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Simultaneous removal and recovery of copper(II) from acidic wastewater by hollow fiber renewal liquid membrane with LIX984N as carrier

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ABSTRACT

Hollow fiber renewal liquid membrane (HFRLM), a new liquid membrane technique inspired from surface renewal theory, is used to simultaneously remove and recover copper from acidic wastewater. The commercial extractant, LIX984N, is used as a carrier in liquid membrane phase, kerosene used as a diluent. $CuSO_4$ solutions is used to simulate acidic industrial wastewater, in which the pH is adjusted by dilute H_2SO_4. The mass transfer mechanisms of the process are investigated. As a carrier-facilitated transport process, the addition of LIX984N in the liquid membrane phase can greatly improve the transport performance; the organic/aqueous stripping volume ratio from 1:10 to 1:7 on lumen side mixture is better in terms of the renewal effect and diffusion resistance. The higher pH in the feed phase (>3) and H_2SO_4 concentration in the stripping phase around $2.0\,\mathrm{mol\,L^{-1}}$ are favorable for the transport process due to the increase of mass transfer driving forces. The mass transfer fluxes increase with increasing flow rates on two sides. The countercurrent cascade experiments show that the HFRLM process could carry out the simultaneous removal and recovery of copper from wastewater successfully. The modeled results based on the surface renewal theory demonstrate a good agreement with experimental data.

1. Introduction

The discharge of industrial acidic effluents containing copper may cause serious environmental problems due to its highly toxicity and non-biodegradability, and expensive heavy metal is also being wasted too [1,2]. The efficient and cost effective removal and recovery of copper from acidic industrial effluents is an urgent affair for the industrial development, such as hydrometallurgy, electroplating, electronic industry, etc. However, the inherent disadvantages, i.e. poor selectivity, inefficiency, high investment and/or operation costs, etc., obstruct the applications of traditional treatment methods [1–4], such as chemical precipitation, liquid–liquid solvent extraction, adsorption, ionic exchange, etc.

Liquid membrane techniques have become an attractive alternative for the removal and recovery of copper from wastewater, due to the specific characteristics of simultaneous extraction and stripping processes in the same stage, non-equilibrium mass transfer, "up-hill" effect, high selectivity, low solvent inventory, etc. [5–8]. However, the poor stability and difficult operations have obstructed the industrial applications of supported liquid membrane (SLM) [9] and emulsion liquid membrane (ELM) [10]. Although researchers have been working on the compositions of liquid membrane phase and operation parameters to improve the stability of ELM and SLM processes [11–13], the issues have not been well solved yet. Since 1980s, a lot of new types of LM techniques have been proposed based on ELM and SLM, such as hollow fiber contained liquid membrane [14], flowing liquid membrane [15], supported emulsion liquid membrane [16,17], supported liquid membrane with strip dispersion [18], etc. Among those LM types, hollow fiber renewal liquid membrane technique is more promising, which is proposed by Zhang et al. [19–23] based on the surface renewal theory and integrated the advantages of fiber membrane extraction process [24], liquid film permeation process [25], and other liquid membrane systems.

In a HFRLM process, hydrophobic hollow fibers are used, whose pores are filled with the organic phase previously. The stirred mixture of organic phase and stripping phase at a low organic/aqueous volume ratio is pumped through the lumen side of the hollow fiber module. The organic phase droplets are uniformly dispersed in the mixture by stirring. The feed phase flows countercurrently through the shell side. During the fluid flowing through the lumen side, a thin organic film, i.e. liquid membrane layer, is developed in the internal side of fibers [20], due to the wetting affinity of the organic phase and hydrophobic fibers. The solute can be selectively transported across the liquid membrane from the feed phase to the stripping phase. The shear force caused by the flowing fluid will influence coalescence and breakage of organic droplets during the stirred mixture flowing through the lumen side. The film liquid on the surface of the developed liquid membrane layer will form microdroplets, peel off from the surface of the liquid membrane

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layer and enter the lumen side fluid. At the same time, the organic droplets will be supplied to the surface of the liquid film. Then the renewal of the liquid membrane is continuously proceeding. This can greatly reduce the mass transfer resistance of solute across the aqueous boundary layer on the lumen side. The thickness of the developed liquid membrane film is usually thin in the HFRLM process, due to the effects of shear forces caused by fluid flowing. Furthermore, the flow rates on two sides are controlled to maintain a positive pressure on the shell side with respect to the lumen side. The dispersed organic droplets on the lumen side fluid can automatically and continuously replenish the loss of membrane liquid caused by solubility and emulsification to prevent liquid membrane degradation. Thus, HFRLM process could provide good stability [20], and the leakage between phases is less than 0.01%. This process has several potential advantages, including high mass transfer rate, high concentration factor, no leakage occurs between phases, no secondary pollution, low extractant consumption, easy scale-up, etc.

The mass transfer mechanism and model studies on the simultaneous removal and recovery of copper from acidic wastewater by hollow fiber renewal liquid membrane have been carried out in order to provide more theoretical bases and help for the intensification of mass transfer, design, scale-up and industry application of the HFRLM technique. $CuSO_4$ solutions are used to simulate acidic industrial wastewater, in which the pH is adjusted by dilute H_2SO_4 solutions. The commercial extractant, LIX984N, dissolved in kerosene is used as the organic phase, which is a particularly attractive extractant for extraction of copper by combining the most desirable features of its components. The active components of LIX984N are 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime. The extractive strength and fast kinetics of salicylaldoximes are combined with the proven excellent physical performance and stability of ketoximes [26]. Compared to the extractant of D2EHPA in our previously studies [20], it can be used directly for the acidic systems without buffer solutions. H_2SO_4 aqueous solution is used as stripping phase. The effects of several process parameters on the mass transfer characteristics of the HFRLM process are investigated. The process parameters considered here include LIX984N concentration in the organic phase, pH in the feed phase, H_2SO_4 concentration in the stripping phase, organic/aqueous volume ratio (O/A), flow rates of two sides, etc. The transport results are studied in countercurrent cascade experiments to verify the application of HFRLM technique. The mass transfer model of the HFRLM process is presented based on the surface renewal theory, resistance-in-series model and mass balance law.

2. Experimental

2.1. Reagents and apparatus

The extractant of LIX984N, a mixture of LIX860N and LIX84I with volume ratio of 1:1, is supplied by Cognis, Ireland. Kerosene, from Tianjin Damao chemical reagent plant of technical grade reagent, is washed twice with 20 vol% H_2SO_4 to remove aromatics and then washed three times with deionized water. $CuSO_4{\cdot}5H_2O$, from Guangdong Xilong Chemical Factory, is an analytical grade reagent with a purity > 99.0%. Other reagents are all analytical grade reagent. The feed phase is prepared by dissolving a weighted amount of $CuSO_4{\cdot}5H_2O$ in aqueous solutions to simulate the industrial acidic wastewater containing copper, in which the pH was adjusted by dilute H_2SO_4 solution. The stripping phase is prepared by diluting H_2SO_4 in deionized water. The organic phase is prepared by dissolving of LIX984N in kerosene.

Table 1
Characteristics of the hollow fiber modules.

Shell characteristics	
Material	Glass
Length, L	20.2 cm
Internal diameter, D_i	1.0 cm
Outer diameter, D_o	1.3 cm
Fiber characteristics	
Material	PVDF
Number of fibers, N	30
Effective length, L	20.0 cm
Internal diameter, d^{int}	812 μm
External diameter, d^{ext}	886 μm
Effective surface area, A	1.37×10^{-3} m^2
Membrane porosity, ε	0.82
Membrane tortuosity, τ	2.0

All the experiments were conducted using the self-designed systems. The experimental set-up was the same as described in our previously work [21]. The used hollow fiber module was self-manufactured with small laboratory scale versions (with two 0–1 dm^3 peristaltic pumps and flow meters) that were specifically designed for the experimental purposes. The small size makes it possible to evaluate the transport performance of the technology without having to prepare large amount of feed, stripping and organic phases. The membrane supports used in HFLRM process were PVDF, supplied by Tianjin Polytechnic University. The Additional information about hollow fiber module 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 a 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 copper concentration analysis. The concentration of copper in the organic phase was calculated by mass balance. For the back-extraction process, the organic phase were taken from extraction process and mixed with the same volume of H_2SO_4 aqueous solution. The distribution coefficient of extraction and back-extraction processes, m and m', can be calculated as follows:

$$m = \frac{[\mathrm{Cu}]_{O,eq}}{[\mathrm{Cu}]_{A,eq}} \tag{1}$$

$$m' = \frac{[\mathrm{Cu}]_{A,eq}}{[\mathrm{Cu}]_{O,eq}} \tag{2}$$

For the HFRLM experiments, hydrophobic fibers used in the hollow fiber module were pre-wetted with organic phase more than 0.5 h in order to make the pores of fibers fully filled with organic phase. The stirred mixture of organic phase and stripping phase at a low organic/aqueous volume ratio was pumped through the lumen side of the hollow fiber module. The feed phase flowed countercurrently through the shell side of the hollow fiber module. 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 of the copper transport across the liquid membrane from the feed phase to the stripping phase, J, was determined by the following equation:

$$J = \frac{\mathrm{d}C_s V_s}{A \cdot \mathrm{d}t} = \frac{Q_s\ \Delta C_s}{A} \tag{3}$$

where ΔC_s represents the variation of copper concentration in the stripping phase, A is the mass transfer area, Q_s is the volumetric flow

Table 2
The effect of the initial pH in the feed phase on the extraction process.

pH_{init}	pH_{eq}	$C_{f,init/mg\,L}^{\;-1}$	$C_{f,eq/mg\,L}^{\;-1}$	m	$E/\%$
5.63	3.22	70.22	0.41	171.25	99.42
4.68	3.09	70.22	0.23	309.38	99.68
3.79	2.96	70.22	0.23	309.38	99.68
2.75	2.58	70.22	0.25	282.62	99.65
2.00	2.08	70.22	0.25	280.01	99.64
1.01	1.05	70.22	18.29	2.87	74.15

rate of the stripping phase, and V_s is the volume of the stripping phase flowing through the lumen side at time interval dt.

The removal efficiency of copper based on the feed phase is:

$$E = \frac{C_f^{in} - C_f^{out}}{C_f^{in}} \times 100\% \tag{4}$$

where C_f^{in} and C_f^{out} are the inlet and outlet copper concentration of the feed phase, respectively.

In order to indicate the tendency of mass transfer characteristic of the HFRLM process, in some case, the normalized concentration, X, was defined as following:

$$X_{\mathrm{Cu}} = \frac{C_{\mathrm{Cu}}}{C^{in}} \tag{5}$$

2.3. Sample analysis

The copper(II) concentration in the aqueous solution was analyzed with sodium diethyldithiocabamate spectrophotometric method (GB7474-87, P.R. China). And a digital precision ionometer model PXS-450 (Shanghai Dapu Co. Ltd.) with a combined glass electrode was used for pH measurements (±0.01 pH). The meter was standardized against 4.01, 6.85, and 9.14 standard buffer solutions.

3. Results and discussion

3.1. Extraction equilibria

The solvent extraction of copper with LIX984N dissolved in kerosene from aqueous solutions can be written as follows:

$$2\mathrm{RH}_{(\mathrm{org})} + \mathrm{Cu}^{2+}_{(\mathrm{aq})} \rightleftharpoons R_2\mathrm{Cu}_{(\mathrm{org})} + 2\mathrm{H}^{+}_{(\mathrm{aq})} \tag{6}$$

The initial copper concentration in the feed aqueous solution is 70.22 mg L^{-1}; the organic phase is the mixture of 10% LIX984N in kerosene; the stripping phase is H_2SO_4 aqueous solution. All extraction experiments are carried out three times under identical condition at room temperature of 20.5 °C. The results are listed in Tables 2 and 3. The extraction efficiency of copper with LIX984N as extractant increases with the increasing of initial pH in the feed solution. When the initial pH is bigger than 2.0, the distribution coefficient of extraction process maintains a relative high value (>150); the extraction efficiency is bigger than 99.4%. Then in the HFRLM process, the initial pH in the feed phase should be bigger than 2.0 to get high mass transfer driving force and good transport result. It is different from the extraction process with D2EHPA as extractant in our previous work [27]. The initial pH in the feed phase must be adjusted by acetate buffer solution to a narrow pH range around 4.44 in order to get better extraction efficiency. In general, the pH in the industrial sulfuric acidic wastewater containing copper is around 2.5. The extractant of LIX984N can be used directly without any addition agent to adjust the pH in the aqueous solution.

Table 3
The effect of H_2SO_4 concentration in the stripping phase on the back-extraction process.

$[H^+]$/mol L^{-1}	$C_{org,init}$/mg L^{-1}	$C_{S,eq}$/mg L^{-1}	m'	$E/\%$
1.0	63.77	58.66	11.46	91.98
2.0	63.77	63.49	228.88	99.56
3.0	63.77	63.76	7412.50	99.99
4.0	63.77	63.76	7412.50	99.99
6.0	63.77	62.96	77.24	98.72

As listed in Table 3, the back-extraction efficiency increases with the increasing of H_2SO_4 concentration in the stripping phase. However, the distribution coefficient decreases at H_2SO_4 concentration of 6.0 mol L^{-1}. It is mainly because of the higher diffusion resistance caused by higher viscosity and the degradation of LIX984N resulted from the oxidizability of sulfuric acid [28,29] at higher H_2SO_4 concentration.

3.2. Stability of HFRLM process

In order to explore the stability of HFRLM process, a series of experiments were conducted in single-pass mode. The stirred mixture of organic phase (10 vol% LIX984N + kerosene) and stripping phase (2.0 mol L^{-1} H_2SO_4 solution) at a volume ratio of 1:10 was pumped through the lumen side of the hollow fiber module. The volumetric flow rate was of 2.7 mL min^{-1}. The feed phase flowed countercurrently through the shell side of the hollow fiber module at volumetric flow rate of 2.2 mL min^{-1}. The initial copper(II) concentration is 64.03 mg L^{-1} at pH of 2.60. Also the experiments with reverse operation mode were studied. That is, the organic phase and feed phase flowed through the lumen side of the hollow fiber module, and the stripping phase flowed countercurrently through the shell side. Results showed that the stable copper(II) concentration profiles were developed both in the feed phase and the stripping phase after 20 min. That is, the stable mass transfer performance was achieved, and the mass transfer mechanisms and characteristics of the HFRLM process can be studied at this status. Then in later experiments, the initial stabilization time is set more than 30 min in order to get the more stable and reliable experimental results. On the other hand, the renewal and regeneration of the liquid membrane layer can automatically and continuously replenish the loss of membrane liquid caused by solubility and emulsification to prevent liquid membrane degradation. The flow rates of two sides are controlled to maintain a positive pressure on the shell side with respect to the lumen side to prevent the leakage between two sides when the hydrophobic fibers are used. The HFRLM process is stable and can run for long-term without any difficulty [20,23].

3.3. Influence of pH in the feed phase

As described above, the pH in the feed phase has significant influence on the extraction equilibrium of copper between 10% LIX984N + kerosene and aqueous solution. Then the influence of pH in the feed phase on the mass transfer of HFRLM process is studied at pH range from 0.5 to 5.5, the results are shown in Fig. 1. At lower pH value (<3), the removal efficiency and the mass transfer flux increase sharply with the increasing of pH. It is mainly because that the mass transfer driving force increases sharply with the increasing of pH in the feed solution. At higher pH value (>3), the removal efficiency and the mass transfer flux increase slowly with the increasing of pH in the feed phase. This is similar with the behavior of extraction equilibrium, while the amplitude of variation of mass transfer performance in the HFRLM process is slow. Because the extraction chemistry involved in liquid membranes is basically the same as that found in solvent extraction, while the overall transport process is governed by kinetic rather than equi-

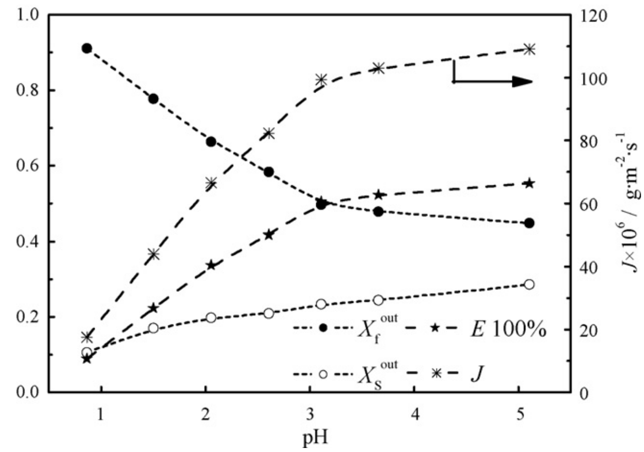

Fig. 1. The effect of pH in the feed phase on the HFRLM process—feed solution: 70.48 mg L^{-1} $CuSO_4$ solution; organic phase: 10% LIX984 + kerosene; stripping solution: 2.0 mol L^{-1} H_2SO_4 solution; O/A = 1:10; shell side flow rate: 2.3 mL min^{-1}; lumen side flow rate: 2.8 mL min^{-1}.

librium parameters. It is different to our previous studies on the transport of copper through HFRLM with D2EHPA as carrier, in which there is a maximum transport rate at pH of 4.44 in the feed phase [20].

3.4. Influence of H_2SO_4 concentration in the stripping phase

In order to study the influence of stripping phase on the mass transfer of HFRLM process, a series of HFRLM experiments in one-through mode are conducted at H_2SO_4 concentration range from 0.0 to 4.0 mol L^{-1}. The results are shown in Fig. 2. When the pure water is used as the stripping phase, there is almost no mass transfer occurring, because the mass transfer driving force caused by distribution equilibrium is very small. With the increasing of H_2SO_4 concentration in the stripping phase, the removal efficiency and the mass transfer flux increase, and reach a maximum value at H_2SO_4 concentration of 2.0 mol L^{-1}, then decrease. It is because that the differential concentration of hydrogen ion (i.e. hydrogen ion concentration gradient) between the stripping phase and the feed phase is also one of the mass transfer driving forces in the HFRLM process. Mass transfer driving force caused by hydrogen concentration gradient increases with the increasing of proton concentration in the stripping phase. However, the high sulfuric acid concentration would result in the high viscosity of the stripping phase, the diffusion resistance of copper across the stripping boundary layer will increase, and it is not benefit for the HFRLM process.

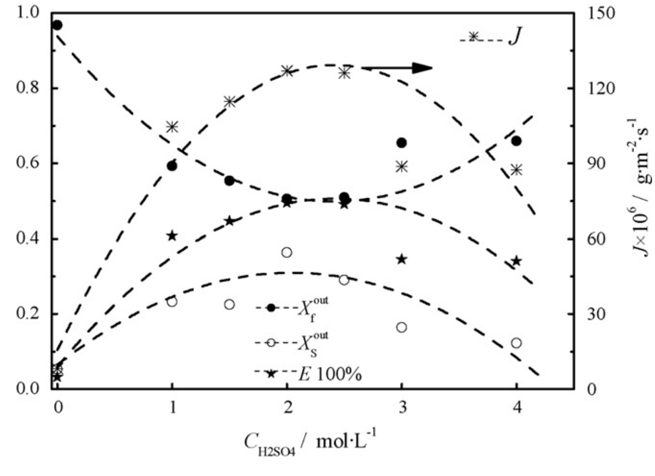

Fig. 2. The effect of H_2SO_4 concentration in the stripping phase on the HFRLM process—feed solution: 91.72 mg L^{-1} $CuSO_4$ solution at pH of 2.6; organic phase: 10% LIX984 + kerosene; stripping solution: H_2SO_4 solution; O/A = 1:10; shell side flow rate: 2.3 mL min^{-1}; lumen side flow rate: 2.8 mL min^{-1}.

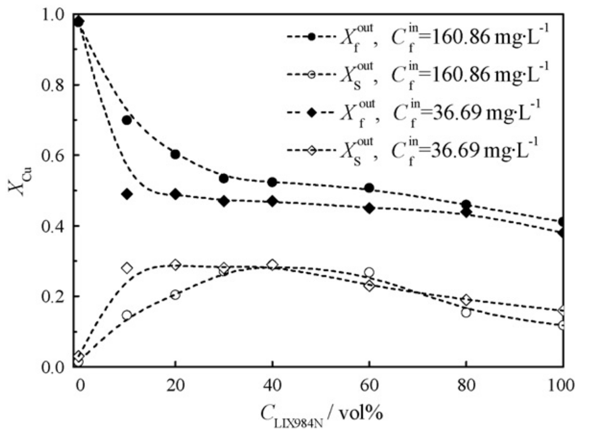

Fig. 3. The effect of LIX984N in the organic phase on the HFRLM process—feed solution: $CuSO_4$ solution at pH of 2.6; organic phase: LIX984 + kerosene; stripping solution: 2.0 mol L^{-1} H_2SO_4 solution; O/A = 1:10; shell side flow rate: 2.3 mL min^{-1}; lumen side flow rate: 2.9 mL min^{-1}.

3.5. Influence of the LIX984N concentration in the organic phase

The mass transfer mechanism of the HFRLM process is a carrier-facilitated transport. The carrier concentration in the organic phase can effect these factors of facilitated transport capacity, chemical reaction rate, mass transfer driving force caused by distribution equilibria, diffusion of complex in liquid membrane phase and membrane phase, renewal capacity of liquid membrane, etc. These factors are corresponding to the mass transfer resistance within the lumen side and membrane phase. The mass transfer rate usually increases with the increasing of carrier concentration in the organic phase.

Prior to the experiment to study the effects of LIX984N concentration in the liquid membrane phase on the mass transfer performance of the HFRLM process, hollow fibers used in the module were pre-wetted with organic phase at different LIX984N concentrations more than 0.5 h. The results are shown in Figs. 3 and 4. When the pure kerosene without carrier is used as organic phase, there is almost no mass transfer occurring in the HFRLM process. With the addition of LIX984N in the organic phase, the removal efficiency and the mass transfer flux increase sharply.

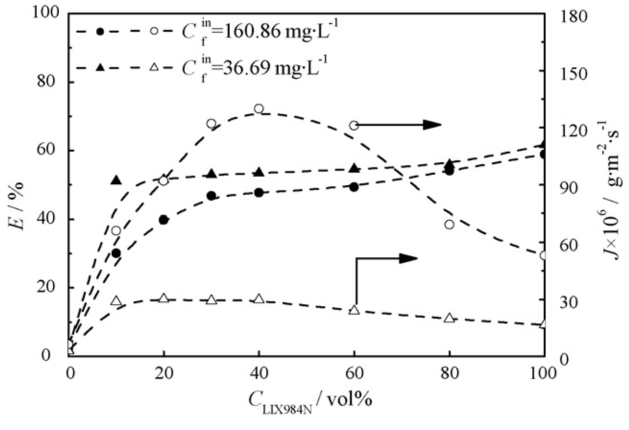

Fig. 4. The effect of Lix984N concentration in the organic phase on the removal efficiency and mass transfer flux.

At lower LIX984N concentration, the driving force of mass transfer increases sharply with the increasing of distribution coefficient of copper between the aqueous solution and organic phase caused by increasing LIX984N concentration. The increasing quantity of carrier in the liquid membrane phase and in mixture can accelerate the rates of complex reaction and carrier-facilitated transport. For the higher initial copper concentration in the feed phase, the higher LIX984N concentration in the organic phase is needed. When the LIX98N concentration in the organic phase increases from 0.0 to 10.0 vol%, the removal efficiency and the mass transfer flux increase from 1.8% to 42.5% and 1.81×10^{-6} to $43.7 \times 10^{-6}\,\mathrm{g\,m^{-2}\,s^{-1}}$ at initial copper concentration in the feed phase of $36.69\,\mathrm{mg\,L^{-1}}$, respectively. When the LIX98N concentration in the organic phase increases from 0.0 to 20.0 vol%, the removal efficiency and the mass transfer flux increase from 2.3% to 39.8% and 10.5×10^{-6} to $135.6 \times 10^{-6}\,\mathrm{g\,m^{-2}\,s^{-1}}$ at initial copper concentration in the feed phase of $160.86\,\mathrm{mg\,L^{-1}}$, respectively.

At higher LIX984N concentration in the organic phase, as shown in Figs. 3 and 4, although the removal efficiency increases slowly with the increasing of LIX984N concentration in the organic phase, the outlet copper concentration of feed phase decrease with the increasing of LIX984N concentration slowly; while the outlet copper concentration of stripping phase and the mass transfer flux decrease with the increasing of LIX984N concentration. Because the viscosity of the organic phase is higher at higher LIX984N concentration, this will increase the diffusion resistances of copper across the liquid membrane phase and membrane phase. On the other hand, the distribution quantity of copper ion in the organic phase is higher at higher LIX984N concentration in kerosene. That is, the accumulation of copper in the liquid membrane phase and membrane phase increase with the increasing of LIX984N concentration in the organic phase. Furthermore, the higher LIX984N concentration in the organic phase will increase the consumption of solvent.

3.6. Influence of organic/aqueous volume ratio

In a HFRLM process, the renewal effect between the organic droplets dispersed in the lumen side fluid and the surface of developed liquid membrane layer can greatly accelerate the mass transfer rate. The organic/stripping volume ratio (O/A) is one of important operation parameters. The amount of the organic phase dispersed in the lumen side fluid will influence the thickness of the developed liquid film, which is corresponding to the mass transfer resistance within the lumen side. Then in this paper, the organic/stripping aqueous volume ratio of 0, 1:50, 1:20, 1:10, 1:7, 1:5 are studied. The results are shown in Fig. 5. In the case of O/A = 0, the process is changed to hollow fiber supported liquid membrane. The removal efficiency and the mass transfer flux are lower. With the addition of organic phase dispersed into the stripping phase, the mass transfer rate is intensified. The removal efficiency and the mass transfer flux increase with the increasing amount of organic phase in the lumen side fluid, because of the renewal effect of liquid membrane in the lumen side and the large mass transfer area arising by the direct contact between organic droplets and aqueous phase. While at the higher O/A volume ratio, the consumption of the organic phase is large, this will increase the thickness of the developed liquid membrane layer and the mass transfer resistance within the lumen side. There is a favorable O/A range from 1:10 to 1:7 for the HFRLM process under the range studied, in which the removal efficiency and the mass transfer flux are higher, and the consumption of the organic phase is smaller.

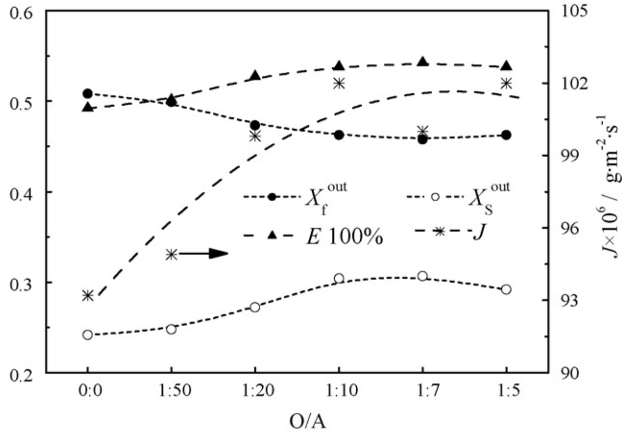

Fig. 5. The effect of organic/aqueous volume ratio on the mass transfer of HFRLM—feed solution: $70.75\,\mathrm{mg\,L^{-1}}$ $CuSO_4$ solution at pH of 2.6; organic phase: 10% LIX984 + kerosene; stripping solution: $2.0\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solution; Shell side flow rate: $2.2\,\mathrm{mL\,min^{-1}}$; lumen side flow rate: $2.7\,\mathrm{mL\,min^{-1}}$.

3.7. Influence of flow rates of two sides

The flow rates both on the lumen side and shell side are the important hydrodynamic parameters, which relate to the contact time (residence time), the thickness of liquid membrane layer, and renewal rate of the liquid membrane in the HFRLM process. As shown in Fig. 6, the mass transfer flux and the removal efficiency increase with the increasing of flow rate on the lumen side. Because at a fixed flow rate on the shell side, the higher flow rate on the lumen side leads to the higher shear force, which will reduce the thickness of the liquid membrane layer and increase the renewal rate of the liquid membrane. These can intensify the mass transfer of the HFRLM process. The mass transfer flux also increases with the increasing of flow rate on the shell sides; while the removal efficiency decreases. Because at a fixed flow rate on the lumen side, the mass transfer intensification due to the renewal effect within the lumen side is fixed. With the increasing of flow rate on the shell side, more fresh feed phase contact with membrane phase; the contact time of feed phase and membrane phase decreases. The mass transfer flux increases with the increasing of mass transfer driving force caused by copper concentration gradient between the feed phase and the stripping phase increases. However, the amount of transport copper with respect to the initial total copper reduces. As described in Eq. (4), the removal efficiency decreases. It is indicated that the residence time of feed phase in the hollow fiber module must be enough for a better transport result.

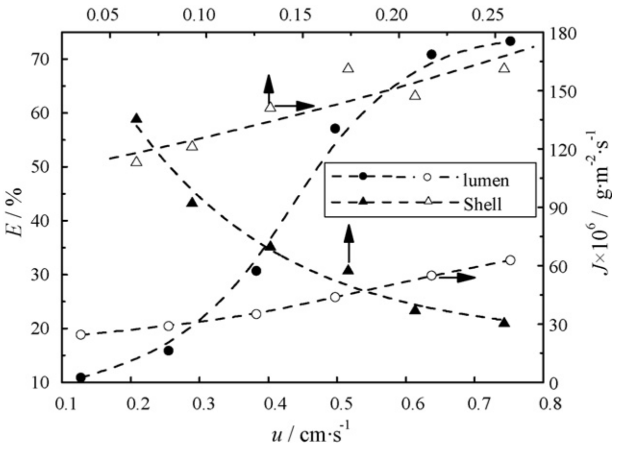

Fig. 6. The effect of flow rates of two sides on the removal efficiency—feed solution: $71.83\,\mathrm{mg\,L^{-1}}$ $CuSO_4$ solution at pH of 2.6; organic phase: 10% LIX984 + kerosene; stripping solution: $2.0\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solution; O/A = 1:10.

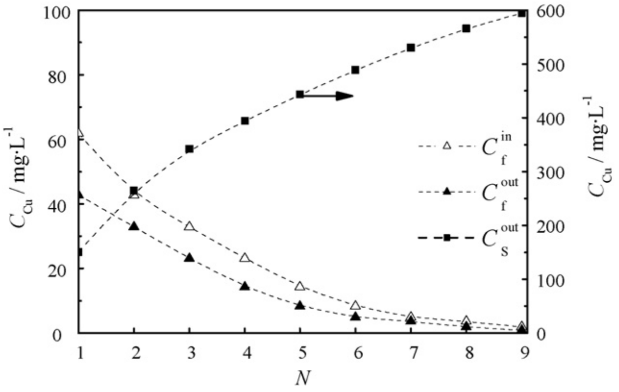

Fig. 7. The copper concentration profiles of countercurrent cascade experiments.

3.8. Transport studies

The ability of copper transport from the feed phase to the receiver phase through HFRLM is studied with countercurrent cascade experiments. The feed phase, 2500 mL $CuSO_4$ aqueous solutions with initial copper(II) concentration of 61.9 mg L^{-1} at pH 2.61, is pumped through the shell side of the module in single-pass mode. The outlet of the N^{th} stage is used as the inlet of $(N+1)^{th}$ stage, and so on. The stirred mixture, 250 mL 2.00 mol L^{-1} H_2SO_4 and 10% LIX984N + kerosene at a volume ratio of 10:1, flows through the lumen side of the hollow fiber module operated in countercurrent recycling mode. The volumetric flow rates both on the lumen side and the shell side are 3.1 and 15.0 mL min^{-1}, respectively.

Fig. 7 gives the copper concentration profiles in the outlet of the stripping phase, inlet and outlet of the feed phase of each stage. Fig. 8 gives the removal efficiency, the mass transfer flux and enrichment factor of each stage. At the 1st stage, the "uphill" effect was occurred. The copper concentration in the feed phase decreased from 61.9 to 42.7 mg L^{-1}, the copper concentration in the stripping phase increased from 0 to 150.6 mg L^{-1}. This characteristic shows the feasibility of simultaneous extraction and concentration of solute from dilute solutions. At later stages, the mass transfer flux decreases sharply, mainly because the decreasing of inlet copper concentration in the feed phase and the increasing of inlet copper concentration in the stripping phase reduce the mass transfer driving force of the process. At 9th stage, the removal efficiency is up to 98.6%. The copper concentration in the outlet of feed phase is 0.80 mg L^{-1}, which is lower than the nation standard of discharge for copper ions. The enrichment factor is up to 9.7. It should be noted that the size of used hollow fiber module is small, and the residence time of the feed phase in the hollow fiber module is short (<30 s). When a large-scale hollow fiber module packed with more hollow fibers and enough effective length is used, the above transport results can be attained in one stage. The transport results show that HFRLM is a promising method for simultaneous removal and recovery of copper from aqueous solutions.

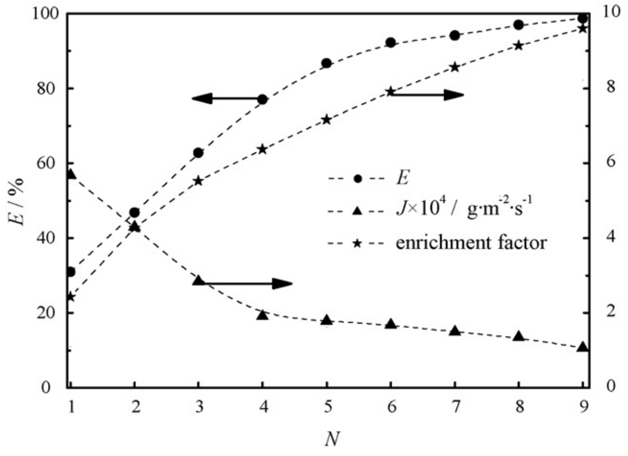

Fig. 8. The removal efficient and mass transfer flux of countercurrent cascade experiments.

3.9. Modeling the transport of copper through hollow fiber renewal liquid membrane

As the rate of complex reaction at interfaces is faster, the mass transfer resistance resulted from complex reaction can be ignored compared to the mass transfer resistance of diffusion mobility across the aqueous phase or organic phase. The transport of copper across HFRLM can be considered as four sequential steps [20], including the diffusion of metal ion across the aqueous boundary layer on the shell side, diffusion of metal-complex across the membrane phase, transport of copper in liquid membrane renewal process and back-extraction process on the lumen side. Because of the fast back-extraction kinetic, huge mass transfer area caused by the direct contact between organic droplets and stripping solution, and the vigorous mixing arising by the flowing fluid, the individual mass transfer resistance of back-extraction process could be neglected compared with the total mass transfer resistance.

Based on the surface renewal theory, resistance-in-series model and mass balance law, the differential mass transfer flux of copper at time interval Δt, dJ_{Cu}, could be calculated as follows:

$$dJ_{Cu} = K_f \, d\left(C_f^{in} - \left(\frac{m'}{m}\right) C_s^{out}\right) \tag{7}$$

$$Q_f(C_f^{in} - C_f^{out}) + Q_S(C_S^{in} - C_S^{out}) = 0 \tag{8}$$

The overall mass transfer coefficient, K_f, based on the feed phase is:

$$\frac{1}{K_{f,\,Cu}} = \frac{1}{k_S} + \frac{1}{mk_m} + \frac{1}{mk_R} \tag{9}$$

where C_f^{in} and C_f^{out} are the inlet and outlet copper concentration in the feed phase, respectively; C_S^{in} and C_S^{out} are the inlet and outlet copper concentration in the stripping phase, respectively; Q_f and Q_S are the volumetric flow rate of the feed phase and the stripping phase, respectively; k_S, k_m and k_R are the individual mass transfer coefficient on the shell side, membrane phase and renewal process, respectively.

In general, the value of m'/m is small, then $C_f^{in} \gg (m'/m)C_s^{out}$. The effect of outlet copper concentration in the stripping phase on the transport results of HFRLM process can be negligible in calculation.

For the countercurrent cascade experiments, it is an unsteady process. The copper concentration in the tank of the stripping phase is:

$$C_{s,\,t+\Delta t} = C_{s,\,t} - \left(\frac{A}{V_s}\right) \Delta J_{Cu} \;\; \Delta t \tag{10}$$

where

$$\Delta J_{Cu} = K_f \frac{(C_{f,t}^{in} - (m'/m)C_{s,t+\Delta t}^{out}) - (C_{f,t}^{out} - (m'/m)C_{s,t}^{in})}{\ln((C_{f,t}^{in} - (m'/m)C_{s,t+\Delta t}^{out})/(C_{f,t}^{out} - (m'/m)C_{s,t}^{in}))} \tag{11}$$

The value of overall mass transfer coefficient at time interval Δt, K_f, can be obtained by Eq. (9). The copper concentrations in the feed phase can be calculated by the mass balance law:

$$C_f^{out} = C_f^{in} - \frac{A \, \Delta J_{Cu}}{Q_f} \tag{12}$$

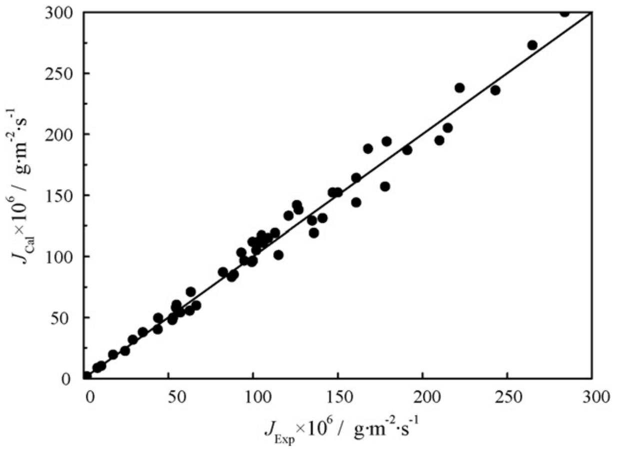

Fig. 9. Comparison of calculated and experimental results.

For the whole process of HFRLM, the mass balance equation is:

$$V_S(C_{S,t+\Delta t}-C_{S,t})=Q_f\ \ \Delta t(C_f^{in}-C_f^{out}) \tag{13}$$

The individual mass transfer coefficient on the shell side, k_S, is [30]:

$$\frac{k_S d_H}{D}=8.58\left(\frac{d_H^2 u_S}{\mu L_H}\right)\left(\frac{\mu}{\rho D}\right)^{1/3} \tag{14}$$

The individual mass transfer coefficient in the membrane phase, k_m, is [31]:

$$k_m=\frac{D\varepsilon}{\tau(d^{\mathrm{ext}}-d^{\mathrm{int}})/2} \tag{15}$$

The individual mass transfer coefficient of renewal process on the lumen side, k_R, is [20]:

$$k_R=aD^{0.5}S^{0.25}=aD^{0.5}\ \mathrm{Re}^{0.25}\,\Phi^{-0.25} \tag{16}$$

where a is the enhancement factor calculated from experimental data with value of 0.0005 [20], A is the effective mass transfer surface area of the hollow fiber module, D is the diffusion coefficient, d_H is the hydraulic diameter, u_S is the velocity on the shell side, L_H is the effective length of hollow fiber module, μ is the viscosity, ρ is the density, τ is the membrane porosity, ε is the membrane tortuosity, S is the renewal factor, Φ is the hold-up of organic droplets in the stripping phase, d^{ext} and d^{int} are the external and internal diameters of the hollow fibers, respectively.

By solving Eqs. (7)–(13), J, K_f and copper concentration profiles in the feed phase and the stripping phase of the HFRLM process could be calculated. As shown in Fig. 9, the modeled results are in a good agreement with experimental data; the weighted standard deviation is less than 12%. Such deviations maybe result from the accuracy of model parameters especially the simplification of m and m' in the calculation which were considered as constant in the entire hollow fiber module for each transport process. It is indicated that the proposed mass transfer model is validity.

4. Conclusions

In this paper, a new liquid membrane technique, namely hollow fiber renewal liquid membrane (HFRLM), is used for simultaneous removal and recovery of copper from acidic wastewater. $CuSO_4$ aqueous solution is used as simulated sulfuric acidic effluent containing copper. A commercial extractant LIX984N is used as the carrier, kerosene as the diluent, and sulfuric acid solution as the stripping phase.

The results show that LIX984N has good performance for the extraction of copper from the acidic and dilute aqueous solutions. The HFRLM process is more stable because of the automatically and continuously replenishment of membrane liquid by the dispersed organic droplets on the lumen side fluid. As a carrier-facilitated transport process, the addition of LIX984N in the organic phase can greatly improve the transport performance of the HFRLM process. The removal efficiency and the mass transfer flux increase with the increasing of LIX984N concentration in the organic phase. There is a favorable organic/aqueous volume ratio range from 1:10 to 1:7 on the lumen side mixture for the HFRLM process under the range studied. The higher pH value (>3) in the feed phase facilitate the transport results of copper through HFRLM; the removal efficiency and the mass transfer flux increase with the increasing of H_2SO_4 concentration in the stripping phase, and reach a maximum value at H_2SO_4 concentration of 2.0 mol L^{-1}, then decrease. It mainly results from the mass transfer driving force caused by distribution equilibrium and hydrogen ion concentration gradient between shell side and lumen side. The mass transfer fluxes increase with the increasing flow rates on two sides, while the removal efficiency increases with the increasing flow rate on lumen side and decreases with the increasing flow rate on shell side.

The transport results in countercurrent cascade experiments show that the HFRLM process can carry out the simultaneous removal and recovery of copper from wastewater successfully. The mass transfer model based on the surface renewal theory is presented by considering the renewal process of liquid membrane layer, diffusion across membrane phase and aqueous boundary layer on the shell side. The modeled results demonstrate a good agreement with experimental data. The results also show that HFRLM is a promising method for the treatment of acidic wastewater containing copper.

Acknowledgements

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