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PURIFICATION OF LACTIC ACID FROM CASSAVA BAGASSE FERMENTATION USING ION EXCHANGE

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ABSTRACT

Polylacticacid (PLA) is used extensively for the design of drug delivery systems for peptides and vaccines, for the manufacture of medical devices and wound dressings, as well as for fabricating scaffolds in tissue engineering. Moreover, the polymer can be formulated with a variety of desirable physical properties and degradation rates, making it extremely versatile. PLA is traditionally manufactured in a three-phase process: (1) fermentation by various strains of *Lactobacillus* to produce lactic acid; (2) recovery of lactic acid from the fermentation broth, and (3) polymerization of the lactic acid. In this study, in order to achieve the low cost production, using the inedible waste from cassava waste as the substrate, lactic acid fermentation was conducted. Afterward, the lactic acid in the fermentation broth was separated by ion exchange resin. The model solutions were hydrolyzed to convert oligomers to monomer. The results of this research show that in batch adsorption of lactic acid (HLa) solution, the resin WA30 has the highest value of adsorbed concentration solutioncompared to the resins of Amberlite IRA A 400, SA 10A, WK 10 and PK 228. The amount of lactic acid exchanged decreases with increasing temperature. The maximum resin capability of lactic acid on WA 30 resin is much higher than the theoretical value which is separately measure with HCL method. Calculated from Langmuir equation; it was found that the adsorbed capacity for model was 128.8 mg/g-resin while for fermentation broth of 100 mg/g-resin.

Keywords: purification, lactic acid, cassava bagasse, ion exchange.

INTRODUCTION

Lampung Province is one of the major producer for cassava in Indonesia, therefore amount of waste from cassava tapioca industry is huge. The waste from cassava not only can be applied as adsorbent of heavy metal ions [1] but also as raw material of production of lactic acid.

Lactic acid is widely used in food and nonfood industrial applications [2]. There is increased interest in using lactic acid as a starting material for the synthesis of polylactic acid (PLA), a biodegradable plastic [3, 4]. PLA is traditionally manufactured in a three-phase process: (1) fermentation by *Streptococcus bovis* to produce lactic acid [5-7]; (2) recovery of lactic acid from the fermentation broth [8, 9], and (3) polymerization of the lactic acid.

The conventional process for fermentative production of lactic acid is a discontinuous process with low productivity and high capital and operating costs. Therefore, alternatives to this manufacturing process are being studied. To reduce these costs, many studies on lactic acid separation have been conducted using different separation techniques, such as reactive extraction, membrane technology, electro dialysis [10], distillation [9] and ion exchange. Ion exchange is widely used in bioseparations, and different processes for lactic acid recovery based on previous reports as the following paragraphs. Kulprathipanja [11] patented a process for lactic acid recovery from a fermentation broth using anionic polymeric. Evangelista and Nikolov [12] recovered lactic acid from fermentation broth using weak base anion exchangers (MWA-1, IRA-35, VI-15). Ye *et al*. [13] also proposed a process for lacticacid production combining a membrane bioreactor and membrane filtration. Previously, we reported the purification of lactic acid and lactate on membrane bioreactor using single and two step [8, 9].

Kumar and Mahajani [14] described the esterification of lactic acid with-butanol by reactive distillation catalyzed by acid ion-exchange resin. They used pseudo-homogeneous model to simulate the kinetic data also without considering the nonideality of the liquid mixture. Sanz *et al.* [15] investigated the reaction of lactic acid with methanol using Amberlyst 15 as catalyst. Zhang *et al*. [16] studied the esterification of lactic acid with ethanol in the presence of five acid ion-exchange resins.

In this study adsorption of l-(+)-lactic acid on several of ion exchange, strongly and weak basic was studied. The adsorption isotherm, breakthrough curve, washing condition, and column separation process for lactic acid were described.

MATERIALS AND METHODS

Batch adsorption

Batch adsorption experiments were conducted by equilibrating 4 g resin with 15 mL lactic acid solution or cell-free fermentation broth in 50 mL Erlenmeyer flasks. Flasks were kept well mixed at 24 in a shaker bath overnight at various initial lactic acid concentrations. After the adsorption experiment was completed, batch desorption experiments were performed by diluting the solution in each flask with 15 mL of water, and equilibrating the flasks at 24 h in a shaker bath. After 24h, the supernatant was sampled and the lactic acid was measured.

Continuous adsorption/columnadsorption

Column adsorption experiments were conducted in an insulated brass fixed-bed column of 1.3 cm diameter and 72.0 cm length. The column was packed with 56.27g of fresh resin pellets. A peristaltic pump transported either broth or lactate solution to the column at an average flow rate of 3.0 mL/min (Figure-1). Glass wool was put on the top and bottom of the bed to obtain a good liquid distribution. The adsorption step was performed at 25 ºC, and then, the column was regenerated by preheating it to 95 ºC using heating tape, then passing steam through the bed at a flow rate of 6.5 g/L and a temperature of 138 ºC. Samples of the effluent condensate were collected and analyzed for lactate concentration.

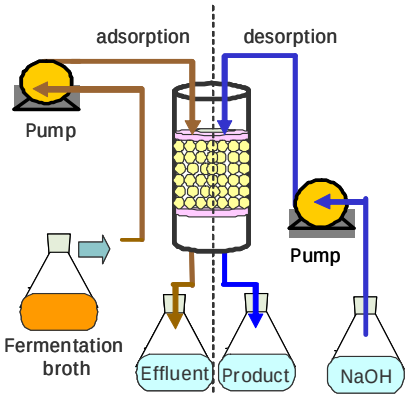

Figure-1. Column adsorption apparatus.

RESULTS AND DISCUSSIONS

Batch adsorption with various resins

A selection procedure was designed to obtain the most favorable resin or adsorbent for lactic acid separation. The objective is the sorption capability of lactic acid (Figure-2). Among the strong-base and weak-base anion ion-exchange resin appears to be the best one for lactic acid separation. The results from the batch adsorption were shown in Figure-2. The resin WA 30 adsorbed lactic acid up to 254 mg/g in aqueous. This adsorptive capacity is high compared to the amount of 210 g/mg reported for lactic acid adsorption on Amberlite IRA-35[17].

Figure-2 shows the capacities of the resins in their different forms. The WA 30 is weak base resin presented the highest adsorption capacity. However, the strong base resin in OH- form had higher adsorption capacities than the weak base ones in free base form. Amberlite IRA A 400, SA 10A, WK 10 and PK 228 not be obtained in OH- form (remained in free base form at pH higher than 9). Resin WA 30 was selected for the other studies.

Batch adsorption with various temperatures

Resin isotherms at different temperatures were measured and the results were shown in Figure-3 and Table-1. The amount of lactic acid exchanged decreases with increasing temperature, which indicates that lactic acid separation should be done at low temperatures. The maximum resin capability of lactic acid on WA 30 resin is much higher than the theoretical value which is separately measure with HCl method. The results indicate that a certain degree of physical adsorption must have existed in addition to resin.

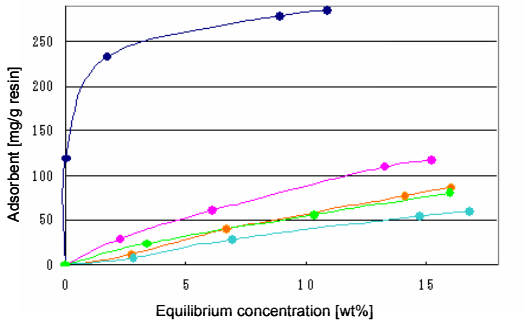

Figure-2. Adsorption isotherm for HLa solution with various resins (♦: WA 30, ♦:SA 10A, ♦: WK 10, ♦: PK 228,♦:IRA A400).

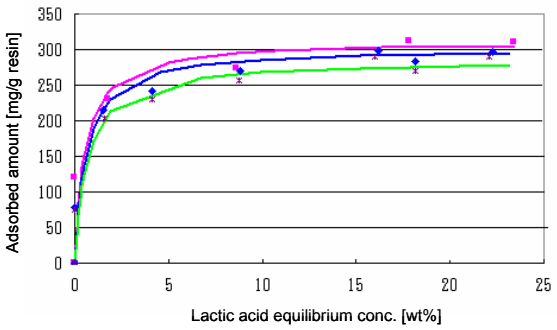

Figure-3. Resin equilibrium of lactic acid on WA 30 and comparison of experimental data and model. (■: 23 ºC, ♦:30 ºC,x:40 ºC).

Since WA30 adsorption isotherm follows Langmuir adsorption, it is simple to summarize the equilibrium constant (K) and saturation adsorption quantity (q_∞) by plotting the Langmuir equation $q = q_\infty \frac{K \cdot c}{1 + K \cdot c}$ in the $\frac{c}{q} = \frac{1}{q_\infty} c + \frac{1}{K \cdot q_\infty}$ form [18] and previous reports of the Langmuir equationaplication [19-23]. The slope is $1/q_\infty$and the intercept is $1/(K.q_\infty)$, the result is shown Table-1. As can be seen in Figure 3, the selectivity at 23 ºC was slightly higher than the selectivity of the anion exchanger at 40 ºC. At this temperature, lactate concentration in the effluent soon reached the feed concentration and a higher volume was treated before chloride appeared in the effluent. Adsorption of lactic acid from fermentation broth on zeolite molecular sieve was conducted by Aljundi *et al*. [24]. Batch experiments were used to measure the adsorption isotherm of lactic acid adsorption which has Henry's constant of 2±0.7 L/kg and 1±0.5 L/kg for the aqueous and broth.

Table-1. Resin equilibrium of lactic acid on WA 30 with different temperatures.

T [ºC]	q_∞[mg/g-resin]	K [1/wt%]
23	312.50	1.882
30	303.03	1.650
40	285.71	1.522

Column adsorption isotherm

This effect of components in the fermentation broth on lactic acid adsorption was studied by plotting the adsorption isotherms of standard lactic acid and lactic acid in the fermentation broth (Figure-4). Figure-4 shows the result of column adsorption using ammonium lactate (NH_4La) solution and fermentation broth. From Figure-4, it can be observed that the experimental data obtained under the conditions correspond with simulations well especially for lactic acid in the fermentation broth.

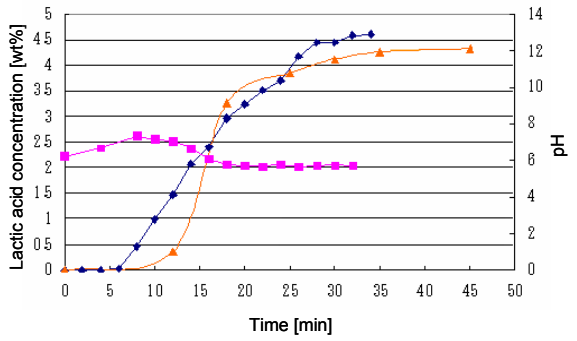

Figure-4. Adsorption isotherm of NH_4La, and fermentationbroth by WA 30 resin (■: pH, ♦: Lactic acid concentration, ▲:40 ºC).

Calculated from Langmuir equation, it was found that the adsorbed capacity for model was 128.8 mg/g-resin while for fermentation broth, 100 mg/g-resin. There is a difference between the model and the fermentation broth, because the difference values (~28.8%) of the q_{max} results obviously from the competitive adsorption of some components in the fermentation broth containing anion ions like some proteins, amino acids, salts, pigments, DNA, RNA, other impurities exist in fermentation broth such as organic acids, microorganism, salt from medium [25].

Column adsorption and desorption

The equilibrium curves obtained from desorption from the WA 30 resin were lower than those obtained from adsorption. Thiswas the result of the shape of the openings to the pores of the solid or of the complex phenomenon of the wetting of the solid by the adsorbate. As shown in Figs. 5 and 6, the adsorption of lactic acid from fermentation broth was clearly irreversible and the hysteresis loop was even wider than that of the aqueous solution. This may be due to the presence of chemical species in the broth (nutrients necessary for bacterial growth such as yeast extract, meat extract, etc.) that alters the intermolecular forces.

Lactic acid concentrations from the bed regeneration were shown in Figure-6. The average recovery of lactic acid from the amount retained in the column was 60 and 70%, for the broth and aqueous solutions, respectively. It is believed that by choosing a high enough temperature, the speed of desorption front can be made faster than the speed of the thermal wave. In this case, desorbed species is accumulated at the front and a high concentration peak with less tail can be expected. On the other hand, when the temperature of desorption is not high enough, desorption gradually occurs and a long tailing will be expected.

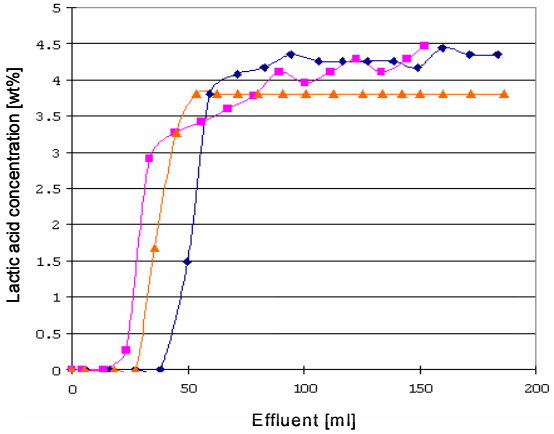

Figure-5. Comparison of column adsorption data (■: NH_4La, ♦: HLa, ▲:Fermentation broth).

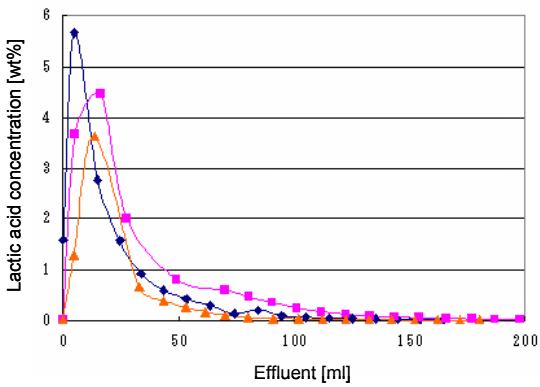

Figure-6. Comparison of column desorption data (■: NH_4La, ♦: HLa, ▲: Fermentation broth).

From the breakthrough curve (Figure-5), it was found that breakthrough point for NH_4La was reached after 13.8 mL of effluent in 6 minutes, while in fermentation broth case; the breakthrough point was reached after 27.35 mL of effluent in 10 minutes. The adsorbed lactic acid in HLa case was 154.73 mg/g-resin and in NH_4La and fermentation broth were 148.22 mg/g-resin and 96.96 mg/g-resin.

Adsorption feed analysis using HPLC

The fermentation broth containing lactic acid was produced from cassava bagasse by *Streptococcus bovis*. In this fermentation broth, there were many components such as glucose, protein, organic acid, pigment, amino acid, salt, etc. The chromatogram of organic acids by HPLC with a column AminexHPX-87H is shown in Figure-6. In Figure-6, it can detected 7 peaks which represent oxalic acid, glycolic acid, lactic acid, citric acid, succinic acid, fumaric acid,acrylic acid, and unknown in the order of retention volume. The concentration of lactic acid in the fermentation broth (pH 6.0) is about 80 mg/mL and the purity is about 80%, respectively.

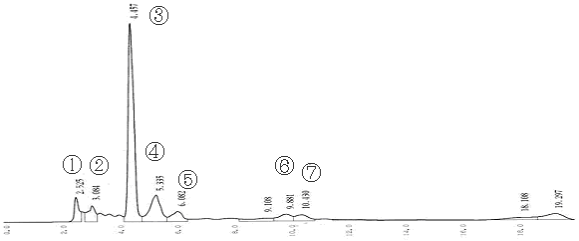

Figure-7. Cromatogram of fermentation broth (1: Oxalic acid, 2: Glycolic acid, 3: Lactic acid, 4: Citric acid, 5: Succinic acid, 6: Fumaric acid, 7: Acrylic acid)

CONCLUSIONS

The resin of WA 30 gives the highest amount of adsorbed concentration of lactic acid compared to the resins of Amberlite IRA A 400, SA 10A, WK 10 and PK 228. It was best suited to be used in adsorption of lactic acid from fermentation broth. The amount of lactic acid exchanged decreases with increasing temperature, which indicates that lactic acid separation should be done at low temperatures. The maximum resin capability of lactic acid on WA 30 resin is much higher than the theoretical value which is separately measure with HCL method. From the column adsorption data, the adsorbed lactic acid is 154.73 mg/g-resinin the HLa, 148.22 mg/g-resin in NH_4La, and 96.96 mg/g-resin in the fermentation broth.

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