



Purification of organic acids by chromatography: Adsorption isotherms and impact of elution flow rate



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ABSTRACT

Bio-based organic acids are identified as very promising sources of renewable carbon. Currently their production costs are a major obstacle to their development and particularly because of complex downstream processes, using distillation or crystallization. Preparative chromatography was studied as an alternative to those processes. Two different ion exchange resins (anionic and cationic) were tested on synthetic solutions, a first step before studying the purification of a real fermentation broth. Firstly, adsorption isotherms were determined for each organic acid in single solute solution. They all fitted with the Langmuir model. Moreover in a first approximation, they could be considered as linear on cationic resin. Affinity coefficients, obtained by fitting, were compared to affinity coefficients determined during pulse tests. They were generally in good agreement, confirming that both methods are accurate. However, wider is the peak tailing on the pulse test and greater are the differences between measured values. In a second phase, the effect of the liquid flow rate on the column efficiency was studied for salts, glucose and lactic acid. The results were consistent with Van Deemter equation for lactic acid and glucose; salts were not retained at all. The linear part of Van Deemter equation is observed for liquid velocities between 0.4 and 4 m/h.

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1. Introduction

The chemical industry has shown rapid growth in the 20th century thanks to petroleum as carbon source. Oil has indeed become the base for almost every product made by industrial chemistry. However this field is now facing a new challenge because it is a fossil resource whose world stocks are inevitably sinking while its price soars. This is the reason for why green chemistry is growing in many fields including, carbon economy, more efficient syntheses but also finding new renewable carbon sources.

Bio-based organic acids are identified as very promising sources of renewable carbon. They were especially highlighted by the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) in 2004 in their famous report "Top Value Added Chemicals From Biomass – Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas" [1]. They are considered as important building-blocks for chemical industry and more specifically for the polymer industry. Current markets for bio-based organic acids are small owing to their relative high cost of synthesis in comparison with their petroleum-derived

homologues [2]. But as prices will become competitive, their markets should increase very fast. That is the reason why there is a huge demand from industry to reduce their production costs.

These molecules have been already produced for a long time by microbial fermentation for food industry. However, new applications need a much higher purity, especially in the field of polymer synthesis. Nowadays industry uses distillation [3,4], esterification [5–7] and crystallization [8] to reach the purity required [9]. These methods are energy-consuming and have relatively small recovery rates. Alternative downstream processes using preparative chromatography seem then to be promising due to advantages of this technique. This powerful separation method was initially developed for extraction and purification of complex mixtures of vegetal origin [10]. Nowadays it is more and more used in various fields, from biotechnology to production of fine chemicals, and in particular in the sugar industry. Reductions in the energy consumption, effluent volumes and chemical consumption may be considered as some of the advantages of chromatography over the above mentioned techniques. Therefore it might help to reach the same purity as other techniques, but generally with better yields, and is more economical and environmentally friendly. In addition chromatography is interesting in our case as it is able to separate mineral salts, sugars and organic acids by using ion exchange resins (cationic and anionic) without performing ion exchanges. Counter-ions

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fixed on the resin are the same as ions in solution. So the resin is in equilibrium with the solution and there is no global ion exchange. However partition phenomena happen between the solid and liquid phases. It results in compound slowdown, according to their affinity for the resin, and thus in a compound separation. This property is used in the sugar industry to separate sucrose from salts with cationic resins, as well as sugars from each other, as the famous glucose–fructose separation and in the citric acid purification with anionic resins. Mechanisms are complex, coupling size exclusion, ligand exchange, hydrophilic or hydrophobic interactions and ions exchange [11,12].

The behavior of a compound can be described by two types of features. The first one is directly related to the compound itself and the adsorbent. It is the affinity that each molecule has for the adsorbent, the reason why one compound is more retained than another. These thermodynamic data are typical of adsorption equilibrium. The second one concerns hydrodynamic dispersion giving the width of each peak.

The goal of this work was to study the separation of organic acids from glucose from both points of view (thermodynamic and kinetic) in order to better understand separation mechanisms and kinetics impacts, and to be able to make reliable scale up calculations.

Lactic, succinic and citric acids were chosen for two reasons. They are major organic acids produced by fermentation. So their production cost optimization is nowadays of big concern to develop the market. Moreover they are respectively mono-, di- and triacids.

2. Theory of chromatography

For a given chromatographic system, the distribution at equilibrium of each compound between both phases is characterized by the affinity coefficient given by the equation $K = q/C$. q and C are respectively the compound concentrations in solid and liquid phases at equilibrium. Differences in affinity coefficients result in disparities in migration velocities along the resin bed and so in a separation of the compounds.

The common unit used in preparative chromatography is the bed volume (BV) [13–15]. It corresponds to the ratio of the total eluted volume to the resin bed volume.

2.1. Retention volume

Consider the injection of a solution containing the studied compound at the concentration C_0 . At the outlet of the column, the compound concentration is zero until the retention volume V_R is reached. If dispersion is ignored, it can be considered that at t_R , when V_R is reached, the concentration at the end of the column directly passes from zero to C_0 . A mass balance at that time gives:

$$Q_{\text{tot}} = V_R C_0 = V_M C_0 + V_S q \quad (1)$$

with Q_{tot} total quantity of compound injected; V_M bed void volume; V_S solid phase volume;

Given V_L the bed volume and ε its voidage, the previous equation becomes:

$$V_R C_0 = \varepsilon V_L C_0 + (1 - \varepsilon) V_L q \quad (2)$$

Yet at equilibrium $q = KC_0$, Eq. (3) in BV can be simply deduced from (2).

$$v_R = \frac{V_R}{V_L} = \varepsilon + (1 - \varepsilon)K \quad (3)$$

with v_R reduced retention volume (in BV). This Eq. (3) is also true in pulse test according to classical models of linear chromatography without competition [16].

K is the thermodynamic equilibrium coefficient (affinity), relating the concentrations in both phases at equilibrium. It can depend on the compound concentration for concentrated phases. However in diluted solutions, K may be considered as constant. So v_R may be constant for a given compound. This is the principle used in HPLC to identify a compound, assuming that the retention time is constant.

2.2. Adsorption isotherm

Langmuir isotherm (4) is classically used to model adsorption [15,17–19]. In diluted conditions, the term $K_1 C$ is negligible with respect to 1 and Langmuir isotherm is linear (5).

$$q = \frac{q_{\text{max}} K_1 C}{1 + K_1 C} \quad (4)$$

$$q = q_{\text{max}} K_1 C \quad (5)$$

$q_{\text{max}} K_1$ corresponds then to K the affinity coefficient previously introduced.

2.3. Dispersion sources

Hydrodynamics and adsorption kinetics tend to disperse a peak. In the case of a linear isotherm (K constant), they are the only phenomena affecting the peak shape. This is the reason why in these conditions, the peak is symmetrical and the distribution is gaussian.

Van Deemter Eq. (6), widely used, takes those dispersion phenomena into account with H the height equivalent to a theoretical plate and u the elution velocity [20,21].

$$H = A + \frac{B}{u} + Cu \quad (6)$$

- The A term represents the flow anisotropy.
- The B term is linked to axial diffusion.
- The C term corresponds to the mass transfer resistance from the liquid bulk to the resin.

This equation was initially developed in 1956 for gases but has since been successfully extended to liquids. Several other equations have been developed as Giddings and Knox equations. The theoretical basis of each equation is different but they all model dispersion along the column and most of them can be applied successfully to fit experimental dispersion data [21]. We chose to work with Van Deemter equation.

The Van Deemter curve (Fig. 1) is classically used to evaluate column efficiency and to scale up from lab to industry scale without theoretically needing a pilot phase. This curve gives an optimal efficiency (minimum of H) for relatively low velocities; but finding

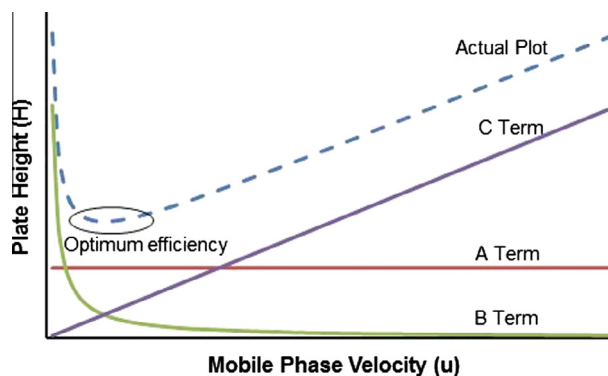


Fig. 1. The Van Deemter curve.

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