

Mass Transfer Coefficients in Pulsed Column for Separation of Samarium and Gadolinium

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ABSTRACT: *The mass transfer performance of a pulsed disc and doughnut column for extraction of samarium and gadolinium from aqueous nitrate solution with D2EHPA was investigated. The effects of operating parameters such as pulsation intensity, continuous and dispersed phase velocities on column performance were investigated. The axial dispersion model was used to obtain the overall mass transfer coefficient. The previous models for overall mass transfer coefficient were reviewed and compared with experimental data. A new correlation was derived for prediction of the overall mass transfer coefficients. The presented model was compared with the experimental results and a good agreement between them was obtained. The mass transfer experiments revealed the feasibility of operating the separation of samarium and gadolinium in the pulsed disc and doughnut columns.*

KEYWORDS: *Mass transfer; Mathematical modeling; Solvent extraction; Axial mixing; Pulsed column; Rare metals.*

INTRODUCTION

Rare earth have an ever growing variety of applications in the modern technology. Rare earth have been extensively used in chemical, medical, nuclear as well as in metallurgy, electronics, and ceramic technology.

The rare earth elements are found in main minerals such as bastnasite, monazite, xenotime, etc; these metal ions are not radioactive, they always coexist with radioactive elements, such as uranium and thorium [1-3].

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The escalating demand for rare earth metals in various applications and their continuous depleting minerals have laid emphasis on producing metals from their complex resources by developing energy efficient and eco-friendly processes [4].

Solvent extraction is at present one of the major techniques on the industrial scale for the extraction and separation of rare earth metals. This technique is characterized by its high effectiveness in the mutual separation of metals as well as its smooth and continuous operation [5-7]. This method for recovery of metal ions is known as a succinct process with the low cost and recyclability of components [8].

The classical extractors such as mixer-settlers and different types of extraction columns are available for solvent extraction. However, the selection of proper equipment is very important depending upon the nature of the application. The mixer-settlers are unique extractors used for rare earth purification and separation in industry. *Parmentier* and co-workers were investigated the continuous process for selective metal extraction with an ionic liquid in the mixer-settler systems [9]. However, the large numbers of stages in a series of mixer-settlers are required for the preparation of high-purity products, because the chemical properties of adjacent elements are very similar [10]. But nowadays, the use of extraction columns is of particular interest in that they are potential alternatives to overcome the disadvantages of mixer-settlers such as large space requirement, long residence time, large solvent inventory, poor sealing of the system and slow response to the change in process control [11].

With the development of rare earth applications, commercial products develop gradually from primary products to single high-purity and high value-added products. The extraction columns are suitable for rapid development in process control to produce individual rare earth in high purity [1].

Among the various types of columns, pulsed extraction columns are recommended for a lot of applications in the field of radioactive solutions due to the absence of moving parts inside the column and facility of keeping the pulsing unit away from the column. The other advantages of the pulsed columns are their simple operation, considerable flexibility, reduction in organic losses and organic inventory, high throughputs and small

footprint for multistage extraction systems. The pulsed disc and doughnut solvent extraction column were originally described by *Van Dijck* [12]. The pulsed disc and doughnut solvent extraction columns are attractive from both safety and economic standpoints, in particular, its simplicity of design [13].

Benedetto et al. [14] investigated the separation of samarium and gadolinium by mixer-settlers in 16 stages. A comparative study on batch and continuous scale has been carried out with three extractants. *Takahashi et al.* [15] investigated the multistage extraction of samarium and gadolinium by means of a mixer-settler extraction column. Then the stage efficiency based on hydrodynamics and mass transfer within the column was studied. *Abdeltawab et al.* [16] studied the separation of La and Ce with PC88A from nitrate media by using a multistage counter-current mixer-settler extraction column in seven stages.

The recovery of Dy with 98% purity and Y with 93% purity from rare earth chloride solution with mixer-settlers in 20 stages has been reported [17]. *Liao et al.* [18] showed that the reciprocating extraction column is highly promising as an alternative of mixer-settlers in the extraction and separation of rare earth elements (Nd group/Sm group) with D2EHPA extract.

Pulsed disc and doughnut columns are representatives of the extraction column in which the discs and doughnuts are alternately arranged along the column equipped with a mechanically imposed pulsation. An installation of these columns to treat of uranium solutions from Western Mining Corporations in South Australia has shown that they have a clear advantage over the mixer-settlers [19,20]. The applications of such columns have rarely been referred to the literature for extraction of rare earth elements. Moreover, the knowledge concerning the design and performance of the pulsed disc and doughnut column is still far from satisfactory. To shed more light on the extraction behavior in these columns, it is necessary to understand properly the hydrodynamics and mass transfer characteristics. Determination of the mass transfer coefficient as one of the fundamental parameters is of great importance in an appropriate design. Accurate prediction of the volumetric mass transfer coefficient in extraction columns can help to find the optimal performance, economy, and safety of these industrial extraction columns [11].

There is no correlation available for prediction of mass transfer coefficient in the pulsed disc and doughnut column for extraction of rare earth elements. Thus, the objective of our work is to interpret the mass transfer performance of the column for extraction and separation of samarium from gadolinium.

The effects of pulsation intensity and dispersed and continuous phase velocities on the mass transfer coefficients, separation factors and stripping efficiencies were investigated. The axial diffusion model has been used to calculate overall mass transfer coefficients. The most commonly used equations were reviewed in line with the mass transfer coefficient prediction. An empirical correlation for prediction of the overall dispersed phase mass transfer coefficients is derived in terms of the Reynolds, dispersed phase holdup and Eötvös number. The calculated values of mass transfer coefficient from the previous equations and proposed equation are compared with the experimental data.

Previous work

Mass transfer in the dispersed phase is generally affected by a combination of molecular diffusion and natural/forced convection within the drop. A large number of equations have been proposed for calculation of the overall mass transfer coefficient of dispersed phase. These equations usually have been based on three mechanism models as follows:

Gröber [21] presented the following equation for molecular diffusion in stagnant drops.

$$K_{od} = -\frac{d}{6t} \ln \left[6 \sum_{n=1}^{\infty} B_n \exp \left(-\frac{4\lambda_n^2 D_d t}{d^2} \right) \right] \quad (1)$$

This model expanded by *Kronig & Brink* [22] to account for laminar circulation within drops with molecular diffusion is presented as follows:

$$K_{od} = \frac{d}{6t} \ln \left[\frac{3}{8} \sum_{n=1}^{\infty} B_n^2 \exp \left(-\frac{64\lambda_n^2 D_d t}{d^2} \right) \right] \quad (2)$$

Where β_n and λ_n are determined by *Elzinga & Banhero* [11].

Handles & Baron [23] presented another form of correlation for calculation of dispersed phase mass transfer coefficient by accounting for turbulent

circulation with eddy diffusion according to the equation given below:

$$K_{od} = \frac{d}{6t} \ln \left[6 \sum_{n=1}^{\infty} B_n^2 \exp \left(-\frac{\lambda_n V_t t}{128d(1+\kappa)} \right) \right] \quad (3)$$

The resulting equation for long contact times shows that K_{od} is independent of the molecular diffusivity.

$$K_{od} = \frac{0.00375 \times V_s}{1 + (\mu_d/\mu_c)} \quad (4)$$

Where V_s is the steady state slip velocity between the phases.

Many researchers attributed the experimentally observed high mass transfer coefficient values to the turbulent conditions of the drop and adopted the eddy diffusivity approach to quantify that impact.

The equation for effective diffusivities or enhancement factor applicable in the rigid drop model is obtained by an empirical combination of molecular diffusivity and an equivalent diffusivity. *Johnson & Hamielec* [24] studied the transfer of ethyl acetate to vigorously circulating water drops. The resulting expression for mass transfer coefficients is given by the following equation:

$$K_{od} = -\frac{d}{6t} \ln \left[6 \sum_{n=1}^{\infty} B_n \exp \left(-\frac{4\lambda_n^2 R D_d t}{d^2} \right) \right] \quad (5)$$

In their experiment, they considered only the first term of the series in the above equation and determined the R -value, as follows:

$$R = \frac{dV_t}{2048D_d(1+\kappa)} \quad (6)$$

Several correlations for estimating the enhancement factor (or effective diffusivity) in single drop systems and different types of extraction columns can be found in the literature. These correlations are listed in Table 1.

EXPERIMENTAL SECTION

Reagents

The commercial extractant, 2-ethylhexyl phosphoric acid (D2EHPA) was supplied from Aldrich. This extractant was dissolved in kerosene to achieve the required concentration. The stock standard solutions

Table 1: Previous correlations for estimation of enhancement factor, effective diffusivity and dispersed phase mass transfer coefficient in single drop systems and different types of extraction columns.

Investigator	Correlations	Comment
Calderbank and Korchinski [25]	$K_{od} = -\left(\frac{d}{6t}\right) \ln \left[1 - \left\{ 1 - \exp\left(-\frac{4\pi^2 RD_d t}{d^2}\right) \right\}^{\frac{1}{2}} \right] \quad (7)$	Single drop system
Skelland and Welke [26]	$\frac{K_{od} d}{D_d} = 31.4 \left(\frac{4D_d t}{d^2}\right)^{-0.338} \left(\frac{dV_t^2 \rho_c}{\sigma}\right)^{-0.338} Sc_d^{-0.125} \quad (8)$	Single drop system
Lochiel and Calderbank [27]	$R = 1 + \left[dV_t / 2048(1 + \kappa) D_d \right] \left\{ 1 - \left[\frac{(2 + 3\kappa)}{1 + (\mu_d \rho_d / \mu_c \rho_c)} \right] \frac{1.45}{Re^{0.5}} \right\} \quad (9)$	Single drop system
Boyadzhiev et al. [28]	$R = 0.003 \left(\frac{\rho_c dV_t}{\mu_c} \right) \left[1 / (1 + \kappa) \right]^2 \quad (10)$	Single drop system
Steiner [29]	$R = 1 + 0.177 Re^{0.43} Sc_d^{0.23} \left[1 / (1 + \kappa) \right]^2 \quad (11)$	Single drop system
Temos et al. [30]	$RD_d = D_d + 0.44D_E \quad (12)$ $\rho_d D_E / \mu_d = 3.29 \times 10^{-4} \left(\rho_d dU_i / \mu_d \right) \left[1 - \exp\left(-3.29 \times \rho_d dU_i / \mu_d\right) \right]$ $U_i = \left\{ 1 - \left[\frac{(2 - 3\kappa)}{1 + (\mu_d \rho_d / \mu_c \rho_c)^{0.5}} \right] \frac{1.45}{Re^{0.5}} \right\} V_t$	Single drop system
Kumar and Hartland [31]	$\frac{K_{od} d}{D_d} = 17.7 + \frac{3019 \times 10^{-3} \left(Re Sc_d^{\frac{1}{3}} \right)^{1.7}}{1 + 1.43 \times 10^{-2} \left(Re Sc_d^{\frac{1}{3}} \right)^{0.7}} \times \left(\frac{\rho_d}{\rho_c} \right)^{\frac{2}{3}} \times \frac{1}{1 + \kappa^{2/3}} \left\{ 1 + C_2 \left\{ \frac{\psi}{g} \left(\frac{\rho_c}{g\sigma} \right)^{1/4} \right\}^{n_2} \right\} \quad (13)$	Pulsed, Karr, Kühni, RDC Column
Bahmanyar et al. [32]	$RD_d = 4.5151 \times 10^{-9} \exp(0.0067 Re) \quad (14)$	Pulsed sieve plate column
Torab-Mostaedi and Safdari [33]	$R = -2.57 + 1326.07 Re^{0.5} Sc_c^{-0.94} (1 + \kappa)^{-0.8} \quad (15)$	Pulsed packed column
Amanabadi et al. [34]	$RD_d = 0.4755 \times 10^{-9} Re^{0.65} \quad (16)$	Rotating Disc Column
Torab-Mostaedi et al. [35]	$R = 5.33 + 97.97 Re^{-0.13} (1 - \phi) E_o^{-0.92} \quad (17)$	Pulsed sieve plate column
Torab-Mostaedi et al. [36]	$R = -11.86 + 63.38 Re^{-0.237} (1 - \phi) E_o^{-0.3} \quad d \rightarrow c \text{ transfer} \quad (18)$ $R = -13.33 + 36.69 Re^{-0.135} (1 - \phi) E_o^{-0.16} \quad c \rightarrow d \text{ transfer} \quad (19)$	Disc and Doughnut Column

were prepared by diluting gadolinium and samarium nitrate hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Middle East Ferro Alloy Company, 99.9% purity) in deionized water. The initial concentrations of two metals in aqueous nitrate media were maintained at 500 mg/L.

The pulsed disc and doughnut column experiments

The batch experiments were carried out for determination of effective parameters in the extraction of samarium and gadolinium with D2EHPA extractant. The results were reported in the previous works [37-39].

The continuous experiments were performed at room temperature in a pilot plant by the pulsed disc and doughnut column extraction. The continuous phase was fed at the top of the column to flow counter-currently in the dispersed phase fed at the bottom. The schematic arrangement of column and auxiliary equipment is shown diagrammatically in Fig. 1.

In extraction experiments, the nitrate solution of samarium and gadolinium with 500 mg/L concentration was prepared for continuous phase. The dispersed phase organic solution contained 0.12 M D2EHPA extractant diluted with kerosene.

In stripping experiments, the nitrate solution with 0.1 M concentration was prepared for continuous phase. The loaded organic phase of samarium and gadolinium with 500 mg/L concentration was used for the dispersed phase organic solution.

The values for the concentration of D2EHPA, initial aqueous pH, a nitric acid agent in stripping stage were selected based on the result of the batch experiments.

The main column section comprised a 76 mm internal diameter glass tube and the effective height of the column was 74 cm. The column was divided into 30 pairs of disc and doughnut made of stainless steel with a thickness of 2 mm.

The discs and doughnuts were arranged alternately and spaced 10 mm apart which resulting in a 20 mm compartment height; the structure was held in place by means of three tie rods (3.2 mm O.D.) with SS spacer sleeves. The discs and doughnut apertures were 67 and 36 mm in diameter, respectively. The open free area was obtained 23.5% based on this arrangement.

Two settlers with 112 mm diameter at each end of the column permitted the liquids to coalesce and decant separately. Pulsation was applied by compressed air at the

required amplitude and frequency to the pulse leg. The frequency of the pulses was controlled using two solenoid valves while the air pressure was controlled by a regulator to provide pulses of the required amplitude.

The flow rates of the organic and liquid phases were controlled by two rotameters. The inlet and outlet of the column were connected to four tanks, each of 80 L capacity. The liquid-liquid interface was maintained approximately 250 mm above the top compartment by using an optical sensor. A solenoid valve was installed in the outlet streamline of the heavy phase. When the interface location was going to vary, the optical sensor sent a signal to the solenoid valve and the aqueous phase was allowed to leave the column by opening the diaphragm of the solenoid valve. Consequently, the organic phase was allowed to leave the column with overflow.

The holdup of dispersed phase was measured by shutdown method, the pulsation was turned off and the inlet and outlet flows were stopped simultaneously after reaching the steady state. The dispersion then coalesced at the interface and the holdup was then measured by determining the change of interfacial height.

The Sauter mean drop diameters (d_{32}) were determined by photographing drops with a Nikon D5000 digital camera. The dimensions of drops were then determined using AutoCAD software and were compared with reference size inside the column such as disc and doughnut thickness and spacing. At least 500 drops were analyzed from each photo. The Sauter mean drop diameter is obtained by using the following equation:

$$d_{32} = \frac{\sum_{i=0}^n n_i d_i^3}{\sum_{i=0}^n n_i d_i^2} \quad (20)$$

Where n_i is the number of droplets of mean diameter d_i within a narrow size range i . In the case of non-spherical droplets, the major and axes, d_1 and d_2 were measured and the equivalent diameter, d_e , was calculated from Eq. (21):

$$d_e = \left(d_1^2 d_2 \right)^{1/3} \quad (21)$$

The amount of gadolinium and samarium transferred to the organic phase in the outlet column was estimated

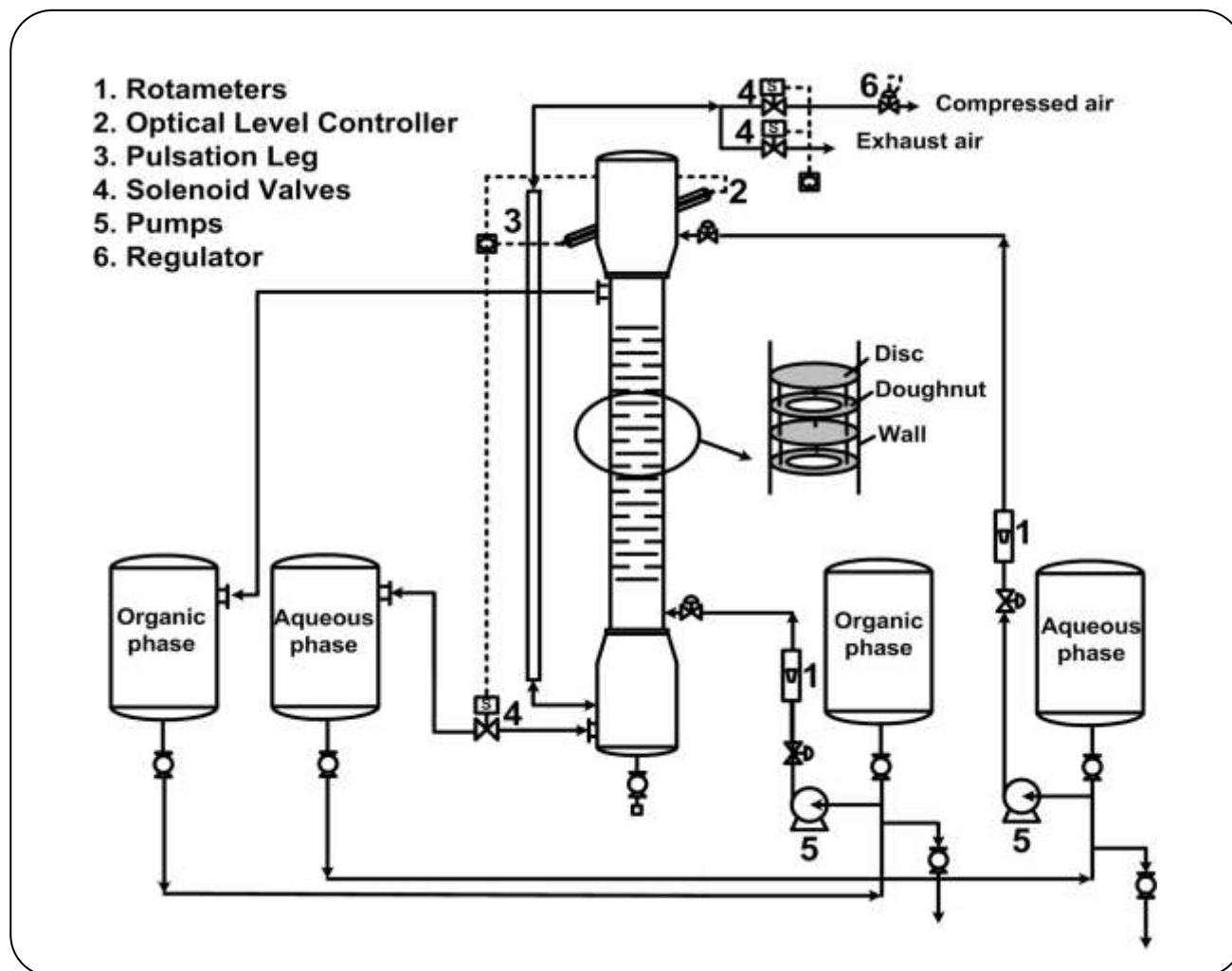


Fig. 1: Schematic flow diagram of pulsed disc and doughnut column.

after stripping with 3 M HNO₃; so that the gadolinium and samarium concentrations in the inlet and outlet phases were analyzed by using a Perkin-Elmer model 5500 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The distribution coefficient ($D_{distribution}$), separation factor (β) and stripping efficiency (S) are determined as follows:

$$D_{distribution} = \frac{|M|_t - |M|_a}{|M|_a} \quad (22)$$

$$\beta = \frac{D_1}{D_2} \quad (23)$$

$$\%S = \frac{[M]_{aq,a} V_{aq}}{[M]_{org,o} V_{org} + [M]_{aq,a} V_{aq}} \times 100 \quad (24)$$

Where $[M]_i$ and $[M]_a$ express the initial and final concentrations of metal ions in the aqueous phase, D_1 and D_2 are the distribution coefficients for Gadolinium and Samarium in extraction experiments. V_{aq} and V_{org} are the volumes of the aqueous and organic phases, $[M]_{aq,a}$ is the equilibrium concentration of metal ion in the stripping acid and $[M]_{org,o}$ is the equilibrium concentration of metal ion in the loaded organic phase, respectively.

The densities of the aqueous and the organic phases were determined by the pycnometer method. The interfacial tension measurements were obtained with a Krüss tensiometer. The viscosity of both phases was measured with DVI-Prime viscometer. Table 2 lists the physical properties of the two phases. In this table, D_c and D_d represent the samarium or gadolinium diffusivities in the continuous and dispersed phases estimated by *Wilke & Chang* [40] equation.

Table 2: Physical properties of the phases used in the system, at 25 °C.

Physical properties	Values
ρ_c (kg/m ³)	1003-1005
ρ_d (kg/m ³)	786-789
$\mu_d \times 10^3$ (Pa.s)	0.9216-0.9301
$\mu_c \times 10^3$ (Pa.s)	1.2501-1.2587
$\sigma \times 10^3$ (N/m)	22.5
$D_c \times 10^{10}$ (m ² /s)-Samarium	7.6841
$D_c \times 10^{10}$ (m ² /s)-Gadolinium	7.4205
$D_d \times 10^{10}$ (m ² /s)-Samarium	2.0755
$D_d \times 10^{10}$ (m ² /s)-Gadolinium	2.0871

Mathematical modeling

Samarium and gadolinium are extracted into the solvent phase by reaction with D2EHPA at the drop/aqueous phase interface [41]. The formatted soluble complex then diffuses into the solvent phase. The reactive extraction of rare earth ions with D2EHPA reagent are so rapid that the process may be classified as purely diffusion-controlled. The axial dispersion model was selected for simulating the mass transfer in the present study. The equations of this model for dispersed and continuous phases can be written as:

$$E_c \frac{d^2 c_c}{dz^2} - \frac{Q_c}{S} \frac{dc_c}{dz} - aK_{oc} (c_c - c_{c,eq}) = 0 \quad (25)$$

$$E_d \frac{d^2 c_d}{dz^2} + \frac{Q_d}{S} \frac{dc_d}{dz} + aK_{oc} (c_c - c_{c,eq}) = 0 \quad (26)$$

The three boundary conditions are as follows:

At the top of the column ($z=0$):

$$-E_c \frac{dc_c}{dz} + \frac{Q_c}{S} c_c = \frac{Q_c}{S} c_{co} \quad (27)$$

At the bottom of the column ($z=L$):

$$-E_d \frac{dc_d}{dz} + \frac{Q_d}{S} c_d = \frac{Q_d}{S} c_{do} \quad (28)$$

$$\frac{dc_c}{dz} = 0 \quad (29)$$

In these equations, c_c and c_d are samarium or gadolinium in the aqueous and organic phases, $c_{c,eq}$ is the

aqueous phase solute concentration in equilibrium with the organic phase, S is the cross sectional column area, Q_c and Q_d are the aqueous and organic phases volumetric flow rates, E_c and E_d represent the continuous and dispersed phases of axial mixing coefficients, respectively, a is the specific interfacial area obtained by Eq. (30) and K_{oc} is the overall mass transfer coefficient of the continuous phase.

$$a = \frac{6\phi}{d_{32}} \quad (30)$$

In this equation, d_{32} represents the Sauter mean diameter of dispersed phase drops and ϕ denotes the dispersed phase holdup.

In the present study, E_d was assumed to be negligible, E_c was estimated by the following correlation given by *Yue-yun et al.* [42]:

$$E_c = 0.026\phi^{-0.92} H^{-0.45} A^{1.13} f^{0.98} \quad (31)$$

The differential equations were solved numerically by the central finite difference method. The value of K_{oc} was obtained by minimizing an objective function defined as:

$$\text{error} = \sum (c_{c,\text{calculation}} - c_{c,\text{experimental}})^2 \quad (32)$$

The dispersed phase overall mass transfer coefficients (K_{od}) are then calculated by the following equation:

$$\frac{1}{mK_{od}} = \frac{1}{K_{oc}} \quad (33)$$

The m represents the samarium and gadolinium distribution ratio between the aqueous and the organic phases at the equilibrium.

RESULTS AND DISCUSSION

The operating parameters such as pulsation intensity, dispersed phase, and continuous phase velocities varied to investigate the effect of these parameters on mass transfer coefficients, separation factors and stripping efficiencies in extraction and stripping stages.

The pulsed disc and doughnut extraction column can operate in three different flow regimes such as mixer-settler, dispersion, and emulsion, depending on the pulse intensity. The preliminary tests in the pulsed disc and doughnut column were carried out by utilizing different pulse intensities. The different flow regimes were created

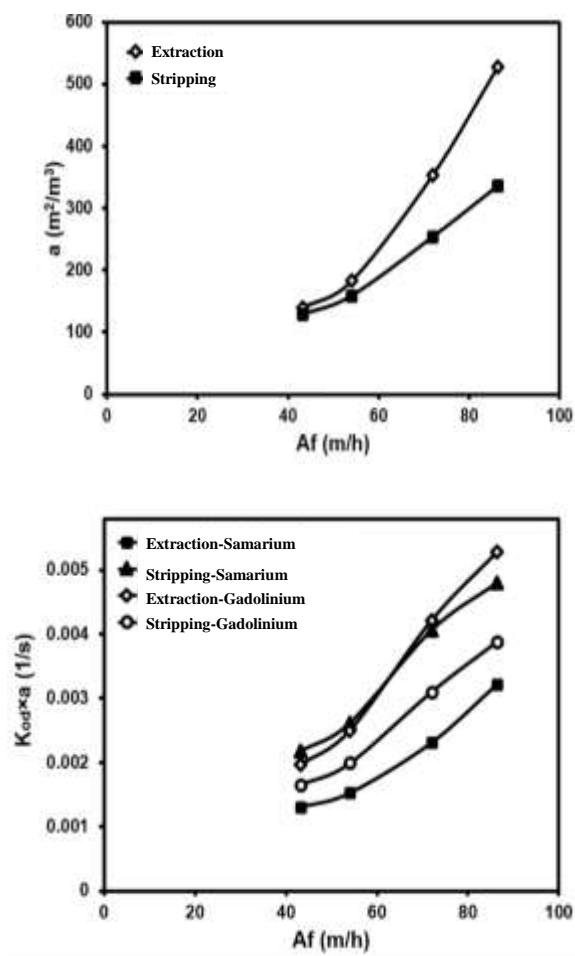


Fig. 2: Effect of pulsation intensity on the interfacial area and volumetric overall mass transfer coefficient ($V_c = V_d = 3.97$ m/h).

on the column depending on the use of A and f. Thus, values for Af leading to the dispersion regime were selected since the main concern of this study was to determine the column performance under industrial operating condition.

Mass transfer performance of pulsed disc and doughnut column

The effect of pulsation intensity on the interfacial area and volumetric overall mass transfer coefficients for samarium and gadolinium in the extraction and stripping stages is shown in Fig.2. As expected, the rise of the pulsation intensity leads to intense drop breaking and the lower value of the Sauter-mean drop diameter.

In addition, the values of holdup increase with a decrease in relative velocity between the dispersed and

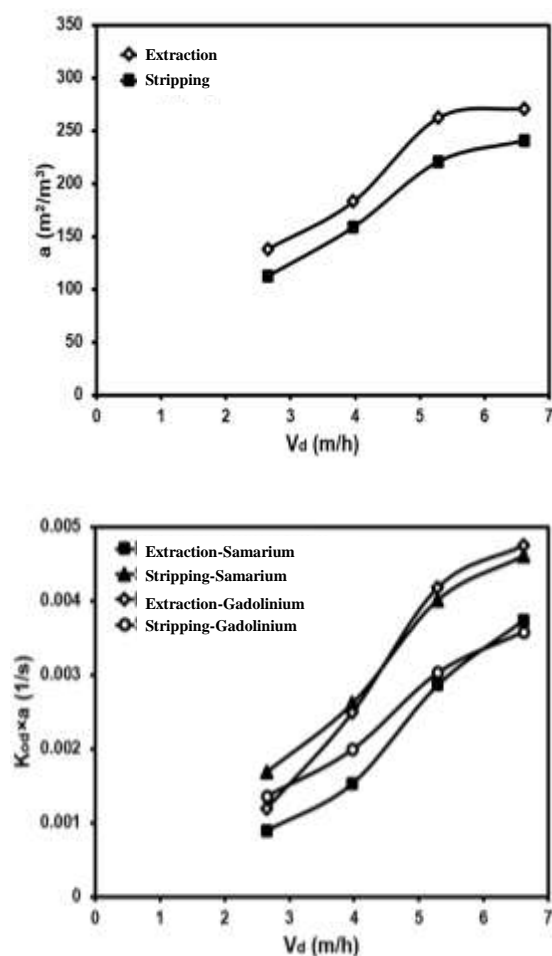


Fig. 3: Effect of dispersed phase velocity on the interfacial area and volumetric overall mass transfer coefficient ($V_c = 3.97$ m/h, $A_f = 54$ m/h).

continuous phases. So it can be concluded that the value of interfacial area increases with both effects. The decrease of drop size leads to a reduction of internal circulation and turbulence in the drops and the higher pulsation intensity results in a reduction in the overall dispersed mass transfer coefficient.

The results show that the effect of interfacial area on the mass transfer performance is larger than that of mass transfer coefficient and consequently, the column performance increases with an increase in pulsation intensity. Fig. 3 shows the variation of volumetric mass transfer coefficients along the pulsed disc and doughnut column, highlighting the effect of the dispersed phase velocity on the column performance. The drop size, hold up and volumetric overall mass transfer coefficient increase with an increase in dispersed phase velocity for

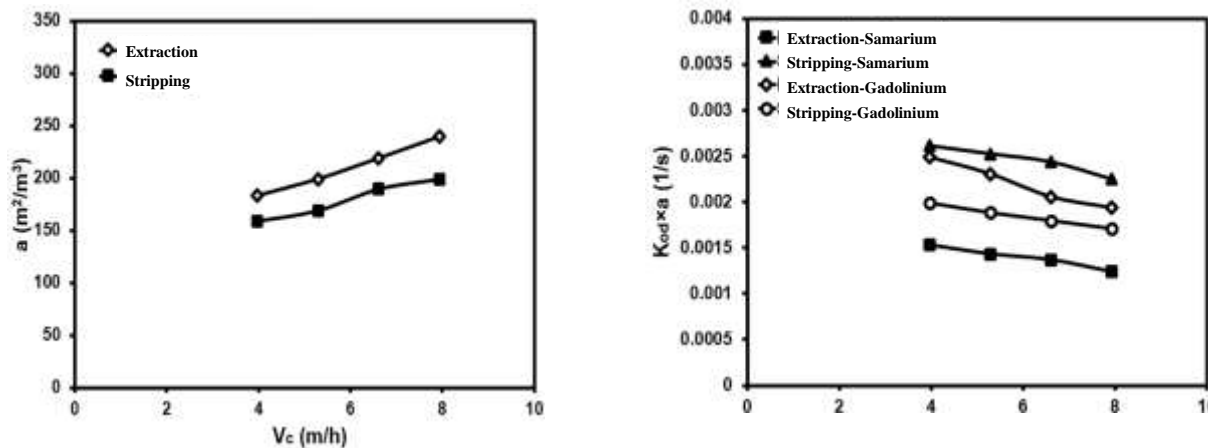


Fig. 4: Effect of continuous phase velocity on the interfacial area and volumetric overall mass transfer coefficient ($V_d=3.97$ m/h, $A_f=54$ m/h).

extraction and stripping stages. The effect of the holdup on interfacial area is larger than that of drop size and consequently, interfacial area increases with an increase in dispersed phase velocity.

The effect of continuous phase velocities on the interfacial area and volumetric overall mass transfer coefficients is given in Fig. 4. The dispersed phase holdup increases with an increase in continuous phase velocity due to an increase of the drag forces and a decrease of slip velocities between the drops and the continuous phase. Moreover, the experiments showed that mean drop size varies slightly with continuous phase velocity. Consequently, the interfacial area increases with an increase in continuous phase velocities. It is also observed that the overall mass transfer coefficient decreases with an increase in continuous phase velocities. The effect of overall mass transfer coefficient is more significant than interfacial area. So, the column performance decreases with an increase in continuous phase velocity in extraction and stripping stages.

Prediction of the overall dispersed phase mass transfer coefficient

The experimental results for the dispersed phase overall mass transfer coefficient in the extraction and stripping stages are compared with the previous models are shown in Figs. 5 and 6. As seen in these figures, the equations obtained for single drop systems and mechanical extraction columns show considerable deviation

from the experimental results, because, in the extraction and stripping stages, as the reaction occurs between the drops and continuous phase at the interface, the formatted complex diffuses from the interface to the aqueous or organic phase depending upon the direction of mass transfer. This matter of mass transfer with chemical reaction is not studied in the previous equations.

The values of the Average Absolute Relative Error (AARE) of the predicted values of the overall dispersed phase mass coefficient obtained by the previous models (Eqs. (1) to (19)) with the experimental results are listed in Table 3.

It is observed that these models do not have enough accuracy for the design of pulsed disc and doughnut column. For this reason, it is of paramount importance to derive a new correlation for prediction of overall dispersed mass transfer coefficient for extraction of samarium and gadolinium. So, experimental data of dispersed phase overall mass transfer coefficients were used in Eq. (5) to determine the enhancement factor (R). The following equation is derived in terms of dispersed phase holdup, Reynolds, and Eötvös number by using the least squares method.

$$R = -14.9 + 41.1(1-\phi)^{-0.95} Re^{-0.158} Eo^{-0.31} \quad (34)$$

for extraction stage

$$R = -11.68 + 34.67(1-\phi)^{-0.95} Re^{-0.161} Eo^{-0.209} \quad (35)$$

For stripping stage

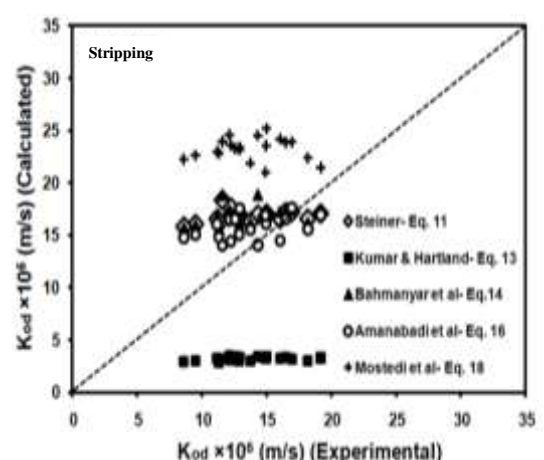
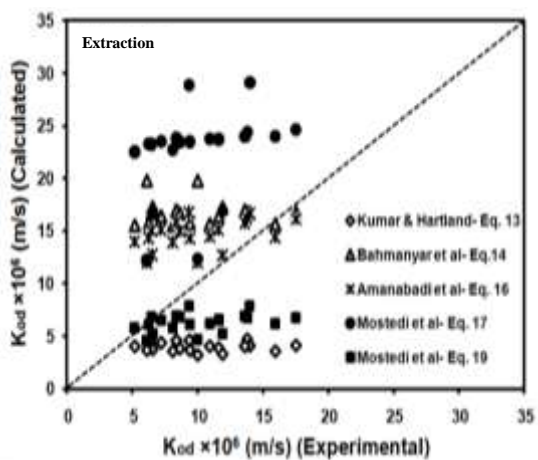
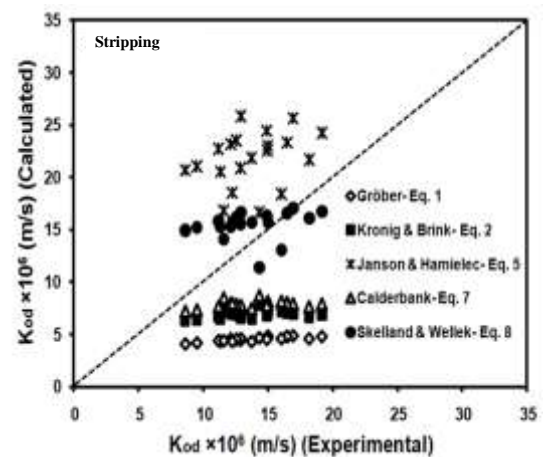
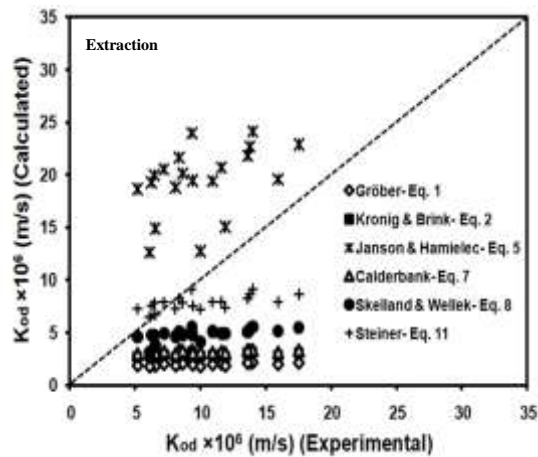


Fig. 5: Comparison of the values calculated previous models with experimental results in extraction stage.

Fig. 6: Comparison of the values calculated previous models with experimental results in stripping stage.

where

$$Re = \frac{\rho_c V_s d_{32}}{\mu_c} \quad (36)$$

$$E_o = \frac{g \Delta \rho d_{32}^2}{\sigma} \quad (37)$$

$$V_s = \frac{V_d}{\phi} + \frac{V_c}{(1-\phi)} \quad (38)$$

Where V_s is the slip velocity between the two phases through the column.

The comparison of calculated values by applying Eqs. (5), (34) or (35) with experimental results is shown in Fig. 7. It is observed that the experimental data are in good agreement with calculated values and the present

model estimates experimental results with an average relative error of 9.68%.

Effect of operating conditions on separation factors and stripping efficiencies

The effect of operating conditions on the extraction and separation of Sm (III) from Gd (III) was studied. The results are shown in Table 4.

It is observed that the separation factors and stripping percent increase with an increase in dispersed phase velocities and pulsation intensities. So, from the experimental data, it concluded that the separation of the two metals can be improved using high pulsation the intensity and high dispersed phase velocity. The maximum separation factor was equal to 4.3 when the values of A_f , V_c and V_d were 1.5 cm/s, 1.102 and 1.102 mm/s,

Table 3: The values of AARE in the previous models of overall mass transfer coefficient with the experimental results.

Stage	Gröber Eq. (1)	Kronig & Brink Eq. (2)	Handlos & Baron Eq. (3)	Janson & Hamielec Eq. (5)	Calderbank & Korchinski Eq. (7)	Skelland & Wellek Eq. (8)
Extraction	78.49	68.29	619.87	112.15	64.69	47.94
Stripping	66.23	48.87	495.07	64.28	41.45	22.03
Stage	Steiner Eq. (11)	Kumar & Hartland Eq. (13)	Bahmanyar et al. Eq. (14)	Amanabadi et al Eq. (16)	Torab-Mostaedi et al. Eq. (17)	Torab-Mostaedi et al Eq. (18) and (19)
Extraction	23.39	55.82	84.34	61.52	32.64	142.32
Stripping	27.49	75.99	28.82	21.62	74.34	539.71

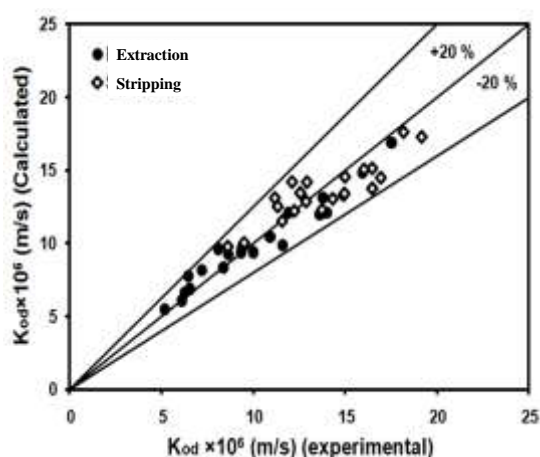


Fig. 7: Comparison between experimental data and the proposed equations (34) and (35).

respectively. This value of β was higher than the reported value by *Benedetto et al.* [4] in mixer-settlers. In the same conditions, samarium and gadolinium reached the maximum stripping percent values of 95.5 and 52.7, respectively.

The hydrodynamic conditions such as flow rates and pulse intensity in disc and doughnut column lead to an increase in back extraction reaction rate for samarium in comparison with gadolinium. The Sm-D2EHPA complex was weaker than Gd-D2EHPA complex and its complex is easier to be broken than Gd-D2EHPA complex. Therefore, the high stripping percent $> 95.5\%$ for samarium is achieved in stripping stage with disc and doughnut column.

The increase in the separation factors and the decrease in stripping percent with an increase in the continuous phase velocity is observed from Table 4. The effect of

continuous phase velocity showed slight improvement with respect to metal selectivity. This behavior is related to the direction of mass transfer and reaction rate. In extraction stage, the forward reaction rate was faster than backward reaction rate. The turbulence of continuous phase around droplets increases with continuous phase velocity and this effect helps to increase the rate of mass transfer and separation factors. In stripping stage, the slow backward reaction rate is more effective than the turbulence of continuous phase and it leads to the decrease in stripping percent for samarium and gadolinium.

The results show that the highly promising pulsed disc and doughnut column can be viewed as an alternative for mixer-settlers in regards to save space and reduce energy cost in rare earth extraction and separation procedures.

CONCLUSIONS

The experiments in pulsed disc and doughnut column allowed a better understanding of the effective operating conditions on mass transfer performance and separation of the two metals. A comparative evaluation of the previous models was carried out to predict the overall dispersed phase mass transfer coefficients. The deviation of the experimental results from the calculated values is due to a chemical reaction that has not been investigated in previous studies. An empirical correlation to predict the overall mass transfer coefficients has been developed based on the experimental data and evaluated values predicted by the proposed correlation are in good compatibility with the experimental results.

The results of separation factors and stripping efficiencies in the pulsed disc and doughnut column,

Fig. 4: Effect of operating conditions on separation factors and stripping efficiencies.

Parameters	Af (cm/s)	V _d (mm/s)	V _c (mm/s)	[Gd] _{aq} ppm	[Sm] _{aq} ppm	D ₁ for gadolinium	D ₂ for Samarium	β	Stripping Efficiency (%)	
									Sm	Gd
V _d	1.5	0.735	1.102	308.6	179.98	1.78	0.62	2.87	54.02	31.48
	1.5	1.102	1.102	352.44	221.92	1.25	0.42	2.99	64.64	35.48
	1.5	1.469	1.102	421.98	313.28	0.60	0.18	3.22	77.56	37.02
	1.5	1.837	1.102	486.42	448.87	0.11	0.03	4.08	89.64	46.36
V _c	1.5	1.102	0.735	352.44	221.92	1.25	0.42	2.99	64.64	35.48
	1.5	1.102	1.102	382.84	254.08	0.97	0.31	3.16	60.26	25.56
	1.5	1.102	1.469	373.04	239.91	1.08	0.34	3.19	55.66	20.16
	1.5	1.102	1.837	349.35	202.71	1.47	0.43	3.4	42.66	13.81
Af	1.2	1.102	1.102	336.36	236.11	1.12	0.49	2.3	41.18	18.66
	1.5	1.102	1.102	352.44	221.92	1.25	0.42	2.99	64.64	35.48
	2	1.102	1.102	416.56	282.85	0.77	0.20	3.83	93.98	41.98
	2.4	1.102	1.102	440.05	320.72	0.56	0.14	4.3	95.48	52.68

showed the feasibility of the column for rare earth separations, with a separation factor of 4.3 and stripping efficiencies of 95.5 % and 52.7 % for Sm (III) and Gd (III), respectively.

V_s Slip velocity, m/s
 %S Stripping efficiency
 V Superficial velocity, m/s
 V_t Terminal velocity, m/s
 t Time, s

Nomenclature

g Acceleration due to gravity, m/s²
 A Amplitude of pulsation, cm
 E Axial mixing coefficient, m²/s
 S Cross section area, m²
 D_{distribution} Distribution coefficient
 m Distribution ratio
 H Effective height of the column, m
 R Enhancement factor for mass transfer
 Eö Eötvös number = $g\Delta\rho d_{32}^2/\sigma$
 K_{eq} Equilibrium constant
 Q Flow rate of the continuous or dispersed phase, m³/s
 f Frequency of pulsation, 1/s
 a Interfacial area, m²/m³
 [M] Metal concentration, mol/L
 D_d Molecular diffusivity, m²/s
 B_n nth coefficient in equations (1-3)
 K Overall mass transfer coefficient, m/s
 Re Reynolds number
 d₃₂ Sauter mean drop diameter, m
 Sc Schmidt number

Greek Letters

ρ Density, kg/m³
 Δρ Density difference between phases, kg/m³
 φ Dispersed phase holdup
 σ Interfacial tension, N/m
 λ_n nth coefficient in equations (1-3)
 ψ Power dissipated per unit mass, m².s³
 β Separation factor
 μ Viscosity, Pa.s
 κ Viscosity ratio, μ_d/μ_c

Subscripts

c Continuous phase
 d Dispersed phase
 o Overall value

Superscripts

* Equilibrium value

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