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Adsorption of Lactic Acid on Weak Base Polymeric Resins

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Abstract: Sorption of lactic acid from a simulated broth has been investigated using weak base ion exchange polymeric resins which behave as functionalized polymers because of tertiary amino groups on the polymer matrix. The equilibrium data for the uptake of lactic acid are represented by Langmuir-Freundlich combination isotherm. The sorption has been modeled by a phase equilibrium approach using the extended Flory-Huggins theory of polymer solutions. The interaction of media components, such as glucose and inorganic salts, with the resins and their effect on lactic acid sorption, also has been investigated.

Keywords: Ion exchange resin, lactic acid, Langmuir-Freundlich combination isotherm, Molecular modeling, Extended Flory-Huggins theory, sorption

INTRODUCTION

Lactic acid ($CH_3CH(OH)COOH$) is a naturally occurring hydroxycarboxylic acid with applications in a variety of fields (1, 2). A major amount of lactic acid is produced by fermentation which is influenced by two important factors. First, it is a product inhibited fermentation which limits the productivity and second, its highly hydrophilic structure makes its recovery from aqueous solutions difficult. Conventionally, the acid is recovered by precipitation as calcium lactate followed by treatment with a mineral acid (3). The process suffers from several disadvantages, such as product loss during

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crystallization, consumption of a large quantity of chemicals and generation of a considerable amount of solid waste (4). Several strategies have been suggested in literature for the recovery of the acid, including solvent extraction (5–9), liquid emulsion membrane extraction (10, 11), aqueous two-phase extraction (4, 12), electro-dialysis (13–15), adsorption (16–18), ion exchange (3, 19) and reactive distillation (20).

In the present study, an attempt has been made to exploit weakly basic ion exchange resins as functionalized polymers to sorb lactic acid selectively from aqueous solutions. The acid-loaded resins can be regenerated with alcoholic solvents. There is an expected reduction in the net consumption of chemicals and no waste is generated. Also, unlike the strongly anionic resins the salts do not hinder the uptake of the acid by the polymeric resins.

A wide variety of polymer resins are commercially available with different support matrices and a range of functional groups giving flexibility of selecting the resin for the required separation. One can also design a resin if the basic interactive forces responsible for the adsorption are identified. In the present study, the sorption of the acid is by molecular interaction(s) as shown in Fig. 1(a, b). The nitrogen of the tertiary amino functional group on the resin carries a partial negative charge because of the lone pair of electrons. This nitrogen can have Lewis acid-base interaction with partially positively charged hydroxyl as well as acidic hydrogen of lactic acid. If the acid can donate the proton to the weak base site the acidic anion and the protonated base can interact electrostatically.

The sorption capacity of the resins and the effect of temperature, and media components such as glucose, $MgSO_4$ and $MnSO_4$, on uptake of lactic

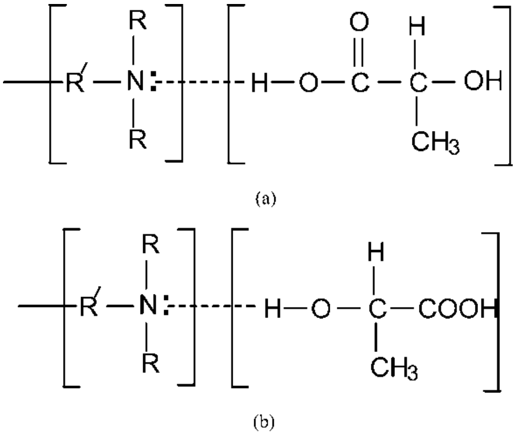

Figure 1. (a) Schematic representation of the interaction between the lactic acid and weak base resin (Carboxylic ‘H’ bonded with ‘N’ of functional group) (b) Schematic representation of the interaction between the lactic acid and weak base resin (Hydroxyl ‘H’ bonded with ‘N’ of functional group).

acid, have been investigated in detail in the present work. The sorption of the acid was also tested from a simulated broth in a packed adsorption column.

Materials and Reagents

Resins used in this study were, Indion 860 and Indion 850, which are weak base resins (WBR), and a strong base resin (SBR), Indion 810. A strong acid resin (SAR), Indion 190 was also tried for comparison. The resin characteristics are given in Table 1. Lactic acid, glucose, methanol, and other media components were of analytical grade and purchased from S. D. Fine Chemicals, Mumbai.

Analytical Methods

Lactic acid concentration was determined by titrating the solution against standardized NaOH solution using phenolphthalein as an indicator. The presence of inorganic salts had no effect on the analysis of the acid. Glucose was analyzed by UV-Spectrophotometer with dinitrosalicylic acid as a reagent (21). Aqueous solutions of magnesium and manganese sulphates were analyzed by colorimetric detection by a UV-Spectrophotometer using barium chloranilate as a reagent. The accuracy and precision of this method is within 1% (22).

EXPERIMENTAL METHOD

Conditioning of Resins

The resins were kept soaked in 5% (w/v) aq. NaOH solutions for 8 hrs followed by washing with distilled water in a fluidized bed column till the pH of the outlet solution became neutral. The resins were then thoroughly washed with methanol and dried in an oven for 6 hrs at 333 K and subsequently cooled to room temperature of 303 K. The resins' structure and properties were not affected by this pretreatment, as the conditions were not allowed to go beyond the physical limits of the resins. The acidic resins were conditioned by soaking in aq. HCl acid solutions and following similar steps as those for basic reasons.

Determination of Sorption Equilibria

A known weight (0.1 gm) of the pretreated resins was soaked in distilled water and then contacted with 10 cm^3 of aqueous solution of lactic acid on an orbital shaker at 180 rpm at a constant temperature for up to 4 h. The samples of the

Table 1. Characteristics of ion exchange resins

Properties[a]	Indion 850	Indion 860	Indion 810	Indion 190
Type	Weak base macroporous	Weak base macroporous	Strong base macroporous	Strong acid macroporous
Matrix structure	Styrene-divinylbenzene copolymer	Styrene-divinylbenzene copolymer	Styrene-divinylbenzene copolymer	Styrene-divinylbenzene copolymer
Functional group	$-NR_2$	$-NR_2$	$-N^+ R_3$	$-SO_3H^+$
Ionic form	Free base	Free base	OH^-	Hydrogen
Moisture content (%)	47–55	52–56	56–63	50–55
Surface area, (m^2/gm)	35	Na	27.7	30–40
Pore volume, (ml/gm)	0.52	Na	0.26	0.3–0.4
Pore diameter, (Å)	339	Na	290	250–350
Exchange capacity, (meq/ml)	1.5	1.4	1.0	1.9
Cross linking (%)	7–8	NA	7–8	NA
Elasticity parameter (η) (mol/dm^3)	3.19	NA	3.58	NA
Max. operating temp., (°C)	60	60	60	100
Particle size, (mm)	0.3–1.2	0.3–1.2	0.3–1.2	4–5

[a] Values as available from manufacturers.

NA = not available.

solutions were periodically taken and analyzed for the acid concentration. The sorption experiments were repeated at different temperatures.

The swelling of the resins in water and acid solutions was determined separately from the difference in the volumes. Since in the fermentation broth, glucose and inorganic salts such as magnesium and manganese sulphates, are also present, it is important to know their influence compounds on the sorption of lactic acid. The batch sorption studies were also conducted for these components individually as well as for the lactic acid-glucose, lactic acid-magnesium sulphate and lactic acid-manganese sulphate binary mixtures in aqueous solutions.

Column Studies

A glass column of 1.0 cm diameter was filled with water and then the slurry of conditioned Indion 860 resins was poured into the column up to 20 cm height. The top and the bottom zones of the column were packed with small glass beads (1 mm diameter) to minimize the dead volumes and the end effects. A lactic acid solution of 0.15 $\mathrm{kmol/m^3}$ concentration was passed through the column at a constant flow rate of 4.0 $\mathrm{cm^3/min}$, in upward direction using a peristaltic pump. Initially, the samples were withdrawn from the exit stream at regular time intervals of 1 min each and analyzed for the acid content. The sorption was continued until the bed was saturated. The column was then drained to remove the unsorbed solution followed by the desorption run with methanol as a regenerating solvent. The methanol also was passed through the column in the upward direction at a constant flow rate of 4.0 $\mathrm{cm^3/min}$ until the outlet acid concentration reduced to zero.

RESULTS AND DISCUSSIONS

Uptake of Lactic Acid on Different Resins

All the four resins have a common styrene-divinyl benzene copolymer matrix but they differ in functional groups. Indion 850 and Indion 860 resins have *tert*-amino functional groups, while Indion 810 has quaternary ammonium functional groups. To check whether there is any interaction of the acid with the polymeric backbone of the resin, sorption was also carried out with acidic Indion 190 resin, having -SO_3H^+ functional group, that should have a minimum attractive interaction with lactic acid.

The uptake of the acid by the resins at equilibrium was calculated from the residual acid concentration. An equilibrium exists between the molecular lactic acid and its dissociated form and the former is mainly responsible for lactic acid uptake by the weak base resins at a given pH condition. The degree of ionization of lactic acid in the solutions was estimated using the relation between pKa of the acid (3.86) and the pH of the solution (23).

$$\%\text{Ionized} = \frac{100}{1 + \exp^{(pK_a - pH)}} \qquad (1)$$

Figure 2 shows the adsorption isotherms of molecular lactic acid on different resins. The acid was strongly sorbed on all the three basic resins but did not show any sorption on the acidic Indion 190 resin. The lactic acid uptake by weak base polymer resins can thus be attributed to specific interaction of the acid with the basic functional group in the resins and the contribution of the styrene-divinylbenzene polymer matrix is negligible. The uptake of the acid is

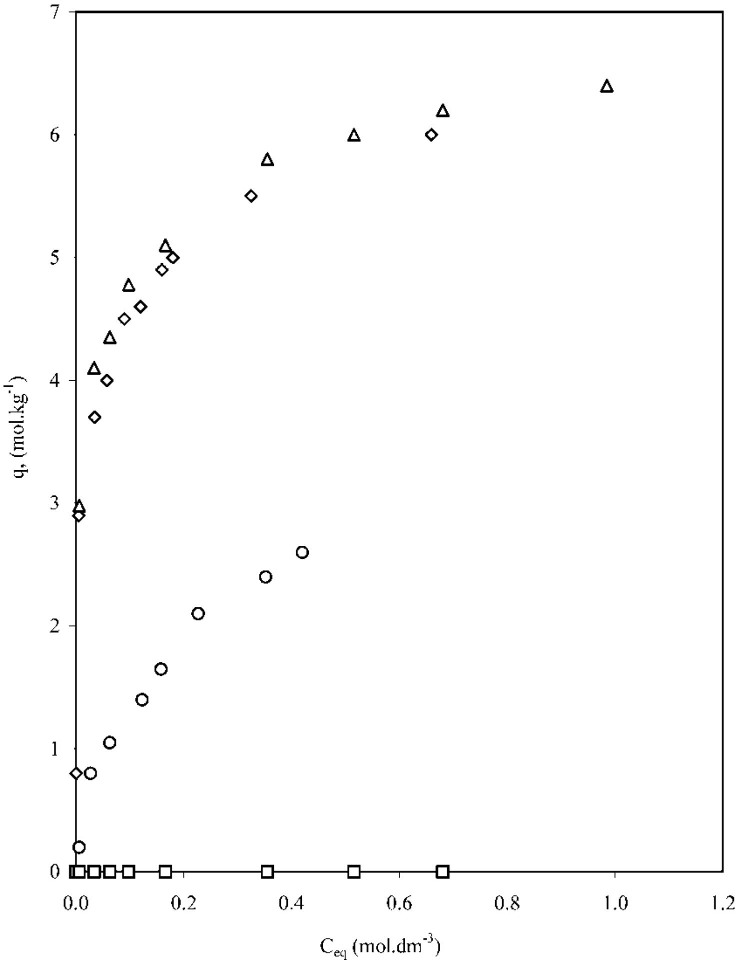

Figure 2. Uptake of lactic acid on different resins. ◇: Indion 860; □: Indion 190; ○: Indion 810; △: Indion 850.

expected to be because of hydrogen-bonding between the nitrogen of amino group of the resins and acidic as well as the hydroxyl hydrogen of lactic acid. The stability of such complexes would be dependent on the medium and how closely the interactive centers are allowed to approach each other. The nitrogen of the functional tertiary amino group should be relatively easily accessible than the nitrogen of quaternary group in a strongly basic resin (24).

The uptake of the acid is higher for the tertiary amine based basic resins than the strong base resins with quaternary groups. The latter should interact mainly with the ionized lactate ions through electrostatic forces but should show relatively poor attractive interaction with the molecular form of the acid. It may, however, induce a shift in the ionization of the acid locally. For weak base resins, the interaction is influenced by the ease with which the interacting centers approach each other. With an increasing degree of substitution on nitrogen, this ease reduces which indeed is the observation in the case of the resins in tertiary and quaternary groups. Indion 850 and Indion 860 resins, which contain *tert*-amino functional groups, have the lactic acid uptakes of ~6.5 mol/kg and ~6.0 mol/kg, respectively, while the Indion 810 resin, which contains quaternary ammonium groups, showed a much lower acid uptake of ~2.5 mol/kg at saturation. The nitrogen of the functional quaternary ammonium group, although positively charged, can not be easily approached by the partially negative oxygen of the acid due to the steric hindrance provided by bulky alkyl groups on the nitrogen. The primary and secondary functional groups can give a better uptake than the tertiary group resins but the hydrogen-bonded complexes would be more stable and would resist desorption, which is required in the subsequent stages. The *tert*-amino group shows the Lewis acid-base interaction, which is strong enough to take up a large quantity of the acid and weak enough so that the resins can be solvent-regenerated. Between the two WBRs, the Indion 850 resin showed a slightly higher uptake of the acid than the Indion 860 resin, because of a higher number of functional groups present than that in the latter.

Since a large amount of lactic acid was sorbed from the solution phase into the resin phase, the uptake only by surface adsorption is debatable. The surface coverage, as mono-/multilayer, can be estimated from the specific surface area (A_s) offered by the adsorbent to a molecule of cross-sectional area (σ) at the saturation capacity 'q_m' (25).

$$\theta = \frac{q_m N_A \sigma}{A_s} \tag{2}$$

N_A is the Avogadro's number and σ can be estimated using McClellan and Harnsberger correlation (26),

$$\sigma = 1.091\left(\frac{M}{\rho N_A}\right)^{2/3} \tag{3}$$

Substituting the molecular weight of lactic acid ($M = 90.08$) and density ($\rho = 1.206\ \mathrm{gm/cm^3}$) the corresponding area (σ) of a lactic acid molecule is approximately 27 Å^2. Available micropore surface areas for Indion 850 and Indion 810 resins are 35 m^2/gm and 27.7 m^2/gm, respectively. From monolayer adsorption, therefore, the estimated capacity of the resin cannot be more than 0.22 mol/kg for the Indion 850 resin and 0.17 mol/kg for the Indion 810 resin. The experimental capacity of these resins, 6.5 mol/kg and 2.5 mol/kg, respectively, far exceeds the monolayer coverage several times. It is also unrealistic to assume that the formation of multiple layers on the surface can reach high values, because it is unlikely for the solute-surface interaction to extend beyond a few molecular layers. The solute uptake by these functionalized polymers may not be due to surface adsorption only. So the sorption into the polymeric matrix has to be considered to explain a high uptake of lactic acid by the resins. A similar observation was made for these resins for the sorption of acetic acid from non-aqueous phases earlier (24).

Swelling of the Resins

During the sorption process, the resin beads swell significantly because of the penetration of the solvent and also that of the acid into the polymeric network of the resin. This swelling is because of the solvation of hydrophilic functional groups (or fixed and mobile ions) of the resin. Stretching of the matrix due to the repulsive electrostatic interactions between the ionic groups also contribute to the swelling. However, cross-linking limits the swelling and an equilibrium is attained when the elastic forces of the matrix balance the dissolution tendency. Since the swelling of the resin makes the adsorption sites easily accessible to the solute, all resins were swollen in water prior to adsorption. The swelling ratio is defined as the ratio of volume of the wet resin to that of the dry resin. Although the three resins have the same matrix and same % of cross-linking, they exhibit different extents of swelling. The maximum swelling in water alone, was exhibited by the Indion 850 resins (20%), followed by the Indion 860 (18%) while the Indion 810 resin exhibited the least swelling (2%). The Indion 850 resin has a slightly higher number of functional groups as compared to the Indion 860 resin. The least swelling in the case of the SBR as compared to WBR is probably due to poor solvation of quaternary ammonium groups as compared to that of *tert*-amino groups. The contribution of the polymeric backbone i.e. styrene-divinylbenzene matrix, to the swelling in aqueous solutions is minimal due to nonpolarity of the matrix. The Indion 860 resin, however, swells more in methanol than in water. The solvation by methanol of the styrene-divinylbenzene structure is more than that of water, which also accounts for a higher swelling ratio in the presence of methanol.

The water-swollen resins further swell in the acidic solutions. The relaxation of the polymer matrix to accommodate the acid-base complexes as well as some associated solvent contributes to the extended swelling. Again the swelling in acidic solutions was more for the Indion 850 resin (35–55%), followed by the Indion 860 resin (32–50%), while the Indion 810 resin showed the least swelling (14–16%).

If it is assumed that an additional volume because of the swelling of the resin along with the pore volume is occupied by the solution having the same concentration as the external liquid phase, then the acid actually associated with the resin polymer structure and/or functional sites can be estimated. Figure 3 gives such adsorbed and absorbed amounts of lactic acid per kg of the dry resins in the resin phase at equilibrium. The difference in the absorbed lactic acid for the three resins is because of the different extents of swelling that these resins exhibit. At saturation, the adsorbed lactic acid is almost 5 times higher than the absorbed lactic acid. The interaction with the functional groups is, therefore, mainly contributing to uptake of the acid. Indion 850 resin gives the highest adsorbed amount (~5.6 mol/kg) followed

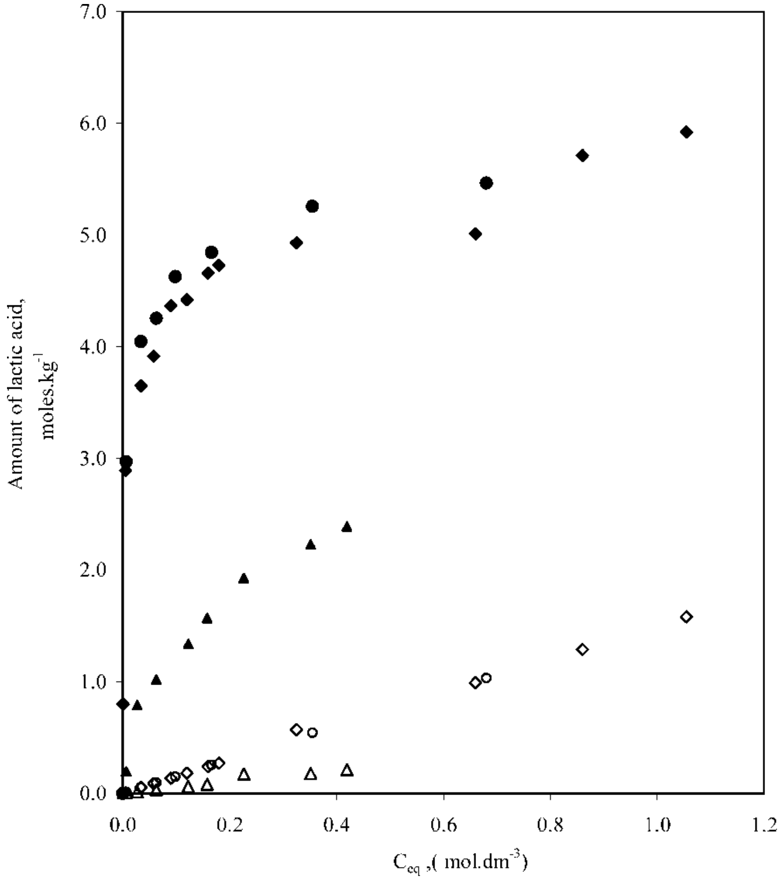

Figure 3. Adsorbed vs Absorbed lactic acid on different resins. (Hollow symbol – Absorption, Filled symbol – Adsorption). ◇: Indion 860; ○: Indion 850; △: Indion 810.

by the Indion 860 resin (~5.0 mol/kg) and the least is for Indion 810 resin (~2.3 mol/kg). These amounts are still significant indicating specific interactions between the functional sites within the resin phase and lactic acid.

To quantify the separation efficiency of the resins, a separation factor between lactic acid and water was calculated in a manner analogous to the relative volatility in distillation using mole fractions of the components (X) in two phases. The separation factor is defined as

$$\text{Separation factor } (\alpha_{1,2}) = \frac{X_1^s/X_2^s}{X_1^l/X_2^l} \tag{4}$$

The superscripts, '*S*' and '*l*' indicate the sorbed and liquid phases, respectively, while subscripts *1* refers to the acid and *2* refers to solvent. The separation factor is defined with respect to the solvent. For an ideal Langmuir system, the separation factor is constant (27). However, Fig. 4 shows the separation factor to be a strong function of the acid concentration in dilute solutions and approaches a constant value only at higher acid concentrations for all the three resins. With the increase in the bulk solution concentration the interaction between solute-solute and solute-solvent molecules increases while the solute-solid interaction may decrease. The possibility of interaction between the adsorbed species was checked by the treatment suggested by Ihm and Lee (28). The interaction energy (W) between the adsorbed molecules can be obtained by plotting $\ln(\alpha_{12})$ vs $(1 - 2 \times X_1^s)$, (Fig. 5) for the equation,

$$K^0 - \ln(\alpha_{12}) + (1 - 2X_1^s) \times \left(\frac{cW}{2kT}\right) = 0 \tag{5}$$

where, c is number of neighboring sites, k is the Boatman's constant, T is absolute temperature and K^0 is constant. The nonzero slopes of the plots are strong indications of the interaction among the adsorbed molecules. In the absence of admolecular interactions, a horizontal line with zero slope is expected.

The adsorbed amounts of lactic acid could not be fitted into the Langmuir as well as the Freundlich adsorption isotherms for the three resins. The equilibrium data deviate significantly from both the isotherms. As discussed earlier, the basic assumptions of these models are not fulfilled by the system. The Langmuir model assumes that each adsorption site can hold only one adsorbate molecule. However, in the present case, a single site may be associated with two or more molecules of lactic acid as the sorption capacity of the resins is indicating. Further, the Langmuir approach assumes no interaction amongst the adsorbed molecules. On the other hand, the Freundlich model predicts that an adsorbent can have almost infinite capacity. But the adsorption, in the present case, is due to specific interactions between lactic acid and the functional groups on the resin. Because of the limited number of the functional groups on the resin, the adsorption capacity should be limited. At high concentrations a finite capacity, although higher than expected from the monolayer coverage, is indeed reached in all the cases.

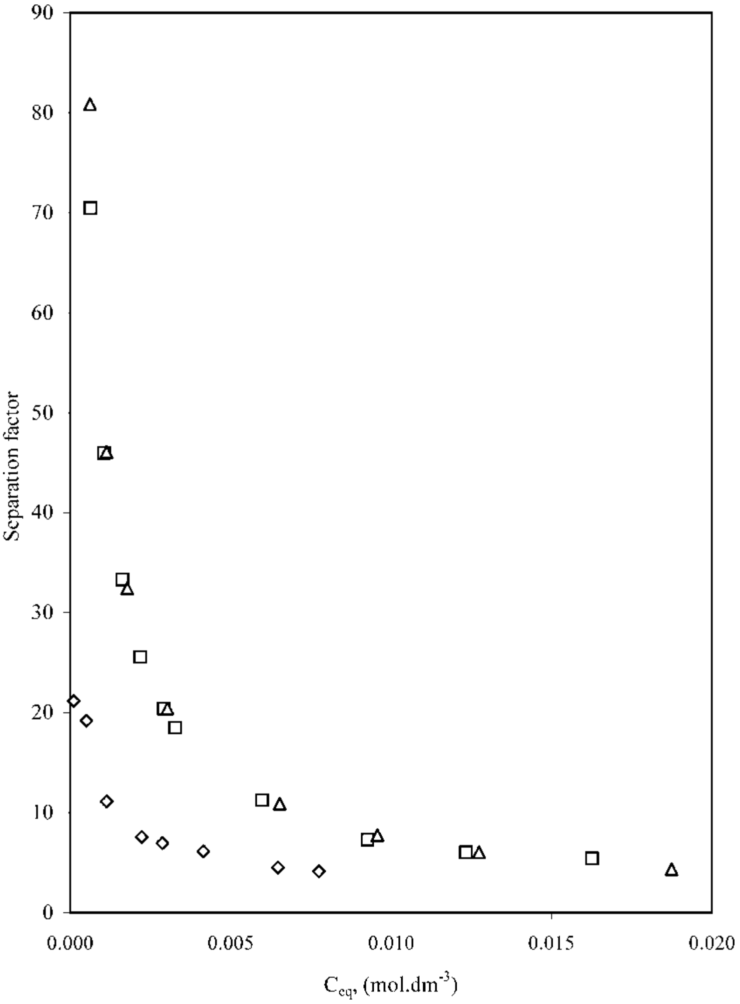

Figure 4. Separation factor of lactic acid with respect to water during sorption on different resins. ◇: Indion 810; □: Indion 860; △: Indion 850.

Since both models did not fit the equilibrium data satisfactory, an empirical Langmuir-Freundlich combination isotherm was used.

$$\frac{q}{q_m} = \frac{KC_{eq}^n}{1 + KC_{eq}^n} \tag{6}$$

where K is equivalent to the Langmuir adsorption constant, q_m is the saturation adsorption capacity and n is equivalent to Freundlich adsorption constant. The lines shown in Fig. 6 are the fitted curves, and the fitted parameters are reported in Table 2. The higher values of the Langmuir

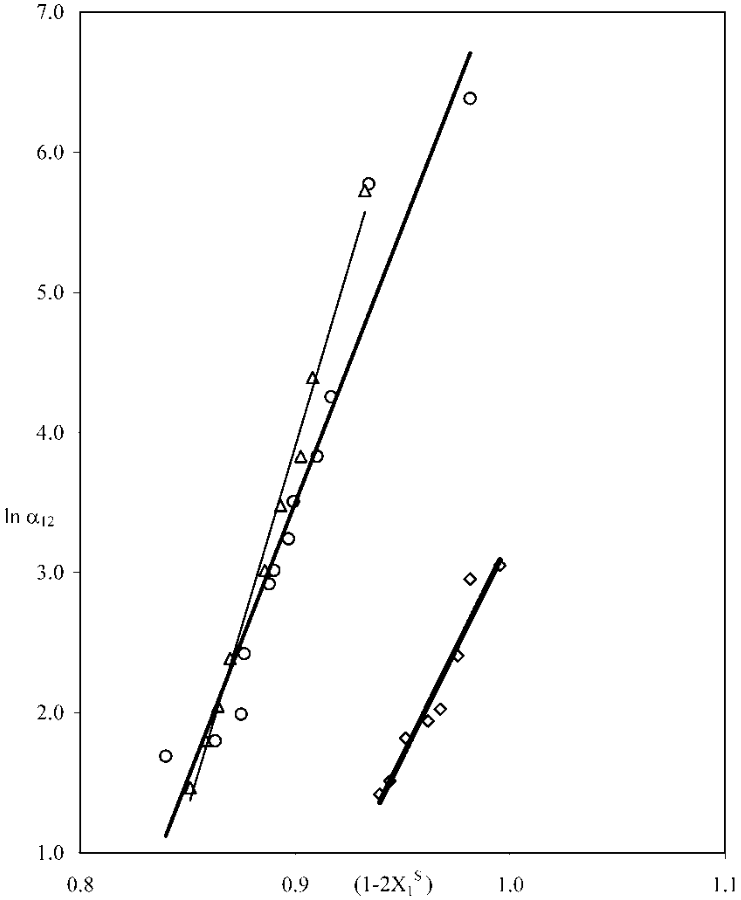

Figure 5. Interaction energy plot for sorption of lactic acid on WBRs. (α is separation factor between acid and solvent and X^s is surface excess of the acid on the resin). ◇: Indion 810; ○: Indion 860; △: Indion 850.

adsorption constant (*K*), and the lower value (less than 1) of Freundlich constant (*n*), indicate favorable interaction of the acid with the sorbent. For both the weak base resins, the isotherm parameters are almost the same. The saturation capacity of the Indion 850 resin is marginally higher than the Indion 860 resin because of its higher exchange capacity. The saturation capacity of the Indion 810 resin is the least amongst all.

Although the experimental equilibrium data were well represented by a Langmuir-Freundlich Isotherm combination, it is a thermodynamically inconsistent and empirical equation (27). There is also a non-ideal behavior in the adsorbed phase. Further, these models do not take into account the swelling of resins which is a critical phenomena affecting the capacity and selectivity of

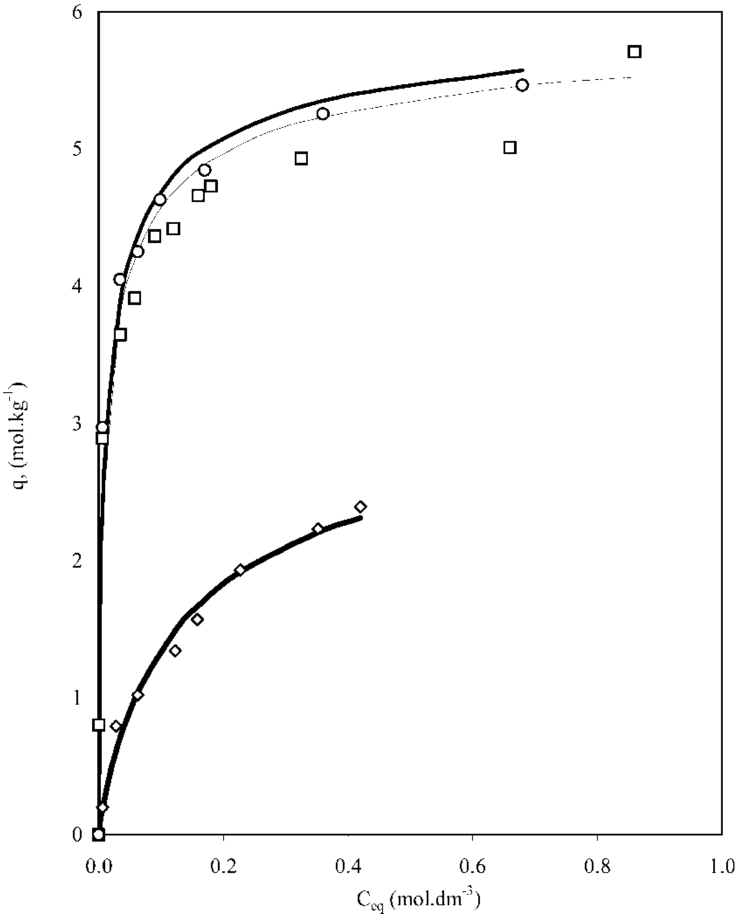

Figure 6. Adsorption equilibria for lactic acid on three resins predicted by Langmuir-Freundlich combination isotherm. Experimental - ◇: Indion 810; □: Indion 860; ○: Indion 850; Predicted - ——: Indion 850; ——: Indion 860; ——: Indion 810.

Table 2. Langmuir-Freundlich combination isotherm parameters for sorption of lactic acid on different resins

Resin	K (dm^3/mol)^n	q_m (mol/kg)	n
Indion 850	12.6	6.1	0.58
Indion 860	12.3	6.0	0.59
Indion 810	5.3	3.2	0.88

the resins. It was, therefore, decided to consider the phase equilibrium between the solution phase and the swollen phase using an equilibrium sorption model (29–33).

Equilibrium Sorption Model

This model treats the sorption process as an equilibrium partitioning of a solute between the external solution phase and the swollen resin phase. The resin phase is considered as a *pseudo*-homogeneous phase consisting of the solute, the solvent, the polymer matrix, and functional groups while the external phase consists of all compounds except the polymer.

The equilibrium is described by equating the activities of each component in the two phases, i.e.

$$a_i^P = a_i^L \qquad (i = 1, N) \tag{7}$$

where, the superscripts P and L indicate the polymer and liquid phases, respectively, N is the number of components excluding the polymer. The solution phase activity of the solute can be estimated by any molecular liquid phase model such as UNIFAC group contribution method considering molecular lactic acid without significant ionization in the aqueous phase.(34). The model is completed by the following mass balance equation

$$n_i^P + n_i^L = n_i^o \qquad (i = 1, N) \tag{8}$$

where, n_i is the number of moles of *ith* component and the index o refers to the initial values. The volume fractions of 'v_i' of each species in the polymer phase can be computed as follows

$$v_i = \frac{n_i^P V_i}{V_P^o + \sum_{j=1}^{N} n_j^P V_j} \qquad (i = 1, N) \tag{9}$$

where V_i is the molar volume of the *ith* component, which has been assumed to be constant and V_P^o is the volume of the dry resin. The denominator of the above equation represents the total volume of the swollen resin particles.

The behavior of the polymeric phase has been described in the framework of the extended Flory –Huggins model (29–33) which gives the activity of the component in the polymeric solution (31)

$$\ln a_i^P = 1 + \ln v_i - \sum_{j=1}^{N+1} m_{ij} v_j + \sum_{j=1}^{N+1} \chi_{ij} v_j - \sum_{j=1}^{N+1} \sum_{k=1}^{j-1} m_{ik} v_k v_j \chi_{kj} + \eta V_i \left(\frac{5}{3} v_P^{1/3} - \frac{7}{6} v_P \right) \tag{10}$$

The first three terms on the right hand side of equation (10) represent the entropic contributions of the free energy of mixing, computed by regarding the system as a lattice with the interchangeable polymer units and solvent molecules (31–33). The fourth and fifth terms describe the energetic interactions between the molecules through the binary interaction parameter, (χ_{ij}), and accounts for the enthalpy of mixing (32), whereas the last term represents the elastic deformation contribution which limits the swelling of the resins. It is represented by a free energy expression developed by Gusler and Cohen (35). The elasticity parameter (η) represents the number of moles of active elastic chains per unit volume and is defined as $\eta = \rho_p/M_c$ where ρ_P is the polymer density (1410 kg/m^3) (24). The parameter M_c represents the molar mass of the active elastic chain accounting for the degree of cross-linking and concentration of the functional group sites in the resin.

For the system, the model involves four binary interaction parameters, lactic acid-polymer (χ_{LP}), water-polymer (χ_{WP}), lactic acid-water (χ_{LW}), and water-lactic acid (χ_{WL}). These parameters were evaluated by fitting the experimental sorption data in the above model using a least square fitting method. The following equation was used as an objective function for the optimization.

$$\text{Objective Function} = \sum \left(a^P_{i,\exp} - a^p_{i,Theo} \right)^2 = 0 \tag{11}$$

The fitted parameters, as reported in Table 3, show stronger and attractive interaction of lactic acid with the basic resin. The interaction parameter between acetic acid and the same WBR was reported to be −3.10 (24). From the p*K*a values of acetic acid (4.76) and lactic acid (3.86) the latter is a stronger acid and its interaction with the resin is expected to be stronger, which is indeed indicated by the interaction parameters of the sorption model.

The interaction parameters were also fitted at higher temperatures, 313 K and 323 K. A theoretical relationship between the binary interactions parameters (χ_{ij}) and the temperature (*T*) has been suggested by Flory (32),

$$\chi^T_{ij} = \chi^{298}_{ij} \times \frac{298}{T} \tag{12}$$

Table 3. Interaction parameters for the Flory-Huggins model for predicting the polymer phase activity

Interaction parameters (χ_{ij})	303 K	313 K	323 K
χ_{LW}	19.07	20.72	21.56
χ_{LP}	−10.92	−11.23	−11.25
χ_{LW}	−2.06	−2.49	−2.25
χ_{WP}	1.50	1.51	1.50

However, the values predicted by this approach and those obtained from the experimental data fitting do not match. Figure 7 shows the fitted sorption data as the $X^L - X^P$ diagram, which represents the mole fraction of lactic acid in the two phases at equilibrium. The lines are the fitted curves while the points are the experimental values. The fit is reasonably good. The line $X^L = X^P$ represents equal mole fractions of lactic acid in the two phases. In the region above the diagonal line, lactic acid is selectively sorbed by the resins in comparison to the solvent. The equilibrium curve lies far above the diagonal line indicating that lactic acid is selectively sorbed in the resin phase.

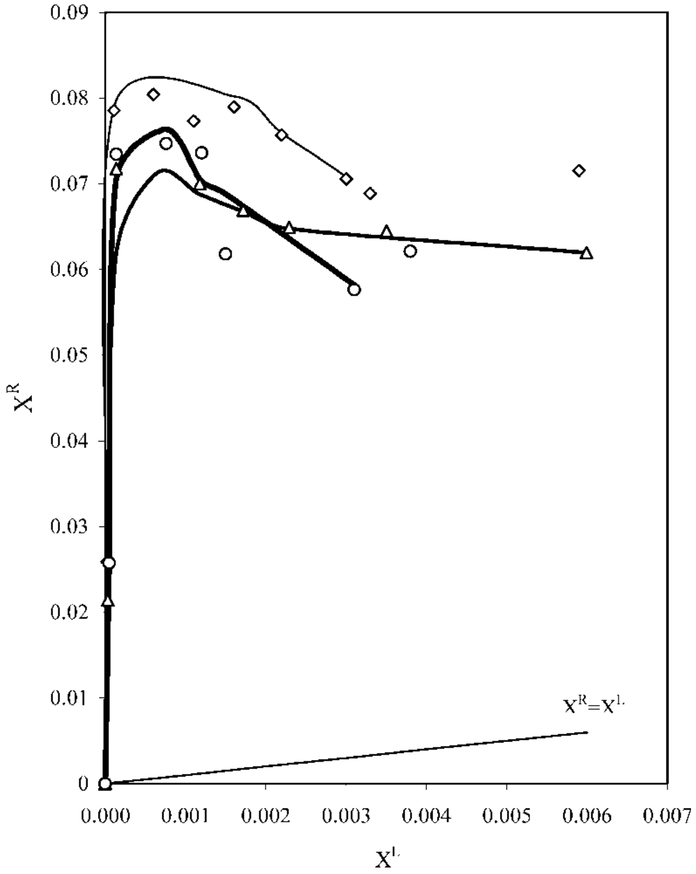

Figure 7. Equilibrium sorption data for lactic acid sorption from water resins at different temperatures. Experimental - ◇: 30°C; △: 40°C; ○: 50°C. Predicted - ——: 30°C; ——: 40°C; ——: 50°C.

Single Component Batch Sorption Study for other Media Components

Lactic acid is present along with other media components such as glucose and inorganic salts, $MgSO_4$, $MnSO_4$, and $FeSO_4$ in the fermentation broth. Single component batch adsorption studies conducted for these components show that the resins pick up a substantial amount of glucose.(Fig. 8 and Table 4) Glucose thus can compete with lactic acid for the adsorption sites. There is, however, no possibility that the resins can sorb $MgSO_4$ or $MnSO_4$, as Indion 860 was expected to have nonionizable *tert*-amino functional group. However, a small uptake of sulphate by the resin indicates the presence of a small number quaternary ammonium groups in the resin matrix. Equilibration with sodium chloride solutions showed almost 0.2 mol/kg exchange capacity

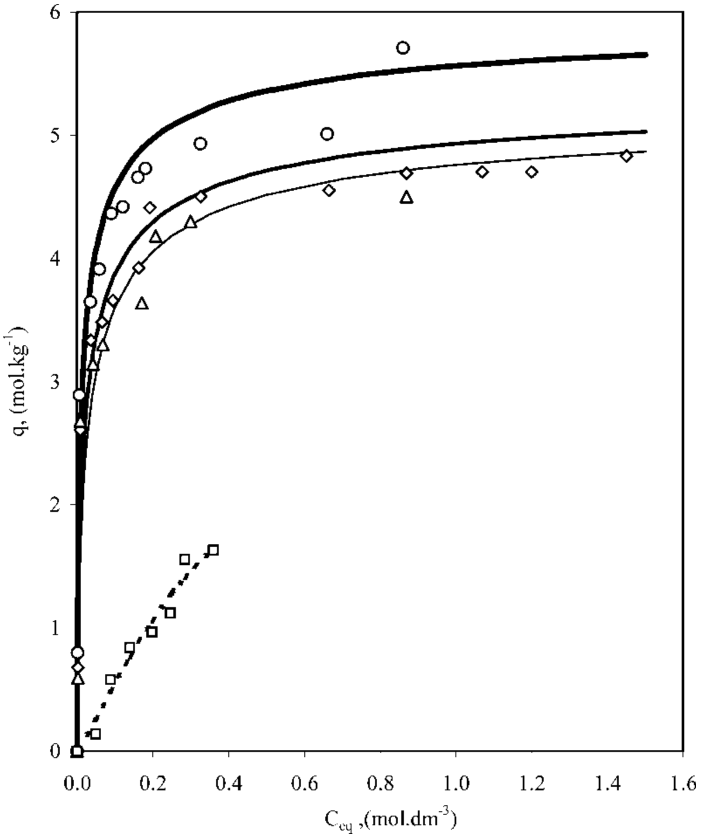

Figure 8. Effect of temperature on sorption of lactic acid. Lactic acid experimental - ○: 30°C; ◇: 40°C; △: 50°C. Lactic acid predicted - ——: 30°C; ——: 40°C; ——: 50°C; □: Glucose experimental; - - - -: Glucose predicted.

Table 4. Langmuir-Freundlich combination isotherm parameters as a function of temperature

Component	Temperature (K)	Isotherm parameters K' $(dm^3 \cdot mol^{-1})^n$	q_m $(mol \cdot kg^{-1})$	n'
Lactic acid	303	12.61	6.12	0.589
	313	12.34	6.01	0.590
	323	5.32	3.23	0.876
Glucose	303	3.4	3.1	1.2

for chloride ions confirming the presence of an equivalent amount of quaternary groups in the resins.

Effect of Media Components on Sorption of Lactic Acid

Figure 9a shows that the sorption of lactic acid from solutions containing 0, 5.0, and 12.5% (w/v) glucose. The sorption of the acid decreased with increase in glucose concentration in the solution due to competitive uptake of glucose. On the other hand, an opposite trend was observed for the uptake of lactic acid in the presence of inorganic salts. Figures 10b and 10c show an increased uptake of lactic acid in the presence of the salts because of the salting-out effect.

Sorption of Lactic Acid from Simulated Broth

The typical media for the fermentation contains 100 gm of glucose, 5 gm of yeast extract, 0.1 gm $MgSO_4$, 0.05 $MnSO_4$, 0.03 gm $FeSO_4 \cdot 7H_2O$ and 5 gm of sodium acetate per dm^3 of the solution. Figure 10 shows that sorption of lactic acid from the simulated broth, containing $50gm \cdot dm^{-3}$ of acid and glucose each, is lower than that from the aqueous solutions in the absence of glucose. The sites available for the acid are reduced because of competitive sorption of glucose. Also, molecular lactic acid available in the broth is less because of the higher pH conditions. However, almost 3.5 moles of acid were sorbed per kg of dry resin which is a significant amount. This confirms that the sorption of lactic acid can be carried out from the fermentation broth effectively, using these resins even at higher pH conditions.

Column Study

Figure 11 shows breakthrough curves for the sorption and desorption of lactic acid from aqueous solutions and from the simulated broth in the packed

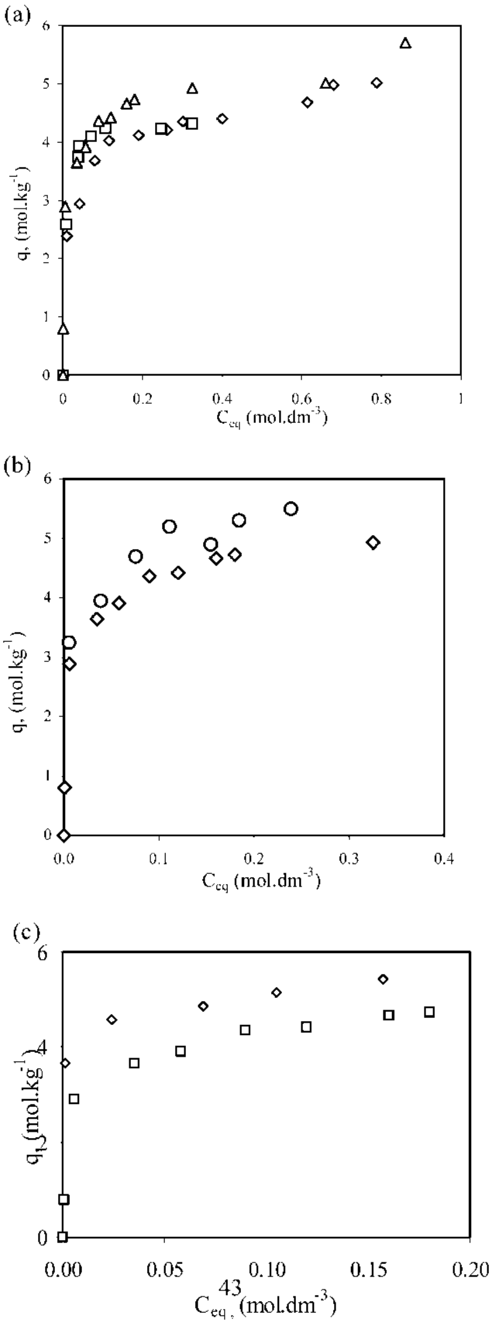

Figure 9. (a) Effect of glucose on sorption of lactic acid. △: 0% Glucose; □: 4% Glucose; ◇: 12.5% Glucose. (b) Effect of $MnSO_4$ on sorption of lactic acid. ◇: without $MnSO_4$; ○: 60 ppm $MnSO_4$. (c) Effect of $MgSO_4$ on sorption of lactic acid. ◇: 120 ppm $MgSO_4$; □: without $MgSO_4$.

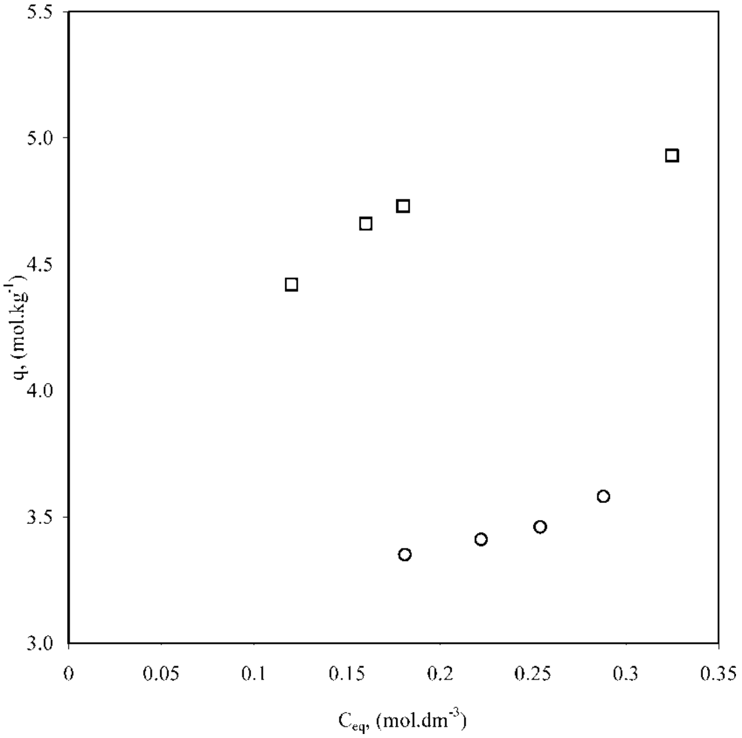

Figure 10. Adsorption of lactic acid from simulated broth and from aqueous solution. □: aqueous solution; ○: simulated broth.

column. In the case of sorption from aqueous solutions, almost 9 bed volumes were treated at the breakpoint after which the acid leaked into the effluent. At this point, the adsorption was 1.31 mol/kg, which is 22% of the total saturation capacity (6.0 mol/Kg). After passing 25 bed volumes of feed solution the bed was completely exhausted. The sorbed amount of lactic acid at this point was 3.85 mol/kg. In case of sorption from the simulated broth only 5 bed volumes could be treated at breakpoint and 20 bed volumes at exhaustion. The adsorption capacity was 1.84 mol/kg and 3.11 mol/kg, respectively, at the breakpoint and at the bed exhaustion. Though feed concentration in case of broth was 0.42 $\text{mol} \cdot \text{dm}^{-3}$, almost three times of that of the aqueous solution (0.14 $\text{mol} \cdot \text{dm}^{-3}$), the sorption of acid from the broth was less. The presence of glucose competes with the acid for the sites and reduces the sorption of lactic acid.

Desorption of lactic acid was carried out using methanol as the eluent as it can be easily separated from lactic acid by distillation. Figure 11 shows that the rate of desorption was initially high, but reduced in the later stages. Initially, lactic acid, sorbed at the exterior surface, gets desorbed easily.

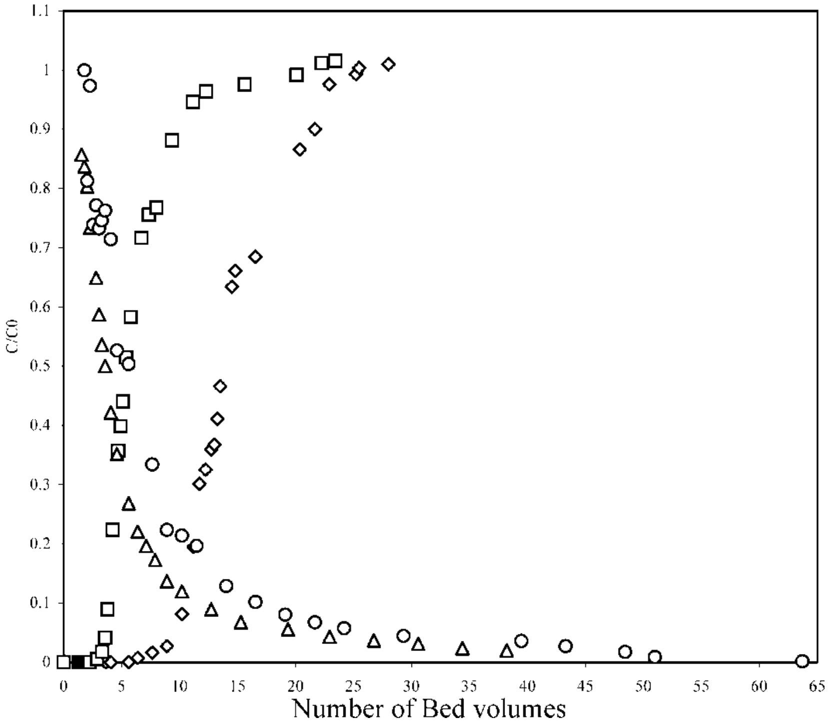

Figure 11. Breakthrough curves for adsorption/desorption of lactic acid in packed column. ◇: Adsorption-aqueous solution; □: Adsorption-simulated broth; ○: Desorption-aqueous solution; △: Desorption-simulated broth.

However, desorption of lactic acid from the interior of the resin bead needs its diffusion to the exterior surface which is slower. Hence the rate of desorption falls in the later stages. After passing about 30 bed volumes of methanol, 86% of the sorbed acid was eluted. Complete removal of the acid required almost 60 bed volumes of methanol in the case of the aqueous solution and 40 in the case of the simulated broth. The temperature of desorption can be manipulated to desorb the acid quickly and to reduce the amount of methanol. The final traces of lactic acid can be removed, if necessary, by an alkali wash followed by a water wash for removal of excess alkali. There will be some loss of lactic acid but complete regeneration of the resin for the next adsorption run is possible. Alternatively, the resin can be dried using hot air and condensing the solvent for recycling.

A typical fermentation broth also contains a significant quantity of proteins whose characteristics will be decided by the microbial strain used for lactic acid formation. These proteins can reduce the capacity of the resin, if present in proportionately large amounts, by depositing on the resin surface. Investigations will be required therefore for a typical strain and for proteins produced by it. The interference of proteins by competitive adsorption on the resin and their subsequent removal by desorption from the resin to regenerate it may become decisive factors in the implementation of simultaneous recovery of lactic acid from the fermentation broth.

CONCLUSION

The WBRs show selective and higher uptake of lactic acid mainly by sorption reinforced by specific interaction with the functional groups in the resin phase. Although. the equilibrium data are well represented by the Langmuir-Freundlich combination isotherm, the equilibrium sorption model explains the sorption data better. The nutrients, glucose and inorganic salts such as $MgSO_4$ and $MnSO_4$, in the broth have opposite effects on the sorption of lactic acid. Although, temperature adversely affects the lactic acid uptake, it is advisable to carry out the adsorption at broth temperature (40–45°C) in order to avoid a substantial cost of cooling that will be required before adsorption as well as heating that will be required before recycling the stream to the fermenter. Continuous adsorption was carried out in a resin filled glass column and a resin bed was regenerated successfully using methanol. Molecular modeling results suggest either a multilayer adsorption or possibly strong interaction amongst admolecules.

NOMENCLATURE

A_s	Specific surface area of resin, m^2/gm
a_i^L	Activity of ith in liquid phase
a_i^P	Activity of ith in polymer phase
C_{eq}	Equilibrium concentration, mol/dm^3
C_{in}	Initial concentration, mol/dm^3
c	Number of neighboring sites
K	Langmuir adsorption constant of Langmuir-Freundlich combination isotherm
k	Boltzmann's constant
M	Molecular weight of solute, gm/gmol
M_C	Molar mass of active elastic chain, kg/mole
N	Number of components excluding polymer
N_A	Avogadro's number
n	Freundlich isotherm constant of Langmuir-Freundlich combination isotherm
n_i^L	Number of moles of ith component in liquid phase.
n_i^P	Number of moles of ith component in polymer phase
q	Amount adsorbed, mol/kg of dry resin
q_m	Amount adsorbed at saturation, mol/kg of dry resin
R	Universal gas constant, 1.98 $kcal/gmol \cdot K$

T	Temperature, K
V	Volume of solution for adsorption, cm^3
V_i	Molar volume of ith component, cm^3/mol
V_P^o	Volume of dry resin, cm^3
W	Weight of resin for adsorption, gm
X_i^L	Mole fraction of *i*th component in the liquid phase
X_i^S	Mole fraction of *i*th component in the polymer phase

Greek Letters

θ	Number of monolayers formed
σ	Cross-sectional area of solute, m^2/molecule
ρ	Solute density, gm/cm^3
σ_p	Polymer density, kg/m^3
α_{1-2}	Separation factor of solute (1) with respect to solvent (2)
χ_{ij}	Interaction parameter between i and j
χ_{ij}^T	Interaction parameter between i and j at temperature T
η	Elasticity parameter, mol/cm^3

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