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Mass transfer characteristics of citric acid extraction by hollow fiber renewal liquid membrane

Zhongqi Ren, Weidong Zhang*, Haoshu Li, Wei Lin

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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ABSTRACT

A new liquid membrane technique, hollow fiber renewal liquid membrane (HFRLM), is used for simultaneous extracting and concentrating citric acid from dilute solutions. The organic phase of 30% N235 + 20% *n*-octanol + 50% kerosene was used as liquid membrane phase, NaOH as stripping phase. Experiments were performed as a function of operation mode, carrier concentration in the organic phase, initial citric acid concentration in the feed phase, NaOH concentration in the stripping phase, etc. The results showed that the HFRLM process was very stable. The transport of citric acid from membrane phase to the stripping phase was the rate-controlling step for this process. The stirred mixture of the stripping phase and the organic phase flowed through the lumen side of the module could provide a higher mass transfer rate. The transport studies with a recycling experiment indicated that HFRLM was a promising recovery method for separation and concentration of compounds from dilute solutions.

1. Introduction

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid, $C_6H_8O_7{\cdot}H_2O$, H_3A) is one of the important organic acids successfully developed by fermentation process. The principal uses of citric acid are food, pharmaceutical, and industrial. The world market of citric acid is growing every year [1]. The recovery of citric acid from fermentation broth is one of important steps in a commercial process of citric acid production, especially from dilute solutions. Now, the only commercially viable technique on large-scale processes is precipitation technique using calcium salt followed by filtration and subsequently treated with sulphuric acid, but the common calcium salt precipitation process for isolation of citric acid produces 2.5 tons of waste per ton of citric acid [1–4]. Other recovery methods for this purpose, such as, solvent extraction, ionic exchange, absorption, electrodialysis, membrane separation, etc., encounter various difficulties [1,2]. Therefore, it is necessary to look for an efficient, economic and lower waste residual disposal process for recovery of citric acid from fermentation broth.

Recently, liquid membrane techniques have become an attractively alternative method for this purpose [5–11]. Boey and Garcia Del Cerro [5] studied the recovery of citric acid using emulsion liquid membrane technique. Alamine 336 was used as carrier, *n*-heptane as diluent, Span-80 and Lubrizol as addition agent, and Na_2CO_3 solution as stripping phase. More than 80% of citric acid was extracted from aqueous solutions. Other researchers also investigated this recovery process using emulsion liquid membrane [6–8]. Juang and Chen [9,10] and Guo and Zhang [11] studied the transport process of citric acid across a supported liquid membrane. However, due to the lack of their long-time stability, difficult operation of the emulsification and de-emulsification steps in ELM processes, etc., liquid membrane techniques have not been adopted for large-scale industrial processes [12–14].

In order to overcome these difficulties arising in the conventional liquid membrane systems, Zhang et al proposed a new liquid membrane technique, called hollow fiber renewal liquid membrane (HFRLM) [15–18], based on the surface renewal theory, which also integrated the advantages of fiber membrane extraction process, liquid film permeation process, and other liquid membrane systems [15].

In a HFRLM process, hydrophobic hollow fibers are used, whose pores are filled with organic phase, i.e. liquid membrane phase. The stirred mixture of organic phase and stripping phase (or feed phase) at a high aqueous/organic volume ratio is pumped through the lumen side of the module. The organic droplets are homogeneously dispersed in the mixture by stirring. The feed phase (or the stripping phase) flows through the shell side, usually in countercurrent mode. The flow rates of two sides are controlled to maintain a positive pressure on the shell side with respect to the lumen side. During the fluid flowing through the lumen side, a thin organic film,

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* Corresponding author. Tel.: +86 10 64423628; fax: +86 10 64436781.
E-mail addresses: renzq@mail.buct.edu.cn, renzhongqi@yahoo.com.cn (Z. Ren), zhangwd@mail.buct.edu.cn (W. Zhang).

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Nomenclature

A	mass transfer area (m^2)
A/O	aqueous/organic volume ratio
C	concentration ($mol\,L^{-1}$)
ΔC	driving force of mass transfer
D	distribution coefficient
H_3A	citric acid
J	mass transfer flux ($mol\,m^{-2}\,s^{-1}$)
K_f	overall mass transfer coefficient base on the feed phase ($m\,s^{-1}$)
L	volumetric flow rate ($m^3\,s^{-1}$)
m	distribution coefficient of extraction process
m'	distribution coefficient of stripping process
t	time (s)
T	temperature (K)
u	velocity ($m\,s^{-1}$)
V	volume (m^3)
Superscripts	
eq	equilibrium
exp	experimental
O	organic
W	aqueous
Subscripts	
f	feed
in	inlet
init	initial
out	outlet
st	stripping phase
S	shell side
T	tube side

i.e. liquid membrane layer, is developed in the internal side of fibers as shown in Fig. 1 due to the wetting affinity of the organic phase and hydrophobic fibers. The shear force caused by the flowing fluid in the lumen side will influence the coalescence and breakage of organic droplets during the stirred mixture flowing through the lumen side. That is, the shear force will cause the film liquid to form microdroplets on the surface of the liquid membrane layer, which will peel off from the surface of the liquid membrane layer and enter into the lumen side fluid. At the same time, the organic droplets will fill the surface of the liquid film. Then the renewal of the liquid membrane is continuous proceeding. This can enhance the mass transfer rate and greatly reduce the diffusion resistance across the aqueous boundary layer within the lumen side. The thickness of the developed liquid membrane film is thin due to the effects of shear forces caused by fluid flowing in the HFRLM process. The solute can be selectively transported across the liquid membrane from the feed phase to the stripping phase. Furthermore, the dispersed organic droplets in the lumen side fluid can automatically and continuously replenish the loss of membrane liquid caused by solubility and emulsification to prevent liquid membrane degradation. The leakage between phases is less than 0.01%. Then the HFRLM process can provide good stability.

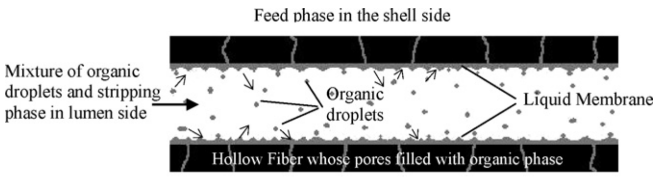

Fig. 1. Principle of hollow fiber renewal liquid membrane technique.

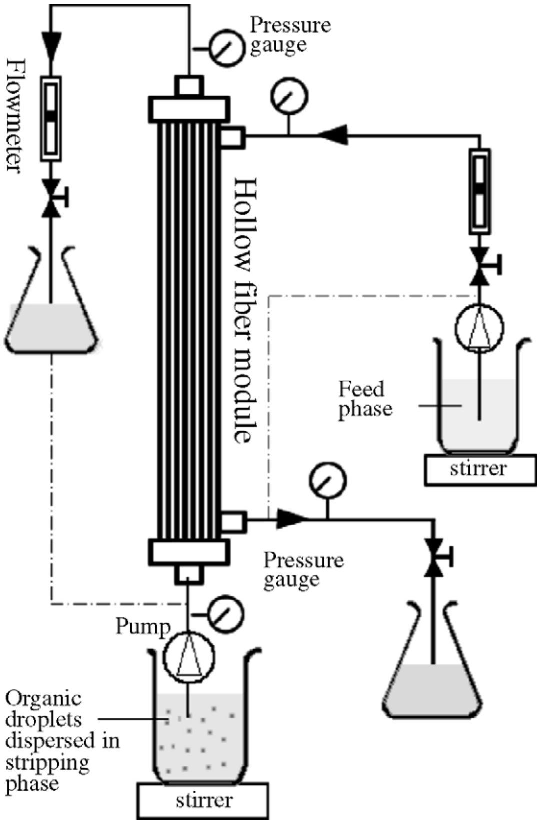

Fig. 2. Experimental set-up of the HFRLM process.

Hollow fiber renewal liquid membrane process has several potential advantages of high mass transfer rate, high concentration factor, long-time stability, no leakage occurs between phases, no secondary pollution, low extractant consumption, low capital, maintenance and operation costs, low energy consumption, easy scale-up, etc.

In this paper, hollow fiber renewal liquid membrane technique was used for simultaneous extraction and concentration of citric acid from dilute aqueous solutions. The system of citric acid + N235/*n*-octanol/kerosene + NaOH solution was used to study the mass transfer characteristics of HFRLM process. The stability and effects of operation mode, carrier concentration in the organic phase, initial citric acid concentration in the feed phase, NaOH concentration in the stripping phase, etc. on mass transfer performance of the HFRLM process were studied. The mechanism of mass transfer in the HFRLM process was also discussed.

2. Experimental

2.1. Reagents and apparatus

Citric acid (Beijing Beihua Refined Chemical Co. Ltd.), NaOH (Beijing Beihua Refined Chemical Co. Ltd.) and *n*-octanol (Guangdong Shandou Xilong Chemical Reagent Plant) are all analytical grade reagents. Kerosene (Tianjin Damao Chemical Reagent Plant) and N235 (Shanghai Laiyashi Chemical Reagent Plant) is technical grade reagent.

All the experiments were conducted using the self-designed systems. The experimental set-up was shown in Fig. 2. The used hollow fiber modules were self-manufactured with small laboratory

Table 1
Characteristics of the hollow fiber module

Shell characteristics	
Material	Glass
Length	30.2 cm
Internal diameter	1.50 cm
Outer diameter	1.70 cm
Fiber characteristics	
Material	PVDF
Number of fibers in module	80
Effective length	29.8 cm
Internal diameter	814 μm
External diameter	886 μm
Effective surface area of module	0.0544 m^2
Packing density	0.387
Membrane porosity	0.82
Membrane tortuosity	2.0

scale versions (with two 0–1 dm^3 min^{-1} peristaltic pumps and flow meters) that were specifically designed for the experimental purposes. The small size made it possible to avoid the influence of non-ideal flow in the shell side of the module. The PVDF hollow fibers were used from Tianjin Polytechnic University. Additional information about these modules was provided in Table 1.

2.2. Experimental procedures

To determine the distribution coefficient, equal volume (25 mL) of aqueous phase and organic phase were added to each flask. The flask containing the mixture was vigorously mixed by a shaker for about 5 min, and then the mixture was transferred to a separating funnel and allowed to settle for at least 15 min. After separation of the phases, the aqueous phase sample was taken for citric acid concentration analysis with neutralization titration method. The concentration of citric acid in the organic phase was calculated by mass balance law. The distribution coefficient can be calculated as follows:

$$\mathrm{D} = \frac{[\mathrm{A}^{3-}]_{\mathrm{O,eq}}}{[\mathrm{A}^{3-}]_{\mathrm{W,eq}}} \qquad (1)$$

For the HFRLM process, the used hydrophobic fibers were pre-wetted with organic phase more than 48 h in order to make the pores of fibers fully filled with organic phase. The stirred mixture of stripping phase and organic phase at a high aqueous/organic volume ratio was pumped through the lumen side of the module; the feed phase flowed through the shell side of the module. In all experiments, both sides were contacted in countercurrent mode. When a stable flow was achieved, aqueous samples were taken from outlet of lumen side and shell side at preset time intervals.

The experimental mass transfer flux J of the transport of citric acid across the liquid membrane from the feed phase to the stripping phase was determined by the following equation:

$$J = \frac{\mathrm{d}C_{\mathrm{st}}V_{\mathrm{st}}}{A\ \mathrm{d}t} = \frac{L_{\mathrm{st}}\,\Delta C_{\mathrm{st}}}{A} \qquad (2)$$

where ΔC_{st} represents the variation of the citrate concentration in the stripping phase at time interval Δt, L_{st} the volumetric flow rate of the stripping phase, A the mass transfer area, and V_{st} is the volume of the stripping solution.

The overall mass transfer coefficient based on the feed phase can be calculated as follows:

$$K_{\mathrm{f}} = \frac{J}{\Delta C_{\mathrm{lm}}} \qquad (3)$$

Table 2
Distribution coefficient of citric acid extraction with various organic phases

No.	Organic composition	*D*
1	N235	18.02
2	Kerosene	0.04
3	*n*-Octanol	0.03
4	30% N235 + 70% kerosene	13.50
5	30% N235 + 20% *n*-octanol + 50% kerosene	27.50

where

$$\Delta C_{\mathrm{lm}} = \frac{\Delta C_1 - \Delta C_2}{\ln(\Delta C_1/\Delta C_2)} = \frac{(C_{\mathrm{f}}^{\mathrm{in}} - (m'/m)C_{\mathrm{st}}^{\mathrm{out}}) - (C_{\mathrm{f}}^{\mathrm{out}} - (m'/m)C_{\mathrm{st}}^{\mathrm{in}})}{\ln((C_{\mathrm{f}}^{\mathrm{in}} - (m'/m)C_{\mathrm{st}}^{\mathrm{out}})/(C_{\mathrm{f}}^{\mathrm{out}} - (m'/m)C_{\mathrm{st}}^{\mathrm{in}}))}$$

where $C_{\mathrm{f}}^{\mathrm{in}}$, $C_{\mathrm{f}}^{\mathrm{out}}$ are the inlet and outlet citric acid concentration in the feed phase, respectively, $C_{\mathrm{st}}^{\mathrm{in}}$, $C_{\mathrm{st}}^{\mathrm{out}}$ the inlet and outlet citrate concentration in the stripping phase respectively, m and m' the distribution coefficient of extraction and stripping process, respectively, ΔC_{lm} is the logarithmic mean driving force of mass transfer.

3. Results and discussion

3.1. Extraction equilibria

Determination of liquid membrane composition is a very important step in HFRLM process. Extraction equilibria experiments were conducted for this purpose. Citric acid ($C_6H_8O_7$, H_3A) is a Lewis acid. Then the solvent with Lewis base functional group is better for citric acid extraction process, such as TBP, TOA, N235, etc. [19–23]. In this paper, N235, a mixture of tertiary amine-based extractant, is used. The extraction experimental results are shown in Table 2. Although the distribution coefficient of citric acid between 100% N235 and aqueous phase is higher, it is found in the experiments that the phase splitting became very difficult due to the heavy emulsification effect when the 100% N235 was used as solvent [24]. The results show that the pure *n*-octanol and kerosene without carrier could extract few citric acids from aqueous phase; the distribution coefficient is less than 0.05. The addition of *n*-octanol in the mixture of N235 and kerosene could increase the distribution coefficient of extraction process. This indicated that *n*-octanol had the synergistic extraction effect for this process, which also reported by Yang et al. [23].

Fig. 3 shows the effect of carrier concentration in the organic phase of (N235 + 20% *n*-octanol + kerosene) on the distribution equilibria of citric acid extraction. The distribution coefficient increases with increasing N235 concentration in the organic phase.

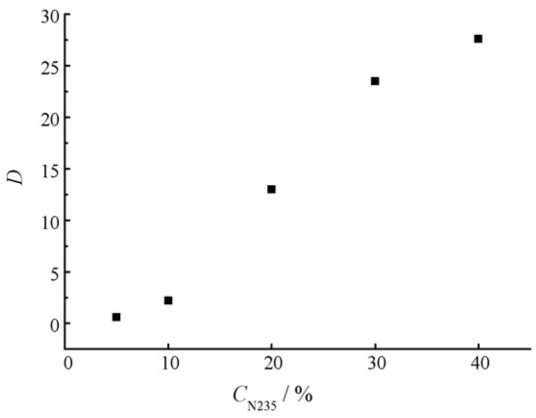

Fig. 3. The effect of the N235 concentration on distribution equilibrium of citric acid (T = 295 K, $C_{\mathrm{inti,citric\ acid}}$ = 0.10 mol L^{-1}).

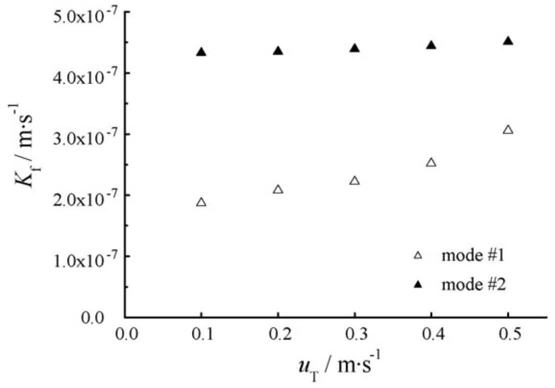

Fig. 4. The effect of operation mode on the overall mass transfer coefficient of HFRLM process ($u_S = 0.10\,\mathrm{cm\,s^{-1}}$).

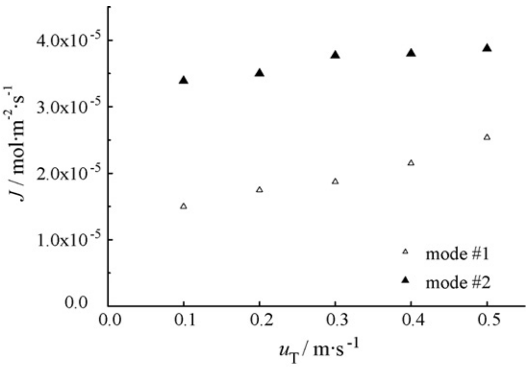

Fig. 5. The effect of operation mode on the mass transfer flux of HFRLM process ($u_S = 0.10\,\mathrm{cm\,s^{-1}}$).

When the N235 concentration increasing from 5% to 40%, the distribution coefficient increases from 0.5 to 27.6. As mentioned above, higher N235 concentration leaded to higher emulsification, the phase splitting and analysis were all difficult. Then in later HFRLM experiments, the organic solution of 30% N235 + 20% *n*-octanol + 50% kerosene was used as liquid membrane composition.

3.2. *Stability of HFRLM process*

In order to study the stability of HFRLM process, a set of experiments were conducted in single-pass mode. The stirred mixture of 0.11 mol L^{-1} NaOH aqueous solution and 30% N235 + 20% *n*-octanol + 50% kerosene (20:1, v/v) was pumped through the lumen side of the module. The feed phase of 0.1 mol L^{-1} citric acid solution flowed through the shell side. Also the reverse operation mode, that is, the organic phase and feed phase flowed through the lumen side of the module and the stripping phase flowed through the shell side, was studied. Results showed that after 20 min stable citric acid concentration profiles were developed both in the feed phase and the stripping phase. That is, the stable mass transfer performance was achieved for this process. It was indicated that the mass transfer rate of citric acid from the feed phase across the liquid membrane to the stripping phase is high. Also, the HFRLM process could run for over 11 h without any difficulty, mainly due to the continuously and automatically replenishment of membrane liquid by the renewal and regeneration of the liquid membrane. It was suggested that the HFRLM process had long-term stability [15]. In later experiments, all the operation time was set more than 30 min in order to get the stabilized and reliable experimental results.

3.3. *Influence of the operation mode*

In order to investigate the mass transfer mechanism of the process, two different operation modes are used in this paper. Mode #1: the stirred mixture of 0.1 mol L^{-1} citric acid aqueous solution and 30% N235 + 20% *n*-octanol + 50% kerosene (20:1, v/v) is pumped through the lumen side of the module; and 0.2 mol L^{-1} NaOH aqueous solution flows through the shell side of the module. Mode #2: the stirred mixture of NaOH aqueous solution and 30% N235 + 20% *n*-octanol + 50% kerosene flows through the lumen side; citric acid aqueous solution flows through the shell side of the module.

The results are shown in Figs. 4 and 5. The overall mass transfer coefficient and mass transfer flux of mode #2 are higher than those of mode #1. It is indicated that main mass transfer resistance of HFRLM process for this system is located in the transport of citric acid from membrane phase to stripping phase. Although the distribution coefficient of citric acid between NaOH aqueous solution and organic phase is much higher than that between the citric acid aqueous solution and organic phase, the extraction chemistry involved in liquid membranes is basically the same as that found in solvent extraction, but the overall transport process is governed by kinetic rather equilibrium parameters.

As shown in Fig. 4, the influence of lumen side flow rate on the overall mass transfer coefficient of operation mode #2 is slight. It is indicated that the transport of citric acid from membrane phase to the stripping phase is not governed by the diffusional mobility of citrate complex through aqueous boundary layer from liquid membrane phase to stripping phase interface, but the rate of decomplexation chemical reaction at the interface. On the contrary, the overall mass transfer coefficient of operation mode #1 increases with increasing lumen side flow rate. It is indicated that in the transport of citric acid from feed phase to the membrane phase is mainly governed by the diffusional mobility of citrate complex through aqueous boundary layer from feed phase to liquid membrane phase interface, not the rate of complexation chemical reaction. Certainly the low values of overall mass transfer coefficient for both operation modes also indicate the diffusion of citrate complex across the pores of membrane plays a definite role in the transport of citric acid in HFRLM process. These agree with the Juang and Chen's [19] study about the transport rates of citric acid through a supported liquid membrane containing tri-*n*-octylamine. They indicated that the transport process was governed by mixed interfacial chemical reaction and membrane diffusion.

In the case of operation mode #2, the renewal of the liquid membrane, i.e. the repeatable exchange of organic droplets between the stirred mixture and liquid membrane layer, and large mass transfer area due to the fully direct contact between the organic droplets and stripping aqueous solution, will intensify the complexation chemical reaction rate and mass transfer rate in HFRLM process. These can greatly reduce the resistance of mass transfer of citric acid from liquid membrane phase to the stripping phase. However, in the case of operation mode #1, the effect of mass transfer intensification is on the transport of citric acid from feed solution to the membrane phase, which is not the main mass transfer resistance in the HFRLM process.

In addition, for the treatment of large amount of low citric acid concentration aqueous solutions, such as fermentation broth, wastewater, etc., the operation mode #1 would increase the consumption of solvent and enhance the difficulties of solvent recovery, while the operation mode #2 could avoid these problems and carry out the concentration of solute simultaneously. Therefore, the operation mode #2 is adopted in later experiments.

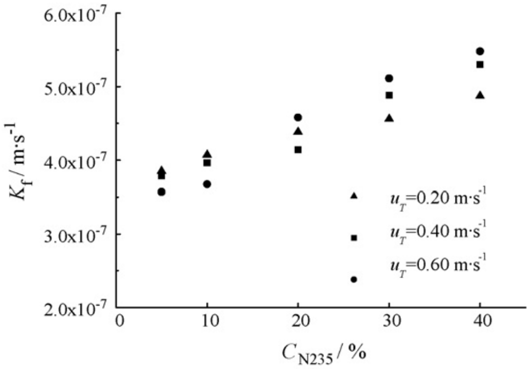

Fig. 6. The effect of the N235 concentration in the organic phase on K_f ($u_S = 0.1$ cm s^{-1}, $c_{init,H3A} = 0.1$ mol L^{-1}, $c_{NaOH} = 0.2$ mol L^{-1}, A/O = 20:1).

3.4. Influence of carrier concentration in the organic phase

Prior to the experiments to study the effect of N235 concentration in liquid membrane phase on the mass transfer characteristic of HFRLM process, hollow fibers used in the module were pre-wetted with organic phase in different N235 concentrations more than 48 h. Results are shown in Figs. 6 and 7.

In the HFRLM process, the overall mass transfer coefficient and mass transfer flux of HFRLM process mainly dependent on facilitated transport capacity of the organic phase, which is also corresponding to the carrier concentration in the organic phase. And the carrier concentration could also affect the chemical reaction kinetic, distribution equilibria, diffusional mobility of complex in the aqueous boundary layer, liquid membrane phase, membrane phase, etc. Usually, the mass transfer rate of HFRLM process increases with increasing carrier concentration due to the mass transfer mechanism of carrier-facilitated transport.

The distribution coefficient of citric acid between the aqueous solution and organic phase increases with increasing N235 concentration in the organic phase; higher N235 concentration leads to higher driving force of mass transfer in HFRLM process. And the increasing quantity of carrier in liquid membrane phase and in mixture can also enhance the rates of complex reaction and carrier-facilitated transport of citric acid. Then as indicated in Figs. 6 and 7, the overall mass transfer coefficient and mass transfer flux increase with increasing N235 concentration in the organic phase in the N235 concentration range of 0–40% (v/v) as expected.

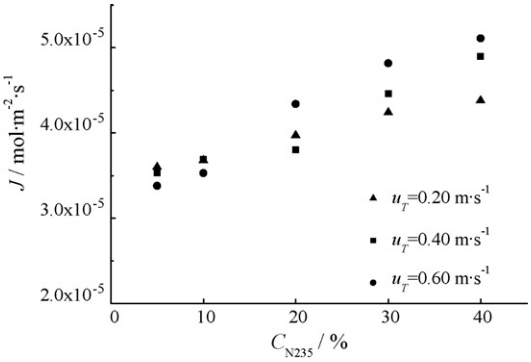

Fig. 7. The effect of the N235 concentration in the organic phase on J ($u_S = 0.1$ cm s^{-1}, $c_{init,H3A} = 0.1$ mol L^{-1}, $c_{NaOH} = 0.2$ mol L^{-1}, A/O = 20:1).

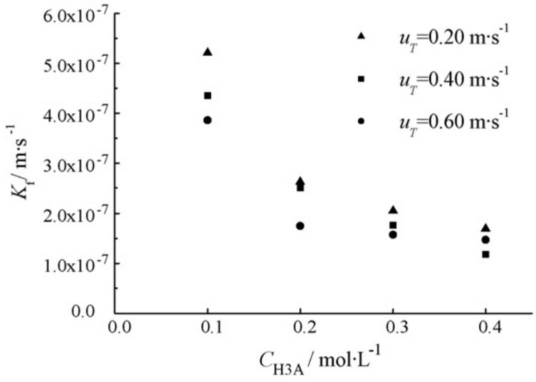

Fig. 8. The effect of the initial citric acid concentration in the feed phase on K_f ($u_S = 0.1$ cm s^{-1}, $c_{N235} = 30\%$ (v/v), $c_{NaOH} = 0.2$ mol L^{-1}, A/O = 20:1).

3.5. Influence of initial citric acid concentration in the feed phase

The effect of initial citric acid concentration in the feed phase on the mass transfer performance of the HFRLM process is also studied. The overall mass transfer coefficient decreases with increasing initial citric acid concentration in the feed phase as shown in Fig. 8. Because the higher initial citric acid concentration in the feed phase leads to higher citric acid concentration in the organic phase by distribution equilibrium, which results in the saturation in the liquid membrane and the pore liquid by the complex molecules. Then the rate of decomplexation chemical reaction at the stripping interface is presumably the rate-limiting step in specific operation conditions. However the mass transfer flux of citric acid increases with increasing initial citric acid concentration in the feed phase as shown in Fig. 9. It is because that the distribution coefficient decreases with increasing initial citric acid concentration in the feed phase, the driving force of mass transfer caused by the distribution coefficient increases with increasing initial citric acid concentration in the aqueous solution. This behavior is similar with our previous study on the transport of copper in HFRLM process [15].

3.6. Influence of NaOH concentration in the stripping phase

Figs. 10 and 11 give the effects of NaOH concentration in the stripping phase on the mass transfer performance of the HFRLM process. The NaOH concentration in the stripping phase almost have no influence on the overall mass transfer coefficient and mass transfer flux in this process at range of 0.20–0.75 mol L^{-1}. Because

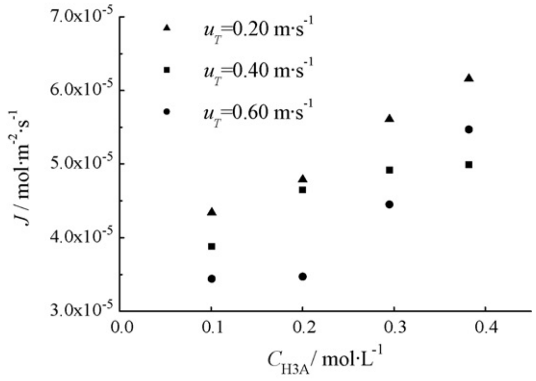

Fig. 9. The effect of the initial citric acid concentration in the feed phase on J ($u_S = 0.1$ cm s^{-1}, $c_{N235} = 30\%$ (v/v), $c_{NaOH} = 0.2$ mol L^{-1}, A/O = 20:1).

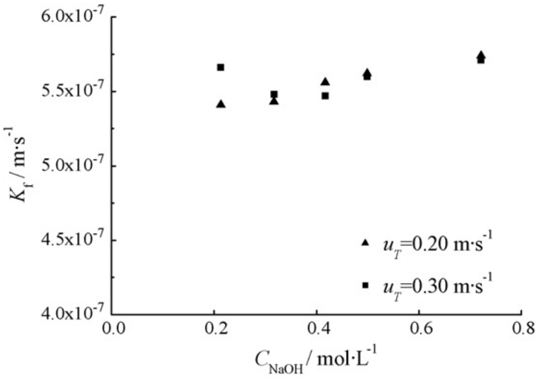

Fig. 10. The effect of NaOH concentration in the stripping phase on K_f (u_S = 0.1 cm s^{-1}, $c_{init,H3A}$ = 0.1 mol L^{-1}, c_{N235} = 30% (v/v), A/O = 20:1).

the relative excess stripping phase has not significant benefit for the rate of decomplexation chemical reaction, which governed the transport of citric acid from membrane phase to stripping phase as discussion above. The mass transfer intensification for this case caused by effects of renewal of liquid membrane and fully contact between organic droplets and stripping solution is fixed.

3.7. Transport studies

The ability of HFRLM technique to the transport of citric acid from the feed phase to the receiver phase is studied in recycling mode. A small self-manufactured hollow fiber module with 20 hollow fibers is used. The feed phase of 300 mL 0.10 mol L^{-1} citric acid solutions is pumped through the shell side of the module. The stirred mixture of 150 mL 1.50 mol L^{-1} NaOH aqueous solution and 15 mL 30% N235 + 20% *n*-octanol + 50% kerosene flows through the lumen side of the module. Both sides are operated in countercurrent recycling mode. The results are shown in Fig. 12.

"Up-hill" effect, which means the solute can be transported from low to high concentration solutions, is an important characteristic of liquid membrane techniques. This characteristic provides the advantages of simultaneous extraction and concentration of solute from dilute solutions. The results show that the transport process appears the up-hill effect at 5 h, the citric acid transports from low concentration solution (feed phase) to high concentration solution (stripping phase); at 8.5 h, the enrichment effect is observed. At 18 h, the citric acid concentration in the feed phase becomes 0.0015 mol L^{-1}, the recovery efficiency is up to 98.8%. Although the mass transfer flux of this recycling experiment decreases with time, it can remain a relative higher value in the whole process. It is indicated that the transport rate of citric acid through HFRLM is high. Furthermore, it should be noted that the size of used hollow fiber module is so small that operation time is long in this experiment.

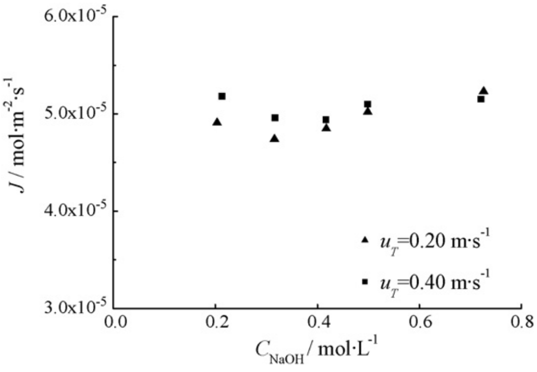

Fig. 11. The effect of NaOH concentration in the stripping phase on J (u_S = 0.1 cm s^{-1}, $c_{init,H3A}$ = 0.1 mol L^{-1}, c_{N235} = 30% (v/v), A/O = 20:1).

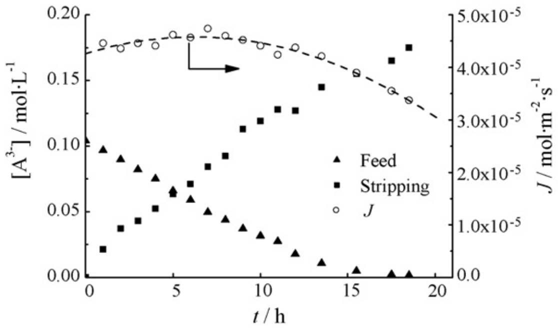

Fig. 12. Transient concentration of citric acid in the feed phase and stripping phase during a transport experiment of HFRLM process.

4. Conclusions

A new liquid membrane technique, hollow fiber renewal liquid membrane, is used for the recovery of citric acid from dilute solutions. The organic solution of 30% N235 + 20% *n*-octanol + 50% kerosene was used as liquid membrane phase, NaOH aqueous solution was used as stripping phase.

Results show that HFRLM process is very stable due to the automatic and continuous replenishment of membrane liquid. It is better for the HFRLM process that the stirred mixture of the stripping phase and the organic phase flows through the lumen side of the module, because the main mass transfer resistance is located in the transport of citric acid from membrane phase to the stripping phase, which is mainly governed by the rate of decomplexation chemical reaction. The overall mass transfer coefficient and mass transfer flux increase with increasing carrier concentration in the organic phase. And the overall mass transfer coefficient decreases with increasing initial citric acid concentration in the feed phase, while the mass transfer flux increases with increasing initial citric acid concentration in the feed phase. The effect of NaOH concentration in the stripping phase on the mass transfer performance of this process is slight.

The transport results show that the recovery of citric acid by HFRLM can carry out enrichment of the citric acid and the mass transfer rate is high. HFRLM technique has good prospects in the recovery process of citric acid from dilute solutions.

Acknowledgements

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References

[1] M. Pazouki, T. Panda, Recovery of citric acid—a review, Bioprocess Eng. 19 (1998) 435–439.
[2] Y.L. Peng, S.Z. Yao, S.L. Ji, C.F. Ma, Review on separation of citric acid from fermentation broth, J. Beijing Polytech. Univ. 28 (2002) 46–51.
[3] U. Bauer, R. Marr, W. Rueckl, M. Siebenhofeer, Extraction of citric acid from aqueous solutions, Chem. Biochem. Eng. 2 (1988) 230–232.
[4] U. Bauer, R. Marr, W. Rueckl, M. Siebenhofeer, Reactive extraction of citric acid from aqueous fermentation broth, Ber. Bunsen-Des. Phys. Chem. 93 (1989) 980–984.
[5] S.C. Boey, M.C. Garcia Del Cerro, Extraction of citric acid by liquid membrane extraction, Chem. Eng. Res. Des. 65 (1987) 218–223.

[6] P.R. Patnaik, Liquid emulsion membranes: principles, problems and applications in fermentation processes, Biotechnol. Adv. 13 (1995) 175–208.
[7] A.G. Anicuta, J. Gheorghe, F. Octavian, Batch extraction of citric acid with liquid surfactant membranes, Chem. Eng. Technol. 22 (1999) 65–69.
[8] B. Yordanov, L. Boyadzhiev, Pertraction of citric acid by means of emulsion liquid membranes, J. Membr. Sci. 238 (2004) 191–197.
[9] R.S. Juang, L.J. Chen, Transport of citric acid across a supported liquid membrane containing various salts of a tertiary amine, J. Membr. Sci. 123 (1997) 81–87.
[10] R.S. Juang, L.J. Chen, Analysis of the transport rates of citric acid through a supported liquid membrane containing tri-*n*-octylamine, Ind. Eng. Chem. Res. 35 (1996) 1673–1679.
[11] C.Z. Guo, J.M. Zhang, Mass transfer condition of citric acid extraction by polypropylene supported liquid membrane, Technol. Water Treat. 33 (2007) 33–36.
[12] A.M. Sastre, A. Kumar, J.P. Shukla, R.K. Singh, Improved techniques in liquid membrane separations: an overview, Sep. Purif. Methods 27 (1998) 213–298.
[13] Z.M. Gu, State of the art and recent progress of liquid membrane separation processes, Membr. Sci. Technol. 23 (2003) 214–223.
[14] T. Franken, Liquid membranes-academic exercise or industrial separation process? Membr. Technol. 85 (1997) 6–10.
[15] Z.Q. Ren, W.D. Zhang, Y.M. Liu, Y. Dai, C.H. Cui, New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater, Chem. Eng. Sci. 62 (2007) 6090–6101.
[16] W.D. Zhang, A.M. Li, X.M. Li, Z.Q. Ren, Principle of liquid membrane and hollow fiber renewal liquid membrane, Mod. Chem. Ind. 25 (2005) 66–68.
[17] W.D. Zhang, A.M. Li, Z.Q. Ren, Study on mass transfer characteristics of hollow fiber renewal liquid membrane, J. Chem. Eng. Chin. Univ. 20 (2006) 843–846.
[18] Z.Q. Ren, J.T. Liu, W.D. Zhang, C.S. Du, J.N. Ma, Treatment of chromium(VI)-containing wastewater with hollow fiber renewal liquid membrane process, Electroplat. Finish. 11 (2006) 49–51.
[19] R.S. Juang, W.T. Huang, Catalytic role of water immiscible organic acid on amine extraction of citric acid from aqueous solutions, Ind. Eng. Chem. Res. 35 (1996) 546–552.
[20] V. Bizek, J. Horacek, M. Kousova, A. Heyberger, J. Prochazka, Mathematical model of extraction of citric acid with amine, Chem. Eng. Sci. 47 (1992) 1433–1440.
[21] V. Bizek, J. Horacek, M. Kousova, Amine extraction of citric acid: effect of diluent, Chem. Eng. Sci. 48 (1993) 1447–1457.
[22] R.S. Juang, W.T. Huang, Equilibrium studies on the extraction of citric acid from aqueous solutions with tri-*n*-octylamine, J. Chem. Eng. Jpn. 27 (1994) 498–501.
[23] D. Yang, C.Z. Lin, L.J. An, C.F. Zhou, L.S. Chen, Study on the mechanism of citric acid extracted by N_{235}–*n*-octanol–petroleum ether cooperatively, Chin. J. Spectrosc. Lab. 16 (1999) 378–381.
[24] A. Heyberger, J. Procházka, E. Volaufova, Extraction of citric acid with tertiary amine—third phase formation, Chem. Eng. Sci. 53 (1998) 515–521.