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Liquid–Liquid Extraction of Phosphoric Acid from Aqueous Solutions in Pulsed Columns

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ABSTRACT

Extraction of phosphoric acid from aqueous solutions, by using *n*-butanol as a solvent, has been studied in a pulsed packed column. The variables studied are feed flow rate, solvent flow rate, pulsation frequency, and amplitude. Based on the results obtained, pulsation was found to increase the rate of mass transfer. Better extraction efficiencies were obtained when the column was pulsed. The aqueous-phase flow rate was found to affect the extraction efficiency slightly whereas the solvent flow rate appreciably increased the extraction efficiency. The effects of pulse amplitude and frequency are interdependent. When operating at low frequencies, the amplitude should be larger than the packing size if any enhancement in the extraction efficiency is to be achieved. But, generally, an increase in either the amplitude or the frequency was found to increase the extraction efficiency.

INTRODUCTION

Phosphoric acid is a major commodity in the production of phosphatic fertilizers. It is produced by two methods: the electric-arc-furnace process and the wet process. The wet-process method depends on the acidulation of phosphate rock with an inorganic, sulfuric, nitric, or hydrochloric acid.

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The resulting wet-process acid is characterized by its high impurity content. A liquid–liquid extraction step is frequently involved in the manufacturing process. This step is much more essential when hydrochloric acid or nitric acid is used in recovering the acid from the soluble calcium-salt solution produced.

Many investigators (e.g., Refs. 1–7) have studied the extraction of phosphoric acid from the acidulation liquors by various solvents. Examples of successful solvents include short-chain aliphatic alcohols, some ketones, amides, and some alkyl phosphates. Some of these solvents are used in several industrial plants (8, 9). Most of these extraction steps are carried out on a batch scale in a battery of mixer settlers. To the best of the present authors' knowledge, only three studies (10–12) have reported work on the extraction of phosphoric acid in packed columns, employing *n*-butanol as the solvent. However, limited efficiency in the extraction of the acid was reported. To the best of the present authors' knowledge, this study represents the first reported attempt to study the employment of pulsed columns in the extraction of phosphoric acid by *n*-butanol.

The use of pulsed columns in extraction was patented in 1935 (13). Pulsed columns generally enhance mass transfer rates and thus lead to better extraction efficiencies. Pulsed columns can be classified into pulsed packed columns, pulsed perforated plate columns, and controlled cycling extractors (14). The latter are not widely classified as pulsed columns in the general sense. However, it is the present authors' opinion that these extractors show the general characteristics of other pulsed columns.

Many mass transfer studies appeared in the literature on using pulsed columns of different column design and geometry (15–21). These studies were conducted using different chemical systems. An increase in the rate of mass transfer occurs and a reduction in the height of transfer unit (HTU_{OE}) of 50–80% was reported when pulsed columns were used. This increase in the rate of mass transfer is a natural outcome of the increased turbulence, interdroplet coalescence, and redispersion as well as the increased surface area and holdup. This fact, however, is countered by the effect of axial mixing which is also increased by pulsation.

The objective of this work was to explore the use of a pulsed packed column in the extraction of phosphoric acid from its aqueous solution by *n*-butanol and to study the behavior of such a system under pulsed conditions.

EXPERIMENTAL

Materials

Simulated phosphoric acid solutions were prepared using a general purpose grade acid produced by Vorsichtl Citemikalten der Abt 3, West Germany. The *n*-butanol employed is a general purpose reagent produced by Prolabo. The concentration of the acid solution used is about 12%, which is similar to that produced in hydrochloric acid acidulation. The concentrations of the acid content of the extract and raffinate samples were determined spectrophotometrically by the phospho vando molybdate method (22). The reagents required by the analytical technique are: 1) ammonium vanadate (AR) supplied by Riedel-De-Haen AG, 2) ammonium molybdate (AR) supplied by BDH, 3) nitric acid (AR) purchased from May & Baker Ltd., and 4) phosphoric acid (AR) supplied by VEB.

Absorbency measurements were performed using a Pharmacia LKB Ultrospec IIE UV/VIS spectrophotometer.

Experimental Setup

The experimental setup shown in Fig. 1 consists of the extraction unit, the pulsing device, tanks, and pumps. The extraction unit consists of two parts. These are the extraction packed column (C) and the pulse transmitting side arm (B).

The column is made from Pyrex glass tubing (3.8 cm i.d.). The column diameter was selected on the basis of economic considerations since this study is only exploratory. The column is divided into three sections. In the lower section, *n*-butanol solvent is admitted through a nonreturn valve. Raffinate is withdrawn by gravity through valve V6. The bottom end of this section is connected to the pulse transmitting side arm, which in turn is connected to the pulsator.

The middle section is filled with packing, polyethylene Raschig rings (6 mm diameter and 10 mm high) to a height of 75 cm. Along this section, five 8-mm diameter sampling points, spaced 15 cm apart, were drilled so that samples could be withdrawn along the column height. These sampling points were not used in this study.

The top section contains the aqueous feed distributor. This section extends to a spherical glass section which serves to reduce entrainment of the dispersed phase with the continuous phase. The extract was withdrawn by overflow through valve V5.

The pulsator used is a reciprocating plunger actuated by an eccentric. The eccentric is attached to a gear box driven by a motor through a belt.

Chemically resistant pumps were used to pump the aqueous feed and the solvent from reservoirs T1 and T2 to constant-head tanks T3 and T4.

Experimental Procedure

The extraction column as well as the pulse transmitting side arm were first filled with *n*-butanol as the continuous phase. The dispersed phase (acid solution) was then admitted to the column. Both phase flow rates

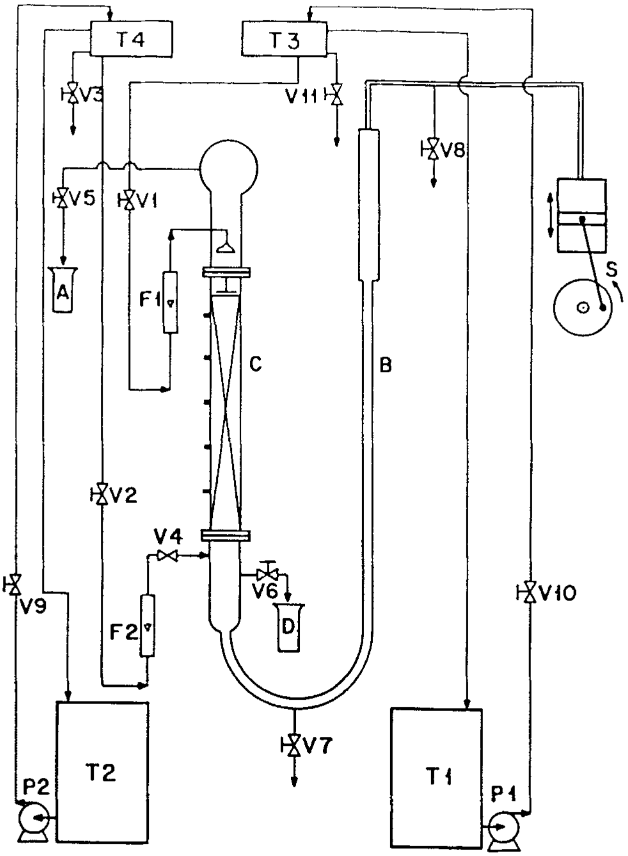

FIG. 1 Schematic diagram of the experimental setup. A: Receiving flask for extract phase. B: Pulse transmission side arm. C: Packed column. D: Receiving flask for raffinate phase. F1: Aqueous-phase flowmeter. F2: Solvent flowmeter. P1: Aqueous-phase pump. P2: Solvent pump. S: Pulsator. T1: Aqueous-phase reservoir. T2: Solvent reservoir. T3: Aqueous-phase overhead tank. T4: Solvent overhead tank. V1: Aqueous-phase inlet valve. V2: Solvent inlet valve. V3: Tank (T4) drain valve. V4: Solvent line check-valve. V5: Extract-phase outlet valve. V6: Raffinate-phase outlet valve. V7: Extraction unit drain valve. V8: Amplitude adjusting valve. V9: Pump (P2) downstream valve. V10: Pump (P1) downstream valve. V11: Tank (T3) drain valve.

were then set to the desired values. The pulsator was then started and the frequency was set and measured by a tachometer. Following that, the amplitude was adjusted with the help of valve V8.

After 2 L of each phase (extract and raffinate) were collected, the flow rates of both streams were measured. Next, samples of both phases were collected. The operation was continued until another 0.5 L of each phase was collected. A second sample was then taken from each phase to confirm the attainment of steady-state. Finally, hold-up measurements were performed by the displacement method (23, 24).

Experimental work was carried out to determine the equilibrium distribution of phosphoric acid between the aqueous and the organic layers. The runs were performed at different ratios of organic to aqueous phases to cover the whole range of the operation in the column.

The height of a transfer unit, defined as the height of the column that produces a change in concentration which is numerically equal to the mean driving force over one transfer unit, is calculated by the following equation:

$$\mathrm{HTU_{OE}} = V_E/K_E a \tag{1}$$

where K_E is the overall mass-transfer coefficient based on the extract phase and a is the mass transfer area. The product $K_E a$ is known as the volumetric mass-transfer coefficient. $K_E a$ is calculated by an overall mass balance using the measured end concentrations.

RESULTS AND DISCUSSION

The variables studied in this work are aqueous phase flow rate, solvent flow rate, pulsation amplitude, and pulsation frequency.

Aqueous Phase Flow Rate

Figure 2 depicts a typical effect of the aqueous phase superficial velocity on the height of a transfer unit ($\mathrm{HTU_{OE}}$). It is clear that at low superficial velocities the pulsation caused a larger reduction in the $\mathrm{HTU_{OE}}$ than at higher velocities. For example, at a superficial velocity of 0.037 m/min, the $\mathrm{HTU_{OE}}$ was reduced by about 52 and 67% when the column was pulsed at frequencies of 37 and 64 rpm, respectively. Alternatively, at a velocity of 0.067 m/min, the reduction is only 30 and 41% at the same two frequencies. This may be explained as follows: When the column was unpulsed, the increase in superficial velocity of the aqueous phase would cause an increase in the degree of turbulence and hence result in higher mass-transfer rates and lower values of $\mathrm{HTU_{OE}}$. When the column is

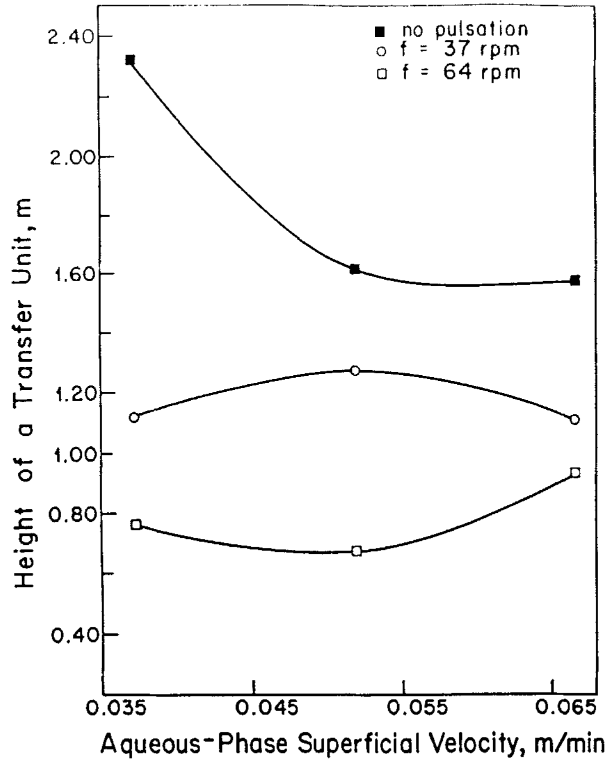

FIG. 2 Effect of aqueous-phase superficial velocity on the height of a transfer unit at different pulsation frequencies and an amplitude of 0.08 m.

pulsed, turbulence is effected mainly by energy introduced by pulsation and not by the flowing liquids. Thus, the effect of increasing the aqueous-phase superficial velocity on extraction efficiency is higher with no pulsation.

At lower frequencies (viz., 37 rpm) the aqueous-phase superficial velocity has a slight effect on the extraction efficiency (cf. Fig. 2). However, at the higher frequency of 64 rpm, as the superficial velocity approaches 0.067 m/min, a reduction in extraction efficiency is observed. This reduction at the higher frequency may be attributed to the increased degree of axial mixing. Axial mixing was increased primarily by an increase in pulse intensity and was further increased by an increase in the superficial velocity. Thus, poorer mass-transfer rates at the higher superficial velocity is obtained. A slight influence of the aqueous-phase (dispersed) superficial velocity on the extraction efficiency in pulsed columns was reported for the extraction of benzoic acid from toluene by water (16). However, this was not the case with the results reported in Ref. 17 for two different liquid systems (MIBK–acetic acid–water and ethyl acetate–acetic acid–water). It is very important to note here that the direction of mass transfer employed in Ref. 16 was from the dispersed phase to the continuous phase (similar to this study), whereas that in Ref. 17 was from the continuous phase to the dispersed phase.

Solvent Flow Rate

Solvent superficial velocity affected the column performance in a more pronounced manner than the aqueous-phase superficial velocity. This is shown in Fig. 3 where HTU_{OE} is reduced as the solvent superficial velocity is increased. The reduction in HTU_{OE} is gradual at the lower aqueous-

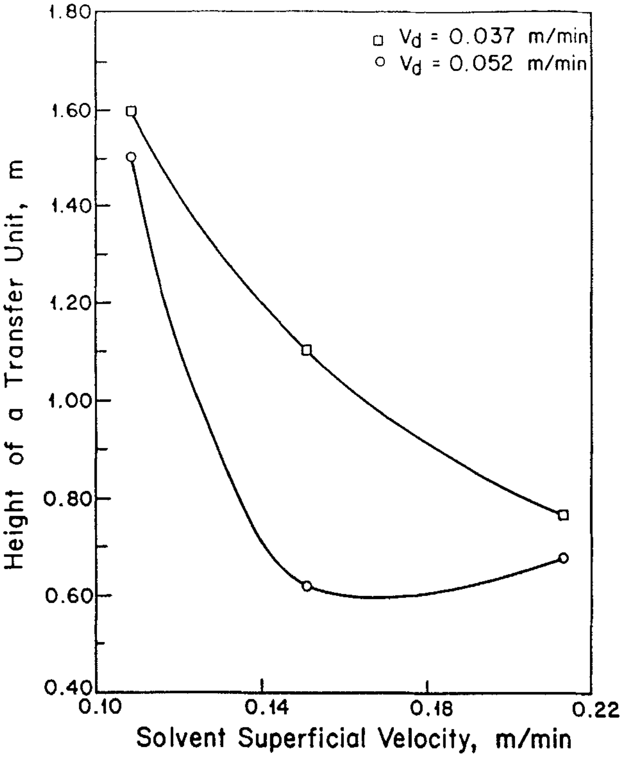

FIG. 3 Effect of solvent superficial velocity on the height of a transfer unit at different aqueous-phase superficial velocities, an amplitude of 0.008 m, and a frequency of 64 rpm.

phase superficial velocity. However, it rapidly increases at the higher aqueous-phase superficial velocity. At an aqueous-phase superficial velocity of 0.052 m/min, a reversal of the trend of HTU_{OE} was noticed as the solvent superficial velocity was increased from 0.15 to 0.21 m/min. This might be attributed to the increase in the degree of axial mixing and the possible reduction in the contact time between the two phases. The general difference in the effect of the solvent (continuous) phase superficial velocity with that of the aqueous phase may be explained as follows: As was reported earlier (3) and confirmed by our experimental equilibrium tests, the distribution of phosphoric acid between the *n*-butanol phase and the aqueous phase is very low. This may imply that the main resistance to mass transfer lies in the *n*-butanol and not in the aqueous phase. Thus, as the turbulence increases in the *n*-butanol (continuous) phase, the extraction of acid from the aqueous phase to the organic phase is increased owing to the reduction in the continuous-phase interfacial film resistance. Turbulence in the continuous phase would be influenced to a much higher extent by the continuous-phase superficial velocity rather than by the dispersed-phase superficial velocity.

Amplitude and Frequency

Figure 4 shows the effect of the amplitude and frequency on the height of the transfer unit. As can be seen, HTU_{OE} decreased generally with an increase in either the amplitude or the frequency. When the amplitude is increased to 0.006 m at a frequency of 64 rpm, HTU_{OE} decreased from 1.6 to 0.67 m. Any further increase in the amplitude would cause no enhancement in the extraction efficiency. At a frequency of 37 rpm, the increase in extraction efficiency with amplitude is lower and is almost constant in the amplitude range of 0.005 to 0.008 m. A further increase in the amplitude to 0.012 m greatly enhanced the extraction efficiency, where HTU_{OE} decreased from 1.27 m at an amplitude of 0.008 m to 0.58 m at an amplitude of 0.012 m. A very similar amplitude effect, especially at higher frequencies, was reported (25). The height of the transfer unit decreased with increasing amplitude. This decrease is more pronounced at high frequencies but occurs gradually at lower frequencies. The large reduction in HTU_{OE} in the 0.008 to 0.012 m amplitude range at 37 rpm could possibly be related to the height of the packing rings. This can be explained as follows: It was suggested (16) that the packing in a pulsed packed column acts as a stirrer of the oscillating liquids. Thus, if amplitudes lower than 0.01 m (the packing Raschig ring height used in this study) were used, some liquid could be trapped inside the packing rings during the pulsation cycle and would not be completed subjected to agita-

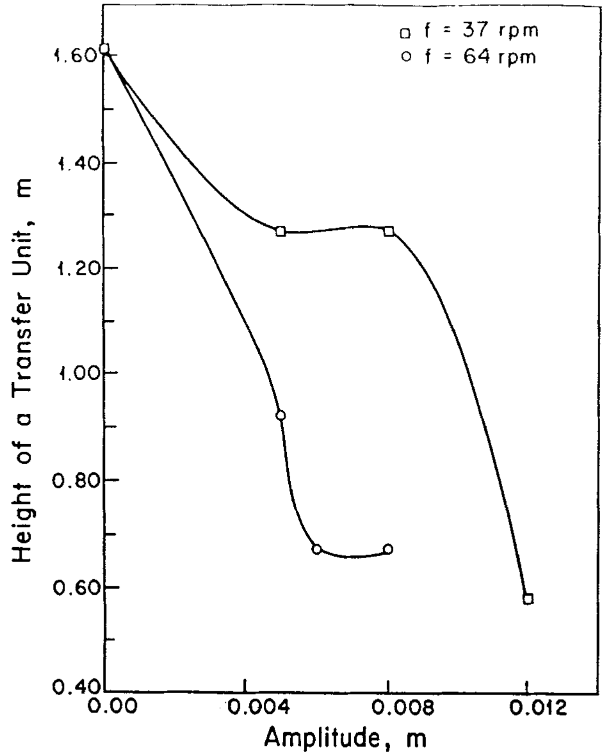

FIG. 4 Effect of pulsation amplitude on the height of a transfer unit at different pulsation frequencies and aqueous-phase and solvent superficial velocities of 0.052 and 0.21 m/min, respectively.

tion. Consequently, only amplitudes higher than 0.01 m would cause larger increases in extraction efficiency. This supposition, of course, only holds at lower frequencies. High pulse frequencies would counteract this effect of the amplitude by the extra energy added to the system.

Pulse Velocity (Rate)

The frequency amplitude product (pulse velocity) is a good measure of the effect of pulsation on extraction columns (26). This is shown in Fig. 5 for HTU_{OE}. This figure indicates that increasing the pulse velocity results in an initial decrease in HTU_{OE}. This may represent the operating conditions where the interfacial turbulence effect on the mass transfer rate is much higher than that of axial mixing.

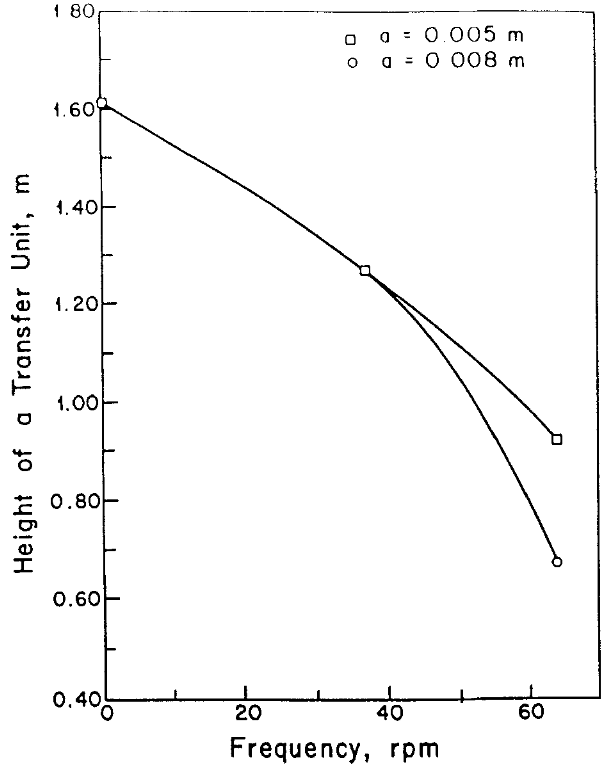

FIG. 5 Effect of pulsation velocity on the height of a transfer unit at different aqueous-phase superficial velocities and a solvent superficial velocity of 0.11 m/min.

A further increase in the pulse velocity caused a reduction in the extraction efficiency with an increase in HTU_{OE}. Here the axial mixing overcame the effect of interfacial turbulence, and hence resulted in reducing the mass-transfer rate.

A further increase in the pulse velocity also results in creating an unstable region in which flooding is approached. In such an unstable region, the change in the value of HTU_{OE} is minor. The unexpected low value of HTU_{OE} at a pulse velocity of 0.9 m/min at the higher aqueous phase superficial velocities is not due to any enhancement in mass-transfer efficiency. It may have resulted from excessive entrainment of fine aqueous (dispersed) phase droplets with the solvent (continuous) phase at this high pulse velocity. This entrained aqueous phase droplets may have given incorrect concentration results. This is supported by the very high value of the dispersed phase holdup (about 0.92) as shown in Fig. 6. This high value of holdup indicates that the column was flooded at the high pulse velocity of 0.9 m/min, since holdup values in the 0.25–0.4 range are only reported before flooding (27–29). Hence, a lot of entrainment is expected.

The effect of increasing the pulse velocity on the extraction efficiency in terms of the height of a transfer unit is similar to that reported in Refs. 17, 18, and 21 for different chemical systems and column geometries. This may imply that the chemical system used has no influence on the shape of the pulse velocity curve. In another study (25), only a reduction in the height of a transfer unit on increasing the pulse velocity until a minimum is reached was reported. The results obtained, however, were at pulse velocity values that are lower than 0.3 m/min, i.e., on the left side of the minimum obtained in this study (cf. Fig. 5).

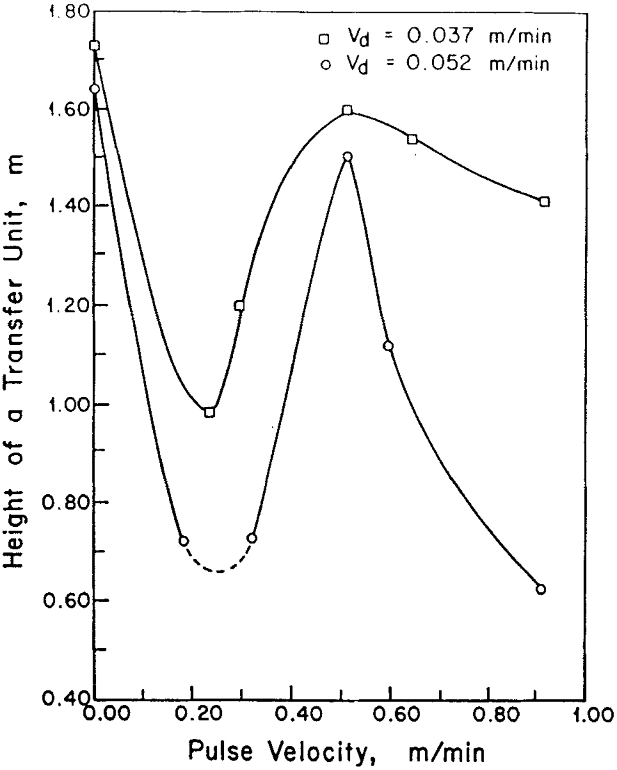

FIG. 6 Effect of pulsation velocity on the dispersed-phase holdup ratio at different aqueous-phase superficial velocities and a solvent superficial velocity of 0.11 m/min.

CONCLUSIONS

The application of pulsation to the extraction of phosphoric acid in a packed column has been found to increase the extraction efficiency. Depending on the phase flow rates, a reduction of as much as 70% in the height of a transfer unit ($\mathrm{HTU_{OE}}$) was achieved when the column was pulsed. The dependence of the operation of the column on the aqueous (dispersed) phase flow rate has been found to be less critical when the column was pulsed. The solvent, *n*-butanol, flow rate affected the column efficiency to a much greater extent than the aqueous phase. Generally, higher solvent superficial velocities resulted in better extraction efficiencies.

An increase in either the pulse frequency or the amplitude was generally found to result in a higher degree of extraction. The effect of any one of these parameters is dependent on the other. The influence of the pulse amplitude, as suggested, is related to the packing size (Raschig ring height) at low pulse frequencies. Amplitudes higher than the packing size were found to greatly increase the extraction efficiency.

The frequency amplitude product (pulsation velocity), rather than either one of them, was found to explicitly explain the effect of pulsation on the mass transfer rates in pulsed columns. As the pulsation velocity was increased, three regions could be identified:

A region where the mass-transfer rates increased to a maximum.
A region where mass-transfer rates decreased because of the excessive increase in axial mixing.
A region of unstable operation where entrainment was greatly increased as flooding was approached.

NOMENCLATURE

a	pulsation amplitude (m)
f	pulsation frequency (rpm)
$\mathrm{HTU_{OE}}$	height of a transfer unit (m)
V_c	solvent superficial velocity (m/min)
V_d	aqueous-phase superficial velocity (m/min)
V_{eff}	volumetric efficiency of the pulsed column (min^{-1})

Subscripts

E	extract phase
O	overall
c	solvent
d	aqueous phase

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