Comparison of Mass Transfer Performance of Pulsed Columns with Tenova Kinetics Internals and Standard Disc and Doughnut Internals

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Abstract

One of the limitations to the application of columns to solvent extraction in the minerals industry is their relative inefficiency in slow kinetic systems such as those used for the separation of copper. In order to overcome this, this work examines the performance of a new kinetic internal and compares it to standard column internals for both a fast and slow kinetic system.

The mass transfer performance of a pilot scale pulsed solvent extraction column with Tenova Kinetics Internals (TKI) and standard disc and doughnut internals (DDI) are compared, including the effect of pulsation intensity, continuous and dispersed phase velocities using the H₂SO₄ – Alamine® 336 system, a fast kinetic system, and CuSO₄ – LIX® 84 system, a slow kinetic system. The height of mass transfer unit (H_{oc}) for the CuSO₄ – LIX 84 system increased with continuous and dispersed phase velocity and decreased with the increase of pulsation intensity. The H_{oc} for TKI was lower than the DDI for the same operating conditions and the TKI reduced the impact of both phase velocities on mass transfer. TKI can maintain the mass transfer performance for fast kinetics H₂SO₄-Alamine 336 system compared to standard disc and doughnut internals and improve mass transfer performance for slow kinetics CuSO₄- LIX® 84 system. An empirical correlation to predict the height of mass transfer unit in both internals was developed with absolute

25 relative errors of 28.0% and 19.2% for the H_2SO_4 – Alamine 336 system and CuSO_4 – LIX 84
26 system, respectively.

27 **Keywords:**

28 Height of mass transfer unit, mass transfer coefficient, Tenova kinetics internals, solvent
29 extraction

30

1. Introduction

Solvent extraction is one of the most effective separation processes to be applied widely in industries such as hydrometallurgy, pharmaceuticals and waste treatment [1]. In the extraction process, two immiscible liquid phases, typically an aqueous solution and an organic solvent, are contacted to extract a desirable solute. One of the most common types of contactors are pulsed solvent extraction columns due to their low maintenance, easy operation, smaller footprint and lower loss of organic. Different types of pulsed solvent extraction columns are available, including pulsed packed columns, pulsed perforated plate columns and pulsed disc and doughnut columns. The design of pulsed column internals can significantly affect column performance.

Pulsed disc and doughnut columns have been successfully applied to kinetically fast systems, such as the extraction of Uranium by Alamine 336 and Nickel by Cyanex 301. Trials with slower kinetic systems, such as copper with a range of oximes, has not been as successful due to the high height required to achieve sufficient recoveries.

Recently, Tenova Kinetics Internals (TKI) have been developed to improve column performance, particularly in kinetically slower systems. TKI have “teeth” on the edges of disc and doughnut sheets which are designed to enhance breakage of the dispersed phase droplets, and therefore achieve less backmixing and improved mass transfer for the same flux. Our previous studies of the hydrodynamic [2, 3] and axial dispersion performance [4] of TKI showed that the kinetic internals have higher potential throughput and similar axial dispersion coefficients compared with the standard disc and doughnut internals.

This study investigates the potential of using columns for a kinetically slow system, particularly with the newer design internals. The mass transfer performance of the TKI and DDI are compared. The height of mass transfer unit (H_{oc}) was measured and analysed over a wide range of column

working conditions, including pulsation intensities, dispersed and continuous phase velocities, in a 2 m high and 76 mm diameter pilot scale pulsed column. To provide the overall mass transfer performance of pulsed columns for two liquid – liquid systems, sulphuric acid (aq) – 3 v/v % Alamine 336, 1 v/v % isodecanol in ShellSol 2046 (org) and copper sulphate (aq) – 6.4 v/v % LIX 84 in ShellSol 2046 (org) systems are used. The sulfuric – Alamine system is representative for a fast kinetics system (first order kinetic reaction rate around 1.4 s^{-1} [5]) and the copper sulfate – LIX 84 system is representative for a slow kinetics system with (first order kinetic reaction rate around $2.1 \times 10^{-2} \text{ s}^{-1}$ [6]).

2. Background

The mass transfer performance of pulsed solvent extraction columns is influenced by the interfacial area (a), the concentration driving force (Δc_c or Δc_d) and the overall mass transfer coefficient (k_{oc} or k_{od}). The mass transfer rate can be expressed as Eq. 1 where c_c^* and c_d^* are concentration of solute at interface of continuous and dispersed phases, respectively[7].

$$\text{Transfer rate} = k_{oc}a(c_c^* - c_c) = k_{od}a(c_d - c_d^*)$$

Eq. 1

The overall mass transfer coefficients, k_{oc} and k_{od} , based on the continuous and dispersed phase respectively are presented in Eq. 2 and Eq. 3; where k_c and k_d are the individual mass transfer coefficients for continuous phase and dispersed phase, respectively, r is the reaction rate of the liquid-liquid system and m is the slope of the equilibrium line. If the reaction rate of the liquid-liquid system is fast enough ($\frac{1}{r} \ll \frac{1}{k_c} + \frac{1}{mk_d}$ or $\frac{m}{k_c} + \frac{1}{k_d}$), the overall mass transfer coefficients depend mainly on the individual mass transfer coefficients. Otherwise the overall mass transfer coefficients are controlled by both mass transfer rate and the reaction rate.

$$\frac{1}{k_{oc}} = \frac{1}{k_c} + \frac{1}{mk_d} + \frac{1}{r}$$

Eq. 2

$$\frac{1}{k_{od}} = \frac{m}{k_c} + \frac{1}{k_d} + \frac{1}{r}$$

Eq. 3

During practical operation of most pulsed liquid-liquid extraction columns, the axial dispersion of the continuous phase is significant inside the active section of pulsed columns. This leads to a concentration jump near the continuous phase inlet, which impacts the mass transfer outcomes. The diffusion model presented by Sleicher (1959)[8] (Eq. 4 and Eq. 5) keep the material balances with incorporation of axial dispersion is given as follows.

$$E_d \frac{d^2 c_d}{dz^2} - v_d \frac{dc_d}{dz} - k_{od} a (c_d - c_d^*) = 0$$

Eq. 4

$$E_c \frac{d^2 c_c}{dz^2} + v_c \frac{dc_c}{dz} + k_{oc} a (c_c - c_c^*) = 0$$

Eq. 5

The diffusion model may be solved using boundary conditions (Eq. 6 to Eq. 9) proposed by Danckwerts[9] (1950) and later justified by Wehner and Wilhelm[10] (1956) as:

$$\frac{dc_d}{dz} = 0 \text{ at } z = 0$$

Eq. 6

$$\frac{dc_d}{dz} = \text{Pe}_d (c_d^{\text{in}} - c_d) \text{ at } z = 1$$

Eq. 7

$$\frac{dc_c}{dz} = 0 \text{ at } z = 1$$

Eq. 8

$$\frac{dc_c}{dz} = \text{Pe}_c(c_c - 1) \text{ at } z = 0$$

Eq. 9

Both the height of a mass transfer unit (H_{oc}) and overall mass transfer coefficient (k_{oc} or k_{od}) are usually used to estimate and compare of mass transfer performance in a pulsed solvent extraction column. The relationship between the height of mass transfer unit based on continuous phase H_{oc} and the overall mass transfer coefficient of continuous phase can be determined by using Eq. 10. The interfacial area (a) can be calculated from the holdup (x_d) and Sauter mean diameter (d_{32}) as shown in Eq. 11.

$$H_{oc} = \frac{l}{N_{oc}} = \frac{v_c}{k_{oc}a}$$

Eq. 10

$$a = \frac{6x_d}{d_{32}}$$

Eq. 11

Numerous empirical and theoretical correlations for both individual mass transfer coefficients (k_c and k_d) and overall mass transfer coefficients (k_{oc} and k_{od}) have been reported for the prediction of mass transfer performance. However, empirical correlations for individual mass transfer coefficients found in literature are often not accurate for extraction columns due to complicated dispersed phase droplet interaction [11].

114 Kumar and Hartland[12] (1999) developed semi-empirical correlations for the individual mass
 115 transfer coefficients for the continuous and dispersed phase as a function of the Sherwood number
 116 as shown in Eq. 12 and Eq. 13; where $C_1 = C_2 = 4.33$ for pulsed columns, ψ is mechanical power
 117 dissipation per unit mass and other dimensionless numbers are defined via Eq. 14 to Eq. 18.

$$118 \quad \frac{\frac{Sh_c}{1-x_d} - Sh_{c,rigid}}{Sh_{c,\infty} - \frac{Sh_c}{1-x_d}} = 5.26 \times 10^{-2} Re^{\frac{1}{3} + 6.59 \times 10^{-2} Re^{\frac{1}{4}}} Sc_c^{\frac{1}{3}} \left(\frac{v_s \mu_c}{\gamma} \right)^{1/3} \left(\frac{1}{1 + (\frac{\mu_d}{\mu_c})^{1.1}} \right) [1 + C_1 \left(\frac{\psi}{g} \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right)^{1/3}]$$

119 Eq. 12

$$120 \quad Sh_d = 17.7 + \frac{3.19 \times 10^{-3} (Re Sc_d^{1/3})^{1.7}}{1 + 1.43 \times 10^{-2} (Re Sc_d^{1/3})^{0.7}} \left(\frac{\rho_d}{\rho_c} \right)^{2/3} \left(\frac{1}{1 + (\frac{\mu_d}{\mu_c})^{2/3}} \right) [1 + C_2 \left\{ \frac{\psi}{g} \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right\}^{1/3}]$$

121 Eq. 13

$$122 \quad Sh_{c,rigid} = 2.43 + 0.775 Re^{1/2} Sc_c^{1/3} + 0.0103 Re Sc_c^{1/3}$$

123 Eq. 14

$$124 \quad Sh_{c,\infty} = C_1 + \frac{2}{\sqrt{\pi}} (Pe_c)^{1/2}$$

125 Eq. 15

$$126 \quad \text{Schmidt number, } Sc_c = \frac{\mu_c}{\rho_c D_c}$$

127 Eq. 16

$$128 \quad \text{Reynolds number, } Re = \frac{d_{32} v_s \rho_c}{\mu_c}$$

129 Eq. 17

$$130 \quad \text{Peclet number, } Pe_c = \frac{d_{32} v_s}{D_c}$$

Eq. 18

van Delden, et al.[13] (2007) successfully applied the mass transfer correlations (Eq. 12 and Eq. 13) of Kumar and Hartland[12] (1999) to the mass transfer performance in a 40 mm diameter pulsed disc and doughnut column for the extraction of caprolactam with toluene in operating range of $Af = 0.016$ and 0.0218 m/s.

Liu, et al.[14] (2015) determined the experimental mass transfer coefficient in an annular pulsed disc and doughnut column with pulsation intensity ranges from 0.0115 to 0.0148 m/s. Only the mass transfer coefficient of the stripping process was adequately predicted with a relative error of 57% . The relative error for extraction process was between 442 and 1007% .

Torab-Mostaedi, et al.[15] (2011) was unable to fit the existing correlations to the overall mass transfer coefficient for the toluene-acetone-water system in a 76 mm diameter pulsed disc and doughnut column. Thus, they derived empirical correlations to predict the overall mass transfer coefficients of the continuous phase in terms of the overall Sherwood number, Reynolds number and dispersed phase holdup for different directions of mass transfer. These relationships are presented as follows:

For $d \rightarrow c$ direction of mass transfer and $11.73 < Re < 69.43$,

$$Sh_{oc} = -121.56 + 103.62Re^{0.16}(1 - x_d)$$

Eq. 19

For $c \rightarrow d$ direction of mass transfer and $9.45 < Re < 57.08$,

$$Sh_{oc} = -119.50 + 113.30Re^{0.12}(1 - x_d)$$

Eq. 20

152 where

$$Sh_{oc} = \frac{k_{oc}d_{32}}{D_c}$$

153 Eq. 21

154 The correlation constants were calculated using the least squares method with “Eviews software”.
155 Model predictions obtained had a relative deviation of 10.52% upon comparison with the
156 experimental data.

157 Jahya[16] (2002) and Jahya, et al.[17] (2009) presents an empirical correlation for the height of a
158 mass transfer unit based on the continuous phase for a 72.5 mm diameter pulsed disc and doughnut
159 column for various liquid-liquid systems, and pulsation intensity from 0.025 ~ 0.3 m/s. Equation
160 (Eq. 22) was correlated with operating conditions, column geometry and physical properties of the
161 liquid-liquid systems:

$$162 \quad H_{oc} = 1.378 \left(\frac{\gamma}{\mu_c v_c} \right)^{0.155} \left(\frac{v_d}{v_c} \right)^{0.341} \left(\frac{v_c^3 \rho_c}{g \mu_c x_d^3} \right)^{-0.049} \left(\frac{Af}{v_d} \right)^{-0.525}$$

163 Eq. 22

164 Recently, Wang, et al.[11] (2017) developed empirical correlations for H_{oc} (Eq. 23) and Sh_{oc} (Eq.
165 24) by operating a 72.5 mm diameter 1 m high pulsed disc and doughnut column for H_2SO_4
166 extraction by Alamine 336-isodecanol-ShellSol 2046. The pulsation intensity was set in the range
167 of 0 – 0.018 m/s and the $(Af)_m$ in the scenario was set as 0.0075 m/s. The correlations developed
168 were based on trend analysis and Jahya’s correlation[16] (Eq. 22) with the absolute average
169 relative error of 17% and 21.9% for H_{oc} and Sh_{oc} , respectively.

$$170 \quad H_{oc} = 9.35 \times 10^{-3} \times \exp[(-73.1) \times |Af - (Af)_m|] \left(\frac{\gamma}{\mu_c v_c} \right)^{0.612} \left(\frac{v_d}{v_c} \right)^{-0.219} \left(\frac{v_c^3 \rho_c}{g \mu_c x_d^3} \right)^{-0.112}$$

171 Eq. 23

$$Sh_{oc} = 9.62 \times 10^{-5} \times \exp[101 \times |Af - (Af)_m|] Re^{2.75} \left(\frac{v_d}{v_c}\right)^{1.61} Sc_c^{\frac{1}{3}} (1 - x_d)$$

Eq. 24

3. Experimental

3.1 Liquid-liquid systems

Two liquid-liquid systems were selected for investigation in this study, one slow and one fast kinetics systems. The fast system selected was ~ 0.04 M sulphuric acid solution (aqueous phase). The solution was prepared via dilution of 98% sulphuric acid (Sigma Aldrich) with Milli-Q water. The organic phase was a mixture of 3 v/v % Alamine 336 (tri-n-octylamine) (BASF) and 1 v/v % isodecanol (ExxonMobil) in ShellSol 2046 (Shell). The isodecanol was added to eliminate the formation of third phase and accelerate the phases separation. The relatively slow kinetics system used was ~ 2 g/L copper sulphate solution (aqueous phase) (Sigma Aldrich) and the organic phase was 6.4 v/v % LIX 84 (2-hydroxy-5-nonylacetophenone oxime) (BASF) in ShellSol 2046. The densities, viscosities and interfacial tensions of both liquid-liquid systems were measured and are displayed in **Table 1**. Densities of aqueous and organic phases were measured three times to obtain an average value using 25 mL pycnometers. A Cannon portable viscometer was used to obtain the viscosity of each phase. Interfacial tensions between aqueous and organic phases were analysed with a Theta Attension Tensiometer.

Table 1 Physical properties of two liquid-liquid systems

Liquid-liquid system	Aqueous Phase	Organic Phase	ρ_{aq} (kg/m ³)	ρ_{org} (kg/m ³)	μ_{aq} (Pa·s)	μ_{org} (Pa·s)	γ (N/m)
I	~ 0.04 M H ₂ SO ₄	Alamine, isodecanol in ShellSol 2046	1000.5	801.2	1.02 x 10 ⁻³	2.30 x 10 ⁻³	0.007 ^a 0.007 ^b

II	$\sim 2 \text{ g/L CuSO}_4$	LIX 84 in ShellSol 2046	961.1	810.3	0.96×10^{-3}	2.08×10^{-3}	0.023^a 0.022^b
	a. aqueous drop in organic background (aq – dispersed; org – continuous)						
	b. organic drop in aqueous background (aq – continuous; org – dispersed)						

3.2 Equipment

A 2-metre-high pilot scale pulsed solvent extraction column was used in this study. The detailed column design was reported in our previous works [2-4]. The column consisted of four QVF® precision pipeline components, including one unequal tee piece, two 1 metre high 76 mm diameter precision bore glass tubes and a concentric reducer. The stainless-steel distributors for the aqueous and organic phase were enclosed and connected to rotameters, flameproof pumps and 150 L stainless steel (SS) storage tanks. A pulsation unit was connected to the bottom of column section with pulsation intensity (Af) ranging from 0 m/s to 0.03 m/s.

The two different structures of column internals, which are TKI and DDI (see to Figure 1 for the internal structures), were inserted and fastened inside the main section of the pulsed column as required. Both sets of internals were made of PVDF (polyvinylidene fluoride) and comprised of 77 discs of 68 mm diameter and 76 doughnut shape plates with apertures of 36 mm diameter, which were arranged alternately with 9.8 mm spacing. All pilot-scale column experiments were conducted at room temperature (15 – 25 °C).

Figure 1 Schematic drawing for standard disc and doughnut internal (top) and Tenova kinetics internals (bottom)

3.3 Operation

Prior to commencing operation, the main section of pulsed column was filled with the organic continuous phase. Following this, the pulsation intensity (pulsing amplitude and frequency) and the flowrates of the continuous (v_c) and dispersed phases (v_d) were set to the desire values. The interface between the two immiscible phases was maintained at a specific level by adjusting the exit flowrate of aqueous phase. The system was operated until steady state was reached, which was approximately 3 – 5 times the residence time, based on the column volume and column

throughput [11, 18]. Following this, the inlet and outlet samples for both the dispersed phase and continuous phase were taken for further analysis.

The concentration of solute for H₂SO₄ – Alamine 336 system (H₂SO₄) in aqueous and organic phases were measured by titration in triplicate with pre-calibrated sodium hydroxide solution at 0.0198 M and the average taken for each operating condition. The concentration of solute in the CuSO₄ – LIX 84 system (CuSO₄) was diluted and analysed via Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES), whilst the concentration of CuSO₄ loaded in organic phase was first stripped by 1 M H₂SO₄ solution and then diluted and analysed by ICP. These tests were conducted in triplicate and the average taken.

To estimate the mass transfer performance, the equilibrium data for both liquid-liquid systems were measured via lab-scale isothermal shake up tests. Figure 2 shows the equilibrium data for H₂SO₄ – Alamine 336 system at 15 °C and 28 °C. The equilibrium data was well predicted by the Langmuir model (Eq. 25) with equilibrium constant (K) and maximum sorption capacity (Γ_{max}) summarised in Table 2.

$$C_{org} = \frac{K\Gamma_{max}C_{aq}}{1 + KC_{aq}}$$

Eq. 25

236
237

Table 2 Parameters of Langmuir models for H₂SO₄ – Alamine system (I) (Figure 2) and CuSO₄ – LIX 84 system (II) (Figure 3)

Liquid-liquid system	Aqueous Phase	Organic Phase	Conditions at equilibrium	K (L/mol)	$\Gamma_{\max}$ (mol/L)
I	H ₂ SO ₄	3 v/v% Alamine 336, 1 v/v% isodecanol in ShellSol 2046	T = 15°C	41.7	0.0476
			T = 28°C	42.6	0.0451
II	CuSO ₄	6.4 v/v% LIX 84 in ShellSol 2046	pH = 1.80 (20 ± 2°C)	4.2	3.18
			pH = 2.50 (20 ± 2°C)	32.5	4.23
			pH = 4.60 (20 ± 2°C)	162.8	5.19

238

Figure 2 Experimental equilibrium relationship and Langmuir prediction of sulphuric acid in water and 3 v/v % Alamine 336, 1 v/v % isodecanol in ShellSol 2046 at temperature 15°C and 28°C

Figure 3 and Table 2 presents the equilibrium data for CuSO₄ – LIX 84 system at pH 1.8, 2.5 and 4.6, as shown all three series of data can be well predicted by the Langmuir model. The extraction reaction for the CuSO₄ – LIX 84 system is showed below:

According to the reaction, the pH will decrease with more cupric ions extracted and low pH will slow the extraction rate of cupric ions from aqueous phase to organic phase. Therefore, it is necessary to keep the pH of the pilot-scale system stable so that the mass transfer performance can be estimated with the equilibrium line for a given pH. Particularly in this study, the pH buffer sodium acetate was added to the aqueous phase before column operation to maintain the extraction pH condition at range of 4.4 to 4.8.

Figure 3 Experimental equilibrium relationship and Langmuir prediction of copper sulphate in water and 6.4 v/v % LIX 84 in ShellSol 2046 at pH 1.80, 2.50 and 4.60 (at ambient temperature $20 \pm 2^\circ\text{C}$)

The height of mass transfer unit (H_{oc}) were calculated via a mas transfer performance programme which also considered the impact of axial dispersion model (Eq. 5). Within the program, H_{oc} at a specified continuous phase velocity (v_c) was calculated via Eq. 10. The active height of the column (l) was 1.96 m and the total stage number (N_o) was calculated from Eq. 5. The axial dispersion coefficients (E_c) in diffusion model (Eq. 5) is predicted via the correlations (Eq. 26 to Eq. 28) [4]. The correlations for axial dispersion model was summarised in Supplementary document S1.

$$\frac{E_c \Delta \rho}{\mu_c} = k_1 \exp(k_2 \Psi) \left(\frac{V_d \mu_c}{\gamma} \right)^{k_3} \left(\frac{\mu_c}{\mu_d} \right)^{k_4} \left(\frac{\mu_c}{(\gamma \Delta \rho h)^{0.5}} \right)^{k_5} \left(\frac{V_c}{V_d} \right)^{k_6}$$

Eq. 26

$$\Psi = \left[\frac{Af - (Af)_m}{(Af)_m} \right]^3 - \left[\frac{Af - (Af)_m}{(Af)_m} \right]^2$$

Eq. 27

$$(Af)_m = 9.69 \times 10^{-3} \left(\frac{\gamma \Delta \rho^{0.25} \varphi}{\mu_d^{0.75}} \right)^{0.33}$$

Eq. 28

4. Results and discussion

The effect of pulsation intensity, the continuous and dispersed phase velocities on the height of mass transfer unit and overall mass transfer coefficient based on the continuous phase with DDI and TKI using H₂SO₄-Alamine 336 system and CuSO₄-LIX 84 system have been studied under a wide range of operating conditions. The pulsation intensity was varied from 0.005 m/s to 0.03 m/s, and the continuous and dispersed phase velocities were varied from 6.62 x 10⁻⁴ m/s to 1.43 x 10⁻³ m/s and 7.35 x 10⁻⁴ m/s to 1.47 x 10⁻³ m/s, respectively.

4.1 Height of mass transfer unit H_{oc}

It is shown in Figure 4 that the height of mass transfer unit (H_{oc}) for the slow kinetics CuSO₄-LIX 84 system, with DDI, decreases significantly with the increase of pulsation intensity at different Aqueous/Organic (A/O) ratios. This could be explained by the slow kinetic properties of CuSO₄ – LIX 84 system that requires the high pulsation intensity to enhance the mass transfer efficiency (meaning lower height of mass transfer unit).

Alternatively, the H_{oc} for the fast kinetics H₂SO₄ – Alamine 336 system remains steady from pulsation intensity 0.005 m/s to 0.03 m/s at approximately 1.3 m, similarly for the TKI experiment as seen in Figure 5.

Figure 4 The effect of pulsation intensity on the height of mass transfer unit based on continuous phase (H_{oc}) at different A/O ratios for both H₂SO₄-Alamine 336 system and CuSO₄-LIX 84 system with DDI

Figure 5 The effect of pulsation intensity on the height of mass transfer unit based on continuous phase (H_{oc}) at different A/O ratios for both H_2SO_4 -Alamine 336 system and $CuSO_4$ -LIX 84 system with TKI

To compare the impact of the different column internals, the height of a mass transfer unit for H_2SO_4 -Alamine 336 and $CuSO_4$ -LIX 84 is presented in Figure 6 and Figure 7. For the H_2SO_4 -Alamine 336 system, the H_{oc} data for both column internals at the specified A/O ratio and pulsation intensity are consistent, showing that the TKI almost have no impact to the mass transfer efficiency of this fast kinetics system. With regards to the $CuSO_4$ -LIX 84 system, the H_{oc} for both column internals decreased with the increase of pulsation intensity. Under the same operating conditions, the height of mass transfer unit for TKI (open symbols) are lower than that of the DDI (filled symbols), within the experimental error. This suggests that the TKI enhanced the mass transfer performance of the column.

Figure 6 The effect of pulsation intensity on the height of mass transfer unit based on the continuous phase (H_{oc}) at different A/O ratios with two types of column internals for H_2SO_4 – Alamine 336 system

Figure 7 The effect of pulsation intensity on the height of mass transfer unit based on the continuous phase (H_{oc}) at different A/O ratios with two types of column internals for CuSO_4 – LIX 84 system

Figure 8 The effect of continuous phase velocity on the height of mass transfer unit based on the continuous phase (H_{oc}) at $v_d = 7.35 \times 10^{-4}$ m/s and $A_f = 0.01$ m/s

The effect of the continuous phase velocity on the height of mass transfer unit (H_{oc}) at 7.35×10^{-4} m/s dispersed phase velocity and 0.01 m/s pulsation intensity is presented in Figure 8. For H_2SO_4 – Alamine 336 system, the height of mass transfer unit for both DDI and TKI are found to be independent of continuous phase velocity. For $CuSO_4$ -LIX 84 system with DDI, the H_{oc} increased with the continuous phase velocity. This could due to the insufficient reaction time for $CuSO_4$ mass transfer, the slow kinetic system, at high column throughput. However, the impact of v_c on mass transfer of $CuSO_4$ – LIX 84 system is negligible when using TKI at the studied range of continuous phase velocity as shown in Figure 8.

Figure 9 The effect of dispersed phase velocity on the height of mass transfer unit based on the continuous phase (H_{oc}) at $v_c = 6.62 \times 10^{-4}$ m/s and $Af = 0.01$ m/s

Similarly, the dispersed phase velocity (v_d) also had no observable effect on the height of mass transfer unit H_{oc} of H_2SO_4 – Alamine 336 system for both DDI and TKI as seen in Figure 9. However, when v_d increased from 7.35×10^{-4} m/s to 1.47×10^{-3} m/s, the H_{oc} for $CuSO_4$ – LIX 84 system also increased from 7 m to 8.7 m and 13.3 m when using DDI and TKI, respectively. This, again, demonstrates that the kinetics internals reduced the impact of dispersed phase velocity on the mass transfer performance of the $CuSO_4$ – LIX 84 system.

4.2 Correlation

The empirical correlation for H_{oc} developed by Wang, et al.(2017) [11] (Eq. 29) was refitted with the ~ 100 experimental data points collected in this study for two different liquid-liquid systems

and two column internals. The holdup value (x_d) was predicted via correlations (Eq. 30) developed in our previous studies [2, 3]. The correlated constants k_1 and k_2 were shown in Table 3 which varied with the liquid – liquid systems. As can be seen in Figure 10, the predicted H_{oc} (calculated from Eq. 29) was compatible with the experimental H_{oc} (obtained from axial dispersion model). The absolute average relative error (AARE) of experimental H_{oc} and predicted H_{oc} are 28.0% and 19.2% for H_2SO_4 – Alamine 336 and $CuSO_4$ – LIX 84 systems, respectively. The AARE for H_2SO_4 – Alamine 336 system is relatively larger due to its fast kinetics and the operating curves being too close to equilibrium curve.

$$H_{oc} = k_1 \cdot \exp[k_2 \cdot |Af - (Af)_m|] \left(\frac{\gamma}{\mu_c V_c} \right)^{0.001} \left(\frac{V_d}{V_c} \right)^{-0.129} \left(\frac{V_c^3 \rho_c}{g \mu_c x_d^3} \right)^{-0.112}$$

Eq. 29

$$x_d = k_1 \exp[k_2 |Af - (Af)_m|] \left(\frac{v_d^4 \rho_c}{g \gamma} \right)^{0.31} \left(\frac{v_c + v_d}{v_d} \right)^{0.32} \left(\frac{\Delta \rho}{\rho_c} \right)^{-0.98} \left(\frac{\mu_d}{\mu_c} \right)^{0.18}$$

Eq. 30

Table 3 Regressed parameters k_1 and k_2 in Eq. 29

Liquid-liquid system	k_1	k_2	AARE (%)
H_2SO_4-Alamine 336 system	1.18	-73.1	28.0
$CuSO_4$-LIX 84 system	7.65	-57.8	19.2

Figure 10 Comparison of experimental H_{oc} and predicted H_{oc} by Eq. 29.

The overall mass transfer coefficient (k_{oc}) was also calculated via Eq. 10 with the interfacial area a obtained from Eq. 11. The holdup and drop size distribution values were predicted via correlations (Eq. 30 and Eq. 31) developed in our previous studies [2, 3]. The constants in above correlations (k_i and C_i) were summarised in Supplementary document S1. Again, the experimental and predicted overall mass transfer coefficient are quite compatible as shown in Figure 11. The absolute average relative error (AARE) of experimental k_{oc} and predicted k_{oc} are 41.2% and 20.4% for H_2SO_4 – Alamine 336 and $CuSO_4$ – LIX 84 systems, respectively.

$$d_{32} = C_1 \varepsilon^{0.3} \left(\frac{\gamma}{\Delta \rho g} \right)^{0.5} \left(h \frac{\sqrt{\rho_* g}}{\gamma_*} \right)^{0.18} \left(\frac{\mu_d g^{0.25}}{\rho_*^{0.25} \gamma_*^{0.75}} \right)^{0.14} \left(\frac{\gamma}{\gamma_*} \right)^{0.06} \left[C_2 + \exp \left\{ C_3 \frac{Af}{\varepsilon \left(\frac{\gamma_* g}{\rho_*} \right)^{0.25}} \right\} \right] \left(\frac{v_d}{v_c} \right)^{0.118}$$

Eq. 31

Figure 11 Comparison of experimental k_{oc} and predicted k_{oc}

5. Conclusions

The conclusions from this work can be summarized as follows:

1. For CuSO_4 – LIX 84 system, the height of mass transfer unit (H_{oc}) decreases with increasing pulsation intensity (Af) and increases with either increasing continuous or dispersed phase velocities for both DDI and TKI using the CuSO_4 – LIX 84 system. In comparison with DDI, the TKI reduced the H_{oc} at the same operating conditions and also reduced the impact of phase velocity on the H_{oc} making them more efficient.

2. For H_2SO_4 -Alamine 336 system, the H_{oc} was constant with increasing Af , v_c or v_d due to the fast kinetics liquid-liquid system reaching the equilibrium state inside a 2 m high pulsed solvent extraction column.
3. A correlation (Eq. 29) was introduced to predict the height of mass transfer unit of different internals and kinetics liquid-liquid systems. The absolute average relative error of the correlation to predict H_{oc} for H_2SO_4 – Alamine 336 and CuSO_4 – LIX 84 with both internals are 28.0% and 19.2 %, respectively.

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7. Nomenclature

a	Interfacial area, m^2
A	pulsation amplitude, m
c	solute concentration in liquid phase, M
d	drop equivalent sphere diameter, m
d_{32}	Sauter-mean drop diameter, m
D	molecular diffusivity, m^2/s
E	actual axial mixing coefficient, m^2/s
f	pulsation frequency, Hz
g	gravity acceleration, m/s^2
H_{oc}	height of mass transfer unit based on continuous phase, m
k_d/k_c	individual mass transfer coefficient of dispersed phase/continuous phase, m/s
k_{od}/k_{oc}	overall mass transfer coefficient of dispersed phase/continuous phase, m/s

395	K	equilibrium constant in Langmuir equation, L/mol
396	l	active column height, m
397	m	slope of equilibrium line, dimensionless
398	N	total number of stage, dimensionless
399	r	reaction rate of liquid – liquid system, m/s
400	Re	Reynolds number, $Re = \frac{d_{32} V_s \rho}{\mu}$ for droplets dispersion, dimensionless
401	Pe	Péclet number, $Pe_c = \frac{d_{32} V_s}{D_c}$ for droplets dispersion, dimensionless
402	Sc	Schmidt number, $Sc = \frac{\mu}{\rho D}$, dimensionless
403	Sh	Sherwood number, $Sh = \frac{k_d}{D}$, dimensionless
404	v_d/v_c	dispersed phase velocity/continuous phase velocity, m/s
405	v_s	slip velocity, m/s
406	x_d	volume fraction holdup of dispersed phase, dimensionless
407	ε	the fractional free area, dimensionless
408	γ	interfacial tension, N/m
409	μ_d/μ_c	viscosity of dispersed phase/continuous phase, Pa·s
410	π	constant equal to 3.1416
411	ρ_d/ρ_c	density of dispersed phase/continuous phase, kg/m ³
412	$\Delta\rho$	density difference between phases, kg/m ³
413	$\Gamma_{\max}$	maximum sorption capacity, mol/l
414	ψ	mechanical power dissipation per mass unit, W/kg

415 **Subscripts or superscripts**

416	c	continuous phase
417	d	dispersed phase
418	in	an inlet to column
419	outlet	an outlet from column
420	rigid	rigid drop conditions
421	*	equilibrium value

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471

SUPPLEMENTARY DOCUMENT S1

- ❖ Prediction of holdup and Sauter mean diameter in TKI and DDI for H₂SO₄ – Alamine 336 and CuSO₄ – LIX 84 systems [2, 3]

$$x_d = k_1 \exp[k_2 |Af - (Af)_m| (\frac{v_d^4 \rho_c}{g\gamma})^{0.31} (\frac{v_c + v_d}{v_d})^{0.32} (\frac{\Delta\rho}{\rho_c})^{-0.98} (\frac{\mu_d}{\mu_c})^{0.18}$$

$$(Af)_m = 9.69 \times 10^{-3} (\frac{\gamma \Delta\rho^{0.25} \varphi}{\mu_d^{0.75}})^{0.33}$$

Table S1 Parameters for predicting the dispersed phase holdup x_d

Internals	Operation	Operating regime	k ₁	k ₂
Standard disc and doughnut internals	Organic continuous system	mixer-settler	7.65	77.30
		transition & emulsion	6.34	39.17
Tenova kinetics internals	Organic continuous system	mixer-settler	7.71	6.49
		transition & emulsion	6.11	21.97
	Aqueous continuous system	mixer-settler	3.75	91.48
		transition & emulsion	1.64	43.80

$$d_{32} = C_1 \varepsilon^{0.3} \left(\frac{\gamma}{\Delta\rho g} \right)^{0.5} \left(h \frac{\sqrt{\rho_* g}}{\gamma_*} \right)^{0.18} \left(\frac{\mu_d g^{0.25}}{\rho_*^{0.25} \gamma_*^{0.75}} \right)^{0.14} \left(\frac{\gamma}{\gamma_*} \right)^{0.06} [C_2 + \exp \left\{ C_3 \frac{Af}{\varepsilon (\frac{\gamma_* g}{\rho_*})^{0.25}} \right\}] \left(\frac{v_d}{v_c} \right)^{0.118}.$$

Table S2 Parameters for predicting the Sauter mean diameter d_{32}

Constants	Operation	C ₁	C ₂
Standard disc and doughnut internals	Organic continuous system	0.0105	0.2368
	Organic continuous system	0.0243	0.0215

Tenova kinetics	Aqueous continuous system	0.02	0
internals			

❖ Axial dispersion correlation in TKI and DDI for H₂SO₄ – Alamine 336 and CuSO₄ – LIX 84 systems [4]

$$\frac{E_c \Delta \rho}{\mu_c} = k_1 \exp(k_2 \Psi) \left(\frac{V_d \mu_c}{\gamma} \right)^{k_3} \left(\frac{\mu_c}{\mu_d} \right)^{k_4} \left(\frac{\mu_c}{(\gamma \Delta \rho h)^{0.5}} \right)^{k_5} \left(\frac{V_c}{V_d} \right)^{k_6}$$

$$\Psi = \left[\frac{Af - (Af)_m}{(Af)_m} \right]^3 - \left[\frac{Af - (Af)_m}{(Af)_m} \right]^2$$

Table S3. Parameters for predicting axial dispersion coefficient E_c

Parameters	k ₁	k ₂	k ₃	k ₄	k ₅	k ₆
Mixer-settler	23	1.58	0.16	-0.37	0.015	0.16
Emulsion	42	3.50				