

ANALYSIS OF EQUILIBRIUM DISPERSIVE MODEL OF LIQUID CHROMATOGRAPHY CONSIDERING A QUADRATIC-TYPE ADSORPTION ISOTHERM

by

Jamil UR REHMAN^a, Adeel MUNEER^{b*}, and Shamsul QAMAR^a

^aDepartment of Mathematics, COMSATS University Islamabad, Islamabad, Pakistan

^bChair of Applied Mathematics (Continuous Optimization),
Friedrich-Alexander-Universitat Erlangen-Nurnberg (FAU), Erlangen, Germany

Original scientific paper
<https://doi.org/10.2298/TSCI201229179U>

A single-component equilibrium dispersive model of liquid chromatography is solved analytically for a quadratic-type adsorption isotherm. The consideration of quadratic isotherm leads to a non-linear advection-diffusion PDE that hinders the derivation of analytical solution. To overcome this difficulty, the Hopf-Cole and exponential transformation techniques are applied one after another to convert the given advection-diffusion PDE to a second order linear diffusion equation. These transformations are applied under the assumption of small non-linearity, or small volumes of injected concentrations, or both. Afterwards, the Fourier transform technique is applied to obtain the analytical solution of the resulting linear diffusion equation. For detailed analysis of the process, numerical temporal moments are obtained from the actual time domain solution. These moments are useful to observe the effects of transport parameters on the shape, height and spreading of the elution peak. A second-order accurate, high resolution semi-discrete finite volume scheme is also utilized to approximate the same model for non-linear Langmuir isotherms. Analytical and numerical results are compared for different case studies to gain knowledge about the ranges of kinetic parameters for which our analytical results are applicable. The effects of various parameters on the mechanism are analyzed under typical operating conditions available in the liquid chromatography literature.

Key words: *single-solute elution, quadratic isotherm, Hopf-Cole transformation, analytical solutions, moment analysis, numerical solutions*

Introduction

Liquid chromatography is a technique of separating mixture components that is based on different adsorptivities of the components to a specific adsorbent which is fixed inside a chromatographic column. The simplest process is the column liquid chromatography which involves a single column charged with pulses of feeded sample (mixture). These injected sample is carried through the column by some liquid desorbent. While traveling through the column, the more adsorptive component of the sample is retained longer by the adsorbent and, thus, leaves the column after the less adsorptive components. This technique is widely used by various researchers in the fields of biology, chemistry, biochemistry, as well as in environmental and clinical sciences. Such a popularity is due to its exceptional success in solving one of the most important problem of the experimental chemist, the physical separation of mixtures

* Corresponding author, e-mail: adeel.muneer@fau.de

components rapidly, completely, and rather inexpensively, even when complex compounds are involved at either laboratory or at large-scales.

Models based on advection-diffusion equations are widely used with tremendous success for describing such separation processes [1, 2]. Various chromatographic models have been developed in the literature to simulate chromatographic processes. The most famous of them are the general rate model, various kinetic models, and the equilibrium dispersive model (EDM) [3-5]. For linear adsorption isotherm, the analytical solutions of models are widely available in [5-10].

There is close correlation between the equilibrium isotherm of a solute in a chromatographic system and the elution profile of its high concentration bands [5, 11-14]. Various systematic investigations have proved good agreement between the experimental band profiles and the profiles calculated from the equilibrium isotherms [13, 15, 16]. In all studied cases, the isotherms were convex upward. The Langmuir isotherm is also convex upward and has no inflexion point. Simple statistical thermodynamics describes that the general form of an isotherm equation should be the ratio of two polynomials of the same exponent [13, 14, 17].

The analytical solutions for fast equilibrium with axial dispersion and non-linear isotherm have been attempted in [18]. The authors have derived approximate results with single boundary, no solution being obtained for diffuse rear boundary. Band shapes in non-linear chromatography with axial dispersion are also investigated in [19]. Furthermore, to answer the question about the peak shape and retention equilibrium, the statistical moments are very useful. In the literature, moment analysis approach is widely analyzed by a number of researchers [5, 7, 20-30].

The goal of this paper is to analytically solve the single-component EDM utilizing a polynomial-type quadratic adsorption isotherm. The inclusion of this quadratic-type isotherm in the mass balance equation leads to a non-linear advection-diffusion PDE like a viscous Burger equation. It is known that analytical solution of Burger's equation can be derived by applying a method discovered independently by Eberhard Hopf (1950) and Julian Cole (1951). As our EDM equation has resemblance to Burger's equation, both Hopf-Cole and exponential transformations are applied one after another to convert the given advection-diffusion EDM to a second order linear diffusion equation. These transformations are applied under the assumption of small non-linearity, or small volumes of injected concentrations, or both. Afterwards, the Fourier transform technique is applied to obtain the analytical solution of the resulting linear diffusion equation. Due to the importance of moment analysis, numerical moments are also derived in this work because of the non-possibility of analytical moments. Lastly, the HR-FVS is extended to solve the non-linear isothermal model of liquid chromatography for comparison and validation of our assumptions [7, 31]. Several test problems of practical interest are conducted.

The non-linear equilibrium dispersive model

Consider the combined transport mechanisms of advection and diffusion for a single-component solute along with the following basic assumptions:

- The chromatographic process is isothermal and the mobile phase is incompressible, which holds for the liquid chromatography.
- The concentration gradients along the radial axis are neglected and band broadening is due to axial dispersion only.
- The packing material of stationary phase are porous spherical particles of same size and the bed is isotropic and homogeneous.
- There is no interaction between the solid (stationary) phase and solvent (mobile) phase.
- The flow rate is assumed to be independent of axial dispersion coefficient.

In the case of single-solute EDM, the equation of mass balance for the transport of solute in the bulk of fluid is given:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} = D_z \frac{\partial^2 c}{\partial z^2} - F \frac{\partial q}{\partial t} \quad (1)$$

where c and q are the concentration of the mobile and adsorbed phases, respectively. Further, $F = (1 - \epsilon)/\epsilon$ is the phase ratio in terms of the total porosity ϵ , u – the interstitial velocity, D_z – the axial dispersion coefficient, while t and z are the time and axial co-ordinates.

Moreover, the following dimensionless quantities are introduced to reduce the number of variables:

$$x = \frac{z}{L}, \quad \tau = \frac{ut}{L}, \quad \text{Pe} = \frac{Lu}{D_z} \quad (2)$$

where L is the length of the column, Pe – the Peclet number for the concentration, and τ – the mean retention time of non-retained component. On using eq. (2) in eq. (1), we get:

$$\frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial x} = \frac{1}{\text{Pe}} \frac{\partial^2 c}{\partial x^2} - F \frac{\partial q}{\partial \tau} \quad (3)$$

The simplest isotherm model used in adsorption studies is the first order Langmuir isotherm [5, 13, 14, 17]:

$$q(c) = \frac{ac}{1+bc} \quad (4)$$

Assuming a fast injection of the sample as a rectangular profile of height c_{inj} and width τ_{inj} such that the product $c_{\text{inj}}\tau_{\text{inj}}$ expresses the sample size. Thus, we have to set the initial condition:

$$c(x, 0) = \begin{cases} c_{\text{inj}}, & 0 < x \leq \tau_{\text{inj}} \\ 0, & \text{otherwise} \end{cases} \quad (5)$$

where the symbols $\tau_{\text{inj}} = ut_{\text{inj}}/L$ stands for the dimensionless time of injections. The boundary conditions for a hypothetically infinite length column are expressed:

$$c(0, t) = 0, \quad c(\infty, t) = 0 \quad (6)$$

Quadratic isotherm and Hopf-Cole transformation

Assuming small changes in the concentration, we can expand the non-linear Langmuir adsorption isotherm around a reference value c_0 by applying Taylor expansion up to second order:

$$q(c) = q(c_0) + \left. \frac{\partial q}{\partial c} \right|_{(c=c_0)} (c - c_0) + \left. \frac{\partial^2 q}{\partial c^2} \right|_{(c=c_0)} \frac{(c - c_0)^2}{2!} \quad (7)$$

After some manipulations and simplifications, the previous equation simplifies to:

$$q(c) = \gamma_1 + \gamma_2 c + \gamma_3 c^2 \quad (8)$$

where

$$\gamma_1 = \frac{ab^2 c_0^3}{(1+bc_0)^3}, \quad \gamma_2 = \frac{a+3abc_0}{(1+bc_0)^3}, \quad \gamma_3 = \frac{-ab}{(1+bc_0)^3} \quad (9)$$

The assumed quadratic isotherm has an edge that it is concave to the adsorbed solute for positive γ_3 , while concave to the concentration axis for negative γ_3 , and becomes linear for

$\gamma_3 = 0$. In order to approximate the highly curved isotherm without the use of higher order polynomial isotherms, the constant γ_1 , has been used. Using eq. (8) in eq. (3), we get:

$$R \frac{\partial c}{\partial \tau} - \frac{1}{(1 + \lambda c)} \frac{\partial c}{\partial x} = \frac{1}{(1 + \lambda c) \text{Pe}} \frac{\partial^2 c}{\partial x^2} \quad (10)$$

where $R = 1 + \gamma_2 F$ and $\lambda = (2F\gamma_3)/R$. Here, λ is a leaning parameter. Assuming $|\lambda c| \ll 1$, and also the quadratic and high order powers of λc can be neglected, thus, we get:

$$(1 + \lambda c)^{-1} \approx 1 - \lambda c \quad (11)$$

Moreover, for larger Peclet number (*e.g.* $\text{Pe} \geq 500$), we can assume that $\lambda c/\text{Pe} \approx 0$. After simplification, eq. (10) becomes:

$$R \frac{\partial c}{\partial \tau} + (1 - \lambda c) \frac{\partial c}{\partial x} = \frac{1}{\text{Pe}} \frac{\partial^2 c}{\partial x^2} \quad (12)$$

As a next step, we introduce a well known Hopf-Cole transformation eliminate the non-linear advection term from eq. (12). Let us define:

$$c(x, \tau) = \frac{2}{\lambda \text{Pe}} \frac{\omega_x(x, \tau)}{\omega(x, \tau)} \quad (13)$$

After some simplifications, the new dependent variable ω can be expressed:

$$\omega(x, \tau) = \exp \left(\frac{\lambda \text{Pe}}{2} \int_{-\infty}^x c(y, \tau) dy \right) \quad (14)$$

where y is an auxiliary integration variable and $c(y, \tau)$ represent axial distribution of solute at τ .

According to eq. (5), we have to set $c(y, 0) = c_{\text{inj}} \tau_{\text{inj}} \delta(y)$ with $\delta(y)$ being a Dirac pulse function. It is defined:

$$\delta(y) = \begin{cases} 0, & y < 0 \\ 1, & y > 0 \end{cases} \quad (15)$$

Thus, eq. (14) for $\tau = 0$ becomes:

$$\omega(x, 0) = \exp \left(\frac{\lambda \text{Pe}}{2} \int_{-\infty}^x c_{\text{inj}} \tau_{\text{inj}} \delta(y) dy \right) \quad (16)$$

By incorporating eq. (13) in eq. (12), the non-linear advection-diffusion PDE in eq. (12) reduces to the following linear advection-diffusion PDE:

$$R \frac{\partial \omega}{\partial \tau} + \frac{\partial \omega}{\partial x} = \frac{1}{\text{Pe}} \frac{\partial^2 \omega}{\partial x^2} \quad (17)$$

Now, we can simplify the aforementioned advection-diffusion equation by introducing another transformation containing a new dependent variable $\phi(x, \tau)$, that is:

$$\omega(x, \tau) = \phi(x, \tau) \exp \left(\frac{\text{Pe} x}{2} - \frac{\text{Pe} \tau}{4R} \right) \quad (18)$$

The previous transformation converts the linear advection-diffusion in eq. (17) to a linear diffusion equation of the form:

$$\frac{\partial \phi}{\partial \tau} = \frac{1}{\widetilde{\text{Pe}}} \frac{\partial^2 \phi}{\partial x^2} \quad (19)$$

where $\widetilde{\text{Pe}} = R\text{Pe}$.

Analytical solution by Fourier transformation

The Fourier transformation is applied as a primary tool to derive analytical solutions of eq. (19). It is defined:

$$\mathcal{F}[\phi(x, \tau)] = \bar{\phi}(k, \tau) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(ikx)\phi(x, \tau)dx \tag{20}$$

where $\bar{\phi}$ and ϕ shows the solution profiles in Fourier-transformed and actual-space domains, respectively. After applying Fourier transformation on eq. (19) we get:

$$\bar{\phi}(k, \tau) = \bar{\phi}(k, 0) \exp(-\tau \widetilde{Pe} k^2) \tag{21}$$

here, $\bar{\phi}(k, 0)$ is constant of integration at $\tau = 0$. By taking Fourier inverse of eq. (21) and using initial conditions (IC) of eq. (16) we reached:

$$\phi(x, \tau) = \int_{-\infty}^{\infty} \phi(x', 0) \sqrt{\frac{\widetilde{Pe}}{4\pi\tau}} \exp\left(\frac{-(x-x')^2}{\frac{4\tau}{\widetilde{Pe}}}\right) dx' \tag{22}$$

where x' is the auxiliary variable. By using eq. (22) in eq. (18), we get:

$$\omega(x, \tau) = \int_{-\infty}^{\infty} \sqrt{\frac{\widetilde{Pe}}{4\pi\tau}} \exp\left[\left(\frac{-(x-x')^2}{\frac{4\tau}{\widetilde{Pe}}}\right) + \left(\frac{Pe x}{2} - \frac{Pe x'}{2} - \frac{Pe \tau}{4R}\right) + \left(\frac{\lambda Pe}{2} \int_{-\infty}^{x'} c_{inj} \tau_{inj} \delta(y) dy\right)\right] dx' \tag{23}$$

After some algebraic manipulations, we get the following simplified form of aforementioned equation:

$$\omega(\xi, \tau) = \int_{-\infty}^{\infty} \sqrt{\frac{\widetilde{Pe}}{4\pi\tau}} \exp\left[\left(\frac{-(\xi-x')^2}{\frac{4\tau}{\widetilde{Pe}}}\right) + \left(\frac{\lambda Pe}{2} \int_{-\infty}^{x'} c_{inj} \tau_{inj} \delta(y) dy\right)\right] dx' \tag{24}$$

where $\xi = x - \tau/R$. After inserting the previous equation in eq. (13) and performing some algebraic manipulations, we get the following simplified solution in term of the actual concentration $c(x, \tau)$:

$$c(\xi, \tau) = \frac{\int_{-\infty}^{\infty} \frac{(\xi-x')}{\frac{\lambda\tau}{R}} \exp\left\{-\left[\frac{(\xi-x')}{2\sqrt{\frac{\tau}{\widetilde{Pe}}}}\right]^2 + \frac{\lambda Pe}{2} \int_{-\infty}^{x'} c_{inj} \tau_{inj} \delta(y) dy\right\} dx'}{\int_{-\infty}^{\infty} \exp\left\{-\left[\frac{(\xi-x')}{2\sqrt{\frac{\tau}{\widetilde{Pe}}}}\right]^2 + \frac{\lambda Pe}{2} \int_{-\infty}^{x'} c_{inj} \tau_{inj} \delta(y) dy\right\} dx'} \tag{25}$$

The integral terms in the aforementioned equation can be simplified by utilizing the definition of Dirac step function given in eq. (15) and by introducing a new parameter

$\beta = (\lambda Pe/2)c_{inj}\tau_{inj}$ [32]. After calculating the aforementioned four integrals, we finally obtain the analytical solution of the form:

$$c(\xi, \tau) = \frac{\frac{-2}{\lambda Pe} \exp\left(-\frac{\xi^2}{4\tau}\right) + \frac{2}{\lambda Pe} \exp\left(\beta - \frac{\xi^2}{4\tau}\right)}{\sqrt{\frac{\pi\tau}{Pe}} \operatorname{erfc}\left(\frac{-\xi}{2\sqrt{\frac{\tau}{Pe}}}\right) + \sqrt{\frac{\pi\tau}{Pe}} \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\frac{\tau}{Pe}}}\right)} \quad (26)$$

where erf is the error function and erfc is the complementary error function, *i.e.* $\operatorname{erfc}(\zeta) = 1 - \operatorname{erf}(\zeta)$.

Moment analysis

In this section, temporal moments are discussed which are useful for analyzing and estimating the behavior of band profiles. Such moments provide overall information about the adsorption equilibrium and kinetic data. In the case of quadratic and non-linear isotherms, analytical expressions of temporal moments are not obtainable. Therefore, numerical moments are calculated by numerically integrating their concentration profiles.

Numerous groups have worked on higher moments of chromatographic peaks in the mid nineties. Kubin [20] and Kučera [21] calculated the moment equations independently. Furthermore, Grushka *et al.* [33, 34], and Boniface and Ruthven [35] have worked on temporal moments.

In this study, the first four temporal moments are considered. The zeroth moment gives information about peak areas and total mass and the first moment μ'_1 corresponds to retention time. The second μ'_2 , third μ'_3 , and fourth μ'_4 central moments give the information about variance (spreading), skewness, and kurtosis of the profiles, respectively.

The formulas for the numerical temporal moments at the column outlet are given:

$$\mu_0 = \frac{L}{u} \int_0^\infty c(x=1, \tau) \tau d\tau \quad (27)$$

$$\mu_n = \left(\frac{L}{u}\right)^n \int_0^\infty c(x=1, \tau) \tau^n d\tau, \quad n = 1, 2, 3, \dots \quad (28)$$

The normalized n^{th} temporal moments are expressed:

$$\mu_n = \left(\frac{L}{u}\right)^n \frac{\int_0^\infty c(x=1, \tau) \tau^n d\tau}{\int_0^\infty c(x=1, \tau) d\tau}, \quad n = 1, 2, 3, \dots \quad (29)$$

The n^{th} central moment are obtained:

$$\mu'_n = \left(\frac{L}{u}\right)^n \frac{\int_0^\infty c(x=1, \tau) (\tau - \mu_1)^n d\tau}{\int_0^\infty c(x=1, \tau) d\tau}, \quad n = 2, 3, \dots \quad (30)$$

The aforementioned formula will be used to calculate numerical moments for the concentration profiles generated by analytical and FVS solutions.

Discussion on numerical test problems

This section presents a few case studies to analyze the applicability range of our derived analytical results. In the test problems, regenerated systems, *i.e.* $c_{init} = 0$ mol/l, and pulse injections of concentration $c_{inj} = 1$ mol/l and duration $t_{r,minj} = 2$ minutes are considered. The analytical solutions are compared with the numerical solutions which are obtained through high resolution finite volume scheme of Koren considering either fully non-linear isotherm, *c.f.* eq. (4), or quadratic isotherm, *c.f.* eqs. (6) and (10), [36].

The numerical moments are obtained from the proposed finite volume scheme using the moments formulas mentioned previously. The trapezoidal rule is applied to numerically approximate the integral terms of these equations. A comparison of linear and quadratic numerical moments for different values of non-linearity coefficients and flow rates are given. The parameters used for comparison are listed in tab. 1.

Table 1. Used parameters in the considered test problems

Lightgray parameters	L	a	b	u	ϵ	D_z	c_{init}	c_{inj}	c_0	t_{inj}
Lightgray	[cm]	[-]	[l/mol ⁻¹]	[cmmin ⁻¹]	[-]	[cm ² min ⁻¹]	[molL ⁻¹]	[molL ⁻¹]	[molL ⁻¹]	[min]
Values	10	1.5	0.5	1.2	0.4	0.02	0	1	0.0001	2.0

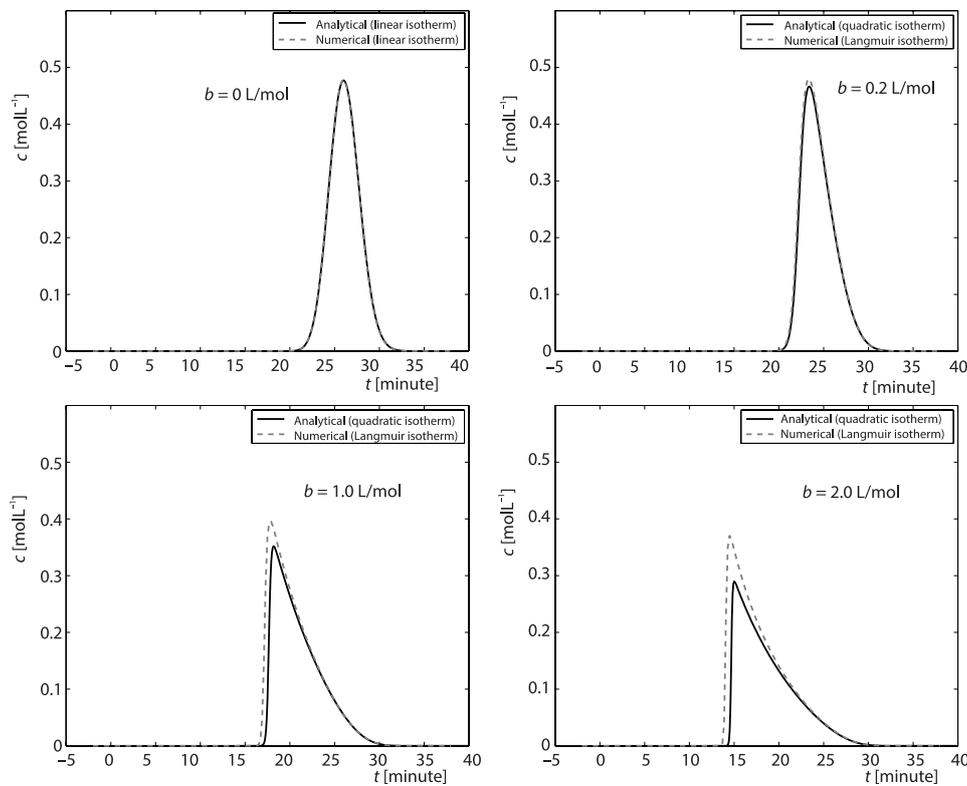


Figure 1. Effects of non-linearity coefficient on concentration profile, where $Pe = 600$; other parameters are given in tab. 1

Effect of the non-linearity coefficient b : Figure 1 shows the results for different values of non-linearity coefficient, *i.e.* for $b = 0, 0.2, 1, 2$. For $b = 0$ both quadratic and Langmuir isotherms become linear, *c.f.* eqs. (4) and (6), and hence, a good agreement can be seen between the analytical and numerical results. While, plots for other values of b show that the results for quadratic isotherm start deviating from the results for Langmuir isotherm with the increase in the value of non-linearity coefficient b . As the non-linearity coefficient increases, the adsorption front of the profile becomes sharper and the desorption fronts becomes tailed. The results obtained endorse the use of quadratic isotherm for moderate values of the non-linearity coefficient.

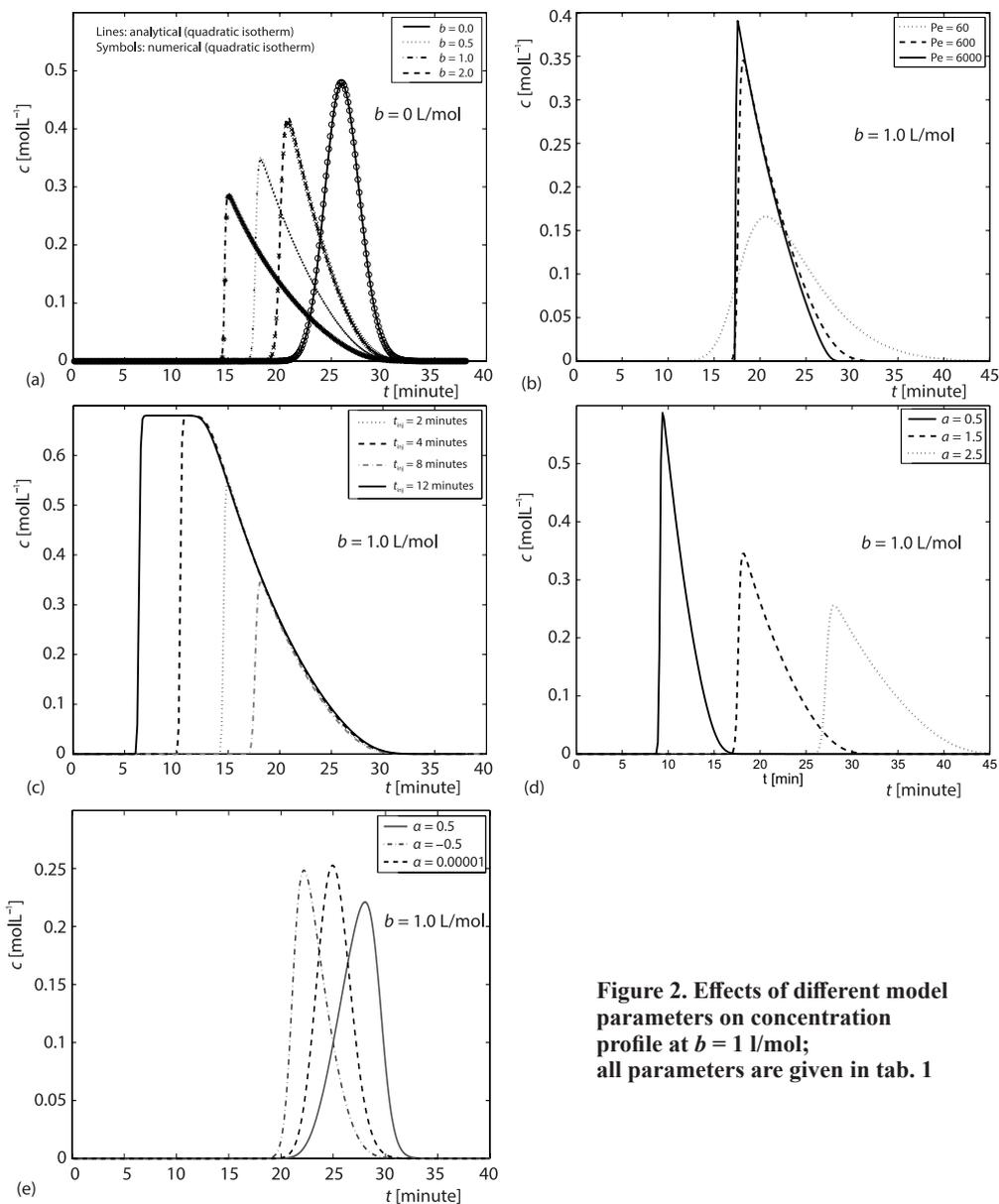


Figure 2. Effects of different model parameters on concentration profile at $b = 1$ l/mol; all parameters are given in tab. 1

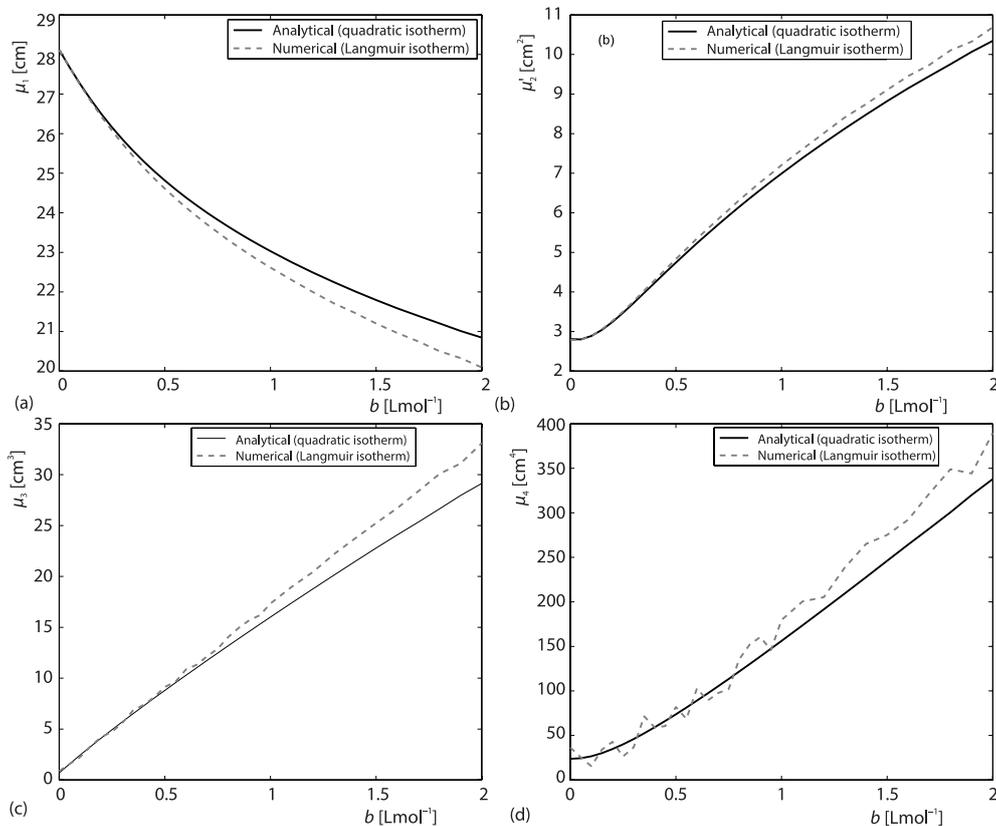


Figure 3. Temporal moments as functions of non-linearity coefficient b ; other parameters are given in tab. 1

Effects of different model parameters: In fig. 2 the effects of different model parameters are shown. Figure 2(a) displays the effect of non-linearity coefficient on the solution profiles, and also the analytical and numerical results for quadratic isotherm are compared with each other. A good agreement in the results verify the correctness of our analytical solution and accuracy of the proposed numerical algorithm. Figure 2(b) demonstrates the effect of Peclet number (or axial dispersion coefficient) on the solution profiles. It can be seen that solutions are diffusive for small value of the Peclet number (or larger axial dispersion coefficient), while profiles are narrower and sharper for large value of the Peclet number (or smaller axial dispersion coefficient). Figure 2(c) shows the influence of injection time on the profiles. It can be seen that profiles become wider on increasing the injection time or injection volume. In fig. 2(d), the plot of concentration profiles for different values of Henry's constant are displayed. It can be seen that for larger value of a , the retention time and spreading of concentration profile increases. In fig. 2(e) the various effects of leaning parameter λ are shown. It can be observed that when value of λ approaches to zero the shape of peak gets very close to Gaussian distribution and for the positive value of λ *i.e.* 0.5 peak of the profile is left tailed, where as it is right tailed for -0.5 .

Effect of the non-linearity coefficient on first four moments: Figure 3 shows the first four numerical moments obtained for different values of the non-linearity coefficient b . It can be seen that moments for quadratic and Langmuir isotherms deviate from each other for larger

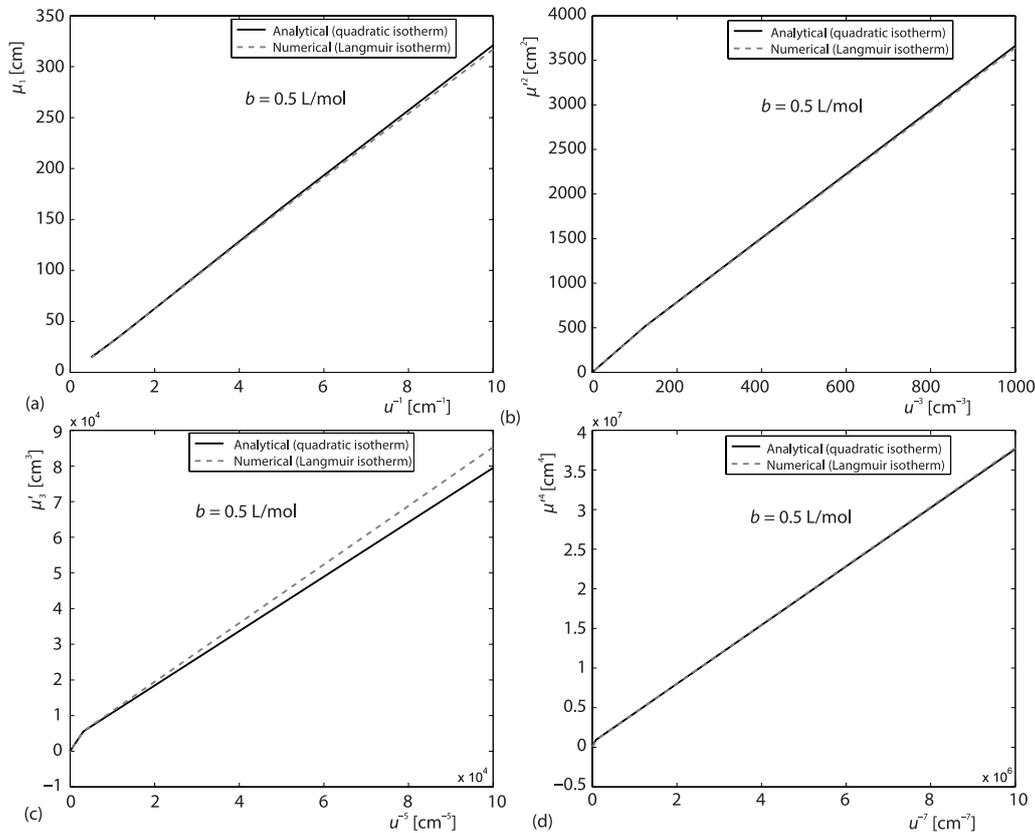


Figure 4. Temporal moments as functions of interstitial velocity at fixed $b = 0.5$ l/mol; other parameters are given in tab. 1

values of the non-linearity coefficient. Thus, it is once again verified that our analytical results for quadratic isotherm are useful for moderate values of the non-linearity coefficient:

Effects of interstitial velocity on first four moments: Figure 4 gives a comparison of first four moments obtained by using quadratic and Langmuir isotherms at different values of flow rates u , while keeping the non-linearity coefficient fixed as $b = 0.5$ l/mol. It can be seen that only third moments, representing asymmetry of the profiles, are deviating from each other:

Conclusion

A single-component liquid chromatography model, based on quadratic isotherm, was solved analytically by using Hopf-Cole, exponential, and Fourier transformation techniques. To gain confidence on the generated profiles of concentration, the model equations were also solved numerically by applying a high resolution finite volume scheme. It was found that a better agreement between analytical and numerical solutions occurs up to a sufficiently large value of the non-linearity coefficient. Furthermore, to investigate about the effects of transport parameters on the elution profiles, numerical temporal moments were obtained. Such moments are useful to interpret and understand the behavior of profiles inside the fixed-bed column. This study provides a feasible procedure of analyzing the column overloading and to determine the

experimental operating conditions which will provide the optimum production rate in preparative liquid chromatography considering moderate changes in the concentrations. The results obtained are very helpful for better understanding of the physicochemical processes involved in liquid chromatography.

Acknowledgment

Adeel Muneer was partially funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project (ID) 416229255 – SFB 1411.

Nomenclature

a	– Henry's constant, [–]	L	– column length, [cm]
c_0	– reference concentration, [mol ⁻¹]	Pe	– Peclet number, [–]
c_{init}	– initial concentrations [mol ⁻¹]	t	– time co-ordinate, [min],
c_{inj}	– inlet concentrations, [mol ⁻¹]	u	– interstitial phase velocity, [cmmin ⁻¹]
$D_{z,j}$	– axial Dispersion coefficient, [cm ² min ⁻¹]	z	– axial co-ordinate, [–]
F	– phase ratio, [–]	ϵ	– external porosity, [–]

References

- [1] Van Genuchten, M. T., Analytical Solutions for Chemical Transport with Simultaneous Adsorption, Zeroth-Order Production and First Order Decay, *Journal Hydrology*, 49 (1981), 3-4, pp. 213-233
- [2] Van Genuchten, M. T., Alves W. J., Analytical Solutions of the 1-D Convective-Dispersive Solute Transport Equation, Technical Bulletin No. 1661, US Department of Agriculture, 1982
- [3] Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, John Wiley and Sons, Wiley-Interscience, New York, USA, 1984
- [4] Guiochon, G., Lin, B., *Modelling for Preparative Chromatography*, Academic Press, New York, USA, 2003
- [5] Guiochon, G., et al., *Fundamentals of Preparative and Non-Linear Chromatography*, 2nd ed., Elsevier Academic press, New York, USA, 2006
- [6] Carta, G., Exact Analytic Solution of a Mathematical Model for Chromatographic Operations, *Chem. Eng. Sci.*, 43 (1988), 10, pp. 2877-2883
- [7] Javeed, S., et al., Analytical and Numerical Investigation of Two Dynamic Models for Liquid Chromatography, *Chem. Eng. Sci.*, 90 (2013), Mar., pp. 17-31
- [8] Qamar, S., et al., Analytical Solutions and Moment Analysis of Chromatographic Models for Rectangular Pulse Injections, *Journal Chromatogr. A*, 1315 (2013), Nov., pp. 92-106
- [9] Qamar, S., et al., Theoretical Investigation of Thermal Effects in an Adiabatic Chromatographic Column Using a Lumped Kinetic Model Incorporating Heat Transfer Resistances, *Ind. Eng. Chem. Res.*, 57 (2018), 6, pp. 2287-2297
- [10] Qamar, S., et al., Analytical Solutions and Moment Analysis of General Rate Model for Linear Liquid Chromatography, *Chem. Eng. Sci.*, 107 (2014), Apr., pp. 192-205
- [11] Rhee, H. K., et al., *First-Order Partial Differential Equations*, Courier Corporation, North Chelmsford, Mass., USA, 2014, Vol. 1
- [12] Golshan-Shirazi, S., et al., Comparison between Experimental and Theoretical Band Profiles in Non-Linear Liquid Chromatography with a Pure Mobile Phase, *Anal. Chem.*, 60 (1988), 23, pp. 2630-2634
- [13] Katti, A. M., et al., Prediction of Binary, Overloaded Elution Profiles Using the Simple Wave Effect, *AIChE J.*, 36 (1990), 11, pp. 1722-1730
- [14] Guiochon, G., et al., Non-Linear Chromatography Recent Theoretical and Experimental Results, *Talanta*, 36 (1989), 1-2, pp. 19-33
- [15] Golshan-Shirazi, S., Guiochon, G., Solutions of the Equilibrium and Semi-Equilibrium Models of Chromatography, *Journal Chromatogr. A*, 506 (1989), 51, pp. 495-545
- [16] Jacobson, S., et al., Chromatographic Band Profiles and Band Separation of Enantiomers at High Concentration, *Journal Am. Chem. Soc.*, 112 (1989), 18, pp. 6492-6498
- [17] Ruthven, D. M., Goddard, M., Sorption and Diffusion of C₈ Aromatic Hydrocarbons in Faujasite Type Zeolites I, Equilibrium Isotherms and Separation Factors, *Zeolites*, 6 (1989), 4, pp. 275-282
- [18] Lightfoot, E. N., Equilibrium Operation of Chromatographic Columns with Longitudinal Diffusion: *Final form Fronts*, *Journal Phys. Chem.*, 61 (1957), 12, pp. 1686-1686

- [19] Houghton, G., Band Shapes in Non-Linear Chromatography with Axial Dispersion, *Journal Phys. Chem.*, 67 (1963), 1, pp. 84-88
- [20] Kubin, M., Beitrag zur Theorie der Chromatographie II, Einfluss der Diffusion Ausserhalb und der Adsorption Innerhalb des Sorbens-Korns (in German), *Collect. Czech. Chem. Commun.*, 30 (1965), pp. 2900-2907
- [21] Kučera, E., Contribution the Theory of Chromatography: Linear Non-Equilibrium Elution Chromatography, *Journal Chromatogr. A*, 19 (1965), pp. 237-248
- [22] Kubin, M., Beitrag zur Theorie der Chromatographie (in German), *Collect. Czech. Chem. Commun.*, 30 (1965), pp. 1104-1118
- [23] Lenhoff, A. M., Significance and Estimation of Chromatographic Parameters, *Journal Chromatogr. A*, 384 (1987), Jan., pp. 285-299
- [24] Miyabe, K., Guiochon, G., Influence of the Modification Conditions of Alkyl Bonded Ligands on the Characteristics of Reversed-Phase Liquid Chromatography, *Journal Chromatogr. A*, 903 (2000), 1-2, pp. 1-12
- [25] Miyabe, K., Guiochon, G., Measurement of the Parameters of the Mass Transfer Kinetics in High Performance Liquid Chromatography, *Journal Sep. Sci.*, 26 (2003), 3-4, pp. 155-173
- [26] Miyabe, K., Moment Analysis of Chromatographic Behavior in Reversed-Phase Liquid Chromatography, *Journal Sep. Sci.*, 32 (2009), 5-6, pp. 757-770
- [27] Qamar, S., Seidel-Morgenstern, A., Extending the Potential of Moment Analysis in Chromatography, *Trends Analyt. Chem.*, 81 (2016), July-Aug., pp. 87-101
- [28] Schneider, P., Smith, J. M., Adsorption Rate Constants from Chromatography, *AIChE J.*, 14 (1968), pp. 762-771
- [29] Suzuki, M., Notes on Determining the Moments of the Impulse Response of the Basic Transformed Equations, *Journal Chem. Eng. Japan*, 6 (1973), 6, pp. 540-543
- [30] Wolff, H.-J., *et al.*, Weighted Moments and the Pore-Diffusion Model, *Chem. Eng. Sci.*, 35 (1980), 6, pp. 1481-1485
- [31] Javeed, S., *et al.*, Parametric Study of Thermal Effects in Reactive Liquid Chromatography, *Chem. Eng. J.*, 191 (2012), May, pp. 426-440
- [32] Jaulmes, A., *et al.*, Study of Peak Profiles in Non-Linear Gas Chromatography, Derivation of a Theoretical Model, *Journal Phys. Chem.*, 88 (1984), 22, pp. 5379-5385
- [33] Grushka, E., *et al.*, Moments Analysis for the Discernment of Overlapping Chromatographic Peaks, *Anal. Chem.*, 42 (1970), 1, pp. 21-26
- [34] Grushka, E., *et al.*, Computer Characterization of Chromatographic Peaks by Plate Height and Higher Central Moments, *Anal. Chem.*, 41 (1969), 7, pp. 889-892
- [35] Boniface, H. A., Ruthven, D. M., The use of Higher Moments to Extract Transport Data from Chromatographic Adsorption Experiments, *Chem. eng. sci.*, 40 (1985), 9, pp. 1401-1409
- [36] Javeed, S., *et al.*, Efficient and Accurate Numerical Simulation of Non-Linear Chromatographic Processes, *Journal Comput. & Chem. Eng.*, 35 (2013), Nov., pp. 2294-2305