

Recovery of Lactic Acid by Sorption

Resin Evaluation

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ABSTRACT

Weak-, moderate-, and strong-base resins were evaluated for their sorption capacities of lactic acid from solutions with different pHs. Composite isotherms and breakthrough curves 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 the result of the decrease in concentration of undissociated lactic acid, the species preferentially adsorbed by the resin, as the pH of the feed increases. The sorption capacity of the strong-base resin remained constant in the same pH range (pH 2-6).

Index Entries: Lactic acid; recovery; sorption; ion exchange.

INTRODUCTION

The use of polylactic acid (PLA) for biodegradable plastics and controlled-release drugs and pesticides is a potential multimillion dollar market (1). The commercial success of PLA hinges on the purity (heat-stable grade) and the cost of the fermentation-produced lactic acid. Therefore, one of the major challenges in lactic acid production is to reduce the cost of the acid recovery and purification, which could amount to almost 50% of the final product cost.

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Adsorption is a process suitable for the recovery of substances produced in dilute concentrations and complex aqueous solutions, such as fermentation broth. A substantial number of publications in the last 12 yr have addressed the use of ion-exchangers and other adsorbents in the recovery of organic acids (2–16). The more recent studies have dealt specifically with lactic acid recovery (11–16). The manufacture of lactic acid currently uses ion-exchange adsorbents mainly for demineralization of thin crude lactic acid.

The adsorption of lactic acid, and carboxylic acids in general, on basic adsorbents is strongly affected by the pH of the process stream. This is because of the pH effect on the equilibrium of the undissociated and dissociated acid forms (3–4,7–9). Therefore, the adsorbent that will maximize the recovery of lactic acid is expected to depend on the processing pH as well as on the adsorbent's basicity.

The objective of our research is to investigate the use of polymeric adsorbents containing basic functional groups in the primary recovery and/or purification of lactic acid from fermentation broth. In this article, the effect of pH of the lactic acid solution on the adsorption capacities of ion-exchange resins with varying degrees of basicity is evaluated. The uptake mechanism of the selected resins occurs by both adsorption and absorption (10); thus, the lactic acid uptake in this work will be referred to as sorption, and the ion-exchange resins as sorbents.

METHODOLOGY

Resin Preparation

Weak-base (VI-15 and Reillex 425), moderate-base (MWA-1, WGR-2, and XUS 40283), and strong-base (XUS 40196) resins (Table 1) were used in this study. The hydrated resins were transferred into a 1-L column (30 × 6 cm). The resin bed was backwashed with deionized water to remove the fine particles. This step was followed by washing (downflow) of the bed with three bed-volumes of 5% HCl, five bed-volumes of deionized water, three bed-volumes of 4% NaOH, and another five bed-volumes of deionized water. The flow rate was adjusted to allow at least 30 min of contact time between the resin 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 resin (in hydroxyl form) was drained under vacuum through a filter and stored in a capped plastic bottle. The strong-base resin was not oven-dried because the quaternary ammonium group in hydroxide form is susceptible to thermal degradation when subjected to temperatures over 60°C (18). The moisture content of the resins was determined by Karl Fischer titration (19).

Table 1
Properties of Selected Basic Adsorbents

Resin	Manufacturer	Type/Matrix	Functional group	pK _a
Reillex 425	Reilly Industries, Indianapolis, IN	Macroporous/PVP-DVB	Pyridine	4.9 ^a /5.2 ^b
VI-15	Riedel-de-Haen, Seelze, Germany	Gel/methylene-bis-acrylamide	Imidazole	6.9 ^c
MWA-1	Dow Chemical, Midland, MI	Macroporous/SDVB	3°-amine	8.8 ^a
WGR-2	Dow Chemical	Gel-Macroporous/Epoxy	3°-amine	8-10
XUS 40283	Dow Chemical	Macroporous/SDVB	3°-amine	8-10
XUS 40196	Dow Chemical	Gel/SDVB	4°-amine, Type I	> 10

^aData from Kuo et al. (4).

^bData from Chanda et al. (3).

^cWeast (17).

Analytical Methods

Lactic acid and glucose concentrations were analyzed by using HPLC (Waters, Milford, MA) equipped with a refractive index detector and Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) (Bio-Rad Chemical Division, Richmond, CA). The column temperature was maintained at 65°C by using a column oven. The mobile phase was 6 mM H₂SO₄ 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, Pittsburg, 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 using 10M NaOH. The lactic acid broth was produced by *Lactobacillus casei* (ATCC 11443) in a stirred-batch fermentor. The medium consisted of 80 g glucose, 10 g yeast extract, 0.6 g MgSO₄·7H₂O, 0.03 g MnSO₄·H₂O, 1 g sodium acetate, and 0.5 g K₂PO₄ dissolved in 1 L of deionized water. The temperature was kept at 37°C, and the pH was maintained at 5 by using 8M NaOH.

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* (20).

Batch Sorption

Composite sorption isotherms (4,21) 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) was used as a starting solution. 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 using the following equation:

$$q = (C_0 - C_e) V/W \quad (1)$$

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), and W = weight of dry resin (g).

Fixed-Bed Sorption

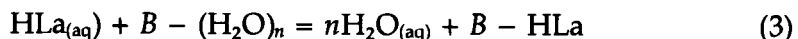
A jacketed 30 × 1 cm id column (Kontes Scientific Glassware/Instruments, Vineland, NJ) equipped with adjustable plungers was charged with hydrated resin (2 g dry resin). The air trapped in the sorbent was removed, and the plunger was lowered to the top of the sorbent bed. The column was drained under vacuum to estimate the interstitial volume of the bed and 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, Pittsburg, PA) was used to maintain the temperature (30°C) of water in the jacket. Fractions of 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 were determined. Column capacities at saturation were calculated by using the following equation:

$$q_s = \{[\Sigma(C_f - C_i) V_i] - C_f V_{st}\} / W \quad (2)$$

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), and W = dry weight of the resin in the column (g).

Modeling of Composite Sorption Isotherms

The Langmuir model (22) was used to describe the competition between lactic acid and n molecules of water for a basic site on the sorbent (10):



where HLa represents the undissociated lactic acid form, B represents a basic functional group, and (aq) refers to the bulk liquid phase. In addition to the standard Langmuir model assumptions, it was further assumed that:

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:

$$q/q_m = KC_{\text{HLA}}/(1 + KC_{\text{HLA}}) \quad (4)$$

where q = composite uptake calculated from Eq. (1) (mg/g), q_m = total sorbent capacity for lactic acid (mg/g), K = association constant of the (B-HLa) complex (mL/mg), and 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 Eq. (4).

RESULTS AND DISCUSSION

Batch Sorption

The composite sorption isotherms of a weak- and a moderate-base sorbent were generated with lactic acid solutions of different starting pHs (Fig. 1). The pH values in parentheses represent the range of equilibrium values that were measured at each experimental point. The sorption capacities of VI-15 and MWA-1 decreased markedly with increasing pH of lactic acid solution. The largest deviations from the initial pH occurred in dilute lactic acid solutions because of the depletion of HLa from the bulk fluid. The pH range of the lactic acid solution at equilibrium was greater for MWA-1 than for VI-15, which correlates to the difference in basicity (pK_a) between MWA-1 and VI-15 (Table 1). A more dramatic decrease in sorption capacity between pHs 2.8 and 3.8 was observed with VI-15 than with MWA-1 because the imidazole group of VI-15 has a lower pK_a than the tertiary amine of MWA-1. The "negative" sorption values measured with VI-15 at pH 5.8 were the result of the resin's greater uptake of water than of lactic acid. The polyacrylate matrix of VI-15 binds a substantial amount of water. At the same time, a negligible amount of HLa is available at this pH for complexation with the imidazole group of VI-15. As a result, the measured lactic acid concentration in the bulk solution at equilibrium was higher than that in the initial solution. Composite isotherms underestimate the capacity of hydrophilic resins because of their inherent affinity for water. For high sorbent selectivities, the composite uptake (q) approaches the actual surface concentration of the acid (10). The composite isotherms of the sorbents listed in Table 1 also exhibited decreased sorption capacity with increasing initial pH. The major reason for the observed decrease in sorption capacity is the pH effect on the concentration of HLa. HLa is the form that interacts with basic functional groups of the resin (3); therefore, lactic acid uptake is expected to decrease as the solution pH approaches or exceeds the pK_a of the acid.

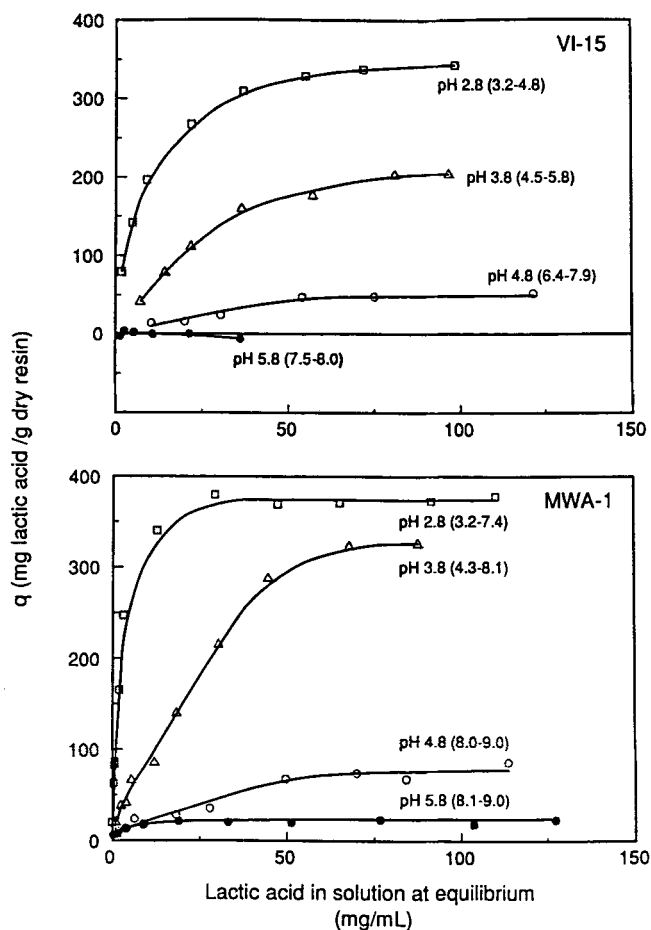


Fig. 1. Composite sorption isotherms of lactic acid at different initial pHs. Numbers in parentheses are range of pH values at equilibrium.

To eliminate the pH effect on lactic acid uptake, the equilibrium concentrations of HLa were calculated by using the Henderson-Hasselbach equation (23). The equilibrium sorption data for the six resins were replotted as a function of equilibrium HLa concentration (Fig. 2). Experimental uptakes were fitted with the Langmuir equation (Eq. [4]), and model parameters were estimated (Table 2). Except for those of Reillex 425 and XUS 40196, the model equation predicted the experimental data very well. The Reillex 425 and XUS 40196 isotherms showed a good fit when a linear term was added to the Langmuir equation [$q/q_m = KC_{HLA} / (1 + KC_{HLA}) + K_1 C_{HLA}$]. This deviation from the Langmuirian behavior suggests that mechanisms other than acid-base interactions may be involved in the lactic acid uptake. A similar sorption behavior was observed by Ernst and McQuigg (16) with Reillex 425 and by Chanda et al. (3), who

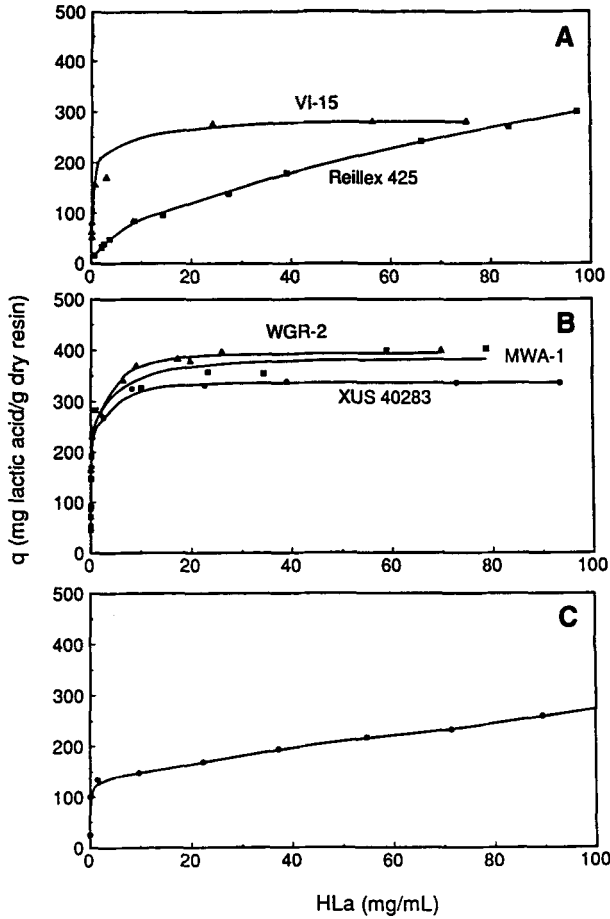


Fig. 2. Composite sorption isotherms of lactic acid: (A) weak-base, (B) moderate-base, and (C) strong-base anion exchangers. HLa is the undissociated lactic acid concentration at equilibrium.

investigated the sorption of carboxylic acids on a gel-type poly(4-vinylpyridine). The association constant (K) values (Table 2) increased with increasing basicity of the polymeric resins (Table 1). The K of VI-15 was higher than that of Reillex 425. For moderate-base resins, the K value of XUS 40283 was higher than those of MWA-1 and WGR-2. As would be expected, the strong-base resin (XUS 40196) had the highest K among the resins evaluated. The total lactic acid capacities of VI-15 and the moderate-base resins were similar, and ranged between 3.1 and 4.2 meq/g. The total sorption capacities of Reillex 425 and XUS 40196 cannot be compared directly with other resins because a different model was used to estimate their values. Compared with the other resins, Reillex 425 and XUS 40196 had substantially smaller equilibrium capacities at HLa concentrations

Table 2
Calculated Values of the Langmuir Model Parameters and Resin Capacities

Resin	K_1 , mL/mg	q_m , mg/g dry resin	Total capacity for HCl, meq/g dry resin	Total capacity for lactic acid ^a , meq/g dry resin
Reillex 425	0.2 2.1 ^b	102	6.1	1.1
VI-15	2.2	280	7.9	3.1
MWA-1	8.4	365	3.8	4.0
WGR-2	10.4	376	8.3	4.2
XUS 40283	16.5	335	4.4	3.7
XUS 41096	459 1.4 ^b	136	4.7	1.5

^aCalculated from q_m values.

^bValues of K_1 in the modified Langmuir equation.

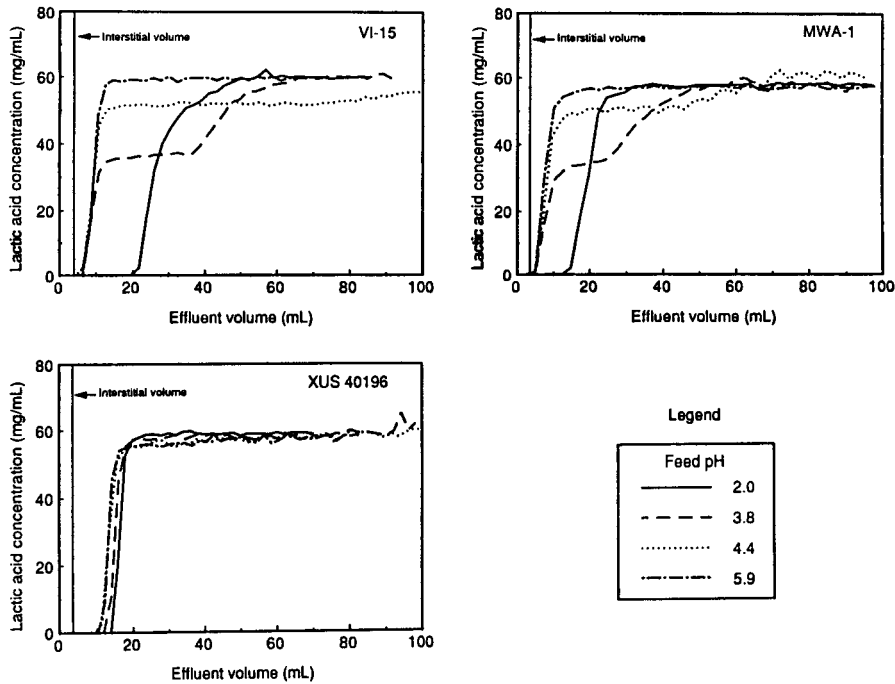


Fig. 3. Breakthrough profiles of lactic acid feed (60 mg/mL) at different pHs.

below 40 mg/mL (Fig. 2). Reillex 425, VI-15, and WGR-2 exhibited much smaller capacities for lactic acid compared with their total capacities for HCl. This may indicate that some of the functional groups in these resins are not accessible to lactic acid molecules. On the other hand, the capacities for lactic acid of MWA-1 and XUS 40283 were about the same as their total capacities for HCl.

Fixed-Bed Sorption

Determining the breakthrough curves is a common industrial practice in designing an adsorption process. The breakthrough profiles (Fig. 3) show the outlet concentration of lactic acid that results from a step input of 60 mg lactic acid/mL. Three resins, representing each basicity group, were used to determine the effect of pH on their breakthrough points (Fig. 3) and saturation capacities (q_s) (Fig. 4).

Breakthrough profiles for VI-15 and MWA-1 show that these resins preferentially bind the HLa form. Two distinct concentration plateaus were observed: (1) VI-15 at pH 3.8, and (2) 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 (La^-) 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 breakthrough points for both resins at pHs > 2 were the result of La^- breakthrough at void volume. In spite of the slight shift in the breakthrough points, the breakthrough profiles of XUS 40196

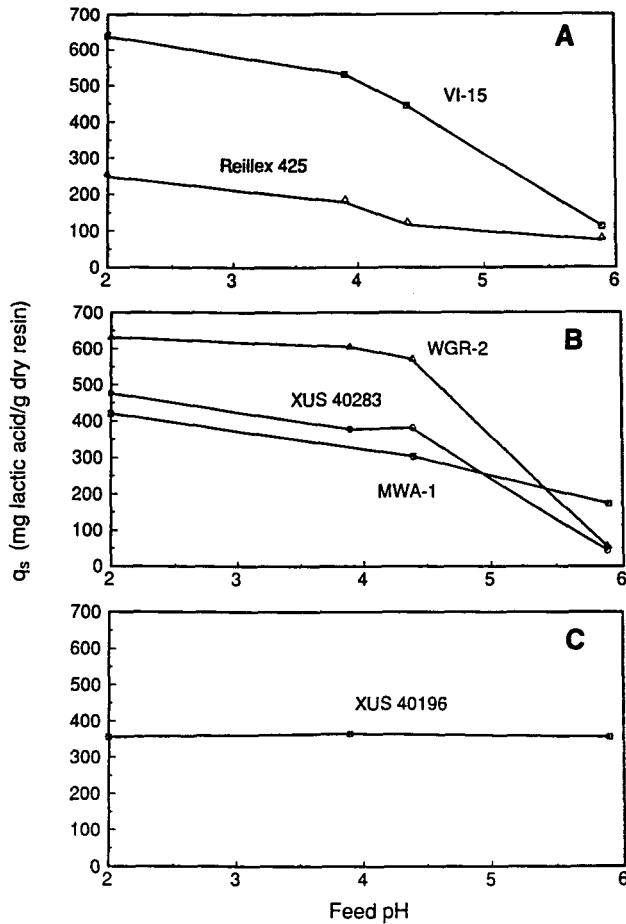


Fig. 4. Effect of pH on saturation capacity of lactic acid (60 mg/mL) on (A) weak-base, (B) moderate-base, and (C) strong-base anion exchangers.

were similar and were not significantly affected by pH of the feed (Fig. 3). The strong-base functional group of XUS 40196 resin apparently interacts with both HLa and La⁻ forms of lactic acid. With HLa, the mechanism is an acid-base neutralization reaction, whereas with La⁻, an anion-exchange (OH⁻) prevails (24). 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 of VI-15 at different feed pHs were always higher than those of Reillex 425 (Fig. 4A). Chanda et al. (3) observed the same trend in their study of carboxylic acid sorption with polybenzimidazole and poly(4-vinylpyridine) resins. The resin capacities of VI-15 and Reillex 425 decreased with increasing pH of the lactic acid feed. A significant drop in saturation capacities of WGR-2 and XUS 40283 occurred at pHs >4.5, whereas the capacity of MWA-1 slowly decreased throughout the pH range investigated (Fig. 4B). The experimental data indicated that the weak-base sorbents can be used up to pH 3.8 without substantial loss

in capacity, but for the moderate-base resins, it is up to pH 4.5. The sorption capacity of the strong-base sorbent (XUS 40196) was not affected by the pH of the feed up to pH 5.8 (Fig. 4C).

The sorption capacities estimated from the breakthrough curves (Fig. 4) were generally higher than those from the batch experiments. There are two reasons for this discrepancy. First, the saturation capacity values calculated by Eq. (2) also include the lactic acid retained in the solution in the pores of the resin 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 VI-15, which exhibited the highest water uptake. The actual saturation concentration on the resin surface, 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 resin pore volume is difficult to determine because of the swelling of the resin in the presence of lactic acid. We estimated the pore volumes of hydrated MWA-1 and Reillex 425 resins by drying them at 110°C and corrected 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 breakthrough curves of fermentation broth containing 60 mg lactic acid/mL and 17 mg glucose/mL at pH 4.4 (Fig. 5) showed that the lactic acid, glucose, and pH profiles of the effluent were similar for both sorbents. Unlike MWA-1, the breakthrough point of glucose in VI-15 occurred somewhat later than that of the lactate. This suggests some glucose uptake by VI-15, but not by MWA-1.

CONCLUSIONS

For efficient utilization of the sorption capacity, weak- and moderate-base sorbents should be used at feed pH below the pK_a of lactic acid (3.86), because only the undissociated acid form interacts specifically with the resin (Eq. [3]). Lactic acid fermentation is usually carried out at pH $> pK_a$, and a large fraction of the acid is present as lactate ion (salt). Therefore, acidification of the broth will be required before using weak- or moderate-base sorbents.

Of the weak-base sorbents, VI-15 exhibited significantly greater sorption capacity for lactic acid than did Reillex 425. A potential disadvantage of VI-15 is the excessive swelling and shrinking that may occur during adsorption, desorption, and regeneration cycles. Because of the high resin capacity at low lactic acid concentrations, VI-15 could be used for *in situ* extraction and pH control of lactic acid fermentation. Moderate-base resins, if needed, could be utilized for lactic acid recovery from solutions with pHs up to 4.5. Strong-base anion exchangers are applicable in a

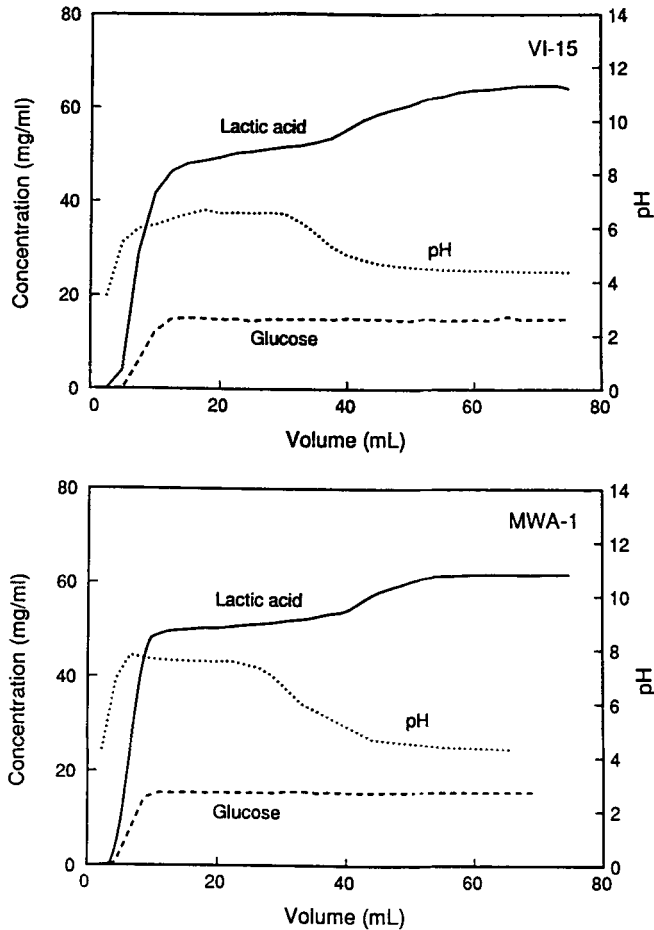


Fig. 5. Breakthrough profiles of lactic acid and glucose using fermentation broth as feed at pH 4.4.

broader pH range with no significant reduction in capacities. The moderate- and strong-base resins have higher selectivities for lactic acid, but stronger eluants will be needed to desorb the lactic acid. In selecting the best resin for lactic acid recovery, one should also consider physical and mechanical properties of the sorbent, the ease of lactic acid desorption, and the costs of the various eluants used in the desorption and regeneration cycles, as well as the cost of their disposal.

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