1994

Recovery and purification of lactic acid from fermentation broth by adsorption

Roque Lagman Evangelista
Iowa State University

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Recovery and purification of lactic acid from fermentation broth by adsorption

Evangelista, Roque Lagman, Ph.D.

Iowa State University, 1994

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Recovery and purification of lactic acid from fermentation broth by adsorption

by

Roque Lagman Evangelista

A Dissertation Submitted to the

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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1994

To my dearest wife, MILA...

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Most of all, to the ALMIGHTY, for the countless blessings that make dreams come true.

ABSTRACT

Weak- (Reillex 425 and Riedel-de-Haen VI-15), moderate- (Dowex MWA-1, Dowex WGR-2, Dowex XUS-40283, and Dowex XUS-43432), and strong- (Dowex XUS 40196 and Amberlite IRA-958) base resins were evaluated for their sorption capacities of lactic acid from solutions with different pHs. Composite isotherms and fixed-bed sorption indicated that the sorption capacities of weak- and moderate-base resins decreased markedly as the pH of the feed exceeded the pK_a of lactic acid. The decrease in capacity was mainly due to the decrease in concentration of undissociated lactic acid as the pH of the feed increases. The strong-base sorbents exhibited significantly higher sorption capacities for free lactic acid than for lactate. The higher capacities at low pHs were due to the swelling of the resin, thus exposing more sorption sites and creating more space for sorption. The capacity of strong-base resin in fixed-bed sorption remained constant from pH 2 to 6.

Riedel-de-Haen VI-15, Dowex MWA-1 and Amberlite IRA-35 were employed in a lactic acid recovery scheme using model fermentation broth. The starting broth (pH 4.5) contained 1% yeast extract, 10% ammonium lactate and 1% glucose. The broth was acidified by using cation exchange resin (Duolite C-464) in H^+ form, producing 0.4 bed volume (BV) of acidified broth. The acidified broth (pH 2.9) containing 6% lactic acid and 0.7% glucose was passed through the column until the basic sorbent was saturated. The sorbed lactic acid in the column was eluted using methanol or 5% NH_4OH. Lactic acid was completely recovered from VI-15 column after 7 BV of methanol while only 64% was recovered from MWA-1 after 4.5 BV. The 5% NH_4OH

eluted all lactic acid from MWA-1 column in 1.5 BV with a maximum effluent concentration of 115 mg/mL. High-purity, heat-stable lactic acid was recovered from Riedel-de-Haen VI-15 when the broth was treated with activated carbon and styrene divinylbenzene resin before the acidification step using a strong cation exchanger in H^+ form. The lactic acid obtained from real fermentation broth was also high in purity but not heat-stable.

I. INTRODUCTION

As the world's crude oil resources diminish and the prices of petroleum products continue to increase, the production of chemicals by biological processes is becoming more competitive. Lactic acid has been produced by fermentation for over a century, but obtaining pure and heat-stable lactic acid cheaply remained a big problem. The huge demand for heat-stable lactic acid prompted the commercial production of lactic acid by chemical synthesis fifty years ago (Benninga, 1990). The usage of lactic acid in food and industrial applications has reached a standstill and it has remained as a specialty chemical.

The use of polylactic acid (PLA) for biodegradable plastics and controlled-release drugs and pesticides are potential multimillion dollar markets (Lipinsky and Sinclair, 1986). The commercial success of PLA, however, hinges on the cost of producing heat-stable lactic acid. Therefore, one of the major challenges in lactic acid production is to reduce the cost of acid recovery and purification, which could amount to almost 50% of the final product cost.

Adsorption is a process suitable for recovering substances produced in dilute concentrations and complex aqueous solutions such as fermentation broth. Because the adsorption of solutes can be selective, preliminary purification is also performed at the same time. The polymeric sorbents are non-toxic to microorganisms, thus it can be used directly in the fermentor. The manufacture of lactic acid currently uses adsorbents mainly for demineralization of thin crude lactic acid.

Lactic acid fermentation is usually conducted at pHs between 4.5-6. This is done by adding an alkali to neutralize the acid as it is produced. The lactic acid in the broth is, therefore, produced as a salt of the base used (lactate). A strong-base ion exchanger appears to be the obvious choice because it adsorbs lactates. Recovering lactate from the sorbent, however, requires a stronger desorbent. For example, if NaOH is used, the product is sodium lactate. But, if the desired product is the acid, further processing is necessary. Weak-base adsorbents, on the other hand, adsorb only free lactic acid; therefore, they are not effective at pHs where only lactates are present. Acidifying the broth with mineral acids will only introduce competing acids. The advantage of weak-base sorbents is that the free lactic acid adsorbed is easily recovered by using alcohols (e.g., methanol and ethanol) or acetone. An acid product is produced after evaporating the alcohol or acetone. Concentrating lactic acid is also cheaper since the low-boiling solvents require less energy to evaporate than water. The solvents, in turn, can be recycled, thus no regenerant is wasted. Another concern in using polymeric adsorbents is fouling. The broth contains numerous potential fouling substances that can reduce the service life of the adsorbents.

Research Objectives

The main objective of this research was to investigate the use of weak-base polymeric adsorbents in the primary recovery and/or purification of lactic acid from fermentation broth. The specific objectives were: (1) to evaluate the ability of the weak-base sorbents to recover and produce purified lactic acid; and (2) to develop a process that would avoid or minimize generating salt in the waste stream.

Explanation of Dissertation Format

This manuscript is divided into six chapters. The general introduction, statement of the problem, and research objectives are presented in Chapter I. The review of literature pertinent to this research is in Chapter II. The methodology (Chapter III) was divided into three sections and the results and discussion (Chapter IV) was presented in the same order as in Chapter III. Each section in the results and discussion includes a summary. A separate overall conclusion is provided in Chapter V. The recommendations for future work are in Chapter VI. The literature cited in this manuscript are listed in references section. The data used in making the figures and tables are in the appendix.

II. REVIEW OF LITERATURE

Properties of Lactic Acid

Lactic acid (2-hydroxypropionic acid) was first discovered in sour milk by Carl Wilhelm Scheele, a Swedish scientist, in 1780 (Holten, 1971). It is a naturally-occurring organic acid, commonly present in many fermented products, and is a constituent in animal blood and muscle tissue. It occurs as dextrorotatory L(+) lactic acid, as levorotatory D(-) lactic acid, or as a mixture of both isomers in varying proportions (Figure 2.1). Lactic acid is soluble in water and alcohol, less soluble in ether, and practically insoluble in chloroform, petroleum ether and carbon disulfide. Other physical properties of interest are listed in Table 2.1.

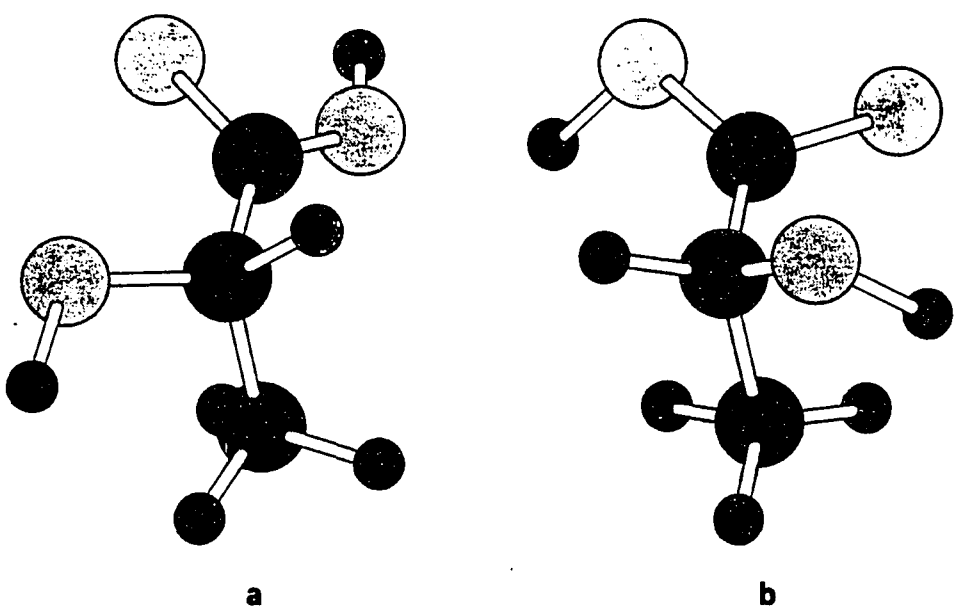


Figure 2.1. Models of (a) L-(+)-, and (b) D-(-)- lactic acid (Holten, 1971)

Table 2.1 Physical properties of lactic acid[a]

Molecular weight	90.08
Melting point, D(-) or L(+)	52.8-54°C
Boiling point (at 14 mm Hg)	122°C
Dissociation constant (K) at 25°C	1.37×10^{-4}
Density at 25°C	1.221 g/mL
Viscosity (88.6% aqueous solution) at 25°C	36.9 cp

[a] Holten, 1971

Lactic acid is available in technical, food (FCC), and pharmaceutical (USP) grades and is commonly sold as 50% or 88% aqueous lactic acid solution. The price of 88% food-grade and technical-grade lactic acid are $1.15 and $1.12 per pound, respectively (Chemical Marketing Reporter, 1994). Crystalline lactic acid is difficult to produce. It is not stable at room temperature because it readily forms intermolecular esters, releasing water in the process in amounts sufficient to completely solubilize lactic acid. At concentrations greater than 20%, the lactic acid solution is a mixture of polylactic acid having varying lengths (Figure 2.2).

Uses of Lactic Acid

Lactic acid was commercially produced by fermentation from 1881 to 1949. Early uses include deliming of hides in leather manufacture, dyeing and printing of textiles, and 'brightening' of silk and rayon. Lactic acid is also used in treating metal surfaces and electrostatic painting. In plastics manufacture, lactic acid is used

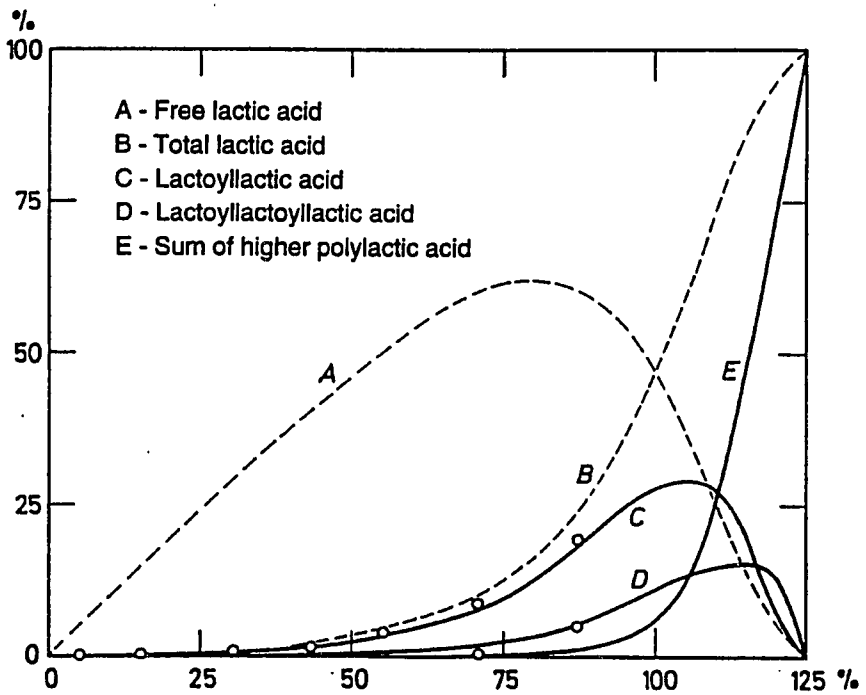


Figure 2.2. Composition of aqueous lactic acid (concentrations in per cent by weight) (Holten, 1971)

in controlling the pH in the film-coating bath for cellophane films, and in the production of phenol-formaldehyde resins and polyesters (Vickroy, 1985). In pharmaceutical products, lactic acid has been used in preparation of buffer solutions, ointments, and cosmetic products.

In 1950, the United States started synthetic lactic acid manufacture to meet the demand for heat-stable lactic acid (Benninga, 1990). The food-grade lactic acid produced by fermentation was not suitable for "Verv" (stearoyl-2-lactylate, an emulsifier and dough conditioner) manufacture because the residual sugars, proteins and other readily-carbonizable substances, and the high reaction temperature required

in the process produced a dark-colored product. About 20% of the total lactic acid produced is converted into stearoyl-2-lactylate and over 50% is used by the food industry as an acidulant and preservative. Lactic acid can also be converted to 2,3-pentanedione, a high-value flavoring ingredient (Miller *et al.*, 1994).

Another application of lactic acid with huge market potential is in the manufacture of poly(lactic acid) (PLA), a biodegradable thermoplastic polymer. This biocompatible polymer is currently used in medical applications such as prosthetic devices, resorbable sutures, and implants. PLA, in combination with other copolymers, has huge potential in biodegradable plastics application. Because PLA is currently made from high-purity lactic acid, its cost is prohibitive and cannot compete with the cheaper petroleum-based plastics (Lipinsky and Sinclair, 1986).

Lactic Acid Manufacture

Lactic acid is commercially produced either by fermentation or by synthesis. As of 1989, total world production was over 30,000 tons/year, of which about 55% is from fermentation. Most of the lactic acid produced in the United States is from a synthetic process (Benninga, 1990).

Fermentation

Biosynthesis of lactic acid from glucose or glycogen does not require oxygen. In animals, plants, and aerobic microorganisms, the anaerobic conversion of glucose or glycogen to pyruvic acid is called glycolysis. The pyruvic acid is then converted to lactic acid by lactate dehydrogenase; which also converts NADH to NAD. This

process is known as lactic fermentation (Holten, 1971). Lactic acid fermentation that yields 2 lactic acid per glucose is considered homolactic fermentation (*Pediococcus*, *Streptococcus*, *Leuconostoc*, and some *Lactobacillus*). Lactic fermentation that produces other by-products (e.g. acetic acid, ethanol, and CO_2) in about equal molar concentrations is called heterolactic fermentation (some *Lactobacillus*) (Buchta, 1983). The homofermentative organisms are employed for lactic acid manufacture. The specific strains of these microorganisms used in the industry are proprietary, but some general principles of strain selection are known. The selection of microorganism depends primarily on the carbohydrate to be fermented. For glucose, *L. delbrueckii* is commonly used. For whey, *L. bulgaricus* is the bacterium of choice as it is able to ferment lactose efficiently (Vickroy, 1985). The high salt content of whey, however, results in higher purification cost.

A large number of carbohydrate-containing substances have been used in lactic acid fermentation. Some common carbohydrate sources are sucrose from cane and beet sugar, lactose from whey, and maltose and glucose from hydrolyzed starch. Refined sucrose, although the most expensive, is the most commonly used substrate, followed by dextrose (Vickroy, 1985). The use of 12-18% sucrose results in the purest medium and the lowest cost for product isolation (Buchta, 1983). Nitrogenous components, such as malt sprouts, malt extract, corn steep liquor, barley, yeast extract, or undenatured mild must, are used to supplement most carbohydrate sources to give rapid and luxuriant growth. In commercial practice, minimal amounts of these substances are used to simplify the recovery process.

Batch fermentation is the method used commercially. Fermentor volume ranges from 20-100 m^3. The fermentation conditions vary depending on the microorganism used. For *L. debrueckii*, the temperature ranges 45-55°C and the pH between 5-6. The acid formed is neutralized by calcium hydroxide or calcium carbonate, either added in little excess at the beginning of the fermentation or added intermittently during the fermentation in response to pH or acid measurements. The fermentation takes two to six days to metabolize 15% glucose or sucrose or one to two days for 5% lactose. The rate of acid production varies from 1-3 $kg/m^3/h$ with a yield of 90-95% based on initial sugar or starch concentration. The residual sugar is about 0.1% and the cell mass ranges from 15% to as high as 30% depending on the initial sugar concentration and the bacteria employed (Vickroy, 1985).

Recovery and purification processes

Various recovery and purification schemes used in industry were discussed by Vickroy (1985) and Benninga (1990). The first step in all recovery processes is to raise the broth's temperature to 80-100°C and increase the pH to 10-11 (using $Ca(OH)_2$) to inactivate the microorganisms, coagulate the protein, solubilize calcium lactate, and degrade some of the residual sugars. The cells and coagulated protein are removed by filtration to produce a crude lactic acid extract. This crude extract is processed further by any of the following methods.

Filtration, carbon treatment, and evaporation. Activated carbon is mixed with the crude extract to remove the colored components. The spent carbon is then

filtered out and the filtrate is sent to the evaporator where excess water is evaporated under mild vacuum at moderate temperature (0.57 atm and 70°C) to 37% calcium lactate concentration. This preparation is then acidified with 63% sulfuric acid to precipitate calcium sulfate, which is filtered out. The lactic acid is bleached a second time and then evaporated to 52 or 82% concentration. Food-grade lactic acid is treated with sodium sulfide to remove heavy metals and is bleached again before packaging. This process produces only food-grade and technical-grade lactic acid. It is also energy-intensive because the concentration process relies heavily on evaporation of excess water. Furthermore, large amounts of salt ($CaSO_4$) are also produced, which create a big waste disposal problem.

Calcium lactate crystallization. The crude extract is bleached with activated carbon and then acidified slightly before undergoing a second bleaching. Excess water is evaporated under vacuum to obtain a density of 1.12 kg/m^3. At this concentration, calcium lactate crystallizes upon cooling. The crystals may be redissolved, treated with sodium sulfide to remove heavy metals, bleached, and recrystallized to improve purity. The product is low in residual sugars but may contain ash, which is mainly calcium sulfate. The yield is 75% based on crude calcium lactate. This rather low recovery is due to losses that occur during the washing step.

Liquid-liquid extraction. The crude extract is filtered, acidified with sulfuric acid and the resulting calcium sulfate precipitate is filtered out. The crude lactic acid is bleached with activated carbon and the heavy metals, calcium, and amino acids are

removed by ion exchange. Excess water is evaporated under vacuum to about 44% lactic acid concentration before it enters the countercurrent extraction columns. The lactic acid is extracted by diisopropyl ether in the first countercurrent extraction column. The extracted aqueous solution still contains 20% of the total lactic acid in the crude lactic acid, which can be concentrated further for technical applications. The acid is recovered from the solvent by countercurrent extraction into water in the second countercurrent extraction column. Finally, the remaining solvent is boiled off from the aqueous solution and the acid is concentrated by evaporating the excess water to obtain food-grade lactic acid. The product is relatively free from ash but may contain other impurities from raw materials. The extraction requires large amount of ether due to low partition coefficients. Use of reactive extractants, such as tertiary amines, coextract other broth components. Thus, extraction alone does not produce high-purity lactic acid.

Esterification and distillation. This is a semi-continuous process for recovery and purification of lactic acid. Crude lactic acid is fed into a heated reactor where it reacts with methanol under the influence of small amounts of sulfuric acid. The molar ratio of lactic acid to methanol is kept at 1:1.5. The vapors distilling from the reactor consist of methyl lactate, methanol, and water, with traces of lactic acid. This mixture is introduced into the middle of a fractionating column. Methanol, the most volatile component, rises to the top of the column, and is collected, condensed to a liquid and returned to the reactor. The bottom fraction contains methyl lactate, lactic acid and water, which are collected in a kettle. Hydrolysis of the methyl lactate takes

place in the fractionating column and is completed in the kettle. The methanol is boiled off and sent back to the reactor via the fractionating column. A more efficient esterification is now performed by using high-boiling alcohols (C4 or C5) (Cockrem and Johnson, 1993). This process is capable of producing high-purity heat-stable lactic acid but the production cost is still high. The distillation of lactic acid esters and its hydrolysis back to lactic acid and alcohol require a lot of energy.

Synthesis

In chemical synthesis lactic acid is produced from lactonitrile, which has the chemical formula $CH_3CHOHCN$. The lactonitrile is a by-product from acrylonitrile synthesis, and can also be made directly from acetaldehyde and hydrogen cyanide by the following reaction:

$$CH_3CHO + HCN \text{ -----> } CH_3CHOHCN$$

Lactonitrile is hydrolyzed by a strong acid such as HCl to produce lactic acid and ammonium chloride:

$$CH_3CHOHCN + 2H_2O + HCl \text{ -----> } CH_3CHOHCOOH + NH_4Cl$$

After the synthesis reaction, the lactic acid produced is isolated and purified by esterification and distillation processes as described previously. Methanol, hydrogen

cyanide and other impurities are then removed by a combination of steaming, carbon treatment, and ion exchange (Van Ness, 1981).

Other Processes in Recovery of Lactic Acid

Other methods proposed include electrodialysis, adsorption, ion exchange, and chromatography. Only electrodialysis will be discussed in this section. The rest will be presented separately in succeeding sections.

Electrodialysis or dialysis in the presence of electric field was also used in recovering lactic acid from fermentation broth. The apparatus was made up of anion and cation membranes arranged alternately between a cathode and an anode. The electric potential between the anode (+ charge) and the anions causes the anions to pass through the anion-permeable membrane. Similarly, the electric potential between the cathode (- charge) and the cations makes the cations to move through the cation-permeable membrane. The anions get concentrated on the anode side and the cations on the cathode side. In water-splitting electrodialysis, a bipolar water-splitting membrane is incorporated. As a result, an acid is recovered on the anode side and a base on the cathode side (Glassner and Datta, 1992). The base can then be recycled to the fermentor for pH control. Since other anions also go with lactic acid, and other broth components end up in the product stream by diffusion, further processing is necessary to remove these impurities. Like other membrane processes, electrodialysis suffers from membrane fouling. Glassner and Datta (1992) reported that they were able to electrodialyze succinic acid from whole broth without

experiencing membrane fouling. The cost of building an electrodialysis unit for large-scale operation is not economically feasible at this time.

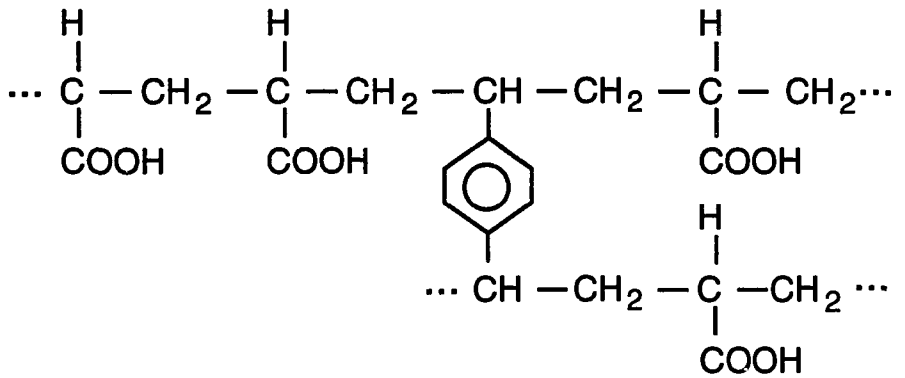
Synthetic Adsorbents

The evolution of synthetic organic ion exchangers started when Adam and Holmes (1935) demonstrated that polar groups can be attached to phenol-formaldehyde matrix, thereby creating both polymeric cation and anion exchangers. These materials were used in series for deionization process. Ion exchangers are now being used in a wide array of applications, from water treatment to recovery and purification steps in most biochemical processes.

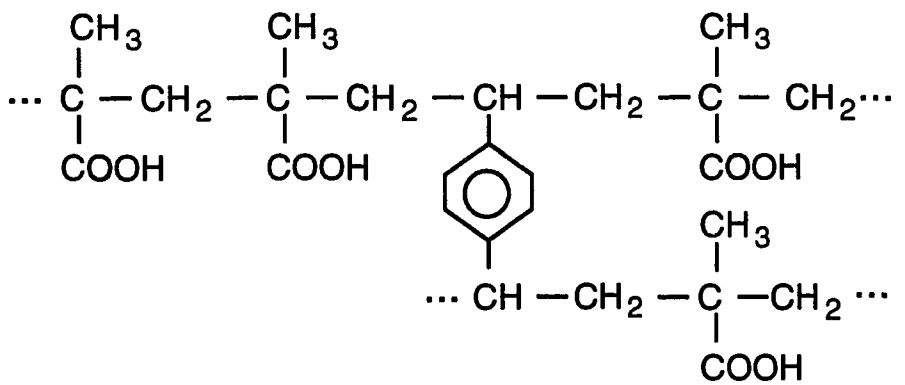
Polymeric adsorbents are classified based on the functionality of their polar groups and the structure of the matrix to which these groups are attached. Based on their polar group, the adsorbent could be a weak-acid or strong-acid cation exchanger, and weak-base or strong-base anion exchanger. In terms of matrix structure, the adsorbent could be gel-type or macroporous (also referred to as macroreticular depending on the manufacturer).

Functional groups

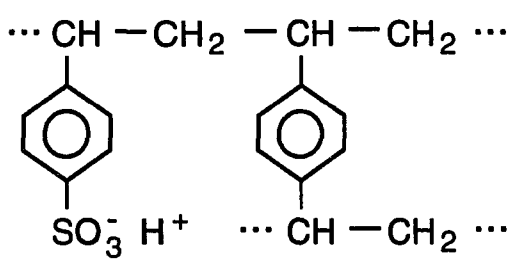
Weak-acid cation exchangers have carboxylic acid groups provided by polyacrylic or polymethacrylic acid (Figure 2.3). In strong cation exchangers, the functional group is sulfonic acid, which is bound to styrene (Figure 2.3). Weak-base adsorbents may have pyridine, imidazole (Figure 2.4), or tertiary amine (Figure 2.5) functional groups, the last group being the most common. Tertiary amines are



(a) Polyacrylic acid-divinylbenzene (DVB)

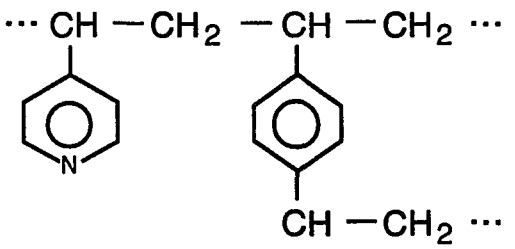


(b) Polymethacrylic acid-DVB

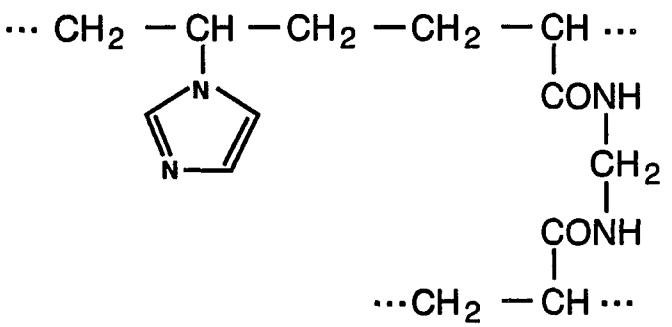


(c) Sulfonic acid in styrene-DVB

Figure 2.3. Chemical structures of cation exchange resins

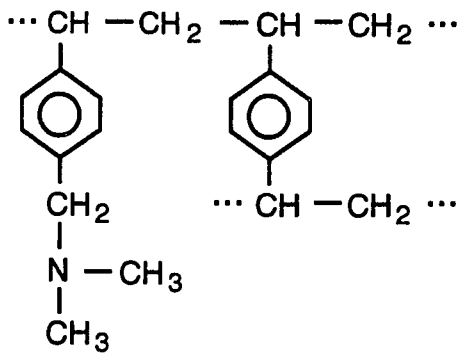


(a) Polyvinylpyridine-DVB

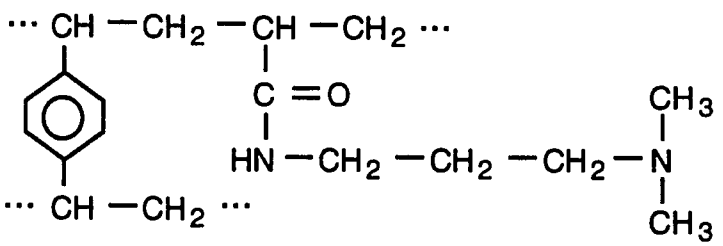


(b) Vinylimidazole-methylene-bis-acrylamide

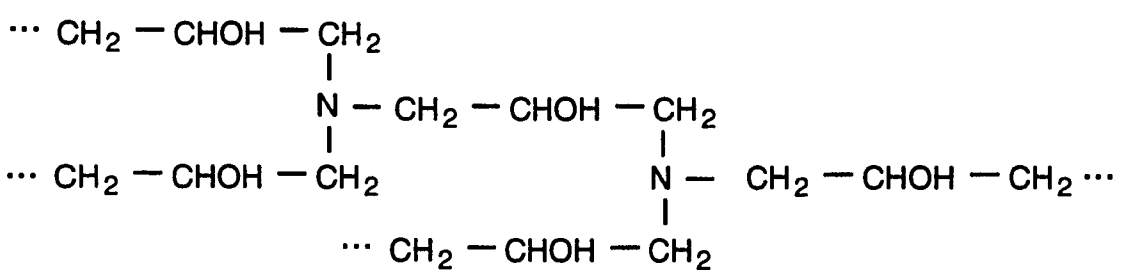
Figure 2.4. Chemical structures of weak-base resins



(a) Tertiary amine-functionalized styrene-DVB



(b) Tertiary amine-functionalized acrylic acid-DVB



(c) Polyamine (Epichlorohydrin-ammonia copolymer)

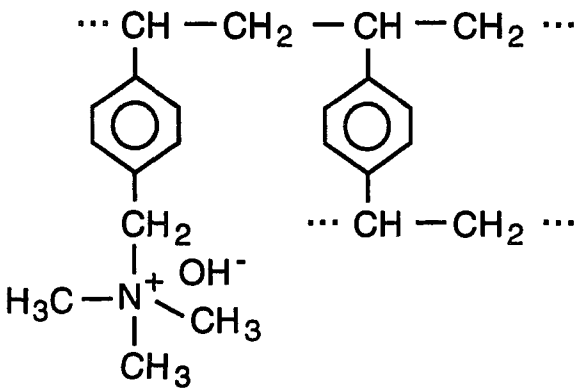
Figure 2.5. Chemical structures of weak-base resins with tertiary amine functionality

either bound to styrene or to acrylate or exist as a polyamine. The strong-base anion exchangers are of quaternary ammonium functionality (Figure 2.6). Quaternary amines are classified further into Type I and Type II. Type I has three alkyl groups attached to nitrogen while in Type II, one of these alkyl groups is replaced with an alkyl alcohol.

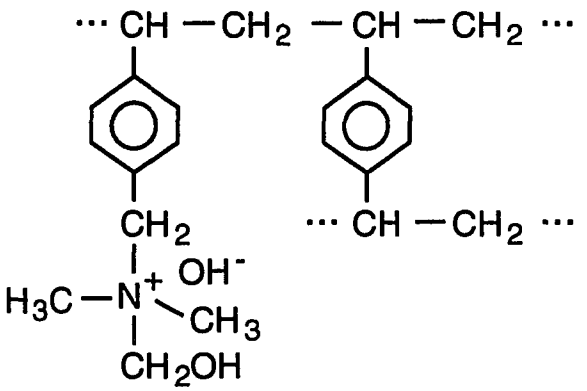
Matrix structure

The three-dimensional structure of the matrix is imparted by the crosslinker that holds the polymers together. Divinylbenzene (DVB) is the most commonly used crosslinker. The degree of crosslinking is expressed in terms of percentage of crosslinker used in producing the resin. The degree of crosslinking determines the mesh width of the matrix and the swelling ability of the resin. Highly crosslinked polymers have good physical stability but suffer from slow kinetics (Helfferich, 1962; Dorfner, 1972)).

The gel-type resin, especially the strong-base anion exchanger, becomes irreversibly fouled by humic acids, a high-molecular-weight electrolyte containing carboxylic and phenolic groups. The aromatic groups in the highly basic anion exchanger (styrene and DVB) have high affinity for aromatic groups in humic acid and fulvic acid. This affinity could not be overcome by caustic regeneration. When an aliphatic polymer was tried in place of styrene, the desorption was improved but the capacity for organic removal was reduced (Calmon, 1984).



(a) Quaternary amine in styrene-DVB (Type I)



(b) Quaternary amine in styrene-DVB (Type II)

Figure 2.6. Chemical structures of strong-base anion exchangers

Adsorption of Carboxylic Acid on Basic Sorbents

Kabawata *et al.* (1981) used dilute aqueous adipic acid (1.5 wt%) to investigate sorption characteristics of poly(4-vinylpyridine) (PVP) crosslinked with DVB. PVP exhibited significant binding capacity for adipic acid. Sorption capacities at breakthrough were scarcely affected by the presence of 1 M NaCl, 0.1 M Na_2SO_4 or 0.1 M HCl. In contrast, the sorption capacities of tertiary amine- and quaternary amine-functionalized resins (IRA-45 and IRA-400, respectively) decreased considerably when inorganic salts were present. PVP had a smaller capacity for adipic acid than IRA-45 or IRA-400, especially at equilibrium acid concentrations below 0.01 M. They attributed this disparity to the stronger interactions of the acid with tertiary and quaternary amine groups than with the pyridyl group of PVP. IRA-400 in OH^- form was also found to have higher capacity than its Cl^- form. No explanation was offered for this behavior. The sorbed organic acid on PVP could be recovered easily by methanol, acetone or 2-propanol, with most of the acid eluted in 2 bed volumes (BV) of eluant.

Kabawata *et al.*'s (1981) study on sorption of monocarboxylic (formic, acetic, propionic, butyric, valeric, acrylic, methacrylic, lactic, and glycolic), dicarboxylic (adipic, malic, and maleic), and tricarboxylic (citric) acids on PVP revealed that the resin's capacity for these acids was a function of the pK_a of the acids and the length of the aliphatic carbon chain. The adsorption capacities of aliphatic acids with similar pK_as increased as the length of the carbon chain increased, suggesting that, in addition to the acid-base interactions, hydrophobic interactions also play a role in the adsorption process. Most of the sorbed organic acids, except citric, maleic, and malic acids, were

easily eluted with 3 BV of methanol. Of the monocarboxylic acids, valeric acid was the easiest to elute, requiring only 1.9 BV of methanol. This behavior seems to confirm the hypothesis of hydrophobic interactions between acids and PVP resins.

Chanda *et al.* (1985) studied the adsorption of formic, acetic, propionic, and butyric acids on polybenzimidazole (PBI) and PVP. At low acid concentrations, PBI exhibited higher sorption capacity than PVP, despite the fact that the total available capacity of PBI is smaller than that of PVP. The higher sorption capacity by PBI was attributed to the higher basicity of benzimidazole (K_b= 0.34 x 10^{-8}) than that of the pyridine (K_b=1.7 x 10^{-9}) in PVP. The acid-base interaction increases with the increase in strength of either the acid or the base, or both. PBI also had faster rate of sorption, and stripping, and regeneration are easily accomplished by using dilute NaOH. The sorption of formic, acetic, propionic, and n-butyric acids on weak-base resins decreased significantly at pHs above the pK_a of these acids. The capacity for butyric acid was the least affected by the pH increase. The lower adsorption capacities of carboxylic acids at pH > pK_a result from the lower equilibrium concentration of the undissociated acid form, which is the species that forms a complex with the functional groups of the weak-base sorbents.

A comprehensive study of the factors that affect the capacity and selectivity for sorption of acetic acid by basic sorbents was reported by Garcia and King (1989). They correlated the sorbent capacity and affinity for acetic acid with the functional group basicity. They reported that resin basicity was a good indicator of sorption affinity, although matrix chemistry and porosity, swelling, and functional group spacing also affected sorbent capacity and selectivity. The elution yield of acetic acid with

methanol inversely correlated with sorption affinities. The elution with methanol worked well only for weak-base sorbents. Only 50% of the acetic acid sorbed on Dowex WGR and MWA-1 (both tertiary amines) was desorbed with methanol at 20:1 solvent to sorbent ratio. Ammonia was more effective in stripping acetic acid from tertiary and quaternary amines, producing ammonium acetate which could be thermally cracked to release ammonia.

Tung (1993) investigated the sorption of lactic and succinic acids on Dowex MWA-1, IRA-35, Duolite A7, and IRA-910 basic sorbents. Resin capacities for HCl were determined experimentally and compared with those of lactic and succinic acids. For Dowex MWA-1, IRA-910, and IRA-35, maximum capacities for lactic acid agreed very well with capacities for HCl. For Reillex 425 and Duolite A7, the available capacity was not fully utilized by lactic acid while only 50% of the available capacities were utilized by succinic acid. The lower capacity for carboxylic acids may be due to steric constraints and to the differences in acidity of carboxylic acids and HCl. The maximum uptakes for succinic acid were generally 8 to 15% higher than the values for lactic acid. Sorbent capacity at pH > pK_a was dependent on sorbent basicity.

Lactic and succinic acids sorbed by Reillex 425, Duolite A7 and Dowex MWA-1 were completely stripped with a stoichiometric amount of trimethylamine (TMA). Stripping lactic and succinic acids from IRA-35 required higher than the stoichiometric amount of TMA because it is more basic than the other tertiary amines. The strong-base resins were not completely regenerable (60 to 75% regeneration) with TMA. Complete removal of TMA from TMA-lactate eluate was unsuccessful because the eluate became increasingly viscous as thermal cracking progressed.

Proposed Processes for Organic Acid Recovery and Purification Using Polymeric Sorbents

Adsorption

Yasuda *et al.* (1984) proposed separation of carboxylic acids by using weak-base resins with pyridine functional groups. Elution of acids with organic solvents was recommended. This method is suitable for separating acids with remarkably different acidities.

Keil *et al.* (1985) used tertiary amine resins to recover lactic and citric acids. The adsorbed acid could be eluted with polar solvents such as lower aliphatic alcohols, methyl ethyl ketones, methyl and ethyl esters of acetic acid. The use of aqueous ammonia and other bases for acid elution was also proposed. In one example, lactic acid fermentation (immobilized *Lactobacillus bulgaricus*) was maintained at pH $\geq$ 4 and the broth was directly adsorbed (extractive fermentation with external loop). The adsorption capacity was 68 g lactic acid per 100 grams of resin. Lactic acid was eluted with methanol and concentrated by distillation to produce "colorless oil" with 99% purity. In another example, fermentation was maintained at pH 6.2 with NaOH. At the end of fermentation, microorganisms were left to consume the remaining glucose and then the cells were filtered. The pH of the filtrate was adjusted to pH 2 with HCl and then, the filtrate was loaded on the sorbent. After the adsorption, the resin was washed with 2 BV of water. Lactic acid was eluted with methanol and concentrated as described earlier.

Obara (1988) described an application of a strong anion exchanger in recovery and purification of lactic acid from fermentation broth. The broth was neutralized with NH_3 to produce ammonium lactate, bleached, and then filtered. The salts were removed by a cation exchange resin, and then the lactic acid was adsorbed on an anion exchange resin. Lactic acid was stripped from the anionic resin by sulfuric acid. The cation exchange and anion exchange resins were regenerated by using 1 M H_2SO_4 and 1 M NaOH, respectively.

Rossiter (1991) used a strong anion exchanger in a continuous moving-bed contactor (ISEP) to recover lactic acid from fermentation broth containing 10-12% NH_4-lactate at pH 5-7. Lactic acid was desorbed by using dilute sulfuric acid to produce 8-12% lactic acid solution. Post-adsorption washing was found to be important for the purity of the lactic acid produced. It was observed that washing was improved with increased fluid velocity and increased residence time of the resin in the wash zone. Also, residence time was more important than the fluid volume employed.

Maeda and Nakasawa (1992) proposed a two-step process for purifying tartaric acid in the presence of gluconic and glycolic acids using strong cation exchange resins crosslinked (4-10%) with DVB. In the first step, salts, carbohydrates, and other impurities were separated from the acids using a cation exchange resin in Na^+ form. In the second step, the organic acid fraction containing Na-carboxylates was converted into free acids and further purified by a strong cation exchanger in H^+ form. High-purity tartaric acid was obtained by crystallization. The pH of the feed containing the organic acid was maintained at a level below the pK_a of the target carboxylic acid. This was achieved by adding sulfuric acid to the feed and the eluant. This process

could be used for desalting an acidified lactic acid fermentation broth and converting the lactate from the first column (Na^+ form) into free acid. Again, Na-sulfate and sulfuric acid will be present in the final product solution.

Ernst and McQuigg (1992) also utilized the ISEP contactor but they used a weak anion exchange resin (Reillex 425) to recover citric and lactic acids from fermentation broth by a temperature swing adsorption process. The resin was loaded with acid at 25°C and desorbed with water at 90°C. In their citric acid purification run, a product stream of 9% purified citric acid was obtained from the feed containing 16% citric acid, a dilution of almost twofold. They claimed that with this process, there is a potential savings of $0.03/lb citric acid.

Mantovani *et al.* (1992) employed a strong-base anion exchanger (IRA-420, quaternary amine-SDVB in bicarbonate (HCO_3^-) form) to adsorb sodium lactate from *Lactobacillus casei* broth (pH 6.4-6.6). The loaded resin was rinsed with 3 BV of water prior to elution with 5% ammonium bicarbonate. This step also converts the resin back to HCO_3^- form. Complete stripping of lactic acid required 3 BV of ammonium bicarbonate resulting in a threefold dilution of lactic acid. Excess ammonium bicarbonate in ammonium lactate solution was removed by heating the solution to 90°C. The ammonium lactate was converted to lactic acid by using a cation exchanger (IRA-120, sulfonate-SDVB in H^+ form). The lactic acid was concentrated by evaporating excess water. The cation exchange resin was regenerated by using 5% HCl.

King and Tung (1992) proposed the use of moderate-base sorbents (MWA-1 and AG3-X4) to extract carboxylic acids (lactic, fumaric, and succinic acids) from

fermentation broth at pHs close to or above the pK_a of the carboxylic acids. They reported that at pH > pK_a, these sorbents maintained high sorption capacities. The carboxylic acids could be stripped from the sorbents by using NH_3 or TMA. Complete recovery of acids from MWA-1 was obtained when the molar ratio of desorbent and carboxylic acid in the column was 2:1. Only 87% was recovered from AG3-X4, a resin that has 10% of sorption sites as quaternary amine. Complete evaporation of TMA from TMA-lactate solution was difficult because of self-esterification of the acid resulting in a viscous solution that apparently imposed severe transport limitations.

Continuous chromatography

Kulprathipanja and coworkers (1988, 1989a, 1989b, 1991) proposed using a continuous countercurrent simulated moving-bed system described in a patent by Broughton (1961) for the recovery of citric and lactic acids from fermentation broth. They evaluated neutral, weak-base (pyridine and tertiary amine) and strong-base (quaternary amine) polymeric sorbents as possible packing materials. Pulse tests on broth containing 10-40% organic acid were performed by using the dynamic testing apparatus packed with adsorbents. The weak-base and strong-base sorbents were prepared in sulfate form by using 0.5 M H_2SO_4. The authors found that, in all cases, the pH of the feed had to be maintained at a pH below the acid pK_a (pK_{a1} for citric acid) to prevent the "breakthrough" of the organic acid with salts and carbohydrates at the beginning of the cycle. A 0.01-0.1 M H_2SO_4 eluant was found to be desirable. The fermentation broth used was acidified by adding sulfuric acid. The sorbent in sulfate form interacts with the undissociated citric and lactic acids by hydrogen

bonding. Although most of the salts and other broth components were separated, minute amounts of some components were still eluted with the acid. A twofold dilution of the acid was also obtained. Water was not effective in eluting either lactic or citric acid from moderate- and strong-base sorbents. The elution of citric acid from a weak-base (pyridine) resin by using water was not practical. The late breakthrough of citric acid resulted in excessive dilution and a longer elution zone, although excellent separation from broth impurities was achieved. Maeda and Nakasawa (1992) suggested using a cation exchanger in H^+ form and eluting with dilute sulfuric acid. The advantage in using a cation exchanger was that no excessive tailing of lactic acid peak was observed.

A similar process was also proposed by Collin and Buresch (1990) using IRA-900 (quaternary amine) and IRA-67 (tertiary amine). The separation of lactic and citric acids from fermentation broths was performed in a simulated moving-bed contactor at 70° and 75°C. Concentrated lactic acid broth (40% lactic acid) was separated on IRA-900 in sulfate form by using water as eluant. Purification of over 95% was achieved, but the lactic acid concentration was about half that of the feed. Concentrated citric acid (43% citric) was purified on IRA-67 with 0.1% sulfuric acid as the eluant. Sulfuric acid was the major impurity at 0.27%.

Extractive fermentation by using sorbents

Yates (1981) proposed a process for continuous recovery and concentration of low-molecular weight organic acids produced by fermentation. The cell-free broth from the fermentor containing sodium acetate was contacted countercurrently with a basic

ion exchanger with tertiary amine functional groups (IRA-68) in bicarbonate form. The spent broth was recycled to the fermentor. The acetate was recovered from the resin by using a water-containing polar solvent (with bp of -30° to 90°C) with CO_2 (10-750 psig). Acetic acid was recovered and, at the same time, the resin was regenerated to bicarbonate form. The excess solvent and water were evaporated to obtain a crude acetic acid.

Behrens *et al.* (1984) employed a quaternary ammonium-functionalized belt (polyamide in combination with dimethyl-diallylammonium chloride and NN-methylene-bis-acrylamide) in OH^- form to extract citrate from fermentation broth. During fermentation, the belt was pulled continuously through the fermentor, regeneration bath, and a sterilization chamber. Rubber lips sealed the fermentor and the sterilization chamber from the environment to maintain aseptic operation. The pH of the broth was 5.5 and contained 10 g/L sodium citrate. At the end of fermentation, the regeneration bath contained 2.2 g/L sodium citrate.

Srivastava *et al.* (1992) controlled the pH in batch *L. delbrueckii* fermentation of sucrose by circulating the broth through a column of strong-base anion exchange resin (IRA 400, quaternary amine). Simultaneous extraction of lactic acid by ion exchange increased the lactic acid yield by 12.1% and cell yield by 36.4% when compared with the NaOH-controlled pH process. The fermentation time was reduced by 69.4%. As a result, there was a 5.3-fold increase in overall lactic acid productivity.

Davison and Scott (1992) proposed a biparticle fluidized-bed bioreactor (FBR) for continuous lactic acid fermentation and adsorption. *L. delbrueckii* was immobilized in 4% κ-carrageenan and the density of the gel beads was adjusted by using Fe_2O_3 or

CeO_2. The gel beads were fluidized in one section of the FBR by adjusting the upward flow of the liquid feed. The activated carbon used as adsorbent was denser than the gel beads. It was added on top of the FBR and moved down through the fluidized gel beads, adsorbing the lactic acid produced. The spent adsorbent was then collected from the bottom. Carbon adsorbed less lactic acid than expected, as well as a small amount of glucose.

Tsao *et al.* (1993) also conducted batch fermentation of glucose by *L. delbruickii* coupled to a column of a weak-base adsorbent with pyridine functional group (Reillex 402). Lactic acid productivity of 0.98 g/L/h was achieved, an increase of 80% compared with fermentation without extraction (0.54 g/L/h). Productivity increased when the amount of resin in the column was increased. Excellent results were obtained when Reillex 425 was used instead of Reillex 402. The saturated resin was rinsed with water to remove the broth in the column and lactic acid was desorbed by using methanol.

III. MATERIALS AND METHODS

Evaluation of Basic Sorbents

Resin preparation

Eight basic sorbents were initially chosen for this study (Table 3.1). Reillex 425 and Dowex MWA-1 have been used widely in the sorption of a variety of carboxylic acids. Some are experimental resins (Dowex XUS resins) recommended by the manufacturer. For purposes of discussion, these resins were classified according to their basicities. Weak-base sorbents have pK_as < 7 (VI-15 and Reillex 425). Moderate-base sorbents have pK_as between 7 and 10 (Dowex MWA-1, WGR-2, XUS-43432 and XUS-40283). Strong-base sorbent are those with pK_a > 10 (IRA-985 and XUS-40196).

The hydrated sorbents were transferred into a 1-L column (30 x 6 cm). The sorbent bed was backwashed with deionized water to remove the fine particles. This step was followed by washing (downflow) of the bed with 3 BV of 5% HCl, 5 BV of deionized water, 3 BV of 4% NaOH, and another 5 BV of deionized water. The flow rate was adjusted to allow at least 30 min contact time between the sorbent and HCl or NaOH solutions. These steps were repeated one more time. The final water-rinse was performed until the effluent pH was less than 8. The weak- and moderate-base resins (in free-base form) were dried in a vacuum oven (60°C at 35 mm Hg) and stored in a desiccator until used. The strong-base sorbent (OH^- form) was drained under vacuum through a filter and stored in a capped plastic bottle. The strong-base

Table 3.1. Properties of selected basic adsorbents

Resin	Manufacturer	Type/Matrix	Functional group	Mesh size	pK_a
Reillex 425	Reilly Industries Indianapolis, IN	Macroporous/PVP-DVB	Pyridine	18-50	4.9[a]/5.2[b]
VI-15	Riedel-de-Haen Seelze, Germany	Gel/methylene-bis-acrylamide	Imidazole	32-150	6.9[c]
MWA-1	Dow Chemical Midland, MI	Macroporous/SDVB	3°-amine	20-50	8.8[a]
WGR-2	Dow Chemical	Gel-Macroporous/ Epoxy	3°-amine	20-50	8-10
XUS 40283	Dow Chemical	Macroporous/SDVB	3°-amine	-	8-10
XUS 43432	Dow Chemical	Gel/ SDVB	3°-amine	30-35	8-10
IRA 958	Rohm and Haas Philadelphia, PA	Macroporous/ADVB	4°-amine,Type I	20-50	>10
XUS 40196	Dow Chemical	Gel/SDVB	4°-amine,Type I	30-35	>10

[a]Data from Kuo *et al.*, 1987.

[b]Data from Chanda *et al.*, 1985.

[c]Weast, 1987.

sorbent was not oven-dried because the quaternary ammonium group in hydroxide form is susceptible to thermal degradation when subjected to temperatures over 60°C (Helfferich, 1962). The moisture contents of the sorbents were determined by Karl Fischer titration (ASTM E203-75, 1975).

Total resin capacity for chloride

Weak-base and strong-base resin capacities for chloride ions were measured by following the procedure outlined in the Rohm and Haas Ion Exchange Resin Laboratory Guide (Rohm and Haas, 1988). Resin (5 g) in chloride form was packed into a column. Chloride ions bound to weak-base sorption sites of the resin were eluted first by passing 1 L of 1% NH_4OH through the column. This was followed by passing 1 L of 1M $NaNO_3$ to elute the remaining chloride ions held by the strong-base sites. Chloride ions recovered by each eluate were quantified by titration.

Analytical methods

Lactic acid and glucose concentrations were analyzed by using HPLC (Maxima 820, Waters, Milford, MA) equipped with a refractive index detector and Bio-Rad Aminex HPX-87H column (300 x 7.8 mm) (Bio-Rad Chemical Division, Richmond, CA). The column temperature was maintained at 65°C by using a column heater (Eppendorf CH-30, Brinkmann Instruments, Inc., Westbury, NY). The mobile phase was 6 mM H_2SO_4 at a flow rate of 0.8 mL/min.

Preparation of starting lactic acid solutions

Twenty percent lactic acid solution was prepared from 88% certified-grade lactic acid (Fisher Scientific, Pittsburgh, PA) and heated close to boiling to hydrolyze the lactic acid anhydride present in the concentrated solution. The presence of lactic acid anhydride in the 20% solution was monitored periodically by using HPLC. The pHs of the starting solutions for the batch and fixed-bed experiments were adjusted to the desired levels by using 10 M NaOH.

Batch sorption

Composite sorption isotherms were developed by using a 1:10 (w:v) ratio of dry resin and starting solution. Aqueous lactic acid with concentrations ranging from 2.5 to 150 mg/mL at four different pHs (2.8, 3.8, 4.8 and 5.8) were used as starting solutions. The vials containing the sorbent and lactic acid solution were maintained at 30°C in a shaking water-bath (Model 3450, Lab-Line Instruments, Inc., Melrose, IL) and were allowed to equilibrate for at least 24 h. The pH of the bulk solution at equilibrium was measured, and the lactic acid concentrations were determined by using HPLC.

The amount of lactic acid sorbed by the resin was calculated by using the following equation:

$$q=\frac{(C_o-C_e)V}{W} \tag{3.1}$$

where q - amount of lactic acid sorbed by the resin (mg/g dry resin)

C_0 - initial concentration of lactic acid (mg/mL)

C_e - concentration of lactic acid at equilibrium (mg/mL)

V - initial volume of lactic acid solution (mL)

W - weight of dry resin (g)

Fixed-bed sorption

The set-up for fixed-bed sorption is illustrated in Figure 3.1. The flangeless fittings used to connect the tubings to the distribution valves allowed fast and easy change from downflow to upflow (and vice versa) configuration whenever desired. A jacketed 30 x 1 cm (i.d.) column (Kontes Scientific Glassware/Instruments, Vineland, NJ) equipped with adjustable plungers was charged with hydrated resin (2 g dry resin). The air trapped in the sorbent was removed by stirring the resin, and the plunger was lowered to the top of the sorbent bed. The column was drained under vacuum to estimate the interstitial volume of the bed. The column was refilled with water, then the trapped air was removed. The feed solution containing 60 mg lactic acid/mL was introduced into the column by using a Rabbit peristaltic pump (Rainin Instrument Co., Inc., Woburn, MA) at the rate of 0.5 mL/min. A constant-temperature circulator (Model 800, Fisher Scientific, Pittsburgh, PA) was used to maintain the temperature of water in the jacket at 30°C. Fractions (2.0 mL) were collected from the column, and the lactic acid concentration was analyzed to monitor the saturation point. The sorbent was considered to be saturated when the lactic acid concentration in the effluent was at least 95% of that in the feed. The lactic acid concentration and pH of each fraction

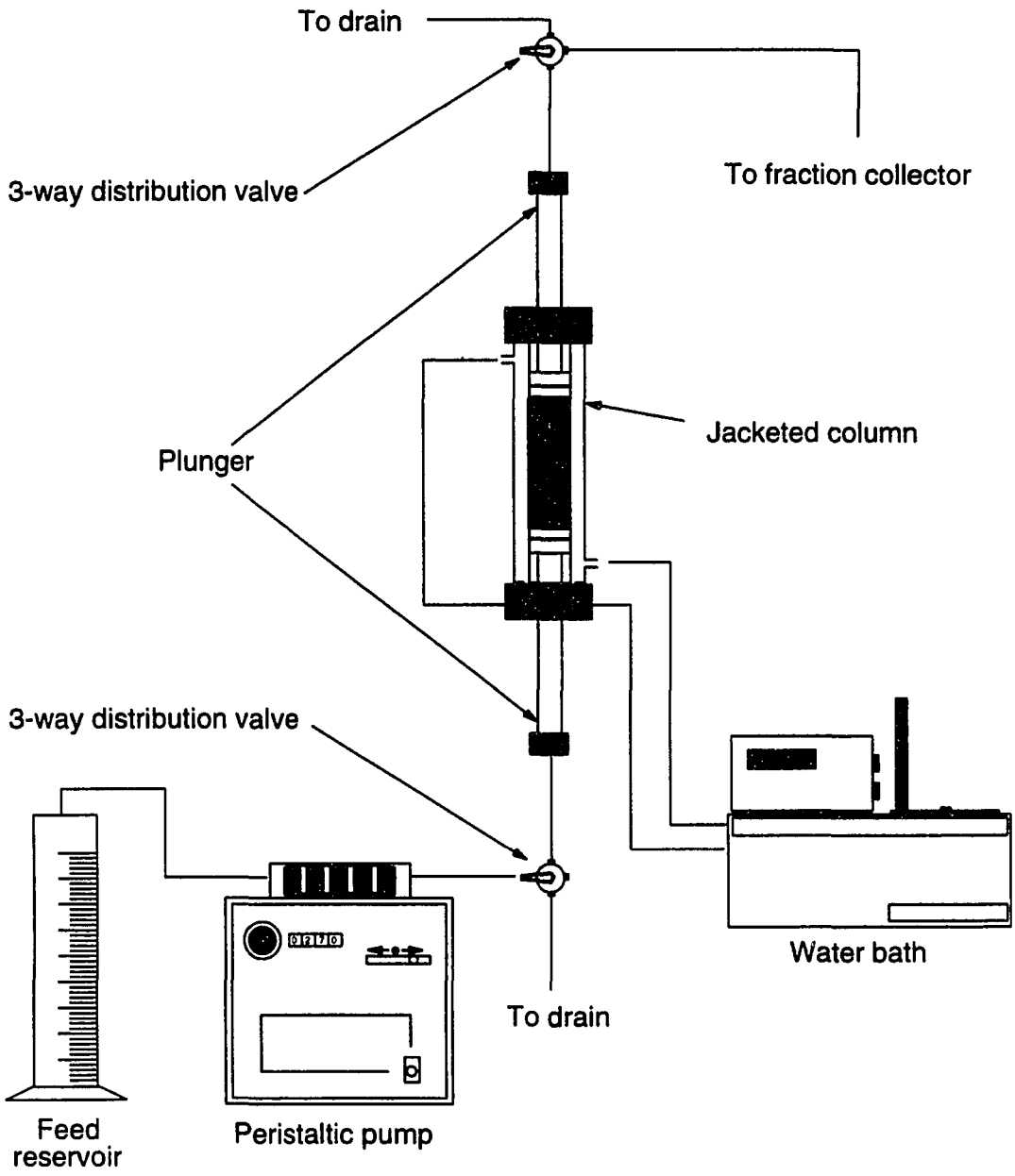


Figure 3.1. Set-up for fixed-bed sorption experiments

were determined. Column capacities at saturation were calculated by using the following equation:

$$q_s = \frac{[\sum (C_f - C_i) V_i] - C_f V_{st}}{W} \qquad (3.2)$$

where q_s - amount of lactic acid sorbed by the resin at saturation (mg/g dry resin)

C_f - concentration of lactic acid in the feed solution (mg/mL)

i - fraction 1 to n; n is the fraction at saturation

C_i - concentration of lactic acid in fraction *i* (mg/mL)

V_i - volume of fraction *i* (mL)

V_{st} - interstitial volume (mL)

W - dry weight of the resin in the column (g)

Lactic Acid Recovery From Fermentation Broth

Lactic acid recovery scheme

A simple scheme using weak- and moderate-base sorbents was used for recovering lactic acid from fermentation broth. The three main steps in the process were: (1) acidifying the broth, (2) adsorbing lactic acid on basic sorbent, and (3) concentrating lactic acid (Figure 3.2). The acidification step was carried out by using a weak-acid cation exchanger prepared in H^+ form. The lactic acid from the acidified broth was then recovered by using a basic sorbent. The exhausted sorbent was rinsed with water to wash out the unbound components of the broth from the voids of

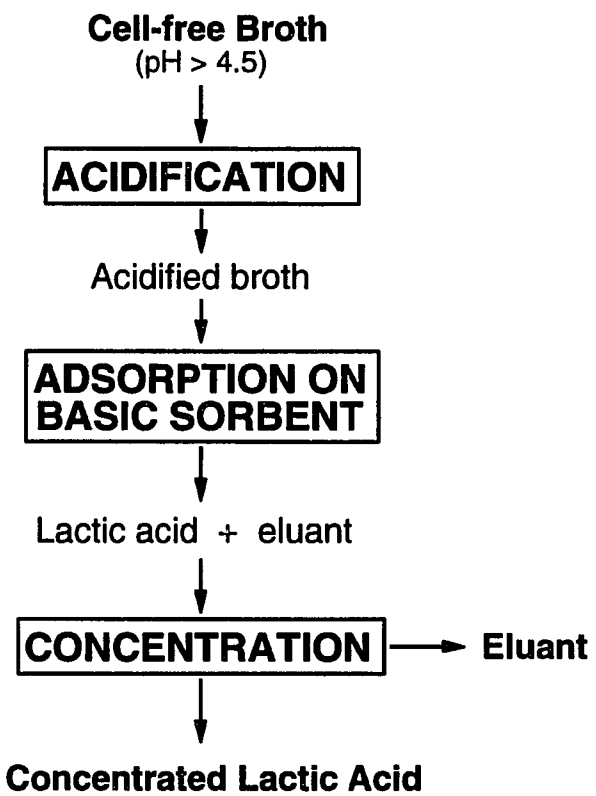


Figure 3.2. Scheme for lactic acid recovery and purification

the bed. The adsorbed lactic acid was eluted by using HPLC-grade methanol (Fisher Scientific, Pittsburgh, PA) or 5% NH_4OH depending on the sorbent used.

Broth preparation

The model lactic acid broth (Table 3.2) used in this study was a glucose-yeast extract (DIFCO Laboratories, Detroit, MI) medium spiked with lactic acid and minerals. The pH of the broth was adjusted to 4.5 by using ammonium hydroxide. Starting broth pH of 4.5 was chosen because the final pH of the broth from batch lactic acid fermentation is typically around this value.

Table 3.2. Composition of model lactic acid broth.

Components	Amount, g/L
Yeast extract	10.00
Glucose	10.00
Lactic acid	100.00
$MgSO_4 \cdot 7H_2O$	0.60
K_2HPO_4	0.50
$MnSO_4$	0.03
NH_4OH	(as required to adjust pH to 4.5)

Column preparation

The resins selected for this study were Riedel-de-Haen VI-15, Dowex MWA-1, and Amberlite IRA-35. The columns for these resins were prepared as described

earlier. One of the intended applications of Duolite C-464 (Rohm and Haas, Philadelphia, PA), a weak-acid cation exchanger (acrylic acid in SDVB matrix) is for removal of ammonia; hence, it was chosen for the acidification step. The Duolite C-464 column was conditioned in a similar manner as the basic sorbents except that the order of NaOH and H_2SO_4 rinsing was reversed to obtain a resin in H^+ form.

Broth acidification

The model broth was passed through the Duolite C-464 column at a flow rate of 3 BV/h. Fractions were collected and analyzed for lactic acid and glucose using HPLC. The pH of each fraction was also measured. Fractions containing acidified lactic acid with a pH < 3.2 were pooled and set aside for sorption on basic sorbents. The column was regenerated by using sulfuric acid. Several cycles were run to produce suffecient amount of acidified broth for the sorption experiments.

Resin regeneration by using carbonic acid

Regeneration of the cation exchange resin by using carbonic acid was also explored. A 1 x 30 cm stainless steel column was packed with Duolite C-464 resin and converted to H^+ form by using 5% HCl. Ten percent aqueous ammonium lactate (with pH 6.3) was introduced into the column upflow by using a piston pump (Minipump NSI-33R, LDC Analytical, Riviera Beach, FL) at 3 BV/h. Effluent fractions were collected and pHs were measured.

The carbonic acid was prepared by bubbling CO_2 in 200 mL water contained in the 300 mL bolted closure reactor (Autoclave Engineers, Inc., Eire, PA) (Figure 3.3)

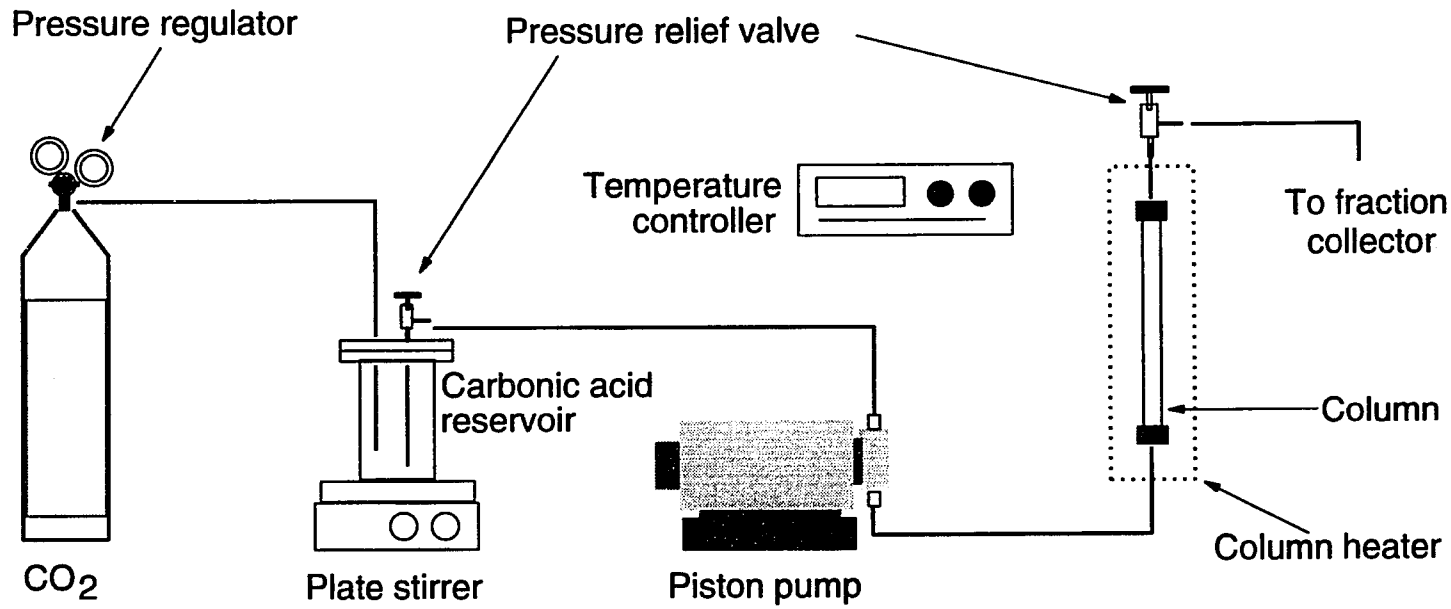


Figure 3.3. Set-up for carbonic acid regeneration

sitting on top of a plate stirrer. A head space pressure of 1724 kPa was maintained by a pressure relief valve. A minimum column back pressure of 1724 kPa was also maintained by a pressure relief valve fitted at the effluent end of the column. After regeneration, the column was loaded again with ammonium lactate, fractions were collected, and pHs were measured. The pH profile of the carbonic-acid-regenerated column was compared with the HCl-prepared column to determine the effectiveness of carbonic acid regeneration. Carbonic acid regeneration at 65°C was also performed by using a column heater (Eppendorf CH-30, Brinkmann Instruments, Inc., Westbury, NY) and a temperature controller (Eppendorf TC-50). The same procedure was repeated using model broth instead of ammonium lactate solution.

Sorption on weak-base sorbents

The acidified broth was introduced onto the basic sorbent column upflow at 3 BV/h. The column was rinsed with water to remove the excess broth and other unbound broth components followed by elution of bound lactic acid with methanol or 5% NH_4OH. Fractions were collected and analyzed for lactic acid, glucose, and pH. Methanol was evaporated from the eluate by using a rotary evaporator. Eluants from NH_4OH desorption were not concentrated. The column was regenerated by using 3 BV 4% NaOH and rinsed with 5 BV water.

Broth Pretreatment

Browning reaction and activated carbon treatment

Model broths at pH 4.5 and 10 (pH was adjusted by using NH_4OH) were placed in 250-mL Erlenmeyer flasks and boiled for 5 h over a hot plate with constant stirring. Water was added periodically to bring the liquid back to its original level. After 5 h, the browned broths were cooled to room temperature and their volumes adjusted to their original level by adding water. Samples of heat-treated broths were analyzed for lactic acid and glucose by using HPLC, and their pHs were measured.

Broth decolorization by using activated carbon

The activated carbon (Calgon Carbon F-400, Calgon Carbon, Pittsburgh, PA) column was conditioned by passing 5 BVs of 10% (by wt) HCl followed by deionized water until the effluent was about pH 7. The heat-treated broths and an unheated broth (pH 4.5) were passed through an activated carbon column at a flow rate of 3 BV/h. Fractions were collected and analyzed for lactic acid and glucose by using HPLC. The pHs of the fractions were also measured.

Broth decolorization by using nonfunctionalized resins

Nonfunctionalized resins with different matrix polarities were chosen for this study (Table 3.3). The sorbents were packed in a 1 x 30 cm column and preconditioned prior to use. The Amberlite XAD-16 and Diaion HP-2MG resins were washed repeatedly with methanol and then rinsed with deionized water. The Duolite

Table 3.3. Nonfunctionalized polymeric sorbents.

Properties	Resin		
	Amberlite XAD-16	Diaion HP-2MG	Duolite S-761
Matrix	Polystyrene-DVB	Polyacrylic acid-DVB	Phenolformal-dehyde
Mean surface area	800 m^2/g	500 m^2/g	100 m^2/g
Pore diameter	100 Å	300-600 Å	600 Å
Applications	hydrophobic compounds up to 40,000 MW; antibiotics; separation of large organic molecules (especially proteins)	hydrophobic compounds; antibiotics; aliphatics; color bodies	removal of proteins; removal of high-molecular weight colorants from sugar solutions, wines, etc.;

S-761 resin was rinsed with methanol, dilute NaOH, dilute H_2SO_4, and deionized water until the effluent was about pH 7.

The model broth was passed through the columns and fractions were collected and analyzed for lactic acid and glucose. The pHs of the fractions were also measured. The columns were rinsed with deionized water to remove the broth, followed by lactic acid elution by using methanol. Samples of methanol eluate were analyzed lactic acid and glucose by using HPLC.

IV. RESULTS AND DISCUSSION

Evaluation of Selected Basic Sorbents

Basic sorbent capacities for HCl

The capacity of the basic sorbent for chloride ions is a measure of the number of its ionogenic group. The value is usually expressed in terms of milliequivalents (meq) per gram dry sorbent in Cl^- form. This value is useful in characterizing the sorbent and in numerical calculations of ion exchange operations (Helfferich, 1962). The measured capacities and the manufacturers' stated capacities are presented in Table 4.1. The manufacturers' values in volume capacities were converted to weight capacities by using the resin's density and water retention data stated in their product literature. Except for Riedel-de-Haen VI-15, all experimental values agreed very well with the manufacturers' values. The experimental capacity for VI-15 was about four times higher than the manufacturers' value. This difference could be due to the high nitrogen content of the resin. The chemical structure of VI-15 (Figure 2.4b) shows that both the imidazole and the crosslinker carry two N each. At very low pHs, all these nitrogens can be protonated, and thus, can adsorb chloride ions. The capacity stated by the manufacturer probably accounted only for one N in the imidazole. Reillex 425 also had high capacity for HCl, which directly translates into the number of pyridyl group in the resin (Figure 2.4a).

The moderate-base sorbents contained considerable amounts of strong-base capacity, which indicated that aside from the tertiary amine functional groups,

Table 4.1. Capacities of sorbents for HCl

Sorbent	Manufacturers' values (meq/g)		Experimental values[a] (meq/g dry resin)	
	Weak-base	Strong-base	Weak-base	Strong-base
Reillex 425	5.5	-	6.2 ± 0.1	-
VI-15	1.7	-	8.0 ± 0.1	-
MWA-1	3.5[b]	-	4.4 ± 0.1	0.6 ± 0.1
WGR-2	5.5[b]	0.6[b]	8.3 ± 0.0	-
XUS 40283	3.8[b]	0.6[b]	4.5 ± 0.1	1.0 ± 0.0
XUS 43432	4.8[b]	-	3.0 ± 0.1	1.2 ± 0.1
IRA-958	-	3.8[b]	2.2 ± 0.0	1.2 ± 0.1
XUS 40196	-	5.0[b]	1.0 ± 0.0	3.6 ± 0.0

[a] Mean ± standard deviation.
[b] Converted from volume capacity.

these resins also had quaternary amine functional groups. Dowex XUS-43432 had the highest strong-base capacity (28% of its total capacity) followed by Dowex XUS-43432 (22%) and Dowex MWA-1 (12%).

The strong-base resins had a considerable fraction of their total capacity as weak-base capacity. Dowex XUS-40196 contained about 22% in weak-base capacity while Amberlite IRA-958 had 65%. Such a high weak-base fraction indicates that a considerable amount of quaternary amine functional groups were degraded. The weak-base capacity level is critical for the performance of strong-base sorbents

because this fraction cannot be utilized at pHs where only ionized ions, which do not interact with the weak-base groups, are present.

Effect of pH on sorption of basic sorbents

The amount of lactic acid sorbed by the resin, calculated using Equation 3.1, was plotted against the total lactic acid in the bulk liquid at equilibrium (Figures 4.1 through 4.9). The final pH values represent the range of equilibrium pHs that were measured at each experimental point.

Reillex 425 exhibited high capacity for lactic acid from solutions with initial pH of 2.8, but practically no sorption was observed from solutions with starting pH of 4.8 (Figure 4.1). At pH 4.8, only 5% of the total lactic acid is present as free lactic acid, so there was not much free lactic acid available for sorption. A similar sorption isotherm was obtained by Chanda *et al.* (1985) for sorption of monocarboxylic acids on a gel-type poly(4-vinylpyridine), and by Ernst and McQuigg (1992) at equilibrium concentrations up to 180 g/L lactic acid.

Riedel-de Haen VI-15 also showed high capacity for lactic acid from solutions with starting pHs of 2.8 and 3.8 (Figure 4.2). Maximum sorbent capacity from solutions at pH of 3.8 was achieved only at about twice the equilibrium concentration needed to attain maximum capacity at pH 2.8. Sorption of lactic acid also decreased dramatically at higher pHs. 'Negative' sorption values were obtained from lactic acid solutions with initial pHs of 5.8. The pH at equilibrium, however, increased significantly, indicating that some lactic acid was adsorbed by the sorbent. Because Riedel-de-Haen VI-15 has a hydrophilic matrix and the sorbent was dry prior to

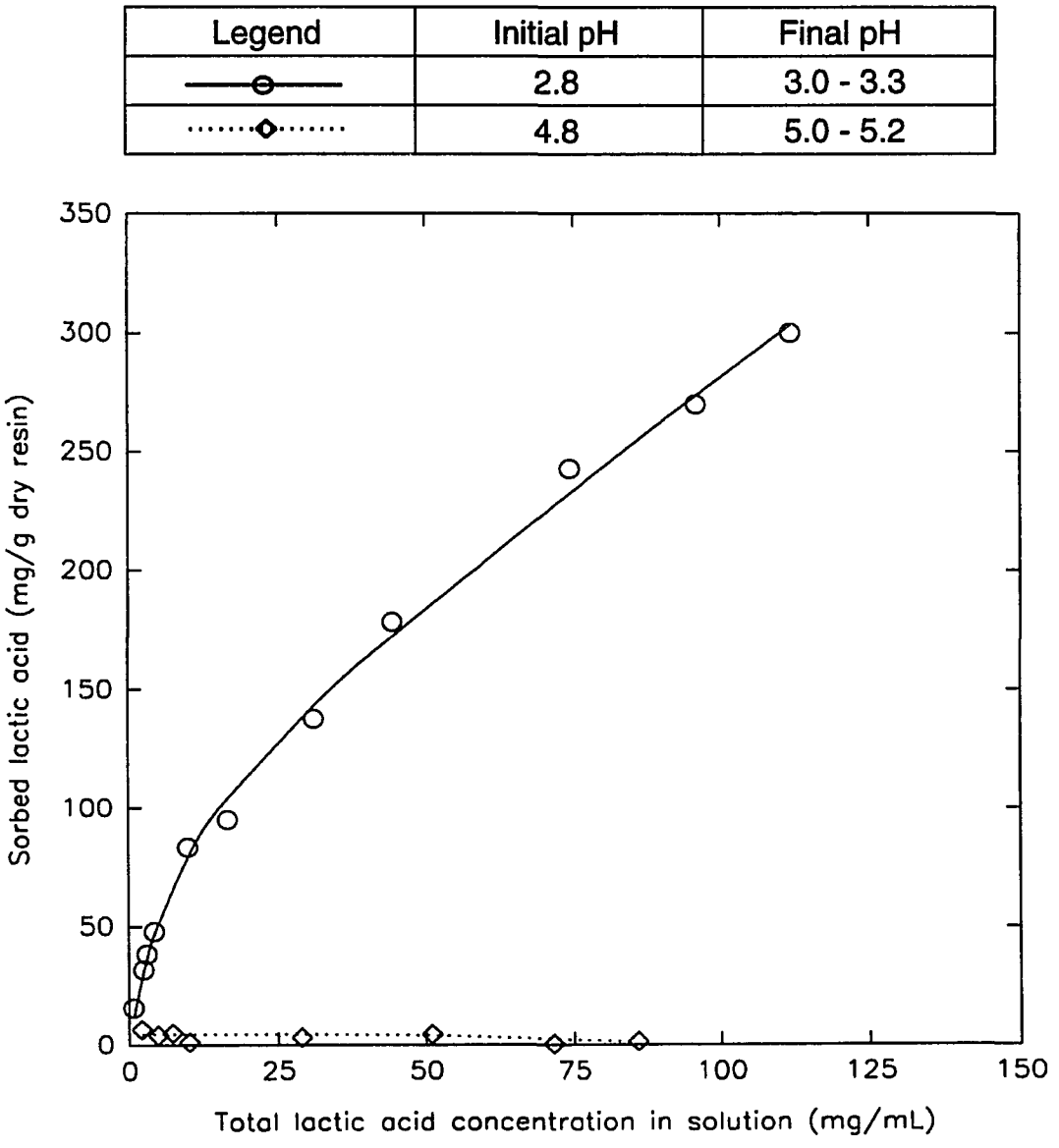


Figure 4.1. Composite sorption isotherms of lactic acid in Reillex 425

Legend	Initial pH	Final pH
—○—	2.8	3.2 - 4.8
-·-▽-·-	3.8	4.5 - 5.8
- -□- -	4.8	6.4 - 7.9
·····◇·····	5.8	7.5 - 8.0

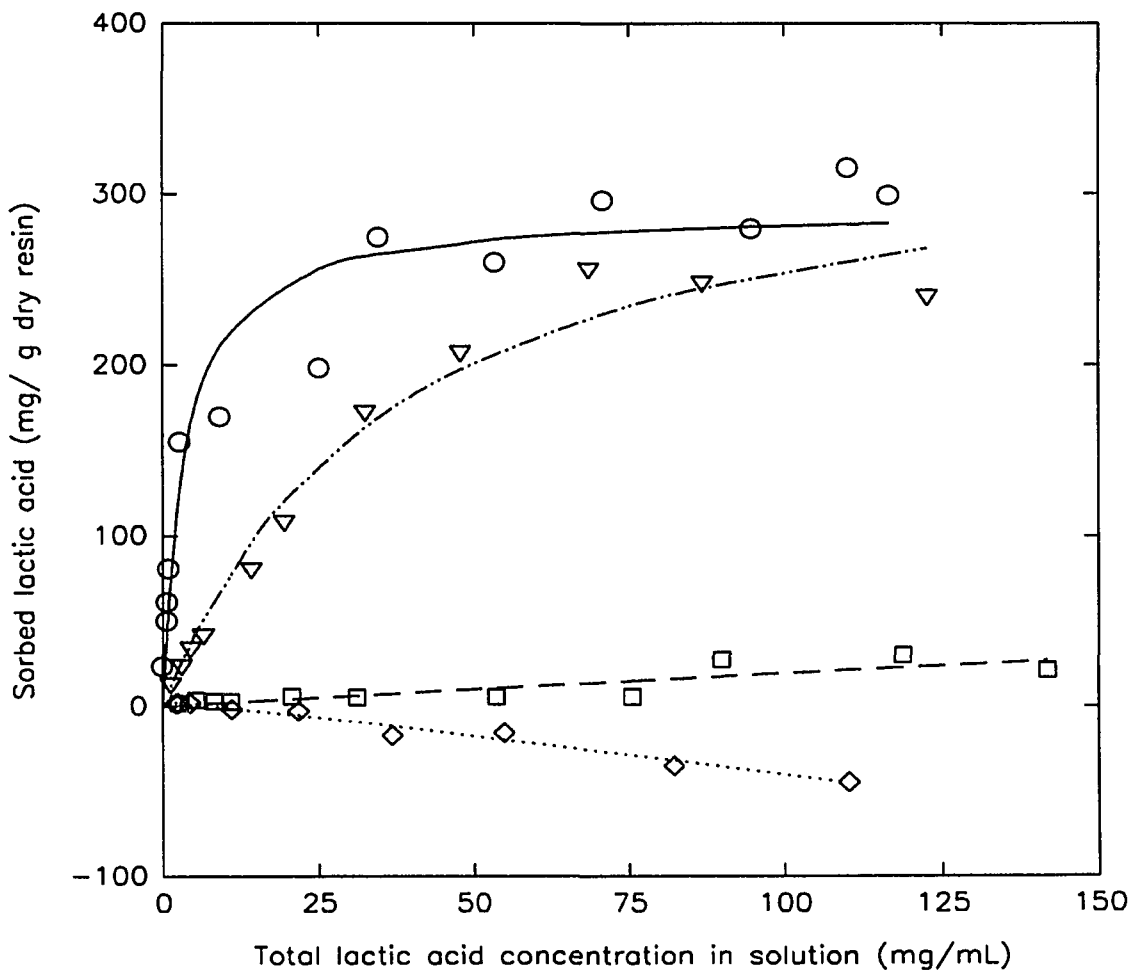


Figure 4.2. Composite sorption isotherms of lactic acid in Riedel-de-Haen VI-15

sorption, the water from the bulk solution was utilized to hydrate the resin. In addition, water was also absorbed in the micropores which are not accessible to lactic acid. As a result of this high water uptake with very little or no lactic acid adsorbed, the final lactic acid concentrations measured were higher than the initial concentrations. This effect was more pronounced at higher equilibrium concentrations of lactic acid.

The three moderate-base resins (Dowex MWA-1, XUS-40283, and XUS-43432) with styrene-DVB matrix and tertiary amine functionality behaved similarly (Figures 4.3-4.5). Their sorption capacities were higher than those of Reillex 425 and Riedel-de-Haen VI-15, but the capacities for lactic acid were just as sensitive to changes in pH. The low sorption capacities observed at high pHs (initial pHs 4.8 and 5.8) were due to the strong-base capacities of these sorbents. For Dowex WGR-2, the isotherms for solutions with starting pHs of 2.8 and 3.8, and pHs of 4.8 and 5.8 approached the same maximum values (Figure 4.6). Like the other moderate-base resins, sorption measured at high pH can be attributed to the strong base-capacity of the sorbent.

The strong-base sorbents (Dowex XUS-40196 and Amberlite IRA-958) also exhibited high capacities at low pHs although the values were much lower than those of the moderate-base sorbents (Figures 4.7 and 4.8). As expected, their capacities at high pHs were considerably higher than the moderate-base sorbents. However, there was a substantial drop in their capacities as the pH increased. The weak-base capacity of Dowex XUS-40196 was only 22% of the total capacity, but the capacity at high pH (initial pH 4.8 and 5.8) dropped by about 50%. It appears that a large portion of the strong-base capacity of Dowex XUS-40196 was not accessible to lactic acid.

Legend	Initial pH	Final pH
—○—	2.8	3.2 - 7.4
-·-▽-·-	3.8	4.3 - 8.1
- —□— -	4.8	8.0 - 9.0
·····◇·····	5.8	8.1 - 9.0

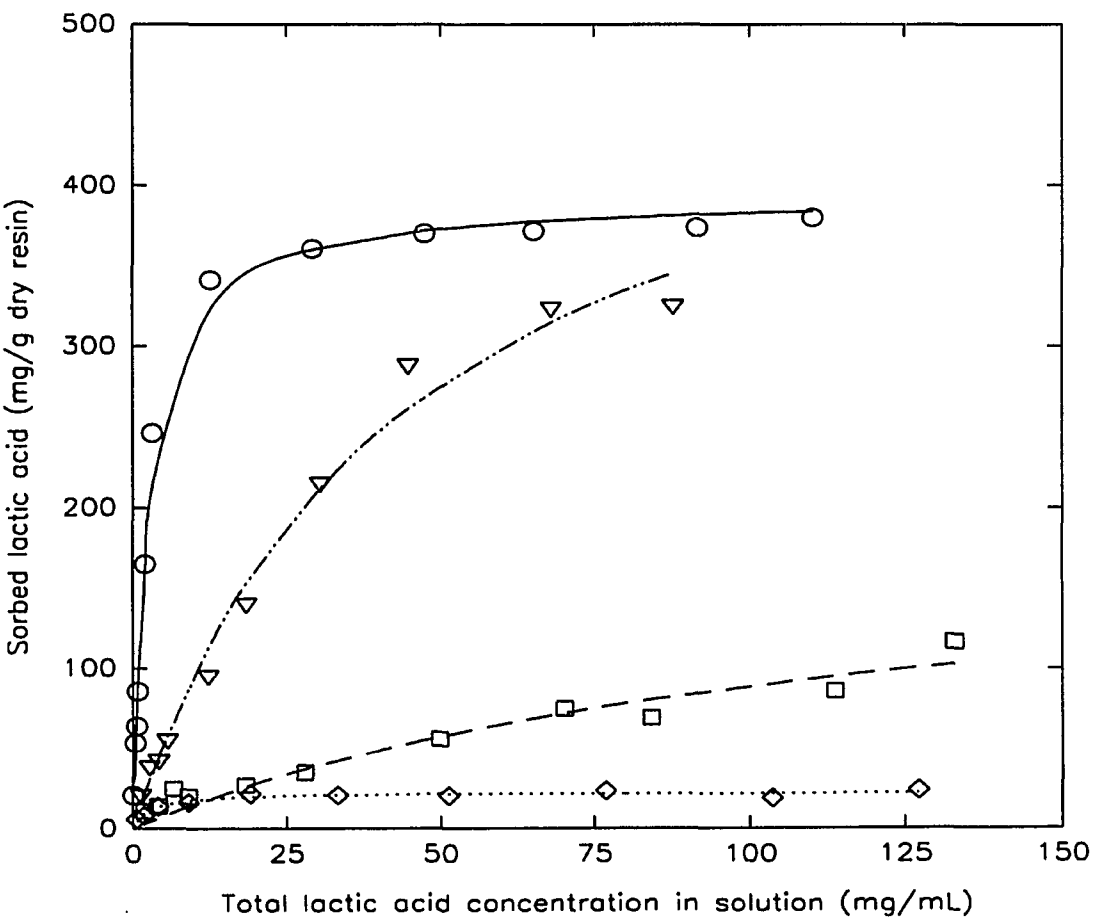


Figure 4.3. Composite sorption isotherms of lactic acid in Dowex MWA-1

Legend	Initial pH	Final pH
—o—	2.8	3.1 - 9.5
—▽—	3.8	4.4 - 10.7
—□—	4.8	7.7 - 11.3
···◇···	5.8	9.3 - 11.4

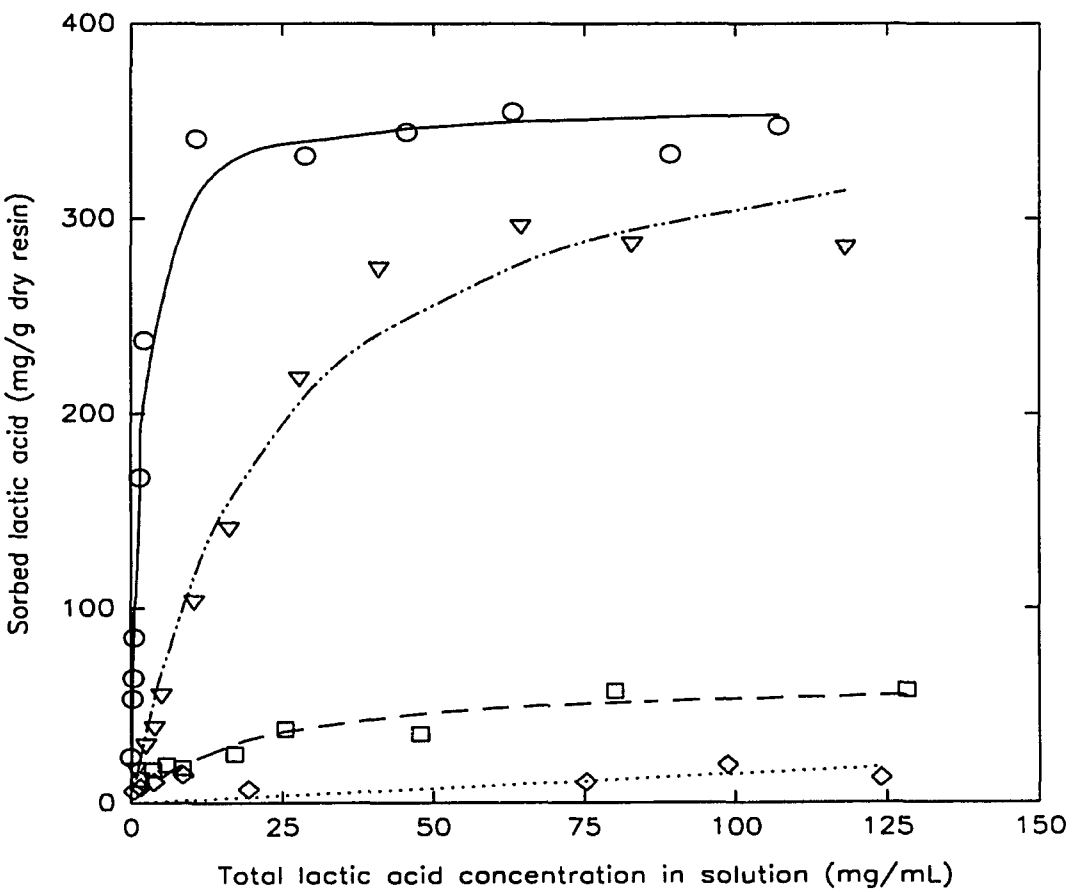


Figure 4.4. Composite sorption isotherms of lactic acid in Dowex XUS 40283

Legend	Initial pH	Final pH
—o—	2.8	3.2 - 7.5
-·▽·-	3.8	4.5 - 8.2
- -□- -	4.8	8.0 - 8.7
····◇····	5.8	8.6 - 9.2

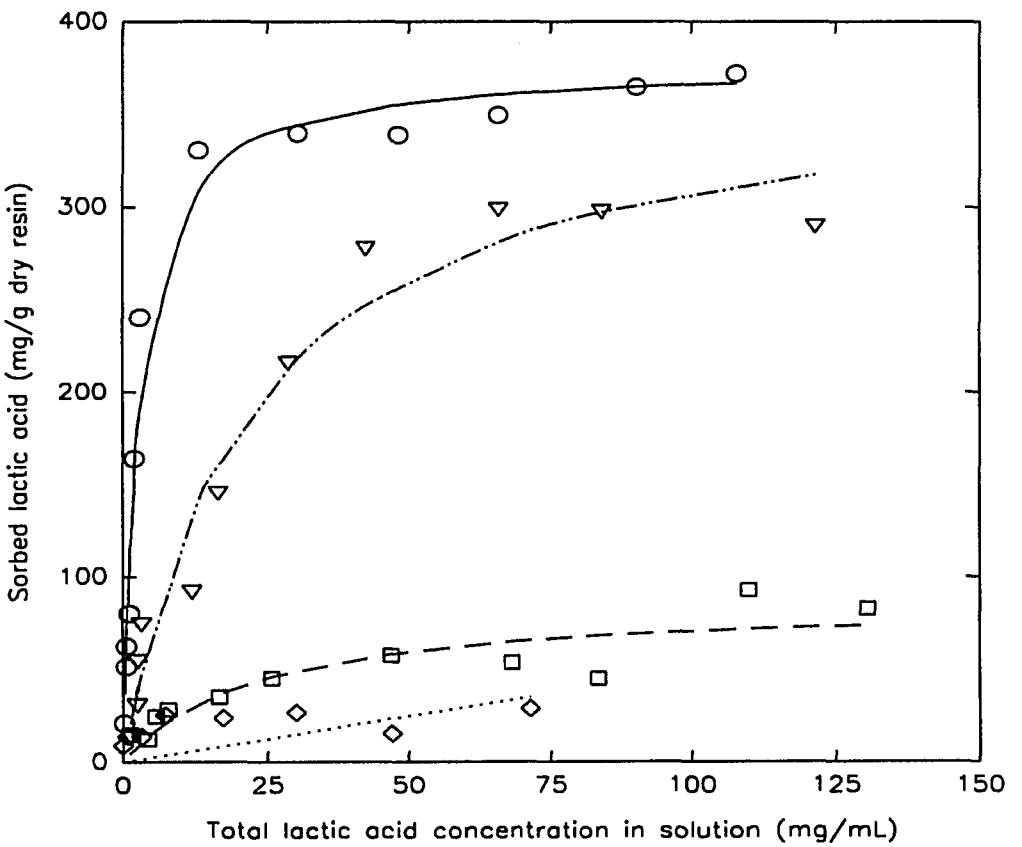


Figure 4.5. Composite sorption isotherms of lactic acid in Dowex XUS 43432

Legend	Initial pH	Final pH
—o—	2.8	3.0 - 6.7
-·-▽-·-	3.8	4.3 - 7.8
- —□— -	4.8	7.3 - 8.4
·····◇·····	5.8	8.1 - 8.4

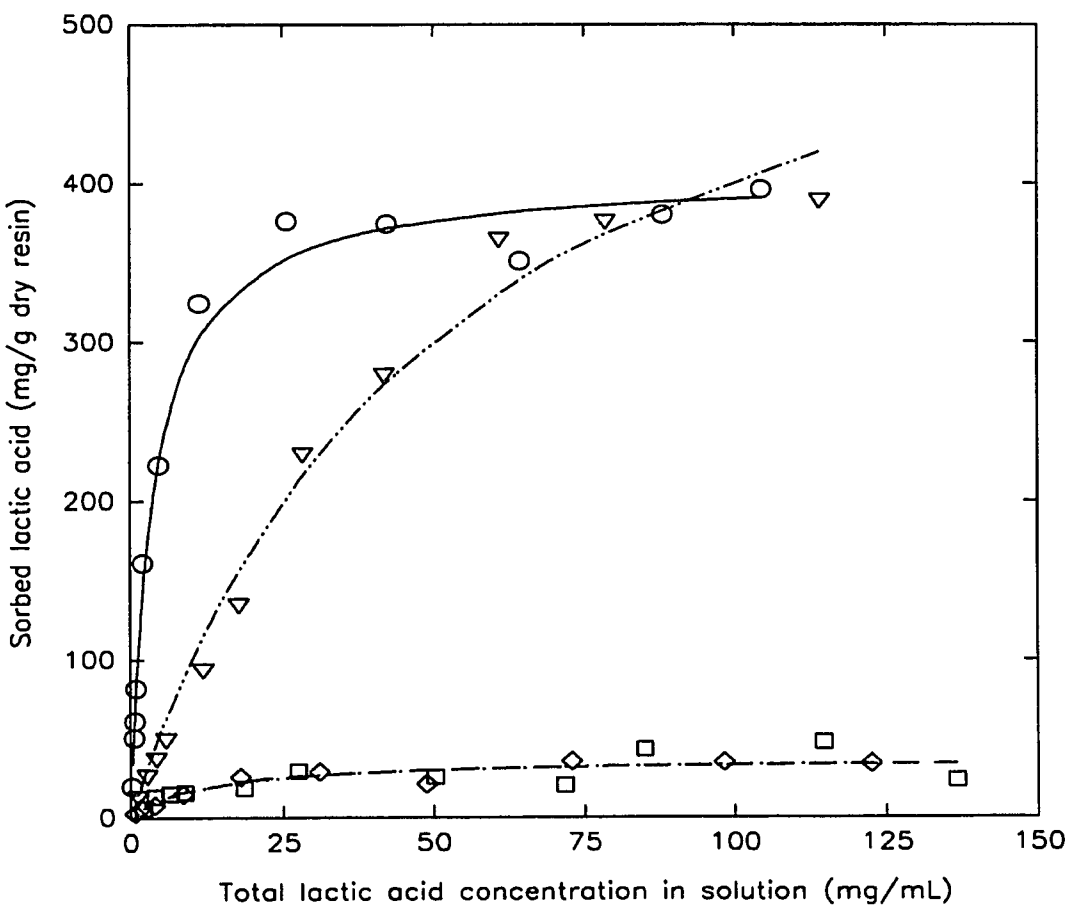


Figure 4.6. Composite sorption isotherms of lactic acid in Dowex WGR-2

Legend	Initial pH	Final pH
—●—	2.8	3.0 - 11.3
-·-▼-·-	3.8	4.0 - 12.1
- -■- -	4.8	6.4 - 8.7
····◆····	5.8	7.8 - 8.6

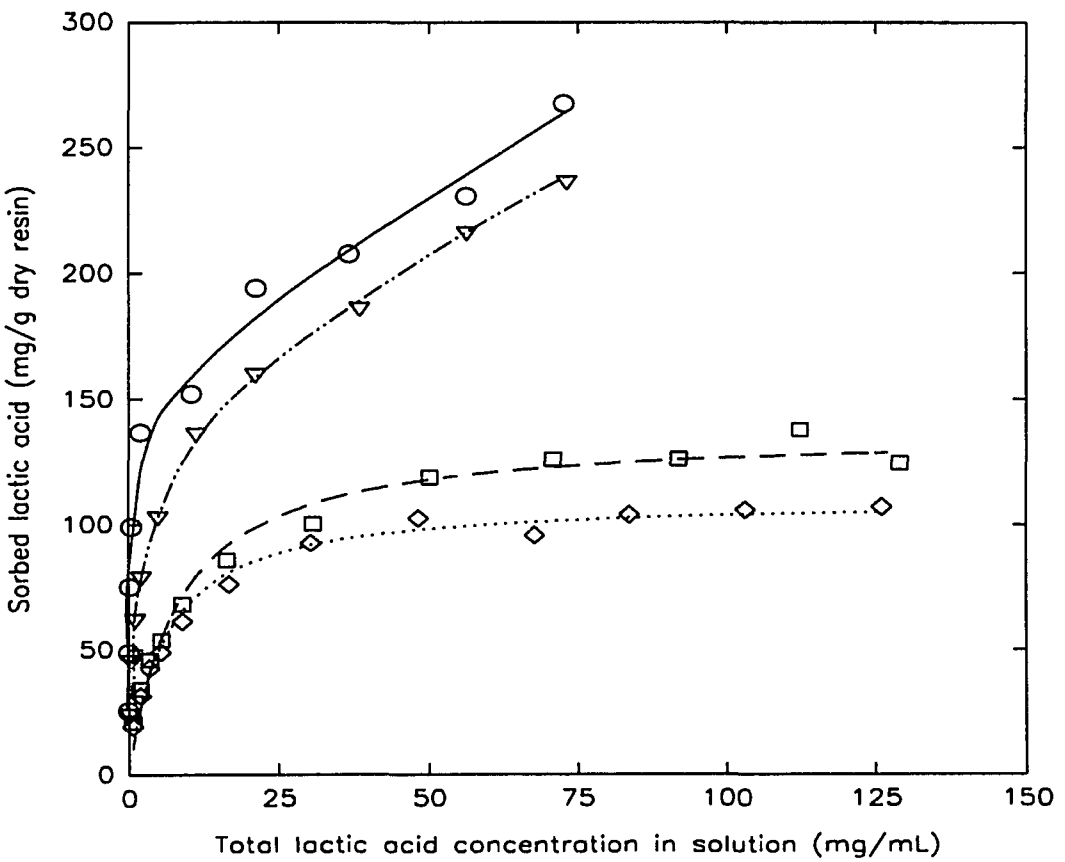


Figure 4.7. Composite sorption isotherms of lactic acid in Dowex XUS 40196

Legend	Initial pH	Final pH
—●—	2.8	3.3 - 10.6
—▼···	3.8	4.3 - 10.8
– –■–	4.8	8.9 - 11.3
····◆····	5.8	11.1 - 11.3

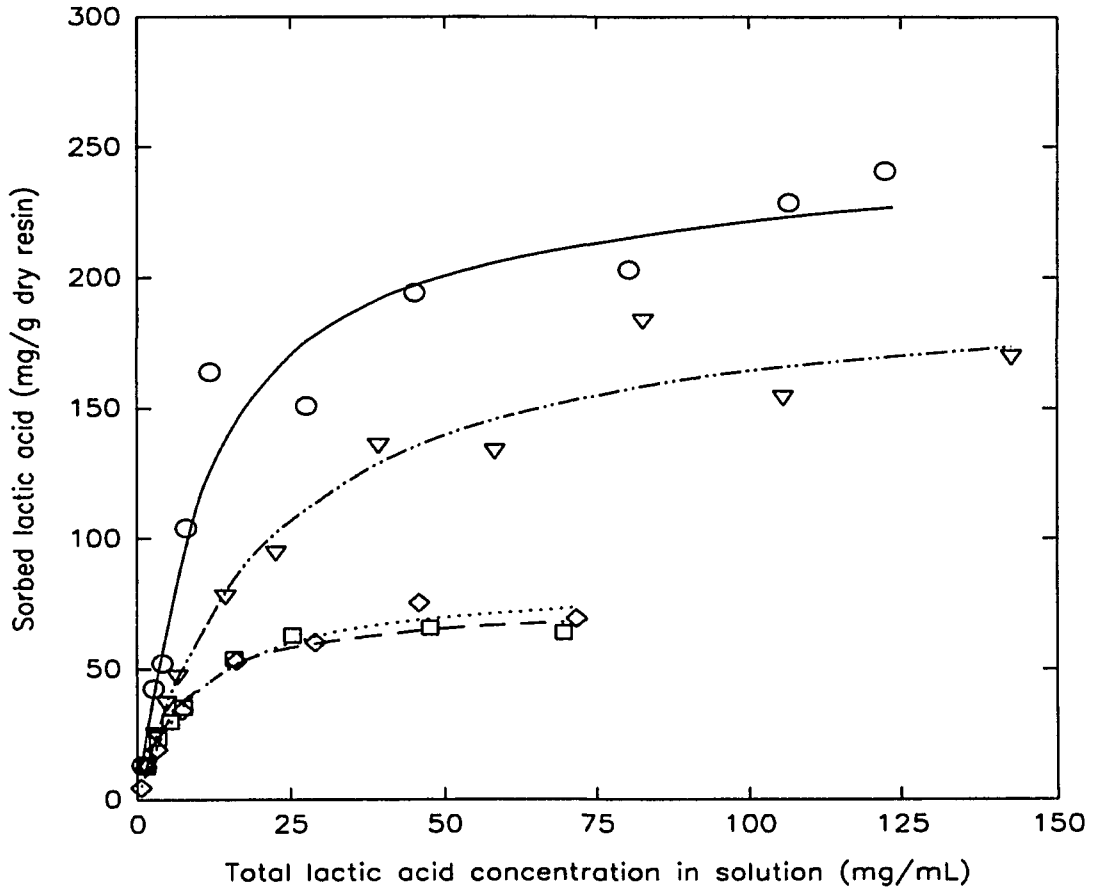


Figure 4.8. Composite sorption isotherms of lactic acid in Amberlite IRA 958

The drop in capacity for Amberlite IRA- 958 was about 70%, which was consistent with the weak-base capacity measured.

To eliminate the pH effect on lactic acid uptake by weak-and moderate-base resins, the equilibrium concentrations of free lactic acid, the species adsorbed by the resin, were calculated by using the Henderson-Hasselbach equation and the composite sorption isotherms were replotted. The Langmuir model was used to describe the competition between lactic acid and *n* molecules of water for a basic site on the sorbent (Ruthven, 1984; Garcia and King, 1989):

$$HLa_{(aq)} + B\text{-}(H_2O)_n \rightleftarrows nH_2O_{(aq)} + B\text{-}HLa \qquad (4.1)$$

where HLa represents the free lactic acid, B represents a basic functional group, and (aq) refers to the bulk liquid phase. The assumptions of the Langmuir model are: (1) only 1:1 complexes are formed, (2) only the HLa form of the lactic acid participates in the complexation reaction with B, (3) basic functional groups have equal basicity and accessibility, and (4) the number of basic functional groups is constant. With these assumptions, the composite sorption isotherm is given by the following equation:

$$q=\frac{q_m * K * C_{HLa}}{1+K * C_{HLa}} \qquad (4.2)$$

where
- q - composite uptake calculated from Equation 3.1 (mg/g)
- q_m - total sorbent capacity for lactic acid (mg/g)
- K - association constant of the (B-HLa) complex (mL/mg)

C_{HLa} - equilibrium lactic acid concentration in the bulk fluid (mg/mL)

The model parameters K and q_m were determined by a nonlinear regression fitting of the equilibrium data to Equation 4.2.

The isotherm for Reillex 425 did not exhibit a Langmuirian behavior (Figure 4.9a). A better fit was obtained when a linear term (K_1*C_{HLa}) was added to the Langmuir model (Equation 4.3). Although the linear term may be interpreted as multi-

$$q=\frac{q_m*K*C_{HLa}}{1+K*C_{HLa}}+K_1*C_{HLa} \qquad (4.3)$$

layer sorption, this may not be the case here. The high solubility of lactic acid in water will probably prevent multilayer formation. Tung (1993) used lactic acid solutions at its natural pH with concentrations up to 12 wt %. The data fit the Langmuir model very well and a q_m of 0.26 g/g dry sorbent (2.86 meq/g) was reported, which is about half of the total capacity of the sorbent. The low capacity for lactic acid was probably due to steric constraints. Lactic acid is much larger than HCl, and therefore, unaccessible to all the available sorption sites in the sorbent. The increase in sorption as the lactic acid concentration increased may have been due to the corresponding increase in swelling of the resin, making more sites accessible for binding in the process. Riedel-de-Haen VI-15 (Figure 4.9a) fit the Langmuir model very well. The calculated K value was much higher than that of Reillex 425 (Table 4.2). The maximum sorption capacity (q_m) for lactic acid was less than half of its HCl capacity and can be attained from solutions with concentrations as low as 10 mg lactic acid/mL.

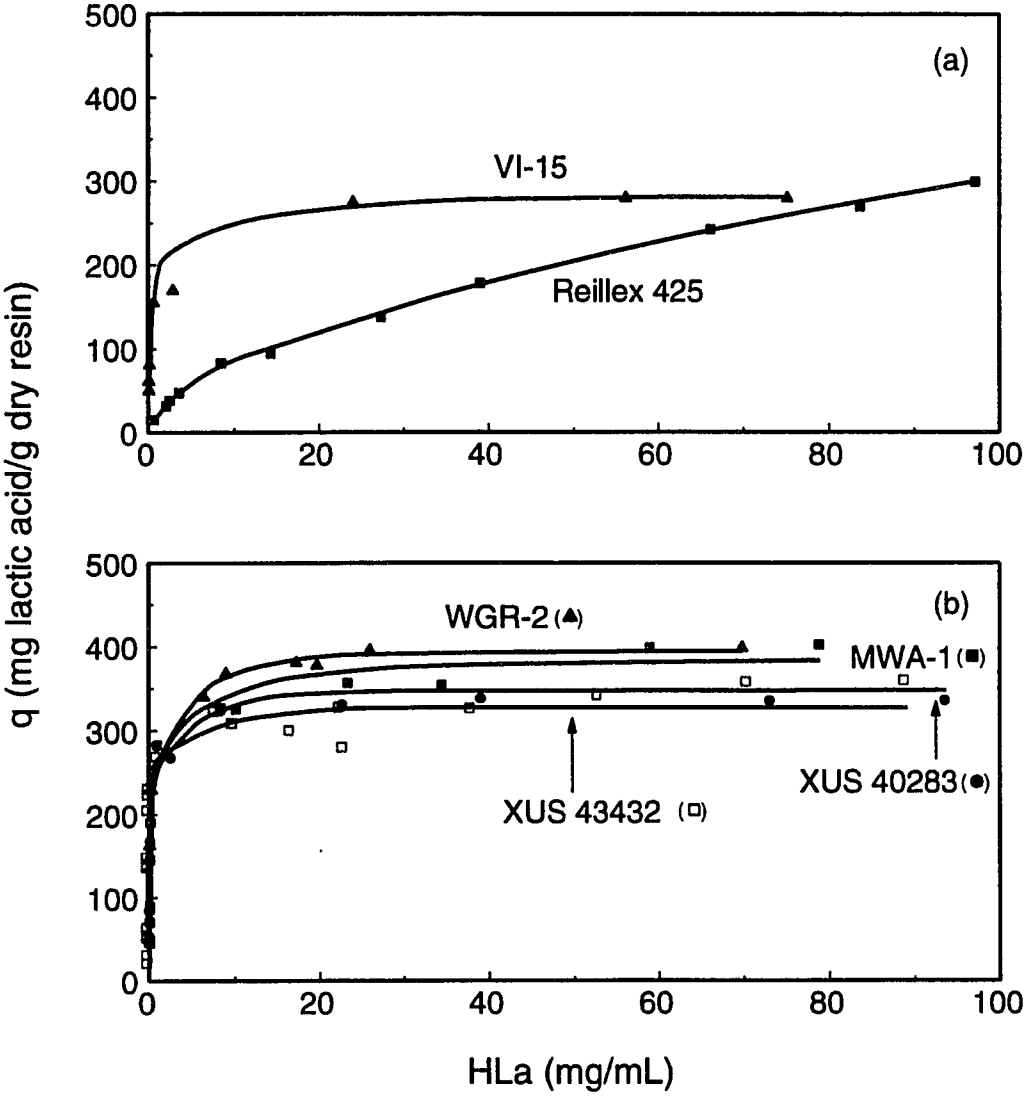


Figure 4.9. Composite sorption isotherms of lactic acid in (a) weak-base, and (b) moderate-base sorbents

Table 4.2. Calculated values of the Langmuir model parameters and resin capacities

Resin	K[a] (mL/mg)	q_m[a] (mg/g dry resin)	Total capacity for HCl (meq/g dry resin)	Total capacity for lactic acid[b] (meq/g dry resin)
Reillex 425	0.2 ± 0.0 2.1[c] ± 0.1	102 ± 11	6.1	N/A
VI-15	2.2 ± 0.7	280[d]	8.0	3.1
MWA-1	8.4 ± 1.7	365 ± 11	4.9	4.0
WGR-2	10.4 ± 3.8	376 ± 16	8.3	4.2
XUS 40283	16.5 ± 3.3	335[d]	4.5	3.7
XUS 43432	16.9 ± 5.6	328 ± 13	4.2	3.6
XUS 40196	7100 ± 2300 0.005[c] ± 0.004	120 ± 8 420[e] ± 200	4.6	N/A
	0.2 ± 0.0	110 ± 3	3.6[f]	1.2
IRA 958	9930 ± 6700 0.03[c] ± 0.02	105 ± 16 158[e] ± 26	3.4	N/A
	0.1 ± 0.0	84 ± 4	1.2[f]	0.9

[a] Mean ± standard error.
[b] Calculated from q_m values.
[c] Values of K_1 or K_2 in the modified Langmuir model.
[d] Value used in Langmuir equation.
[e] Value of q_{m2} in the modified Langmuir model.
[f] Strong-base capacity only.
N/A means not applicable.

The moderate-base sorbents also conformed very well to the Langmuir model (Figure 4.9b). Their K and q_m values were basically similar despite the differences in measured strong-base capacities. The lactic acid capacities of Dowex MWA-1, Dowex XUS-40283, and Dowex XUS-43432 were slightly lower than their HCl-capacity whereas the lactic acid capacity of Dowex WGR-2 was only about half of the capacity for HCl. The low capacity for lactic acid is again due to inaccessibility of the sorption sites since Dowex WGR-2 is also partially microporous.

Equation 4.1 must be rewritten to reflect the sorption mechanism in strong-base sorbent. The quaternary amine can adsorb both free lactic acid (HLa) and lactate (La^-) as shown in the following equations:

$$HLa_{(aq)} + BOH \rightleftarrows H_2O + BLa \qquad (4.4)$$

$$MLa_{(aq)} + BOH \rightleftarrows MOH + BLa \qquad (4.5)$$

BOH is the strong-base in the resin in OH^- form and MLa is the lactate salt. Equation 4.4 is an acid-base neutralization, whereas Equation 4.5 represents a typical ion exchange reaction. Dowex XUS-40196 and Amberlite IRA-958 contained considerable amounts of weak-base capacity; therefore, Equation 4.1 also applies. The presence of weak- and strong-base sorption sites violates the assumption of equal basicity of sorption sites. At pHs below 3, where mostly free lactic acid exist, both weak- and strong-base capacities are utilized. Tung (1993) used a two-site sorption model

$$q=\frac{q_m * K * C_{HLa}}{1+K * C_{HLa}}+\frac{q_{m2} * K_2 * C_{HLa}}{1+K_2 * C_{HLa}} \qquad (4.6)$$

(Equation 4.6) to describe sorption of lactic acid on a polyfunctional Duolite A7 resin.

It was assumed that each type of binding site sorbs acid independent of each other. An equivalent K (K_{avg}) was calculated from the average of the two K values weighted by the corresponding q_m values. The same model was applied here to describe the sorption of free lactic acid on weak-base and strong-base functional groups.

At pHs above 6, where mostly lactates are present, only the strong-base capacity is used for sorption. The Langmuir model is still valid and C_{HLa} was replaced with C_{la^-}. When considerable amount of each species are available, there will be some competition between free lactic acid and lactate for the sorption sites because the quaternary ammonium groups can adsorb either one. However, sorption of free lactic acid will be favored (acid-base neutralization reaction vs ion exchange) since the sorbents were prepared in OH^- form. This case may require a more complicated model to address two-site and competitive sorption mechanisms and will not be considered here.

The sorption isotherms of the strong-base resins (Dowex XUS-40196 and Amberlite IRA-958) from solutions with low pH (initial pH < 3) fit the two-site Langmuir model (Figure 4.10a). The value of K_2 were very small and were not representative of K values obtained for tertiary amines. The high values of K and the large standard errors on these values overshadowed the K_2 values. The K_{avg} values for Dowex XUS-40196 and Amberlite IRA-958 were 1578 and 3964 mL/mg, respectively (Table 4.2). These K_{avg} values were two orders of magnitude greater than the K values for tertiary amines in moderate base resins .

The isotherms of the strong-base resins at high pH fit the Langmuir model very well (Figure 4.10b). Although the strong-base capacity of Dowex XUS-40196 was

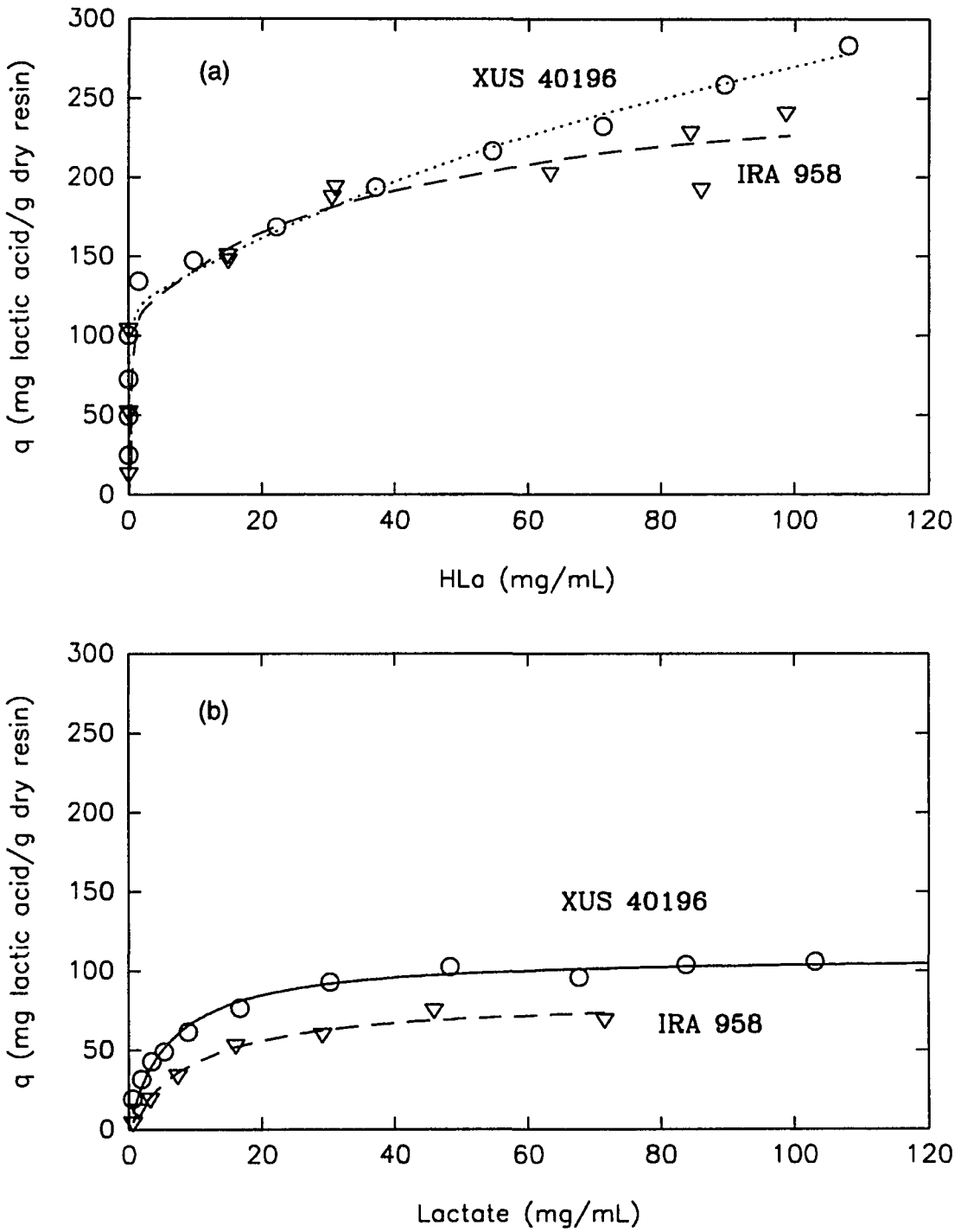


Figure 4.10. Composite sorption isotherms of lactic acid in Dowex XUS 40196 and Amberlite IRA 958 at (a) pHs < 3, and (b) pHs > 6

three times that of Amberlite IRA-958, its capacity for lactate was only slightly greater than that of Amberlite IRA-958. Only 33% of the strong-base capacity of Dowex XUS-40196, a gel-type resin, was utilized for sorption compared with 75% for Amberlite IRA-958, a macroporous resin. The accessibility of strong-base sites in Amberlite IRA-958 also accounts for the high K value despite its having 65% weak-base capacity. It is also interesting to note that the K values were much lower than those obtained for moderate-base sorbents, implying that ion exchange interactions are less specific than of acid-base interactions. The maximum capacities were achieved at lactate concentrations above 30 mg/mL, three times the concentration needed for Riedel-de-Haen VI-15 and moderate-base sorbents.

Fixed-bed sorption

Determining the breakthrough curves is a common practice in designing an adsorption process. The breakthrough profiles of three resins, representing each basicity group are shown in Figure 4.11. The breakthrough profiles for Riedel-de-Haen VI-15 and Dowex MWA-1 clearly showed that these sorbents bind only the free lactic acid form. Two distinct concentration plateaus were observed in Riedel-de-Haen VI-15 (at pH 3.8), and MWA-1 (at pH 3.8 and 4.4). The measured outlet concentration of the first plateau corresponded to the concentration of the lactate anion in the feed at the specified pH, whereas the concentration of the second plateau matched that of the total lactic acid in the feed. The early breakthroughs observed for both resins at pHs greater than 2 were due to lactate breakthrough at void volume. In spite of the slight shift in the breakthrough points, the breakthrough profiles of Dowex XUS-40196 were

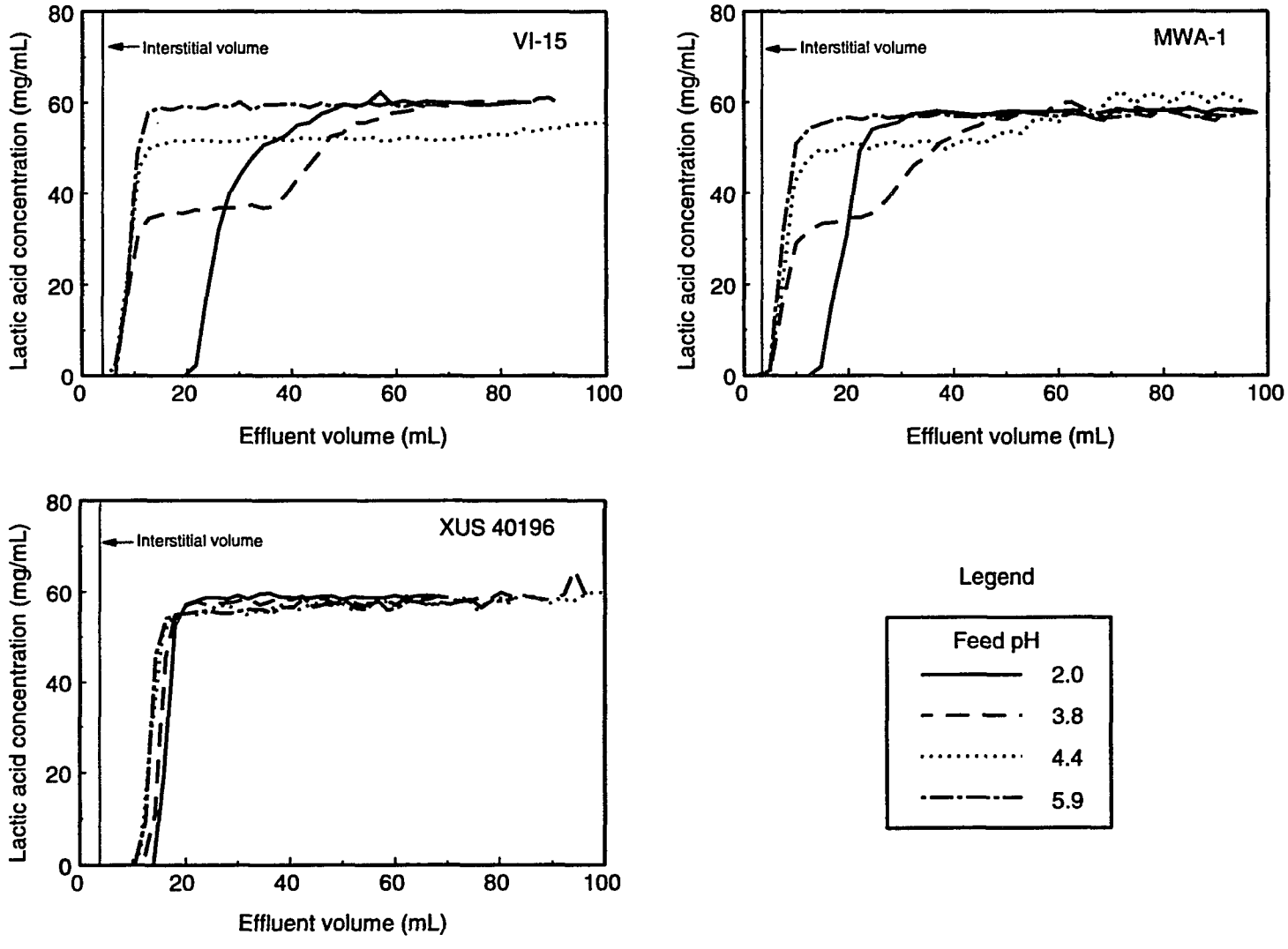


Figure 4.11. Breakthrough profiles of lactic acid feed (60 mg/mL) at different pHs

similar and were not significantly affected by the pH of the feed. The strong-base functional group of Dowex XUS-40196 sorbent interacts with both free lactic acid and lactate. With free lactic acid, the mechanism is an acid-base neutralization reaction, whereas with lactate, an anion-exchange with OH^- prevails. As a result, no early breakthrough at void volume was observed with this sorbent, and a single saturation concentration at 60 mg/mL was measured.

The saturation capacities (q_s) were calculated and plotted against pH (Figure 4.12). The saturation capacities of Riedel-de-Haen VI-15 at different feed pHs were always higher than those of Reillex 425 (Figure 4.12a). Chanda *et al.* (1985) observed the same trend in their study of carboxylic acid sorption with polybenzimidazole and poly(4-vinylpyridine) sorbents. The capacities of Riedel-de-Haen VI-15 and Reillex 425 decreased with increasing pH of the lactic acid feed. Significant drops in saturation capacities of Dowex WGR-2 and Dowex XUS-40283 occurred at pHs > 4.5, whereas the capacity Dowex of MWA-1 slowly decreased throughout the pH range investigated (Figure 4.12b). This is contrary to the higher strong-base capacity measured for these sorbents since Dowex XUS 40283 has higher strong-base capacity than Dowex MWA-1. The experimental data indicated that the weak-base sorbents can be used up to pH 3.8 without substantial loss in capacity, while moderate-base resins can be used up to pH 4.5. It must be emphasized, however, that to minimize leakage of lactate, these resins should be used at pHs $\leq$ 2.8. The sorption capacity of Dowex XUS-40196 remained high despite the high weak-base capacity measured for this resin (Figure 4.12c).

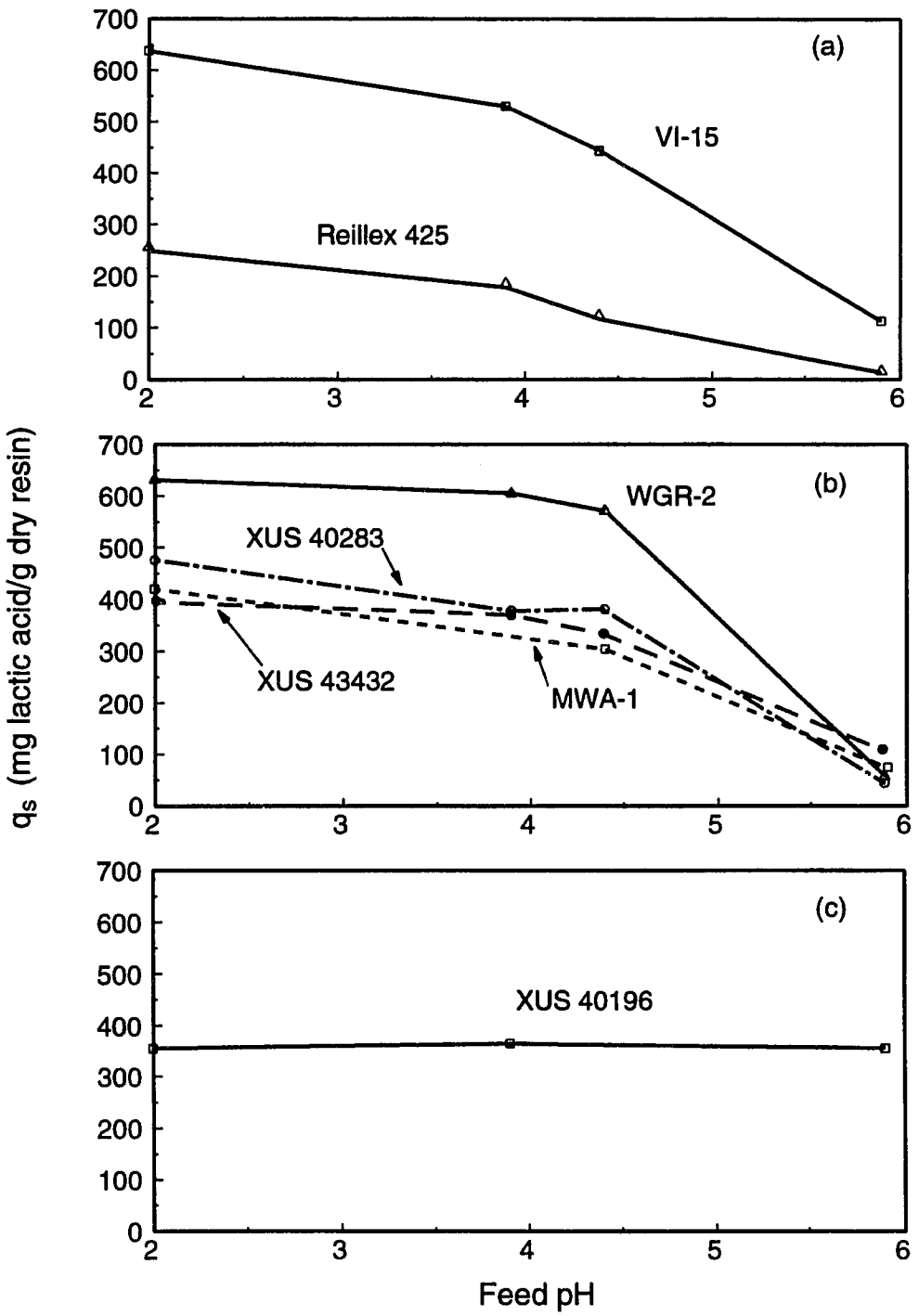


Figure 4.12. Effect of pH on saturation capacity for lactic acid in (a) weak-base, (b) moderate-base, and (c) strong base sorbents

The sorption capacities estimated from the breakthrough curves were generally higher than those from the batch experiments. There are two reasons for this discrepancy. First, the saturation capacity values calculated by Equation (3.2) also include the lactic acid in the solution absorbed in the pores of the sorbents in addition to adsorbed lactic acid. Second, as discussed earlier, the composite isotherm tends to underestimate the sorption capacity, especially for low-specificity sorbents. The greatest discrepancy between the batch and fixed-bed estimated capacities was observed with Riedel-de-Haen VI-15, which exhibited the highest water uptake. The actual saturation capacity of the resin, which represents the specifically adsorbed acid, can be estimated by subtracting the amount of lactic acid retained in the pores from the total sorption capacity. The pore volumes of hydrated Dowex MWA-1 and Reillex 425 resins were estimated by drying them at 110°C and then correcting the respective q_s values for the amount of lactic acid retained in the pores. The corrected saturation concentrations were similar to the total sorbent capacities (q_m) calculated from the composite isotherms. The exact resin pore volume is difficult to determine because of the swelling of the resin in the presence of lactic acid.

Section summary

Weak- and moderate-base sorbents should be used at feed pH below the pK_a of lactic acid (3.86), preferably one to two pH units lower, to minimize leakage of lactate from the column. Of the weak-base sorbents, Riedel-de-Haen VI-15 exhibited significantly greater sorption capacity for lactic acid than Reillex 425. The moderate-

anion exchangers are applicable over a broader pH range with no significant reduction in capacities within the pH range studied.

The high lactic acid capacity of Riedel-de-Haen VI-15 and the ease of regeneration by using low-boiling alcohols make it an attractive sorbent for lactic acid recovery. To maximize the sorbent capacity, the feed stream must be acidified first. Acidification by adding mineral acid to the broth is not desirable because the mineral acid competes with lactic acid for the sorption sites. Another problem that requires consideration is improving the physical stability of the sorbent. Excessive swelling and shrinking of the sorbent during sorption and desorption cycles make it susceptible to attrition.

Recovery of Lactic Acid from Fermentation Broth

Broth acidification

Broth acidification by using a cation exchanger is a good alternative to adding mineral acid directly to the broth because no competing acids are introduced. The cation exchanger can also effect some purification by adsorbing certain impurities besides cations. The Duolite C-464 column was effective in lowering the pH of the broth (Fig. 4.13). The pH of the fraction at the point of breakthrough of lactic acid was around 3.0. The lowest pH achieved was 2.1. Fractions starting at breakthrough were pooled until the pH of the pooled fractions was about 2.8 (one pH unit below the pKa of lactic acid). The last fraction added to the pool had a pH of 3.2 and the lactic acid concentration was about the same as that of the feed. The total volume of the pool

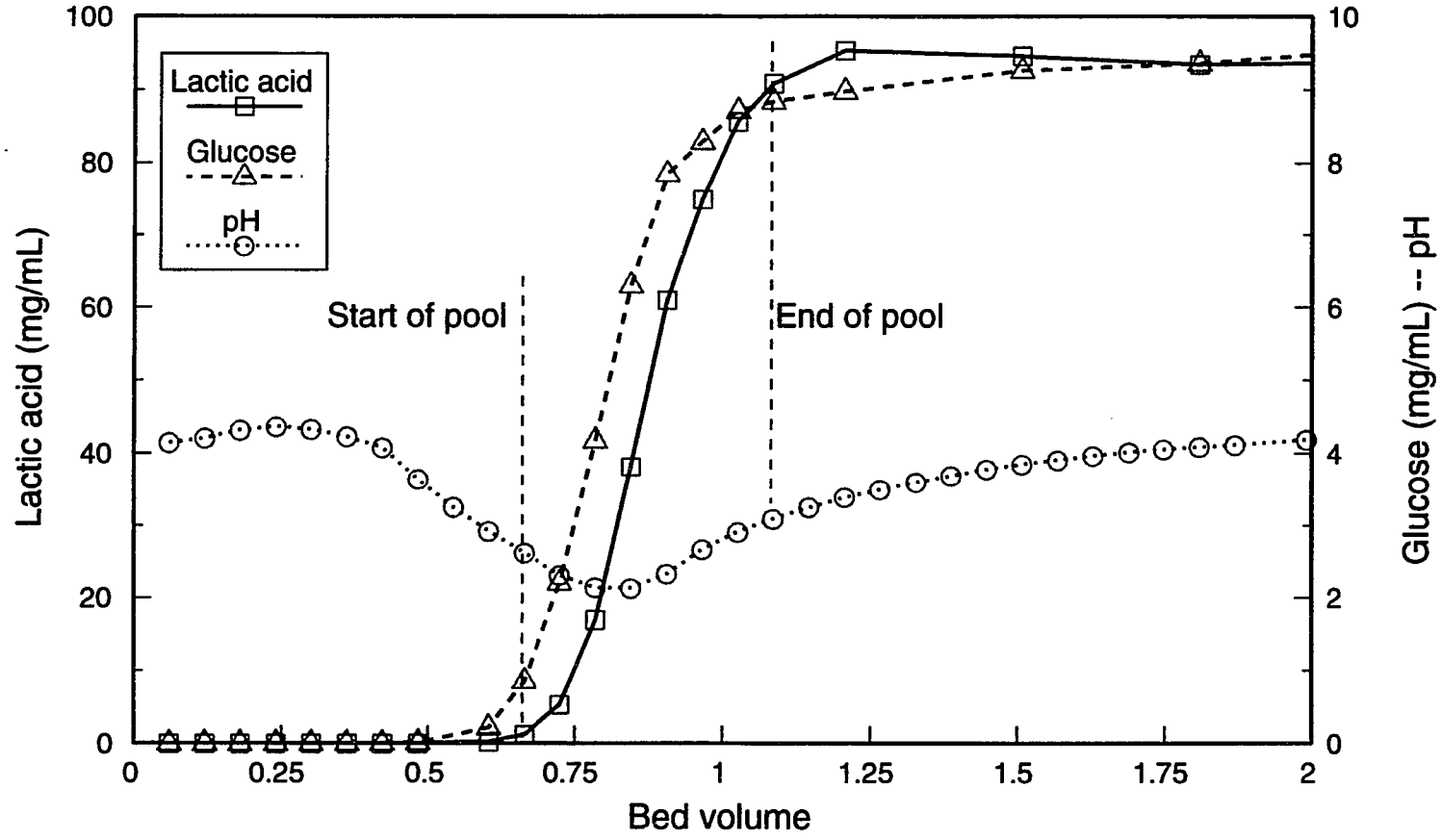


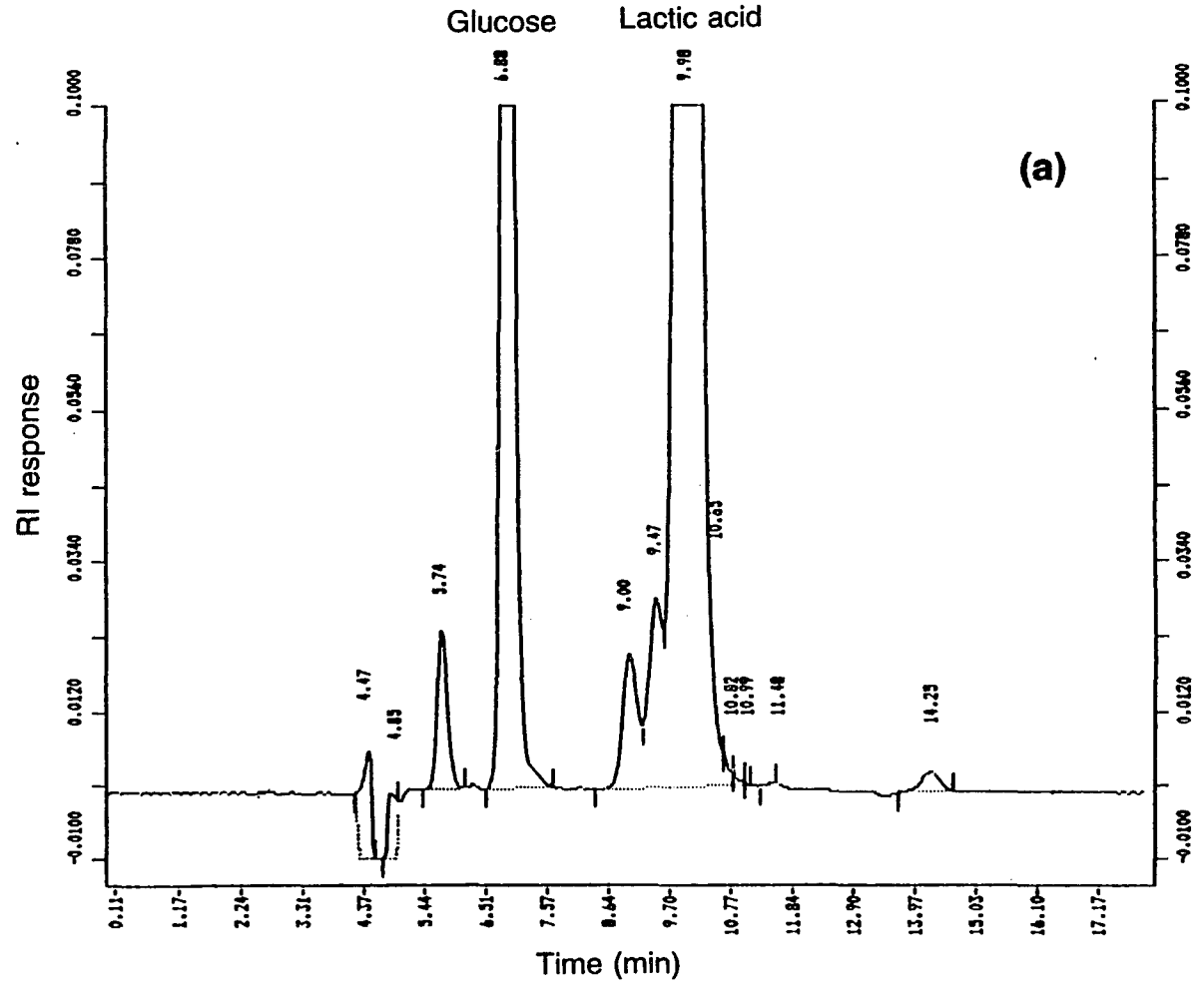
Figure 4.13. Elution profile of model broth on Duolite C 464 column

was about 40% of the column bed volume. The pooled acidified broth had a pH of 2.9 and contained 58.2 mg/mL lactic acid and 6.8 mg/mL glucose. Despite the dilution, the concentration of lactic acid was still above the minimum (about 10 mg/mL) needed to attain q_m for all three basic sorbents. The cut-off pH of the acidified broth may be lowered further as long as the lactic acid concentration does not fall below 10 mg/mL.

Duolite C-464 also removed the colored components, as manifested by the marked color reduction in the broth (from amber to faint yellow). The HPLC chromatograms (Figures 4.14a and 4.14b), however, show no significant decrease in the number of broth components. The faint yellow color in the pooled acidified broth came from the fractions approaching the cut-off point. By lowering the cut-off point closer to the minimum concentration required to obtain q_m, the amount of colored impurities loaded into the basic sorbents will be reduced. These compounds may not be adsorbed by the basic sorbents, but may still appear in the concentrated product if not removed completely during the wash step. If they do adsorb on the basic sorbent, they may elute with lactic acid during desorption.

Column regeneration by using carbonic acid

One advantage of weak-acid cation exchanger is that almost any acid, including carbonic acid, may be used to regenerate it (Kunin, 1984). This prospect is very appealing considering that the generation of waste salt can be minimized. At atmospheric pressure, the NH_4HCO_3 can be easily decomposed to NH_3 and CO_2 at 60°C (Walkup *et al.*, 1991). This possibility was explored by regenerating the exhausted Duolite C-464 column by using carbonic acid.


Glucose
Lactic acid
(a)
RI response
Time (min)

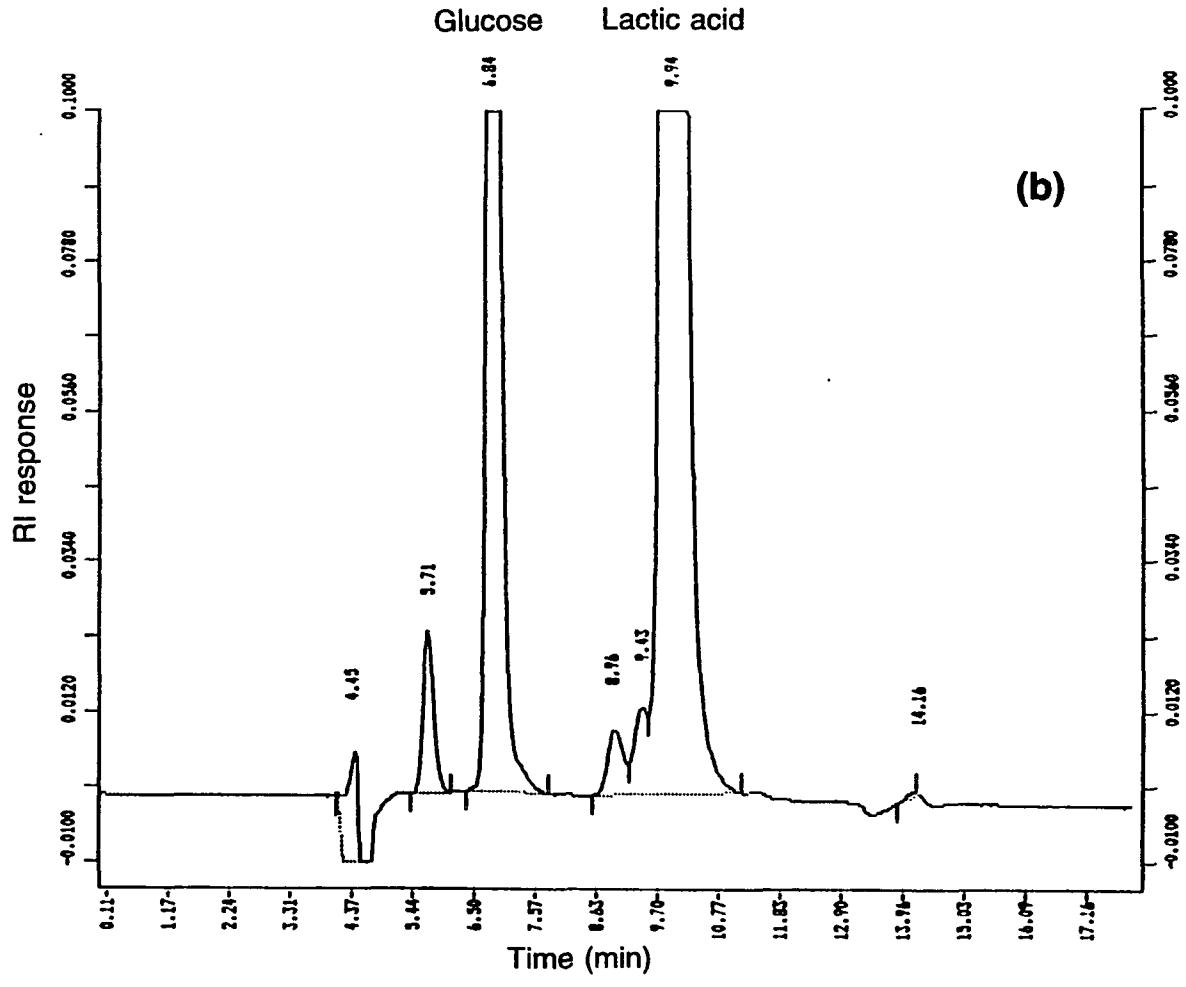


Figure 4.14. Chromatogram of (a) model lactic acid broth, and (b) Duolite C-464 column-acidified model lactic acid broth

Ten percent aqueous ammonium lactate (with pH 6.3) was acidified by using the Duolite C-464 column regenerated with 5% HCl or carbonic acid. The pH profile of the acidified broth from HCl-regenerated column showed that a minimum pH of about 3.1 was achieved (curve labelled HCl in Figure 4.15) while a minimum pH of about 4.5 was obtained from the carbonic acid-regenerated column (curve labelled H_2CO_3 -25°C in Figure 4.15). This indicated that carbonic acid did not regenerate the column to H^+ form completely. Regeneration was significantly improved when the column temperature was raised to 65°C. This time, the minimum pH of the acidified broth obtained was about 3.5 (curve labelled H_2CO_3 - 65°C in Figure 4.15). However, the desired pH of $\leq$ 2.8 still could not be attained.

The same procedure was repeated by using the model broth at pH 4.5 instead of pure ammonium lactate solution with a pH of 6.3. The back pressure was also increased to 2758 kPa to keep more carbonic acid in solution at 65°C. Amberlite IRC-50, a cation exchanger that is slightly weaker than Duolite C-464, was also evaluated. The lowest pHs obtained from sulfuric acid-regenerated column were 2 and 2.5 for Duolite C-464 and IRC-50, respectively (Figures 4.16a and 4.16b). This difference is due to the higher acidity of Duolite C-464 (pK=5.5) than IRC-50 (pK=6.1). No improvement in minimum pH was observed in carbonic acid-regenerated columns. The pH minima were still about 3.5. The shift of the minimum pH was longer in Duolite C-464 than in IRC-50, indicating that Duolite C-464 is more difficult to regenerate with carbonic acid than IRC-50. The model broth also contained divalent cations (Mg^{2+} and Mn^{2+}), amino acids, and peptides, which could not be desorbed easily by carbonic acid. At 1724 kPa, the pH of carbonic acid solution is only 3.3

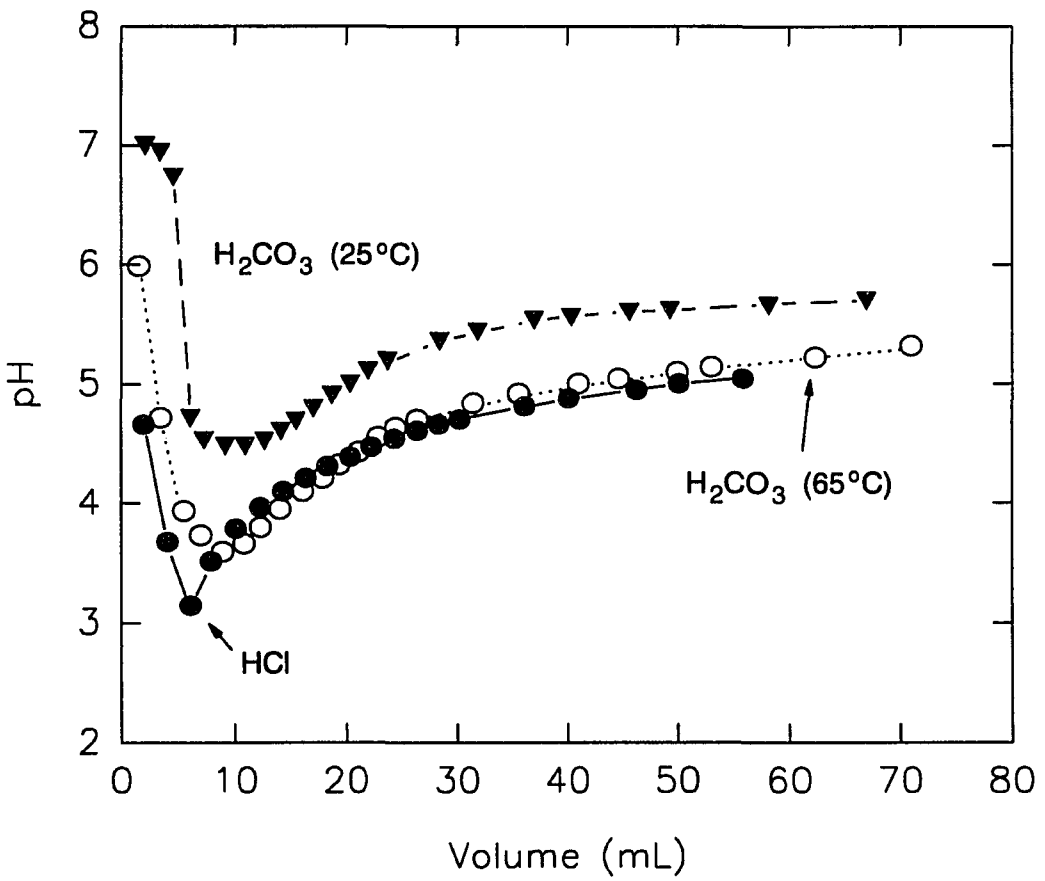


Figure 4.15. pH profiles of acidified effluent of lactate (pH 6.5) from Duolite C 464 column after regenerating with HCl and H_2CO_3

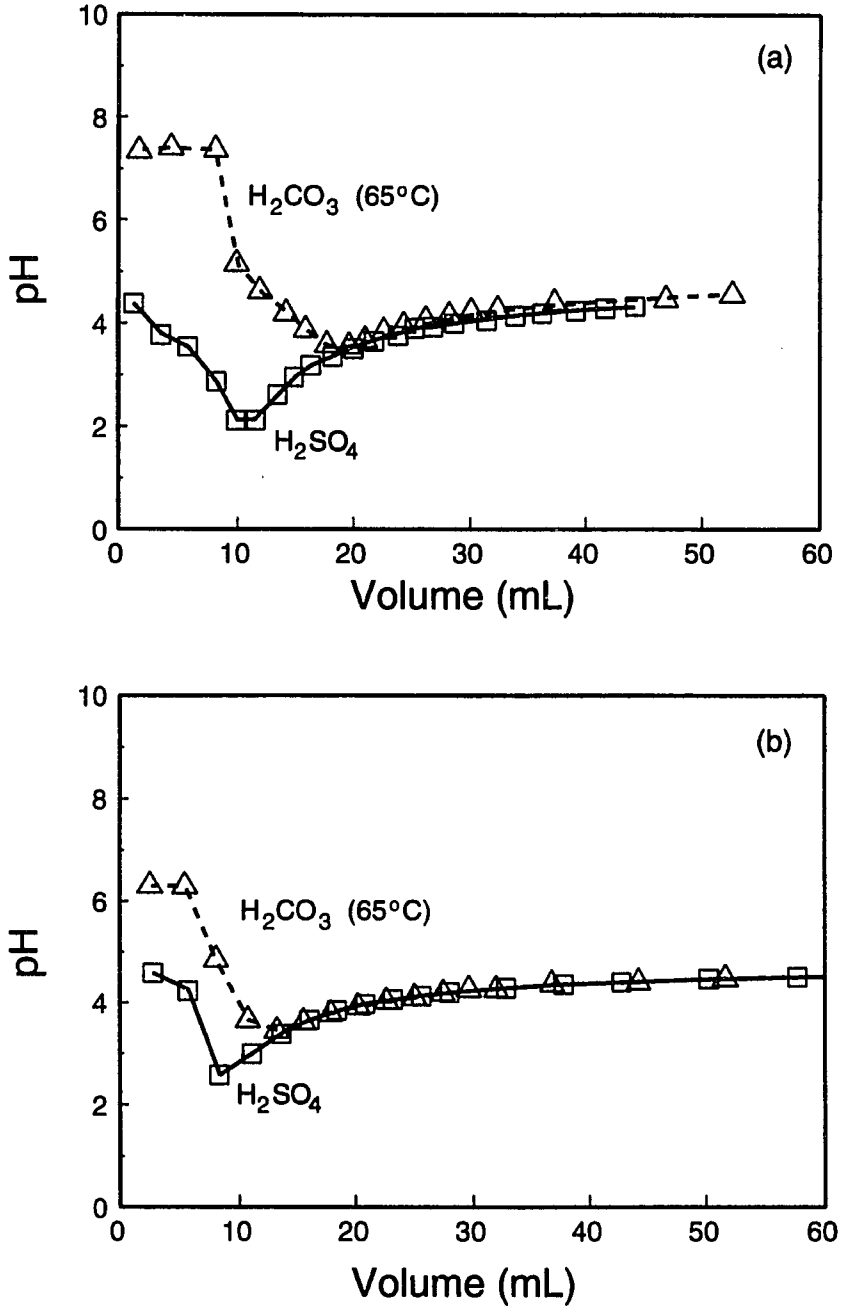


Figure 4.16. pH profiles of acidified model broth effluent from (a) Duolite C 464, and (b) IRC 50 after H_2SO_4 and H_2CO_3 regeneration

(Meyssami *et al.*, 1992). The H^+ concentration is not high enough to effectively regenerate the column.

Recovery of lactic acid from acidified broth by using basic sorbents

Riedel-de-Haen VI-15. The resin column required 6 BV of acidified broth to reach saturation (Figure 4.17). At this point, the bed volume increased by 30%. No glucose was detected in the water-rinse effluent after 4 BV. About 55% of the total lactic acid in the column went out with the rinse water. In practice, this fraction can be recycled back to the adsorption column since the pH was still low - even lower than the pH of the acidified broth. The slightly lower pH in the rinse effluent indicated that some adsorbed lactic acid was also eluted.

The lactic acid was completely desorbed with 6.8 BV of methanol. The highest lactic acid concentration of the effluent was 31 mg/mL, which would be the expected concentration of lactic acid during desorption in a countercurrent operation. A cloudy effluent was observed near the end of the first bed-volume of the methanol eluant, which could be due to the shrinking of the sorbent beads upon contact with methanol. The shrinking excludes the liquid from the sorbent including the micropores. Because the micropores are accessible to smaller ions but not to lactic acid, the cloudiness may have been caused by other salts (such as sulfates) that are insoluble in methanol.

The cloudy fractions contained 29% of the total lactic acid recovered from the column. These fractions were not included in the pool that was subsequently concentrated. The concentrated product contained 98% lactic acid and 0.05% glucose. The viscous product had a very light yellow tint but was not turbid. The

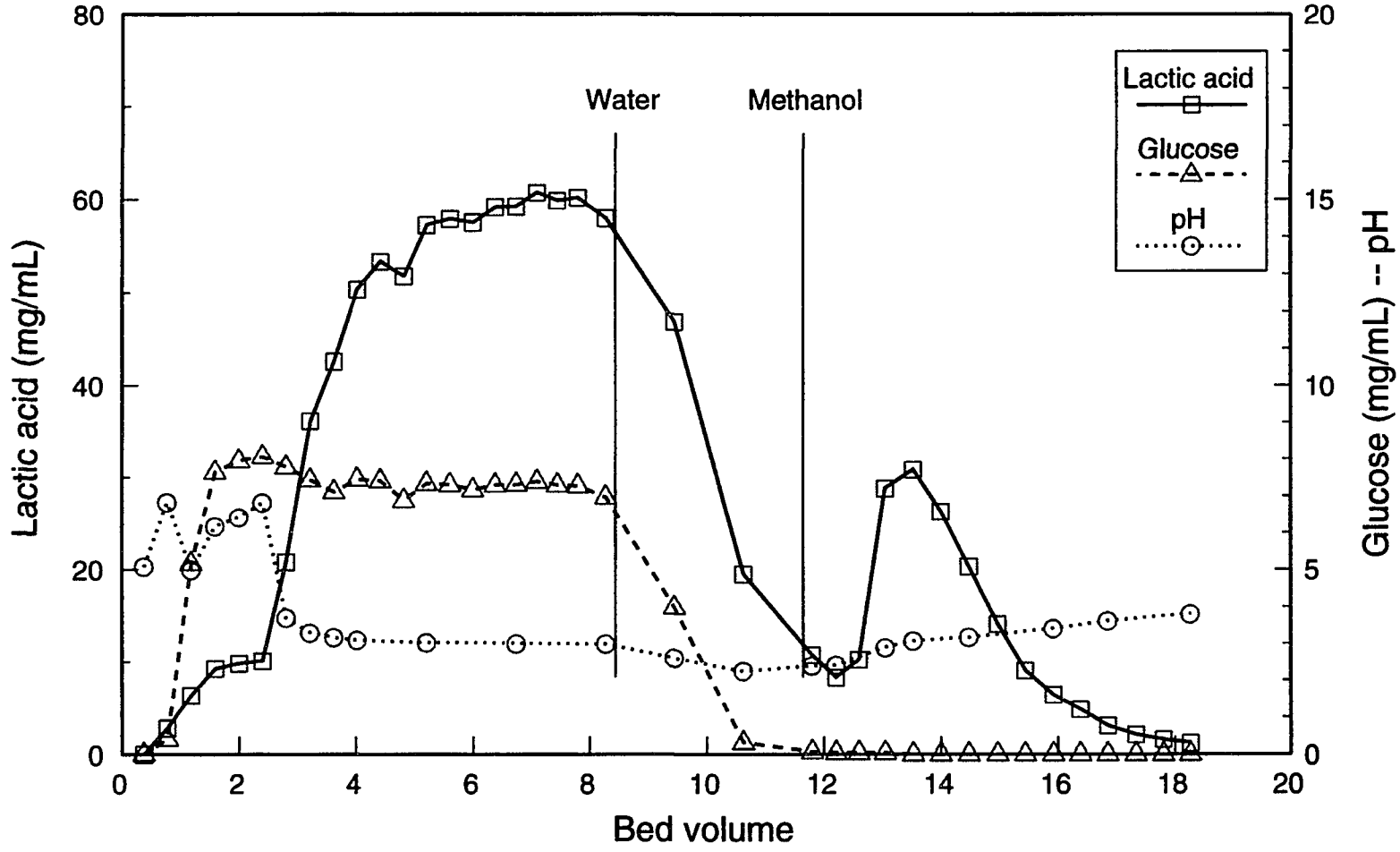


Figure 4.17. Effluent profile for VI-15 column

chromatogram (Figure 4.18) shows that, aside from glucose, small amounts of other impurities (retention times of 4.86, and 11.16 to 14.23 min) were also present. Peaks with retention times of 9.05 and 9.54 min were originally present in the lactic acid solution used and were possibly lactides. The presence of readily carbonizable residues was verified by the positive result (formation of brown layer at the interface of sulfuric acid and lactic acid) of the sulfuric acid test.

The column was rinsed with 1 M NaOH to remove broth components not desorbed by methanol. The rinse effluent collected was yellow. The chromatogram (Figure 4.19) shows that, aside from lactic acid (retention time 9.93 min) and methanol (retention time 14.11 min), other components were strongly adsorbed by the resin. The dominant broth component retained in the resin had a retention time of 4.66 min. These results suggested that the column required periodic regeneration with a strong base to remove these strongly bound broth components to restore its capacity. A 30% decrease in column capacity for lactic acid was observed after a ten-cycle run without NaOH rinse.

The shrinking of the sorbent during desorption also led to compaction of the sorbent in the column and a decrease in sorption capacity since the beads cannot swell freely. The sorbent had to be loosened by backwashing with water at high flow rate to prevent compaction of the sorbent bed during the next loading cycle. The backwashing step also removed the methanol remaining in the column.

Dowex MWA-1. The resin column reached saturation after 3.5 BV of acidified broth (Figure 4.20), which is about half the volume needed to saturate the

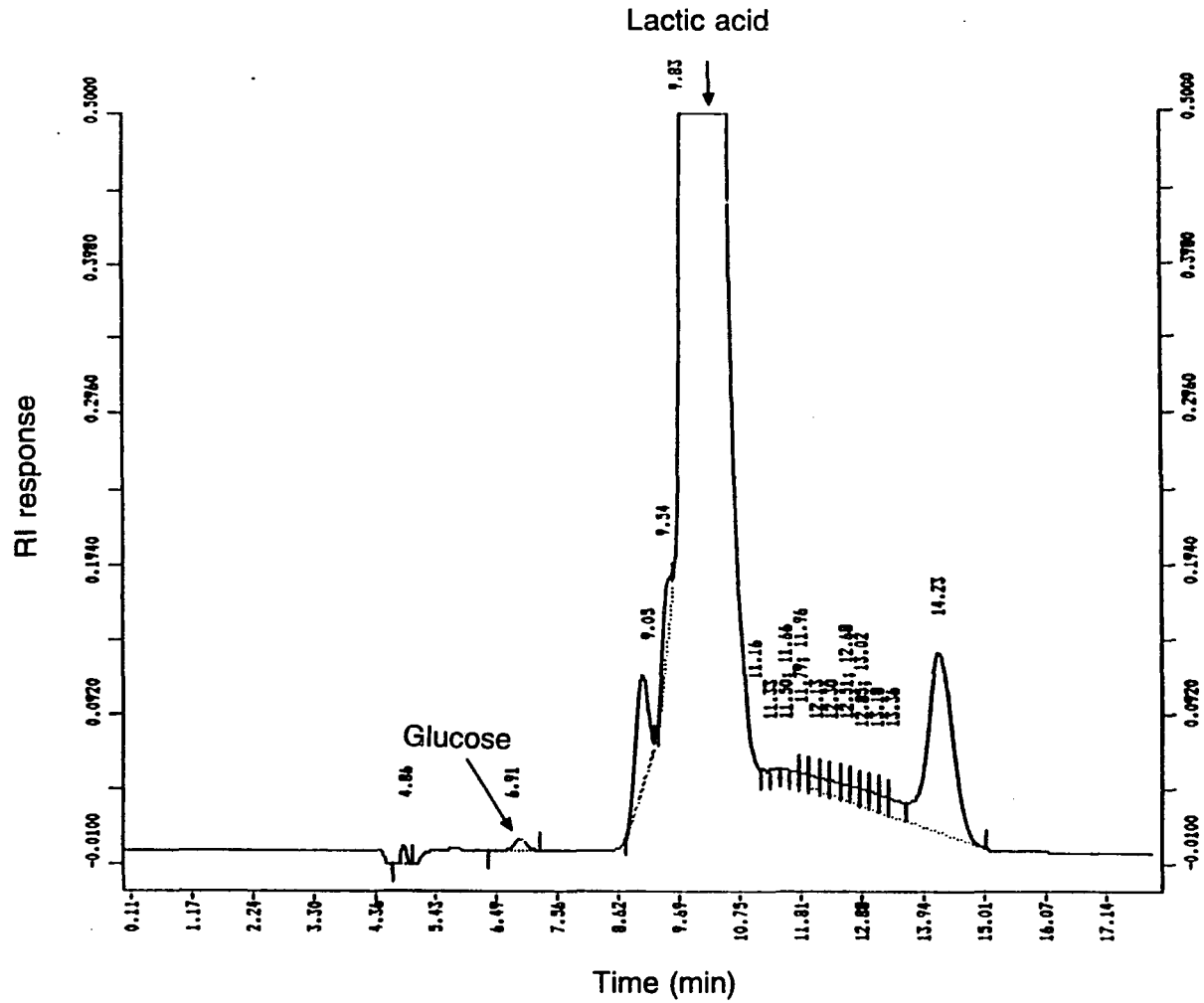


Figure 4.18. Chromatogram of lactic acid eluted by methanol from VI-15 column

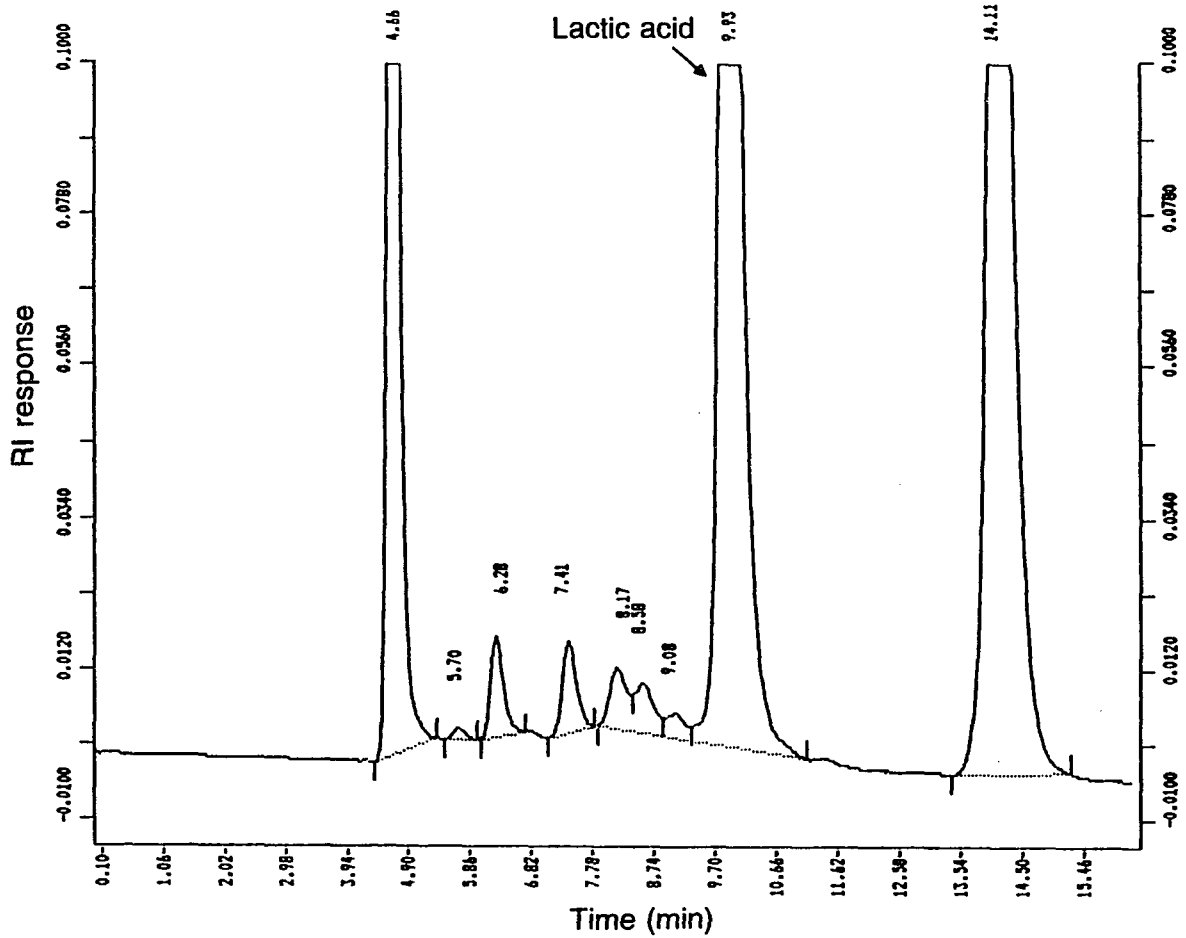


Figure 4.19. Chromatogram of NaOH rinse of VI-15 column after methanol elution

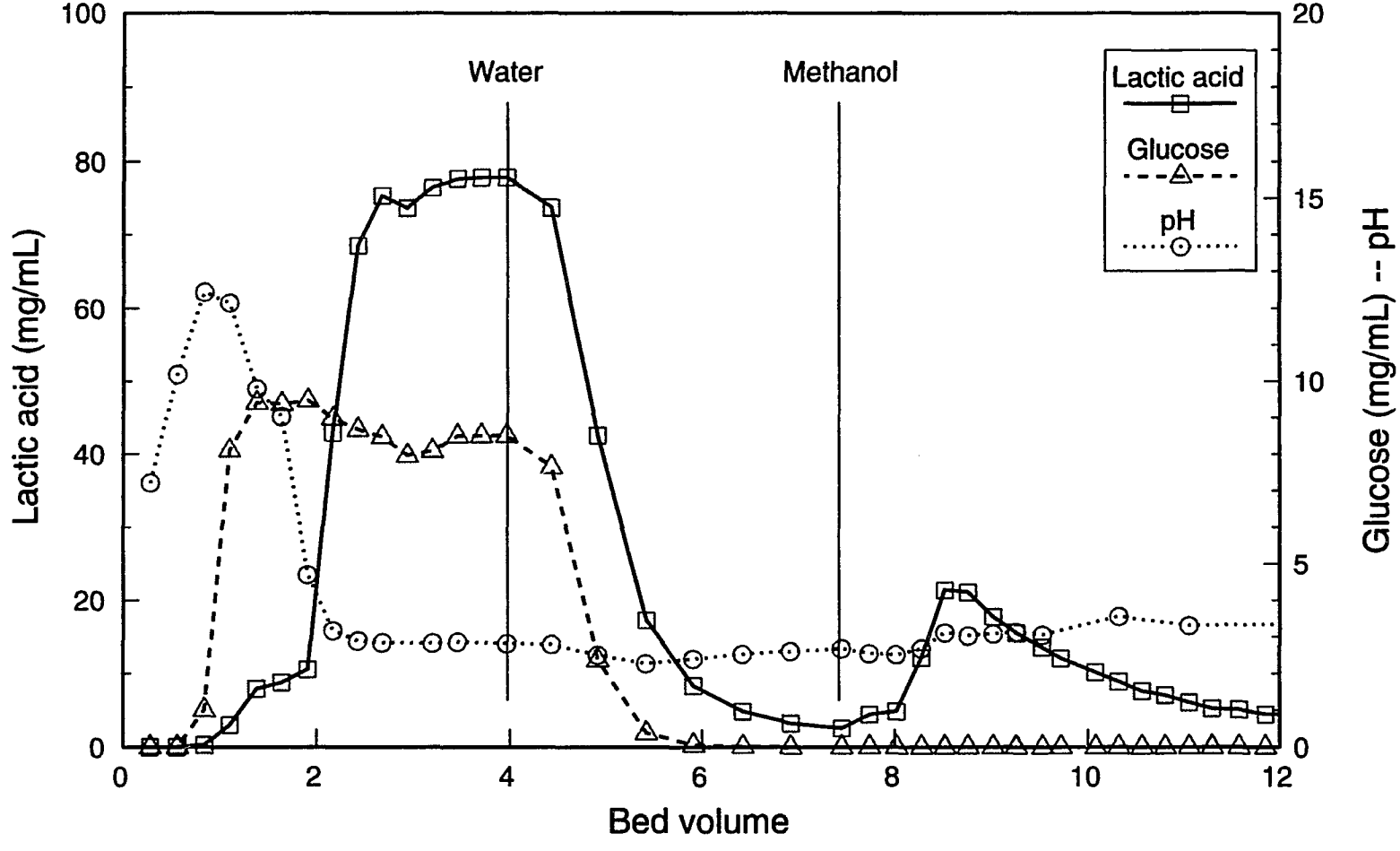


Figure 4.20. Effluent profile for MWA-1 column

Riedel-de-Haen VI-15 column. The faster sorption on MWA-1 was the combined effect of its having a macroporous matrix and a more basic functional group compared with Riedel-de-Haen VI-15. The rinse effluent was free of glucose after 3 BV and the lactic acid concentration at this point was around 4 mg/mL. About 51% of the total lactic acid in the column after loading came out with the rinse water. The column adsorbed 72 mg lactic acid/mL resin (310 mg/g dry resin).

Methanol was not effective in desorbing lactic acid from Dowex MWA-1 column despite the higher temperature (50°C) used. Only 64% of the adsorbed lactic acid was recovered after 4.5 BV. The maximum concentration of lactic acid in the eluate was only 21 mg/mL. The cloudy fractions, which contained 12% of the total lactic acid recovered, were not included in the pool that was concentrated. The concentrated lactic acid was cloudy and yellow. The chromatogram (Figure 4.21) of the product shows that no glucose was present, but other broth components (retention times 6.52, 8.15, and 10.98 to 15.61 min) were detected. The sulfuric acid test for readily carbonizable residues also came out positive. Since no glucose was detected, the other impurities found in the concentrated lactic acid product were also readily carbonizable residues.

When 5% NH_4OH was used as the desorbent, 100% recovery was attained in 1.5 BV of eluant (Figure 4.22). The maximum concentration was 113 mg/mL, about 50% higher than the lactic acid concentration in the feed. However, NH_4OH also desorbed other broth components (retention times 4.44 to 8.35 min) adsorbed by the resin (Figure 4.23), resulting in a product with more impurities than the one desorbed

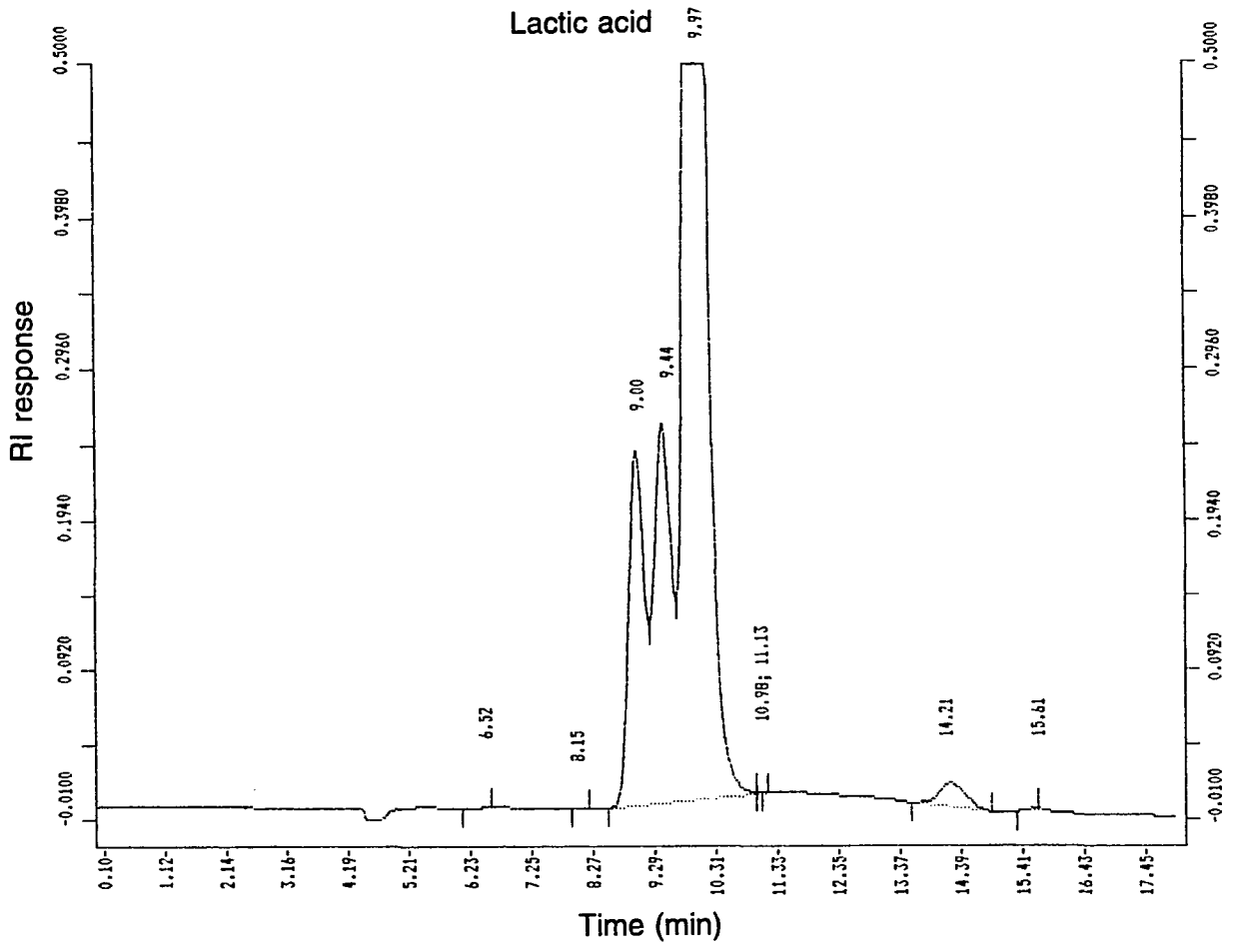


Figure 4.21. Chromatogram of lactic acid eluted by methanol from MWA-1 column

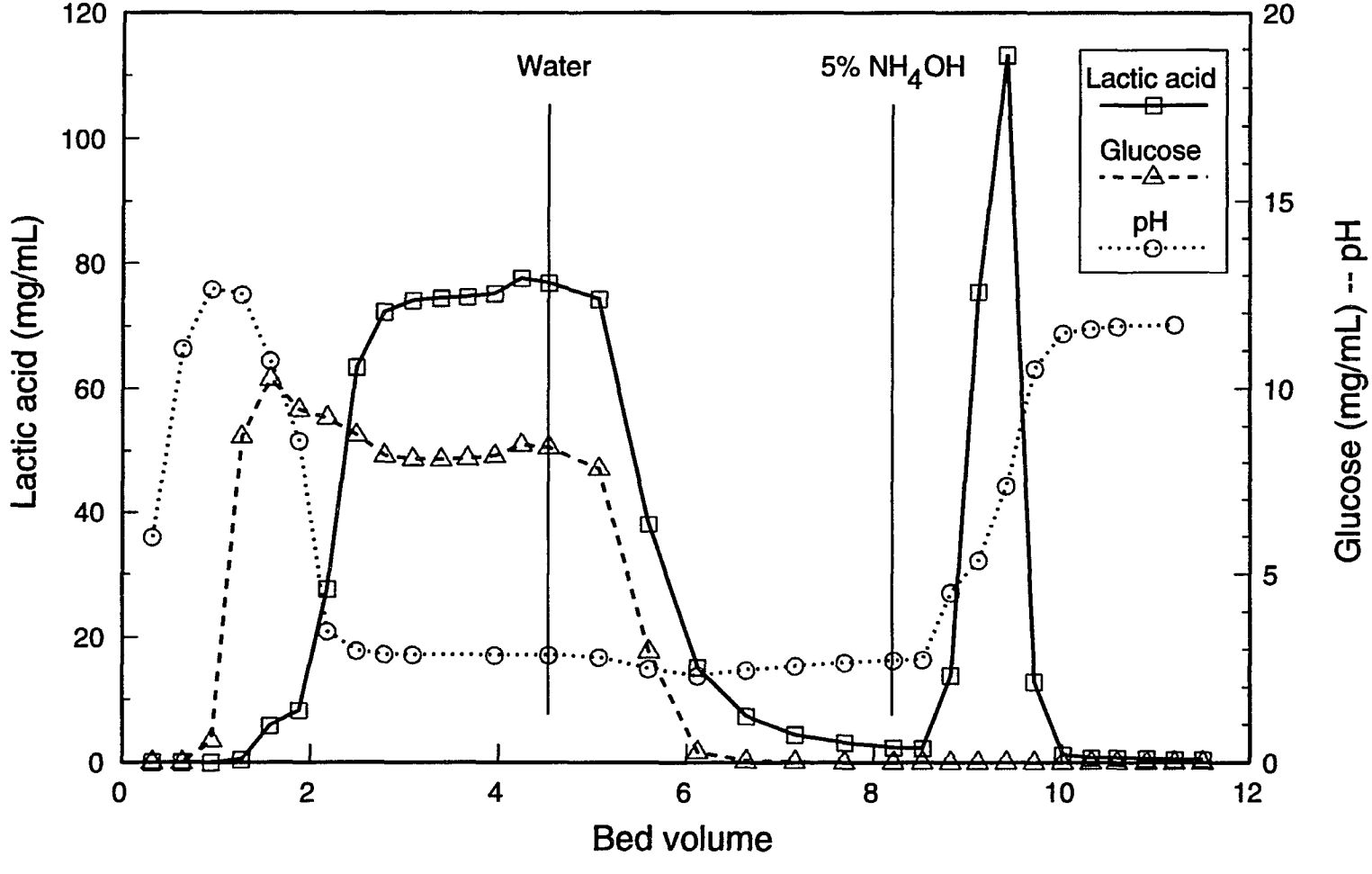


Figure 4.22. Effluent profile for MWA-1 column with NH_4OH as desorbent

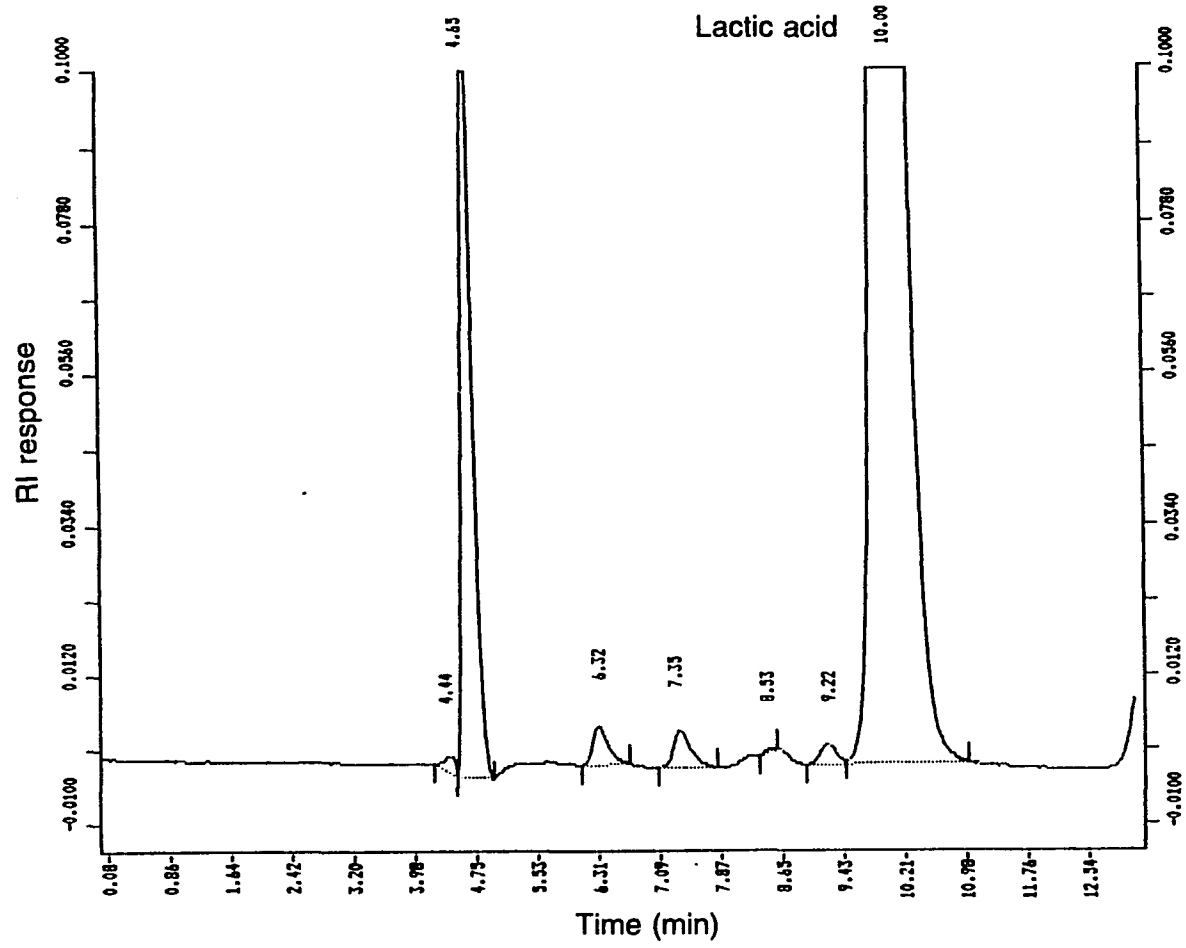


Figure 4.23. Chromatogram of lactic acid eluted by 5% NH_4OH from MWA-1 column

with methanol. The sulfuric acid test for readily carbonizable residues also turned out positive, despite the absence of glucose.

Amberlite IRA 35 column. The Amberlite IRA-35 column required about the same amount of acidified broth (3.2 BV) as Dowex MWA-1 to reach saturation (Figure 4.24). The rinse effluent was free of glucose after about 3 BV and the lactic acid concentration at this point was about 1 mg/mL. About 48% of the lactic acid in the column was washed out with the rinse water. The column adsorbed 75 mg/mL resin (410 mg/g dry resin). Methanol eluted only 18% of the adsorbed lactic acid after 5 BV. The maximum lactic acid concentration in the effluent was 5 mg/mL. The chromatogram of the eluted lactic acid revealed that no glucose was present but other broth components (retention times 4.96 to 8.45 and 11.47 to 15.65 min) were also eluted (Figure 4.25). The sulfuric acid test for readily carbonizable residue was also positive despite the dilute concentration of lactic acid used in the test.

The much lower recovery of lactic acid from Amberlite IRA-35 by methanol was not surprising since Amberlite IRA-35 has a higher pK_a (Gustafson et al., 1970; Clifford and Weber, 1983) and higher association constant (K) for lactic acid than MWA-1 (Tung, 1993). These earlier studies explained that the styrene ring and the quaternary ammonium group in MWA-1 have base-weakening effects on the amine group. In contrast, the aliphatic backbone and the presence of carboxylates in IRA-35 increase the basicity of the amine group.

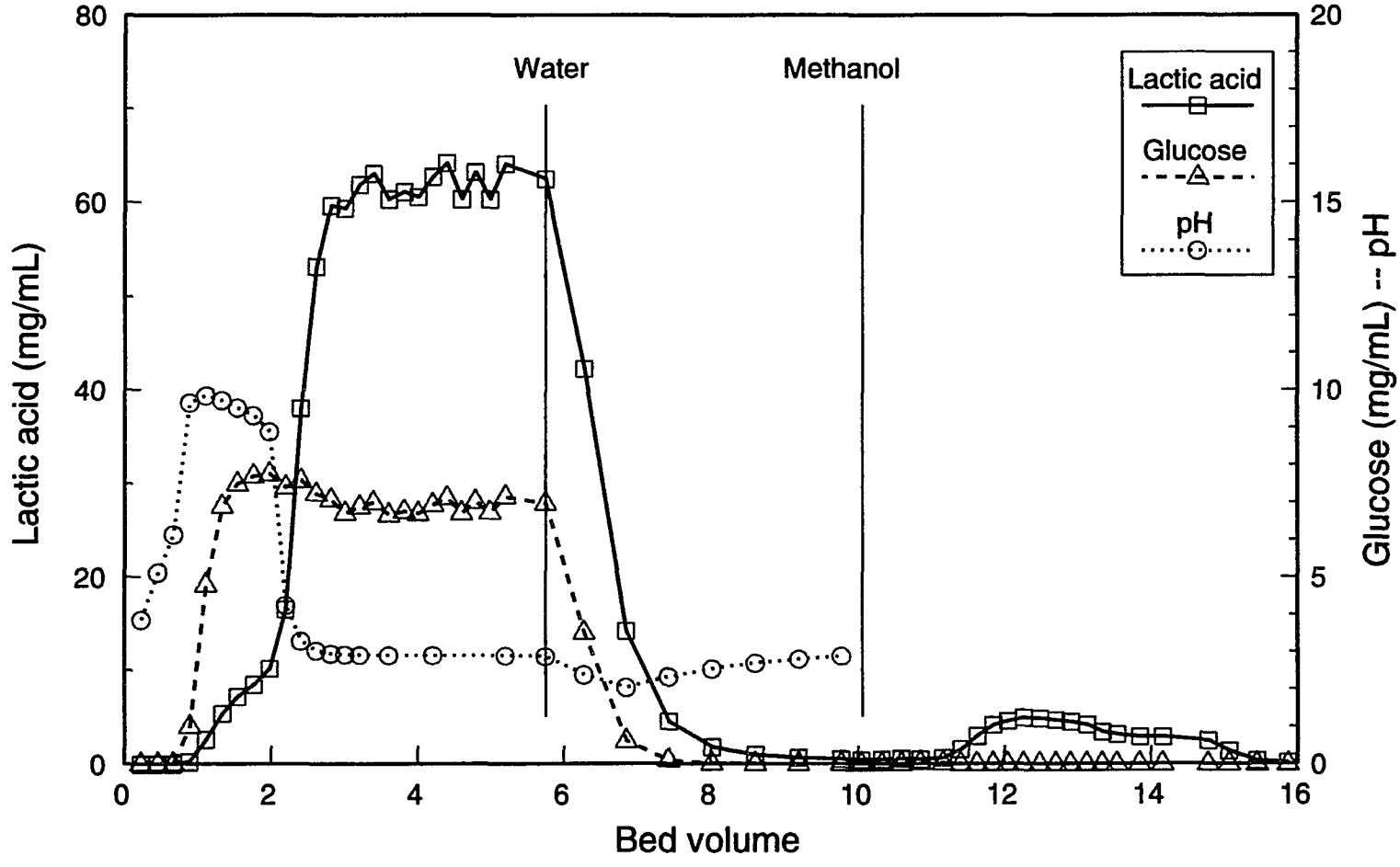


Figure 4.24. Effluent profile for IRA-35 column with methanol as desorbent

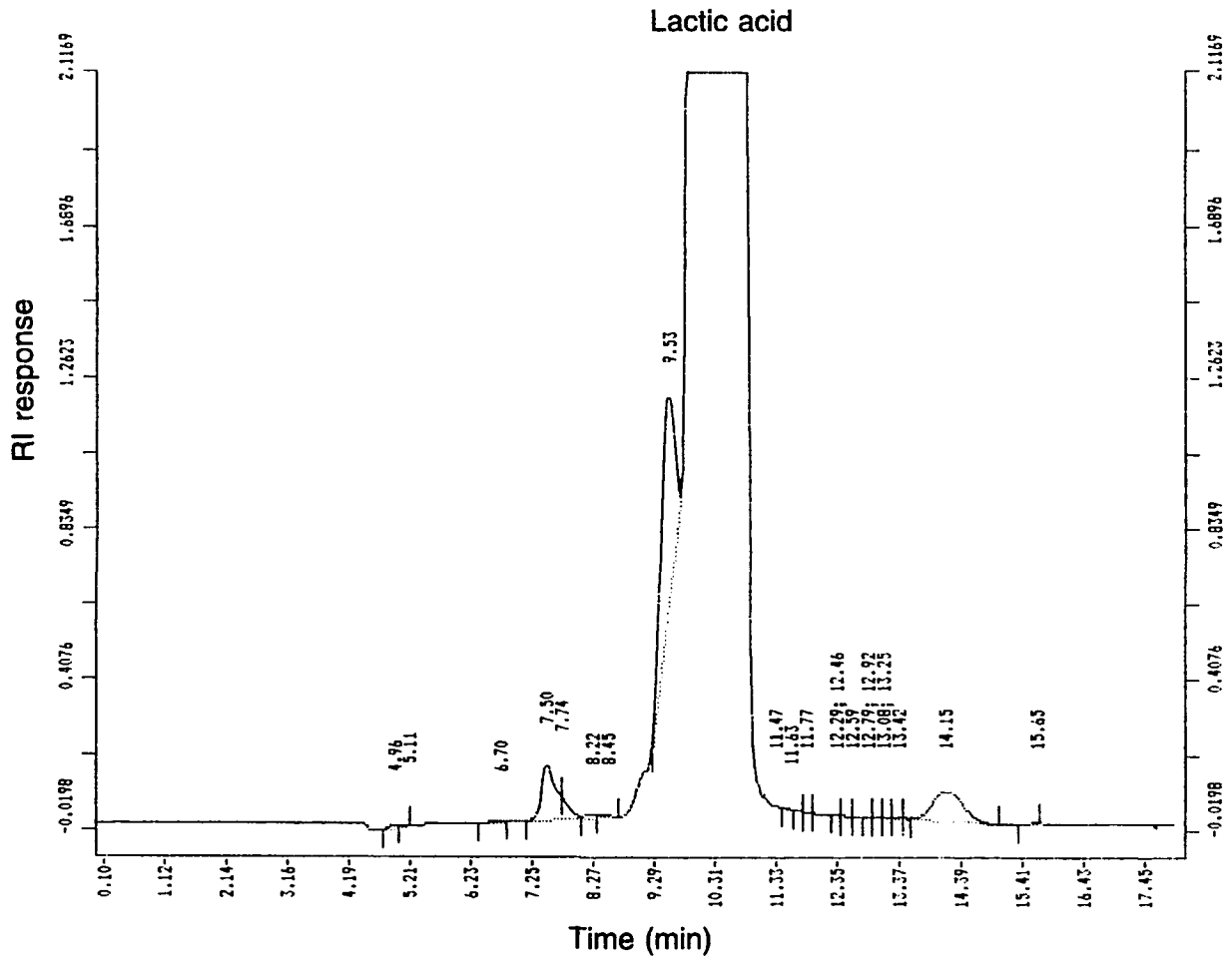


Figure 4.25. Chromatogram of lactic acid eluted by methanol from IRA-35 column

Section summary

Duolite C-464 was able to reduce the pH of the broth from 4.5 to 2.9, but produced only 0.4 BV of partially decolorized acidified broth. Lactic acid dilution was about 1.5 times but this concentration was still above the level (10 mg/mL) needed to achieve maximum capacity of Riedel-de-Haen VI-15, Dowex MWA-1, and Amberlite IRA-35. However, to generate 1 BV of feed stream for basic sorbent, the acidifying column must be 2.5 times the size of the lactic acid sorption column.

Methanol eluted lactic acid from Riedel-de-Haen VI-15 completely but with significant dilution. Methanol and NH_4OH also desorbed other broth components adsorbed by the sorbent, thus some impurities remained in the product. Another problem that needs to be addressed is the cloudy effluent obtained at the beginning of the desorption cycle of Riedel-de-Haen VI-15 and MWA-1 columns.

The recovery scheme employed was not sufficient to produce pure lactic acid. Pretreatment of the broth and/or a polishing step(s) is necessary to improve the purity of the product.

Use of basic sorbent to control the pH in continuous fermentation has been suggested by several researchers (Yates, 1981; Srivastava *et al.*, 1992; Tsao *et al.*, 1993). As demonstrated earlier, the sorbents also adsorb other broth components. These compounds could be nutrients needed by the microorganisms, and therefore, must be replenished continuously. Since the sorbent is also exposed directly to untreated broth, fouling may be a big problem.

Broth Pretreatment

in the preceding section, it was learned that broth components other than lactic acid also bind to the basic sorbent. Furthermore, these broth components were eluted with lactic acid during desorption and impurities remained in the final product. Because the two-stage purification did not result in heat-stable lactic acid, the process was modified to include broth pretreatment. The modified process consists of four main steps: (1) broth pretreatment, (2) broth acidification, (3) adsorption on basic sorbent, and (4) lactic acid concentration (Figure 4.26). This phase of the study investigated the possibility of removing the undesirable broth components before reaching the final lactic acid sorption step. Broth pretreatments such as browning reaction, decolorization using activated carbon, and by using nonfunctionalized resins were explored.

Browning and activated carbon treatment

The increase in brown color in the broth after heating close to boiling (95°C) for 5 h was due to caramelization and/or Maillard reaction. The Maillard reaction requires reducing sugars and amino group-bearing compounds such as amino acid, peptide and protein. The amino group must be unprotonated for the carbonyl-amine condensation reaction to occur. The rate of browning increases with increasing pH up to about pH 10, with little, if any, browning occurring below pH 6 (Ashoor and Zent, 1984). Caramelization, on the other hand, results from heating of glucose. Heating glucose at about pH 4 produces polymeric or condensed-ring compounds (Whistler and Daniel, 1985).

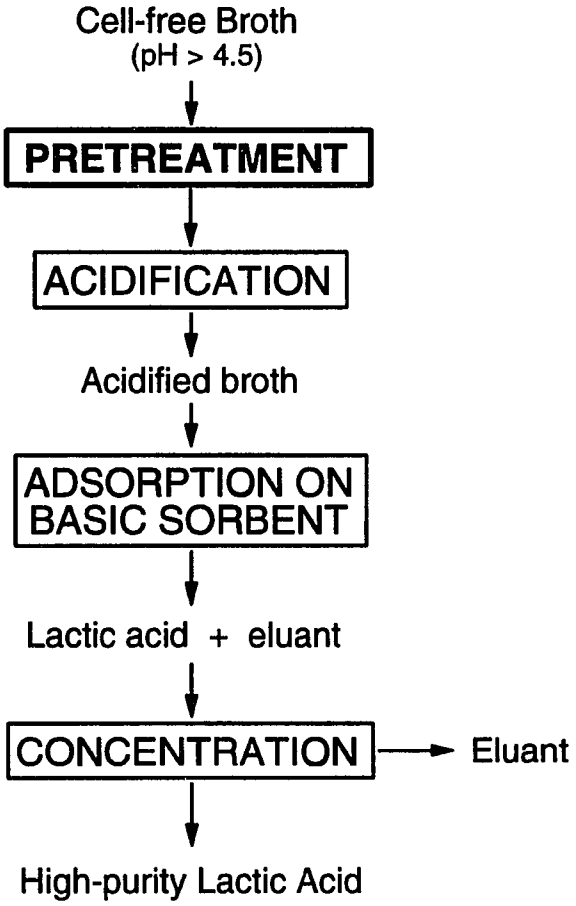


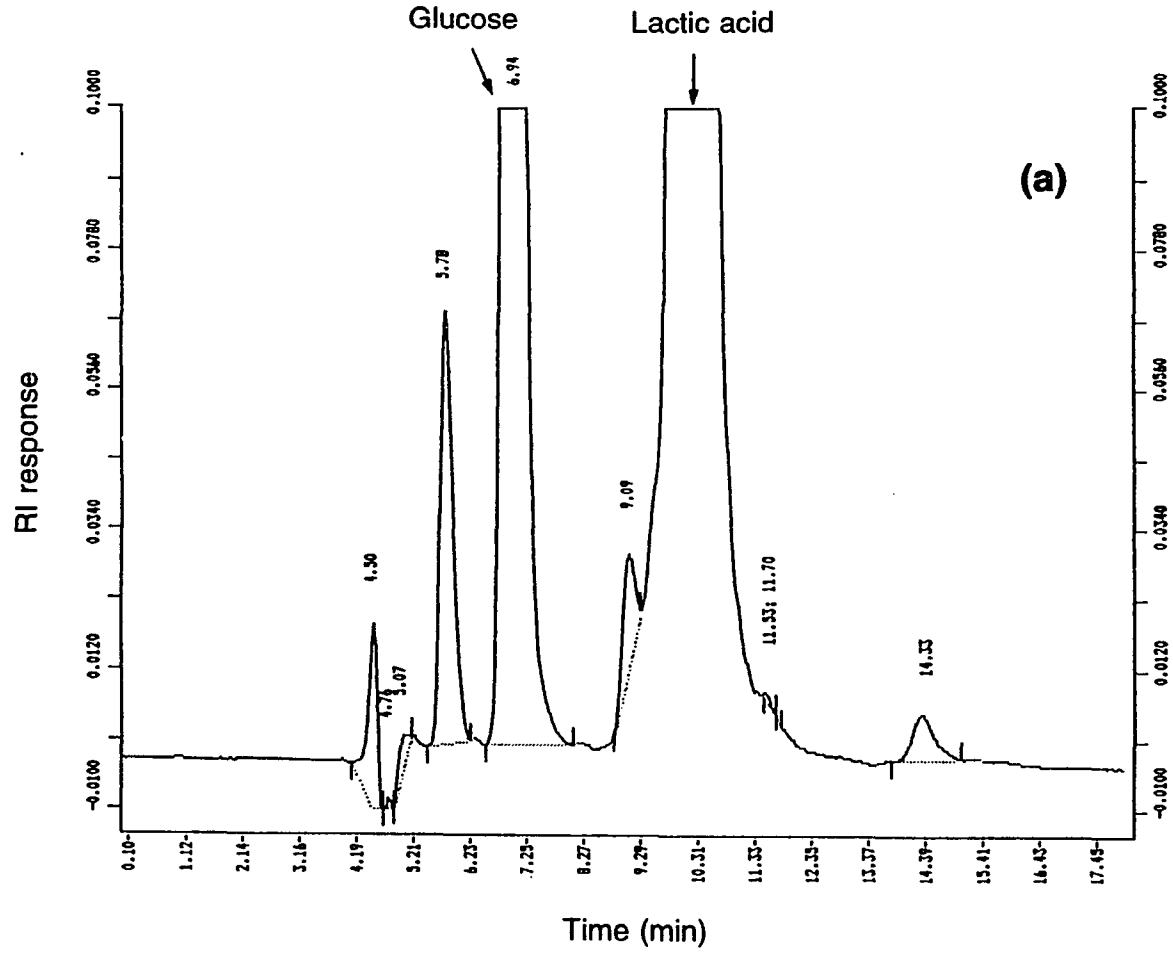
Figure 4.26. Modified scheme for lactic acid recovery and purification

During heating, the broth with an initial pH of 10 turned brown much faster and the color was much darker than the one with a pH of 4.5. The pH of the basic broth at the end of heating time decreased to 5.3, whereas that of the acidic broth remained the same. The significant pH decrease of the basic broth was caused by NH_3 liberated during heating.

The glucose concentration in the broth browned at basic pH was 58% lower than that in the starting broth while lactic acid concentration remained the same. The chromatograms of the broth before and after heat treatment (Figure 4.27) show that several new compounds were formed, with peaks A, B, C, and D being the most prominent. Some compounds present originally show an increase in peak heights (retention times 4.52, 4.83, and 5.79 min). There was also a reduction of the peak (9.2 min retention time) on the left shoulder of the lactic acid peak.

The glucose concentration in the browned broth with a pH of 4.5 was 32% lower than the initial broth. Since little or no Maillard reaction is expected to occur at pHs lower than 6, the color change observed could be attributed largely to caramelization. The chromatograms (Figure 4.28) show that new compounds (peaks A and B) similar to those observed in browned basic broth were also present, but in much smaller quantities.

The activated carbon decolorized the model broth and browned broths effectively. However, the activated carbon sorbed 103 and 109 mg lactic acid/mL of bed from unheated broth and browned broth (both at pH 4.5), respectively. The saturation points were not achieved even after 2 BV of decolorized broth (Figures 4.29a and 4.29b). The amount of lactic acid sorbed from broth with a pH of 5.3 was


Glucose
Lactic acid
(a)
RI response
Time (min)
4.30
5.07
5.78
6.94
9.09
11.53
11.70
14.33

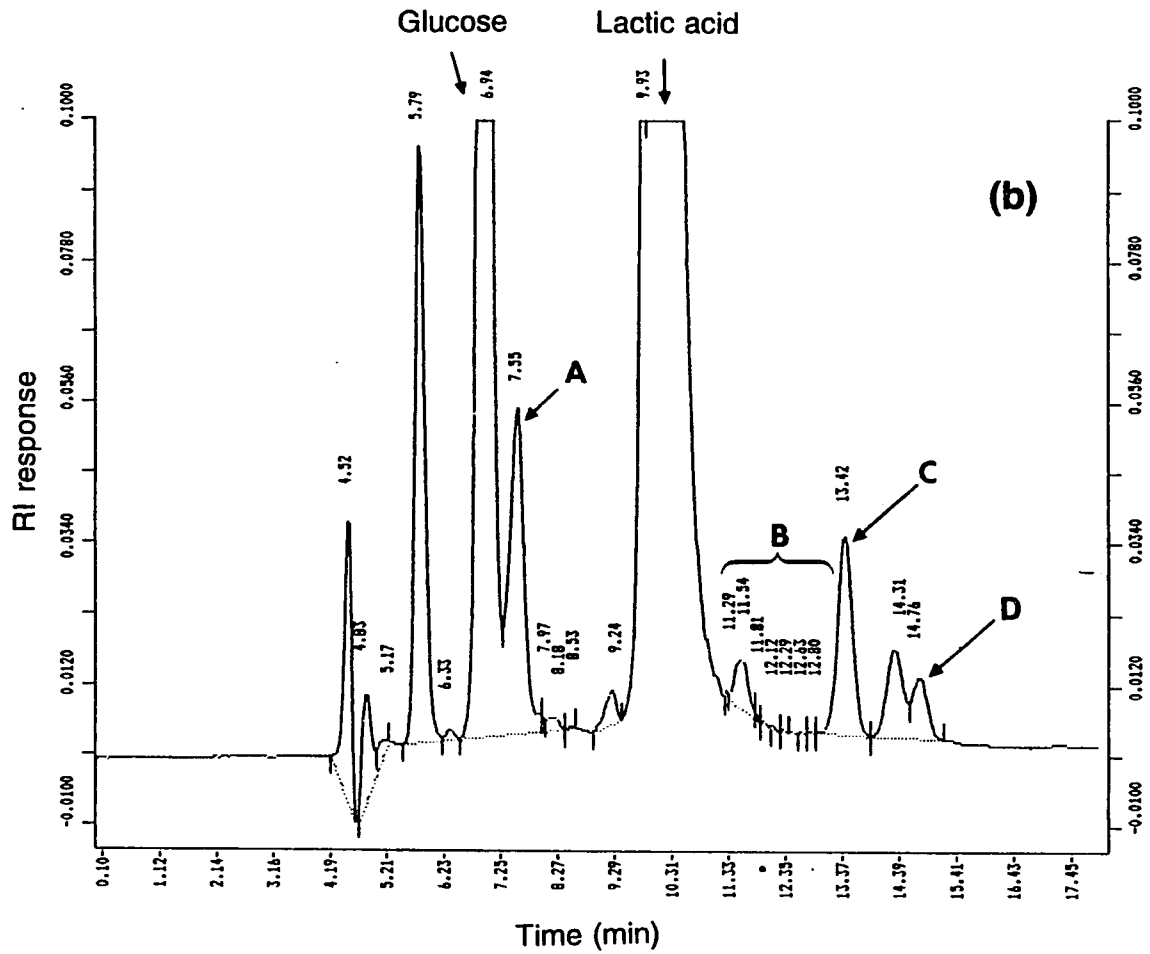
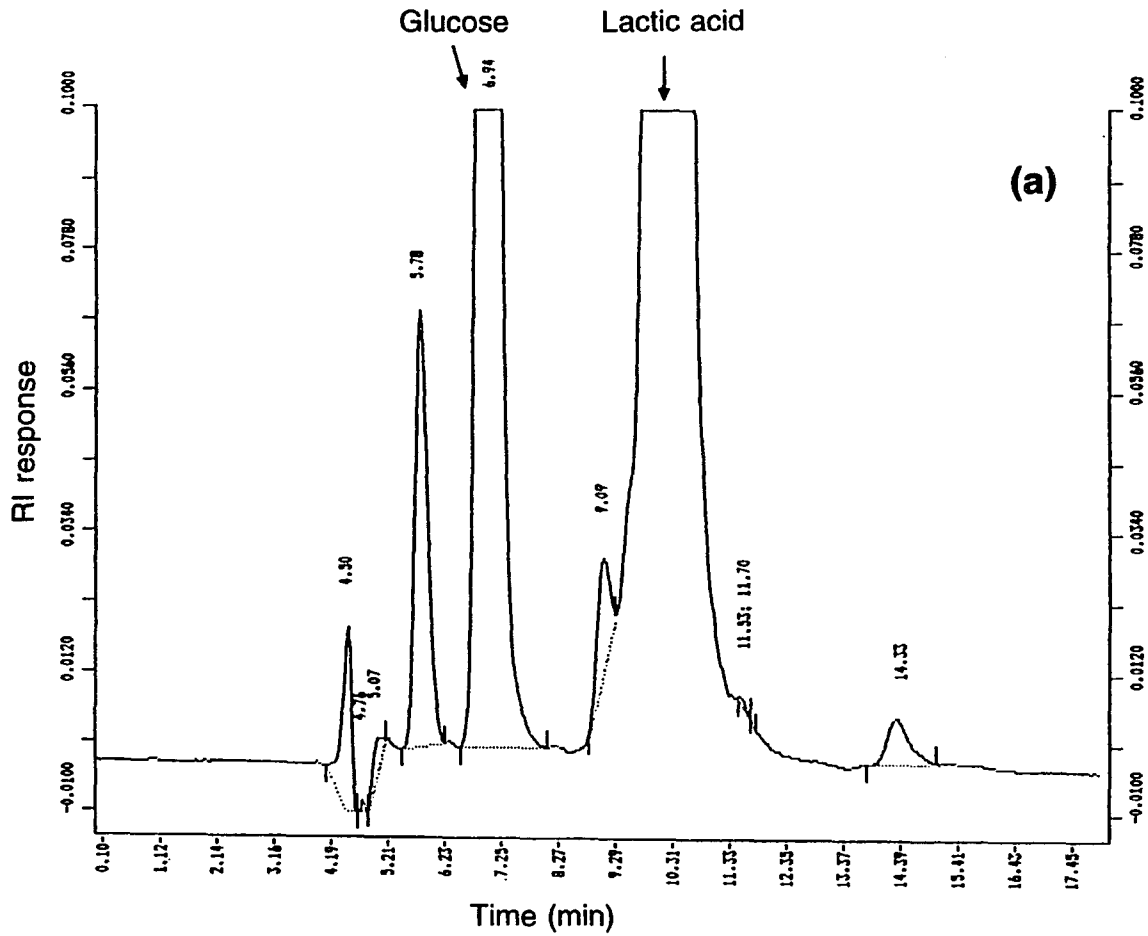


Figure 4.27. Chromatograms of model lactic acid broth (pH 10) (a) before, and (b) after heating for 5 h


Glucose
Lactic acid
(a)
RI response
Time (min)

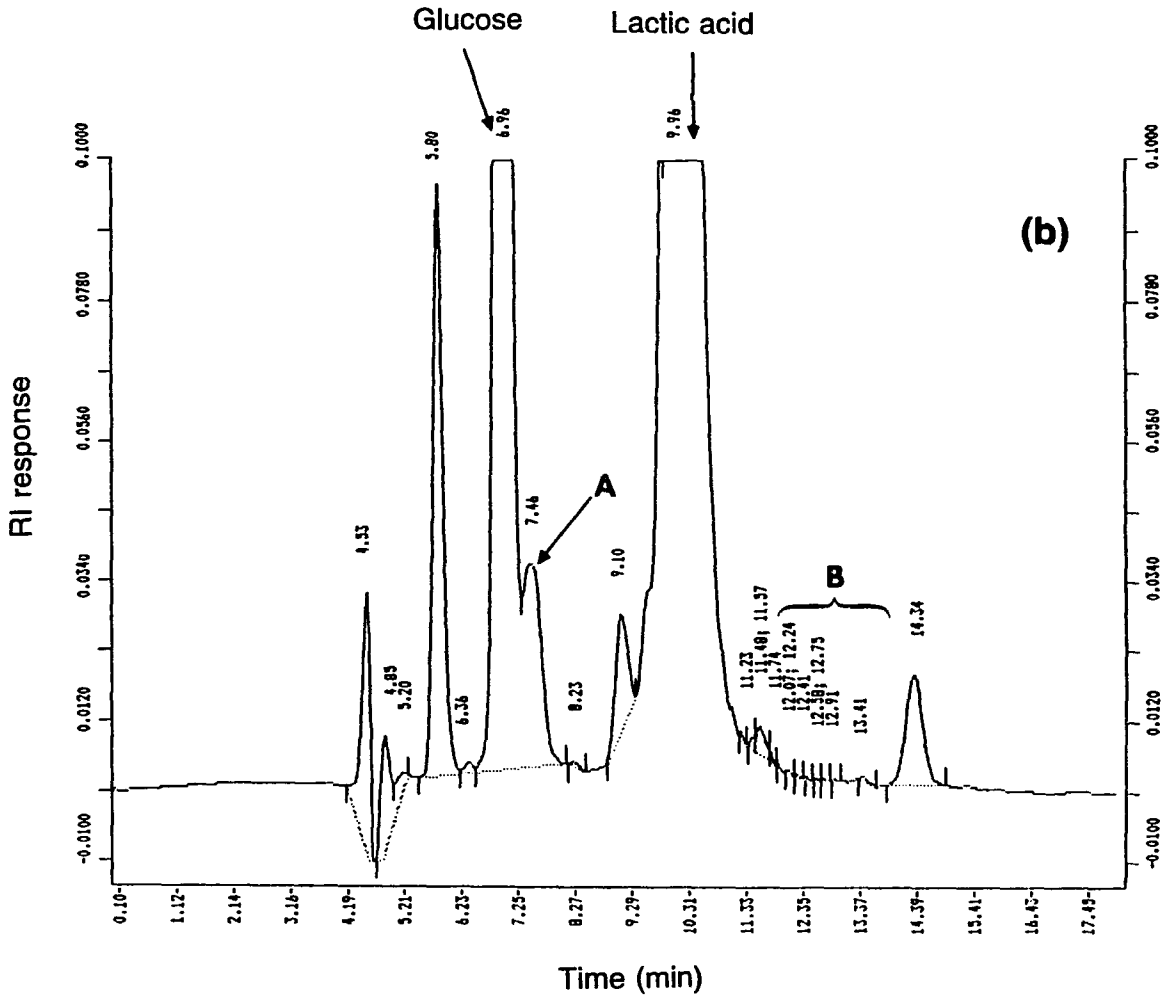


Figure 4.28. Chromatograms of model lactic acid broth (pH 4.5) (a) before, and (b) after heating for 5 h

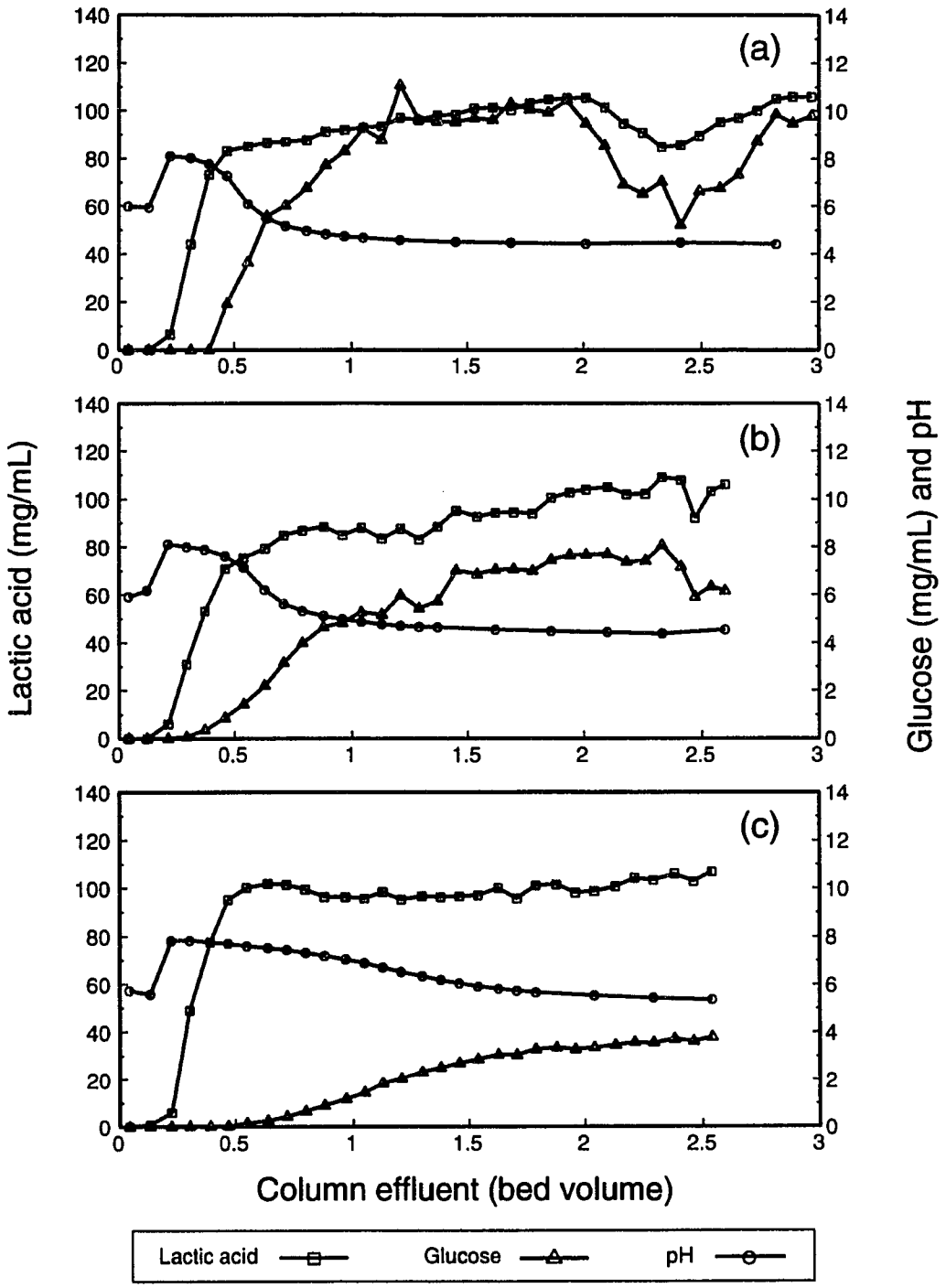


Figure 4.29. Effluent profiles of (a) unheated lactic acid broth (pH 4.5), and browned broths at (b) pH 4.5 and (c) pH 5.3 on activated carbon column

about 80 mg/mL of bed and saturation was achieved after 0.5 BV of decolorized broth (Figure 4.29c).

The chromatograms (Figures 4.30 to 4.32) of the activated carbon column effluent show that browning and activated carbon treatment had no significant advantage over decolorized unheated broth as far as removal of undesirable broth components is concerned. Browning at basic pH generated more problem compounds (peaks designated as A) close to lactic acid peak (Figure 4.32) and were not removed completely by activated carbon. These peaks were not present in the decolorized unheated broth and browned broth at pH 4.5. (Figures 4.30 and 4.31).

Broth pretreatment by using nonfunctionalized resins

The three nonfunctionalized resins used were all effective in decolorizing the broth. The columns (except Duolite S-761 column, which was brown in color) progressively turned darker as the broth flowed through, indicating that colored compounds were being adsorbed. Amberlite XAD-16, Diaion HP-2MG, and Duolite S-761 retained 62, 110, and 105 mg lactic acid/ml of bed, respectively. Since these resins are nonfunctionalized and the pH of the effluent basically remained the same as that of the feed (Figure 4.33), the lactic acid retained by the columns was mostly unbound and can be recovered readily by rinsing the columns with water. The chromatograms of column effluent appeared to be the same as that of the feed (Figures 4.34 to 4.36). The columns were rinsed with methanol after washing the column with at least 3 BV of deionized water. The methanol eluate was golden in color. Methanol was evaporated at low temperature from the fraction with the darkest

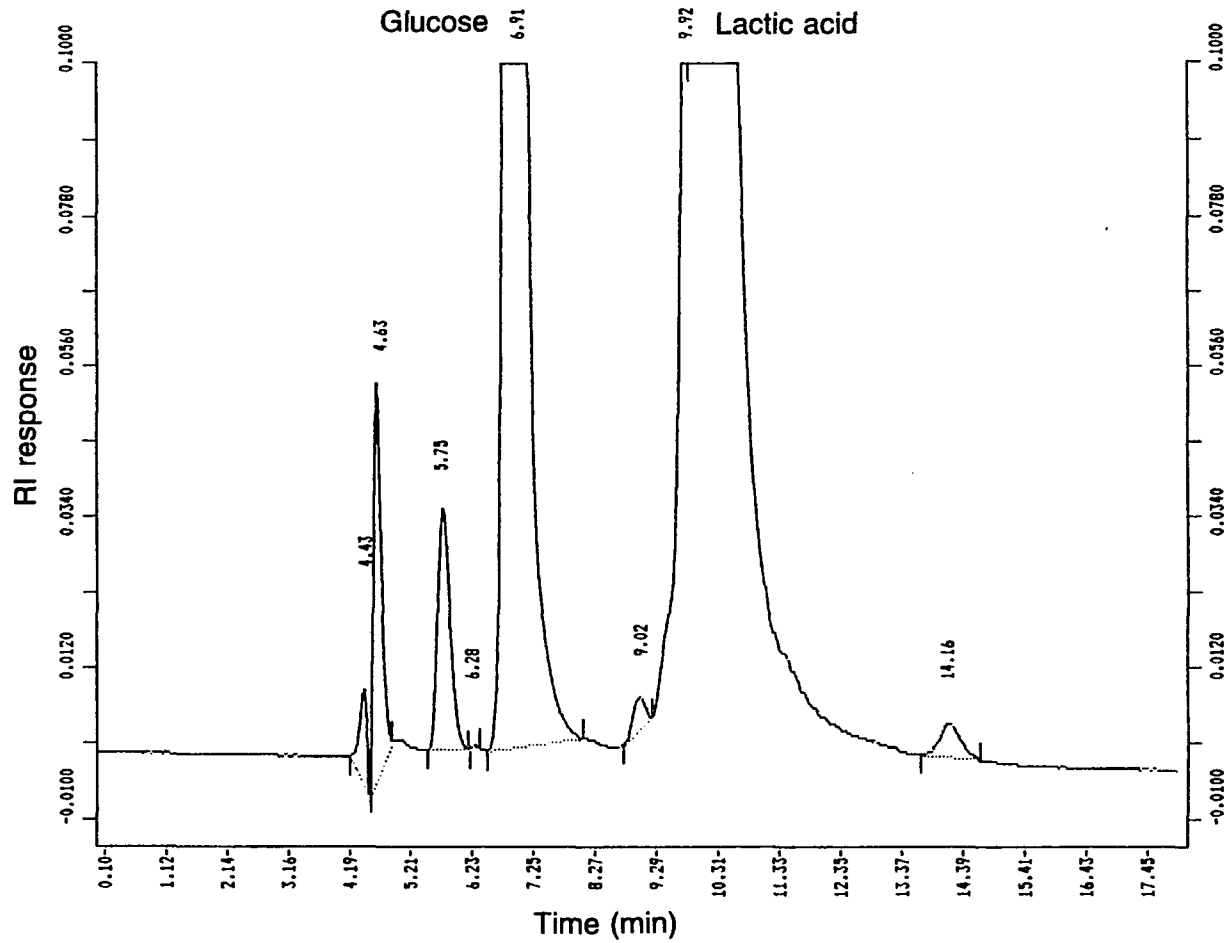


Figure 4.30. Chromatogram of unheated broth effluent from activated carbon column

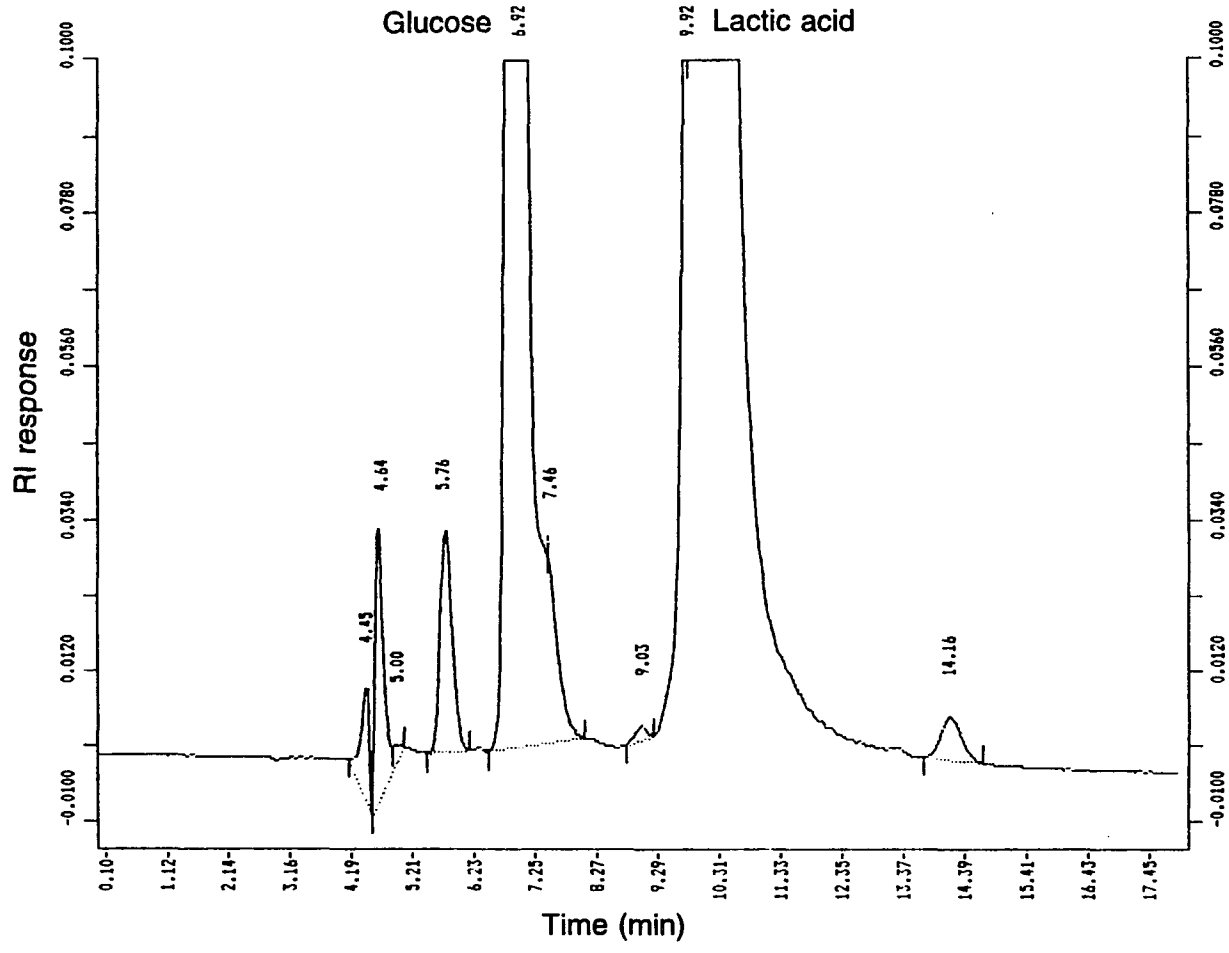


Figure 4.31. Chromatogram of browned broth (pH 4.5) effluent from activated carbon column

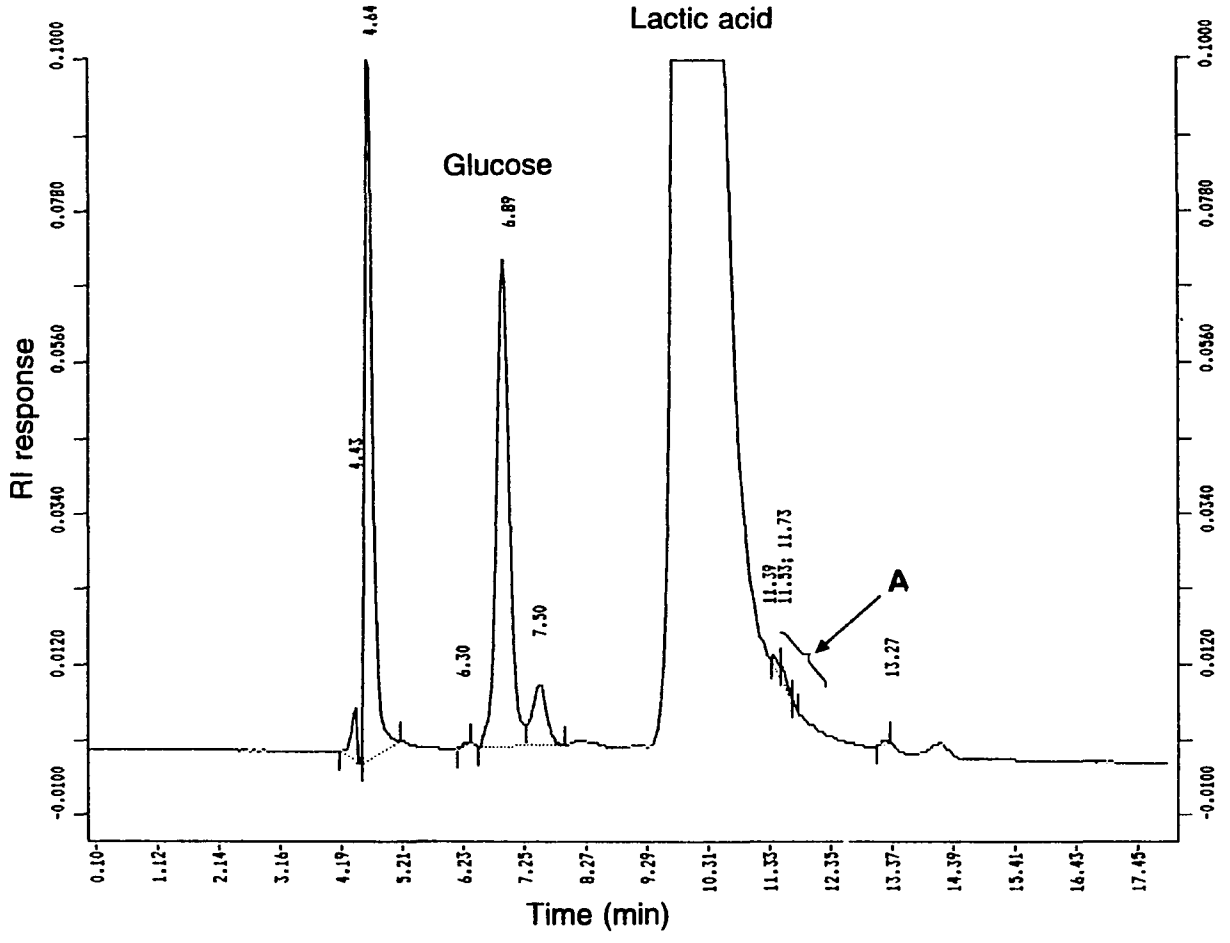


Figure 4.32. Chromatogram of browned broth (pH 10) effluent from activated carbon column

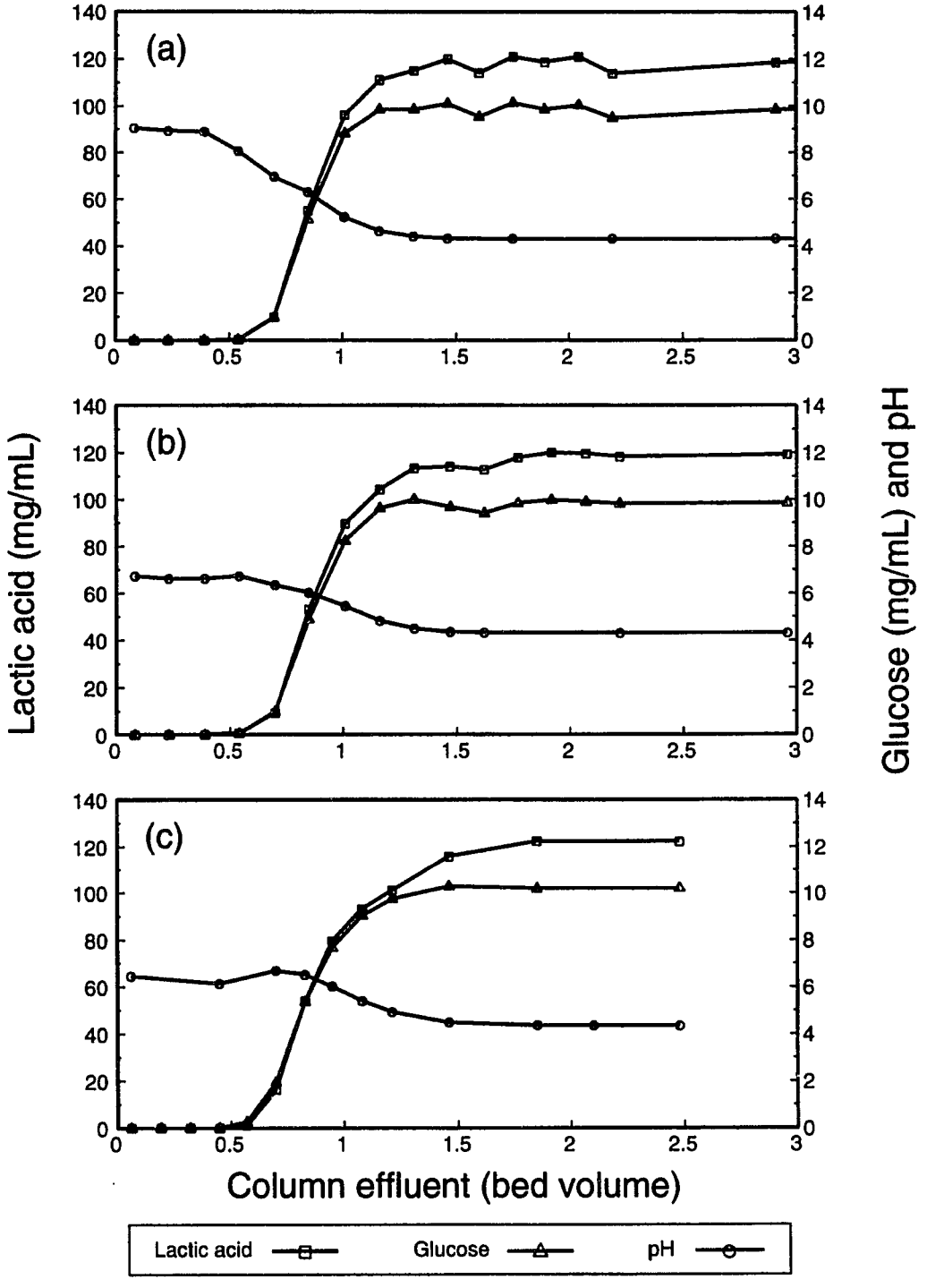


Figure 4.33. Effluent profiles of model lactic acid broth in (a) Duolite S-761, (b) Diaion HP-2MG, and (c) Amberlite XAD 16 columns

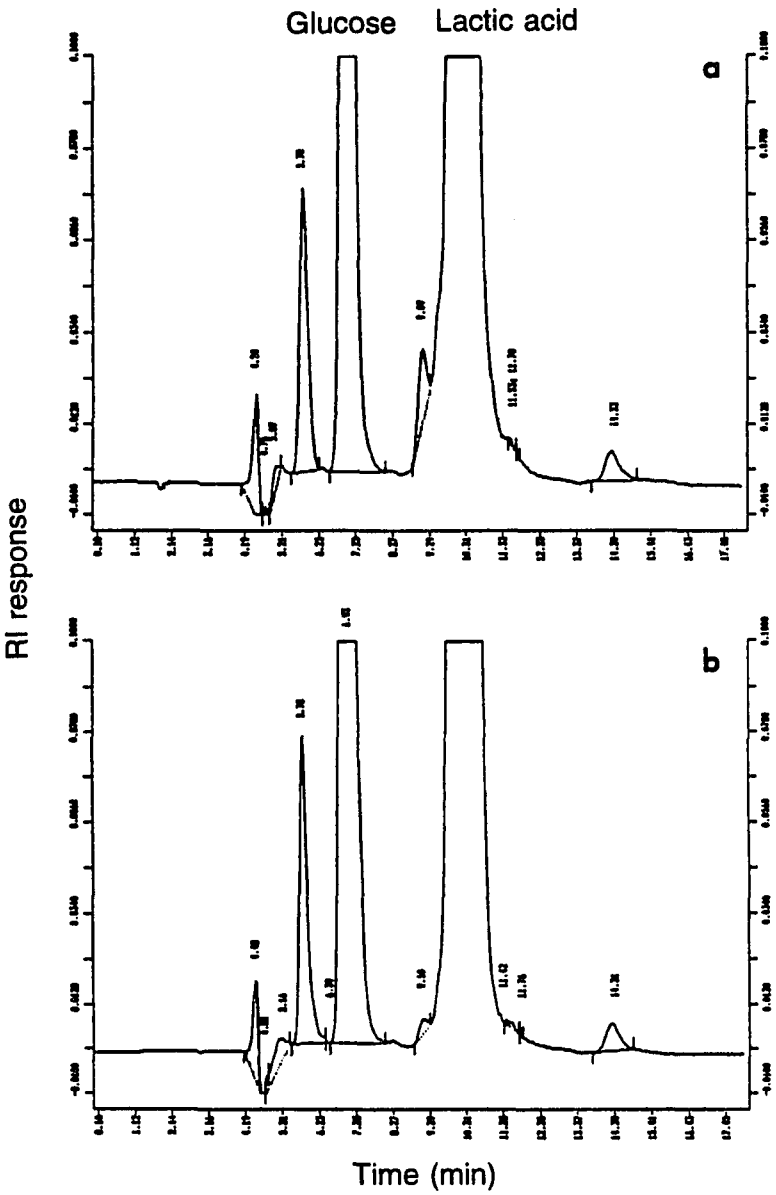


Figure 4.34. Chromatograms of model lactic acid broth (a) before, and (b) after passing through Amberlite XAD 16 column

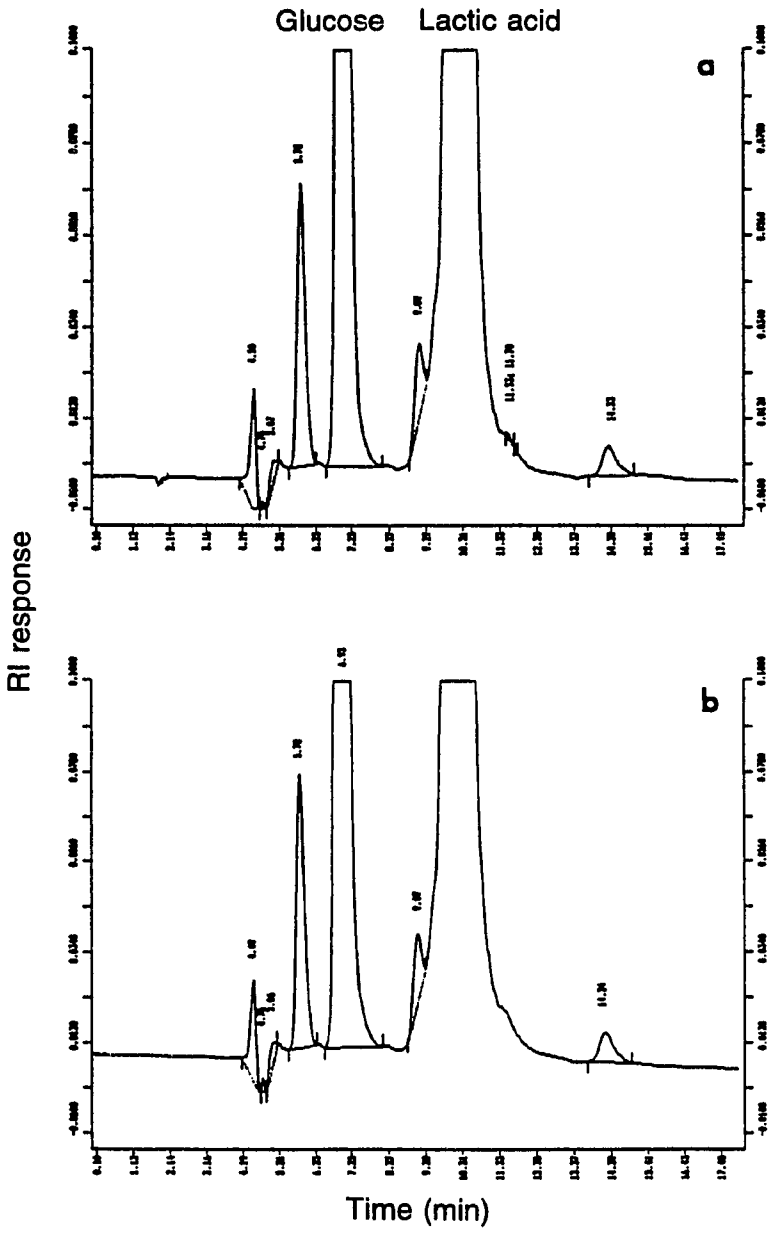


Figure 4.35. Chromatograms of model lactic acid broth (a) before, and (b) after passing through Diaion HP-2MG column

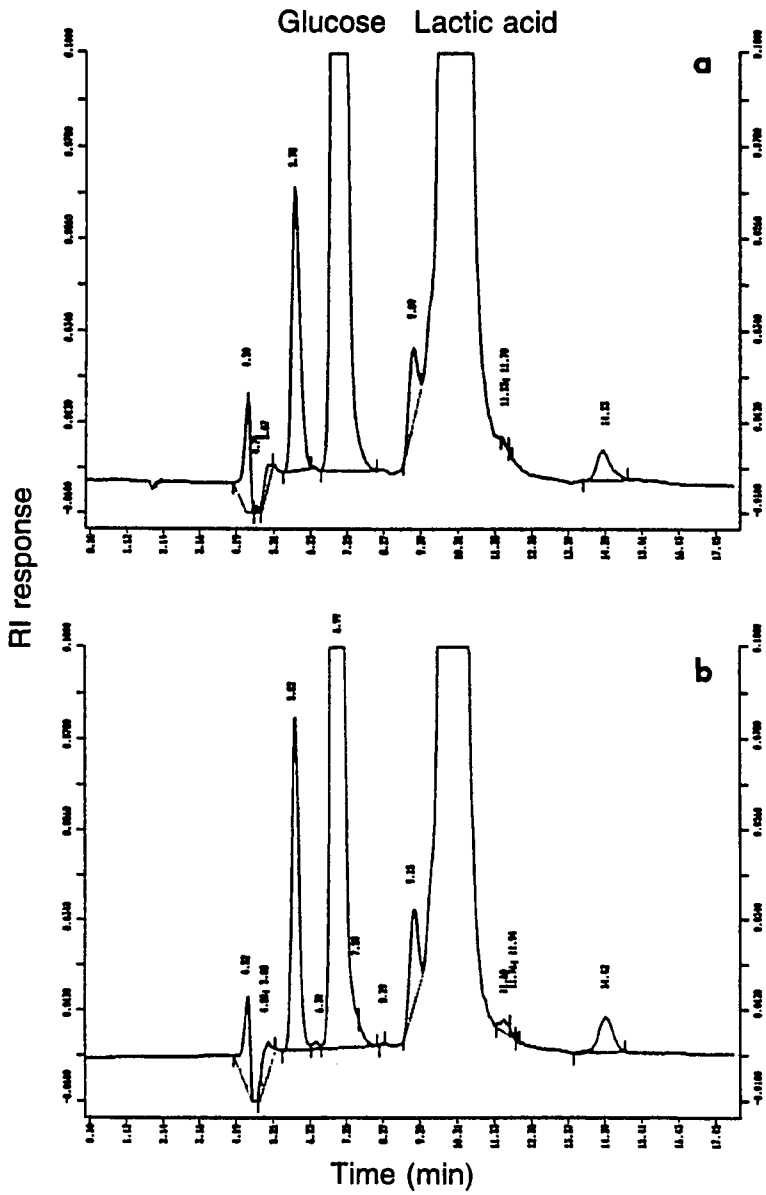


Figure 4.36. Chromatograms of model lactic acid broth (a) before, and (b) after passing through Duolite S-761 column

color and analyzed by HPLC. The chromatograms show that the dominant peak, common to all three resins, has a retention time of about 14.2 min (Figures 4.37 to 4.39). This is the most likely compound responsible for the yellowish color of the broth. Methanol also desorbed two other components (retention times 9.12 and 9.58 min) right before the lactic acid peak from Amberlite XAD-16 (Figure 4.37). However, the binding capacity of XAD-16 for these compounds is apparently very small since they were still present in the column effluent (Figure 4.34b). Other broth components (retention times 4.57 and 4.72 min) were also adsorbed by Amberlite XAD-16 but not by the other two resins.

The hydrophilic resin, Duolite S-761, appeared to be more selective for the smaller compounds (peaks that appear towards the end of the chromatogram), adsorbing other compounds not picked up by the hydrophobic Amberlite XAD-16 resin. The moderately polar Diaion HP-2MG behaved more like Duolite S-761 resin. Among the three non-functionalized resins, Amberlite XAD-16 had more impact on purification, specifically, its ability to pick up compounds very close to lactic acid.

Section summary

Browning may be beneficial in producing heat-stable lactic acid by reducing, if not eliminating, glucose and other readily carbonizable compounds from the broth. However, browning also created new compounds that may create more separation problems. The heat-treated broth must be close to neutral pH to minimize sorption of lactic acid on activated carbon. Activated carbon was very effective in decolorizing the broth.

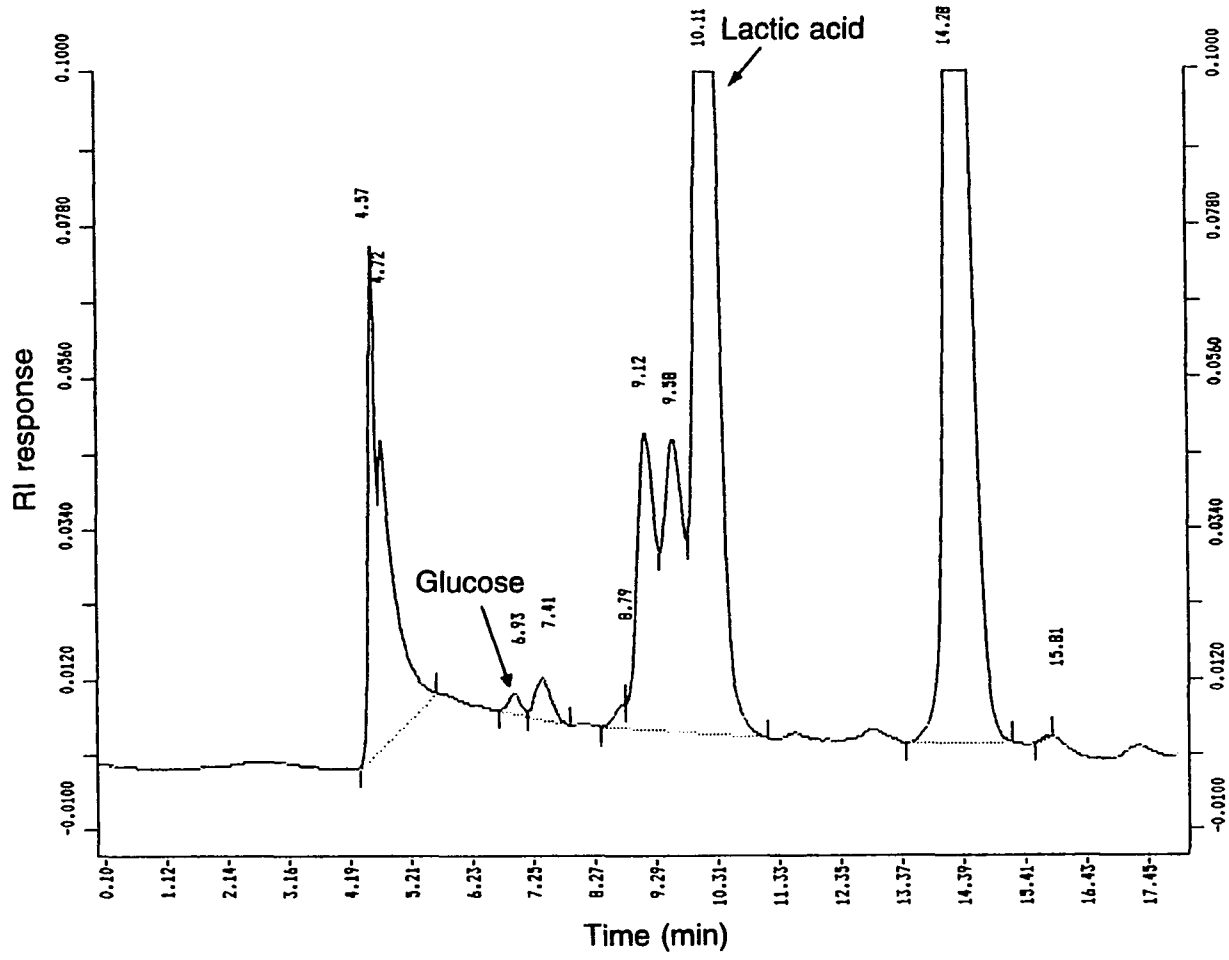


Figure 4.37. Chromatogram of methanol rinse from Amberlite XAD 16 after model lactic acid broth sorption

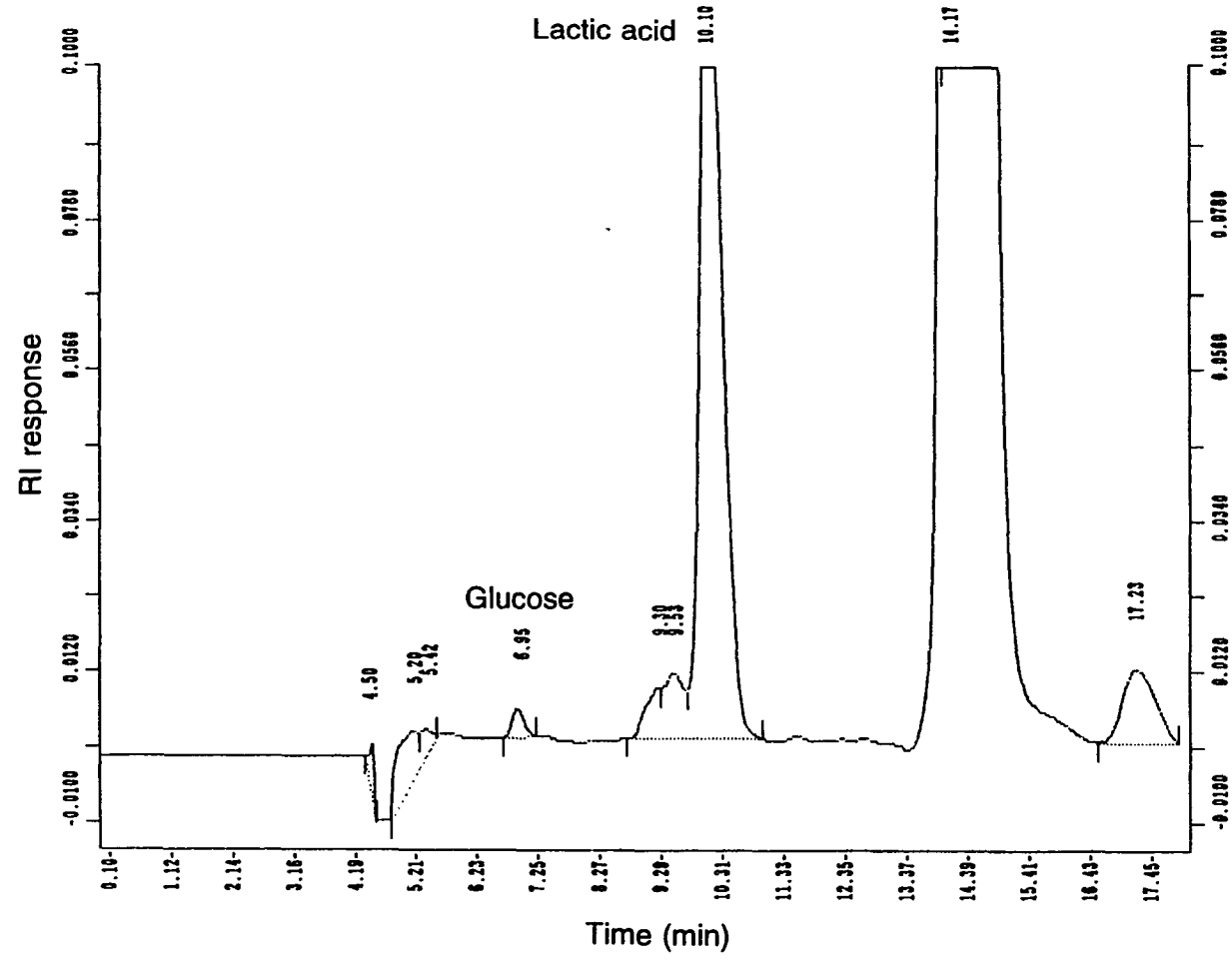


Figure 4.38. Chromatogram of methanol rinse from Diaion HP-2MG after model lactic acid broth sorption

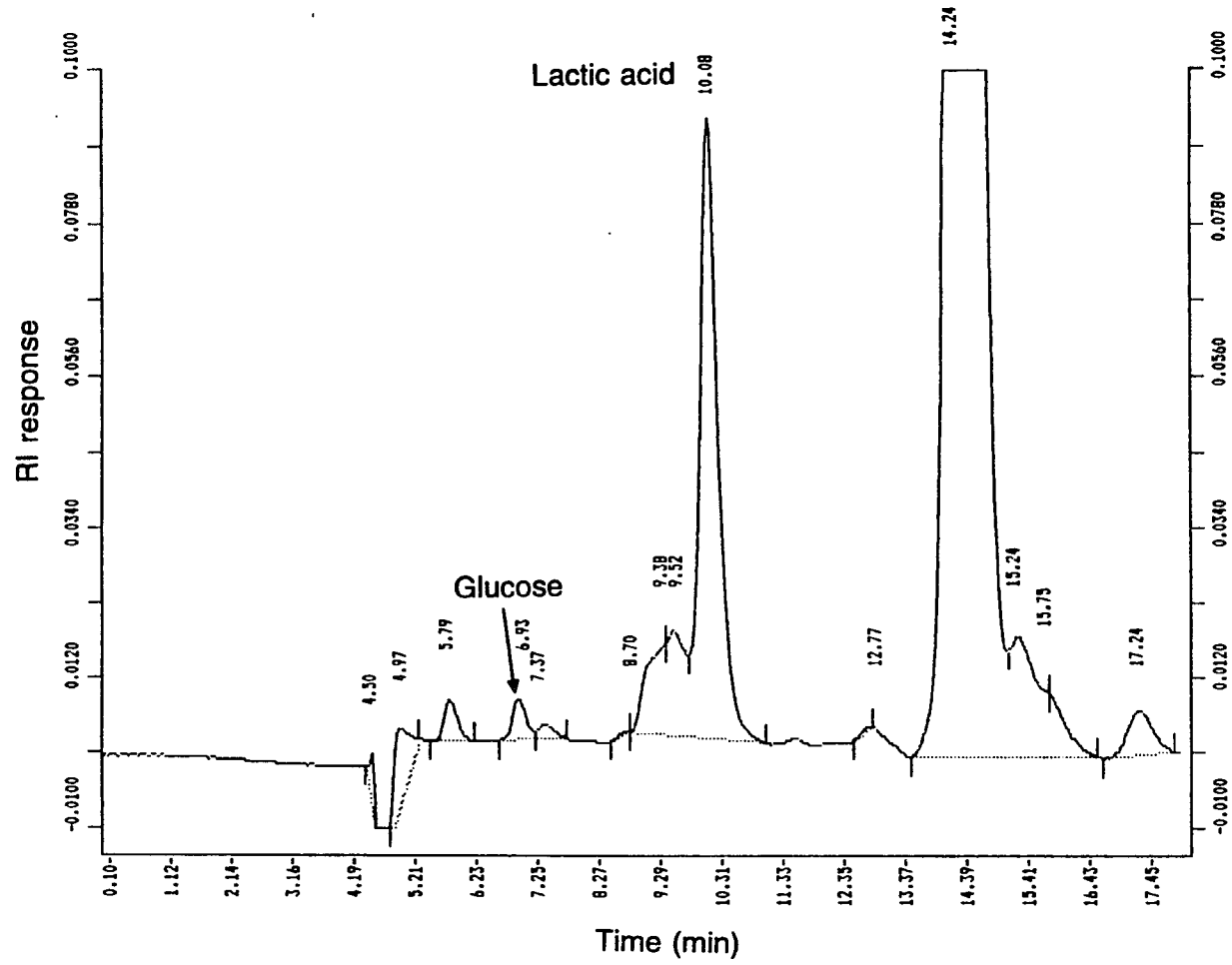


Figure 4.39. Chromatogram of methanol rinse from Duolite S-761 after model lactic acid broth sorption

Among the nonfunctionalized sorbents, Amberlite XAD-16 was able to adsorb more broth components than Duolite S-761 or Diaion HP-2MG, especially the problem compounds. The XAD-16 can also be used as precolumn for styrene-DVB-based ion exchangers. Duolite S-761 adsorbed other broth components that Amberlite XAD 16 did not. A combination of XAD-16 and Duolite S-761 will be able to adsorb a wide range of colored and other undesirable broth components

Proposed Lactic Acid Recovery and Purification Scheme

Based on the results of the pretreatment study, the lactic acid recovery scheme was revised to include two broth pretreatment steps (Figure 4.40). The cell-free broth was decolorized by using activated carbon, followed by sorption of hydrophobic compounds on Amberlite XAD-16. The Amberlite XAD-16 column also served as a precolumn for the cation exchanger. The weak-acid sorbent (Duolite C-464) was replaced with a strong cation exchanger (Dowex XUS 40406) to increase the volume of acidified broth. Riedel-de-Haen VI-15 was used as the weak-base sorbent. The resulting product obtained from this process was crystal clear even after evaporating methanol. The product was analyzed by HPLC and the chromatogram (Figure 4.41) shows no glucose peak, but three other peaks other than the lactic acid were present. One of the three peaks was probably residual methanol (retention time 14.19 min), while the other two were originally present in the lactic acid used in making the model broth. The result of the test for readily carbonizable substances was negative.

The outlined process was applied to the purification of lactic acid from "real" fermentation broth produced by repeat-fed-batch fermentation of glucose by

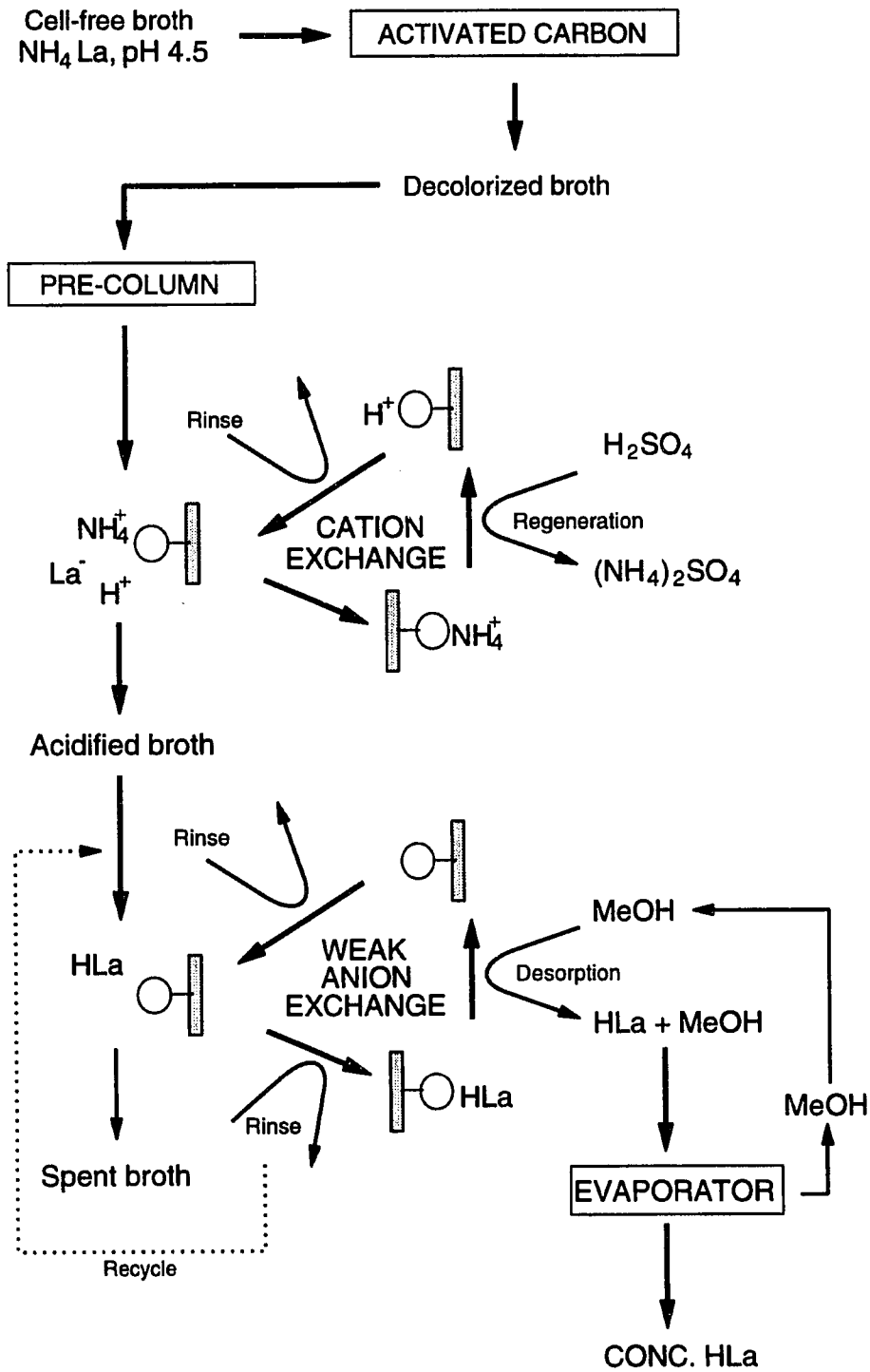


Figure 4.40. Proposed process for lactic acid recovery and purification

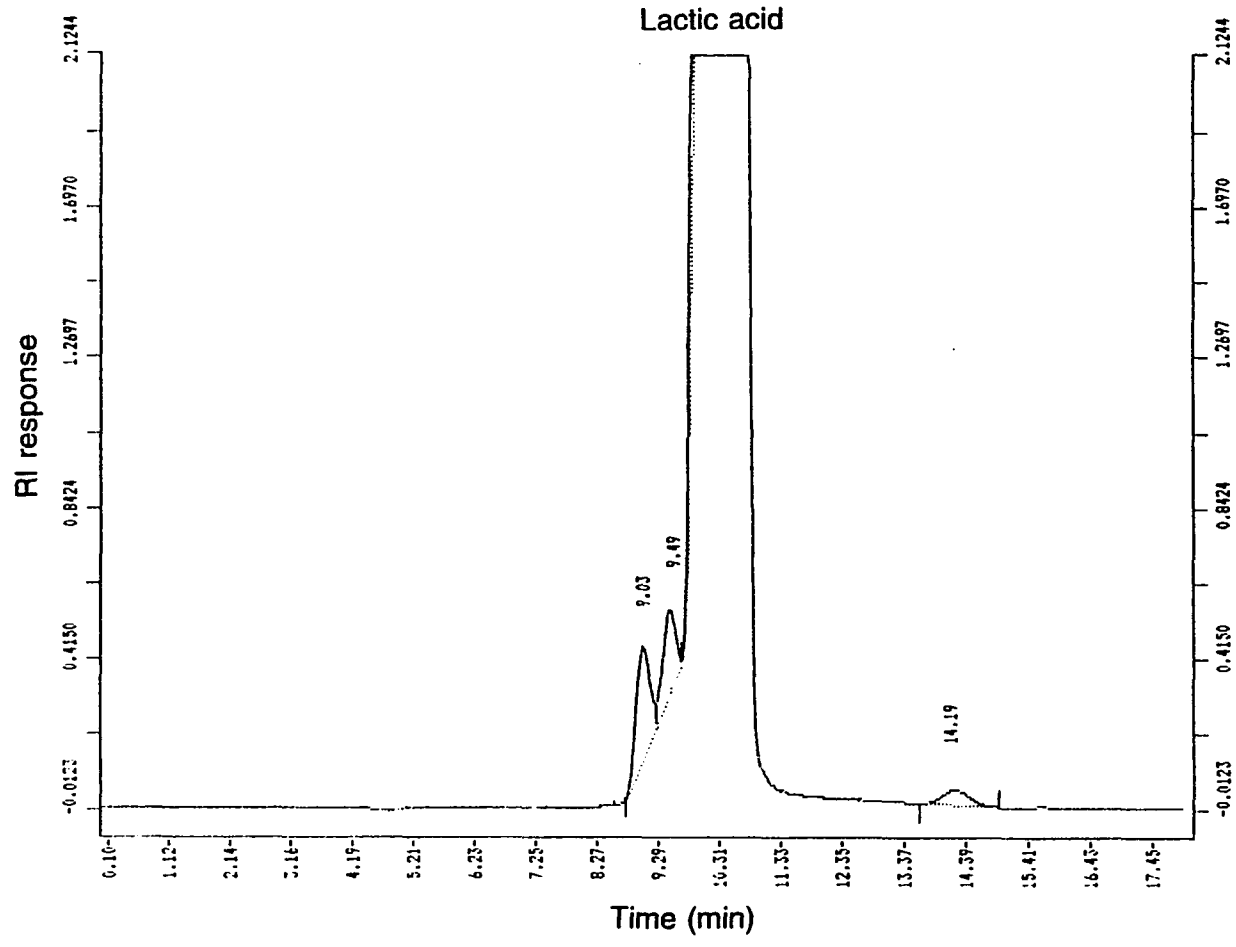


Figure 4.41. Chromatogram of lactic acid recovered from model broth pre-treated with activated carbon and Amberlite XAD-16

Lactobacillus casei (ATCC 11443). The broth was centrifuged (5000 x *g* for 10 min) to remove the cells. The cell-free broth had a pH of 5.3 and contained 5.5% lactate and 0.1% glucose. The decolorized broth was still cloudy and remained hazy even after acidification. The strong cation exchange resin column produced 1 BV of acidified broth with a pH of 1.95. At this pH, 99% of the lactic acid is in free acid form. The methanol eluate from VI-15 was colorless but turned cloudy once methanol was evaporated. The HPLC chromatogram revealed that no glucose was present but some large compounds (peaks in void volume) and smaller compounds (after the lactic acid peak) were still present. The test for readily carbonizable substances also came out positive.

The failure to produce heat-stable lactic acid from real fermentation broth was attributed to inadequate broth pretreatment, as manifested by the hazy acidified broth. The fermentation broth was more complex than the model broth. The contaminants that were not removed during the broth pretreatment steps were also sorbed by Riedel-de-Haen VI-15 resin. These contaminants were not removed completely during the water rinse step, either because of insufficient rinse time or the strong interaction with the resin. Incorporating a precolumn for Riedel-de-Haen VI-15 column may improve the purity of the product. This precolumn may be part of a stratified bed with Amberlite XAD-16 or employed as a separate unit after the acidification step.

The product purity can be improved with further process optimization. Employing a less-swelling macroporous Riedel-de-Haen VI-15 instead of the gel-type resin used in this study may decrease uptake of broth contaminants by pore filling and improve the efficiency of the rinse and desorption steps.

V. GENERAL SUMMARY AND CONCLUSIONS

Weak- (Reillex 425 and Riedel-de-Haen VI-15), moderate- (Dowex MWA-1, Dowex WGR-2, Dowex XUS 40283, and Dowex XUS 43432), and strong-(Dowex XUS 40196 and Amberlite IRA-958) base resins were evaluated for their sorption capacities of lactic acid from solutions with different pHs. Composite isotherms and fixed-bed sorption indicated that the sorption capacities of weak- and moderate-base resins decreased markedly as the pH of the feed exceeded the pK_a of lactic acid. Weak- and moderate-base sorbents should be used at feed pH below the pK_a of lactic acid (3.86) to minimize leakage of lactate from the column.

Riedel-de-Haen VI-15 exhibited significantly greater sorption capacity for lactic acid than Reillex 425. Dowex XUS 40196 can be used in a broader pH range with no significant reduction in capacity. The moderate- and strong-base resins had higher capacities for lactic acid, but required stronger eluants to desorb the lactic acid.

Riedel-de-Haen VI-15 was the most attractive sorbent for lactic acid recovery because of its high capacity and the ease by which it can be regenerated by using low-boiling alcohols. However, for this resin to be effective, the broth must be acidified first, but not by adding mineral acid, which competes with lactic acid for sorption sites. Another undesirable characteristic of this resin is its excessive swelling during sorption and shrinking during elution with methanol. The increase in internal void volume only increases sorption of other broth components by pore filling. These impurities, if not removed during the rinse step, may be trapped inside or may elute slowly with lactic acid as the bead shrinks once the resin comes in contact with methanol.

Duolite C-464, a weak-acid cation exchanger, was effective in decolorizing the broth but produced only 0.4 BV acidified broth with the desired pH of 2.9 from broth with a pH of 4.5. To generate 1 BV of feed stream for basic sorbent, the column must be 2.5 times the size of the lactic acid sorption column. Dowex XUS 40406, a strong-acid cation exchanger, produced 1 BV of acidified broth with pH 1.9.

Carbonic acid employed at 1724 kPa and 65°C was unable to regenerate Duolite C-464 and Amberlite IRC-50. The ineffectiveness of carbonic acid regeneration can be attributed to the low concentration of H^+ in carbonic acid solution, and presence of divalent cations and positively charged organic compounds in the broth. Carbonic acid may be better utilized by applying it directly in the broth. However, carbonic acid acidification alone may not be able to produce the low pH level desired. A combination of carbonic acid and strong cation exchange acidification will minimize consumption of sulfuric acid and generation of ammonium sulfate waste during regeneration of the cation exchanger.

Methanol completely desorbed lactic acid from Riedel-de-Haen VI-15 even at ambient temperature, but the elution required about 7 BV of methanol, which produced an eluate with half the lactic acid concentration than that of the feed. Methanol did not completely desorb lactic acid from Dowex MWA-1 and Amberlite IRA-35. NH_4OH desorbed lactic acid from Dowex MWA-1 in less than 2 BV and will probably be just as effective with Amberlite IRA-35. However, methanol and NH_4OH also desorbed other broth components that were adsorbed by the sorbent; thus, some impurities still remained in the product. The cloudy effluent at the beginning of the desorption cycle of Riedel-de-Haen VI-15 column indicated that the recovery scheme employed was not

sufficient to produce pure lactic acid. Pretreatment of the broth and/or a polishing step(s) is necessary to improve the purity of the product.

The browning reaction may be beneficial in producing heat-stable lactic acid by reducing, if not eliminating, glucose and other readily carbonizable compounds from the broth. The heat-treated broth must have close to neutral pH to minimize sorption of lactic acid on activated carbon. Browning, however, produced new compounds that create additional purification problems.

Among the nonfunctionalized sorbents, the hydrophobic Amberlite XAD-16 adsorbed more broth components than the hydrophilic Duolite S-761 or the moderately non-polar Diaion HP-2MG. However, Duolite S-761 also adsorbed other broth components that Amberlite XAD-16 did not.

Based on the results described in the preceding sections, a process for the recovery and purification of lactic acid from fermentation broth was evaluated. The scheme involved broth pretreatment by using activated carbon and nonfunctionalized resin as precolumns. A strong cation exchanger effectively acidified the broth without introducing competing acids. Lactic acid was recovered from the dilute acidified broth by using weak-base sorbent. The sorbed acid was then eluted by using a low-boiling alcohol (methanol) that can be evaporated readily and reused. With process optimization, a high-purity, heat-stable lactic acid can be produced. Another problem that needs to be addressed is improving the physical stability of the sorbent. Excessive swelling and shrinking of the sorbent during loading and desorption cycles make it susceptible to attrition.

VI. RECOMMENDATIONS

One of the objectives of the study was to develop a method that would minimize salt generation in the waste stream. Employing a strong-acid cation exchanger in acidifying ammonium lactate broth results in the production of ammonium sulfate when the column is regenerated with sulfuric acid. The amount of ammonium sulfate produced can be lessened by incorporating a carbonic acid acidification step before the cation exchange acidification step of the proposed process. Lowering the pH of the feed stream further will reduce the frequency of column regeneration. The pressure and temperature for carbonic acid broth acidification have to be optimized.

Another possibility of improving the proposed process is to run the acidified broth through a chromatographic separation step by using a nonfunctionalized resin as described by Kulprathipanja (1988). Water will be used as eluant, so no additional separation problem is created. This step is expected to greatly reduce the undesirable broth components going into the lactic acid adsorption by basic sorbent.

The evaluation of the proposed process for the recovery and purification of lactic acid was mainly qualitative in nature. No attempt was made to identify the so-called problem compounds. Identifying these compounds may lead to strategies to minimize, if not eliminate, their presence in the broth. Other resins with similar basicity as Riedel-de-Haen VI-15 but with hydropohobic and macroporous matrix are also worth investigating.

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APPENDIX

Nomenclature

Batch sorption data

W - dry weight of the resin (g).

C_o - concentration of lactic acid in the initial solution (mg/mL).

C_f - concentration of lactic acid in the bulk solution at equilibrium (mg/mL).

q - lactic acid sorbed by the resin (mg/g dry resin).

pH - bulk solution pH at equilibrium.

HLa - concentration of free lactic acid in the bulk solution at equilibrium calculated by using the Henderson-Hasselbach equation (mg/mL).

Fixed-bed sorption data

V_f - volume of fraction (mL).

V_{mp} - cummulative average volume (mL).

C_f - concentration of lactic acid in the fraction (mg/mL).

Data

Table A.1. Total capacities of basic sorbents for HCl

Resin	Weight (g)	Moisture Content (%)	Bed Height (cm)	Capacity for HCL (meq/g dry resin)		
				Weak-base	Strong-base	Total
Reillex 425	5.006	53.6	11.6	6.2	-	6.2
	5.000	53.6	12.7	6.1	-	6.1
Riedel-de-	5.001	63.8	8.7	8.0	-	8.0
Haen VI-15	5.001	63.8	9.1	7.9	-	7.9
Dowex	5.040	59.2	10.2	4.3	0.6	4.9
MWA-1	5.040	59.2	10.2	4.4	0.5	4.9
Dowex	5.053	31.4	19.1	8.3	-	8.3
WGR-2	5.002	36.5	22.6	8.3	-	8.3
Dowex XUS	5.023	50.0	9.6	4.4	1.0	4.5
40283	5.013	50.0	9.9	4.6	1.0	4.7
Dowex XUS	5.011	33.3	9.6	2.9	1.3	4.2
43432	5.043	33.3	9.7	3.1	1.2	4.3
Dowex XUS	5.046	62.1	9.1	3.6	1.0	4.6
40196	5.040	62.1	9.0	3.6	1.0	4.6
Amberlite	5.012	52.8	6.6	2.2	1.2	3.4
IRA- 958	5.017	52.8	5.1	2.2	1.3	3.5

Table A.2. Experimental data for composite sorption isotherm of lactic acid in Reillex 425

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.83	1	1.008	2.392	0.809	15.706	3.29	0.64
	2	1.006	5.706	2.505	31.837	3.22	2.04
	3	1.009	6.921	3.046	38.408	3.21	2.49
	4	1.009	9.124	4.300	47.821	3.17	3.57
	5	1.004	18.380	10.002	83.418	3.12	8.46
	6	1.003	26.142	16.617	94.989	3.08	14.25
	7	1.004	45.136	31.322	137.658	3.03	27.29
	8	1.006	62.412	44.476	178.294	3.01	38.97
	9	1.004	98.868	74.497	242.719	2.96	66.17
	10	1.001	123.065	96.045	269.847	3.03	83.67
	11	1.007	142.140	111.959	299.866	3.04	97.24
4.83	1	1.009	2.733	2.074	6.538	5.20	0.09
	2	1.008	5.208	4.801	4.041	5.24	0.19
	3	1.008	7.765	7.258	5.030	5.26	0.28
	4	1.000	10.150	10.034	1.160	5.26	0.38
	5	1.002	29.304	28.996	3.079	5.19	1.30
	6	1.005	51.378	50.933	4.434	5.15	2.48
	7	1.003	71.589	71.563	0.257	5.14	3.57
	8	1.005	86.056	85.922	1.337	5.12	4.48

Table A.3. Experimental data for composite sorption isotherm of lactic acid in Riedel-de-Haen VI-15

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.83	1	1.004	2.392	0.000	23.815	4.62	0.00
	2	1.006	5.706	0.617	50.592	4.80	0.06
	3	1.008	6.921	0.703	61.680	4.84	0.07
	4	1.006	9.124	0.962	81.104	4.74	0.11
	5	1.007	18.380	2.736	155.342	4.43	0.58
	6	1.006	26.142	9.046	169.903	4.20	2.84
	7	1.007	45.136	25.135	198.564	3.73	14.43
	8	1.008	62.412	34.699	275.071	3.51	23.98
	9	2.005	79.653	53.557	260.262	3.21	43.76
	10	2.007	100.839	70.892	296.466	3.17	58.87
	11	1.008	123.065	94.863	279.898	3.28	75.11
	12	1.008	142.140	110.316	315.589	3.24	88.97
	13	1.007	146.912	116.761	299.410	3.18	96.58
3.83	1	1.004	2.361	1.230	11.261	5.77	0.02
	2	1.003	5.586	2.974	26.040	5.86	0.03
	3	1.006	8.026	4.334	36.701	5.89	0.04
	4	1.004	11.477	6.338	51.182	5.81	0.07
	5	1.002	23.645	14.016	96.098	5.46	0.34
	6	1.008	31.531	19.405	120.302	5.16	0.93
	7	1.008	49.011	32.528	163.517	4.90	2.72
	8	1.007	67.789	47.933	197.177	4.65	6.69
	9	1.005	91.352	68.555	226.837	4.54	11.85
	10	1.006	111.548	86.909	244.921	4.50	16.20
	11	1.005	149.695	122.737	268.237	4.47	24.19
4.83	1	1.008	2.715	2.534	1.796	7.86	0.00
	2	1.007	5.662	5.300	3.591	7.69	0.00
	3	1.008	8.391	8.093	2.953	7.58	0.00
	4	1.002	11.064	10.795	2.684	7.57	0.00
	5	1.003	21.207	20.635	5.699	7.35	0.01
	6	1.000	31.713	31.183	5.290	7.19	0.02
	7	1.006	54.265	53.714	5.470	6.94	0.04
	8	1.008	76.096	75.525	5.663	6.79	0.09

	9	1.006	92.709	89.957	27.368	6.70	0.13
	10	1.009	121.929	118.916	29.851	6.52	0.26
	11	1.005	143.951	141.827	21.132	6.35	0.46
5.83	1	1.006	1.094	2.034	1.752	7.16	0.00
	2	1.002	2.625	2.431	1.935	7.93	0.00
	3	1.001	5.113	4.322	1.848	7.17	0.00
	4	1.007	10.741	10.928	-1.855	7.69	0.00
	5	1.008	21.425	21.703	-2.758	7.55	0.00
	6	1.005	35.147	36.900	-17.443	7.57	0.01
	7	1.002	53.397	54.993	-15.939	7.55	0.01
	8	1.003	78.757	82.298	-35.299	7.56	0.02
	9	1.002	105.866	110.369	-44.925	7.53	0.02

Table A.4. Experimental data for composite sorption isotherm of lactic acid in Dowex MWA-1

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.83	1	2.040	2.343	0.212	20.888	7.35	0.00
	2	2.039	6.016	0.550	53.623	7.17	0.00
	3	2.039	7.264	0.737	64.036	7.15	0.00
	4	2.028	9.602	0.898	85.837	6.62	0.00
	5	2.027	18.843	2.122	165.007	5.41	0.06
	6	2.028	28.285	3.308	246.336	4.88	0.29
	7	2.026	47.336	12.771	341.137	3.60	8.24
	8	2.059	66.501	29.390	360.449	3.32	22.81
	9	2.038	85.242	47.528	370.031	3.11	40.35
	10	2.036	103.183	65.344	371.596	3.19	53.84
	11	2.017	129.280	91.572	373.914	-	-
	12	2.030	148.878	110.320	379.829	-	-
3.83	1	2.026	3.434	1.335	20.707	8.14	0.00
	2	2.029	6.567	2.647	38.643	8.05	0.00
	3	2.016	8.419	4.133	42.521	7.91	0.00
	4	2.019	11.195	5.600	55.773	7.97	0.00
	5	2.033	21.942	12.241	95.428	7.66	0.00
	6	2.034	32.727	18.468	140.178	6.85	0.02
	7	2.020	52.311	30.557	215.378	6.14	0.16
	8	2.041	74.215	44.786	288.363	5.22	1.87
	9	2.020	100.796	68.107	323.590	4.50	12.69
	10	2.033	120.715	87.655	325.299	4.32	22.57
4.83	1	2.030	2.958	1.866	10.756	8.96	0.00
	2	2.024	5.579	4.156	14.062	8.97	0.00
	3	2.005	9.048	6.585	24.564	8.86	0.00
	4	2.020	11.072	9.054	19.980	8.67	0.00
	5	2.026	21.121	18.402	26.868	8.57	0.00
	6	2.035	31.612	28.045	35.035	7.86	0.00
	7	2.018	55.505	49.834	56.234	7.31	0.02
	8	2.005	77.701	70.197	74.838	7.23	0.03
	9	2.016	91.135	84.152	69.264	8.38	0.00
	10	2.016	122.482	113.827	85.901	7.95	0.01

	11	2.023	144.731	132.944	116.547	-	-
5.83	1	2.031	1.227	0.630	5.879	8.88	0.00
	2	2.005	2.631	1.823	8.060	9.00	0.00
	3	2.024	5.409	4.032	13.607	8.93	0.00
	4	2.007	10.679	9.054	16.186	8.88	0.00
	5	2.023	21.304	19.130	21.495	8.59	0.00
	6	2.024	35.479	33.387	20.673	8.20	0.00
	7	2.020	53.334	51.293	20.195	8.24	0.00
	8	2.036	79.269	76.868	23.580	7.91	0.01
	9	2.029	105.587	103.671	18.890	7.85	0.01
	10	2.027	129.666	127.254	23.808	8.14	0.01

Table A.5. Experimental data for composite sorption isotherm of lactic acid in Dowex WGR-2

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (g/mL)
2.83	1	1.003	2.334	0.345	19.826	9.36	0.00
	2	1.003	5.829	0.779	50.346	7.94	0.00
	3	1.004	6.981	0.843	61.133	7.56	0.00
	4	1.004	9.268	1.073	81.624	6.92	0.00
	5	1.005	18.452	2.245	161.266	5.44	0.06
	6	1.006	27.246	4.852	222.605	4.60	0.75
	7	1.003	44.077	11.534	324.454	3.75	6.49
	8	1.005	63.620	25.802	376.294	3.41	19.05
	9	1.002	80.017	42.491	374.507	3.25	34.12
	10	1.005	99.840	64.540	351.248	3.17	53.60
	11	1.001	126.333	88.258	380.369	3.18	73.00
	12	1.001	144.440	104.774	396.265	3.14	88.00
3.83	1	1.002	2.620	1.263	13.539	10.17	0.00
	2	1.007	5.490	2.772	26.995	9.87	0.00
	3	1.003	8.100	4.309	37.794	9.71	0.00
	4	1.004	10.913	5.904	49.886	9.38	0.00
	5	1.003	21.426	11.977	94.205	7.93	0.00
	6	1.002	31.253	17.698	135.283	7.58	0.00
	7	1.004	51.438	28.339	230.065	5.96	0.22
	8	1.008	70.197	41.987	279.862	5.18	1.92
	9	1.005	97.715	60.994	365.379	4.65	8.51
	10	1.006	116.489	78.596	376.667	4.44	16.37
	11	1.003	153.291	114.176	389.977	4.42	24.66
4.83	1	1.005	2.724	2.142	5.789	10.87	0.00
	2	1.005	5.436	4.093	13.363	11.20	0.00
	3	1.003	8.078	6.564	15.094	11.06	0.00
	4	1.006	10.607	9.006	15.915	11.07	0.00
	5	1.006	20.381	18.517	18.532	10.94	0.00
	6	1.008	30.511	27.534	29.530	10.94	0.00
	7	1.007	52.821	50.216	25.864	10.25	0.00
	8	1.004	73.842	71.807	20.267	9.12	0.00
	9	1.003	89.380	85.044	43.228	8.46	0.00

	10	1.005	119.530	114.747	47.591	8.14	0.01
	11	1.006	139.018	136.631	23.727	8.06	0.01
5.83	1	1.006	1.000	0.722	2.762	10.76	0.00
	2	1.006	2.416	1.786	6.266	11.04	0.00
	3	1.007	4.810	4.011	7.937	11.15	0.00
	4	1.004	10.205	8.704	14.945	11.46	0.00
	5	1.003	20.499	17.913	25.779	11.49	0.00
	6	1.003	33.952	31.047	28.966	11.68	0.00
	7	1.009	51.027	48.885	21.231	11.76	0.00
	8	1.003	76.527	72.949	35.675	11.63	0.00
	9	1.003	101.760	98.264	34.859	11.56	0.00
	10	1.006	125.930	122.506	34.040	11.45	0.00

Table A.6. Experimental data for composite sorption isotherm of lactic acid in Dowex XUS 40283

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.83	1	1.007	2.392	0.000	23.751	6.68	0.00
	2	1.002	5.706	0.347	53.504	5.60	0.01
	3	1.004	6.921	0.483	64.135	5.87	0.00
	4	1.003	9.124	0.606	84.943	5.62	0.01
	5	1.005	18.380	1.575	167.188	5.21	0.07
	6	1.004	26.142	2.315	237.391	4.78	0.24
	7	1.003	45.136	10.939	340.942	3.59	6.05
	8	1.007	62.412	28.976	332.119	3.27	23.00
	9	1.004	80.412	45.833	344.323	3.14	39.01
	10	1.002	98.868	63.310	354.740	3.08	54.50
	11	1.006	123.065	89.557	333.219	3.10	76.50
	12	1.004	142.140	107.246	347.723	3.06	93.55
3.83	1	1.003	2.575	0.782	17.865	7.77	0.00
	2	1.002	5.392	2.385	30.011	6.47	0.01
	3	1.006	7.764	3.838	39.031	7.30	0.00
	4	1.002	10.551	4.977	55.655	7.18	0.00
	5	1.002	20.759	10.362	103.723	6.88	0.01
	6	1.002	30.336	16.179	141.333	6.57	0.03
	7	1.005	49.840	27.895	218.453	5.91	0.25
	8	1.003	68.688	41.118	274.762	5.06	2.48
	9	1.004	94.288	64.544	296.346	4.46	12.87
	10	1.001	111.885	83.119	287.287	4.30	21.69
	11	1.003	146.844	118.178	285.678	4.32	30.71
4.83	1	1.003	2.733	1.524	12.056	8.35	0.00
	2	1.006	5.208	3.510	16.871	8.24	0.00
	3	1.003	7.765	5.819	19.410	8.20	0.00
	4	1.005	10.150	8.331	18.115	8.20	0.00
	5	1.004	19.554	17.035	25.084	8.01	0.00
	6	1.003	29.304	25.501	37.926	7.78	0.00
	7	1.004	51.378	47.825	35.433	7.73	0.01
	8	1.003	86.056	80.308	57.339	7.53	0.02
	9	1.002	134.085	128.302	57.740	7.30	0.05

5.83	1	1.004	0.906	0.470	6.231	8.23	0.00
	2	1.003	2.209	1.585	8.105	8.53	0.00
	3	1.003	4.507	3.702	10.780	8.51	0.00
	4	1.004	9.666	8.530	14.552	8.55	0.00
	5	1.005	19.574	19.373	6.960	8.56	0.00
	6	1.002	74.300	75.322	10.749	8.32	0.00
	7	1.004	97.650	98.682	19.489	8.21	0.00
	8	1.003	121.740	124.016	12.872	8.20	0.01

Table A.7. Experimental data for composite sorption isotherm of lactic acid in Dowex XUS 43432

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.83	1	1.007	2.392	0.317	21.228	7.29	0.00
	2	1.001	5.706	0.722	51.882	7.02	0.00
	3	1.008	6.921	0.789	62.546	7.01	0.00
	4	1.005	9.124	1.288	80.424	6.89	0.00
	5	1.006	18.380	2.020	164.127	6.28	0.01
	6	1.002	26.142	3.082	240.565	5.24	0.09
	7	1.003	45.136	13.020	330.542	3.58	7.92
	8	1.004	62.412	30.420	339.661	3.29	22.82
	9	1.006	80.412	48.328	338.815	3.20	38.50
	10	1.005	98.868	65.776	349.583	3.15	53.59
	11	1.002	123.065	90.418	364.836	3.20	71.31
	12	1.007	142.140	107.920	372.145	3.18	85.79
3.83	1	1.006	2.575	1.312	14.449	8.11	0.00
	2	1.002	5.392	2.407	31.563	8.11	0.00
	3	1.004	7.764	2.555	55.473	8.10	0.00
	4	1.004	10.551	3.221	75.352	8.07	0.00
	5	1.003	20.759	11.759	92.580	7.90	0.00
	6	1.002	30.336	16.388	145.830	7.69	0.00
	7	1.003	49.840	28.709	216.513	7.12	0.02
	8	1.006	68.688	42.497	278.300	5.42	1.09
	9	1.004	94.288	65.792	299.468	4.58	10.03
	10	1.005	111.885	84.203	298.195	4.44	16.84
	11	1.007	146.844	121.550	290.267	4.47	23.20
4.83	1	1.005	2.733	1.212	14.956	8.69	0.00
	2	1.007	5.208	4.143	12.340	8.64	0.00
	3	1.005	7.765	5.556	24.696	8.65	0.00
	4	1.004	10.150	7.671	28.360	8.60	0.00
	5	1.004	19.554	16.536	35.153	8.45	0.00
	6	1.005	29.304	25.759	45.216	8.42	0.00
	7	1.002	51.378	47.027	57.665	8.30	0.00
	8	1.002	71.589	68.146	53.878	8.26	0.00

	9	1.002	86.056	83.542	45.128	8.20	0.00
	10	1.002	117.140	109.894	92.773	8.14	0.01
	11	1.005	134.085	130.598	82.801	8.04	0.01
5.83	1	1.005	0.906	0.000	9.012	8.75	0.00
	2	1.004	2.209	0.822	13.820	9.05	0.00
	3	1.002	4.507	3.137	13.680	9.07	0.00
	4	1.005	9.666	7.122	25.315	9.21	0.00
	5	1.007	19.574	17.183	23.743	9.14	0.00
	6	1.008	32.764	30.076	26.669	9.03	0.00
	7	1.000	48.657	47.113	15.435	9.03	0.00
	8	1.003	74.300	71.399	28.916	8.84	0.00

Table A.8. Experimental data for composite sorption isotherm of lactic acid in Dowex XUS 40196

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.0	1	1.002	7.272	0.003	72.516	7.15	0.00
	2	1.002	10.060	0.028	100.154	4.47	0.01
	3	1.001	14.999	1.575	134.075	2.79	1.45
	4	1.002	24.743	9.991	147.236	2.34	9.70
	5	1.001	39.587	22.725	168.431	2.14	22.30
	6	1.002	57.155	37.753	193.717	2.03	37.20
	7	1.001	77.145	55.254	218.667	1.91	54.64
	8	1.002	95.442	72.165	232.314	1.85	71.47
	9	1.002	116.199	90.299	258.515	1.79	89.54
	10	1.001	137.238	108.896	283.076	1.73	108.10
2.8	1	1.002	2.616	0.049	25.627	11.32	0.00
	2	1.002	4.992	0.087	48.950	11.56	0.00
	3	1.001	7.789	0.241	75.390	11.61	0.00
	4	1.007	10.506	0.517	99.227	11.52	0.00
	5	1.001	15.683	1.976	136.890	4.10	0.72
	6	1.001	25.710	10.471	152.232	3.23	8.48
	7	1.002	40.777	21.319	194.246	3.10	18.16
	8	1.001	57.485	36.699	207.657	3.00	32.25
	9	1.001	79.402	56.300	230.745	2.95	50.13
	10	1.001	99.514	72.727	267.576	2.95	64.76
3.8	1	1.001	2.571	0.137	24.313	12.08	0.00
	2	1.001	5.074	0.490	45.802	12.30	0.00
	3	1.003	7.309	1.060	62.321	12.39	0.00
	4	1.002	10.009	2.067	79.242	12.43	0.00
	5	1.002	15.238	4.897	103.233	12.32	0.00
	6	1.001	24.880	11.234	136.343	11.65	0.00
	7	1.001	37.192	21.172	160.040	4.47	4.17
	8	1.002	57.071	38.415	186.234	4.12	13.62
	9	1.002	78.034	56.355	216.301	4.01	23.36
	10	1.002	96.985	73.292	236.528	3.98	31.62

4.8	1	1.002	2.737	0.638	20.936	8.40	0.00
	2	1.000	5.278	1.867	34.110	8.32	0.00
	3	1.000	8.053	3.465	45.879	8.33	0.00
	4	0.999	10.728	5.345	53.857	8.74	0.00
	5	1.000	15.778	8.948	68.312	7.93	0.00
	6	1.000	24.987	16.389	85.997	7.64	0.00
	7	1.000	40.746	30.713	100.349	7.35	0.01
	8	1.000	62.075	50.195	118.785	7.15	0.03
	9	1.000	83.570	70.966	126.044	7.08	0.04
	10	1.000	104.694	92.067	126.258	6.25	0.37
	11	1.000	126.333	112.538	137.904	6.21	0.50
	12	1.000	141.494	129.026	124.680	6.39	0.38
5.8	1	1.001	2.557	0.630	19.250	10.02	0.00
	2	0.999	5.057	1.908	31.506	9.74	0.00
	3	1.001	7.691	3.422	42.657	9.62	0.00
	4	1.000	10.211	5.309	49.037	9.36	0.00
	5	1.001	15.058	8.905	61.483	7.83	0.00
	6	1.000	24.359	16.723	76.367	6.37	0.05
	7	1.000	39.600	30.320	92.777	4.05	11.90
	8	1.000	58.499	48.257	102.475	3.74	27.44
	9	1.000	75.458	67.869	75.906	3.60	43.80
	10	0.999	94.208	83.812	104.031	3.51	57.93
	11	1.000	113.789	103.202	105.927	3.49	72.34
	12	0.999	138.317	126.103	122.205	3.46	90.20

Table A.9. Experimental data for composite sorption isotherm of lactic acid in Amberlite IRA-958

Initial pH	Sample No.	W (g)	Co (mg/mL)	Cf (mg/mL)	q (mg/g)	pH	HLa (mg/mL)
2.8	1	1.006	2.274	0.922	13.452	10.57	0.00
	2	1.006	7.041	2.756	42.598	10.03	0.00
	3	1.001	9.420	4.190	52.248	9.77	0.00
	4	1.008	18.531	8.029	104.180	8.61	0.00
	5	1.001	28.337	11.916	164.114	6.23	0.05
	6	1.007	43.000	27.792	151.039	3.80	14.85
	7	1.008	64.813	45.226	194.321	3.52	31.04
	8	1.004	100.839	80.447	203.092	3.29	63.39
	9	1.006	129.630	106.612	228.867	3.28	84.41
	10	1.007	146.761	122.485	240.977	3.24	98.79
3.8	1	1.003	2.665	1.326	13.346	10.84	0.00
	2	1.008	5.586	3.015	25.508	10.61	0.00
	3	1.002	8.432	4.685	37.407	10.48	0.00
	4	1.005	11.271	6.493	47.543	10.33	0.00
	5	1.001	22.101	14.272	78.245	9.85	0.00
	6	1.009	32.174	22.600	94.908	9.03	0.00
	7	1.008	53.026	39.311	136.097	7.95	0.00
	8	1.001	71.706	58.296	133.932	4.83	5.64
	9	1.009	101.140	82.611	183.693	4.44	17.20
	10	1.003	121.105	105.613	154.517	4.31	27.66
	11	1.006	159.730	142.647	169.900	4.33	36.10
4.8	1	1.003	2.715	1.441	12.700	11.32	0.00
	2	1.002	5.662	3.305	23.532	11.28	0.00
	3	1.001	8.391	5.394	29.932	11.21	0.00
	4	1.008	11.064	7.500	35.360	11.20	0.00
	5	1.009	21.207	15.773	53.862	11.03	0.00
	6	1.002	31.713	25.409	62.908	10.90	0.00
	7	1.003	54.265	47.662	65.802	10.62	0.00
	8	1.008	76.096	69.646	63.979	10.36	0.00

5.8	1	1.006	1.094	0.633	4.579	11.49	0.00
	2	1.008	2.625	1.362	12.529	11.49	0.00
	3	1.007	5.113	3.165	19.343	11.49	0.00
	4	1.006	10.741	7.308	34.115	11.47	0.00
	5	1.009	21.425	16.067	53.126	11.47	0.00
	6	1.001	35.147	29.119	60.212	11.45	0.00
	7	1.000	53.397	45.851	75.451	11.53	0.00
	8	1.005	78.757	71.780	69.431	11.42	0.00

Table A.10. Experimental data for fixed-bed sorption of lactic acid in Reillex 425 column

Fraction No.	pH 2.0			pH 3.8			pH 4.4			pH 5.8		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	5.2	2.6	0.000	1.5	0.8	0.000	1.8	0.9	0.000	2.2	1.1	0.000
2	5.1	7.7	3.585	1.9	2.5	0.000	1.9	2.7	0.000	2.3	3.4	0.000
3	4.8	12.6	32.982	1.9	4.4	6.006	1.8	4.5	6.030	2.4	5.7	23.466
4	4.6	17.3	54.834	1.9	6.2	25.860	1.8	6.3	34.971	2.4	8.1	55.362
5	4.6	21.9	58.461	1.8	8.1	34.038	1.8	8.1	48.081	2.3	10.5	57.726
6	4.8	26.6	59.085	1.8	9.9	35.763	1.8	9.9	50.199	2.4	12.8	57.954
7	4.7	31.3	59.073	1.8	11.7	38.565	1.9	11.7	50.691	2.4	15.2	59.445
8	4.7	36.0	58.716	1.8	13.5	43.845	1.8	13.5	49.857	2.4	17.6	59.208
9	4.6	40.7	58.695	1.8	15.3	45.900	1.8	15.3	50.904	2.4	20.0	59.610
10	4.7	45.3	59.283	1.8	17.1	49.980	1.8	17.0	52.407	2.4	22.4	57.888
11	4.7	50.0	58.560	1.8	18.9	53.286	1.8	18.8	53.475	2.4	24.8	59.745
12	4.7	54.7	59.103	1.8	20.6	54.078	1.8	20.6	54.822	2.4	27.2	57.633
13	4.7	59.4	59.298	1.8	22.4	55.296	1.8	22.4	55.662	2.5	29.7	58.386
14	4.7	64.1	59.271	1.8	24.1	55.998	1.8	24.1	56.382	2.4	32.1	58.632
15	4.6	68.8	59.067	1.8	25.9	57.333	1.8	25.9	56.634	2.4	34.5	58.242
16	4.8	73.4	58.950	1.8	27.6	57.828	1.8	27.6	57.126	2.4	36.9	59.076
17	4.7	78.2	59.337	1.8	29.4	57.954	1.8	29.4	56.847	2.4	39.3	57.987
18	4.7	82.9	58.818	1.8	31.1	58.425	1.8	31.2	57.768	2.5	41.8	59.454
19	4.5	87.5	58.548	1.8	32.9	57.810	1.8	32.9	57.159	2.4	44.2	59.718
20	3.5	91.5	58.644	1.8	34.6	57.888	1.9	34.7	58.383	2.4	46.6	58.371

Table A.11. Experimental data for fixed-bed sorption of lactic acid in Riedel-de-Haen VI-15 column

Fraction No.	pH 2.0			pH 3.8			pH 4.4			pH 5.8		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.2	1.1	0.000	2.1	1.1	0.000	2.1	1.1	0.000	2.1	1.1	0.000
2	2.2	3.3	0.000	2.2	3.2	0.000	2.1	3.2	0.000	2.1	3.2	0.000
3	2.2	5.5	0.000	2.1	5.4	2.372	2.2	5.3	1.800	2.1	5.3	0.000
4	2.2	7.7	0.000	2.1	7.5	16.981	2.2	7.5	20.679	2.1	7.4	16.125
5	2.2	9.9	0.000	2.2	9.6	31.374	2.2	9.7	45.666	2.1	9.5	48.516
6	2.2	12.1	0.000	2.1	11.8	34.643	2.2	11.9	50.286	2.1	11.6	57.691
7	2.2	14.3	0.000	2.2	13.9	35.403	2.2	14.1	50.784	2.1	13.7	59.052
8	2.1	16.5	0.000	2.2	16.1	35.805	2.2	16.3	51.513	2.2	15.8	58.422
9	2.1	18.6	0.000	2.2	18.3	35.707	2.2	18.5	51.372	2.2	18.0	59.172
10	2.1	20.7	2.253	2.2	20.5	36.371	2.2	20.7	51.723	2.2	20.2	59.010
11	2.2	22.8	18.111	2.2	22.7	35.979	2.2	22.9	51.645	2.2	22.4	58.743
12	2.1	25.0	32.107	2.1	24.9	36.784	2.2	25.1	51.288	2.2	24.6	59.583
13	2.2	27.1	40.010	2.1	27.0	36.806	2.2	27.3	51.332	2.2	26.8	58.923
14	2.2	29.3	44.571	2.2	29.1	36.859	2.3	29.6	51.595	2.2	29.0	60.105
15	2.2	31.5	47.973	2.2	31.3	37.460	2.3	31.9	52.472	2.2	31.2	58.320
16	2.1	33.7	50.699	2.2	33.5	36.781	2.3	34.2	52.392	2.2	33.4	59.520
17	2.1	35.8	51.570	2.1	35.7	37.146	2.2	36.4	51.846	2.3	35.7	59.595
18	2.1	37.9	52.765	2.1	37.8	39.494	2.2	38.6	51.579	2.2	37.9	59.739
19	2.2	40.0	55.065	2.1	39.9	42.752	2.2	40.8	52.127	2.2	40.1	59.685
20	2.2	42.2	55.659	2.2	42.0	45.971	2.2	43.0	52.015	2.2	42.3	58.928
21	2.3	44.5	57.450	2.1	44.2	48.868	2.2	45.2	51.915	2.2	44.5	59.922

22	2.3	46.8	58.492	2.2	46.3	52.514	2.2	47.4	52.610	2.2	46.7	59.142
23	2.2	49.0	59.517	2.2	48.5	53.143	2.3	49.7	51.828	2.3	49.0	59.658
24	2.3	51.3	59.198	2.2	50.7	55.491	2.2	51.9	51.867	2.2	51.2	58.929
25	2.2	53.5	59.965	2.2	52.9	55.693	2.2	54.1	52.463	2.2	53.4	60.000
26	2.3	55.8	62.211	2.2	55.1	56.470	2.3	56.4	51.381	2.3	55.7	59.493
27	2.2	58.0	59.727	2.2	57.3	57.535	2.2	58.6	51.795	2.1	57.9	60.037
28	2.2	60.2	60.430	2.2	59.5	57.988	2.2	60.8	52.449	2.1	60.0	58.923
29	2.2	62.4	59.782	2.2	61.7	58.307	2.2	63.0	52.158	2.2	62.1	59.763
30	2.2	64.6	60.291	2.2	63.9	59.564	2.3	65.3	51.702	2.2	64.3	59.121
31	2.2	66.8	60.028	2.1	66.1	59.634	2.3	67.6	51.759	-	-	-
32	2.3	69.1	59.958	2.2	68.2	59.204	2.2	69.8	51.864	-	-	-
33	2.2	71.3	59.868	2.2	70.4	59.568	2.2	72.0	52.404	-	-	-
34	2.2	73.5	59.544	2.2	72.6	60.134	2.2	74.2	52.362	-	-	-
35	2.2	75.7	59.591	2.2	74.8	60.359	2.2	76.4	52.962	-	-	-
36	2.3	78.0	59.662	2.2	77.0	59.976	2.3	78.7	52.992	-	-	-
37	2.2	80.2	59.904	2.2	79.2	60.157	2.2	80.9	52.761	-	-	-
38	2.2	82.4	60.086	2.2	81.4	60.296	2.2	83.1	54.189	-	-	-
39	2.2	84.6	59.954	2.3	83.7	59.531	2.3	85.4	53.607	-	-	-
40	2.2	86.8	73.008	2.2	85.9	60.867	2.1	87.6	54.435	-	-	-
41	-	-	-	2.2	88.1	61.058	2.1	89.7	54.276	-	-	-
42	-	-	-	2.2	90.3	59.603	2.2	91.8	55.080	-	-	-
43	-	-	-	-	-	-	2.2	94.0	55.398	-	-	-
44	-	-	-	-	-	-	2.2	96.2	55.527	-	-	-
45	-	-	-	-	-	-	2.2	98.4	55.602	-	-	-

Table A.12. Experimental data for fixed-bed sorption of lactic acid in Dowex MWA-1 column

Fraction No.	pH 2.0			pH 3.8			pH 4.4			pH 5.9		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.5	1.2	0.000	2.5	1.3	0.000	2.4	1.2	0.000	2.5	1.3	0.000
2	2.5	3.7	0.000	2.5	3.8	0.712	2.4	3.6	0.000	2.5	3.8	1.063
3	2.5	6.1	0.000	2.5	6.3	16.632	2.4	6.0	19.147	2.5	6.3	31.590
4	2.5	8.6	0.000	2.5	8.8	29.280	2.4	8.4	42.269	2.5	8.8	50.993
5	2.5	11.0	0.000	2.5	11.3	32.182	2.4	10.8	47.176	2.5	11.3	54.349
6	2.5	13.5	2.005	2.5	13.8	33.496	2.4	13.2	49.581	2.5	13.8	55.291
7	2.5	15.9	17.955	2.5	16.3	33.832	2.4	15.6	48.939	2.5	16.3	56.293
8	2.5	18.4	30.999	2.5	18.8	34.658	2.4	18.0	50.606	2.5	18.8	56.766
9	2.5	20.8	49.076	2.5	21.3	34.908	2.4	20.4	51.059	2.5	21.3	56.306
10	2.5	23.3	54.070	2.5	23.8	35.854	2.4	22.8	49.601	2.5	23.8	57.217
11	2.5	25.7	54.967	2.5	26.3	38.762	2.4	25.2	50.960	2.5	26.3	56.675
12	2.5	28.2	55.729	2.5	28.8	42.712	2.4	27.6	51.256	2.5	28.8	56.912
13	2.5	30.6	57.409	2.5	31.3	46.148	2.4	30.0	49.948	2.5	31.3	57.098
14	2.5	33.1	57.682	2.5	33.8	48.322	2.4	32.4	51.405	2.5	33.8	56.898
15	2.5	35.5	58.127	2.5	36.3	51.088	2.4	34.8	51.341	2.5	36.3	57.650
16	2.5	38.0	57.763	2.5	38.8	52.540	2.4	37.2	49.691	2.5	38.8	56.898
17	2.5	40.4	57.562	2.5	41.3	53.968	2.4	39.6	51.122	2.5	41.3	56.872
18	2.5	42.9	57.298	2.5	43.8	55.048	2.4	42.0	51.707	2.5	43.8	56.703
19	2.5	45.3	57.380	2.5	46.3	56.598	2.4	44.4	50.651	2.5	46.3	57.330
20	2.5	47.8	57.886	2.5	48.8	56.442	2.4	46.8	52.838	2.5	48.8	57.257
21	2.5	50.2	58.004	2.5	51.3	57.584	2.4	49.2	53.788	2.5	51.3	57.807
22	2.5	52.7	57.963	2.5	53.8	57.600	2.4	51.6	53.138	2.5	53.8	57.659

23	2.5	55.1	57.889	2.5	56.3	57.660	2.4	54.0	55.988	2.5	56.3	57.287
24	2.5	57.6	57.934	2.5	58.8	59.794	2.4	56.4	56.540	2.5	58.8	57.018
25	2.5	60.0	58.006	2.5	61.3	59.974	2.4	58.8	55.721	2.5	61.3	57.534
26	2.5	62.5	58.168	2.5	63.8	58.462	2.4	61.2	58.010	2.5	63.8	57.183
27	2.5	64.9	56.617	2.5	66.3	57.570	2.4	63.6	58.974	2.5	66.3	56.955
28	2.5	67.4	56.188	2.5	68.8	58.160	2.4	66.0	57.307	2.5	68.8	56.692
29	2.5	69.8	58.599	2.5	71.3	57.720	2.4	68.4	60.670	2.5	71.3	57.062
30	2.5	72.3	58.057	2.5	73.8	58.892	2.4	70.8	62.452	2.5	73.8	57.368
31	2.5	74.7	58.141	2.5	76.3	57.744	2.4	73.2	59.584	2.5	76.3	56.848
32	2.5	77.2	58.201	2.5	78.8	58.094	2.4	75.6	61.642	2.5	78.8	58.576
33	2.5	79.6	58.234	2.5	81.3	57.600	2.4	78.0	61.581	2.5	81.3	57.664
34	2.5	82.1	58.365	2.5	83.8	58.800	2.4	80.4	59.603	2.5	83.8	56.730
35	2.5	84.5	58.326	2.5	86.3	56.630	2.4	82.8	61.892	2.5	86.3	57.036
36	2.5	87.0	57.725	2.5	88.8	56.054	2.4	85.2	61.826	2.5	88.8	57.130
37	2.5	89.4	58.458	2.5	91.3	58.412	2.4	87.6	60.006	2.5	91.3	56.856
38	2.5	91.9	58.156	2.5	93.8	58.318	2.4	90.0	61.839	2.5	93.8	57.422
39	2.5	94.3	57.797	2.5	96.3	57.860	2.4	92.4	60.954	2.5	96.3	57.685
40	2.5	96.8	57.683	2.5	98.8	57.282	2.4	94.8	59.781	2.5	98.8	57.233

Table A.13. Experimental data for fixed-bed sorption of lactic acid in Dowex WGR-2 column

Fraction No.	pH 2.0			pH 3.8			pH 4.4			pH 5.9		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.8	1.4	0.000	2.5	1.25	0.000	2.5	1.25	0.000	2.1	1.1	0.000
2	2.8	4.1	0.000	2.5	3.8	0.000	2.5	3.8	0.000	2.1	3.2	6.388
3	2.8	6.9	0.000	2.5	6.3	10.056	2.5	6.3	3.540	2.1	5.3	35.126
4	2.8	9.6	0.000	2.5	8.8	23.274	2.5	8.8	23.772	2.1	7.4	52.612
5	2.8	12.4	0.000	2.5	11.3	31.209	2.5	11.3	39.141	2.1	9.5	57.553
6	2.8	15.1	0.000	2.5	13.8	33.642	2.5	13.8	43.229	2.1	11.6	59.775
7	2.8	17.9	0.000	2.5	16.3	35.037	2.5	16.3	44.934	2.1	13.7	60.857
8	3.3	20.9	30.402	2.5	18.8	34.278	2.5	18.8	45.543	2.1	15.8	61.149
9	2.5	23.8	54.690	2.5	21.3	34.932	2.5	21.3	45.468	2.1	17.9	58.199
10	2.5	26.3	58.740	2.5	23.8	35.355	2.5	23.8	46.065	2.1	20.0	58.679
11	2.5	28.8	59.976	2.5	26.3	35.337	2.5	26.3	46.317	2.1	22.1	61.571
12	2.5	31.3	60.375	2.5	28.8	36.489	2.5	28.8	46.008	2.1	24.2	58.628
13	2.5	33.8	59.673	2.5	31.3	38.748	2.5	31.3	46.218	2.1	26.3	59.442
14	2.5	36.3	60.684	2.5	33.8	43.554	2.5	33.8	45.435	2.1	28.4	58.259
15	2.5	38.8	59.307	2.5	36.3	48.303	2.5	36.3	45.530	2.1	30.5	58.563
16	2.5	41.3	59.850	2.5	38.8	51.729	2.5	38.8	45.732	2.1	32.6	61.569
17	2.3	43.6	59.808	2.5	41.3	54.789	2.5	41.3	45.993	2.1	34.7	62.147
18	2.3	45.9	59.820	2.5	43.8	56.463	2.5	43.8	47.331	2.1	36.8	62.179
19	2.3	48.1	59.601	2.5	46.3	58.050	2.5	46.3	46.812	2.1	38.9	58.410
20	2.5	50.5	61.050	2.5	48.8	58.647	2.5	48.8	48.012	2.1	41.0	62.198
21	2.5	53.0	59.262	2.5	51.3	58.632	2.5	51.3	48.579	2.1	43.1	59.088
22	2.5	55.5	59.352	2.5	53.8	59.454	2.5	53.8	49.695	2.1	45.2	59.088

23	2.5	58.0	59.325	2.5	56.3	59.265	2.5	56.3	51.296	2.1	47.3	60.343
24	2.5	60.5	60.018	2.5	58.8	59.778	2.5	58.8	52.539	2.1	49.4	58.403
25	2.3	62.9	59.514	2.2	53.8	60.618	2.2	53.8	53.928	2.1	51.5	60.404
26	2.3	65.1	60.015	2.5	63.8	59.412	2.5	63.8	54.843	2.1	53.6	61.716
27	2.3	67.4	59.955	2.5	66.3	59.448	2.5	66.3	55.866	2.1	55.7	62.240
28	2.3	69.6	59.301	2.5	68.8	59.148	2.5	68.8	56.079	2.1	57.8	61.407
29	2.5	72.0	59.166	2.5	71.3	59.679	2.5	71.3	57.486	2.1	59.9	62.076
30	2.5	74.5	59.925	2.5	73.8	59.460	2.5	73.8	57.129	2.1	62.0	58.635
31	2.5	77.0	59.532	2.5	76.3	61.119	2.5	76.3	57.216	2.1	64.1	61.938
32	2.5	79.5	59.709	2.5	78.8	59.880	2.5	78.8	57.483	2.1	66.2	62.319
33	2.4	82.0	60.384	2.5	81.3	60.183	2.5	81.3	58.278	2.1	68.3	58.633
34	-	-	-	2.5	83.8	60.411	2.5	83.8	59.169	2.1	70.4	61.224
35	-	-	-	2.5	86.3	60.021	2.5	86.3	58.101	2.1	72.5	61.904
36	-	-	-	2.5	88.8	60.129	2.5	88.8	58.398	2.1	74.6	59.706
37	-	-	-	2.5	91.3	59.673	2.5	91.3	57.612	2.1	76.7	61.732
38	-	-	-	2.5	93.8	62.901	2.5	93.8	58.341	2.1	78.8	60.113
39	-	-	-	2-.5	96.3	59.676	-	-	-	2.1	80.9	59.388
40	-	-	-	2.5	98.8	55.983	-	-	-	2.1	83.0	61.851

Table A.14. Experimental data for fixed-bed sorption of lactic acid in Dowex XUS 40283 column

Fraction No.	pH 2.0			pH 3.9			pH 4.4			pH 5.9		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.5	1.3	0.000	2.5	1.3	0.000	2.5	1.3	0.000	2.1	1.1	0.000
2	2.5	3.8	0.000	2.5	3.8	18.578	2.5	3.8	23.265	2.1	3.2	6.282
3	2.5	6.3	0.000	2.5	6.3	33.030	2.5	6.3	45.057	2.1	5.3	44.625
4	2.5	8.8	9.749	2.5	8.8	38.205	2.5	8.8	47.430	2.1	7.4	57.479
5	2.5	11.3	19.776	2.5	11.3	39.081	2.5	11.3	48.801	2.1	9.5	59.981
6	2.5	13.8	28.191	2.5	13.8	43.228	2.5	13.8	49.257	2.1	11.6	57.290
7	2.5	16.3	34.522	2.5	16.3	44.468	2.5	16.3	49.944	2.1	13.7	64.485
8	2.5	18.8	39.966	2.5	18.8	46.073	2.5	18.8	50.559	2.1	15.8	62.819
9	2.5	21.3	44.181	2.5	21.3	47.424	2.5	21.3	52.026	2.1	17.9	58.943
10	2.5	23.8	47.404	2.5	23.8	48.503	2.5	23.8	51.609	2.1	20.0	57.090
11	2.5	26.3	50.684	2.5	26.3	50.330	2.5	26.3	52.965	2.1	22.1	59.363
12	2.5	28.8	53.299	2.5	28.8	50.917	2.5	28.8	53.862	2.1	24.2	63.465
13	2.5	31.3	54.910	2.5	31.3	52.894	2.5	31.3	54.417	2.1	26.3	58.441
14	2.5	33.8	56.622	2.5	33.8	52.845	2.5	33.8	55.392	2.1	28.4	58.460
15	2.5	36.3	57.899	2.5	36.3	54.169	2.5	36.3	55.401	2.1	30.5	59.489
16	2.5	38.8	58.782	2.5	38.8	54.547	2.5	38.8	54.528	2.1	32.6	63.520
17	2.5	41.3	59.845	2.5	41.3	55.260	2.5	41.3	54.681	2.1	34.7	62.794
18	2.5	43.8	60.387	2.5	43.8	55.598	2.5	43.8	56.313	2.1	36.8	59.891
19	2.5	46.3	59.098	2.5	46.3	56.230	2.5	46.3	56.634	2.1	38.9	60.013
20	2.5	48.8	61.976	2.5	48.8	58.098	2.5	48.8	56.892	2.1	41.0	62.825
21	2.5	51.3	61.207	2.5	51.3	56.812	2.5	51.3	54.297	2.1	43.1	62.624
22	2.5	53.8	61.707	2.5	53.8	57.722	2.5	53.8	56.466	2.1	45.2	60.158

23	2.5	56.3	61.494	2.5	56.3	58.325	2.5	56.3	57.174	2.1	47.3	58.678
24	2.5	58.8	61.497	2.5	58.8	57.918	2.5	58.8	58.014	2.1	49.4	65.489
25	2.5	61.3	62.381	2.5	61.3	59.112	2.5	61.3	57.240	2.1	51.5	62.907
26	2.5	63.8	62.359	2.5	63.8	58.817	2.5	63.8	57.477	2.1	53.6	65.876
27	2.5	66.3	61.943	2.5	66.3	59.830	2.5	66.3	58.077	2.1	55.7	64.358
28	2.5	68.8	63.937	2.5	68.8	59.489	2.5	68.8	57.969	2.1	57.8	63.115
29	2.5	71.3	62.694	2.5	71.3	59.856	2.5	71.3	58.956	2.1	59.9	63.444
30	2.5	73.8	69.218	2.5	73.8	60.165	2.5	73.8	58.701	2.1	62.0	65.030
31	2.5	76.3	63.599	2.5	76.3	60.952	2.5	76.3	59.343	2.1	64.1	62.731
32	2.5	78.8	62.140	2.5	78.8	60.226	2.5	78.8	59.742	2.1	66.2	62.958
33	-	-	-	2.5	81.3	60.778	2.5	81.3	59.640	2.1	68.3	63.305
34	-	-	-	2.5	83.8	61.152	2.5	83.8	59.163	2.1	70.4	60.003
35	-	-	-	2.5	86.3	60.756	2.5	86.3	59.922	2.1	72.5	62.192
36	-	-	-	2.5	88.8	61.227	2.5	88.8	60.072	2.1	74.6	59.558
37	-	-	-	2.5	91.3	62.237	2.5	91.3	59.619	2.1	76.7	63.478
38	-	-	-	2.5	93.8	61.894	2.5	93.8	60.360	2.1	78.8	59.627
39	-	-	-	2.5	96.3	61.526	2.5	96.3	60.768	2.1	80.9	60.572
40	-	-	-	2.5	98.8	61.367	2.5	98.8	59.862	2.1	83.0	61.373

Table A.15. Experimental data for fixed-bed sorption of lactic acid in Dowex XUS 43432 column

Fraction No.	pH 2.0			pH 3.9			pH 4.4			pH 5.9		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.5	1.3	0.000	2.5	1.3	0.000	2.5	1.3	0.000	2.1	1.1	0.000
2	2.5	3.8	0.000	2.5	3.8	23.955	2.5	3.8	31.905	2.1	3.2	0.000
3	2.5	6.3	15.699	2.5	6.3	32.847	2.5	6.3	42.597	2.1	5.3	32.337
4	2.5	8.8	29.489	2.5	8.8	36.507	2.5	8.8	44.376	2.1	7.4	48.459
5	2.5	11.3	34.240	2.5	11.3	38.679	2.5	11.3	46.227	2.1	9.5	52.290
6	2.5	13.8	38.898	2.5	13.8	43.059	2.5	13.8	46.476	2.1	11.6	54.183
7	2.5	16.3	41.943	2.5	16.3	45.156	2.5	16.3	47.843	2.1	13.7	55.536
8	2.5	18.8	44.303	2.5	18.8	46.497	2.5	18.8	48.414	2.1	15.8	56.643
9	2.5	21.3	46.058	2.5	21.3	48.904	2.5	21.3	49.584	2.1	17.9	56.295
10	2.5	23.8	47.915	2.5	23.8	49.049	2.5	23.8	50.088	2.1	20.0	55.938
11	2.5	26.3	49.621	2.5	26.3	50.034	2.5	26.3	51.417	2.1	22.1	57.378
12	2.5	28.8	51.255	2.5	28.8	50.493	2.5	28.8	50.097	2.1	24.2	57.366
13	2.5	31.3	51.947	2.5	31.3	52.280	2.5	31.3	52.826	2.1	26.3	57.552
14	2.5	33.8	53.043	2.5	33.8	52.915	2.5	33.8	53.467	2.1	28.4	58.245
15	2.5	36.3	53.802	2.5	36.3	53.004	2.5	36.3	52.884	2.1	30.5	58.248
16	2.5	38.8	55.152	2.5	38.8	53.529	2.5	38.8	54.686	2.1	32.6	58.200
17	2.5	41.3	55.816	2.5	41.3	53.823	2.5	41.3	54.655	2.1	34.7	57.156
18	2.5	43.8	55.551	2.5	43.8	54.192	2.5	43.8	54.273	2.1	36.8	58.734
19	2.5	46.3	57.743	2.5	46.3	54.861	2.5	46.3	54.090	2.1	38.9	59.544
20	2.5	48.8	58.055	2.5	48.8	55.506	2.5	48.8	54.422	2.1	41.0	58.428
21	2.5	51.3	57.923	2.5	51.3	54.558	2.5	51.3	54.731	2.1	43.1	58.431
22	2.5	53.8	59.900	2.5	53.8	55.947	2.5	53.8	55.307	2.1	45.2	59.250

23	2.5	56.3	59.786	2.5	56.3	55.371	2.5	56.3	55.688	2.1	47.3	58.860
24	2.5	58.8	59.535	2.5	58.8	56.004	2.5	58.8	55.604	2.1	49.4	58.851
25	2.5	61.3	60.594	2.5	61.3	56.571	2.5	61.3	55.476	2.1	51.5	71.076
26	2.5	63.8	60.426	2.5	63.8	56.304	2.5	63.8	56.133	2.1	53.6	59.607
27	2.5	66.3	60.840	2.5	66.3	56.760	2.5	66.3	56.493	2.1	55.7	59.616
28	2.5	68.8	61.086	2.5	68.8	56.301	2.5	68.8	55.956	2.1	57.8	58.572
29	2.5	71.3	61.169	2.5	71.3	56.763	2.5	71.3	56.267	2.1	59.9	57.951
30	2.5	73.8	62.431	2.5	73.8	56.862	2.5	73.8	55.911	2.1	62.0	57.816
31	2.5	76.3	61.697	2.5	76.3	57.336	2.5	76.3	55.937	2.1	64.1	58.200
32	2.5	78.8	60.724	2.5	78.8	57.582	2.5	78.8	56.582	2.1	66.2	58.182
33	2.5	81.3	61.421	2.5	81.3	58.440	2.5	81.3	56.886	2.1	68.3	58.809
34	2.5	83.8	61.157	2.5	83.8	58.140	2.5	83.8	56.993	2.1	70.4	57.987
35	2.5	86.3	61.251	2.5	86.3	58.884	2.5	86.3	57.134	2.1	72.5	60.012
36	2.5	88.8	61.171	2.5	88.8	58.977	2.5	88.8	56.963	2.1	74.6	61.242
37	2.5	91.3	61.706	2.5	91.3	58.551	2.5	91.3	57.233	2.1	76.7	59.745
38	2.5	93.8	61.146	2.5	93.8	58.866	2.5	93.8	57.129	2.1	78.8	58.584
39	2.5	96.3	60.654	2.5	96.3	59.118	2.5	96.3	56.892	2.1	80.9	59.157
40	2.5	98.8	61.965	2.5	98.8	59.172	2.5	98.8	56.994	2.1	83.0	61.236

Table A.16. Experimental data for fixed-bed sorption of lactic acid in Dowex XUS 40196 column

Fraction No.	pH 2.0			pH 3.9			pH 4.4			pH 5.9		
	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf	Vf	Vmp	Cf
1	2.0	1.0	0.000	2.0	1.0	0.000	1.6	0.8	0.000	2.1	1.1	0.000
2	2.0	3.0	0.000	2.0	3.0	0.000	2.0	2.6	0.000	2.1	3.2	0.000
3	2.0	5.0	0.000	2.0	5.0	0.000	2.0	4.6	0.000	4.1	6.3	0.000
4	2.0	7.0	0.000	2.0	7.0	0.000	2.0	6.6	0.000	2.1	9.4	0.000
5	2.0	9.0	0.000	2.0	9.0	0.000	2.0	8.6	0.000	2.0	11.4	9.144
6	2.0	11.0	0.000	2.0	11.0	0.000	2.0	10.6	2.955	2.0	13.4	45.732
7	2.0	13.0	0.000	2.2	13.1	11.082	2.1	12.7	30.414	2.1	15.5	54.048
8	2.0	15.0	19.722	2.0	15.2	45.036	2.0	14.7	50.631	2.0	17.5	55.013
9	2.0	17.0	52.434	2.0	17.2	55.200	2.0	16.7	54.084	2.0	19.5	55.268
10	2.0	19.0	57.132	2.0	19.2	56.964	2.0	18.7	55.407	2.0	21.5	55.657
11	2.0	21.0	57.972	2.0	21.2	57.783	2.0	20.7	54.984	2.0	23.5	55.664
12	2.0	23.0	58.749	2.0	23.2	56.967	2.0	22.7	55.218	2.0	25.5	55.425
13	2.0	25.0	58.734	2.0	25.2	57.444	2.0	24.7	56.604	2.0	27.5	55.161
14	2.0	27.0	58.362	2.0	27.2	57.510	2.0	26.7	57.132	2.0	29.5	55.710
15	2.0	29.0	59.127	2.0	29.2	58.023	2.0	28.7	55.899	2.0	31.5	56.061
16	2.0	31.0	58.467	2.0	31.2	58.674	2.0	30.7	54.996	2.0	33.5	56.150
17	2.0	33.0	59.547	2.0	33.2	57.029	2.0	32.7	55.677	2.0	35.5	55.223
18	2.0	35.0	59.628	2.0	35.2	57.885	2.0	34.7	55.644	2.0	37.5	56.656
19	2.0	37.0	58.863	2.0	37.2	58.695	2.0	36.7	57.147	2.0	39.5	56.421
20	2.0	39.0	58.761	2.0	39.2	58.206	2.0	38.7	56.691	2.0	41.5	58.565
21	2.0	41.0	58.788	2.0	41.2	58.992	2.0	40.7	56.226	2.0	43.5	56.647
22	2.0	43.0	58.614	2.0	43.2	57.354	2.0	42.7	57.228	2.0	45.5	57.333
23	2.0	45.0	59.028	2.0	45.2	58.710	2.0	44.7	57.489	2.0	47.5	56.871

24	2.0	47.0	59.055	2.0	47.2	57.453	2.0	46.7	57.345	2.0	49.5	58.023
25	2.0	49.0	58.248	2.0	49.2	57.852	2.0	48.7	57.486	2.0	51.5	56.328
26	2.0	51.0	58.869	2.0	51.2	57.471	2.0	50.7	56.079	2.0	53.5	56.163
27	2.0	53.0	58.788	2.0	53.2	56.856	2.0	52.7	56.933	2.0	55.5	58.311
28	2.0	55.0	58.764	2.0	55.2	57.606	2.0	54.7	57.906	2.0	57.5	55.905
29	2.0	57.0	58.608	2.0	57.2	58.152	2.0	56.7	58.086	2.0	59.5	56.543
30	2.0	59.0	59.178	2.0	59.2	57.051	2.0	58.7	57.054	2.0	61.5	58.035
31	2.0	61.0	58.560	2.0	61.2	58.926	2.0	60.7	58.187	2.0	63.5	57.630
32	2.0	63.0	59.073	2.0	63.2	58.158	2.0	62.7	58.158	2.0	65.5	56.931
33	2.0	65.0	59.160	2.0	65.2	58.284	2.0	64.7	57.462	2.0	67.5	57.613
34	2.0	67.0	58.968	2.0	67.2	59.076	2.0	66.7	57.171	2.0	69.5	57.129
35	2.0	69.0	58.704	2.0	69.2	58.035	2.0	68.7	57.132	2.0	71.5	57.878
36	-	-	-	2.0	71.2	58.047	2.0	70.7	58.158	2.0	73.5	58.352
37	-	-	-	2.0	73.2	58.005	2.0	72.7	58.668	2.0	75.5	56.484
38	-	-	-	2.0	75.2	58.812	2.0	74.7	56.220	2.0	77.5	58.014
39	-	-	-	2.0	77.2	58.458	2.0	76.7	57.606	2.0	79.5	57.887
40	-	-	-	2.0	79.2	59.760	2.0	78.7	58.878	2.0	81.5	58.482
41	-	-	-	2.0	81.2	58.941	2.0	80.7	57.579	-	-	-
42	-	-	-	2.0	83.2	59.049	2.0	82.7	59.133	-	-	-
43	-	-	-	2.0	85.2	58.800	2.0	84.7	59.154	-	-	-
44	-	-	-	2.0	87.2	58.305	2.0	86.7	58.191	-	-	-
45	-	-	-	2.0	89.2	58.128	2.0	88.7	57.444	-	-	-
46	-	-	-	2.0	91.2	59.456	2.0	90.7	58.599	-	-	-
47	-	-	-	2.0	93.2	64.824	2.0	92.7	57.684	-	-	-
48	-	-	-	2.0	95.2	59.586	2.0	94.7	59.067	-	-	-
49	-	-	-	2.0	97.2	61.646	2.0	96.7	59.772	-	-	-
50	-	-	-	2.0	99.2	58.134	2.0	98.7	59.799	-	-	-

Table A.17. Experimental data for lactic acid recovery from model broth by using Riedel-de-Haen VI-15

Feed - Model broth acidified by using Duolite C-464
Eluant - Methanol

Fraction No.	Volume (mL)	Avg. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
Feed	100	-	-	58.351	7.006	2.90
L1	4.5	2.3	0.2	0.000	0.000	5.08
L2	4.7	6.9	0.6	2.801	0.406	6.83
L3	5.0	11.7	1.0	6.393	5.161	4.99
L4	4.9	16.7	1.4	9.263	7.638	6.17
L5	4.9	21.6	1.8	9.853	7.946	6.42
L6	4.8	26.4	2.2	10.112	8.059	6.82
L7	4.8	31.2	2.6	20.826	7.781	3.70
L8	4.9	36.1	3.0	36.157	7.430	3.29
L9	4.9	41.0	3.4	42.659	7.116	3.17
L10	4.8	45.8	3.8	50.393	7.451	3.10
L11	4.8	50.6	4.2	53.344	7.398	-
L12-	4.8	55.4	4.6	51.789	6.880	-
L13	4.7	60.2	5.0	57.216	7.336	3.03
L14	4.8	64.9	5.4	57.880	7.298	-
L15	4.7	69.7	5.8	57.479	7.163	-
L16	4.5	74.3	6.2	59.132	7.289	-
L17	4.4	78.7	6.6	59.200	7.306	3.00
L18	4.3	83.1	6.9	60.703	7.383	-
L19	4.2	87.3	7.3	59.845	7.292	-
L20	4.2	91.5	7.6	60.164	7.266	-
L21	5.8	96.5	8.0	57.935	6.966	2.99
R1	14.0	106.4	8.9	46.908	3.972	2.61
R2	14.2	120.5	10.0	19.499	0.306	2.25
R3	14.0	134.6	11.2	10.761	0.062	2.40
met1	4.9	144.1	12.0	8.336	0.044	2.42
met2	4.7	148.9	12.4	10.260	0.042	-
met3	5.4	153.9	12.8	28.835	0.038	2.90

met4	5.7	159.5	13.3	30.830	0.000	3.08
met5	5.7	165.2	13.8	26.304	0.000	
met6	5.8	170.9	14.2	20.350	0.000	3.17
met7	5.8	176.7	14.7	14.123	0.000	-
met8	5.7	182.5	15.2	9.062	0.000	-
met9	5.7	188.2	15.7	6.430	0.000	3.41
met10	5.5	193.8	16.1	4.829	0.000	-
met11	5.7	199.4	16.6	3.071	0.000	3.61
met12	5.7	205.1	17.1	2.101	0.000	-
met13	5.7	210.8	17.6	1.586	0.000	-
met14	5.7	216.5	18.0	1.186	0.000	3.80

Table A.18. Experimental data for lactic acid recovery from model broth by using Dowex MWA-1

Feed - Model broth acidified using Duolite C-464
Eluant - Methanol

Fraction No.	Volume (mL)	Avg. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
Feed	-	-	-	75.117	8.345	2.78
L1	4.8	2.4	0.1	0.000	0.000	7.22
L2	4.9	7.3	0.4	0.000	0.000	10.19
L3	4.8	12.1	0.7	0.278	1.004	12.45
L4	4.6	16.8	1.0	3.035	8.105	12.16
L5	4.7	21.5	1.2	7.929	9.413	9.81
L6	4.6	26.1	1.5	8.775	9.378	9.03
L7	4.7	30.8	1.8	10.571	9.475	4.70
L8	4.5	35.4	2.0	42.972	8.978	3.17
L9	4.4	39.8	2.3	68.509	8.682	2.89
L10	4.4	44.2	2.6	75.337	8.482	2.84
L11	4.4	48.6	2.8	73.660	7.960	-
L12	4.5	53.1	3.1	76.446	8.092	2.83
L13	4.5	57.6	3.3	77.704	8.504	2.86
L14	4.4	62.0	3.6	77.870	8.510	-
L15	4.4	66.4	3.8	77.868	8.511	2.82
R1	8.2	72.7	4.2	73.758	7.652	2.79
R2	8.4	81.0	4.7	42.586	2.371	2.51
R3	8.5	89.5	5.2	17.276	0.382	2.27
R4	8.6	98.0	5.7	8.346	0.060	2.40
R5	8.7	106.7	6.2	4.859	0.013	2.53
R6	8.8	115.4	6.7	3.264	0.005	2.62
R7	9.0	124.3	7.2	2.540	0.000	2.68
MeOH1	5.1	131.4	7.6	4.441	0.000	2.55
MeOH2	4.8	136.3	7.9	4.863	0.000	2.52
MeOH3	4.5	141.0	8.1	12.147	0.000	2.68
MeOH4	4.2	145.3	8.4	21.379	0.000	3.11
MeOH5	4.2	149.5	8.6	21.104	0.000	3.03

MeOH6	4.4	153.8	8.9	17.758	0.000	3.08
MeOH7	4.2	158.1	9.1	15.510	0.000	3.13
MeOH8	4.7	162.6	9.4	13.597	0.000	3.05
MeOH9	3.3	166.6	9.6	12.094	0.000	-
MeOH10	6.1	171.3	9.9	10.208	0.000	-
MeOH11	4.2	176.4	10.2	8.906	0.000	3.56
MeOH12	4.2	180.6	10.4	7.641	0.000	-
MeOH13	4.2	184.8	10.7	7.082	0.000	-
MeOH14	4.2	189.0	10.9	6.092	0.000	3.31
MeOH15	4.2	193.2	11.2	5.283	0.000	-
MeOH16	4.9	197.8	11.4	5.124	0.000	-
MeOH17	4.8	202.6	11.7	4.452	0.000	-
MeOH18	4.4	207.2	12.0	4.380	0.000	3.34

Table A.19. Experimental data for lactic acid recovery from model broth by using Dowex MWA-1

Feed - Model broth acidified by using Duolite C-464
Eluant - 5% NH_4OH

Fraction No.	Volume (mL)	Avg. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		(mL)	BV			
Feed	100	-	-	75.117	8.345	2.84
L1	5.5	2.8	0.2	0.000	0.000	5.99
L2	5.5	8.3	0.5	0.000	0.000	11.07
L3	5.5	13.8	0.8	0.001	0.587	12.65
L4	5.4	19.2	1.1	0.442	8.707	12.50
L5	5.3	24.6	1.4	5.919	10.260	10.75
L6	5.4	29.9	1.7	8.325	9.442	8.60
L7	5.2	35.2	2.0	27.647	9.232	3.50
L8	5.2	40.4	2.3	63.470	8.762	2.98
L9	5.2	45.6	2.6	72.303	8.204	2.88
L10	5.2	50.8	2.9	74.048	8.107	2.87
L11	5.2	56.0	3.2	74.442	8.088	-
L12	4.9	61.1	3.5	74.643	8.130	-
L13	5.0	66.0	3.8	75.189	8.190	2.86
L14	5.0	71.0	4.1	77.640	8.490	-
L15	5.0	76.0	4.4	76.821	8.416	2.86
R1	9.2	83.1	4.8	74.269	7.843	2.80
R2	9.1	92.3	5.3	38.047	2.949	2.50
R3	9.0	101.3	5.9	15.192	0.277	2.31
R4	9.1	110.4	6.4	7.418	0.040	2.46
R5	9.0	119.4	6.9	4.428	0.021	2.58
R6	9.1	128.5	7.4	3.160	0.002	2.66
R7	9.0	137.5	7.9	2.378	0.000	2.72
NH_4OH1	5.4	144.7	8.4	2.266	0.000	2.74
NH_4OH2	5.1	150.0	8.7	13.910	0.000	4.52
NH_4OH3	5.1	155.1	9.0	75.427	0.000	5.38
NH_4OH4	5.2	160.2	9.3	113.116	0.000	7.39
NH_4OH5	5.2	165.4	9.6	12.907	0.000	10.54

NH_4OH6	5.2	170.6	9.9	1.254	0.000	11.48
NH_4OH7	5.2	175.8	10.2	0.738	0.000	11.60
NH_4OH8	4.8	180.8	10.5	0.728	0.000	11.66
NH_4OH9	5.3	185.9	10.7	0.613	0.000	-
NH_4OH10	5.2	191.1	11.0	0.517	0.000	11.71
NH_4OH11	5.2	196.3	11.3	0.483	0.000	-

Table A.20. Experimental data for lactic acid recovery from model broth by using Amberlite IRA-35

Feed - Model broth acidified by using Duolite C-464
Eluant - Methanol

Fraction No.	Volume (mL)	Avg. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
Feed	49.5	-	-	62.088	7.008	2.83
L1	2.1	1.1	0.1	0.000	0.000	3.86
L2	2.1	3.2	0.3	0.000	0.000	5.11
L3	2.0	5.2	0.6	0.000	0.002	6.13
L4	2.0	7.2	0.8	0.235	1.000	9.66
L5	2.0	9.2	1.0	2.596	4.790	9.85
L6	2.0	11.2	1.2	5.383	6.890	9.72
L7	2.0	13.2	1.4	7.170	7.488	9.52
L8	2.0	15.2	1.7	8.451	7.699	9.32
L9	2.0	17.2	1.9	10.174	7.750	8.89
L10	2.0	19.2	2.1	16.544	7.402	4.25
L11	2.0	21.2	2.3	38.050	7.572	3.29
L12	1.9	23.2	2.5	53.202	7.218	3.03
L13	1.8	25.0	2.7	59.640	7.060	2.95
L14	1.8	26.8	2.9	59.328	6.712	2.92
L15	1.8	28.6	3.1	61.828	6.876	2.91
L16	1.8	30.4	3.3	62.980	6.992	-
L17	1.9	32.3	3.5	60.304	6.664	2.90
L18	1.9	34.2	3.7	61.056	6.752	-
L19	1.8	36.0	3.9	60.532	6.696	-
L20	1.8	37.8	4.1	62.656	6.928	2.90
L21	1.8	39.6	4.3	64.140	7.112	-
L22	1.8	41.4	4.5	60.312	6.712	-
L23	1.8	43.2	4.7	63.164	7.016	-
L24	1.8	45.0	4.9	60.296	6.736	-
L25	1.9	46.9	5.1	64.032	7.136	2.89
R1	5.1	50.4	5.5	62.416	6.968	2.87
R2	4.9	55.4	6.0	42.256	3.516	2.38

R3	5.2	60.4	6.6	14.235	0.615	2.04
R4	5.4	65.7	7.1	4.534	0.096	2.32
R5	5.4	71.1	7.7	1.789	0.014	2.54
R6	5.4	76.5	8.3	0.964	0.000	2.69
R7	5.4	81.9	8.9	0.659	0.000	2.79
R8	5.4	87.3	9.5	0.507	0.000	2.88
MeOH1	2.5	91.3	9.9	0.442	0.000	-
MeOH2	2.5	93.8	10.2	0.466	0.000	-
MeOH3	2.5	96.3	10.5	0.543	0.006	-
MeOH4	2.4	98.7	10.7	0.496	0.033	-
MeOH5	2.9	101.4	11.0	0.663	0.022	-
MeOH6	2.2	103.9	11.3	1.564	0.001	-
MeOH7	2.0	106.0	11.5	2.972	0.000	-
MeOH8	2.0	108.0	11.7	4.155	0.000	-
MeOH9	1.9	110.0	12.0	4.572	0.000	-
MeOH10	2.0	111.9	12.2	4.931	0.000	-
MeOH11	2.0	113.9	12.4	4.845	0.000	-
MeOH12	2.0	115.9	12.6	4.690	0.000	-
MeOH13	1.9	117.9	12.8	4.480	0.000	-
MeOH14	2.0	119.8	13.0	4.192	0.000	-
MeOH15	1.9	121.8	13.2	3.405	0.000	-
MeOH16	1.9	123.7	13.4	3.140	0.000	-
MeOH17	2.8	126.0	13.7	2.898	0.000	-
MeOH18	2.9	128.9	14.0	2.861	0.000	-
MeOH19	5.7	133.2	14.5	2.472	0.000	-
NaOH1	2.6	137.3	14.9	1.356	0.000	-
NaOH2	3.5	140.4	15.3	0.372	0.000	-
NaOH3	4.0	144.1	15.7	0.197	0.000	-
NaOH4	5.5	148.9	16.2	21.815	0.000	-
NaOH5	6.4	154.8	16.8	39.258	0.024	-
NaOH6	7.0	161.5	17.6	13.044	0.010	-
NaOH7	7.6	168.8	18.3	1.079	0.000	-

Table A.21. Experimental data for broth pre-treatment by using activated carbon (Unheated broth)

Fraction No.	Volume (mL)	Ave. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
Feed	246.2	-	-	118.34	11.23	4.50
1	6.4	3.2	0.0	0.00	0.00	5.98
2	6.3	9.6	0.1	0.00	0.00	5.94
3	6.3	15.9	0.2	6.53	0.00	8.10
4	6.2	22.1	0.3	44.02	0.00	8.02
5	6.0	28.2	0.4	73.32	0.00	7.76
6	6.0	34.2	0.5	83.07	1.92	7.26
7	6.0	40.2	0.6	85.03	3.65	6.09
8	6.0	46.2	0.6	86.64	5.58	5.47
9	6.0	52.2	0.7	87.05	6.02	5.15
10	6.0	58.2	0.8	87.64	6.77	4.96
11	5.9	64.2	0.9	91.28	7.73	4.83
12	5.9	70.1	1.0	91.95	8.30	4.73
13	5.9	76.0	1.1	92.87	9.25	4.67
14	5.8	81.8	1.1	93.52	8.78	-
15	5.7	87.6	1.2	97.08	11.07	4.58
16	5.8	93.3	1.3	96.04	9.62	-
17	5.8	99.1	1.4	97.98	9.56	-
18	5.8	104.9	1.5	98.44	9.52	4.50
19	5.8	110.7	1.5	101.06	9.70	-
20	5.5	116.4	1.6	101.40	9.62	-
21	5.7	122.0	1.7	100.32	10.31	4.47
22	5.8	127.7	1.8	103.19	10.06	-
23	5.8	133.5	1.9	104.80	9.94	-
24	5.7	139.3	1.9	105.20	10.44	-
25	5.5	144.9	2.0	105.61	9.47	4.42
26	5.9	150.6	2.1	101.46	8.54	-
27	5.9	156.5	2.2	94.68	6.92	-
28	5.9	162.4	2.2	90.80	6.54	-
29	5.9	168.3	2.3	84.86	7.04	-
30	5.9	174.2	2.4	85.64	5.22	4.48

31	5.8	180.0	2.5	89.52	6.64	-
32	5.9	185.9	2.6	95.22	6.78	-
33	5.8	191.7	2.7	96.93	7.33	-
34	5.7	197.5	2.7	100.10	8.72	-
35	5.7	203.2	2.8	105.00	9.86	4.41
36	5.7	208.9	2.9	105.88	9.48	-
37	5.7	214.6	3.0	105.86	9.78	-
38	5.6	220.2	3.1	106.42	10.24	-
39	5.7	225.9	3.1	107.16	9.28	-
40	5.7	231.6	3.2	109.46	10.67	4.39
41	5.9	237.4	3.3	106.40	9.51	-
42	5.9	243.3	3.4	104.84	9.51	-

Table A.22. Experimental data for broth pre-treatment by using activated carbon (Browned broth - pH 4.5)

Fraction No.	Volume (mL)	Ave. Cum. vol.		HLa (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
1	5.6	2.8	0.04	0.00	0.00	5.91
2	6.2	8.7	0.12	0.00	0.00	6.17
3	6.2	14.9	0.21	6.10	0.00	8.11
4	6.0	21.0	0.29	31.11	0.07	8.00
5	6.1	27.1	0.37	53.30	0.36	7.89
6	6.0	33.1	0.46	70.87	0.86	7.62
7	6.1	39.2	0.54	75.34	1.42	7.13
8	6.0	45.2	0.63	79.33	2.22	6.20
9	6.1	51.3	0.71	84.87	3.16	5.62
10	6.0	57.3	0.79	86.85	3.99	5.32
11	6.0	63.3	0.88	88.47	4.64	5.11
12	6.0	69.3	0.96	84.88	4.84	4.97
13	6.0	75.3	1.04	88.04	5.27	4.86
14	6.0	81.3	1.13	83.45	5.16	4.77
15	5.9	87.3	1.21	87.61	5.98	4.70
16	5.9	93.2	1.29	83.07	5.43	4.65
17	5.9	99.1	1.37	88.39	5.74	4.64
18	5.9	105.0	1.45	95.18	7.02	-
19	5.8	110.8	1.54	92.60	6.86	-
20	5.8	116.6	1.62	94.22	7.05	4.54
21	5.8	122.4	1.70	94.52	7.08	-
22	5.8	128.2	1.78	94.00	7.00	-
23	5.7	134.0	1.86	100.53	7.46	4.48
24	5.7	139.7	1.94	102.70	7.66	-
25	5.8	145.4	2.01	103.96	7.67	-
26	5.8	151.2	2.10	104.95	7.70	4.44
27	5.8	157.0	2.18	101.90	7.38	-
28	5.7	162.8	2.26	102.16	7.42	-
29	5.5	168.4	2.33	109.12	8.06	4.38

30	5.2	173.7	2.41	108.03	7.18	-
31	4.5	178.6	2.47	92.12	5.92	-
32	5.1	183.4	2.54	103.16	6.34	-
33	3.0	187.4	2.60	106.02	6.16	4.54

Table A.23. Experimental data for broth pre-treatment by using activated carbon (Browned broth - pH 10)

Fraction No.	Volume (mL)	Ave. Cum. vol.		Lactic acid (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
1	6.1	3.1	0.04	0.00	0.00	5.74
2	6.3	9.3	0.13	0.84	0.01	5.58
3	6.3	15.6	0.22	5.98	0.01	7.82
4	6.2	21.8	0.30	49.08	0.02	7.83
5	6.0	27.9	0.39	77.63	0.02	7.76
6	6.0	33.9	0.47	95.22	0.03	7.69
7	6.0	39.9	0.55	100.19	0.15	7.59
8	6.0	45.9	0.64	101.99	0.26	7.51
9	6.0	51.9	0.72	101.50	0.44	7.43
10	6.0	57.9	0.80	99.50	0.65	7.31
11	5.9	63.9	0.88	96.49	0.90	7.18
12	5.9	69.8	0.97	96.36	1.18	7.03
13	6.0	75.7	1.05	95.68	1.44	6.89
14	5.9	81.7	1.13	98.50	1.84	6.70
15	5.9	87.6	1.21	95.33	2.04	6.52
16	6.0	93.5	1.30	96.66	2.32	6.34
17	5.9	99.5	1.38	96.36	2.51	6.18
18	6.0	105.4	1.46	96.73	2.69	6.04
19	6.0	111.4	1.54	97.10	2.86	5.92
20	6.0	117.4	1.63	100.17	3.07	5.82
21	6.0	123.4	1.71	95.80	3.04	5.74
22	6.0	129.4	1.79	101.26	3.28	5.66
23	6.0	135.4	1.88	101.59	3.36	-
24	6.0	141.4	1.96	98.27	3.28	-
25	6.0	147.4	2.04	98.88	3.36	5.53
26	6.0	153.4	2.13	100.76	3.46	-
27	6.0	159.4	2.21	104.32	3.58	-
28	6.0	165.4	2.29	103.47	3.56	5.43
29	6.0	171.4	2.38	106.16	3.72	-
30	6.0	177.4	2.46	102.92	3.62	-
31	5.8	183.3	2.54	106.96	3.80	5.36

Table A.24. Experimental data for broth pre-treatment by using Amberlite XAD 16 (Unheated broth)

Fraction No.	Volume (mL)	Ave. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		BV	mL			
Feed	2.2	-	-	118.34	11.23	4.35
1		0.1	1.0	0.00	0.00	6.46
2	2.2	0.2	3.3	0.00	0.00	-
3	2.2	0.3	5.5	0.00	0.00	-
4	2.2	0.4	7.7	0.00	0.00	6.14
5	2.2	0.6	9.9	1.21	0.26	-
6	2.2	0.7	12.1	16.26	1.95	6.70
7	2.2	0.8	14.3	53.98	5.37	6.52
8	2.2	1.0	16.5	79.64	7.68	6.03
9	2.2	1.1	18.7	93.35	9.04	5.41
10	2.2	1.2	20.9	101.20	9.75	4.93
11	2.2	1.3	23.1	-	-	-
12	2.2	1.5	25.3	115.88	10.284	4.50
13	2.2	1.6	27.5	-	-	-
14	2.2	1.7	29.7	-	-	-
15	2.2	1.8	31.9	122.46	10.200	4.37
16	2.2	2.0	34.1	-	-	-
17	2.2	2.1	36.3	-	-	4.36
18	2.2	2.2	38.5	-	-	-
19	2.2	2.4	40.7	-	-	-
20	2.2	2.5	42.9	122.26	10.210	4.35

Table A.25. Experimental data for broth pre-treatment by using Diaion HP-2MG (*Unheated broth*)

Fraction No.	Volume (mL)	Ave. Cum. vol. (mL)	Ave. Cum. vol. BV	Lactate (mg/mL)	Glucose (mg/mL)	pH
Feed	-	-	-	118.34	11.23	4.35
1	2.5	1.3	0.1	0.00	0.00	6.73
2	2.5	3.8	0.2	0.00	0.00	6.63
3	2.5	6.3	0.4	0.00	0.00	6.63
4	2.5	8.8	0.5	0.64	0.05	6.74
5	2.5	11.3	0.7	9.30	0.97	6.35
6	2.5	13.8	0.9	53.22	4.91	6.04
7	2.5	16.3	1.0	89.66	8.25	5.46
8	2.4	18.7	1.2	104.22	9.63	4.82
9	2.5	21.2	1.3	113.46	10.00	4.50
10	2.5	23.7	1.5	114.12	9.68	4.35
11	2.4	26.1	1.6	112.72	9.42	4.32
12	2.4	28.5	1.8	117.94	9.84	-
13	2.4	30.9	1.9	120.06	9.98	-
14	2.4	33.3	2.1	119.65	9.90	-
15	2.4	35.7	2.2	118.36	9.83	4.31
16	2.4	38.1	2.4	-	-	-
17	2.4	40.5	2.5	-	-	-
18	2.4	42.9	2.7	-	-	-
19	2.4	45.3	2.8	-	-	-
20	2.4	47.7	3.0	119.19	9.86	4.31

Table A26. Experimental data for broth pre-treatment by using Duolite S-761 (Unheated broth)

Fraction No.	Volume (mL)	Ave. Cum. vol.		Lactate (mg/mL)	Glucose (mg/mL)	pH
		mL	BV			
Feed	-	-	-	118.34	11.23	4.35
1	2.5	1.3	0.1	0.00	0.00	9.04
2	2.5	3.8	0.2	0.00	0.00	8.92
3	2.5	6.3	0.4	0.00	0.00	8.88
4	2.5	8.8	0.5	0.32	0.02	8.06
5	2.5	11.3	0.7	9.79	0.97	6.95
6	2.5	13.8	0.9	55.15	5.15	6.31
7	2.5	16.3	1.0	96.26	8.81	5.24
8	2.4	18.7	1.2	111.04	9.86	4.63
9	2.4	21.1	1.3	114.98	9.86	4.41
10	2.3	23.5	1.5	119.89	10.11	4.33
11	2.3	25.8	1.6	114.02	9.54	-
12	2.4	28.1	1.7	120.87	10.14	4.31
13	2.3	30.5	1.9	118.52	9.87	-
14	2.4	32.8	2.0	120.87	10.04	-
15	2.4	35.2	2.2	113.80	9.50	4.31
16	2.4	37.6	2.3	-	-	-
17	2.3	40.0	2.5	-	-	-
18	2.3	42.3	2.6	-	-	-
19	2.3	44.6	2.8	-	-	-
20	2.3	46.9	2.9	118.44	9.86	4.31
21	2.3	49.2	3.1	-	-	-
22	2.3	51.5	3.2	-	-	-
23	2.2	53.7	3.3	-	-	-
24	2.2	55.9	3.5	-	-	-
25	2.3	58.2	3.6	119.79	9.98	4.31
26	2.4	60.5	3.8	-	-	-
27	2.2	62.8	3.9	-	-	-
28	2.4	65.1	4.0	-	-	-
29	2.3	67.5	4.2	-	-	-
30	2.4	69.8	4.3	117.08	9.66	4.31
31	2.3	72.2	4.5	-	-	-
32	2.3	74.5	4.6	-	-	-

33	2.2	76.7	4.8	-	-	-
34	2.3	79.0	4.9	-	-	-
35	2.4	81.3	5.0	117.90	9.78	4.31
36	2.4	83.7	5.2	-	-	-
37	2.3	86.1	5.3	-	-	-
38	2.3	88.4	5.5	-	-	-
39	2.3	90.7	5.6	-	-	-
40	2.4	93.0	5.8	118.48	9.80	4.31