SEPARATION OF BETAINE FROM MOLASSES

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ABSTRACT

This paper presents the result of an experimental study dealing with the separation of betaine from molasses. It is a part of an ongoing research work desired to design and develop a simulating moving bed (SMB) for the separation of main sugar and non-sugar components from molasses with chromatography intended to optimize sugar industries. In view of this, a series of pluse experiments at different betaine concentrations were carried out in a fixed bed column packed with a strongly anionic exchange resin. The adsorption equilibria for both lower (very dilute) and higher betaine concentrations were identified from the eluted pulse peaks. The first moment, equilibrium constants, solid phase concentrations and equilibrium isotherm are reported.

INTRODUCTION

Nowadays, there is a growing need for optimization of sugar industries by employing effective methods for separating sugar and non-sugar components in molasses mainly due to economic and environmental reasons. In this context, several research works have been carried out and appreciable results have been achieved especially in the recovery of sugar molasses components.

Most sugar factories precipitate quite considerable volume of molasses, frequently used as animal feed and as a raw material for the production of ethanol, while still a large part of it is disposed of. This poses serious environmental problems affecting particularly aquatic life owing to its high organic load and nutrient contents. Molasses is the final sugar solution obtained after repeated crystallization steps. To increase productivity of sugar industries and reduce the adverse environmental impact, the desugarization of molasses through recovery of the dissolved sugar and other valuable non-sugar fractions is gaining increasing importance [3,4,5]. Amino acids are the most interesting non-sugar components of molasses constituents. Betaine is one of the most important amino acids [3,6,7] present in a higher concentration usually between 4 and 7% (w/w) compared to the rest of the amino acids [3]. It has found wide application in pharmaceutical and cosmetic industries among others.

Most of the industrial applications and laboratory scale studies performed so far concerning molasses treatment mainly focused on the separation of sugar and non-sugar components of molasses or on the subsequent separation of sugar components from one another [3,8,10]. Liquid chromatography has been a suitable technique employed for the separation of the components of molasses from one another. This process not only gives a better separation of sucrose from the non-sugar components but also ensures the effective separations of non-sugar from one another [2]. The process provides the possibility to collect the sucrose in one fraction with high purity and recovery as well as the non-sugar fractions according to their properties and importance.

The results of a series of experimental works carried out on beet molasses showed that more than 95% sugar can be recovered. Similar results were also obtained in treating cane molasses. However the separation of cane molasses yields, in addition to the sugar and non-sugar fractions, a third fraction rich in invert sugar [2]. In both cases the quality of the end product depends very much on the quality of the molasses used. For an industrial scale separation of molasses components, a simulated moving bed (SMB) is the commonly employed process technology [3,5,11]. For the design of the separation unit on industrial scale, adsorption equilibrium and mass transfer efficiency are the essential parameters to be considered [12].

In this paper experimental results obtained for the separation of betaine from the reference aqueous solutions carried out in a laboratory unit with fixed-bed column are presented. The data was utilized to evaluate the key parameters that are essential for the industrial scale design of a simulating moving bed unit to be used for the separation of betaine from molasses.

EXPERIMENT

Apparatus and Procedure

The experimental apparatus for the elution chromatography using a single column is schematically shown in Figure 1. Feed pump (3) is used to maintain the eluent (reservoir 1) and the injected pulse streams flow through the column (6). Two three-way valves (5) are used to ensure the required bypass flow. A pulse of desired betaine concentration was injected into the pulse loop by means of a syringe,which flows to the detector (7) via a six-way valve (4). The loop volume is 6.15 cm^3. The column is connected to the thermostat (2) in order to maintain constant column temperature by circulating water from tlie thermostat bath through the column jacket. The column is packed with a DOWEX 50 WX8-400, strongly acidic cation exchanger resins, in the form of K^+, having average particle diameter of about 56 μm.

The bypass and eluted streams were directly conveyed to a refractive index (RT) detector .(model 1047A. HP rmbH). Data acquisition was performed with a personal computer (9) coupled with the unit by means of a Chrom Card software.

Objective of the Experiment

The purpose of this experimental research work is aimed at determining and establishing the adsorption equilibria of the main sugar and non-sugar components with emphasis on one of the most important amino acids, betaine, found in both cane and beat molasses. Since the adsorption equilibrium is one of the key parameters considered for the design of a separation process, its determination is of immense importance. To this end, series of experimental runs were carried out in column and bypass. In the first case, a pulse of a reference aqueous solutions of specific betaine concentrations was injected into the plus loop [11], which was then introduced into the column via a six-way valve with the three-way valves kept open. In the second case, the solution was injected and directly introduced to the detector via the six-way valve bypassing the column with one of the three-way valves being maintained in a closed position. The chromatograms for all pulse experimental runs were observed and evaluated.

The equilibration of the column with eluent or background concentration was performed prior to running each pulse experiment. This was done by

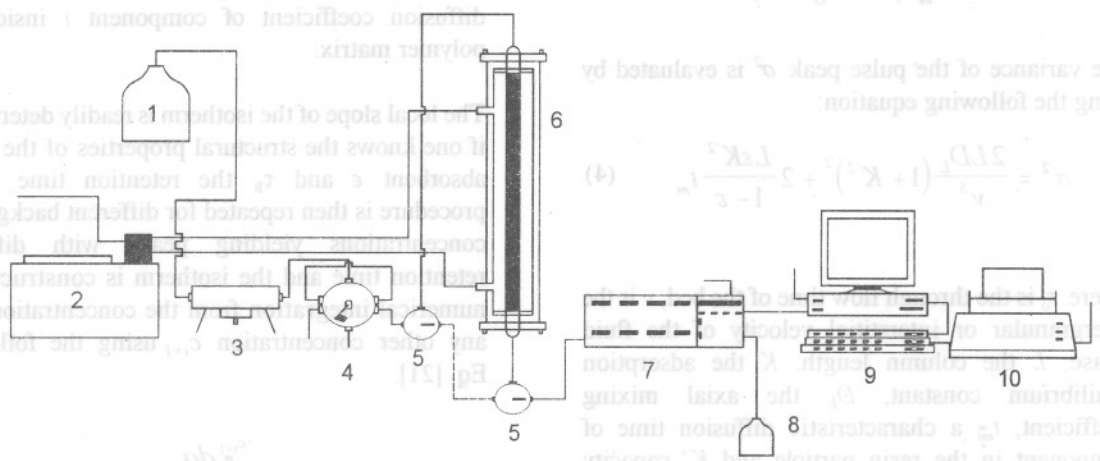

Figure 1 Equipment set-up

1. Feed tank with eluent
2. Thermostat
3. Feed pump
4. Six-way valve
5. Three-way-valve
6. Packed column
7. IR detector (HP 1047A)
8. Storage tank for eluent flow
9. PC with Chrom-Card Soft ware
10. Printer
11. Pulse loop

pumping the eluent or solution of background concentration until a constant baseline was maintained by the detector. The flow rate used for equilibration and experimental runs were the same. All experimental runs were conducted at a constant column temperature of 40°C.

Evaluation

Retention time or equivalently the first moment of the peak τ_R for different pulse concentration was determined. The equilibrium constant or the local slope of the isotherm was also evaluated. It is known [21] that the retention time is given by Eq. (1).

$$\tau_R = \tau_0\left(1+\frac{1-\varepsilon}{\varepsilon}K\right) \quad (1)$$

where $\tau_0 = \frac{L}{u}$ (2)

From Eqs. (1) and (2), it follows that,

$$\tau_R = \frac{L}{u}\left(1+\frac{1-\varepsilon}{\varepsilon}K\right) \quad (3)$$

The variance of the pulse peak σ^2 is evaluated by using the following equation:

$$\sigma^2 = \frac{2LD_L}{v^3}\left(1+K'^2\right)^2 + 2\frac{L\varepsilon K'^2}{1-\varepsilon}t_m \quad (4)$$

where τ_o is the through flow time of the bed, v is the intergranular or interstitial velocity of the fluid phase, L the column length, K the adsorption equilibrium constant, D_L the axial mixing coefficient, t_{mi} a characteristic diffusion time of component in the resin particle and K' capacity factor, defined as

$$K' = K\frac{1-\varepsilon}{\varepsilon} \quad (5)$$

The absorptivity of each component, K_i is readily estimated using Eq. (1) or (3). Moreover, the linearity and non-linearity of the adsorption equilibria were checked by the pulse experiments at different concentrations. In this regard, approximately constant K values are obtained for very dilute betaine concentration. These values are different for higher betaine concentrations thus indicating the non linearity of the process. With regard to transport phenomena, Eq. (4) can also be expressed in terms of the height of equivalent theoretical plate, HETP given by Eq. (6).

$$HETP = \frac{2D_L}{v} + \frac{2v\varepsilon}{1-\varepsilon}\left(\frac{K_i'}{1+K_i'}\right)^2 t_{mi} \quad (6)$$

Eq. (6) is the well-known Van Deemter equation [15]. The efficiency of the column is governed by the factor related to fluid dynamics non-ideality and the interparticle transport phenomena lumped in the time parameter. Its actual expression is determined by the assumed particle morphology [3]. In gel-type ion exchange resins, two diffusion steps are usually identified: transport through the external fluid film and diffusion through the polymeric matrix in the adsorbed phase [3]. Hence the characteristic diffusion time is given by the equation.

$$t_{mi} = \frac{r_p}{3K_i} + \frac{r_p^2}{15K_iD_{si}\rho_p} \quad (7)$$

where r_p indicates the particle radius and D_{si} the diffusion coefficient of component i inside the polymer matrix.

The local slope of the isotherm is readily determined if one knows the structural properties of the of the absorbent ϵ and τ_R the retention time . The procedure is then repeated for different background concentrations yielding peaks with different retention time and the isotherm is constructed by numerical integration from the concentration c_i to any other concentration c_{i+1} using the following Eq. [21].

$$q_i = \int_{c_i}^{c_{i+1}} \frac{dq}{dc}dc \quad (8)$$

where dq/dc is the derivative of the adsorption isotherm. The adsorbed phase concentration q is expressed in units coherent with the units of the liquid phase concentration c, that is, grames adsorbed per unit volume of solid adsorbent.

The peak moments which are referred to in Eqs. (1) and (3) have to account for the effect of chromatographic column only. However, the experimental data are affected by extra column parts of the unit, such as injector, tubing, valves, and detectors [3]. In linear chromatographic theory [3,13] the sulting moments are expressed taking into account the superposition of these effects and the corrected values of the moments to be used in Eqs. (1) and (3) which are evaluated by means of the following equations.

$$\tau_i = \tau_{ic} - \tau_{ibp} \qquad (9)$$

$$\sigma_i^2 = \sigma_{ic}^2 - \sigma_{ibp}^2 \qquad (10)$$

The values of the extra column moments estimated by the bypass pulse experiments were completely equivalent to those described above.

INTERPRETATION OF RESULTS

Illustrative Examples

Figure 2 shows the experimental eluted peaks obtained in pulse bypass (without column) and pulse column runs for 0.7 g/l betaine concentration with eluent pure water. Figure 3 depicts the experimental eluted peaks in the pulse column and bypass runs respectively for 7.3 g/l betaine concentration with background (saturation) solution i.e., when column is saturated with eluent solution.

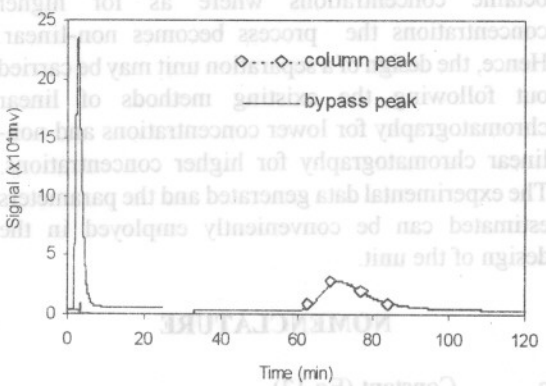

Figure 2: Bypass and eluted peaks for 0.7 g/l betaine concentration with background pure water

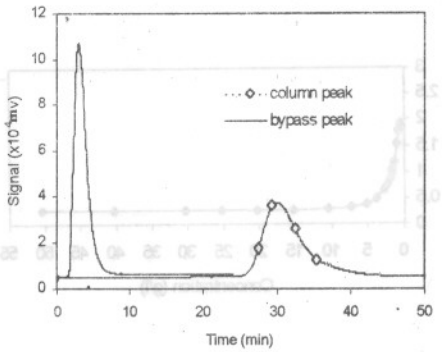

Figure 3: By-pass and eluted peaks for 7.3 gm/l betaine with background concentraion

Parameter Estimation

The data obtained in chromatographic experiments can be used for the design of a simulating moving bed unit desired for the separation of betaine from sucrose and other non-sugar components usually present in molasses. The data was utilized to evaluate the key parameters such as retention time, equilibrium constant, solid phase concentration, and HEPT required for the design of a desired unit for the separation of betaine from molasses. The results are reported graphically.

To identify a possible concentration dependence of the equilibrium constant of betaine, values of equilibrium constant were estimated for the whole series of pulse experiments. The reported values of equilibrium constant are approximately the same for very dilute concentrations thus representing a linearity of the process. It has also become obvious from the results that for higher concentrations the process is non-linear. Figures 4 and 5 represent a plot of equilibrium constant versus concentration for lower and higher concentrations respectively.

Isotherms

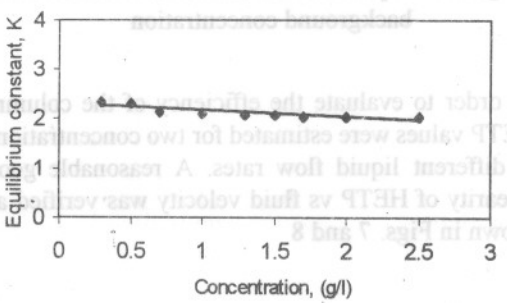

Figure 4 Equilibrium constant vs concentration with background pure water

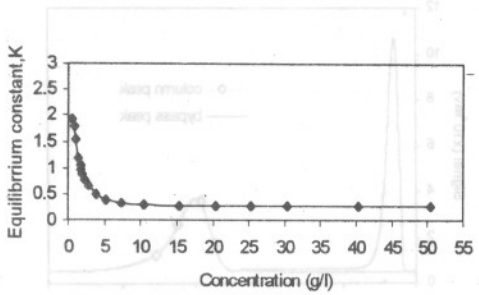

Figure 5 Equilibrium constant vs with background

Isotherms

The solid phase concentrations q at different liquid concentrations c, were calculated and the results are reported. These results are represented by the plot of solid phase concentration vs liquid phase concentration. Figure 6 represents the equilibrium isotherm of betaine at 40°C in accordance with the computed values of q and c. As can be seen from the plot, the isotherm is non-linear. This prevails for all higher concentrations as observed in this work.

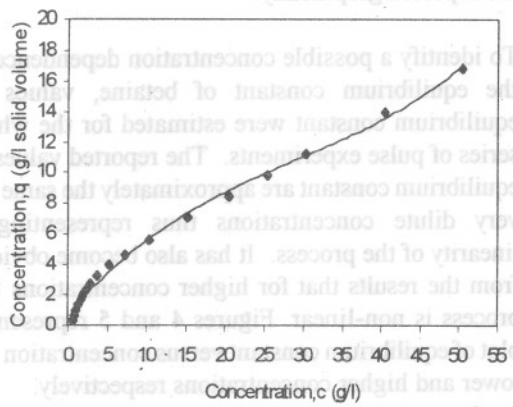

Figure 6 Equilibrium isotherm for betaine with background concentration

In order to evaluate the efficiency of the column, HETP values were estimated for two concentrations at different liquid flow rates. A reasonable good linearity of HETP vs fluid velocity was verified as shown in Figs. 7 and 8

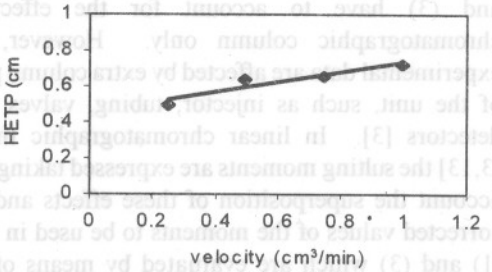

Figure 7 HETP vs fluid velocity for 1.0 g/l betaine concentration

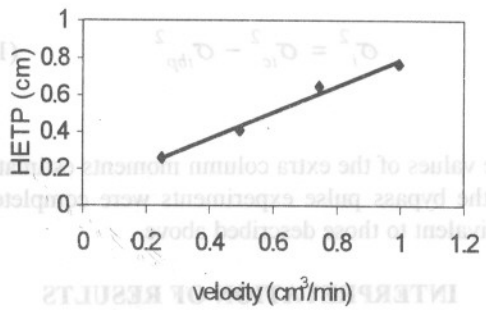

Figure 8 HETP vs fluid velocity for 2.0 g/l betaine concentration

CONCLUSIONS

The results of experimental study for the separation of betaine are presented. This study has shown that the adsorption of betaine follows linear chromatography theory for lower (very diluted) betaine concentrations where as for higher concentrations the process becomes non-linear. Hence, the design of a separation unit may be carried out following the existing methods of linear chromatography for lower concentrations and non-linear chromatography for higher concentrations. The experimental data generated and the parameters estimated can be conveniently employed in the design of the unit.

NOMENCLATURE

a	Constant (Eq.12)
b	Constant (Eq.12)
c	Liquid phase concentration (gm. l^{-1})
D_L	Axial mixing coefficient ($cm^2.s^{-1}$)
D_s	Diffusion coefficient inside the bed particle ($cm^2.s^{-1}$)

d_c	Column diameter (cm)
$HETP$	Height equivalent to a theoretical plate (cm)
K	Equilibrium constant adsorption
K	Capacity factor
L	Column length (cm)
Q	Volumetric flow rate ($l.min^{-1}$)
q	Solid phase concentration (gm. betaine/l of adsorbent)
r_p	Particle radius (cm)
t_m	Characteristic time of diffusion
u	Superficial velocity ($cm.min^{-1}$)
ϵ	Void fraction
τ	First moment (min)
σ	Variance (min^2)
ρ	density of fluid ($gm.\ cm^{-3}$)

SUBSCRIPTS

c	column
bp	bypass
i	the i^{th} component
L	liquid phase
m	average condition (mean)
p	particle
s	solid phase

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