Steady State Population Balance Modeling of Zinc Extraction in a Kühni Liquid-liquid Extraction Column

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A reduced steady state population balance model, based on the Spatially Mixed-Sectional Quadrature Method Of Moments (SM-SQMOM), is developed to model the reactive extraction process of zinc with D2EHPA in a Kühni liquid-liquid extraction column. The numerical flux vectors of the hydrodynamic transport equations are closed using one quadrature point, where an analytical solution based on the algebraic velocity model is used to calculate the required dispersed phase mean droplet velocity along the column height. In addition to this, a multi-sectional grid (w.r.t. droplet diameter) is used to approximate the source terms of the hydrodynamic transport equations, while one section (w.r.t. droplet solute concentration) is used to model the steady state reactive mass transfer behavior inside the column. The proposed model is validated with the experimental data using $ZnSO_4$/D2EHPA in isododecane EFCE chemical test system. The effect of changing the rotational speed, phase ratio and the total throughput on the column performance is investigated. The SM-SQMOM is found able to reconstruct the shape of the droplet size distribution and to predict the zinc reactive concentration profiles along the column height as compared with the experimental data.

1. Introduction

Liquid-liquid extraction is a commonly used separation process for recovery of heavy metals [1, 2]. In contrast to the physical extraction, the mass transfer process occurring during reactive extraction is superimposed by a chemical reaction when using liquid ion exchangers [1, 3]. An alternative to the commonly used mixer-settlers is the use of columns with the advantage of lower foot-print and solvent inventory. Their performance is determined by the coupled hydrodynamics and reactive mass transfer phenomena. In addition to this, the droplet size distribution is the major factor, which affects the available interfacial area and the droplets residence time inside a column. As a result of this, more attention is needed to model the coupled droplet-droplet interactions and the reactive mass transfer phenomena. A first attempt to simulate a reactive extraction column was done by Veglio and Slater [4]. The authors proposed a numerical design procedure and concluded that the most important design factor, which affects the column height, is the zinc ions mass transfer coefficient in the continuous phase. Ji et al. [5] studied the role of kinetics of zinc extraction in a packed bed liquid-liquid extraction column. The authors used the backmixing approach to model the reactive extraction process of zinc with D2EHPA, where they assumed constant dispersed phase integral properties (dispersed phase holdup and mean droplet diameter). Neto and Mansur [6] modeled the reactive extraction of zinc with D2EHPA in a short Kühni liquid-liquid extraction column. The authors used the back and forward mixing models, where the required dispersed phase integral properties were calculated using published correlations [6]. However, assuming constant dispersed phase integral properties is not realistic because the dispersed phase properties change along the column height due to mass transfer and droplet breakage and coalescence. As a result of this, a rigorous mathematical model to describe the dispersed phase behavior is needed. To shed more light on the dispersed phase behavior, Attarakih et al. [7, 8] introduced a comprehensive reduced non-equilibrium bivariate population balance model based on the discrete Sectional Quadrature Method of Moments (SQMOM) which is called OPOSPM. This model was developed to simulate the simultaneous reversible chemical reaction and extraction process of an industrial scale high-pressure oil-splitting reactor with a first-order reversible kinetics. The authors showed that the proposed framework was able to describe the column hydrodynamics as well as the reactive mass transfer behavior as demonstrated by different case studies where the reactor was represented by a spray column in the absence of static or moving internals. Since the droplet size distribution is nearly constant in spray columns, the proposed reduced model conserves the total number concentration (zero moment) and total mass (dispersed phase holdup) of the droplet size distribution and hence no extra droplet-droplet interaction mechanisms are required to reconstruct the shape of the droplet size distribution.

In this contribution, a reduced steady state bivariate population balance algorithm is developed to model the reactive extraction process of zinc with D2EPHA in a lab scale Kühni liquid-liquid extraction column. In this regard, the Spatially Mixed-Sectional Quadrature Method Of Moments (SM-SQMOM) [9], which is based on the SQMOM as a discrete framework for modelling particulate systems [10], is utilized and implemented. To facilitate the source terms implementation, an analytical solution [9], which is based on the algebraic velocity model, is used to calculate the required dispersed phase mean droplet velocity inside the column. The resulting integral spatial numerical flux vector is closed using the mean mass droplet diameter (d_{30}), while the hydrodynamics source terms are closed using the Two-Equal Weight Quadrature (TEqWQ) formula [10]. A multi-sectional grid (w.r.t droplet diameter) is used to approximate the integral hydrodynamics source terms, where 20 sections were found enough to reconstruct the shape of the droplet size distribution. In addition to this, one section is used to model the steady state reactive mass transfer behavior inside the column. At the experimental validation level, the model prediction is compared with the experimental data using the reactive ZnSO4/D2EHPA/isododecane EFCE chemical test system. The SM-SQMOM was found able to predict the column hydrodynamics as well as the mass transfer profiles when compared with the experimental data.

2. Experimental investigations

2.1 Experimental procedure

The experimental investigations were carried out at TU Kaiserslautern using a countercurrent Kühni DN32 liquid-liquid extraction column, where the column dimensions are shown in Table. 1. The chemical test system used in the investigations is $ZnSO_4$ / D2EHPA/ isododecane chemical test system as recommended by Bart et al. [1]. The column is initially filled with the aqueous phase, and then the rotor is started and after that the dispersed phase has been fed to the bottom of the column. In all cases, the dispersed organic phase (here isododecane) was fed at the bottom of the column using a finger distributer with 8 holes, while the continuous aqueous phase was fed at the top of the column. The dispersed phase holdup was measured in the active height of the column using the corresponding pressures method, while a high-speed camera was used to detect the droplet size distribution at the upper settling zone of the column. In this regard, the effect of changing the rotational speed, phase ratio and the total throughput on the column performance is investigated. The zinc ion concentrations and the pH values were measured at five different positions along the column height, where the column was operated at 80 percent away from the flooding point.

Table 1. Kühni column dimensions (all dimensions are in m).

Column diameter	Compartment height	Blade diameter	Stator diameter
0.032	0.028	0.0195	0.026

2.2 Chemical reaction kinetics

The EFCE chemical test system $ZnSO_4$/D2EHPA is commonly used as a standard test system for the extraction of zinc from aqueous solutions [1]. The chemical reaction of the zinc ions and D2EHPA occurs at the liquid-liquid interface as follows [1, 6]:

$$Zn^{2+} + 1.5\,\overline{(RH)_2} = \overline{ZnR_2(RH)} + 2H^+ \tag{1}$$

where $\overline{(RH)}$ and $\overline{ZnR_2(RH)}$ denote the D2EHPA and the zinc complex in the organic phase (see bar) respectively. Here, the D2EHPA dimer and the zinc ions diffuse toward the liquid-liquid interface and react to form the zinc complex in the organic phase and two protons in the aqueous phase. The equilibrium constant of the zinc extraction reaction is given by [1, 5, 6] and depends on the concentration of the pH value:

$$K = \frac{\left[\overline{ZnR_2(RH)}\right]\cdot\left[H^+\right]^2}{\left[Zn^{2+}\right]\cdot\left[\overline{(RH)_2}\right]^{1,5}} \tag{2}$$

It is assumed that both phases are immiscible and the water solubility in the dispersed phase is neglected. In all cases, the zinc (Zn^{2+}) inlet concentration was fixed at a constant value of 0.01mol/l, while the D2EHPA concentration is fixed at 0.25 mol/l as recommended by many authors [1, 5, 6]. In addition to this, the sulfuric acid (H_2SO_4) was added to adjust the pH value inside the column. The physical properties of the chemical test system are shown in in Table (2).

Table 2. Physical properties of the extraction reaction chemical test system.

Chemical compound	Density (kg/m^3)	Viscosity (Pa.s)	Interfacial tension (N/m)
$ZnSO_4$/water	999.6	0.000913	-
D2EHPA/ isododecane	764.8	0.001543	0.02087

3. Mathematical model

Following the efforts of Attarakih et al. [10], Alzyod et al. [9] extended the Sectional Quadrature Method Of Moments (SQMOM) to solve the bivariate nonhomogeneous population balance equation, where they developed a steady state algorithm to model the hydrodynamics and mass transfer behavior of liquid-liquid extraction columns based on the Specially-Mixed Sectional Quadrature Method Of Moments (SM-SQMOM). The steady state moment's system of equations which describe the coupled hydrodynamics and mass transfer along the spatial domain is given by [9]:

$$\frac{\partial}{\partial z}\left(\bar{F}_{r,m}^{\langle i\rangle} - D_y \frac{\partial \mu_{r,m}^{\langle i\rangle}}{\partial z}\right) = \hat{S}_{r,m}^{\langle i\rangle} \quad r,m = 0,..,2\times N_q - 1 \tag{3}$$

Here, the superscript i represents the i^{th} section of the internal coordinate, N_q is the number of secondary particles, D_y is the dispersed phase axial dispersion coefficient, $\mu_{r,m}^{\langle i\rangle}$ is a two dimensional moment transformation (w.r.t droplet diameter and solution concentration), $\bar{F}_{r,m}^{\langle i\rangle}$ is transformed numerical flux and $\hat{S}_{r,m}^{\langle i\rangle}$ is the transformed source term. In this work, the transformed source term and the mixed numerical flux vectors are given as follows [9, 10]:

$$\hat{S}_{r,m}^{\langle i\rangle} = u_y^{in}\mu_{in}^{\langle i\rangle}c_{yin}^{m}\delta\left(z - z_y\right) + S_{B,r,m}^{\langle i\rangle} + S_{C,r,m}^{\langle i\rangle} + S_{M,r,m}^{\langle i\rangle} \tag{4}$$

$$\bar{F}_{r,m}^{\langle i\rangle} = \sum_{j=1}^{Nq}\sum_{n=1}^{Nq}\left[u_y\left(d_{j,n},\alpha_y,P\right)d_{j,n}^{r}c_{y,n}^{m}w_{j,n}\right]^{\langle i\rangle} \tag{5}$$

where u_y^{in} is the superficial inlet velocity of the dispersed phase, c_{yin}^{m} is the solute concentration in the dispersed phase, $S_{B,r,m}^{\langle i\rangle}$ and $S_{C,r,m}^{\langle i\rangle}$ are the breakage and coalescence source terms respectively and $S_{M,r,m}^{\langle i\rangle}$ is the transformed reactive mass transfer source term. The transformed hydrodynamics and mass transfer source terms are given by [9, 10]:

$$S_{B,r}^{\langle i\rangle} = -Dr^{\langle i\rangle}\left[\Gamma^{\langle i\rangle}\bullet w^{\langle i\rangle}\right]^{T} + \sum_{m=i}^{N_{pp}}C_{r}^{\langle i,m\rangle}\left[\Gamma^{\langle i\rangle}\bullet w^{\langle i\rangle}\right]^{T} \tag{6}$$

$$S_{C,r,1}^{\langle i\rangle} = \sum_{k=1}^{i\times N_q}\left\{\sum_{j=k}^{i\times N_q}\psi_{k,j,r}^{\langle i\rangle}\omega_{j,k}w'_j w'_k - \theta_k \times \sum_{n=1}^{N_q\times N_{pp}}\left(d_k'^{r}\right)\omega_{k,n}w'_k w'_n\right\}` \tag{7}$$

$$S_{M,r,m}^{\langle i\rangle} = m\sum_{n=1}^{N_{sp}}c_y^{m-1}\left(\partial c_y/\partial t\right)w_n \tag{8}$$

For more details regarding the source terms, the reader can refer to [9, 10]. In this work, the mixed numerical flux vector is closed using the mean mass droplet diameter (d_{30}) and the resulting set of hydrodynamics moments conservation equations are given by [9]:

$$\frac{\partial \bar{F}_{r,0}^{\langle i\rangle}}{\partial z} = \frac{\partial}{\partial z}\left(u_y^{\langle i\rangle}\left(d_{30}^{\langle i\rangle},\alpha_y,P\right)\mu_{r,0}^{\langle i\rangle}\right) = \hat{S}_{r,0}^{\langle i\rangle} \quad r = 0,..,2\times \mathrm{N}_q - 1 \tag{9}$$

where α_y is the dispersed phase volume fraction and P is the physical properties vector. The mean mass droplet diameter can be directly calculated from Equation (9) as follows [9]:

$$d_{30}^{\langle i\rangle} = \sqrt[3]{\frac{\bar{F}_{3,0}^{\langle i\rangle}\left(d_{30}^{\langle i\rangle}\right)}{\bar{F}_{0,0}^{\langle i\rangle}\left(d_{30}^{\langle i\rangle}\right)}} \tag{10}$$

In this work, the hydrodynamics source terms are closed using the analytical Two Equal Weight Quadrature (TEqWQ) formula as follows [9, 10]:

$$d_{1,2}^{\langle i\rangle} = \hat{F}_{1,0}^{\langle i\rangle} \mp \frac{1}{\sqrt{3}}\sqrt{\frac{\hat{F}_{3,0}^{\langle i\rangle}}{\hat{F}_{1,0}^{\langle i\rangle}} - \left(\hat{F}_{1,0}^{\langle i\rangle}\right)^2} \tag{11}$$

$$w_{1,2}^{\langle i\rangle} = \frac{1}{2}\hat{F}_{0,0}^{\langle i\rangle} \tag{12}$$

Finally, the required dispersed phase mean droplet velocity to close the hydrodynamics model equations is given by [9]:

$$u_y^{\langle i\rangle}\left(F_{3,0}^{\langle i\rangle}, d^{\langle i\rangle}\right) = \frac{1}{3}\cdot\lambda_1^{\langle i\rangle} - \lambda_2^{\langle i\rangle} \tag{13}$$

where λ_1 and λ_2 are functions of droplet diameter, continuous phase velocity and the column internal geometry. For more information, the reader can refer to [9].

4. Results and discussion

In this section, the performance of the presented spatially mixed framework is tested, where the model prediction is validated using the steady state experimental data. The column dimensions and the chemical test system physical properties are discussed in detail in section 2. The simulations were carried out using two different inlet flow ratios ($\lambda_d = Q_d/Q_c = 0.2$ and 1.0 respectively), while the rotational speed was varied from 100 to 300 rpm. In this case study, the single droplet velocity model is given by Vigness velocity model [11]. The slowing effects due to the column internals and droplet's swarm is given by Steinmetz [12]. Concerning the droplet-droplet interactions, the coalescence mechanism between two liquid droplets is modeled using Coulaloglou and Tavlarides [13], while the droplet breakage probability function is given by Fang et al. [14]. Figure 1 shows a comparison between the calculated dispersed phase holdup and the experimental data using different rotational speed values. It can be clearly observed that a higher phase ratio results in a higher holdup values. In addition to this, the holdup values increase with increasing the rotational speed.

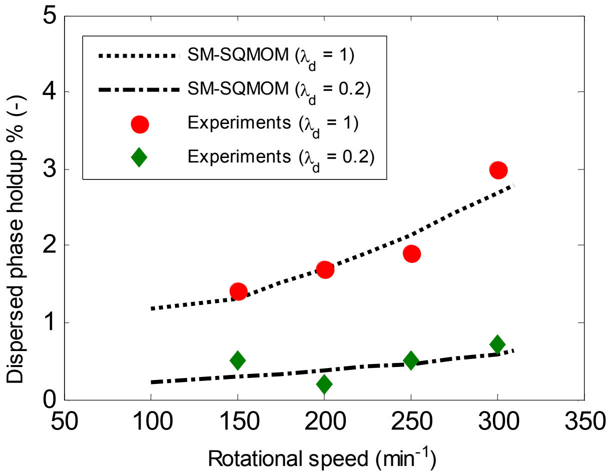

Figure 1. Comparison between the simulated and experimental dispersed phase hold up.

Figure 2 shows a comparison between the simulated droplet size distribution and the experimental data at the top of the column. The simulation was carried out at 350 rpm and a flow ratio of λ_d =1. It can be clearly observed that the SM-SQMOM retains the required information concerning the shape of the droplet size distribution, where 20 sections are found enough to reconstruct the shape of the size distribution. In addition to this, the column hydrodynamics is found dominated by the breakage phenomena at high rotor speeds.

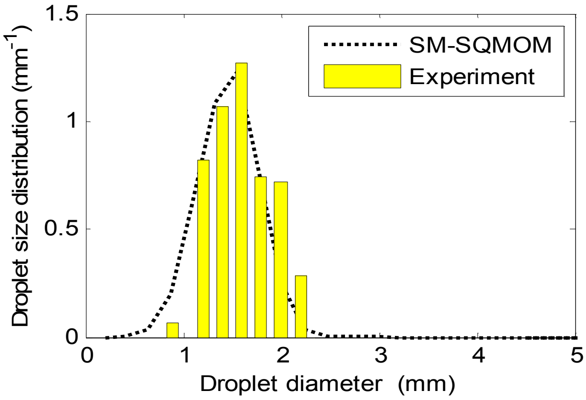

Figure 2. Comparison between the simulated and experimental droplet size distribution.

Based on the converged steady state droplet size distribution, the reactive solute mass transfer profiles can be predicted along the column height. This can be done by adjusting the coalescence model parameters to fit the predicated droplet size distribution at the top of the column with the experimental data. In this case study, the coalescence model parameters are given by c_1 = 0.02 and c_2 = 1.33×10^{11} m^{-2} respectively.

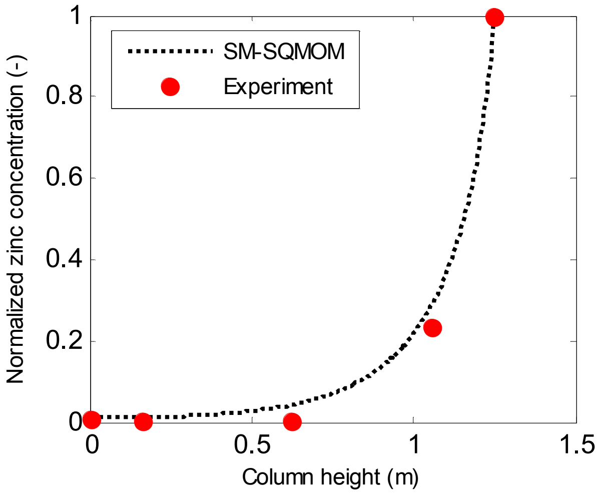

Figure 3. Comparison between the simulated and experimental Zn^{2+} concentration profiles.

Figure 3 shows a comparison between the simulated zinc ions concentration in the aqueous phase and the experimental data. In this case study, the correlation of Heertjes [15] is used to calculate the zinc ions local mass transfer coefficient in the continuous phase, while the correlation of Handlos and Baron [16] is used to calculate the D2EHPA local dispersed phase mass transfer coefficient. As expected the zinc ions concentration decreases along the column height (from the inlet point at the top to the bottom) due to the chemical reaction and the mass transfer process inside the extraction column. In addition to this, one section based on the solute concentration as an internal coordinate is found enough to predict the solute mass transfer profiles as compared with the experimental data.

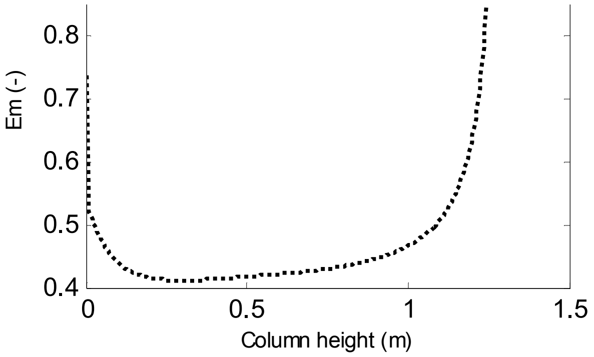

Figure 4. The ratio of the mass transfer resistance to the total resistance.

Figure 4 shows the ratio between the mass transfer resistance and the total resistance (*Em*) along the column height. It can be clearly observed that the extraction process is controlled by the mass transfer mechanism the top of the column, while the extraction process in controlled by the chemical reaction and mass transfer mechanisms at the bottom and the middle of the extraction column.

Figure 5 depicts a comparison between the simulated pH values and the experimental data at five different points along the column height using the same simulation conditions. The pH values decrease along the column height (from top to bottom of the column) until it reach a constant value (around 1.4). A very good agreement between the simulation results and the experimental data is obtained.

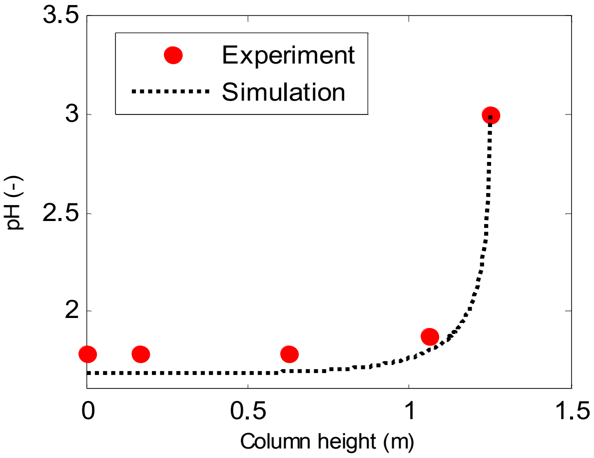

Figure 5. Comparison between the simulated and experimental pH profiles.

4. Conclusions

In this work, a steady state framework to model the reactive extraction process of zinc with D2EHPA in liquid-liquid extraction columns is developed, where the SM-SQMOM is utilized as a reduced population balance mathematical framework. The proposed framework is found able to describe the column hydrodynamics as well as the reactive mass transfer behavior. In this regard, 20 sections (w.r.t droplet diameter) are found enough to predict the column hydrodynamics, while one section (w.r.t solute concentration) is found enough to predict the reactive solute mass transfer profiles as compared with the experimental data. As a final conclusion, the SM-SQMOM is considered as a promising reduced population balance model for the two-phase flow problems.

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