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## Determination of mass transfer coefficients of $^{10}\text{B}$ and $^{11}\text{B}$ isotopes on chelating and weak base anion exchange resins

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### ABSTRACT

The successful design and the operation of chromatographic separations require the optimization of a large number of parameters which affect the separation in a usually nonlinear and interacting fashion. Additionally, modeling studies of chromatographic separations allow prediction of the dynamic behavior of the solute in the column against different operating alternatives without experimental effort, as well as scaling up the separation process. Thus the model based understanding of chromatographic separation, largely prevents the inconveniences of experimenting with the real process whether the operation is batch or continuous. There are several models to be used for chromatographic separations whether it is at the analytical scale or at the preparative/production scale, including the ideal model, the equilibrium dispersive model, the transport dispersive model and the general rate (GR) model. The GR model is widely acknowledged as being the most comprehensive among the chromatography models available in the literature as it accounts for axial dispersion and all the mass transfer resistances, e.g. external mass transfer of solute molecules from bulk phase to the external surface of the adsorbent, diffusion of the solute molecules through the particle, and adsorption-desorption processes on the site of the particles. In this study the mass transfer coefficients of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes are determined for chelating resin of different particle diameter and weak base anion exchange resin. It is concluded that film mass transfer coefficient and homogeneous solid diffusivity coefficients differs from each other both for  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes according to resin type and diameter.

### 1. Introduction

Chromatography is a widely used and highly selective process of separation, employed in the separation of complex mixtures of which the overall product yield of sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods, enantiomers and isomers...etc. is governed by the individual yields of discrete operations. It is admitted by several researchers that no other separation method is as powerful and generally applicable as chromatography is [1-6].

Modelling of chromatographic separations is essential for the prediction of the dynamic behavior of the solute in the column against different operating alternatives without experimental effort, as well as scaling up the separation process. Besides, chromatographic separations are complex processes and so that model based

understanding of this kind of separation, largely prevent the inconveniences of experimenting with the real process.

Several chromatographic models have been established and studied according to their level of complexity and accuracy whether it is at the analytical scale or at the preparative/production scale, including; the ideal model (IM), the equilibrium dispersive (ED) model, the transport dispersive (TD) model and the general rate (GR) model [7-13].

IM based on the equilibrium theory of chromatography, assumes that the equilibration of a solute between the mobile and stationary phase is an infinitely rapid process accounting the chromatographic column has an infinite efficiency and any contributions from hydrodynamic effects or mass transfer phenomena are neg-

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lected. As the highest production and recovery rate allowed by the thermodynamics is estimated by this model, IM may be useful only for the analysis of the qualitative behavior of the process and the influence of some of the process parameters on chromatographic separation for ideal conditions despite the fact that the IM model is far away to simulate realistic conditions within the chromatographic column.

In ED model, similar to the TD model instant equilibrium is assumed between the stationary and the mobile phases hence both models ignore the concentration profile development within the particle [14-17]. Additionally, ED and TD modeling approaches do not directly take into effect the mass transfer resistances individually, instead a lumped mass transfer coefficient is used, where pseudo homogeneous concentration within the particle is assumed. When mathematical modeling of chromatographic separation is brought into play neither the ED model nor the TD model is sufficiently accurate, especially for the separations where slow mass transport kinetics exist, because mass transfer resistances as well as the axial dispersion within the column reflect entirely different mass transfer mechanisms. The internal and external mass transfer resistances and axial dispersion do not usually respond in a harmony to the changes in column operation parameters such that hydrodynamic conditions have a significant effect on both the external mass transfer resistance and axial dispersion terms whereas stationary phase internal mass transfer resistance is almost immune to that of the changes of mobile phase interstitial velocity.

GR model is the most sophisticated model among the others since the GR model accounts external [18] and intraparticle mass transfer resistances, as well as axial dispersion in the column individually as a result the effect of development of particle concentration profile on eluent concentration profiles is reflected to this model equation. GR model is brought wider recognition especially for scaling up of a preparative where mass transfer resistances are high, providing a reliable platform to simulate elution bands [19-21] and accounting

all contributions to band broadening: axial dispersion [22], external [23] and internal mass transport resistances directly into model equations. Despite reflecting the most accurate chromatographic simulation profiles [24, 25], numerical solution of GR model requires lengthy computational time due to the necessity in the solution of coupled partial differential equations representing liquid phase side and stationary phase side mass transfer. For this reason in order to simplify numerical solution of the GR model different approaches are investigated by several researchers [26, 21].

Özdural et al. [28] proposed a new algorithm for numerical solution of GR model in frontal chromatography. When the numerical solution of GR model is considered, the advantage of this methodology lays in the fact that it does not require the solution of coupled partial differential equations; instead the stationary phase concentrations were evaluated through unsteady state component mass balance expressions written in discretization schemes. Thus the number of partial differential equations to be solved reduces to one, which saves considerable machine time.

In order to simplify the model equations several researchers employed local equilibrium assumption, where solute average concentration in the particle, is in instant equilibrium with the solute concentration in the bulk eluent,  $c(x,t)$ . Hence all transient resistances are neglected [28, 29]. Furthermore, in local equilibrium approach based studies in order to represent the band broadening effect all the mass transfer resistances are lumped into a single quantity called lumped axial dispersion coefficient. However axial dispersion and mass transfer mechanisms are different phenomenon that cannot be lumped into a single term. Therefore in this study general rate (GR) based model is followed where Fig. 1 represents the true case, and indicates the formation of concentration gradient within the particle as a result of transient resistances. In GR model equilibrium is only attained at the interface between the liquid and solid phases.

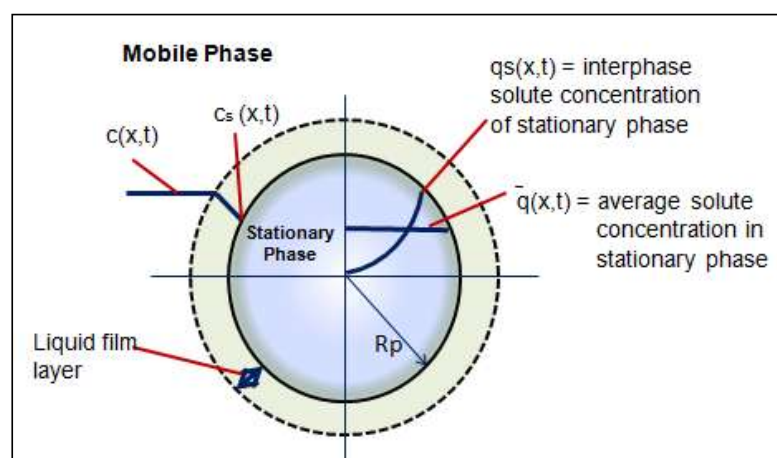


Figure 1. The illustration of the local equilibrium and non-equilibrium adsorption approaches within a spherical particle.

The schematic view of equilibrium conditions for equilibrium [30] and non-equilibrium assumption with regard to liquid and stationary phase concentration profiles is shown in Fig 1. In Fig 1.  $c(x,t)$  and  $c_s(x,t)$  are the bulk liquid concentration and liquid film inner surface concentrations respectively whereas  $q(x,t)$  and  $q_s(x,t)$  are the average and interphase concentrations in stationary phase. All of concentrations whether for liquid phase or stationary phase are the function of axial distance and time.  $R_p$  is the stationary phase radius.

In non-equilibrium modeling also named as general rate model approach, where solid surface concentration,  $q_s(x,t)$  and liquid film inner surface concentration,  $c_s(x,t)$  are in equilibrium, all mass transfer effects including film mass transfer coefficient, solid diffusivity and axial dispersion terms are taken into account individually. Thus the non-equilibrium modeling approach provides a realistic aspect to the dynamic conditions exist in the column.

In the present of general rate model parameters, film mass transfer coefficient and homogeneous solid diffusivity of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes are specified for different particle diameter chelating resin and weak base anion exchange resin. Thus determination of these parameters enable to model the chromatographic enrichment of boron isotopes and allows us to suggest protocols for system operation parameters and/or facilitate scale-up procedures by accounting axial dispersion and all the mass transfer resistances.

## 2. Theoretical and experimental method

### 2.1 Theoretical information

Non-equilibrium conditions exist between the spherical adsorbent particle and the liquid in the perfectly mixed reservoir. The model is based on a dual resistance model combining external mass transfer and intraparticle transport by homogeneous diffusion, and assumes a time dependent parabolic concentration profile within the particle.

The solute mass balance around the reservoir given in Eq. (1).

$$V \frac{dC}{dt} = -m \frac{1}{\rho_p} \frac{d\bar{q}}{dt} \quad (1)$$

where  $C$  is the time dependent bulk liquid concentration ( $\text{mg}/\text{cm}^3$ ),  $m$  is the adsorbent mass within the reservoir (g),  $V$  is the liquid volume in batch adsorbent ( $\text{cm}^3$ ),  $q$  is the time dependent solid average concentration ( $\text{mg}/\text{cm}^3$  solid),  $\rho_p$  is the adsorbent particle density ( $\text{g}/\text{cm}^3$ ) and  $t$  is the time (s). With referring to Fig. 1, the solid uptake rate for spherical adsorbent particles can be expressed as following [29, 31].

$$\frac{d\bar{q}}{dt} = k_f \frac{3}{R_p} (C - C_s) \quad (2)$$

Where  $C_s$  is the time dependent interphase liquid concentration ( $\text{mg}/\text{cm}^3$ ),  $R_p$  is the particle radius (cm) and  $k_f$  is the liquid film mass transfer coefficient (cm/s).

Substitution of Eq. (2) into Eq. (1) gives the following equation [32].

$$V \frac{dC}{dt} = -m \frac{1}{\rho_p} k_f \frac{3}{R_p} (C - C_s) \quad (3)$$

It is generally agreed that, for favorable isotherms, during the early stages of batch uptake from dilute solutions the value of  $C_s$  becomes negligible [26]. Under these conditions integrating Eq. (3) between the limits of  $t = 0, C = C_0; t = t, C = C(t)$  gives:

$$\ln \frac{C}{C_0} = -\frac{m}{\rho_p V} \frac{3}{R_p} k_f t \quad (4)$$

Eq. (4) indicates that  $k_f$  value can easily be determined for short times and low concentration batch experiment uptake data as long as the adsorption isotherm is favorable. For low initial solution concentrations the uptake kinetics is controlled by liquid film resistance at the early stages of adsorption, where all the adsorption sites of the solid that are close to the solid surface are empty. Once the solute molecules pass through the liquid film layer, these solute molecules need not to diffuse further inside the particle instead they are immediately adsorbed near to surface locations. It is obvious that stirred tank adsorption processes do not duplicate the hydrodynamic conditions of a packed bed adsorption column and  $k_f$  values calculated by this technique is limited to stirred batch reactor. However,  $k_f$  value obtained from dilute solution batch adsorption experiments, corresponding to a certain degree of mixing can be used in numerical solution of the uptake equation for batch adsorption in order to find  $D_s$  homogeneous diffusivity,  $D_s$  ( $\text{cm}^2/\text{s}$ ) value. This  $D_s$  value is also valid for a packed-bed adsorption column, since  $D_s$  depends on particle properties rather than the hydrodynamic conditions except concentration.

Once film mass transfer coefficient value is obtained from a low concentration experimental data, then  $D_s$  can be calculated from a high concentration experiment, by keeping all other experimental parameters the same with that of the low concentration run. It is clear that for high concentration experiments the liquid concentration at the interface between liquid and solid,  $C_s^* \approx 0$  assumption is no longer valid. Thus, in order to predict the change of bulk liquid concentration with time, one should incorporate  $C_s(t)$  into the solution of Eq. (3). In this work, the widely used immediate equ-

ilibrium assumption between the solid average concentration and the bulk liquid concentration is ruled out due to the fact that under dynamic conditions this assumption is not valid with realistic mass transfer resistances. However, it is reasonable to assume that immediate equilibrium is attained at the interface since transfer of solute at the interphase to adsorbed state is generally very fast. Eq. (5) gives well known Langmuir adsorption isotherm expression.

$$q_s = \frac{q_m K_L C_s}{1 + K_L C_s} \quad (5)$$

The  $q_m$  (mg/cm<sup>3</sup> solid) and  $K_L$  (cm<sup>3</sup>/mg) terms in Eq. (5) are the Langmuir constants and  $q_s$  is the solid surface concentration in equilibrium with  $C_s$ . As long as Langmuir adsorption isotherm holds, adaptation of methodology to the batch systems shows that interphase liquid concentration,  $C_s$ , can be given by Eq. (6) and Eq.(7) for Langmuir adsorption isotherm [28].

$$C_s = \frac{-M + \sqrt{M^2 + \frac{4}{K_L} \left[ C + \frac{5\bar{q}}{Bi} \right]}}{2} \quad (6)$$

Where Biot number in Eq. (6) is  $Bi = kf R_p / D_s$  and it includes all mass transfer resistances: film mass transfer resistance and homogeneous solid diffusivity.

$$M = \frac{5q_m}{Bi} - \frac{5\bar{q}}{Bi} + \frac{1}{K_L} - C \quad (7)$$

$$V \frac{dC}{dt} = -m \frac{1}{\rho_p} k_f \frac{3}{R_p} \left( C - \frac{-M + \sqrt{M^2 + \frac{4}{K_L} \left[ C + \frac{5\bar{q}}{Bi} \right]}}{2} \right) \quad (8)$$

The non-equilibrium model presented in this study is that it obviates the usually employed solution of coupled ordinary and partial differential equation systems and makes it possible to use the well-known Runge-Kutta algorithms during simulation studies. Eq. (8) can now be solved without assuming  $C_s \approx 0$  since Eq. (6) and (7) gives  $C_s$  value. During the numerical solution procedure, the  $q$  value at  $j$  time panel is evaluated from the  $c$  and  $q$  values at  $(j-1)$  time panel through the mass balance methodology of Özdural et al. [2, 28].

$$\bar{q}_j = \bar{q}_{j-1} + \frac{V\rho_p}{m} (C_j - C_{j-1}) \quad (9)$$

For finding homogeneous diffusivity, model predicted reservoir concentration vs. time data for different  $D_s$  values were numerically generated and compared with the experimentally gathered reservoir concentra-

tion versus time data until the two profiles agree.  $D_s$  value which gives the best fit, was taken as the homogeneous solid diffusion coefficient of the system of interest.

## 2.2 Materials and method

### 2.2.1 Apparatus

Inductively coupled plasma – mass spectrometry (ICP-MS, Perkin Elmer ELAN 9000, U.S.A.) was used for the determination of boron isotopes. Multi-position magnetic stirrer (IKA R010, Germany) was used for reaching the equilibrium between liquid and stationary phase.

### 2.2.2 Materials

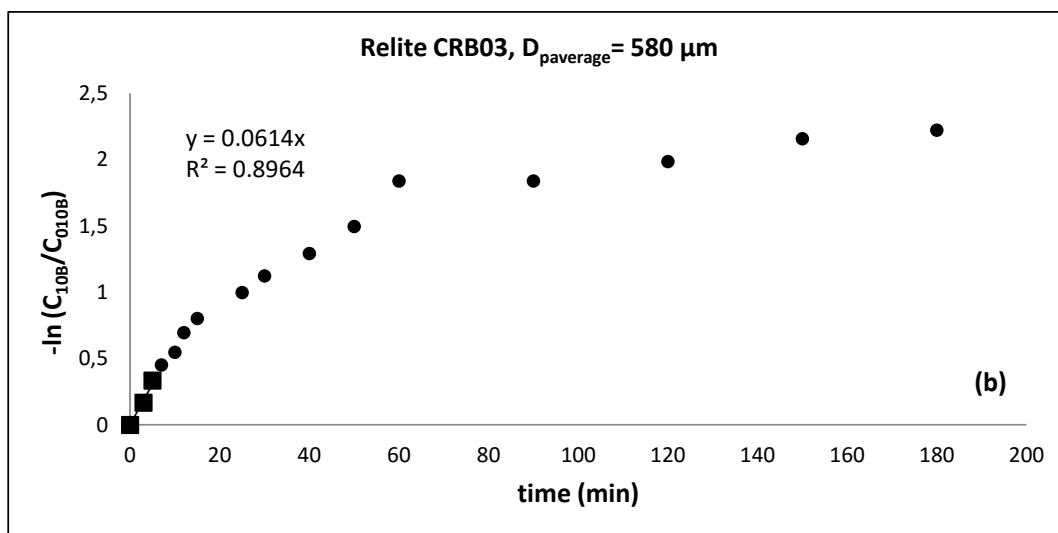
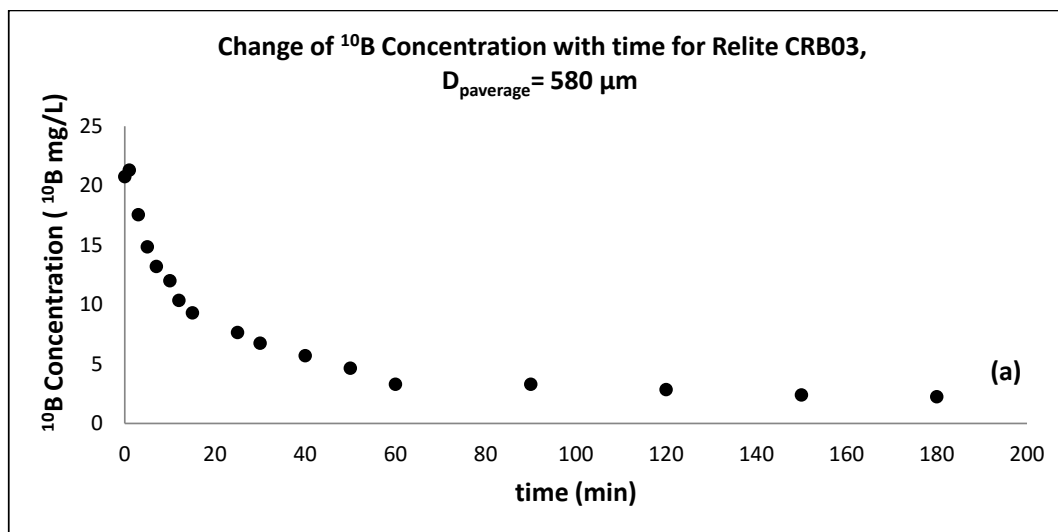
580  $\mu$ m and 270  $\mu$ m particle diameter Relite CRB03 (Mitsubishi Chemical, Japan) chelating resin and 580  $\mu$ m particle diameter Diaion WA21 (Mitsubishi Chemical, Japan) weak base anion exchange resin were used. Boric acid (Eti Mine Works General Directorate) solution is selected as liquid phase medium.

### 2.2.3 Procedure

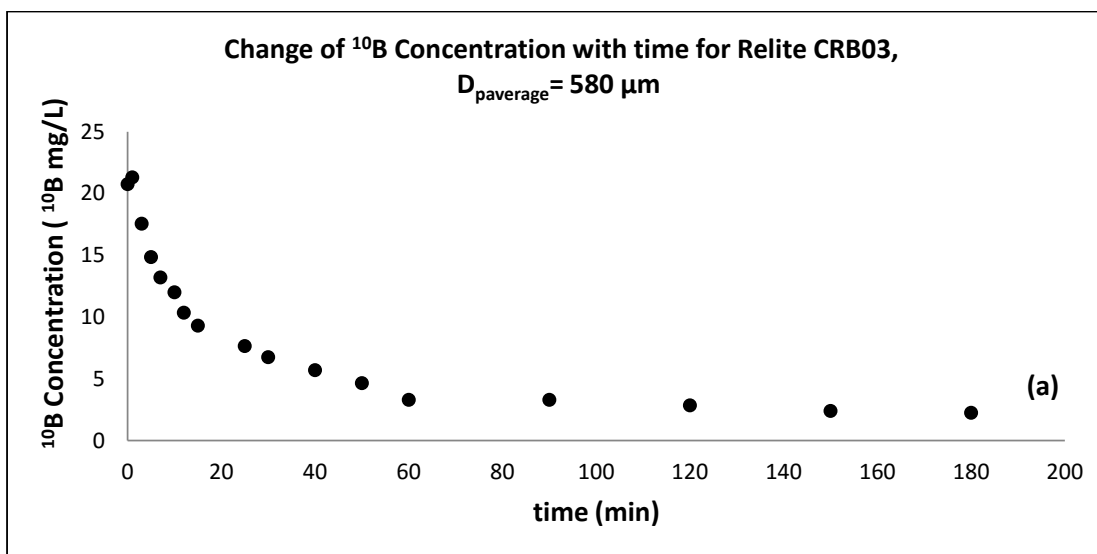
In the experimental part of this study mass transfer resistances of <sup>10</sup>B and <sup>11</sup>B determined separately for 580  $\mu$ m and 270  $\mu$ m particle diameter Relite CRB03 (Mitsubishi Chemical, Japan) chelating resin and 580  $\mu$ m particle diameter Diaion WA21 (Mitsubishi Chemical, Japan) weak base anion exchange resin. Solution volume is 50 mL and rotational speed of batch stirrer is 400 rpm. Experiments are performed in room temperature. The mass of 0.025 M HCl and distillate water regenerated resins are 1 g. The initial concentration of boric acid (Eti Mine Works General Directorate) solution used to determine film mass transfer coefficients,  $k_f$  and homogeneous solid diffusivities,  $D_s$  of boron isotopes is 100 mg/L and 8000 mg/L respectively. Time dependent <sup>10</sup>B and <sup>11</sup>B concentrations are determined with ICP-MS.

## 3. Results and discussions

For the sake of simplicity, change of boron isotopes with time graphs and film mass transfer coefficient calculation graphs are given for only <sup>10</sup>B isotope and for Relite CRB03 ( $D_{paverage} = 580 \mu$ m) and Diaion WA21 ( $D_{paverage} = 580 \mu$ m) resins. From Fig. (2a) and (3a) change of <sup>10</sup>B isotope with time is given for 100 mg/L boric acid initial concentration. As it is given in Eq. 4, in the early steps of adsorption, the slope of time versus  $-\ln(C/C_0)$  graph gives the film mass transfer coefficient,  $k_f$  value of the boron isotopes for the selected resin. Film mass transfer resistance values of <sup>11</sup>B isotope for three different resins are calculated with the same method but not shown this part of the study.



**Figure 2.** (a) Change of <sup>10</sup>B isotope concentration with time for Relite CRB03 (D<sub>paverage</sub> = 580 μm) (b) Linearized film mass transfer calculation curve of <sup>10</sup>B isotope for Relite CRB03 (D<sub>paverage</sub> = 580 μm)



**Figure 3.** (a) Change of <sup>10</sup>B isotope concentration with time for Diaion WA21 (D<sub>paverage</sub> = 580 μm)

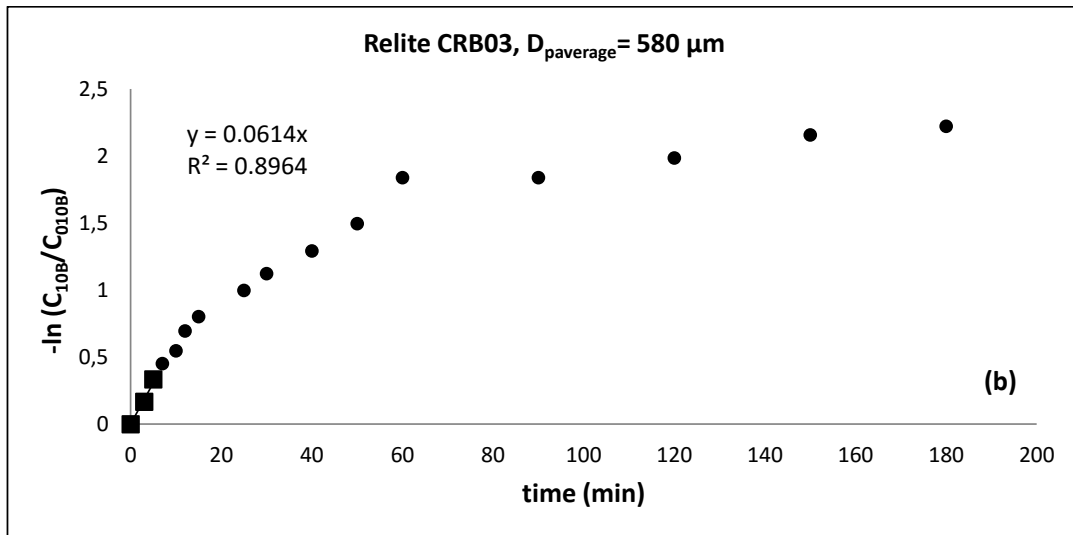


Figure 3. (b) Linearized film mass transfer calculation curve of  $^{10}\text{B}$  isotope for Diaion WA21 ( $D_{\text{paverage}} = 580 \mu\text{m}$ )

The homogeneous solid diffusivity parameter,  $D_s$  is determined from the numerical solution of Eq. (8) and (9) based on the mass balance methodology that is derived by Özdural et al. [28]. Once the model based time versus concentration data adjust with the experimental data the homogeneous solid diffusivity is determined. In Fig 4. the experimental time versus  $^{10}\text{B}$  concentration and numerical solution of the system is given for only  $^{10}\text{B}$  isotopes for the Diaion WA21 weak base anion exchange resin at 8000 mg/L boric acid initial concentration.

In Table 1 and 2 the mass transfer coefficients of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes are given respectively for chelating resin Relite CRB03 with different particle diameters and weak base anion exchange resin, Diaion WA21.

It is seen from the both film mass transfer coefficient and homogeneous solid diffusivity values of  $^{10}\text{B}$  isotope is higher than the that of  $^{11}\text{B}$  isotope. In other words, the mass transfer resistance of resin to  $^{11}\text{B}$  isotope is

high when compared with the mass transfer resistance of resin to  $^{10}\text{B}$  isotope. This situation is logical as the resin phase has higher affinity to  $^{10}\text{B}$  isotope. Also when the particle diameter decreases, the film mass transfer coefficient increases as it is expected whereas the unexpected results for homogeneous solid diffusivity coefficients are obtained. Homogeneous solid diffusivity coefficients must be increased with the decrease of particle diameter as the travelling path of solute molecules within the stationary phase decreases. However in this study the obtained results indicate that the homogeneous solid diffusivity coefficients decreases with the decrease in the stationary phase particle diameter. This can be explained with the change of competitive adsorption mechanism of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes with the particle diameter decrease. It is estimated that the increase of adsorption capacity of resin with the decrease in particle diameter and increase in surface area of resin phase, increase the competitive adsorption of  $^{10}\text{B}$  over  $^{11}\text{B}$  isotopes.

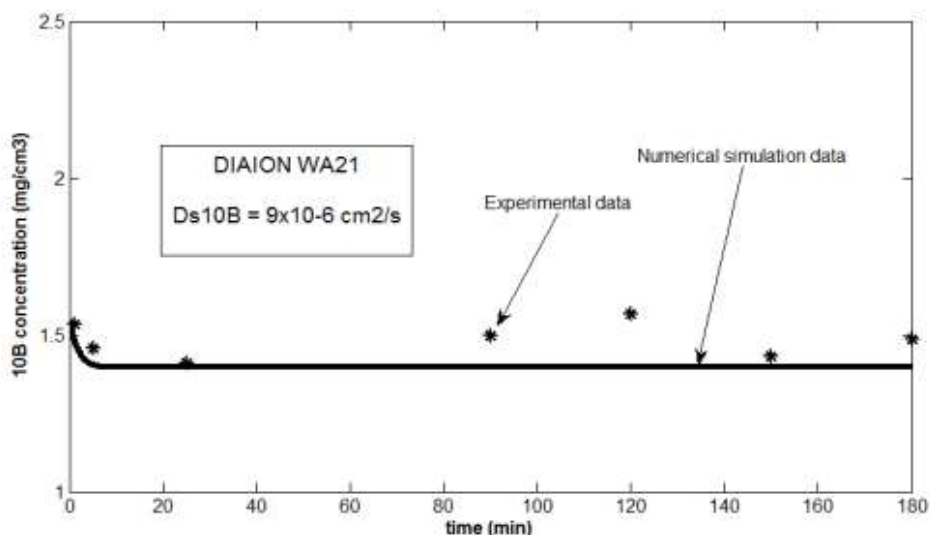


Figure 4. Experimental and numerical simulation data of change of  $^{10}\text{B}$  concentration in liquid phase with time for Diaion WA21 resin.

**Table 1.** Mass Transfer Coefficients of  $^{10}\text{B}$  Isotope

	RELITE CRB03 Resin	RELITE CRB03 Resin	DIAION WA21 Resin
Average Resin Diameter ( $\mu\text{m}$ )	580	270	580
Film Mass Transfer Coefficient, $k_{f10\text{B}}$ (cm/s)	$5.44 \times 10^{-4}$	$3.17 \times 10^{-3}$	$3.31 \times 10^{-4}$
Homogeneous Solid Diffusivity, $D_{s10\text{B}}$ ( $\text{cm}^2/\text{s}$ )	$9.00 \times 10^{-7}$	$9.00 \times 10^{-8}$	$9.00 \times 10^{-6}$

**Table 2.** Mass Transfer Coefficients of  $^{11}\text{B}$  Isotope

	RELITE CRB03 Resin	RELITE CRB03 Resin	DIAION WA21 Resin
Average Resin Diameter ( $\mu\text{m}$ )	580	270	580
Film Mass Transfer Coefficient, $k_{f11\text{B}}$ (cm/s)	$4.93 \times 10^{-4}$	$2.95 \times 10^{-3}$	$2.20 \times 10^{-4}$
Homogeneous Solid Diffusivity, $D_{s11\text{B}}$ ( $\text{cm}^2/\text{s}$ )	$7.00 \times 10^{-7}$	$3.00 \times 10^{-8}$	$5.00 \times 10^{-6}$

In the consequence of literature investigations about this subject, it is concluded that there is no any other study based on the determination of liquid film mass transfer and solid diffusivity coefficients of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes. Thus unfortunately the result which are determined both with experimentally and mathematical model simulation given in this study could not compared with literature.

#### 4. Conclusion

The objective of this study is to apply the methodology that is improved by Özdural et al. [28], for the determination of mass transfer coefficients of  $^{10}\text{B}$  and  $^{11}\text{B}$  isotopes for chelating and weak base anion exchange resins. Once the mass transfer coefficient parameters are determined, the model based simulation of boron isotope enrichment can be solved numerically to optimize the chromatographic system operating parameters whether it is continuous or batch mode.

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