Analysis of mass transfer equations during solid-liquid extraction and its application for vanilla extraction kinetics modeling

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ABSTRACT

Rigorous dimensionless analysis and analytical solution of mass transfer equation (punctual and space averaged) governing the solid-liquid extraction dynamic were performed. Analytical solutions result in continuous and analytical maps between solute mass fractions in extract with respect to time which were used both for solute diffusivity estimation and process modeling. In order to validate the models, experimental extraction at equilibrium of 1 cm long vanilla beans pieces were obtained at 0.1, 0.2, 0.3 and 0.4 g vanilla/mL solvent (60% w/w ethanol-water) and 30, 40 and 50 °C; and extraction kinetics were developed at 0.1 g/mL and 30, 40 and 50 °C. Apparent equilibrium constant and solute effective diffusivity estimation were performed by linear regression on experimental results. Apparent equilibrium constant was 0.86, and diffusivities were 1.22, 1.98, and 2.43 × 10^{-11} m^2/s at 30, 40 and 50 °C respectively. Diffusivities and analytical solutions predicted the experimental results at 30 and 50 °C with 0.3, and 0.4 g/mL respectively.

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1. Introduction

Solid-liquid extraction operation has recently returned to interest due to the extraction of bioactive compounds from natural sources (Cacace and Mazza, 2003; Pinelo et al., 2006; Spigno and De Faveri, 2007; Amendola et al., 2010; Linares et al., 2010) and therefore the mechanistic (mass transfer based) mathematical modeling of the process has been revised. Mass transfer during solid-liquid extraction may be conceptualized as solute diffusion in a media (underflow) contacting a well-stirred solution of finite volume (extract). The analytical solution to this problem in the diffusion media was reported by Crank (1975) for negligible interfacial resistance and by Mikhailov (1977) for a general case. In both cases, the solution for concentration in the well-stirred finite volume solution was not explicitly solved, and the volume of both phases was assumed as constant during process. Independently of the reported analytical solutions (Crank, 1975; Mikhailov, 1977), it has been a common practice the use of empirical models to describe the concentration kinetic of extractable solutes in extract

during solid-liquid extraction (Simeonov et al., 1999; Amendola et al., 2010; Linares et al., 2010; Rakotondramasy-Rabesiaka et al., 2010; Chilev et al., 2014); and, the extractable solutes effective diffusivity has been estimated by different methods: with the concentration at a punctual given time (Seikova et al., 2004; Rakotondramasy-Rabesiaka et al., 2010) which is not convenient because the experimental error is only the punctual error obtained at one time of the whole kinetic; by regression fit of the analytical solutions of diffusion equation considering infinite volume of solvent (Pinelo et al., 2006; Franco et al., 2007); by non-linear regression directly of differential equations (Garcia-Perez et al., 2010); or by an equation valid at very short times ($\tau < 0.0189$) (Cacace and Mazza, 2003). An alternative approach, for solid-liquid extraction modeling and/or effective diffusivity estimation, has been the use of mechanistic models supported in macroscopic (averaged) mass transfer equations (Veloso et al., 2005; Espinoza-Pérez et al., 2007; Rodríguez-Jimenes et al., 2013). Espinoza-Pérez et al. (2007) deduced an analytical solution of averaged mass transfer equations, and Rodríguez-Jimenes et al. (2013) applied this solution during vanilla solid-liquid extraction for the estimation of aromatic compound effective diffusivity in underflow by non-linear regression.

Considering the different point of views of solid-liquid extraction kinetic modeling and diffusivity estimation, it is necessary a unified model that represents the process with a theoretical basis. A unified model must be deduced from fundamental principles of mass transfer and thermodynamics, and it must have the property of predict the phenomenon at different conditions than those used to estimate the mass transfer properties. Therefore, in this paper a deep analysis of mass transfer equation governing the process dynamic is presented. It was declared as dynamic, because the mass transfer equations (local or space-averaged) represent the solid-liquid extraction kinetics in terms of driven forces. The analysis was performed for both, local and space-averaged equations and included dimensionless analysis, analytical solution and experimental validation. Obtained analytical solutions are continuous and analytical maps that relate extractable solutes mass fraction in both phases (extract and underflow) with the process time. These maps were used for the extractable solute effective diffusivity estimation during vanilla solid-liquid extraction and for the prediction of experimental extraction kinetics in the same system at different product/solvent ratios.

2. Model development

2.1. Punctual model

Solid-liquid extraction involves the diffusion of extractable material in media (underflow) contacting with a finite volume of a well-stirred solution (extract). The extractable material diffusion within underflow in a general coordinate system is represented by,

$$\frac{\partial \left(\rho_\beta x_\beta \right)}{\partial t} = D_\beta \nabla \cdot \nabla \left(\rho_\beta x_\beta \right) \quad \text{in} \quad \mathscr{V}_\beta \tag{1}$$

The mass transfer at underflow-extract interface in a general coordinate system is given by,

$$-\mathbf{n} \cdot D_\beta \nabla \left(\rho_\beta x_{\beta i} \right) = k_c \rho_\gamma \left(x_{\gamma i} - x_\gamma \right) \quad \text{in} \quad \mathscr{A}_{\beta\gamma} \tag{2}$$

In which the extractable material must be in phase equilibrium that may be represented by Nernst's law,

$$x_{\gamma i} = K_{eq} x_{\beta i} \tag{3}$$

Alternatively the phase equilibrium could be represented by a more complex relationship, as the Langmuir relation. However, Nernst's law has been universally assumed (Crank, 1975; Mikhailov, 1977; Seikova et al., 2004; Cacace and Mazza, 2003; Veloso et al., 2005; Chilev et al., 2014) when the analytical solution of mass transfer equations are required. Finally, the mass balance of extractable material in extract is,

$$\frac{d \left(\mathscr{V}_\gamma \rho_\gamma x_\gamma \right)}{dt} = k_c \rho_\gamma \mathscr{A}_{\beta\gamma} \left(x_{\gamma i} - x_\gamma \right) \quad \text{in} \quad \mathscr{V}_\gamma \tag{4}$$

The transfer surface ($\mathscr{A}_{\beta\gamma}$) in terms of underflow volume ($\mathscr{V}_\beta$) is,

$$\mathscr{A}_{\beta\gamma} = \frac{n \mathscr{V}_\beta}{l} \tag{5}$$

Particular forms of Eq. (5) are: an infinite flat slab with mass transfer in both sides with l half-thickness and $n = 1$; an infinite cylinder with radius l and $n = 2$; and a sphere with radius l and $n = 3$. The solution volume ($\mathscr{V}_\gamma$) and medium volume ($\mathscr{V}_\beta$) can be represented as a fraction of total system volume ($\mathscr{V} = \mathscr{V}_\gamma + \mathscr{V}_\beta$), and therefore,

$$\mathscr{V}_\gamma = \varepsilon \mathscr{V} \quad \text{and} \quad \mathscr{V}_\beta = (1 - \varepsilon) \mathscr{V} \tag{6}$$

The total mass balance of the whole system (underflow + extract) between initial and equilibrium states results in,

$$\frac{m_{\gamma 0} x_{\gamma 0} - m_{\gamma e} x_{\gamma e}}{m_{\beta 0} x_{\beta 0} - m_{\beta e} x_{\beta e}} = -1 \tag{7}$$

where underflow and extract masses in terms of their volume are,

$$m_\gamma = \rho_\gamma \mathscr{V}_\gamma \quad m_\beta = \rho_\beta \mathscr{V}_\beta \tag{8}$$

It is important to note that Eq. (7) considers that initial underflow ($m_{\beta 0}$: feed) mass and initial extract ($m_{\gamma 0}$: solvent) mass may be different of final underflow ($m_{\beta e}$: at equilibrium) mass and final extract ($m_{\gamma e}$: at equilibrium) mass respectively, as expected in any solid-liquid extraction system due to the solution retained by inert