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# Separation of D-lactic acid from aqueous solutions based on the adsorption technology

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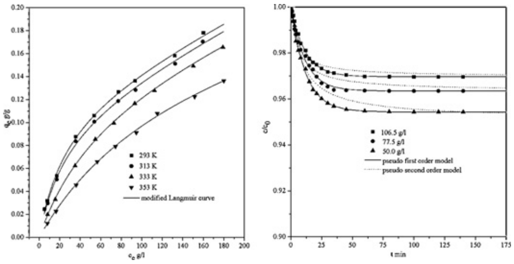
## HIGHLIGHTS

- ► A novel polar macroporous resin was offered with good properties.
- ► A green refining process was proposed since only water was added.
- ► A model was established to design the D-lactic acid adsorption process.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel polar macroporous adsorption resin (AX-1) has been applied for separation of D-lactic acid (DLA) from aqueous solutions in a fixed-bed chromatographic column. The adsorption equilibrium and kinetics were investigated experimentally. A column model was subsequently established and validated by comparison of the simulation results to the experimental data obtained at different operating conditions in terms of feed flow rates and initial concentrations as well as bed heights. At the end of this work, the recycling studies were carried out. It was found that the saturated resin could be washed out DLA completely and repeated use by 353 K hot water. The results show that the AX-1 resin has a high adsorption capacity to DLA while no retention to sulfate ion. Based on this kind of resin, a green-production refining process could be established since only water is added in the entire separation process.

## 1. Introduction

Lactic acid (2-hydroxypropanoic acid), which can be generally found in sour milk, is chiral and has two optical isomers. One is known as L-lactic acid (LLA) and the other, its mirror image, is D-lactic acid (DLA), shown in Fig. 1. It has been attended much attention on its use as a raw material for the production of polylactic acid (PLA), which later has developed application as biodegradable plastic. This renewable plastic has a promising application used for substituting conventional petroleum based plastics because of low emission of carbon dioxide [1,2]. However, due to its low melting temperature and low crystallization ability, the application of PLA in other aspects is restricted [3]. Recently, several researchers [4,5] reported that the stereo-complex of poly (DLA) and poly (LLA) blend could increase the melting point approximately 50 K higher than that of pure PLLA. Karst and Yang [6] also found that this 50/50 PLLA and PDLA blend exhibited a new feature for higher

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## Nomenclature

| | |
|---|---|
| $a$ | Modified Langmuir isotherm model parameter [–] |
| $A$ | Temkin parameter [–] |
| $b$ | Modified Langmuir isotherm model parameter [–] |
| $B$ | Temkin parameter [–] |
| $c$ | DLA concentration in the liquid phase [g/l] |
| $c_e$ | equilibrium DLA concentration in the liquid phase [g/l] |
| $c_0$ | initial concentration of DLA in aqueous solution [g/l] |
| $d_p$ | diameter of the particle of the adsorbent [m] |
| $D_{ax}$ | axial dispersion coefficient [$m^2$/s] |
| $h$ | Modified Langmuir isotherm model parameter [–] |
| $k_1$ | the rate constant of pseudo-first kinetic model [$min^{-1}$] |
| $k_2$ | the rate constant of pseudo-second kinetic model [$min^{-1}$] |
| $k_n$ | the rate constant of pseudo-$n$ kinetic model [$min^{-1}$] |
| $K_0$ | thermodynamic equilibrium constant [–] |
| $L$ | bed height [cm] |
| $m$ | mass of adsorbent [g] |
| $q$ | DLA concentration in the stationary phase [g/g] |
| $q_e$ | equilibrium adsorption capacity [g/g] |
| $Q$ | mobile phase volumetric flow rate [ml/min] |
| $Re$ | Reynolds number [–] |
| $t$ | time [min] |
| $t_0$ | dead time of the column [min] |
| $t_R$ | retention time [min] |
| $T$ | temperature [K] |
| $u$ | superficial velocity [m/s] |
| $v$ | interstitial velocity of the liquid phase [cm/min] |
| $z$ | axial coordinate in the bed [cm] |
| $\triangle q$ | standard deviation [–] |
| $\triangle G$ | free energy change [kJ/mol] |
| $\triangle H$ | enthalpy change [kJ/mol] |
| $\triangle S$ | entropy change [J/mol K] |
| $\rho$ | resin bed density [g/l] |
| $\rho_s$ | fluid density [$kg/m^3$] |
| $\mu$ | viscosity of the solution [cP] |
| $\varepsilon$ | void fraction of bed [–] |

hydrolysis-resistance. The price of optically pure DLA is five to ten times higher than that of pure LLA [7]. Therefore, more attention has been given to the production of DLA, in addition to LLA.

Currently, over 90% of commercial lactic acid is produced via fermentation by lactic acid bacteria [8]. However, the growth of lactic acid bacteria is inhibited by the accumulation of lactic acid in the fermentation process. Calcium carbonate is added to maintain the fermentation broth pH around 5.0–7.0 [9]. Hence, at the end of fermentation, calcium lactate, instead of lactic acid, is formed, which leads to the downstream purification process is not straightforward. The calcium lactate is firstly acidified with sulfuric acid to convert the salt to lactic acid and calcium sulfate precipitates [10]. After filtration, the clarified liquor contains not only the target component DLA but several impurities, i.e., calcium and sulfate ions as well. Sequentially, the cation, i.e., Amberlite IR-120/H [11] and anion, i.e., IRA-94 [12] exchangers are applied to remove the impurities. Since there exists lactate ion in the liquor which can be adsorbed by the anion exchanger as well, recovery of DLA based on this process has the disadvantages of high separation cost and low productivity. Moreover, the wastewater disposal is another serious environmental problem. In literature, several other methods such as extraction [13], electrodialysis [14] and distillation [15] have been reported as well. However, they still need more improvements to meet the demands of the large volume production of lactic acid. However, ion exchanger is a practical technique used in bio-separation.

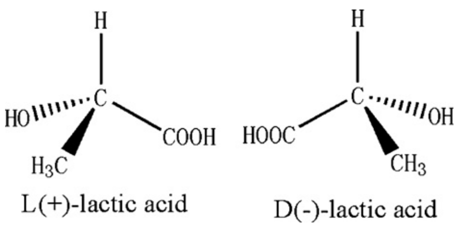

**Fig. 1.** Chemical structure of L-lactic acid and D-lactic acid.

In order to improve the DLA productivity, several alternative adsorbents have been reported in literature. Evangelista and Nikolov [16] separated lactic acid from model fermentation broth by using weak base anion adsorbents VI-5, MWA-1 and IRA-35. They found that VI-5 appeared to be the most attractive adsorbent since it could completely desorb lactic acid by using 6.8 bed-volume of methanol as a desorbent. But the selectivity of VI-5 was below, as other broth components could not be effectively removed. Chen and Ju [17] purified lactic acid from the fermentation broth using polyvinylpyridine (PVP) and activate carbon as adsorbents. The results showed that the solution pH had little effect on the lactic acid adsorption onto PVP. Active carbon was better than PVP due to its higher loading capacity to LLA than that of PVP. The drawback of active carbon was its high adsorption affinity to cell which limited its application. Tong et al. [18] recovered LLA from the fermentation broth with paper sludge using weak anion exchange resin IRA-92, and pH adjusted to 6.0 could increase the recovery yield, purity and productivity. Lee et al. [10] separated a mixture of LLA and acetic acid based on a four-zone laboratory-scale Simulated Moving Bed (SMB) unit. The resin PVP was selected as an adsorbent. The LLA purity of 99.9% could be achieved in the process.

So far the research efforts are mainly focused on the LLA recovery. Good separation performances have been essentially obtained. However, the purification of DLA has been little reported in literature compared with LLA. Hence, it would be important to select a specific adsorbent for the recovery of DLA from the fermentation broth as well.

Separation processes carried out by macroporous adsorption resins have the advantages of low cost, little pollution and easy regeneration [19]. There has been an increased interest in developing various macroporous adsorption resins to separate organic acids [20–22]. DLA is an alpha hydroxyl acid with a hydroxyl group adjacent to the carboxyl group. Since DLA contains hydroxyl and carboxyl groups in its molecular structure, an adsorption resin with polar functional groups on its skeleton would have the properties of large adsorption capacity to DLA by formation of the hydrogenous bond force.

In this paper, an AX-1 polymeric resin with phenolic hydroxyl groups on its skeleton made by our laboratory was applied to remove DLA from the aqueous solutions in a fixed-bed column. The adsorption equilibrium and kinetics were investigated. The commonly used kinetic models in terms of pseudo-first-order and pseudo-second-order were used to describe the DLA adsorption kinetics on the resin. Furthermore, a chromatographic model based on the experimentally determined isotherm model and adsorption kinetics was used to predict the breakthrough curves at different operating conditions, i.e., flow rates, inlet concentrations and bed height. The model was verified by comparing the calculated results with the experimental data. Finally, the regeneration processes were carried out. The aim of this study is not only to offer a potential adsorbent which processes good adsorption properties