

Mass Transfer Studies in Pulsed Sieve Plate Extraction Column for the Removal of Tributyl Phosphate from Aqueous Nitric Acid

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ABSTRACT: Removal of a saturated amount of tributyl phosphate (TBP) from a nuclear reprocessing aqueous waste stream is very important as far as economy of process as well as waste disposal is concerned. The present research work describes the detailed mass transfer studies for the removal of TBP from aqueous stream in a geometrically optimized pulsed sieve plate extraction column (PSPEC). The original industrial system, viz., 0.3 M nitric acid–TBP–normal paraffinic hydrocarbon (NPH), was used for the mass transfer studies. The effect of operating parameters such as continuous to dispersed phase velocity ratio and pulsed velocity on the volumetric mass transfer coefficient was investigated. The effect of operating parameters on the variation in axial concentration and holdup profile is also studied to evaluate the dynamic operation of the column for the attainment of steady state. The experimental results indicate that pulse velocity has a strong effect on the volumetric mass transfer coefficient, while the effect of the continuous phase flow rate is greater than the effect of the dispersed phase flow rate.

1. INTRODUCTION

The Plutonium/Uranium Refining by Extraction (PUREX) process consists of extraction and purification of uranium and plutonium using diluted tributyl phosphate (TBP) as an extractant¹ in pulsed sieve plate columns.² Typically, the separation of uranium and plutonium and other fission products from nitrate solutions from the spent nuclear reactor fuel is carried out by using 30% TBP (by volume) in a hydrocarbon diluent such as dodecane/kerosene/normal paraffinic hydrocarbon (NPH).³ During this operation, a small amount of TBP (150–400 ppm) depending upon the concentration of nitric acid is back-extracted and also entrained as an impurity in a new aqueous acid stream. The presence of traces of this organic compound (TBP) in the aqueous acidic stream can lead to violent reaction during evaporation of the solution leading to “red oil” formation and subsequently runaway reactions.⁴ Moreover, if the organic is used in certain scrubbing operations of the PUREX process, it is detrimental as there is a presence of residual uranium. Therefore, these traces of TBP from aqueous solution must be removed soon after the extraction cycle. The percentage of TBP in aqueous nitric acid is negligible; thus, one can recommend distillation as the separation method. However, TBP has a high boiling point (285 °C) and, moreover, the rate of hydrolysis of TBP increases with the HNO₃ concentration. Depending on the time of exposure to hydrolysis conditions, TBP hydrolyzes to monobutyl phosphate (MBP) and/or butanol and/or dibutyl phosphate (DBP) and/or phosphoric acid; further, this butanol can undergo nitrolysis or oxidation.⁵ The extraction is thus found to be a suitable tool for separation of traces of TBP from 0.3 M HNO₃.

Based on the method of dispersion of phases, equipments used for liquid–liquid extraction are broadly classified as gravity contactors, mechanically agitated contactors, pulse agitated contactors, etc. In spite of the fact that horizontal contactors and mixer–settler equipment are being developed, vertical columns are the preferred extractors. There is always insufficient turbulence in conventional vertical columns as the

energy for phase dispersion is provided by the density difference between the two phases.⁶ The pulse column is an outstanding example of an improvement of the vertical extraction column used for liquid–liquid contacting, invented by Van Dijk.⁷ The addition of a certain frequency pulse to a sieve plate column increases the extraction efficiency while maintaining a high column throughput, which makes it useful for a wide range of applications. Particularly, it finds application in extraction of radioactive and hazardous materials due to its insensitivity toward contamination of the interface and the absence of mechanical moving parts inside the column.⁸

Venkatanarasaiah and Varma⁹ reported that the mass transfer coefficient depends linearly on the drop size and consequently on the dispersed phase holdup, which is a function of the pulse velocity.¹⁰ Various attempts have been made for designing liquid–liquid extraction columns based on the laboratory-scale single-drop experiment.^{11–14} This approach primarily focuses on the determination of the overall mass transfer coefficient based on the dispersed phase drop formation, breakage, coalescence, and sedimentation. Many times, ReDrop^{15,16} and the drop population balance^{17,18} modeling approach have been used to arrive at the design of equipment.

Extensive studies have been reported in the literature covering mass transfer between different phases in a pulsed sieve plate extraction column (PSPEC) using different systems.^{19,20} Li et al.²¹ and Yu et al.²² studied mass transfer in a coalescence–dispersion pulsed sieve extraction column with a working system of 30% TBP (in kerosene)–nitric acid–water. Golding and Lee²³ carried out mass transfer studies for the extraction and separation of cobalt and nickel from aqueous solution by bis(2-ethylhexyl)phosphoric acid (10% D2EHPA in kerosene). The maximum advantage of a pulse column without

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much of the pilot plant studies can be brought about by much greater knowledge of the effects of the physical and chemical properties of both phases employed, and moreover, the dynamic effects under mass transfer conditions have to be well understood. Therefore, scale-up of the height of the column requires knowledge of the mass transfer coefficient variation with height or diffusing component concentration along the height of the column. This information along with its hydrodynamic properties has to be determined as part of engineering research for designing the column.²⁴

It is observed that only one attempt has been made so far, by Manohar et al.,²⁵ for the separation of TBP aqueous stream from the reprocessing origin and that was using a combined airlift based mixer-settler unit (CAL-MSU). However, there are no reports of mass transfer studies for the removal of the TBP in PSPEC. Therefore, the present study has been undertaken to carry out the mass transfer studies for the removal of TBP in PSPEC using the original industrial system, i.e., nitric acid–TBP–NPH system,²⁵ where an attempt has been made to find out the effects of operating parameters such as pulse velocity and superficial velocities of dispersed and continuous phases on the volumetric mass transfer coefficient. The transient axial holdup and concentration behavior plays an important role in relating complete dynamic mass transfer equations.²⁶ Therefore, the studies have also been carried out to identify the effect of operating parameters on the axial phase holdup and concentration variation with time and position in the column. The present study would be useful in the evaluation of the scale-up parameters for the design of the PSPEC.

2. MATERIALS AND METHODS

Nitric acid (HNO_3) and TBP were procured from T. A. Corp., Mumbai, India. Normal paraffinic hydrocarbon (NPH) was supplied by Eastern Petroleum Pvt. Ltd., Mumbai. Deionized (DI) water was used for the experimental study. The materials were used directly without any further purification. The detailed physical properties (viscosity, density, and interfacial tension) of the system components are tabulated in Table 1.

Table 1. Physical Properties of the System Components

system component	viscosity, $\text{Pa}\cdot\text{s} \times 10^2$	density, kg m^{-3}	interfacial tension, N m^{-1}
0.3 M HNO_3	0.109	1028	0.048
NPH	0.104	850	

2.1. Analytical Methods. High performance liquid chromatography (HPLC) and gas chromatography (GC) were used for the analysis of TBP in aqueous and organic phases, respectively. The detailed analysis method can be found in Bajoria et al.²⁷

2.2. Feed Preparation. The aqueous feed (continuous phase) was prepared by saturating 0.3 M nitric acid with TBP in a mixing tank. TBP was added in excess amount (1 L) to make the continuous phase saturated. The concentration of TBP was measured by withdrawing samples from the mixing tank intermittently, and when a concentration of about 160 ppm was achieved, the mixing was stopped with the assumption of homogeneity and excess TBP was separated. This aqueous phase was used for further experimental work.

2.3. Experimental Setup and Procedures. The experiments were carried out in the experimental setup (PSPEC)

shown in Figure 1. The PSPEC consisted of a vertical glass column having 0.076 m diameter and 1.0 m height with two

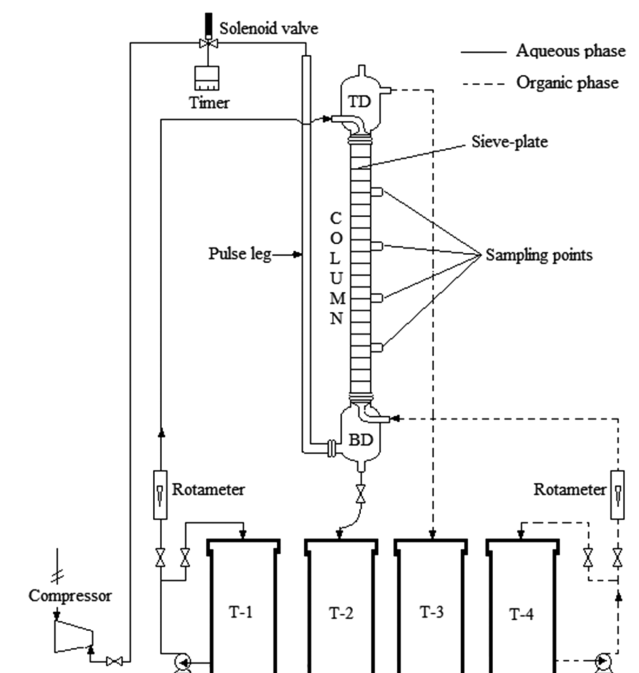


Figure 1. Schematic diagram representing the pulsed sieve plate extraction column (PSPEC). TD, top disengaging section; BD, bottom disengaging section; T1, aqueous phase inlet tank; T2, aqueous phase outlet tank; T3, organic phase outlet tank; T4, organic phase inlet tank.

glass disengaging sections of 0.152 m in diameter and 0.2 m in length, one each at the top and the bottom. The cartridge having 20 stainless steel plates and 20% free area with a perforation diameter of 0.003 m (which is most suitable for high capacity operation) is mounted on a 0.008 m diameter rod at the center of the column. The pneumatic pulsation was used as source of energy for this operation. A pulse leg of 0.0254 m diameter and 1.8 m in length was connected at the base of the bottom disengaging section for pulsing the continuous phase. Four sampling points were provided along the column height at 0.2, 0.4, 0.6, and 0.8 m, measured from the bottom of the column, for taking samples for concentration and holdup measurement.

The wetting characteristics of the plates play an important role in the design and operation of the sieve plate column.^{28,29} Since the column has stainless steel plates which are preferentially wetted by the aqueous phase, satisfactory operation can be achieved only with the aqueous phase as a continuous phase.³⁰ Hence, the aqueous continuous/heavy phase is fed into the top of the column and the organic dispersed/lighter immiscible phase is pumped into the bottom of the column at a certain flow rate by adjusting the predetermined rotameter setting. The surface tension of the aqueous phase will not allow it to fall or flow through the sieve plates by gravity. However, when pulsing is provided as per need by controlling the compressed air flow, the organic phase is pushed up through the holes and the aqueous phase is pulled down through the holes, and in turn droplets of both phases are formed. The pulse amplitude was checked manually by the extreme positions in the graduated pulse leg and thereby calculating that change in the column. The frequency was set at

1 Hz by an electronic timer. The interface level was set roughly midway in the top disengaging section, precisely staying in between the continuous phase inlet and the dispersed phase outlet.

2.4. Experimental Methods. The samples of aqueous phase were collected from the continuous phase outlet at the bottom of column after a 10 min interval to analyze the concentration of TBP in the continuous phase at steady state. The length of a run varied with the throughput and was roughly equal to the time required to attend the steady state (about 50 min), which was ensured by no change in the outlet concentration of the continuous phase. Once steady state was achieved, the stage samples were collected in a 50 mL measuring cylinder from the four sampling points provided along the height of the column. These samples were used to analyze the concentration variation along the height of the column and the stage holdup. The stage holdup along the height is measured by the volume fraction of the dispersed phase in the sample collected in the measuring cylinder. The concentrations at each stage are measured from each of the measuring cylinder by analysing these samples using HPLC. The steady state concentration at the top of the column is considered to be the concentration of TBP at sample collected at 1 m height of the column, whereas at bottom it is considered as 0 m.

Since the organic phase was the dispersed phase, at the top disengaging section the interface level dropped. Both inlet flows were shut off so as to stop the operation. Simultaneously, the pulsing was stopped and both phases were allowed to separate; continuous aqueous phase was fed to the column so that the interface would climb to the normal operating level. The interface was then returned to the operating position, and the organic phase overflow was collected in the 1 L cylinder and was taken as the overall holdup.

3. RESULT AND DISCUSSION

3.1. Mass Transfer Calculations. The PSPEC essentially operates as a stagewise device, whereas a spray column operation may be considered as differential. Significant back-mixing occurs in the PSPEC, because lower resistance to flow is offered even though the plates allow phase separation at each stage. The validity of the assumption of differential operation is reduced by stagewise operation. Moreover, representation by differentials would not present a true picture if the column operated with back-mixing, a phenomenon which effectively reduces the number of countercurrent theoretical stages (efficiency). Back-mixing is essentially a localized reversal of countercurrent flow to concurrent flow which tends to mix higher concentrations of a phase with lower concentrations of that phase. Since back-mixing would therefore tend to lower the driving force for mass transfer throughout the column, it would consequently tend to add the HTU and in turn decrease $K_{oc}a$.

The extraction efficiencies are expressed in terms of the overall volumetric mass transfer coefficient on the basis of continuous phase concentrations. The effective height for the mass transfer in the column can be considered to be equal to 1 m. The following relationships were used in expressing extraction efficiencies based on the aqueous phase. The total height of the column is given as

$$H = (NTU)_{oc}(HTU)_{oc} \quad (1)$$

$$(HTU)_{oc} = \frac{V_c}{K_{oc}a} \quad (2)$$

$$(NTU)_{oc} = \int_{C_2}^{C_1} \frac{dC}{C - C^*} \quad (3)$$

The simplified form of eq 3 is

$$(NTU)_{oc} = \frac{C_{c1} - C_{c2}}{\Delta C_{LM}} \quad (4)$$

where ΔC_{LM} is the log mean concentration difference based on the continuous phase which is calculated as follows:

$$(\Delta C)_{LM} = \frac{(C_{c1} - C_{c1}^*) - (C_{c2} - C_{c2}^*)}{\ln \frac{C_{c1} - C_{c1}^*}{C_{c2} - C_{c2}^*}} \quad (5)$$

The equilibrium concentrations were calculated from the equilibrium data represented by Bajoria et al.²⁷ The final form of eq 1 is given as

$$K_{oc}a = \frac{V_c(C_{c1} - C_{c2})}{H(\Delta C)_{LM}} \quad (6)$$

3.2. Effects of Operating Parameters on Dimensionless Outlet Continuous Phase Concentration Profile with Time.

The kinetics of continuous extraction of TBP in the countercurrent flow PSPEC is an important parameter which has to be checked to know the dynamic approach to the steady state. The steady state of operation is decided by the operating conditions, such as superficial velocities of the continuous phase and dispersed phase and the pulse velocity. The concentration profile can be used to evaluate the axial dispersion coefficient and the mass transfer coefficient by using various numerical methods.³¹

The general observation is that, at all operating conditions, the concentration of the continuous phase decreases with time due to the decrease in chemical potential between the continuous and dispersed phases, as result of continuous mass transfer from the continuous phase to the dispersed phase until steady state is achieved. The concentration of the aqueous phase was measured at 10 min time intervals at the continuous phase outlet. On the basis of those operating conditions, the steady state was achieved between 30 and 40 min. The effects of the continuous phase to dispersed phase velocity ratio and of the pulse velocity on the steady state outlet continuous phase concentration profile with time are observed and discussed in Figures 2 and 3.

3.2.1. Effect of Continuous to Dispersed Phase Superficial Velocity Ratio ($R = V_c/V_d$). The effect of the continuous to dispersed phase superficial velocity ratio on the concentration variation is observed and shown in Figure 2. At a constant pulse velocity of 0.025 m/s, when the continuous phase velocity is increased from 0.0025 m/s ($R = 1$) to 0.0075 m/s ($R = 3$), the time required for achieving the steady state is decreased from 40 to 30 min. Approach to the steady state is faster at the higher values of the phase velocity ratios. This is because at a higher phase velocity ratio the solute present at the initial period of time (until 30 min) is quite high and the lower dispersed phase velocity allows longer contact. It can be observed that, at $R = 3$, the approach to steady state is faster as compared to $R = 0.33$, but the mass transfer is being controlled.

The effect of the dispersed phase superficial velocity (0.0025, 0.005, and 0.0075 m/s, i.e., $R = 1, 0.5$, and 0.33 , respectively) at

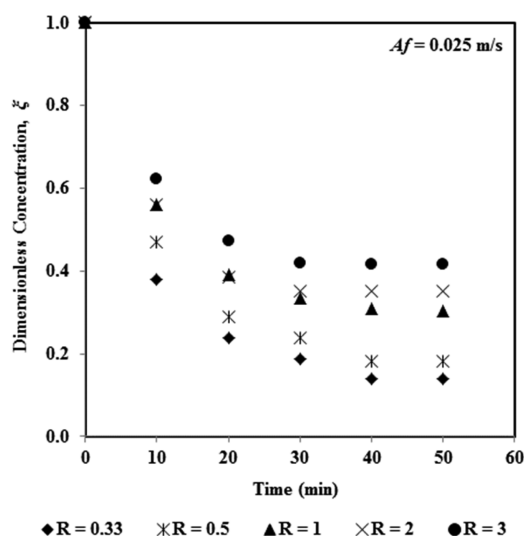


Figure 2. Effect of continuous to dispersed phase superficial velocity ratio ($R = V_c/V_d$) on the dimensionless outlet continuous phase concentration variation with time.

a constant pulse velocity of 0.025 m/s on the continuous phase dimensionless concentration profile is shown in Figure 2. An increase in the dispersed phase superficial velocity (from 0.0025 to 0.0075 m/s) increases the percent extraction of TBP (from 69.6 to 85.9%). This is because an increase in the dispersed phase velocity increases the dispersed phase holdup as result of large number of drops generated at constant pulse velocity. These drops find an oscillation and shear forces at the droplet surface.³² The residence time of the droplets is increased because of oscillation, which in turn helps to increase the mass transfer.³³ Therefore, it can be concluded that the dispersed phase velocity has a strong implication on the overall mass transfer but not on the approach to steady state.

With both effects taken together, it can be summarized that increase in the velocity ratio decreases the overall mass transfer. The lowest mass transfer (percent extraction) of 68.3% was observed at $R = 3$, whereas the highest of 85.9% was observed at $R = 0.33$.

3.2.2. Effect of Pulse Velocity (Af). The mass transfer experiments were performed for different pulse velocities (0.025–0.045 m/s) to study its effect on the concentration profile with time. An increase in pulse velocity decreases substantially the time for attaining steady state as shown in Figure 3. The overall effect of breakup, coalescence, sedimentation, and circulation of drops of dispersed phase which is prominent at higher pulse velocity enhances the mass transfer of TBP from aqueous phase to organic NPH.^{13,34,35} It can be clearly seen that the pulse velocity of 0.035 m/s overlaps at the exit end with the graph of 0.045 m/s. This is attributed to the formation of deformed droplets which in turn form circulating drops of dispersed phase at 0.045 m/s which give the higher mass transfer.³³ This fact can also be extended to the faster approach of steady state at 0.045 m/s (87% extraction). Similarly, there is a higher initial rate of extraction and a higher steady state percent extraction is achieved at 0.035 m/s (85.7%). It can also be observed that, at 0.045 m/s pulse velocity, the steady state (at 30 min) concentration is 20 ppm, but at 20 min, the concentration of TBP is just more than steady state, i.e., 23 ppm. It was evident from visual observation that, at low values of pulse velocity (0.025 m/s), mixer–settler

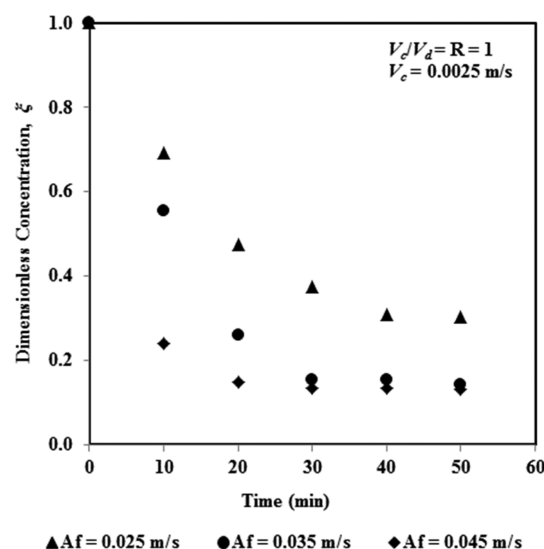


Figure 3. Effect of pulse velocity on the dimensionless outlet continuous phase concentration variation with time.

conditions prevailed under which each phase in turn was forced either up or down through the other, and then settled out below or above the following plate. At higher values of pulse velocity (≥ 0.035), emulsion regime prevailed, which has high mass transfer rates as the drop size is smaller.

3.3. Effects of Operating Parameters on the Steady State Dimensionless Concentration Profile along the Height of Column. The effects of the continuous to dispersed phase superficial velocity ratio and of the pulse velocity on the steady state dimensionless concentration profile along the height of the column are observed and reported in Figures 4 and 5, respectively. Smoot and Babb³⁶ experimentally found the longitudinal concentration profile for evaluation of the mass transfer of a dilute solute from organic to aqueous phases in a 2 in. i.d. PSPEC using the systems methyl isobutyl ketone–acetic acid–water and 1,1,2-trichloroethane–acetone–water. They also studied the effect of operating variables on the longitudinal solute concentration gradients. The mass transfer is enhanced by the overall effect of counterflow of the continuous phase through the holes and the shearing and breakup of drops as they pass through them.¹² The continuous phase travels along the column height from the top to the bottom part of the column whereby transferring TBP to the organic phase at each plate. Moreover, at the bottom of the column, fresh dispersed phase (NPH) is being supplied which gives a higher concentration gradient and hence the concentration varies along the height of the column. It was observed that, at all operating conditions, the concentration of the continuous phase decreased as it moved from the top to the bottom of the column due to the continuous mass transfer of TBP from the continuous phase to the dispersed phase.

3.3.1. Effect of Continuous to Dispersed Phase Superficial Velocity Ratio ($R = V_c/V_d$). The effect of the continuous to dispersed phase superficial velocity ratio (R) on the variation of concentration along the height of the column is depicted in Figure 4 and discussed in two parts. First is the effect of the dispersed phase velocity (0.0025–0.0075 m/s, i.e., $R = 1$ –0.33) at constant continuous phase velocity (0.0025 m/s) and pulse velocity (0.025 m/s). With an increase in the dispersed phase superficial velocity from 0.0025 to 0.0075 m/s, the percentage extraction of TBP from aqueous feed is increased from 69.6 to

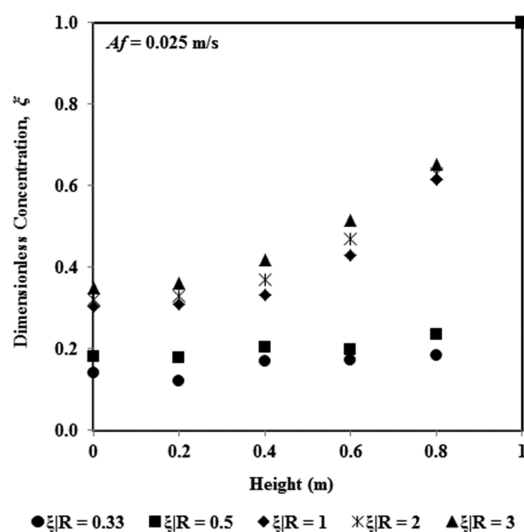


Figure 4. Effect of continuous to dispersed phase superficial velocity ratio ($R = V_c/V_d$) on the concentration variation along the height of the column.

85.9%, respectively. Conversely, the decrease in phase ratio from 1 to 0.33 increases the mass transfer. At the dispersed phase velocity of 0.0075 m/s, the concentration of TBP in the raffinate phase decreased gradually (157.4–22.4 ppm, i.e., $\xi = 1$ to $\xi = 0.14$) along the height of the column (from top to bottom), before attaining the steady state. For different dispersed phase velocities the concentration variation along the height becomes undifferentiated (overlapping trend), indicating that the axial dispersion is not affected by the dispersed phase velocity. The axial dispersion observed in the case of the dispersed phase velocity is far less than the continuous phase velocity; exactly opposite trends were observed by Wang et al.³⁷ for a pulsed column with disks and doughnuts.

Second, the effect of continuous phase superficial velocity (0.0025–0.0075 m/s, i.e., $R = 1$ –3) at constant dispersed phase superficial velocity (0.0025 m/s) and pulse velocity (0.025 m/s) is reported in Figure 4. An increase in the continuous phase velocity essentially increases the holdup of the continuous phase in the column; however, the dispersed phase drop size has minimal influence. This dispersed phase (having similar holdup values and drop size) remains constant at the operating conditions and tends to acquire equal amount of TBP from the continuous phase. This can also be supported by the fact that an increase in the continuous phase superficial velocity increases the axial mixing along the column, which reduces the efficiency of the process by decreasing the solute concentration gradients.³⁸ The concentration variation along the height is less with an increase of continuous phase velocity, which means that the axial dispersion taking place with an increase of continuous phase velocity is significant.

3.3.2. Effect of Pulse Velocity. At a constant continuous to dispersed phase velocity ratio ($R = 1$), the effect of the pulse velocity on the concentration variation along the height of the column was studied, and the results are plotted in Figure 5. At a higher pulse velocity of 0.045 m/s the concentration of TBP decreased from 154.8 to 20.2 ppm (about 87%), whereas at a lower pulse velocity of 0.025 m/s the concentration decreased from 151 to 46 ppm from the top to the bottom (0.2 m) of the column. However, the concentration profile along the height of

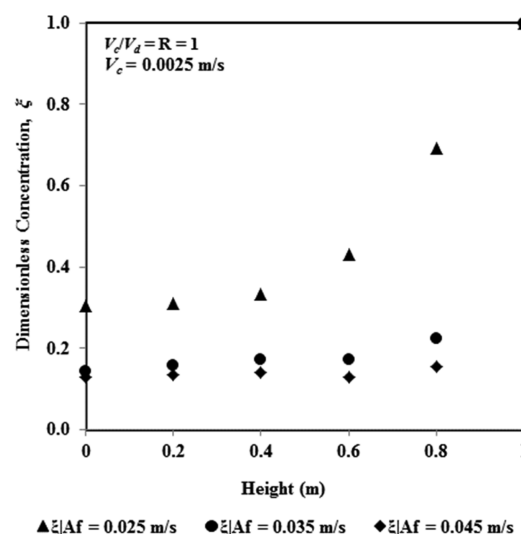


Figure 5. Effect of pulse velocity on the concentration variation along the height of the column.

the column is comparable for 0.035 and 0.045 m/s. With an increase in pulse velocity, axial mixing within the column increases, but at the same time drop size is decreased and consequently holdup increases significantly. This decrease in drop size is the main cause of the increase in the mass transfer, surpassing the effect of axial mixing. Therefore, the steep decrease in concentration at a pulse velocity of 0.045 m/s can be observed and can be supported by the fact that the deformation and coalescence of the drops is much higher at 0.045 m/s compared to 0.025 m/s while passing the sieve plate. This deformation causes some mixing within the droplet (circulation and recirculation) tending to disturb the radial concentration profile, which results in higher mass transfer coefficients. At the top of this section a high rate of TBP transfer exists because of smaller drop size, whereas at the bottom lower rates of TBP transfer prevail as nitric acid transfer takes place. The pulse energy required to produce a good dispersion of the dispersed phase is appreciably greater at the top, where higher mass transfer rates are observed, than in the bottom of the column where little mass transfer takes place. The more pronounced rate extraction at the top of the column was observed because of the ease of dispersion and coalescence of the dispersed phase based on the physical properties of the interface.

3.4. Effects of Operating Parameters on the Steady State Axial Holdup Distribution in the Column. Uniform axial holdup distribution throughout the column is an important assumption for simplification while designing the column.³⁹ This can cause error and reduce the accuracy of design parameters such as the column height and diameter. The fact is that the dispersed phase holdup is variant along the column height, which has to be incorporated while designing the column so as to have an accurate design.^{40,41}

The effects of operating parameters, namely, the continuous to dispersed phase superficial velocity ratio (R) and the pulse velocity, on the stage holdup profile along the height of the column are shown in Figures 6 and 7, respectively. The dispersed phase, which is fed from the bottom of the column, has to pass the sieve plates provided within the column, which also acts as resistance to the flow of phases. Therefore, the shear stress between the dispersed phase and the continuous phase

increases, which leads to a decrease in the drop size. This decrease in the drop size increases the residence time up the column, in turn increasing the dispersed phase holdup from the bottom to the top of the column.

3.4.1. Effect of Continuous to Dispersed Phase Superficial Velocity Ratio ($R = V_c/V_d$). The steady state axial holdup distribution along the height of the column at constant dispersed phase (0.0025 m/s) and pulse velocity (0.025 m/s) for a varying continuous phase velocity ratio is depicted in Figure 6. Khawaja et al.⁴¹ studied the variation of the dispersed

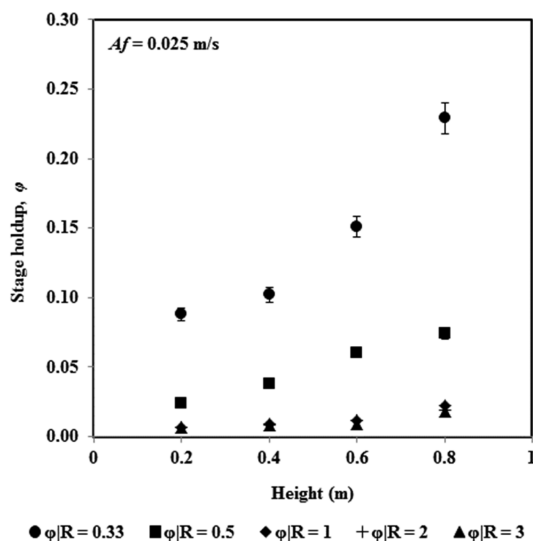


Figure 6. Effect of continuous to dispersed phase superficial velocity ratio ($R = V_c/V_d$) on stage holdup axial distribution along the height of the column.

phase holdup with height and found that there is negligible difference in the holdup for the isoamyl alcohol–water system and the operating conditions considered therein. The steady state stage holdup shows an increasing trend along the height of the column. With an increase in continuous phase velocity; the shear stress between the continuous phase and the dispersed phase drops increases. Thus, the dispersed phase drops break down into smaller drops which have a large residence time. Since this happens continuously in the column, the holdup of the dispersed phase at a particular stage is increased with an increase in the continuous phase velocity.

The effect of the dispersed phase velocity on stage holdup is very large as compared to that of the continuous phase velocity.⁴² When the dispersed phase velocity is increased from 0.0025 to 0.0075 m/s, the total quantity of dispersed phase is continuously increased within the column. It can be also observed that, at all dispersed phase velocities, the holdup at the top of the column is 2–3 times greater than at the bottom side of the column. Increase in the stage holdup is not linear as the residence time of the larger dispersed phase droplets formed as a result of coalescence decrease is different.

3.4.2. Effect of Pulse Velocity. Figure 7 indicates that the holdup along the height is greatly affected by the pulse velocity. An increase in pulse velocity enhances turbulence as result of higher energy dissipation in the column, which reduces the drop size of the dispersed phase. Therefore, the rise velocity of dispersed drops reduces, which increases the residence time of drops as well as the holdup. With an increase in pulse velocity from 0.025 to 0.045 m/s, the holdup at the top side of the

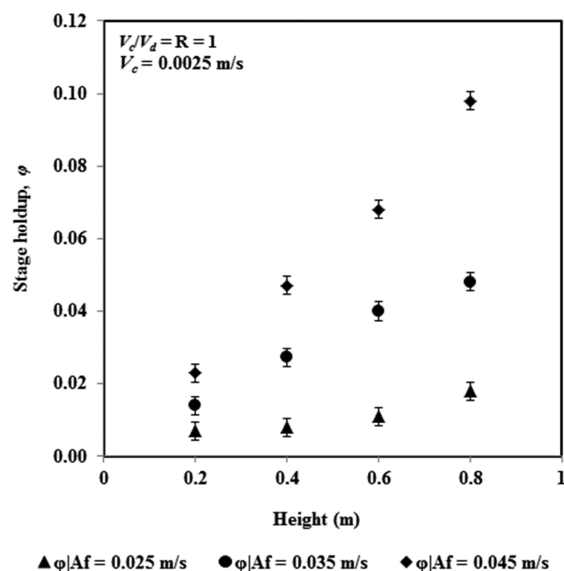


Figure 7. Effect of pulse velocity on stage holdup axial distribution along the height of the column.

column is 3–4 times greater than that at the bottom side of the column.

3.5. Effects of Operating Parameters on Volumetric Mass Transfer Coefficient and Overall Holdup. In the PSPEC, the volumetric mass transfer coefficient mainly depends on the interfacial area and the axial dispersion taking place inside the column. Interfacial area is directly proportional to dispersed phase holdup and inversely proportional to drop diameter. Thus, it is essential to increase holdup at a constant or small drop size for a higher interfacial area. If the drop size increases comparatively with holdup, then they will compensate each other and there will be no significant change in interfacial area; consequently, no change in the volumetric mass transfer coefficient is expected. The dispersed phase holdup in the pulse column is observed to be affected by superficial velocities of continuous and dispersed phase superficial velocities as well as the pulse velocity. Therefore, the effects of the phase velocity ratio (R) and the pulse velocity on the volumetric mass transfer coefficient and overall holdup have been studied and are plotted in Figures 8 and 9, respectively.

3.5.1. Effect of Continuous to Dispersed Phase Superficial Velocity Ratio ($R = V_c/V_d$). The effect of the continuous phase velocity (0.0025–0.0075 m/s, i.e., $R = 1$ –3) at constant dispersed phase velocity (0.0025 m/s) and pulse velocity (0.025 m/s) on the volumetric overall mass transfer coefficient is given in Figure 8. According to Figure 8, the volumetric mass transfer coefficient increases with increasing continuous phase velocity. When the continuous phase velocity increases, the continuous phase does not allow the dispersed phase to pass through the column due to the high resistance offered by the former. Thus, the rise velocity of the drop reduces. Hence, the residence time of the drops increases, which leads to increase in the holdup and the corresponding mass transfer coefficient. With an increase in the continuous phase velocity, the drag force between the dispersed phase drops and the continuous phase increases, so the drop movement is limited, enhancing the residence time, and consequently the holdup is increased. Initially, the holdup is increased rapidly with an increase in the continuous phase velocity from 0.0025 to 0.005 m/s, and then the effect of the continuous phase velocity for the range 0.005–

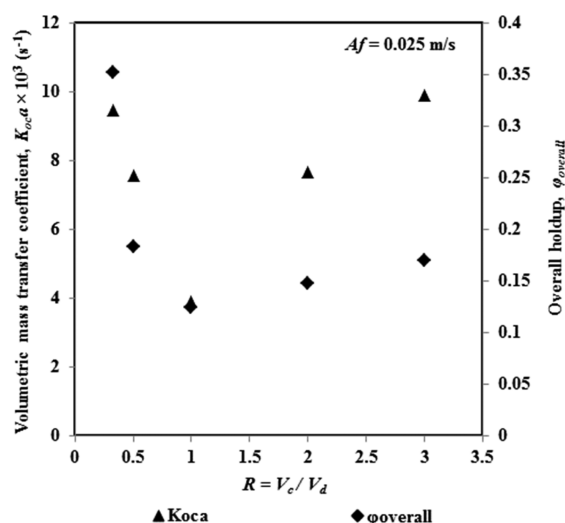


Figure 8. Effect of continuous to dispersed phase velocity ratio on overall volumetric mass transfer coefficient and overall holdup.

0.0075 m/s lessens. Initially, there is intense drop breakage occurring due to the increase in the continuous phase velocity and then the drop breakage is limited and the drop size decreases gradually. Thus, the increase in the holdup is proportionally less with an increase in the continuous phase velocity. A similar effect was observed by many authors, such as Khemangkorn et al.⁴³ and Venkatanarasaiah and Varma.⁹

The effect of the dispersed phase velocity on the overall volumetric mass transfer coefficients is also shown in Figure 8. It indicates that the volumetric mass transfer coefficient increases with an increase in the dispersed phase velocity. However, the effect of the continuous phase is observed to be more because of two reasons. First, when the dispersed phase velocity increases, not only the dispersed phase holdup increases, but also the drop size of the dispersed phase increases simultaneously. However, it is observed that the effect of holdup on the interfacial area is larger than that of drop size; i.e., the interfacial area increases by increasing the dispersed phase flow rate and consequently the mass transfer rate is found to increase. Thus, the effects of holdup and drop size compensate each other and hence there is no significant change in the interfacial area. In the case of the continuous phase, holdup is increased due to the decrease in drop size. The higher mass transfer at higher dispersed phase velocity also can be accounted by phenomena such as oscillation and the internal circulation of drops in the large size drops.¹³ However, the overall volumetric mass transfer coefficient does not show a very net decrease at higher values. The second reason is that the axial dispersion within the column is observed to increase with the dispersed phase velocity, which increases the back-mixing within the column and ultimately reduces the value of the overall volumetric mass transfer coefficients. Torab-Mostaedi et al.⁴⁴ have also reported that in the PSPEC the effect of the continuous phase velocity on the volumetric mass transfer coefficient is more than the effect of the dispersed phase velocity.

The drop population in the column increases with an increase in the dispersed phase velocity.¹⁸ When the dispersed phase velocity is increased from 0.0025 to 0.0075 m/s, the amount of the dispersed phase in the column is continuously increased. The effect of the dispersed phase velocity on holdup is observed to be greater than that of the continuous phase

velocity. Torab-Mostaedi et al.⁴⁴ have also observed a similar effect of both phase velocities on the overall holdup.

3.5.2. Effect of Pulse Velocity. The effect of the pulse velocity (0.025–0.045 m/s) at a constant phase velocity ratio ($R = 1$) on the overall volumetric mass transfer coefficient is given in Figure 9. The overall volumetric mass transfer

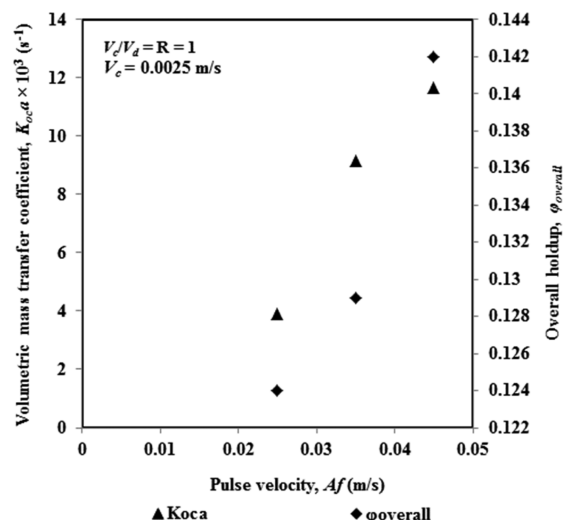


Figure 9. Effect of pulse velocity on overall volumetric mass transfer coefficient and overall holdup.

coefficient was found to increase 3-fold (from 3.89×10^{-3} to $11.66 \times 10^{-3} \text{ s}^{-1}$) when the pulse velocity was increased from 0.025 to 0.045 m/s. More pulsing action prevailed; more droplets of each phase were formed, thereby increasing the surface area and resulting in a more efficient contact. The amount of mass transfer is proportional to the surface area of the two phases in contact. Moreover, the rise velocity of smaller drops is less, which increases their residence time within the column. The droplets of the continuous phase travel down and the dispersed phase rise, and thus sieve plates serve to slow and disperse the droplets of both phases and thereby increase the surface area of contact; hence mass transfer is increased. Thus holdup of the dispersed phase rises at higher pulse velocity. Along with holdup, axial dispersion also increases. However, the former has a greater effect on the overall volumetric mass transfer coefficient. The more prominent steep increase in the mass transfer coefficient is observed at in the lower pulse velocity region (0.025–0.035 m/s) as compared to the higher pulse velocity region (0.035–0.045 m/s). As small droplets suffer little interaction with the sieve plate, the enhancement in mass transfer is lower. The larger droplets are observed in the range of pulse velocity of 0.025–0.035 m/s, and have the tendency to form inner circulation without sieve plates. This effect dominates especially at diffusion controlled mass transfer at a pulse velocity of 0.025 m/s.⁴⁵ Wang et al.,³⁷ Khemangkorn et al.,⁴³ and He et al.⁴⁶ observed that K_{oc} increased with an increase in pulsed velocity. The variation in transfer efficiency and dispersed phase holdup as a function of pulse velocity was studied by Ousmane et al.,⁴⁷ who found that the best efficiency was obtained at the highest pulsed frequency.

The drop size and degree of turbulence are a function of the energy supplied to the system; hence dispersed phase holdup in a PSPEC is affected by the pulse velocity. The increase in pulse velocity leads to higher shear stress and to intense drop

breakage, increasing the number of drops, and consequently holdup is increased. With an increase in the pulse velocity from 0.025 to 0.045 m/s, holdup increases from 12.4 to 14.2%; i.e., holdup is increased by 14.5%. The effect of pulse velocity on overall holdup is greater than the effect of continuous phase and dispersed phase velocities. Mohanty and Vogelpohl,⁴⁸ Prabhakar et al.,¹⁰ and Venkatanarasiah and Varma⁹ observed that the holdup is increased with an increase in the pulse velocity. Khemangkorn et al.⁴³ measured the holdup for the water–iodine–CCl₄ system and reported that the holdup increases with both amplitude and frequency. However, they found that the group $Af^{1.24}$ correlated their holdup data more satisfactorily than Af .

4. CONCLUSIONS

Mass transfer studies with the original nuclear industrial system of 0.3 M nitric acid–TBP–NPH were performed in a PSPEC. In the present work, an attempt has been made to find out the effects of superficial velocities of the dispersed phase and the continuous phase (phase flow ratio) and the pulse velocity on the outlet continuous phase concentration profile with time (dynamic operation of the column), steady state concentration, and stage holdup profile in the column and volumetric mass transfer coefficient. It is observed that the pulse velocity has a strong effect on K_{oc} . The overall volumetric mass transfer coefficient was found to increase 3-fold (from 3.89×10^{-3} to $11.66 \times 10^{-3} \text{ s}^{-1}$) when the pulse velocity was increased from 0.025 to 0.045 m/s. With increases in the dispersed phase velocity and continuous phase velocity (from 0.0025 to 0.0075 m/s), the volumetric mass transfer coefficient increases about 2.5 times (from 3.89×10^{-3} to $9.9 \times 10^{-3} \text{ s}^{-1}$).

On the basis of the results of this investigation, it can be concluded that the increase in the pulse velocity increases holdup and the mass transfer coefficient. Pulse velocity also helps in the attainment of the steady state at a faster rate. The effect of the continuous phase to dispersed phase velocity ratio on the axial steady stage concentration and holdup profile is established.

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Notes

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NOMENCLATURE

H = effective height of the column for extraction (1 m)
 $(HTU)_{oc}$ = overall height of a transfer unit based on the aqueous phase
 $(NTU)_{oc}$ = overall number of transfer units based on the aqueous phase
 K_{oca} = overall volumetric mass transfer coefficient (s^{-1})
 V_c = continuous phase superficial velocity (m/s)
 C_{c1} = concentration of TBP in continuous phase at the inlet of the column (mol/m^3)
 C_{c1}^* = equilibrium concentration of TBP in continuous phase at the inlet of the column (mol/m^3)

C_{c2} = concentration of TBP in continuous phase at the outlet of the column (mol/m^3)

C_{c2}^* = equilibrium concentration of TBP in continuous phase at the outlet of the column (mol/m^3)

$(\Delta C)_{LM}$ = log mean concentration difference (mol/m^3)

ξ = dimensionless concentration (concentration of TBP in continuous phase at the outlet of the column/initial feed concentration)

χ = % extraction; $(1 - \xi)(100)$

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