A New Bubbling Extraction Tower: Toward Liquid–Liquid Solvent Extraction at Large Aqueous-to-Oil Phase Ratios

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Enrichment and recovery of valuable components in industrial waste waters by traditional liquid–liquid solvent extraction is not economic due to extremely low concentrations of those targets. Large-phase-ratio extraction exhibits potential advantages for recovery of small quantities of target components from large volume of aqueous solutions. A novel bubbling extraction tower is proposed toward performing solvent extraction at large aqueous-to-oil phase ratios in this work. Organic extractants were covered onto surface of gas bubbles to form a layer of organic liquid membrane and the dispersed organic phase in tower could be small enough. The target components are extracted from aqueous feed solution onto the surface of the bubbles, and the enrichment ratios could be extremely high. We develop a feasible methodology to calculate tower height and operation phase ratios of the bubbling extraction tower, which is essential for future industrial scale-up. Experimental results in pilot test are highly consistent with calculations. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 3889–3897, 2015

Keywords: large-phase-ratio extraction, bubbling extraction tower, design, calculation

Introduction

Liquid–liquid solvent extraction plays an important role in chemical industrials for separation and enrichment of various target components from complicated solutions.[1,2] Nowadays, advances in practical separation processes stimulate such demands to develop new methods and equipment for performing liquid–liquid extraction processes at large aqueous-to-oil phase ratios, so that target components with extremely low concentration in large volume of feed aqueous solutions can be extracted and enriched with higher enrichment ratios into small volume of organic phases and achieve recovery economically.[3] It is beneficial for applications in the future to treat various industrial waste water containing low content of valuable components needed to be recovered.[4,5] However, structural design for such a large-phase-ratio extractor is difficult to meet practical requirements for dispersing small volume of organic phase thoroughly into large volume of aqueous phase.[6]

The traditional equipment used for solvent extraction can be divided into three types: mixer-settler, extraction tower, and centrifugal extractor. Those equipment were designed primarily according to the requirements of liquid–liquid two-phase separation and mass transfer at lower aqueous-to-oil phase ratios.[7] For improving dispersion of small-volume organic phases, the traditional mixer-settlers have to increase stirring intensity in mixing chamber, so that correspondingly to increase settling area in settling chamber to offset the adverse effects caused by intense agitation. However, those efforts are generally not effective when operating at large aqueous-to-oil phase ratios, such as above 100:1, due to structural limitation for design of mixer and impeller to achieve dispersion of small-volume organic phases.[8] The extraction tower need to increase tower height to achieve mass-transfer equilibrium between dispersed oil droplets and continuous aqueous phases. Operation at large aqueous-to-oil phase ratios may result in severe axial back-mixing or flooding in towers, and therefore decrease mass-transfer efficiency and phase separation rate, especially for those systems easily to cause emulsification.[9]

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Centrifugal extractors strengthen phase separation using centrifugal force instead of gravity. Although centrifugal extractor promote phase separation in emulsification systems, it may cause serious entrainment of organic phase into discharged water when operating at large aqueous-to-oil phase ratios.[10,11] Therefore, aforementioned conventional extraction equipment do not satisfy the demand to perform large-phase-ratio extraction. Low separation efficiency, serious loss of expensive organic extractants, and increased operation costs are always unavoidable.

Recently, some emerging techniques, such as liquid membrane extraction[12,13] and predispersed solvent extraction,[14,15] have been suggested with the aim to improve mass transfer, when targets with lower concentration in large volume of aqueous phase are required to be extracted and enriched into small volume of oil phase. Emulsification Liquid membrane (ELM) extraction takes advantage of amphiphilic surfactants to stabilize dispersed organic extractants by forming a thin layer of organic liquid membrane, on one side of which is feed aqueous solution and the other side is acceptable stripping solution. Enrichment of targets with extremely low concentrations in feed solutions can be achieved by collecting dispersed ELMs and breaking emulsion. Predispersed solvent extraction is to disperse the organic extractants as oil droplets by previously adding surfactants into oil phase before mixing with aqueous feed solutions. Stability of dispersed oil droplets is a crucial parameter for performing large-phase-ratio extraction processes. Those reported techniques exhibit many advantages such as large contacting surface and fast mass-transferring processes. However, they have to face such difficulties how to destroy the emulsion system introduced by surfactants and then promote coalescence of dispersed organic phases after extraction. That turns out to be a main obstacle to restrict practical application and future industrial scale-up.

To solve above problems, our previous works invented a series of new equipment to perform large-phase-ratio extraction.[16–18] A gas-assisted bubbling extraction tower was suggested and it exhibit excellent performance for dispersing small-volume organic phase. The organic extractant was covered onto surface of gas bubbles to form a layer of organic liquid membrane, so that total volume of dispersed organic phase in tower may be small enough, which depend on the thickness of organic layer on surface of gas bubbles and gas containment ratios in per unit of mass-transfer height in tower. Those gas bubbles covered with organic extractant ascend in tower and contact countercurrently with aqueous feed solutions so that target components can be extracted and enriched into the surficial organic liquid membrane layer of the gas bubbles. The dispersion of organic extractant onto the surface of gas bubbles was attributed to interfacial activities of those amphiphilic extractant molecules, which stabilize gas bubbles. Destroying those gas-in-oil bubbles and then those dispersed organic liquid membrane on each bubble aggregating together to form a continuous organic bulk phase can be controlled easily, if appropriate operation parameters of the tower were conducted. That new bubbling extraction tower achieved the purpose to disperse small-volume organic phase thoroughly into large-volume aqueous phase. The water-to-oil phase ratio in the tower could reach an extremely large value which is impossible achieved using traditional extractor. Therefore, target components with extremely low concentration in large volume of feed aqueous solutions can be enriched with higher enrichment ratios into the organic liquid layer covered on the surface of gas bubbles.

Our previous works demonstrated that it was feasible to obtain organic liquid membrane covered gas-in-oil bubbles with almost uniformed size and liquid membrane thickness. And it is also found that mass-transfer kinetics of target components during bubbling extraction process has close relationship with tower height and/or height-to-diameter ratio. However, no feasible theoretical models have been raised until now or could be referred to in the literatures toward design methodology for the tower height and/or height: diameter ratio of this kind of new bubbling extraction tower. A continued lack of theoretical calculation would restrict further optimization, scale-up, and industrial application of that new extraction towers.

The aim of this work is to provide a feasible methodology toward design and calculation of the tower height of the proposed bubbling extraction tower and its operation phase ratios. Here, we develop a theoretical framework based on the plug-flow model[19,20] and the dual resistance model[21] to calculate the tower height. The aqueous-to-oil operation phase ratios in the tower can be calculated when gas containment ratios in the tower are known, if specific tower diameter is given. Experimental results confirm the reasonability of that suggested calculation method. The present works provide fundamental data for future industrial application of that new bubbling extraction tower.

Experimental

Apparatus

The proposed bubbling extraction tower has a structural design as depicted in Figure 1.

The new bubbling extraction tower is composed of these parts: organic bubble film generator (4), main tower (3), organic phase demulsification section (1), aqueous phase clarification section (8), aqueous phase distributor (2), organic phase inlet (7), organic phase outlet (10), aqueous phase inlet (9), aqueous phase outlet (5), gas phase inlet (6), and gas phase outlet (11).

The organic bubble film generator [(4) in Figure 1] consists of a group of gas needles and oil holes, as shown in Figure 2. Gas needles are inserted into the oil holes. The outer diameter of gas needles is smaller than the inner diameter of oil holes. The organic phase passes through the annular gaps between gas needles and oil holes and flow out from the top end of those oil holes. When gas bubbles were blown out from the top end of gas needles, a thin layer of organic liquid extractant membrane could be formed and covered on the surface of gas bubbles. We called those gas-in-oil bubbles covered with organic liquid extractant membrane as “organic bubbles.” The extraction process might be enrichment of target components from aqueous feed solution onto the surfacial organic liquid membrane layer of those dispersed organic bubbles.

The organic phase demulsification section [(1) in Figure 1] located at the top of main tower can destroy organic bubbles and achieve coalescence of dispersed organic phases after extraction. The aqueous phase clarification section [(8) in Figure 1] set at the bottom of the main tower is aimed to clarify the aqueous phase flowing out and decrease oil content within it as little as possible.

Process principle

Experimental operations of the bubbling extraction tower were conducted according to following procedures:

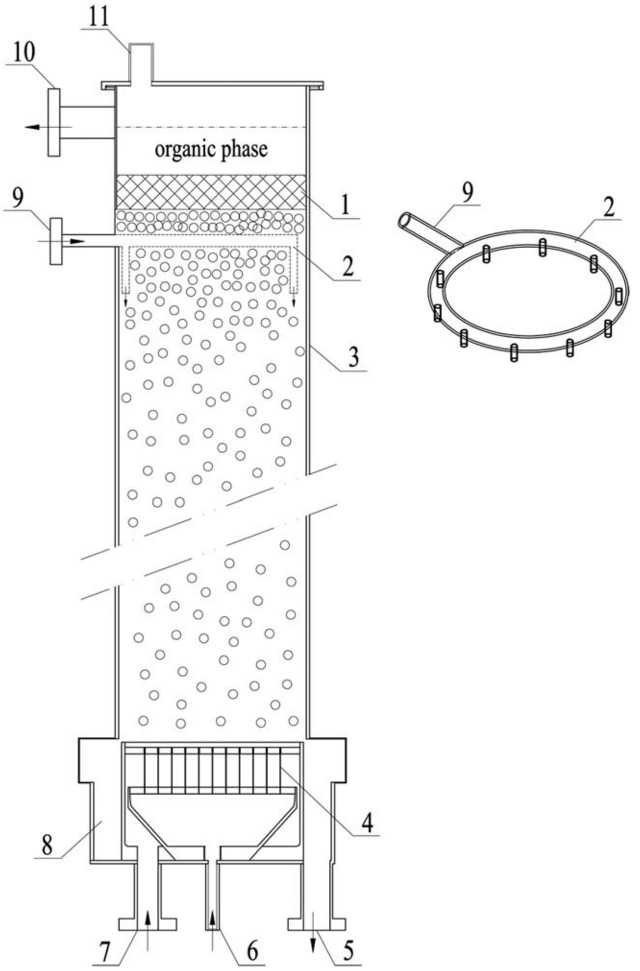

Figure 1. Sketch structure of the bubbling extraction tower.

1-organic phase demulsibility section; 2-aqueous phase distributor; 3-main tower; 4-organic bubble film generator; 5-aqueous phase outlet; 6-gas phase inlet; 7-organic phase inlet; 8-aqueous phase clarification section; 9-aqueous phase inlet; 10-organic phase outlet; 11-gas phase outlet.

The aqueous solutions containing target components flow into the aqueous phase distributor [(2) in Figure 1] from the aqueous phase inlet [(9) in Figure 1] set at the top of main tower, then entering the main tower [(3) in Figure 1] along the inner-wall of main tower. The aim to design such an aqueous phase distributor is to prevent axial back-mixing and flooding of aqueous phase in tower. The aqueous phase flow down along the main tower and contact with dispersed organic bubbles ascending in tower, so that target components in continuous aqueous phase can be entrapped and enriched into the organic liquid membrane layer on the surface of dispersed gas bubbles. The aqueous phases, after contacting with organic bubbles, pass through the aqueous phase clarification section [(8) in Figure 1] to separate out dispersed oil phases and then flow out from the aqueous phase outlet [(5) in Figure 1] set at the bottom of main tower finally.

The organic phase flow into the organic bubble film generator [(4) in Figure 1] from the organic phase inlet [(7) in Figure 1] set at the bottom of main tower, and in the meantime, air or nitrogen gas was also blown into the organic bubble film generator from the gas phase inlet [(6) in Figure 1]. When gas bubbles were blown out from the top end of gas needles, a thin layer of organic liquid membrane could be formed and covered on the surface of gas bubbles. The organic bubbles ascend along the main tower and contact with the aqueous phase flowing down, so that countercurrent extraction could be achieved. After phase contacting, the organic bubbles were destroyed when they pass through the organic phase demulsification section [(1) in Figure 1], and organic liquid membrane on surface of dispersed gas bubbles agglomerate together to form a continuous organic bulk phase and then overflows from the organic phase outlet [(10) in Figure 1] set at the top of main tower. The gas phase flows out from the gas phase outlet [(11) in Figure 1] set at the top of main tower.

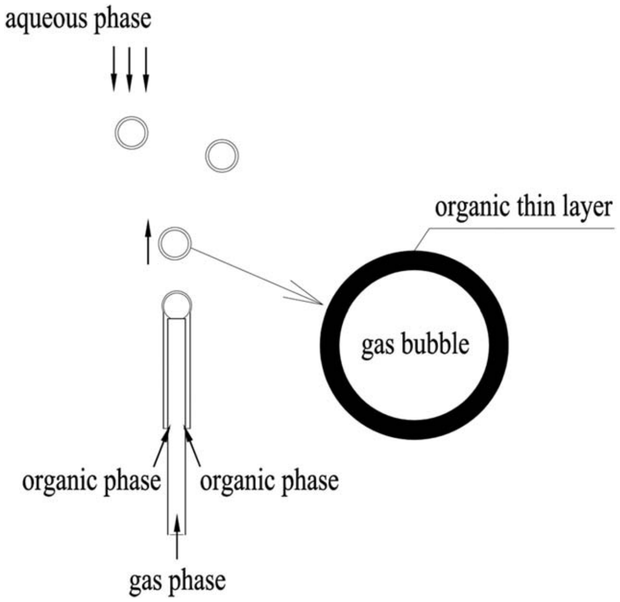

Figure 2. Sketch structure of the organic bubble film generator.

Calculations of Operation Phase Ratios

In this work, we found that it is feasible to achieve dispersion of small-volume organic phase in a form of thin layer organic liquid membrane covered onto surface of gas bubbles if the volume flow rate of gas pumping in the tower and that of organic phase pumping in were carefully controlled at appropriate ratios. The thickness of organic liquid membrane layer on each gas bubble could also be controlled by doing so. Therefore, the total volume of organic phase in the tower can be calculated if we know the total volume of the organic liquid membrane layer on the surface of those dispersed gas bubbles in tower. Unfortunately, it is difficult to determine the average thickness of those organic liquid membrane layer on each gas bubble, and also the total surficial area of those dispersed organic bubbles in tower.

In fact, when volume flow rate of organic phase (L_0) pumping in tower is known, the total volume of organic phase pumping into tower during the time of those dispersed oil bubbles passing through the tower can be calculated as followed

$$V_0 = L_0 t \tag{1}$$

Here, V_o is the total volume of organic phase within per unit of mass-transfer height of the tower. t is the two-phase contacting time within per unit of mass-transfer height of the tower. And we have

$$t=\frac{1}{\mu_g} \tag{2}$$

In Eq. 2, μ_g is the moving velocity of oil bubbles passing through the empty tower (i.e., aqueous phase in tower does not move), and it can be calculated by following equation

$$\mu_g=\frac{L_g}{A} \tag{3}$$

where L_g is the volume flow rate of gas phase pumping in tower. A is the cross-sectional area along the direction of tower diameter. It can be expressed as $A=\frac{\pi d_t^2}{4}$

The volume of aqueous phase (V_a) within per unit of mass-transfer height is

$$V_a=\pi\left(\frac{d_t}{2}\right)^2(1-\varepsilon_g) \tag{4}$$

In Eq. 4, d_t is the tower diameter. ε_g is the gas containment ratio in aqueous phase in per unit of mass-transfer height of the tower, and it can be expressed as[22]

$$\frac{\varepsilon_g}{(1-\varepsilon_g)^4}=0.20\left(\frac{g d_t^2 \rho_W}{\sigma_W}\right)^{\frac{1}{8}}\left(\frac{g d_t^3}{v_W^2}\right)^{\frac{1}{12}}\left(\frac{\mu_g}{\sqrt{g d_t}}\right) \tag{5}$$

In Eq. 5, σ_W is the surface tension of the aqueous phase. v_W is the kinematic viscosity of the aqueous phase. ρ_W is the density of the aqueous phase. The constant g is acceleration of gravity.

Therefore, the aqueous-to-oil phase ratio, $R_{a/o}$, within per unit of mass-transfer height can be calculated by the following equation

$$R_{a/o}=V_a/V_o \tag{6}$$

In Eq. 6, V_a and V_o could be calculated respectively based on the values obtained from Eqs. 1 to 5, therefore, $R_{a/o}$ can be expressed as

$$R_{a/o}=\frac{(1-\varepsilon_g)L_g}{L_0} \tag{7}$$

From above discussion, we know that the values of ε_g depend only on the tower diameter d_t, if the physicochemical properties of the extraction system, such as σ_W, v_W, ρ_W, and so forth, are known previously. Therefore, $R_{a/o}$ can be calculated when d_t is given. The calculation about $R_{a/o}$ provide feasible guidelines for operation of the tower to achieve dispersion of the small volume of organic phase on the surface of gas bubbles by regulating the ratios between the volume flow rate of gas pumping in the tower and that of organic phase pumping in. Therefore, a stable operation to perform liquid–liquid solvent extraction at large aqueous-to-oil phase ratios in that suggested bubbling extraction tower could be achieved.

Calculations of Tower Height

The plug-flow model is usually used to calculate the mass-transfer height in traditional extraction tower.[23] In that process, organic extractant was dispersed as tiny oil droplets to achieve countercurrent contact with aqueous feed solutions. However, extraction reaction in this work was carried on the surface layer of dispersed gas bubbles covered with organic extractant liquid membrane. The novelty of this method is the use of a gaseous phase inside the small organic droplets. The gas bubbles act only as a kind of distribution medium to support organic liquid extractant membrane and do not participate in the reactions. Therefore, the mass-transfer process of target component is in fact from the bulk aqueous phase into the organic liquid membrane covered on the surface of those dispersed gas bubbles. In such conditions, operation model of the suggested bubbling extraction tower is very similar as that of traditional extraction tower. Therefore, the plug-flow model could also be used to calculate the mass-transfer height in present bubbling extraction tower.

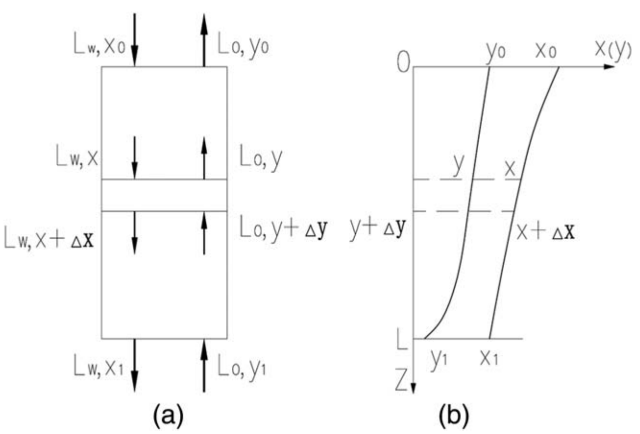

Figure 3. Continuous and countercurrent mass transferring in extraction tower.

(a) Plug-flow model of aqueous and organic phase flow in tower (b) Mass transfer between organic and aqueous phase occur only in the horizontal direction

As shown in Figure 3, we assume that aqueous phase flow and organic phase flow in bubbling extraction tower both follow the plug-flow model. That is to say, the volume flow rate of the two liquid phases both keep in constant, when they pass through each section of the tower along the direction of tower height. The liquid flow moves likes a piston, moving forward regularly and in parallel. Mass transfer between oil and aqueous phase is assumed to occur only in the horizontal direction but not in the vertical direction.[23]

Given that two immiscible liquid phases both undergo plug-flow in the tower, the theoretical height of mass transfer can be expressed as[23]

$$H_W=\frac{L}{KaA}\int_{x_1}^{x_0}\frac{dx}{x-x^*} \tag{8}$$

where, H_W is the theoretical mass-transferring height of aqueous phase. K is the total mass-transfer coefficient. a is the total contacting surface area between organic and aqueous two phases. x_0 and x_1 represent the concentration of target component in aqueous phase entering in the tower (i.e., the inlet concentration) and flowing out the tower (i.e., the outlet concentration), respectively. x represents the concentration of target component in aqueous phase entering in one of sections along the tower height direction. x^* is the mass-transfer equilibrium concentration of target component passing out off each section in the tower.

Equation 8 is composed of two parts: $\int_{x_1}^{x_0}\frac{dx}{x-x^*}$ and $\frac{L}{KaA}$. The former, $\int_{x_1}^{x_0}\frac{dx}{x-x^*}$, is defined as the mass-transfer unit number, which could be represented by the symbol $(\mathrm{NTU})_W$. The mass-transfer unit number depends on detailed requirements from separation processes. The later, $\frac{L}{KaA}$, in Eq. 8 was defined as the mass-transfer unit height, which could be represented

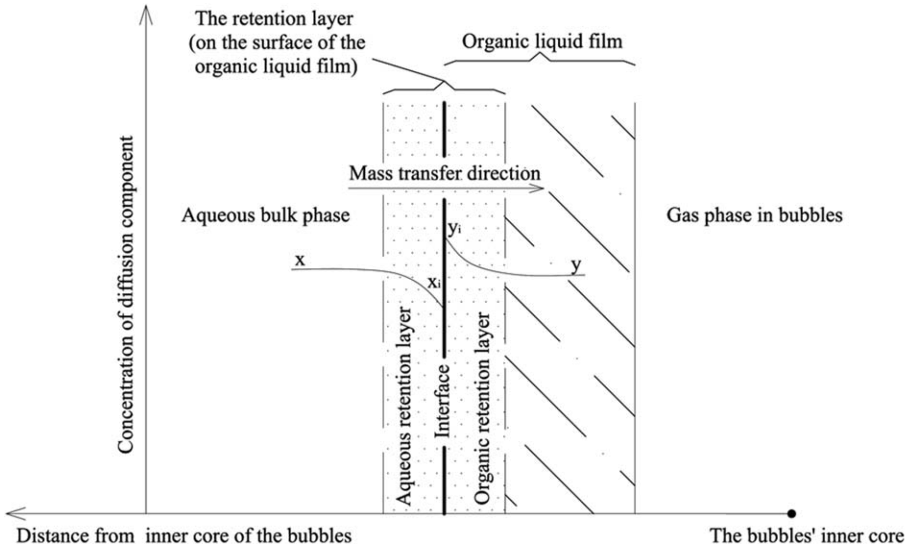

Figure 4. The dual resistance model.

by the symbol $(\mathrm{HTU})_\mathrm{W}$. Therefore, the theoretical mass-transfer height can be expressed as[23]

$$H_\mathrm{W} = (\mathrm{NTU})_\mathrm{W}(\mathrm{HTU})_\mathrm{W} \tag{9}$$

In that case, there is no apparent change in volume flow rate of each phase and no mutual dissolution of the two phases in the extraction process, $(\mathrm{NTU})_\mathrm{W}$ can be expressed as[23]

$$(\mathrm{NTU})_\mathrm{W} = \frac{1}{1-\frac{1}{\varepsilon}}\ln\left[\left(\frac{x_0-\frac{y_1}{D}}{x_1-\frac{y_1}{D}}\right)\left(1-\frac{1}{\varepsilon}\right)+\frac{1}{\varepsilon}\right] \tag{10}$$

In Eq. 10, ε is the extraction factor. It can be expressed as $\varepsilon = \frac{DL_0}{L}$, in which L_o and L represent the volume flow rate of the organic and aqueous phases, respectively. D is the distribution coefficient. y_1 and y_0 represent the inlet and outlet concentration of target component in organic phase, respectively.

$(\mathrm{HTU})_\mathrm{W}$ could be expressed as[23]

$$(\mathrm{HTU})_\mathrm{W} = \frac{L}{KaA} \tag{11}$$

In Eq. 11, the total contacting surface area, a, between organic and aqueous two phases can be calculated by the following equation[24]

$$a = \frac{6\varepsilon_\mathrm{g}}{d_\mathrm{vs}} \tag{12}$$

where, the average bubble diameter,d_vs, can be calculated using the Akita Number Relational Formula[22]

$$\frac{d_\mathrm{vs}}{d_\mathrm{t}} = 26\left(\frac{g d_\mathrm{t}^2 \rho_\mathrm{W}}{\sigma_\mathrm{W}}\right)^{-0.5}\left(\frac{g d_\mathrm{t}^3 {\rho_\mathrm{W}}^2}{v_\mathrm{W}^2}\right)^{-0.12}\left(\frac{\mu_\mathrm{g}}{\sqrt{g d_\mathrm{t}}}\right)^{-0.12} \tag{13}$$

The total mass-transfer coefficient, K, can be calculated based on the Dual Resistance Model.[21] The extraction process is represented in Figure 4.

Assuming that an air circulation inside the small organic droplets was not considered here. According to the dual model resistance assumption for a stable mass transfer across the interface, the mass-transfer rate for target components from aqueous bulk phase to interface is equal to that from interface to organic bulk phase. There is

$$n_\mathrm{A} = k_\mathrm{W}(x-x_i) = k_0(y_i-y) \tag{14}$$

In Eq. 14, n_A is the diffusion rate of target component A on per unit of contacting area. k_W and k_0 are the mass-transfer coefficients of component A in aqueous and organic phases, respectively. Variables x and y are the concentrations of target component A in organic and aqueous bulk phases, respectively. x_i and y_i are the interfacial concentrations of target component A on the side of organic phase and aqueous phases, respectively.

In fact, x_i and y_i are unknown. Assume the mass transfer of target component A has reached equilibrium on the liquid–liquid interface, therefore the target component passes through the interface without any resistance. According to the Dual Resistance Model, the total mass-transfer resistance is composed of two parts: target components transferring from aqueous bulk phase onto the interface, and then the reaction resultants formed on the interface transferring into organic bulk phase. The total mass-transfer resistance of target component from aqueous bulk phase to organic bulk phase across per unit of mass-transfer area can be expressed as[21]

$$\frac{1}{K} = \frac{1}{k_\mathrm{W}} + \frac{1}{Dk_0} \tag{15}$$

According to Eq. 15, the total mass-transfer resistance can be calculated based on mass-transfer coefficients of target component in organic bulk phase, k_0, and that in aqueous bulk phase, k_W.

When organic oil bubbles pass through continuous aqueous phase, the Reynolds Number is $R_e = d_\mathrm{vs}u_\mathrm{s}\rho_\mathrm{W}/v_\mathrm{W}$. Here, u_s is the relative moving velocity of organic and aqueous phases in tower. It can be expressed as follows[21]

$$\mu_s = \frac{\mu_0}{\phi_D} + \frac{\mu}{1-\phi_D} \tag{16}$$

where μ_0 is the moving velocity of organic phase passing through the empty tower. It has $\mu_0 = \frac{L_0}{A}$. μ is the moving velocity of aqueous phase passing through the empty tower. It has $\mu = \frac{L}{A}$.

In Eq. 16, ϕ_D is the flooding retention rate, which has

$$\phi_D = \frac{2}{3+\sqrt{1+\frac{8}{L_R}}} \tag{17}$$

Here, L_R represents the ratio of volume flow rate of oil to aqueous phase, it has $L_R = \frac{L_0}{L}$.

In this work, the calculated values of R_e is 1.62, which is below 10.

Therefore k_0 can be expressed as[25]

$$k_0 = \frac{2\pi^2 D_0}{3d_{vs}} \tag{18}$$

Calderbank and Moo-Young proposed that k_W could be described by the following formula[25]

$$\frac{k_W d_{vs}}{D_W} = 0.42\left(\frac{\upsilon_w}{\rho_W D_W}\right)^{\frac{1}{3}}\left(\frac{g d_{vs}^3 \Delta\rho\rho_W}{\upsilon_W^2}\right)^{\frac{1}{3}} \tag{19}$$

Here, D_0 and D_W are the molecular diffusion coefficients of target component in organic and aqueous phases, respectively. $\Delta\rho$ is the density difference between organic phase and aqueous phase.

Based on the values obtained from Eqs. 10 to 19, the theoretical mass-transferring height, H_W, of aqueous phase in the tower can be calculated. As for a real mass-transferring height, H_{WG}, that is required for practical operation processes, the influence from ε_g should be taken into considered because a large amount of gas bubbles were blown into the tower. Therefore, we have

$$H_{WG} = \frac{H_W}{1-\varepsilon_g} \tag{20}$$

The process of gas bubbling may result in axial mixing in the bubbling extraction tower. Levenspiel and Bischoff suggested a quantitative model to describe the influence from axial gas mixing on the calculation of tower height.[26] Therefore, the mass-transferring height involving in axial gas mixing effect can be described as H_{WZ}, which has a close relationship with the Peclet Number (P_e) and operation efficiency (η_A). Here, P_e can be calculated as follows

$$P_e = \frac{u_g H_{WG}}{E_{GZ}\varepsilon_g} \tag{21}$$

where, E_{GZ} is the axial gas dispersion coefficient.

Pavlica and Olson proposed that E_{GZ} could be calculated as follows[27]

$$E_{GZ} = 5d_t\left(\frac{u_g}{\varepsilon_g}\right) \tag{22}$$

Therefore, H_{WZ} can be obtained from the Levenspiel's quantitative relationship diagram when P_e and η_A are known.

Apart from above discussion, the aqueous phase clarification section and the organic phase demulsification section should also be included in for calculation of the total tower height to achieve complete separation of aqueous and oil phases.

We use H_S to describe the required height for the aqueous phase clarification section.

H_S can be calculated by the following formula

$$H_S = \frac{4V_S}{\pi d_t^2} \tag{23}$$

where, V_S is the volume of the aqueous phase clarification section in tower.

The calculation for V_S should take into account that half of that volume was occupied by aqueous phase

Therefore, we have

$$V_S = \frac{2L_0\tau_0}{\phi_D} \tag{24}$$

τ_0 is the retention time required in the aqueous phase clarification section. It could be calculated using the following formula[23]

$$\tau_0 = 1.32\times10^5 \frac{\upsilon_W d_{vs}}{\sigma_W}\left(\frac{H_{WZ}}{d_{vs}}\right)^{0.18}\left(\frac{\Delta\rho g d_{vs}^2}{\sigma_W}\right)^{0.32} \tag{25}$$

Usually, the height of the organic phase demulsibility section is equal to H_S.

Therefore, the total tower height, H, is a sum of the mass-transferring height involving in axial gas mixing effect, H_{WZ}, and the height of the aqueous phase clarification section and the organic phase demulsibility section

$$H = H_{WZ}+2H_S \tag{26}$$

Regarding the practical processes to operate the tower, those calculations are necessary to achieve effective extraction and enrichment of target components, because we could regulate the volume flow rate of organic phase, aqueous phase, and gas pumping in the tower according to the calculated values of H_{WZ} and H_S, so that to meet the requirements of practical height of the main tower [(3) in Figure 1], the height of the aqueous phase clarification section [(1) in Figure 1] and that of the organic phase demulsibility section [(8) in Figure 1].

Calculation Examples

Calculation of operation phase ratio

The suggested bubbling extraction tower was used for extraction of lanthanum (La) from an industrial waste water obtained from a rare-earth refinery in Shandong Province, P.R. China. The density of aqueous feed solution, ρ_W, was 1060 kg/m^3, and the surface tension of the aqueous solution, σ_W, was 17.5×10^{-3} N/m. v_W was 3.0×10^{-3} pa·s, and g is 9.81 m/s^2. The organic extractant was 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (CAS No.1070-03-7) (denoted as P507) as used in traditional rare-earth solvent extraction processes. Kerosene (CAS No.8008-20-6) was used as a diluent of the organic extractant P507. The concentration of P507 in kerosene was 1.5 mol/L. The aqueous-phase flow rate, L, was 0.10 m^3/h, while the organic-phase flow rate, L_0, was controlled at 0.03 m^3/h. The gas-phase flow rate, L_g, was 20 m^3/h.

According to previous discussion, the operation phase ratio, $R_{a/o}$, can be calculated if the tower diameter, d_t, and gas containment ratios, ε_g, were known. Here, the value of d_t was set equaling to 0.23 m. The calculated results are listed in Table 1.

As shown in Table 1, if the tower diameter, d_t, of the proposed bubbling extraction tower was 0.23 m, the operation phase ratio, $R_{a/o}$, could reach 603. Such a large aqueous-to-oil operation phase ratio is hard to be achieved in traditional extraction equipments.

Calculation of tower height

P507 molecules diluted in kerosene generally occurs in a form of its molecular dimers, which could be expressed as $(HA)_2$. The chemical reaction between P507 molecules and La^{3+} ions includes two step

Table 1. Calculation Results for Operation Phase Ratio

t (s)	μ_g (m/s)	V_o (m^3)	ε_g	V_a (m^3)	$R_{a/o}$
7.58	0.132	0.63×10^{-4}	0.095	0.038	603

Table 2. The Physic-Chemical Parameters of Extraction System

D_0 (m^2/s)	D_W (m^2/s)	$\Delta\rho$ (kg/m^3)	D	η_A (%)
5.85×10^{-9}	0.79×10^{-11}	180	63	0.95

$$(\mathrm{HA})_{2(\mathrm{org})} + 2\mathrm{NaOH} = (\mathrm{NaA})_{2(\mathrm{org})} + 2\mathrm{H_2O} \tag{27}$$

$$3(NaA)_{2(\mathrm{org})} + 2\mathrm{LaCl_3} = (\mathrm{LaA_3})_{2(\mathrm{org})} + 6\mathrm{NaCl} \tag{28}$$

Saponification of P507 molecules with alkali was required prior to extraction of La^{3+}, which would result in the H^+ ion in phosphoric acid group (-POOH) of P507 molecules would be replaced by Na^+ ion, as shown in Eq. 27. Therefore, La^{3+} extraction chemical reaction with P507 is in fact that, La^{3+} in aqueous phase transfer into the organic phase to exchange with Na^+ ion and associate with —POO group, as shown in Eq. 28. In the meantime, Na^+ in the organic phase transfer into the aqueous phase.

According to the Dual Resistance Model, the mass-transfer resistance for La^{3+} ion from the aqueous bulk phase into the organic liquid extractant membrane on the surface of bubbles, and Na^+ ion from organic liquid membrane layer into the aqueous bulk phase, come from the resistance in the organic and aqueous retention layer on the two sides of the surface of the organic liquid membrane layer covered on surface of the bubbles, as depicted in Figure 4. The total mass-transfer resistance for La^{3+} ion transferring is composed of two parts: La^{3+} transferring from aqueous bulk phase onto the interface of those dispersed organic bubbles, and then the reaction resultants formed on the interface transferring into the bulk phase of the organic liquid membrane layer. According to Eqs. 18 and 19, we could obtain the mass-transfer coefficients, k_0 and k_W, of La^{3+} ions passing through the organic and aqueous retention layer in the liquid organic membrane on the surface of those dispersed organic bubbles contacting with aqueous phase, respectively. Therefore, the total mass-transfer resistance for La^{3+} transferring across per unit of the surficial area of the liquid membrane layer on bubbles can be calculated based on Eq. 15.

If we know the inlet concentration of La^{3+} ions in feed aqueous solution, x_0, and the outlet concentration of La^{3+} ions in aqueous solution flowing out of the tower, x_1, the total tower height, H, could be calculated based on Eq. 26. Here, x_0, was set equaling to 7.19×10^{-4} mol/L, and x_1, was 0.36×10^{-4} mol/L. The other physic-chemical parameters required for calculation are listed in Table 2. The calculated results are listed in Table 3.

As shown in Table 3, a required total tower height was 11.12 m, when outlet concentration of La^{3+} in aqueous solution after extraction was set equaling to 0.36×10^{-4} mol/L. The height to diameter ratio of the main tower is 48.

Demonstration in Pilot Test

A new bubbling extraction tower was manufactured to confirm the reasonability of above calculations. The tower diameter d_t was 0.23 m and total tower height H was 4.0 m, H_{WZ} was 3.4 m.

The pilot test was performed according to the following procedures:

About 0.15 m^3 of aqueous feed solution was used for extraction. When all of 0.15 m^3 aqueous feed solutions flow out from the bubbling extraction tower, the mass-transfer height of aqueous phase traveling in the tower is 3.4 m. Then the aqueous solution flowing out was repumped into the tower for recycling from the aqueous phase inlet to contact with dispersed organic extractant bubbles once again. Extraction was end until the aqueous solution recycle four times in tower. For each repeated recycling, two-parallel samples were taken from the aqueous solution flowing out of the tower. The aqueous-phase flow rate, L, the organic-phase flow rate, L_0, the gas-phase flow rate, L_g, and other detailed operating parameters of the bubbling extraction tower were same as mentioned before. Air bubbles were blown into the tower as the support of the organic liquid extractant membrane. Experimental results are shown in Table 4.

From the results listed in Table 4, we see that the concentration of La^{3+} in equilibrating aqueous phase decreased from 7.19×10^{-4} mol/L to 0.20×10^{-5} mol/L when the aqueous phase passed through the tower three times, which means the aqueous phase traveling a total height of 10.2 m in the tower. The experimental data in pilot test for required tower height are highly consistent with the calculation results given in previous discussion. Therefore, the calculation methods established in this study can be appropriate for designing the tower height of our proposed bubbling extraction tower.

In pilot test, the volume flow rate of the organic-phase sprayed into the tower was 0.03 m^3/h, and gas-phase flow rate was 20 m^3/h. Our previous works found that the time for a single gas bubble ascending from the oil spraying-hole at the bottom of the tower to the top end of the tower (tower height is 3.4 m) is about 13 s. Here, that time is defined as phase contacting time in bubbling extraction tower. Therefore, the total volume of organic phase and that of gas phase passing through the tower are 1.08×10^{-4} m^3 and 0.072 m^3, respectively, during the time of two phase contacting in tower. The total volume of aqueous phase in the tower is 0.071 m^3, which is a difference of the total volume of main tower minus the total volume of organic phase and gas phase in tower. Thus, the practical operation phase ratio in bubbling extraction tower is 657. Experimental observation about operation phase ratio is indeed in a good agreement with that calculated values. The calculated error is only 9%.

Pilot test also demonstrated that the new bubbling extraction tower suggested in this work have unique advantage in

Table 3. Calculation Results for Tower Height

d_{vs} (m)	a (m^2/m^3)	μ_0 (m/s)	μ (m/s)	μ_s (m/s)	L_R	ϕ_D	k_0 (m/s)	k_W (m/s)	K (m/s)	ε
2.7×10^{-3}	211	0.2×10^{-3}	0.7×10^{-3}	1.7×10^{-3}	0.3	0.24	1.42×10^{-5}	1.40×10^{-6}	1.40×10^{-6}	18.9
$(NTU)_W$	$(HTU)_W$ (m)	H_W (m)	H_{WG} (m)	E_{GZ} (m^2/s)	H_{WZ} (m)	P_e	τ_0 (s)	V_S (m^3)	H_S (m)	H (m)
3.1	1.82	5.64	6.23	1.60	10.30	5.41	244	0.017	0.41	11.12

Table 4. Pilot Test for Extraction of La in the New Bubbling Extraction Tower

Numbers Aqueous Phase Passing Through the Tower	Concentration of La in Aqueous Phase Flowing out From the Tower (mol/L)	Average Extraction of La (%)
0	7.19×10^{-4}	
1	1.51×10^{-5}	79.0
2	0.51×10^{-5}	92.9
3	0.20×10^{-5}	97.2
4	0.19×10^{-5}	97.4

comparison with traditionally used extraction towers for recovery of small quantities of valuable components diluted in large quantities of water. To perform liquid–liquid extraction using large aqueous-to-oil phase ratios could achieve economic recovery of the target components with extremely low concentrations in industrial waste waters. As an example to illustrate that advantage, we conducted a preliminary analysis about the cost of the new extraction tower. As mentioned above, the initial concentration of La^{3+} in waste water is 7.19×10^{-4} mol/L. That is to say, about 100 g La was in per cubic meter of waste water. We know that the percent recovery of La in the aqueous solution flowing out of the bubbling extraction tower could reach above 97%, as indicated in Table 4. According to economic price of La in China market (about 0.2 RMB yuan per gram), the incomes for treatment of per cubic meter of waste water would be 19.4 RMB yuan, if we could obtain 97 g La from per cubic meter of waste water. Our pilot test demonstrated that the enrichment ratios of La could reach more than 600, by performing large-phase-ratio extraction in that bubbling extraction tower. Therefore, the payback for treatment of per cubic meter of waste water would be 17.4 RMB yuan, due to the cost to treat per cubic meter of waste water in that suggest bubbling extraction tower is less than 2.0 RMB yuan. However, the maximum phase flow ratios in the traditional extraction towers, such as Rotating Disc Column or Pulsed Sieve Plate Extraction Column, are not higher than 15.[28] In addition, the percent recovery are only around 60% using the traditional extraction towers to treat such an industrial waste water containing extremely low concentration of target components.[29] The cost to perform liquid–liquid extraction using traditional extraction towers would be far larger than that suggested bubbling extraction tower. Therefore, the economic benefits brought about using the new bubbling extraction tower is obvious higher than those traditional extraction towers and it does have a decent payback.

Conclusions

In this work, a novel bubbling extraction tower was suggested to perform liquid–liquid solvent extraction at large aqueous-to-oil phase ratios, so that valuable components in industrial waste waters with extremely low concentrations can be effectively extracted and enriched with higher enrichment ratios into the small volume of organic phase and then recovered economically. Experimental results demonstrated that in the bubbling extraction tower, the small volume of organic phase can be dispersed and covered on the surface of gas bubbles to form a layer of organic liquid extractant membrane. The target components are extracted from the aqueous feed solution into the surficial organic liquid membrane of those dispersed oil bubbles, which are ultimately collapsed at the top of the tower and the organic phase is recovered. We developed a theoretical framework to calculate the required tower height of the suggested bubbling extraction tower based on the plug-flow model and the dual resistance model. The aqueous-to-oil operation phase ratios in the tower can be calculated when gas containment ratios in the tower are known, if specific tower diameter is given. In comparison with traditional extraction tower, dispersion characters of organic extractants on the surface of gas bubbles were taken into consideration to calculate the tower height and operation phase ratios. Tower height and operation phase ratio calculated by the proposed new methodology are highly consistent with those experimental results in pilot tests. These works provide a scientific basis for structural design of the new bubbling extraction tower, and it is important for future optimization, scale-up, and industrial application.

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Literature Cited

1. Xie F, Zhang TA, Dreisinger D, Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner Eng*. 2014;56:10–28.
2. Wilson AM, Bailey PJ, Tasker PA, Turkington JR, Grant RA, Love JB. Solvent extraction: the coordination chemistry behind extractive metallurgy. *Chem Soc Rev*. 2014;43:123–134.
3. Sinha MK, Sahu SK, Meshram P, Pandey BD. Solvent extraction and separation of zinc and iron from spent pickle liquor. *Hydrometallurgy*. 2014;147:103–111.
4. Singh VK, Tiwari PN. Removal and recovery of chromium(VI) from industrial waste water. *J Chem Technol Biotechnol*. 1997;69:376–382.
5. Rudnicki P, Hubicki Z, Kołodyńska D. Evaluation of heavy metal ions removal from acidic waste water streams. *Chem Eng J*. 2014; 252:362–373.
6. Leonga MI, Fuhb MR, Huangc SD. Beyond dispersive liquid-liquid microextraction. *J Chromatogr A*. 2014;1335:2–14.
7. Wang JD, Chen JY. *Handbook of Solvent Extraction*, *1st ed*. Beijing: Chemical Industry Press, 2001.
8. Hosseinzadeh M, Ranjbar M, Alizadeh M. Effect of operational parameters and internal recycle on rhenium solvent extraction from leach liquors using a mixer-settler. *Eng Sci Technol Int J*. 2014;17: 45–49.
9. Tang XJ, Luo GS, Wang JD. Mass transfer and axial mixing characteristic in a coalescence-dispersion pulsed-sieve-plate extraction column. *Chin J Chem Eng*. 2004;12:857–861.
10. Zhou JZ, Duan WH, Xu JQ, Yang YY. Experimental and simulation study on the extraction of p-cresol using centrifugal extractors. *Chin J Chem Eng*. 2007;15:209–214.
11. Orpusov GV, Tilyanin FA. Multistage counterflow centrifugal extractor-has chamber manifold with screw plug to give constant phase volume ratio in all stages. US Patent 967506-A, 1983.
12. Ferreira AR, Neves LA, Ribeiro JC, Lopesc FM, Coutinhob JAP, Coelhosoa IM, Crespoa JG. Removal of thiols from model jet-fuel streams assisted by ionic liquid membrane extraction. *Chem Eng J*. 2014;256:144–154.
13. Valenzuela F, Fonseca C, Basualto C, Correa O, Tapia C, Sapag J. Removal of copper ions from a waste mine water by a liquid emulsion membrane method. *Miner Eng*. 2004;18:33–40.
14. Luo JH, Li J, Yang ZP, Liu XF. Removal of chromium(III) from aqueous waste solution by predispersed solvent extraction. *Trans Nonferrous Met Soc China*. 2013;23:524–529.

15. Hu W, Sun Y, Ye RQ. Separation of quercentin by pre-dispersed solvent extraction. *Chin J Chem Eng*. 2003;11:367–370.
16. Huang K, Liu HZ, Tao AZ. A new extraction equipment for liquid-liquid solvent extraction at large aqueous-to-oil phase ratios. Chinese Patent 201110404565.2, 2011.
17. Huang K, Xiao CX, Liu HZ. A new large-phase-ratio extractor by "organic bubbles" covered with liquid organic extractant membrane. Chinese Patent 201410007908.5, 2014.
18. Huang K, Liu J, Wu HZ, Liu HZ. An equipment to generate liquid organic film supported by gas bubbles. Chinese Patent 201410023670.5, 2014.
19. Trebal RE. *Liquid Extraction*, *2nd ed.* New York: McgRAW-Hill, 1963.
20. Coulson JM, Ichardson RJF. *Chemical Engineering, Vol. 2*, *2nd ed.* Oxford: Pergamon, 1979.
21. Whitman WG. A preliminary experimental confirmation of the two-film theory of gas absorption. *Chem Metall Eng*. 1923;29:146–148.
22. Akita K, Yoshida F. Bubble size interfacial area and liquid-phase mass transfer coefficient. *Ind Eng Chem Process Des Dev*. 1974;13:84–91.
23. McCabb WL, Smith JC, Harriott P. *Unit Operation of Chemical Engineering*, *7th ed.* New York: McGraw-Hill, 2004.
24. China Petrochemical Corporation Shanghai Engineering Co., Ltd. *Handbook of Chemical Process Design*, 4th ed. Beijing: Chemical Industry Press, 2009.
25. Calderbank PH, Moo-Young MB. The continuous phase heat and mass-transfer properties of dispersions. *Chem Eng Sci*. 1961;16:39–54.
26. Levenspiel O, Bischoff KB. Backmixing in the design of chemical reactors. *Ind Eng Chem Res*. 1959;51:143–1434.
27. Pavlica RT, Olson JH. Unified design method for continuous-contact mass transfer operations. *Ind Eng Chem Res*. 1970;62:45–48.
28. Rauscher H, Blass E. Operation of a pulsed sieve-plate extraction column with an extreme phase flow ratio. In: Sekine T, editor. *Proceedings of the 10th International Conference on Solvent Extraction (ISEC 90). Kyoto, Japan, July 16–21, 1990. Solvent Extraction 1990, PTS A and B: Process Metallurgy*, Kyoto, Japan: Japan Atom Energy Res Inst. RAUSCHER, 1992: Vol. 7, 1271–1276.
29. Vikesh GL, Achyut DP, Virendra KR. Mass transfer studies in pulsed sieve plate extraction column for the removal of tributyl phosphate from aqueous nitric acid. *Ind Eng Chem Res*. 2014;53:4812−4820.

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