Modeling of Lactic Acid Adsorption Isotherm by Anion Exchange Resin Amberlite IRA-96

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ABSTRACT

In this paper, adsorption isotherm of lactic acid on ion exchange resin and its modeling will be presented. The adsorption isotherm of lactic acid was obtained at pH 2 and 25°C and 40°C. Amberlite IRA-96, a weakly basic anion exchanger, was selected for lactic acid purification from lactic acid solution. It was observed that its removal capacity was higher than that of other known adsorbents. The model for predicting adsorption isotherm of lactic acid on Amberlite IRA-96 by combining effect of physical adsorption and ion exchange was proposed and fitted with the experimental results. In the proposed model, the ion exchange capacity was lower than the physical adsorption capacity at pH 2; hence, the effect of physical adsorption was higher than that of ion exchange. The fitted parameters of this model were the maximum physical adsorption capacity, adsorption separation factor and ion exchange factor. The parameters were obtained by fitting the adsorption isotherm to the model and were found to depend on adsorption temperature. The results and the proposed model would be beneficial for engineers and scientists who would like to improve recovery of lactic acid production.

Keywords: Ion exchange resin, Adsorption isotherm, High capacity

I. INTRODUCTION

Lactic acid is a raw material for biodegradable plastics and is also used in the food industry and production of pharmaceuticals and cosmetics. To reduce the costs, many studies on lactic acid purification have been conducted using different separation techniques, such as reactive extraction, membrane technology, ion exchange, electrodialysis, and distillation. The recovery of lactic acid is rather difficult due to its chemical behavior, as it shows strong affinity to water and low volatility. Therefore, its purification is the most cost-intensive and energy-intensive processing step [1]. The use of ion exchange technique depends on various factors such as pH, temperature and sorbent characteristics such as microporosity and chemical properties [1-5]. The ion exchange technique is widely used in bio-separation and several different ion exchanger resins with the maximum capacity ranging from 3.8 – 5.6 eq kg^{-1} dry resin such as IRA-92 [6], IRA-400 [2,5], Dowex MWA-1 [4], Reillex 425 [4], IRA-35 [4], IRA-900 [2], IRA-96 [2] and IRA-67 [2] were studied for the recovery of lactic acid.

The different forms of resin can affect its adsorption capacity [2]. For example, In Cl$^-$ form, the weakly basic ion exchange resins attained its highest capacities. However, the strongly basic ion exchange resins in OH$^-$ form presented the higher capacities than the free base form [2]. Amberlite IRA-96, a weakly basic anion exchange resin in Cl$^-$ form, was selected for lactic acid recovery from lactic acid solution in this paper. The selectivity between lactic acid and glucose during recovery of lactic acid depends on the basic extractants and polymeric sorbents. Dai et al. [4], studied the carboxylic acid from fermentation broth and found that the lactic acid removal decreased sharply with increasing temperature. Cao et al. [5] studied the lactic acid removal from fermentation broth and found that the lactic acid removal increased sharply with increasing pH. They described the adsorption isotherm by Langmuir model. For adsorption modeling, Carmona et al. [7] were combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420. The adsorption and ion exchange mechanism expressed by Langmuir equation.

In this work, a weakly basic anion exchanger (Amberlite IRA-96) was used for recovery lactic acid from lactic acid solution. According to this work, lactic acid uptake by both the adsorption of the undissociated form and anion exchange effect of the corresponding dissociated lactate ion were studied. Therefore, the equilibrium data for lactic acid on Amberlite IRA-96 in the Cl$^-$ form at different temperature and at pH 2 and 5 were obtained.

II. METERIAL AND METHODS

A. Materials

1) Chemicals

Samples of preset concentrations were prepared from a commercial solution containing 88% lactic

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acid. A commercial Amberlite IRA-96 ion exchange resin supplied by Rohm and Hass was used.

2) Preparation of lactic acid solution

The lactic acid solution was prepared from a commercial lactic acid solution. Initial concentration of lactic acid was 78 g/l. Then, the pH was adjusted to 2 by adding 1 M NaOH and the solution was stored at 4°C until use. Before utilization, the concentration of lactic acid solution was determined by high performance liquid chromatography (HPLC).

3) Preparation of an anion exchange resin

An anion exchange resin Amberlite IRA 96 (free base form) was used for the lactate separation process. The resin was commercially provided with free base. The free base form with a matrix of Styrene divinylbenzene copolymer has a specific gravity of 1.040 to 1.060 (FB form) and a bulk density of 670 g/l having a Harmonic mean size 0.550 to 0.750 mm. The maximum ion exchange capacity of the resin was 1.2 meq g^{-1}dry resin. Before utilization, the resin was washed and converted into their Cl^- form. Resins in Cl^- form were obtained by washing the resins sequentially with 1 M HCl solution, distilled water, 1M NaOH solution, distilled water, 1 M HCl solution and distilled water (until pH=7). The resin in Cl^- form was air dried and assayed for moisture by oven drying at 105°C for 24 h.

4) Analytical methods

The concentration of lactic acid was determined by HPLC using a Hewlett Packard chromatograph fitted with an RI (refraction index) detector (detector temperature, 60°C). Other analysis conditions were: column, Hypersil BDS C18; mobile phase, 0.005 M H2SO4, elution flow, 0.7 ml/min.

B. Experimental Method

A series of samples with different amounts of Amberlite IRA-96, in Cl^- form, were weighed in flasks. Then, the solution 78 g lactic acid/l was added into each flask with a solution of 10 ml at pH 2. Thereafter, all flasks were shaken for 48 h in a shaking water bath at 200 rpm at 25°C (or 40°C). The residual lactic acid concentrations in the solution were measured by an HPLC.

The resin-phase concentration was determined from the mass balance according to Equation (1)

$$q^* = \frac{V}{W}(C - C^*) \tag{1}$$

Where C_0 and C* are the initial concentration and the equilibrium concentration of lactic acid in the liquid phase (mol dm^{-3}), respectively; q* denotes the resin-phase equilibrium concentration of lactic acid (mol kg^{-1} dry resin); V and W are the volume of the solution (dm^3) and weight of dry resin (kg)

C. Modeling of lactic acid adsorption isotherm on Amberlite IRA-96

1) Liquid phase (Manuel Carmona et al., 2006)

For the water dissociation:

$$H_2O \Leftrightarrow H^+ + OH^- \tag{2}$$

For the lactic acid dissociation:

$$\varphi^{LA} \Leftrightarrow \varphi^{L^-} + H^+ \tag{3}$$

If the reaction (4) and (5) are combined to eliminate H+, one obtains

$$\varphi^{LA} + OH^- \Leftrightarrow \varphi^{L^-} + H_2O \tag{4}$$

Eq. (4) becomes

$$\frac{K_{\varphi^{LA}}}{K_W} = \frac{[\varphi^{L^-}]}{[\varphi^{LA}][OH^-]} \tag{5}$$

Where $[\varphi^{LA}]$ is the concentration of undissociated lactic acid, is the concentration of dissociated lactate, and KW are the equilibrium constants for lactic acid and water dissociation in the liquid phase, respectively.

For the measurement of lactic acid, both forms of lactic acid were detected. Mathematically, it can be expressed as:

$$[\varphi^{LA}_{measured}] = [\varphi^{LA}] + [\varphi^{L^-}] \tag{6}$$

Where $[\varphi^{LA}_{measured}]$ is the total concentration of lactic acid measured by HPLC.

Eq. (5) becomes

$$\frac{K_{\varphi^{LA}}}{K_W} = \frac{[\varphi^{L^-}]}{[\varphi^{LA}_{measured} - \varphi^{L^-}][OH^-]} \tag{7}$$

For the hydroxide concentration, the equation is:

$$pOH = 14 - pH \tag{8}$$

Then,

$$[OH^-] = 10^{-(14-pH)} \tag{9}$$

Eq. (7) becomes:

$$[\varphi^{L^-}] = \frac{(K_{\varphi^{LA}} / K_W)\,[\varphi^{LA}_{measured}]\,10^{-(14-pH)}}{1 + (K_{\varphi^{LA}} / K_W)\,10^{-(14-pH)}} \tag{10}$$

2) Solid phase (Manuel Carmona et al., 2006)

In this model, it has been assumed that two mechanisms, ion exchange and another by physical adsorption, for the adsorption of lactic acid into the resin beads take place.

3) The ion exchange process:

The ion exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counter ion which is different from that in the ion exchanger

Counter ion exchange occurs, and the ion Cl^- in the ion exchange partially replaced by L^-.

$$RCl + \varphi^{L^-} \Leftrightarrow R\varphi^{L^-} + Cl^- \tag{11}$$

In this reversible equilibrium, both the ion exchanger and the solution contain both competing counter ion species, Cl^- and L^-.

The adsorption of lactic acid on the resin beads take place due to the ion exchange can be expressed by Langmuir equation.

$$q^*_{\varphi^{L^-}} = \frac{q^\infty_{IE} K_{IE} [\varphi^{L^-}]}{1 + K_{IE} [\varphi^{L^-}]} \tag{12}$$

Where q^∞_{IE} is the maximum ion exchange capacity of the resin ($1.2\, meg\, g^{-1}$ dry resin), KIE the ion exchange separation factor ($dm^3\, mol^{-1}$) and $q^*_{\varphi^{L^-}}$ is the equilibrium concentration of lactic acid in the solid phase.

The physical adsorption process:

$$\varphi^{LA} + S^* \Leftrightarrow S\varphi^{LA} \tag{13}$$

Where S^* and $S\varphi^{LA}$ represent active and occupied adsorption sites of the resin, respectively.

The uptake of lactic acid into the resin beads takes place due to physical adsorption can be correlated by Langmuir equation.

$$q^*_{\varphi^{LA}} = \frac{q^\infty_{Ad} K_{Ad} [\varphi^{LA}]}{1 + K_{Ad} [\varphi^{LA}]} \tag{14}$$

Where q^∞_{Ad} is the maximum adsorption capacity of the resin, K_{Ad} is the adsorption separation factor and $q^*_{\varphi^{LA}}$ is the equilibrium concentration of the undissociated lactic acid in the solid phase.

The mass balance can be evaluated as

$$q^*_{\varphi^{LA}} + q^*_{\varphi^{L^-}} = ([\varphi^{LA}_{initial}] - [\varphi^{LA}_{measured}]) \frac{V}{W} \tag{15}$$

Where $[\varphi^{LA}_{initial}]$ is the initial lactic acid concentration, V the volume of the solution and W is the weight of dry resin.

Introducing Eqs. (6), (10), (12) and (14) in the Eq. (15), the following equation is obtained:

$$\left(\left(\frac{q^\infty_{Ad} K_{Ad} [\varphi^{LA}_{measured}]}{1 + (K_{\varphi^{LA}} / K_W) \quad 10^{-(14-pH)} + K_{Ad} [\varphi^{LA}_{measured}]} \right) + \left(\frac{q^\infty_{IE} K_{IE} [\varphi^{L^-}]}{1 + (K_{\varphi^{LA}} / K_W) \quad 10^{-(14-pH)} \cdot [1 + K_{IE} [\varphi^{L^-}]]} \right) \right) \cdot \frac{W}{V}$$

$$= ([\varphi^{LA}_{initial}] - [\varphi^{LA}_{measured}]) \tag{16}$$

This equation describes the removal of lactic acid by resin in the term of three unknown parameters (KIE, KAd, q^∞_{Ad}) related to ion exchange and adsorption. Experimental data were fitted to the Eq. (16) by a non-linear least-squares regression procedure.

III. RESULTS AND DISCUSSION

It was observed that its removal capacity was higher than the maximum capacity of the resin due to the ion exchange (1.2 eq kg^{-1}). Furthermore, its removal capacity was higher than those of other known adsorbents reported in the literature. The removal capacity of the resin studied at pH 2 and 25°C was 9.4 eq kg^{-1} dry resin. The capacity of the resin studied at pH 2 and 40°C was 5.84 eq kg^{-1} dry resin. Please note that the isotherm was obtained at pH lower than pKa of lactic acid (pKa of lactic acid was 3.86); hence most of lactic acid would present as the undissociated form. The values of the parameters obtained by fitting the experimental data to this model are shown in Table I.

TABLE I. EQUILIBRIUM PARAMETER IN EQ.16 OF LACTIC ACID ON AMBERLITE IRA-96

pH 2	Value of parameter		
Temperature (°C)	q^∞_{Ad} (mol kg^{-1} dry resin)	K_{Ad}($dm^3 mol^{-1}$)	K_{IE}($dm^3 mol^{-1}$)
25	8.20	2.11x10^3	5.78x10^3
40	4.64	4.55x10^4	1.85x10^4

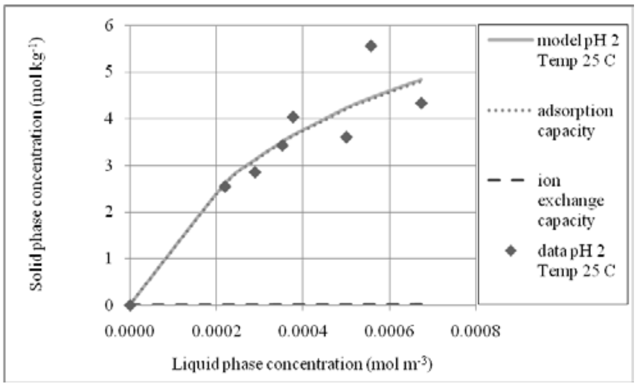

Figure 1 Isotherm of lactic acid removal from liquid phase by Amberlite IRA-96 for pH 2 at temperature 25 °C

Fig. 1 shows the isotherm obtained at pH 2 and 25°C. The lactic acid dissociation is low and, thus, the molecular adsorption process is the predominant one. The amount of lactic acid removed by molecular adsorption is always higher than the removed by ion exchange regardless of the liquid phase concentration.

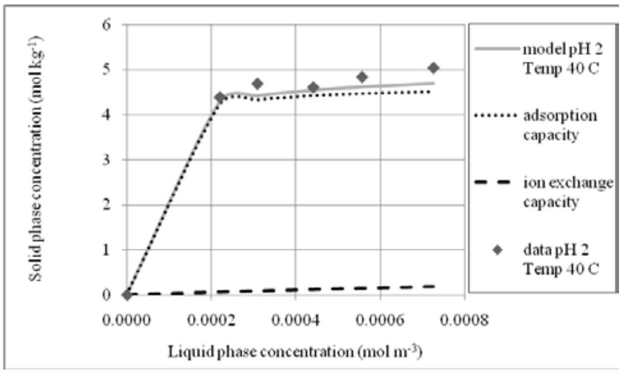

Figure 2 Isotherm of lactic acid removal from liquid phase by Amberlite IRA-96 for pH2 at temperature 40°C

Fig. 2 shows the isotherm obtain at pH 2 and 40°C. The lactic acid dissociation is low and, thus, the molecular adsorption process is the predominant one. The amount of lactic acid adsorbed by molecular adsorption is always higher than that adsorbed by ion exchange regardless of the liquid phase concentration.

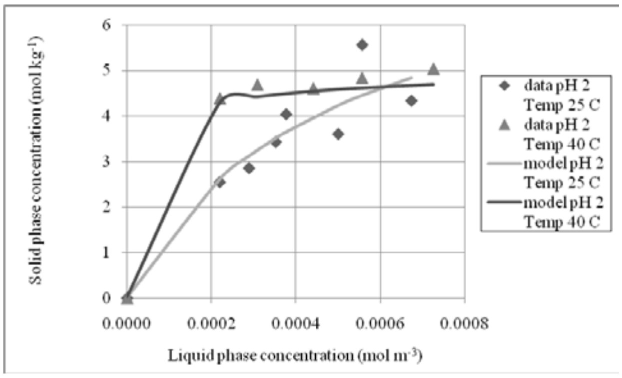

Figure 3. Lactic acid removal from liquid phase by Amberlite IRA-96 for pH2 at temperature 25 °C and 40°C.

From Fig. 3, it was clearly shown that the amount of lactic acid being adsorbed at 40°C was higher than those at 25°C for the liquid lactic acid concentration lower than 0.0006 mol m^{-3} and the amount of lactic being adsorbed would not depend on temperature at higher liquid lactic acid concentration. It should be noted that our finding is different from those reported in Dai and King [4]. Since the mechanism for lactic acid adsorption on Amberlite IRA-96 at pH 2 was mainly the molecular adsorption rather than the ion exchange as studied by Dai and King [4], it was probably that the different mechanisms being investigated were the main reason for these differences. In our cases, it was thought that the increases in the amount of lactic acid adsorped at 40°C is caused by the positive enthalpy change of adsorption of lactic acid on similar material reported by [8] ; hence, the amount of adsorped lactic acid would increase with temperature as indicated by Van't Hoff equation [9]. However, at the higher concentration, this effect is decreased because of the higher dissociation constant.

It should be noted that the experimental results and the model at pH higher than pKa is currently on-going. The modified model that includes the chemical adsorption caused by the stronger interaction of lactate ion and ion exchange resins is also being developed and will be reported subsequently.

IV. CONCLUSION

Lactic acid can be adsorbed on a weak basic anion exchange resin Amberlite IRA-96. It was observed that its removal capacity was higher than that of other known adsorbents. At low concentration of lactic acid, the capacity of lactic acid at pH 2 and 40°C was higher than the capacity of lactic acid at pH 2 and 25°C. The model can predict adsorption isotherm of lactic acid. The amount of lactic acid adsorbed by ion exchange mechanism was lower than that adsorbed by molecular adsorption mechanism. The effect of adsorption mechanism was higher than ion exchange mechanism. This equation describes the removal of lactic acid by the resin in terms of three unknown parameters (q_{Ad}^{∞} , KAd, KIE) related to ion exchange and adsorption. These parameters clearly depend on temperature.

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