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Removal of neodymium(III) from wastewater using microtube ultrafiltration chemical reactor with organic phosphate

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ABSTRACT

Rare-earth mining in Inner Mongolia has produced wastewater containing neodymium, which has caused certain environmental pollution. Aiming at the low removal efficiency of neodymium in wastewater, we developed microtube ultrafiltration chemical reactor (UFCR). UFCR had organic phosphate system containing wastewater part with buffer solution acetic acid and enrichment part with nitric acid solution and organic phosphate(2-ethylhexyl phosphoric acid-mono-2ethylhexyl-ester) dissolved in fuel oil. Many factors of neodymium(III) removal using UFCR need to explore, including hydrogen ion concentration (or pH), cinit of neodymium(III), different ionic strength of rare-earth mine wastewater, volume ratio of organic phosphate with fuel oil and nitric acid solution (O/W), nitric acid concentration, organic phosphate concentration and different acid solution of enrichment part. The advantages of UFCR compared with the traditional removal methods was investigated. The effects of hydrodynamic properties (stablity and flow rate) and UF system parameters (inner diameter of microtube, tubule shell thickness, void ratio) etc. on the mass transfer performance of UFCR process for neodymium(III) removal were also studied. The experimental results show that the best removal conditions of neodymium(III) were obtained as that nitric acid concentration was 4.00 mol L^{-1}, organic phosphate concentration was 0.150 mol L^{-1}, and O/W was 0.5 in the enrichment part, and pH value was 4.50 in the wastewater part. Ionic strength of rare-earth mine wastewater had no obvious effect on neodymium(III) removal. When cinit of neodymium(III) concentration was 1.42×10^{-4} mol L^{-1}, the removal percentage of neodymium(III) was up to 93.5% in 150 min. The results of this study provide theoretical support for the treatment of wastewater containing neodymium in rare-earth mines.

Keywords: Microtube ultrafiltration chemical reactor; Organic phosphate; Neodymium(III); Wastewater part; Enrichment part; Removal percentage

1. Introduction

Rare-earth metals have been widely used in various industries. It can be used alone in some fields or with other substances. Adding a certain amount of rare-earth metals or rare-earth compounds can improve the properties of the alloy. Therefore, rare-earth elements are known as vitamins in the metallurgical industry [1]. For example, adding some rare-earth elements to steel can improve plasticity, toughness, steel resistance, heat resistance, oxidation

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resistance and corrosion resistance. For another example, rare-earth metals can be used to make fire alloys, permanent magnet materials, superconducting materials, dyeing materials, luminescent materials, trace element fertilizers, etc. In addition to being widely used in metallurgy, petrochemical, glass, ceramics, fluorescent materials, electronic materials, medicine and agriculture, rare-earth metals have gradually penetrated into many fields of modern science and technology. With the wide application of rare-earth elements in production and life, the removal and enrichment of rare-earth elements has become very necessary. In recent years, many institutions at home and abroad have studied this aspect [2]. There are many rare-earth mines in China. At present, due to national needs, they are being mined continuously. But it also produces some wastewater that is difficult to purify. There is a neodymium mine in Inner Mongolia, China. There is a lot of neodymium wastewater, which has some impact on the surrounding environment. The discharge of neodymium wastewater did not meet the standard. A certain amount of neodymium was detected in the surrounding crop roots. If this problem is not solved, people eating these plants will cause damage to the skin and internal organs. The removal effects of traditional methods were not good. This study attempted to explore the method of neodymium removal. It provided theoretical support for the purification of neodymium wastewater in the future.

Membrane reactor technology is a new removal method which combines the characteristics of solvent removal and solid membrane removal. Compared with the traditional methods of solvent removal and liquid membrane technology, it has several potential advantages. Rare-earth metal membrane reactor removal has the characteristics of short process, high speed, high enrichment rate, low reagent consumption and low cost. In China, this research began in the early 1980s. The organic solvent for extracting rare-earth metal ion-exchange membrane reactor system adopts kerosene or ordinary fuel oil, the carrier adopts various organic phosphonates, and the removal solution adopts various acids or bases. Rare-earth leaching solution can be grouped, purified and separated according to needs [3].

Some scholars used stearic acid and phosphate as carriers to study the purification of rare-earth element Sm(III) in traditional membrane reactor system and establish migration model [4]. Others had also established a membrane reaction system of rare-earth element Europium with polypropylene porous membrane as the supporting membrane and organic phosphonic acid as the carrier, and established a mathematical model of the membrane reaction system and heavy metal removal process [5]. Some people also used composite membrane reactor to treat lanthanum in rare-earth wastewater [6]. In recent years, some people [7] in China had studied the flat sandwich membrane reaction system, tested the permeability coefficient of extracting rare-earth metals, compared the differences of membrane bodies with different materials and thickness in the removal process, and investigated the removal rate and stability of the membrane reaction system. In China, rare-earth resources are abundant, with many kinds and large quantities. It is a very arduous task to separate, purify and recycle them.

The filtration reactor system is simple to operate without adding expensive surfactant. However, due to the dissolution of organic solutions (organic solvents, extractants and modifiers) in acid-base solutions, the contradiction between the decline of system stability and high permeation flux has not been well solved [8]. In recent years, some experts at home and abroad had turned to explore new reactor structures. They hoped to maintain the characteristics of membrane removal and overcome the instability of ultrafiltration reactor. Therefore, a combined technology of polyacrylonitrile (PAN)-ultrafiltration reactor and organic phosphonic acid was proposed [9,10]. It combined ultrafiltration body or various chemical processes with organic phosphoric acid solution, which can effectively overcome the problem of carrier leakage from ultrafiltration body. In our previous work, we studied the removal of rare-earth in dispersion supported liquid membrane reactor, and the removal results were very obvious [11–13]. Based on the previous work of dispersion supported liquid membrane reactor and hollow fiber strip dispersion reactor technology [14], this paper proposed PAN-microtube ultrafiltration reactor with organic phosphate system (UFCR) with nitric acid as removal agent and organic phosphonic acid dissolved in fuel oil as mobile carrier. In UFCR process, due to the wetting affinity between hydrophobic microtube and organic solution, a very thin organic film was formed on the inner surface of microtube for separating feed part and removal part. Solute was selectively transported from the feed section to the removal section through microtubes. UFCR not only has the advantages of non-equilibrium mass transfer and uphill effect, but also avoids the disadvantages of low removal rate of traditional liquid membrane, such as organic solute loss, difficult operation of emulsification and de-emulsification steps and so on.

At present, the application of UFCR in the removal of neodymium(III) had not been reported. This paper mainly explored and studied the feasibility of extracting neodymium(III) by UFCR. The removal of rare-earth metals was realized through membrane module design, carrier optimization and removal percentage control. The removal process of rare-earth metals was studied, and a new method and system for extracting rare-earth metals by UFCR were established. The research of this paper can provide more theoretical basis for further research, and its results are expected to make a breakthrough in the industrial application of UFCR technology.

2. Theoretical analysis

2.1. UFCR removal process

The wastewater part was prepared by dissolving a certain amount of $Nd(CH_3COO)_3 \cdot 4H_2O$ in acetate buffer solution with adjusted acidity value. The enrichment part take organic phosphonate as the carrier and is dissolved in fuel oil. The extract was 3.0 mol L^{-1} nitric acid solution. Soaked the microtube ultrafiltration body with organic solution for at least 48 h to make the pores of microtube completely filled with organic phosphate solution. In these experiments, there are two operation modes: (I) the extract enters the system through the outer wall of the ultrafiltration tube, and the wastewater enters the system through the ultrafiltration tube. (II) The extract enters the system through the ultrafiltration tube, and the wastewater enters the system through the outer wall of the ultrafiltration tube. Both fluids are transported in opposite directions and in a single path process. Generally speaking, due to the weak surface activity of the removal solution, the use of stirrer can mix the removal solution with organic phosphoric acid solution and form droplets of the removal solution in continuous organic liquid. It is called the enriched part. During the experiment, there was a constant supply of organic phosphoric acid solution, that is, the enriched organic phosphonic acid solution was in contact with the micropores of UF. The continuous supply of this organic phosphonic acid solution ensures the stable and continuous operation of UF. In this way, the complex of rare-earth metal and carrier can diffuse to the interface between removal solution and organic solution in UF pores. Therefore, the direct contact between removal solution and organic phosphonic acid solution provides effective mass transfer for rare-earth metal removal. Secondly, once the removal of the target species is completed, the agitator used for removal will not work. The organic liquid suspension is allowed to separate the enrichment part into two parts: an organic phosphoric acid solution that is easy to wet the carrier hole and a removal solution containing concentrated rare-earth metal ions. The concentrated extract is the product of this process. Fig. 1 is the experimental device of UFCR process.

In order to prevent the leakage of organic phosphoric acid solution from the membrane hole, the pressure on both sides can be controlled through the flow rate to make the pressure outside the ultrafiltration tube slightly positive and form a stable interface.

Based on our previous experiments, a stable neodymium(III) concentration distribution was obtained in the wastewater part and enrichment part after 22 min, and then a stable mass removal performance was realized. Similar results were found when the enriched part flowed through the tube side. In later experiments, the initial stabilization time is set to more than 30 min to obtain more reliable results.

2.2. UFCR removal process principle

Fig. 2 is the principle of UFCR process, which describes the concentration change and removal process. The removal process involves various equilibrium reactions, which are described as follows [13]:

- Neodymium(III) diffuses from the wastewater part to interface X.
- On the wastewater side interface of UFCR, neodymium(III) is extracted from the wastewater solution with carrier organic phosphate [which can be $(\mathrm{HR})_2$] in fuel oil, which can be expressed as [11]:

$$\mathrm{Nd}_f^{3+} + 3\left(\mathrm{HR}\right)_{2,\mathrm{org}} \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} \mathrm{Nd\,R_3} \cdot 3\mathrm{HR} + 3\mathrm{H}_f^{+} \qquad (1)$$

where f and org represent wastewater and organic phosphonic acid solution respectively; $(\mathrm{HR})_2$ shows that the organic phosphorus in fuel oil mainly exists in the form of dimer; K_1 and K_{-1} represent the forward and reverse reaction percentage constants at the interface

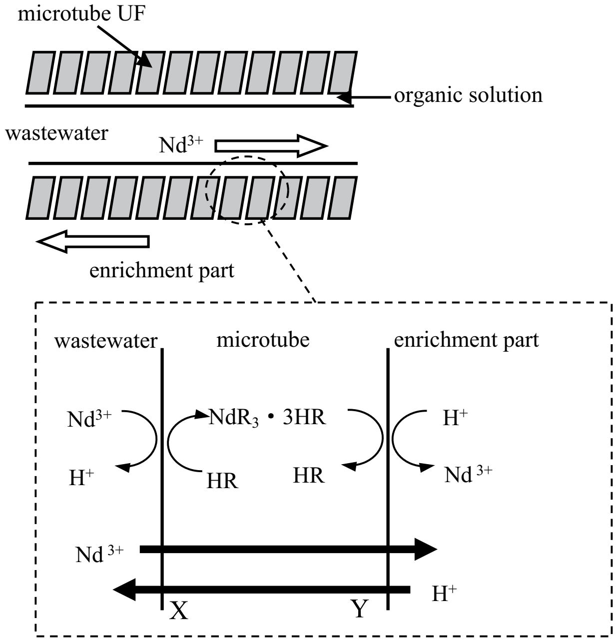

Fig. 2. Schematic principle and description of Nd^{3+} removal UFCR.

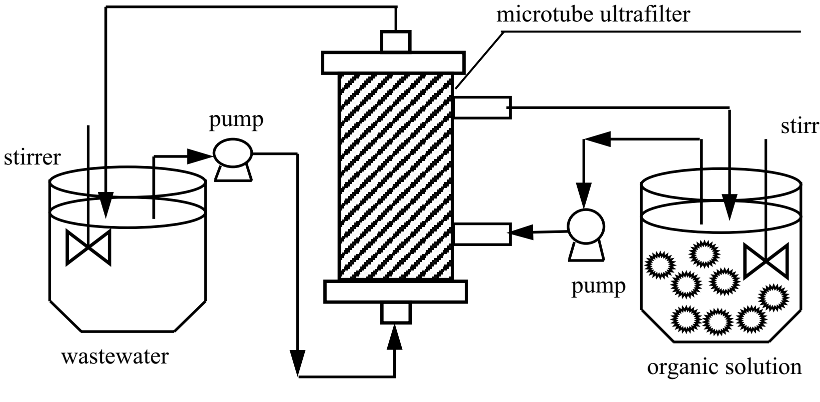

Fig. 1. Experimental installation of microtube ultrafiltration chemical reactor process.

between the wastewater part and the ultrafiltration microtube.
- The metal complex ($NdR_3·3HR$) was extracted by membrane X-Y.
- At the removal side interface of UFCR, $NdR_3·3HR$ and metal ion neodymium(III) dissolved in organic phosphoric acid solution are extracted by extractant.

The removal reaction on the other side of the microtube is as follows:

$$NdR_3 \cdot 3HR + 3H_s^+ \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} Nd^{3+} + 3(HR)_{2,org} \quad (2)$$

where s represents the enrichment part; K_2 and K_{-2} represent the forward and reverse reaction percentage constants at the interface between organic phosphonic acid solution and enrichment part.

- The carrier organic phosphate returns from y to X.

In this mechanism, the removal of neodymium(III) by UFCR will be described by considering the diffusion coefficient of neodymium(III). Because the complex reaction between neodymium(III) and organophosphate at the interface is much faster than the reaction on wastewater and microtube [13].

In order to establish the model, the following assumptions are made:

- Neodymium(III) moves only in the form of $NdR_3·3HR$ complex in organic medium.
- The convection in ultrafiltration microtube has no net flow.
- Metal ions only react with organic phosphate at the microtube interface.
- Organic phosphate monomer and dimer are always in equilibrium in the whole enrichment part.
- We found that the solubility of organic phosphate in acidic solution is negligible. Therefore, it is assumed that the concentration of organic phosphate in UFCR remains unchanged [15].

In this model, it can be considered that the removal of neodymium(III) in UFCR includes four consecutive steps. If the removal process can be described by Fick's law, the removal flux of each step is as follows [15–19]:

The flow of wastewater can be written as:

$$J_f = \frac{D_f}{d_f}\left(c_f - c_{\text{fi}}\right) \quad (3)$$

where J_f, D_f, d_f, c_f and c_{fi} respectively represent the removal flux in the wastewater part, the diffusion coefficient of neodymium(III) in the microtube, the thickness of the interface between the wastewater part and the microtube, the concentration of neodymium(III) in the wastewater part and the concentration of neodymium(III) in the interface between the wastewater part and the microtube.

The removal equilibrium constant K_{ex} in Eq. (1) can be expressed as:

$$K_{\text{ex}} = \frac{\left[H^+\right]^3 c^0_{\text{mf}}}{c_{\text{fi}}\left[(HR)_2\right]^3} = \frac{K_d\left[H^+\right]^3}{\left[(HR)_2\right]^3} = \frac{8K_d\left[H^+\right]^3}{\left[HR\right]^3} \quad (4)$$

where m represents organic phosphonic acid-microtube and K_d represents the distribution ratio of neodymium(III).

The removal flux of the interface layer between the wastewater part and the organic phosphonic acid-microtube can be written as:

$$J_{\text{mf}} = K_1 c_{\text{fi}} - K_{-1} c^0_{\text{mf}} \quad (5)$$

where J_{mf} and c^0_{mf} represent the removal flux and neodymium(III) concentration in the wastewater part and the organic phosphonic acid microtube interface layer.

$$J_m = \frac{D^0_m}{d_m}\left(c^0_{\text{mf}} - c^0_{\text{ms}}\right) \quad (6)$$

where J_m, c^0_{ms}, D^0_m and d_m respectively represent the removal flux at the reaction interface, the concentration of neodymium(III) in the organic phosphonic acid and microtube interface layer, the removal coefficient of neodymium(III) in microtubes and the thickness of microtubes.

In view of the different characteristics of different microtubes, the curvature and porosity of microtubes have an impact on the removal flux of microtubes. The greater the porosity of microtubes, the higher the flux, the greater the curvature of microtubes, and the lower the flux. Therefore, considering the correction coefficient, Eq. (6) can be rewritten as:

$$J_m = \frac{D^0_m \varepsilon}{d_m \tau}\left(c^0_{\text{mf}} - c^0_{\text{ms}}\right) \quad (7)$$

where τ and ε represents the curvature and porosity of microtubes.

In the internal steady-state reaction system under ideal conditions, all the above individual removal fluxes can take the same value [12,15–19].

$$J_f = J_m = J_{\text{mf}} = J_s \quad (8)$$

where J_s represents the removal flux of the dispersed phase.

Combining Eqs. (3), (4), (6), (7) and (8), the following equation can be obtained:

$$J = \frac{1}{\dfrac{d_f}{D_f} + \dfrac{8d_m\tau\left[H^+\right]^3}{D^0_m \varepsilon K_{\text{ex}}\left[HR\right]^3}} c_f \quad (9)$$

According to the definition of permeability coefficient, the removal flux of microtube can also be written as:

$$J = P_C \cdot c_f = -\frac{V_f}{\varepsilon A}\left(\frac{dc_f}{dt}\right) \quad (10)$$

where V_f represents the volume of wastewater, A represents the effective area of microtube and J represents the flux of microtube.

P_C stands for permeability coefficient, which can be defined as:

$$P_C = \frac{1}{\frac{d_f}{D_f} + \frac{8d_m\tau\left[\mathrm{H}^+\right]^3}{D_m^0 \varepsilon K_{\mathrm{ex}}\left[\mathrm{HR}\right]^3}} \tag{11}$$

The d_f/D_f and d_m/D^0_m are defined as follows:

$$\delta_f = \frac{d_f}{D_f} \tag{12}$$

$$\delta_m = \frac{d_m}{D_m^0} \tag{13}$$

Eq. (11) can be simplified as:

$$\frac{1}{P_C} = \frac{8\delta_m\tau\left[\mathrm{H}^+\right]^3}{\varepsilon K_{\mathrm{ex}}\left[\mathrm{HR}\right]^3} + \delta_f \tag{14}$$

In Eq. (14), ε, τ and K_{ex} are constants. Through the removal experiment, K_{ex} 1.5×10^{-10} was obtained. Under the same organic phosphorus concentration, $1/P_C$ has a linear relationship with $[\mathrm{H}^+]^3$. Therefore, the removal coefficient of neodymium(III) in microtubes and the thickness of wastewater microtube interface can be obtained by linear slope method. Similarly, under the same acidity of the wastewater part, the relationship between $1/P_C$ and $[\mathrm{HR}]^3$ was tested as linear.

Then, you can get δ_f, δ_m. D^0_m and d_f values can also be obtained according to Eq. (14) in combination with Eqs. (12) and (13).

The removal percentage of neodymium(III) was obtained by measuring d_{cf}/d_t.

Consider and integrate Eq. (10) as follows:

$$\ln\frac{c_t}{c_0} = -\frac{\varepsilon A}{V_{\mathrm{f}}} P_C \cdot t \tag{15}$$

$$\eta = 1 - e^{-\frac{\varepsilon A}{V_{\mathrm{f}}}P_C \cdot t} \quad \text{or} \quad \ln\left(1-\eta\right) = -\frac{\varepsilon A}{V_{\mathrm{f}}} P_C \cdot t \tag{16}$$

$$\int_{c_0}^{c_t} \frac{dc_f}{c_f} \cdot \frac{-V_{\mathrm{f}}}{\varepsilon A P_C\left(t^*\right)} = t - t_0 \tag{17}$$

where c_t and c_0 represent the concentration of neodymium(III) in the wastewater at $t = 0$ and $t = t$, respectively. t^* represents the average time respectively. Eq. (15) shows that the value of P_C is the slope of the straight line obtained under different operating conditions.

Combining Eqs. (10)–(17), the following formula can be obtained:

$$\eta = 1 - e^{\frac{8\delta_{\mathrm{m}}\tau V_{\mathrm{f}}\left[\mathrm{H}^+\right]^3}{\varepsilon^2 K_{\mathrm{ex}} A t\left[\mathrm{HR}\right]^3} + \frac{\delta_f V_f}{\varepsilon A t}} \tag{18}$$

According to Fick's second law, Eq. (18) can also be written as follows [13]:

$$J\Big|_t = \frac{D_m^0 K_{\mathrm{ex}}\left[\left(\mathrm{HR}\right)_2\right]^3 c_f}{d_m\left[\mathrm{H}^+\right]^3}\left(1 - \frac{d_m^2}{6D_m^0 t}\right) \tag{19}$$

where ε, τ and K_{ex} are constants. η represents the removal percentage of neodymium(III) through UFCR. J represents the removal flux of neodymium(III). c_f is the concentration of the wastewater part. t is the time. D_f represents the movement coefficient of neodymium(III) in microtubes. d_f represents the thickness of the interface layer between the wastewater part and the film phase. D^0_m represents the coefficient of neodymium(III) in microtubes. d_m represents the thickness of microtubes respectively.

3. Experimental

3.1. Reagent

$\mathrm{Nd(CH_3COO)_3{\cdot}4H_2O}$, arsenazo III, $\mathrm{HNO_3}$, $\mathrm{NaH_2PO_4}$, $\mathrm{Na_2HPO_4}$, $\mathrm{CH_3COONa}$ and $\mathrm{CH_3COOH}$ used in this study were of analytical grade. 2-ethylhexyl phosphate mono-2-ethylhexyl ester (organic phosphate) was a commercial extractant (purity > 95%) without further purification. The fuel oil was washed with concentrated sulfuric acid and distilled at 178°C–207°C.

3.2. Preparation of solution

Neodymium(III) stock solution: dissolved $\mathrm{Nd(CH_3COO)_3{\cdot}4H_2O}$ in 1.0 mol $\mathrm{L^{-1}}$ nitric acid to prepare neodymium(III) stock solution, and analyzed it with arsenazo III as chromogenic agent.

Neodymium(III) feed solution: after adding the calculated amount of $\mathrm{CH_3COONa}$ and $\mathrm{CH_3COOH}$ or $\mathrm{Na_2HPO_4}$ and $\mathrm{NaH_2PO_4}$, diluted a certain amount of neodymium(III) stock solution to a given degree with 0.02 mol $\mathrm{L^{-1}}$ nitric acid solution.

Arsenazo III stock solution: arsenazo III stock solution was prepared by dissolving arsenazo III powder in deionized water.

Back removal solution: dissolved with deionized water and diluted to the required amount of nitric acid with known concentration.

3.3. Experimental materials and determination

All experiments were self-designed systems. The microtube ultrafilter was a laboratory scale version with two 0~200 ml $\mathrm{min^{-1}}$ pumps and flowmeters. This make it possible to evaluate the performance without preparing a large amount of wastewater, back extractant and organic phosphoric acid solution, and avoided the influence of non-ideal flow on both sides of the microtube. The microtube ultrafiltration body adopted commercial PAN module, with nominal porosity of 48%, bending degree of 2.15, effective module length of 28 cm, module inner diameter of 4.2 cm and number of fibers of 19. The inner diameter, outer diameter, thickness and effective film area of the microtube were 2.85 mm, 3.18 mm, 0.27 mm and 181 cm^2 respectively.

The ion concentration of the sample containing only neodymium(III) in the feed solution was analyzed with a UV-1200 spectrophotometer and arsenazo III as the developer (detection wavelength: 651 nm).

4. Results and discussion

4.1. Stability of UFCR

In order to determine the stability of UFCR compared with traditional supported liquid membrane, the variation trend of neodymium(III) concentration in wastewater part and enrichment part with time under long-term fixed operation conditions was studied.

In this experiment, two operation modes are studied in mode 1: the enrichment part enters through the outside of the microtube wall and the wastewater part enters through the inside of the microtube. The flow rates of wastewater part and enrichment part were 0.017 and 0.008 m s^{-1}, respectively. The flow velocity of the two parts was maintained in the experiment.

The selected hypothetical experimental condition was to adjust the pH value to 4.60 under the specific pH value of the wastewater part. In the wastewater part, the cinit of neodymium(III) was 1.84×10^{-4} mol L^{-1}, the volume ratio (O/W) of organic phosphoric acid solution/removal solution was 0.3, the concentration of nitric acid in the enriched part was 3.10 mol L^{-1}, and the concentration of organic phosphate was 0.240 mol L^{-1}. The results are shown in Figs. 3 and 4. After 30 min, the change trend of neodymium(III) concentration was stable, so we take samples twice at a time, once every 15 min and once every 30 min. Neodymium(III) concentration and stability of the enrichment part gradually decreased when the traditional supported liquid membrane was used, and the neodymium(III) concentration of the wastewater part and the enrichment part remains stable when UFCR was used. This is because the organic phosphoric acid in the traditional supporting liquid membrane is gradually lost, while UFCR with organic phosphoric acid solution can continuously supplement the system with organic phosphoric acid. Therefore, we can conclude that the stability of UFCR is better than that of traditional supported liquid membrane.

4.2. Effect of flow rate of wastewater part and enrichment part

In order to study the removal mechanism in UFCR, and determine the main part of the total removal resistance, it is necessary to study the hydrodynamic characteristics of the system. The flow rate of wastewater and enrichment plays an important role in the removal of metal ions from wastewater to back removal solution.

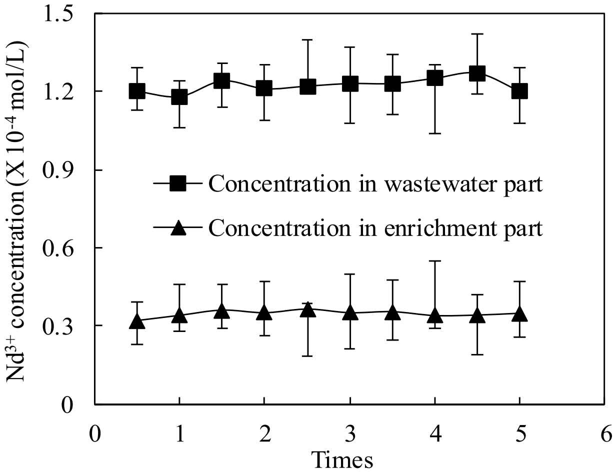

Fig. 3. Stability of UFCR.

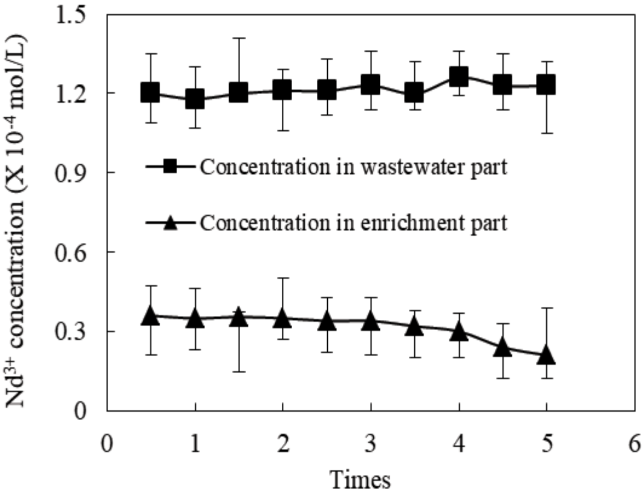

Fig. 4. Stability of traditional SLM.

In the traditional supported liquid membrane, the carrier will be gradually washed away by the high-speed flowing solution. In UFCR, organic phosphoric acid solution helps to provide carrier for microtubes under high-speed flow conditions. Therefore, this section studied the effect of the flow rate of wastewater part and enrichment part on the removal rate of neodymium(III). All other parameters, such as pH value, cinit of neodymium(III) in wastewater, volume ratio of organic phosphonic acid solution/acid solution (O/W) and organic phosphate concentration, were adjusted to 4.50 and 1.75×10^{-4} mol L^{-1}, 0.50 and 0.240 mol L^{-1}, respectively. The effect of the flow rate of wastewater part and enrichment part on the removal percentage of neodymium(III) is shown in Figs. 5 and 6.

We can find that in the traditional supported liquid membrane, the high-speed flowing solution will gradually wash away the organic phosphonic acid carrier, so the higher the flow rate, the lower the removal rate. In UFCR, under the condition of high-speed flow, organic phosphonic acid solution helps to provide carrier for

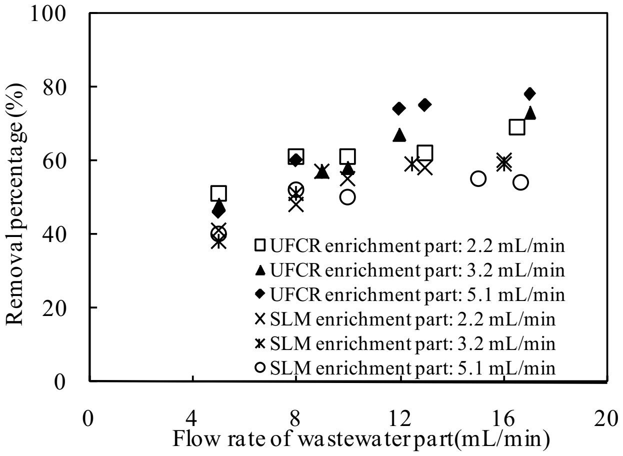

Fig. 5. Comparison between UFCR and traditional SLM about flow rates effect on removal of neodymium(III) in both two part (I).

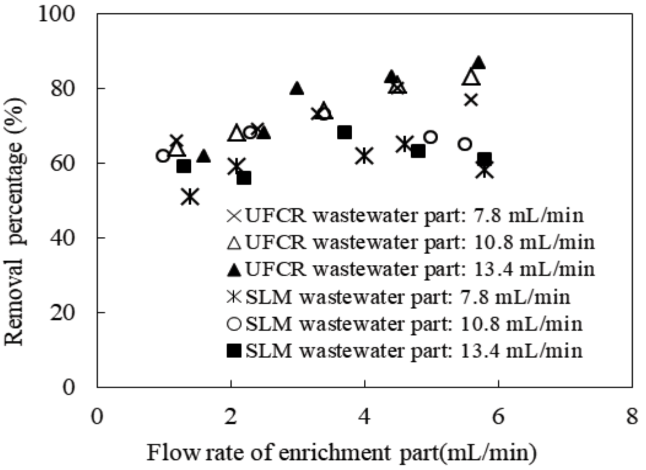

Fig. 6. Comparison between UFCR and traditional SLM about flow rates effect on removal of neodymium(III) in both two part (II).

microtubes. Therefore, the outer wall solution flow rate of microtube has no significant effect on the removal rate of neodymium(III). The flow rate of wastewater solution in microtube has little effect on the removal rate of neodymium(III). Because the diffusion rate of wastewater solution in the inner boundary layer of microtube is an important rate control step in the whole removal process [20,21]. The flow rate of the organic phosphine solution was about 10.2 ml min^{-1} in the outer wall of the micro tube, and the flow rate was limited to about 1.7 ml min^{-1}.

4.3. Effect of wastewater pH

According to the mechanism of the removal process, the concentration difference between the wastewater part and the enrichment part is the driving force of the mass transfer process [11]. Therefore, in the wastewater part, the lower the H^+ concentration, the stronger the driving force of the mass transfer process. Stronger power will promote the removal flux of neodymium(III). Similarly, the higher the pH value of wastewater, the higher the removal flux of neodymium(III). The effect of wastewater pH on neodymium(III) removal was studied in the range of pH 2.60 to 5.00. In the wastewater part, the cinit of neodymium(III) is 1.42×10^{-4} mol L^{-1}. In the enrichment part, the concentration of nitric acid solution was 4.00 mol L^{-1}, the volume ratio of organic phosphonic acid solution/acid solution (O/W) was 0.50, and the concentration of organic phosphate was 0.120 mol L^{-1}. The results are shown in Fig. 7. When the pH value of wastewater increased from 2.60 to 5.00, the removal percentage of neodymium(III) increased, and the maximum removal percentage observed at pH 4.50 within 150 min was 87.3%. When the pH value of wastewater was higher than 4.50, the removal percentage of neodymium(III) was unstable within 150 min due to wastewater emulsification. For all previous cases, the announcement of relevant documents [11,16] proposed the influence of pH value on the partition coefficient of removal process. This is because of the regeneration effect of organic phosphonic acid on microtubes. And when the diffusion mobility of neodymium(III) ions is determined under specific experimental conditions, the removal process is mainly controlled by the mass transfer driving force caused by distribution balance [12,17,18]. We chose the pH value of 4.50 as the optimal feed condition for our study.

4.4. Effect of acid concentration in enrichment part

The stripping reaction of the enriched part plays an important role in extracting metal ions from wastewater to the stripping stage. Therefore, this section studied the effect of the concentration of enriched nitric acid on the removal flux of neodymium(III). All other parameters, such as pH value, cinit of neodymium(III) in wastewater, volume ratio of organic phosphonic acid solution/acid solution (O/W) and organic phosphate concentration, were adjusted to 4.50 and 1.42×10^{-4} mol L^{-1}, 0.50 and 0.120 mol L^{-1} respectively. The effect of nitric acid concentration of enriched part on neodymium(III) removal flux is shown in Fig. 8. The results showed that the removal flux of neodymium(III) increased with the increase of the concentration of enriched acid. It can be seen that the effective acid concentrations for removal were 3.00, 4.00 and 5.00 mol L^{-1}, respectively, which made the removal flux of neodymium(III) about 4.81×10^{-7} mol/(s m^2), 5.71×10^{-8} mol/(s m^2) and 5.33×10^{-8} mol/(s m^2).

Increasing the concentration of nitric acid solution from 1.00 to 2.00 mol L^{-1} had no significant effect on the removal flux of neodymium(III). Because the number of neodymium(III) complexes and the concentration of organic phosphonic acid extracted by microtubes per unit time were determined. Considering the control of acidity and the increase of removal flux, we chose 4.00 mol L^{-1} as the optimal acid concentration of the concentrated part for the later experiments.

4.5. Effect of volume ratio of enriched part (O/W)

The effect of the volume ratio of organic phosphoric acid solution to acid solution (O/W) of enrichment part on the removal of neodymium(III) was studied. It was

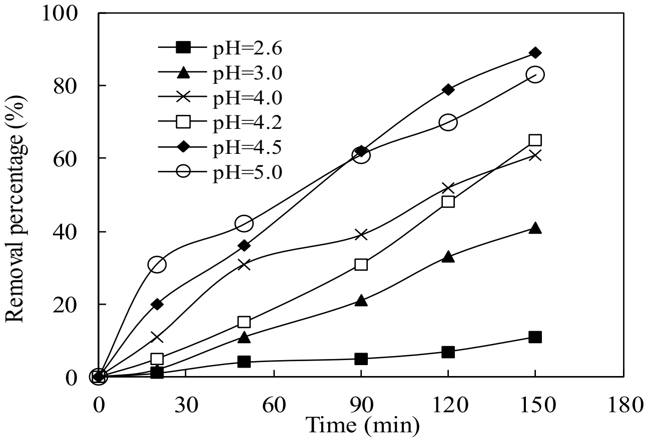

Fig. 7. Effect of wastewater pH.

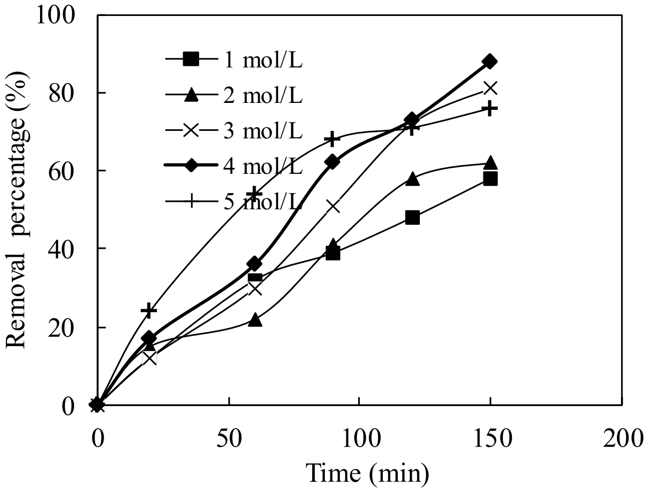

Fig. 8. Effect of nitric acid concentration on separation of Eu(III).

assumed that the selected experimental conditions were the specific pH value of the wastewater part, which was adjusted to 4.50. The cinit of neodymium(III) in wastewater was adjusted to 1.42×10^{-4} mol L^{-1}, the acid concentration of the enrichment part was adjusted to 4.00 mol L^{-1}, and the concentration of organic phosphoric acid was adjusted to 0.120 mol L^{-1}. The effect of the volume ratio (O/W) of the enriched part on the separation of neodymium(III) is shown in Fig. 9. The volume ratio increased from 0 to 2.00. It can be seen that the most effective volume ratio was 0.50, which made the removal flux of neodymium(III) much higher than that of other substances.

This showed that the removal flux of neodymium(III) increases with the increase of the volume ratio of enriched part. When the volume ratio of enriched part increases, the organic phosphoric acid solution is obviously dispersed in microtubes. Therefore, the probability of contact between organic phosphate and neodymium(III) increases. In this way, the mixing of microtubes and enriched parts provides additional regeneration percentage of removal surface and microtube surface carrier. Thus, the efficiency of extracting

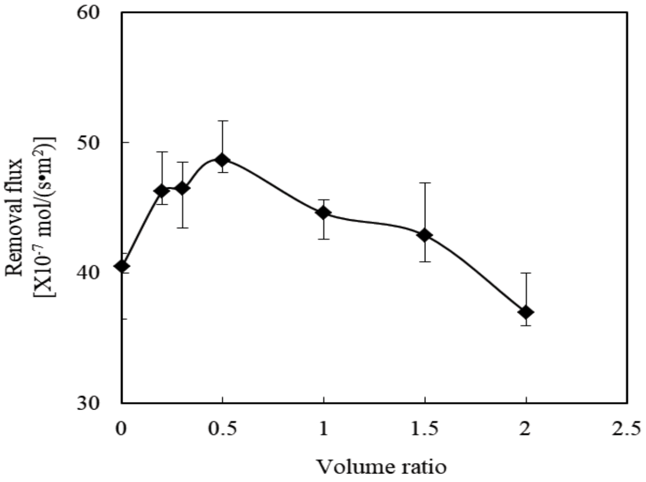

Fig. 9. Effect of volume ratio of organic phosphoric acid solution to acid solution (O/W).

the target heavy metal complex from organic phosphonic acid solution to acid solution is greatly improved. When the volume ratio increases to a certain extent, the flux decreases due to the reduction of H^+ in the enriched part [11]. In the following experiment, we chose 0.50 as the optimal volume ratio (O/W) of organic phosphoric acid solution and acid solution.

4.6. Effects of different acid solutions as stripping agents

The concentrated acid solution plays an important role in extracting metal ions from wastewater to stripping stage. Therefore, the effects of different acids on the removal of neodymium(III) were studied. Adjust the pH value of the wastewater part, the cinit of neodymium(III), the volume ratio (O/W) of the enrichment part and the concentration of organic phosphorus to 4.50 and 1.42×10^{-4} mol L^{-1}, 0.50 and 0.100 mol L^{-1} respectively. The effects of different acids in the enrichment part on the removal rate of neodymium(III) are shown in Fig. 10. Under the same acidity conditions, hydrochloric acid, sulfuric acid and nitric acid were used as stripping agents respectively. It was found that nitric acid was the most effective stripping agent in this study.

4.7. Effect of neodymium(III) cinit in wastewater part

Wuhen the cinit of neodymium(III) was in the range of 7.50×10^{-5} mol L^{-1} to 1.70×10^{-4} mol L^{-1}, the effect of cinit on the removal rate of neodymium(III) was studied. The pH value of the wastewater part was adjusted to 4.50, the volume ratio (O/W) was adjusted to 0.50, the concentration of nitric acid in the enrichment part was also adjusted to 4.00 mol L^{-1}, and the concentration of organic phosphoric acid is 0.100 mol L^{-1}. The results are shown in Table 1. With the neodymium(III) cinit in the wastewater part from 7.50×10^{-5} mol L^{-1} increased to 1.42×10^{-4} mol L^{-1}, the removal rate of neodymium(III) decreased. This is because when the interface between the wastewater part and the microtube is determined, the amount of organic phosphate passing through the microtube is certain. In other words, in this removal process, the amount of neodymium(III) extracted was determined [11]. When the neodymium(III) cinit was 7.50×10^{-5} mol L^{-1}, 1.03×10^{-5} mol L^{-1}, 1.24×10^{-5} mol L^{-1}, 1.42×10^{-4} mol L^{-1} and 1.70×10^{-4} mol L^{-1}, the removal rates in 100 min were 92.1%, 71.4%, 70.3%, 62.9% and 48.7%, respectively.

4.8. Effect of organic phosphoric acid concentration

The concentration of organic phosphoric acid in microtubes and enriched part also has an important effect on the removal of neodymium(III). The effect of organic phosphate acid concentration on the removal rate of neodymium(III) was studied in the range of organic phosphate acid concentration from 0.060 to 0.200 mol L^{-1}. Adjust the pH value to 4.50, and the cinit of neodymium(III) in the wastewater was 1.42×10^{-4} mol L^{-1}, the volume ratio (O/W) of the concentrated part was adjusted to 0.50, and the nitric acid concentration was also adjusted to 4.00 mol L^{-1}. The results are shown in Fig. 11. The removal rate of neodymium(III) increased with the increase of membrane carrier concentration from 0.065 to 0.200 mol L^{-1}. However, when the concentration of organic phosphoric acid increased from 0.150 to 0.200 mol L^{-1}, the removal rate of neodymium(III) did not increase significantly. In the range of organic phosphoric acid concentration from 0.060 to 0.200 mol L^{-1}, the effectiveness of organic phosphoric acid on the partial dispersion interface of wastewater increases with the increase of organic phosphonic acid concentration. Therefore, the chemical reaction is balanced to the left. Similarly, when the concentration of organic phosphoric acid becomes low, the equilibrium moves to the right [13]. When the concentration of organic phosphoric acid increases significantly, the removal flux of neodymium(III) will no longer increase with time [11]. When the concentration of organic phosphoric acid was 0.100, 0.120, 0.150 and 0.200 mol L^{-1}, the removal rates were 86.2%, 91.1%, 92.3% and 93.4%, respectively. The concentration of organic phosphoric acid is directly proportional to the concentration of neodymium(III) on microtubes. When the concentration of organic phosphoric acid in microtube is higher than that of neodymium(III) in wastewater, no neodymium(III) reacts with excess organic phosphoric acid, so the increase of neodymium(III) removal rate will slow down. This shows that when the initial concentration of neodymium(III), the action area and time of the membrane are fixed, the amount of organic phosphate extracted by the membrane per unit time is determined. The optimum concentration of organic phosphonic acid was 0.150 mol L^{-1}. Under these conditions, the removal rate of neodymium(III) was 96.1% within 150 min.

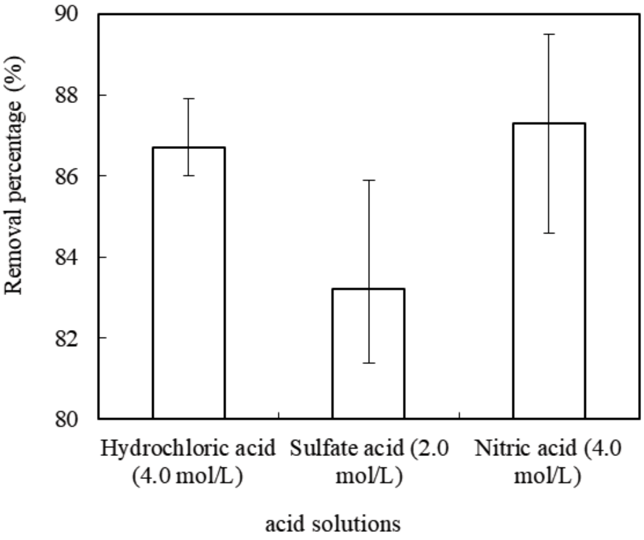

Fig. 10. Effect of different acid solutions as stripping agents.

4.9. Effect of ionic strength in wastewater

In this section, the effect of partial ionic strength of wastewater on the removal rate of neodymium(III) was studied. The results are shown in Fig. 12. The results showed that the ionic strength had no significant effect on the removal flux of neodymium(III). Because the nitric acid effect surrounded by organic phosphonic acid solution is weak, the ionic strength of the enriched part can be ignored. When the ion concentration of the wastewater is low, the ionic strength of the two parts can be ignored. Compared with other removal technologies, the operating conditions can be further simplified [13].

4.10. Reuse of organic phosphonic acid solution

Under the optimum conditions, the reuse of organic phosphonic acid solution was studied. It can be seen from Fig. 13 that the organic phosphonic acid solution in UFCR

Table 1
Effect of neodymium(III) cinit

Time (min)	Removal percentage (%)				
	7.50×10^{-5} mol L^{-1}	1.03×10^{-4} mol L^{-1}	1.24×10^{-4} mol L^{-1}	1.42×10^{-4} mol L^{-1}	1.70×10^{-4} mol L^{-1}
0	0	0	0	0	0
20	31.5	39.7	26.3	27.5	17.3
60	69.8	54.6	52.1	41.7	27.1
100	91.1	71.4	72.3	61.4	48.71
130	–	87.30	80.1	75.3	59.3
150	–	–	93.2	89.2	69.0

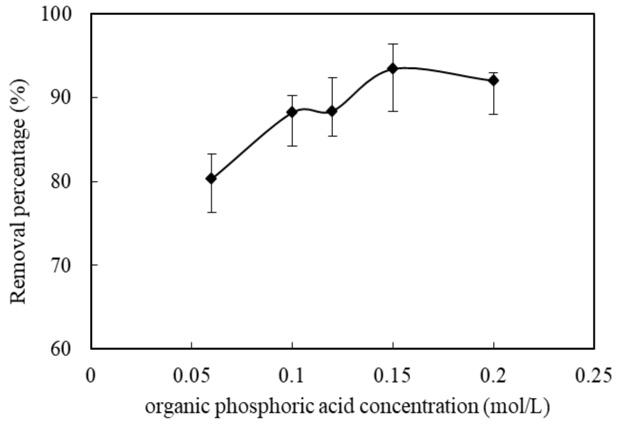

Fig. 11. Effect of organic phosphoric acid concentration.

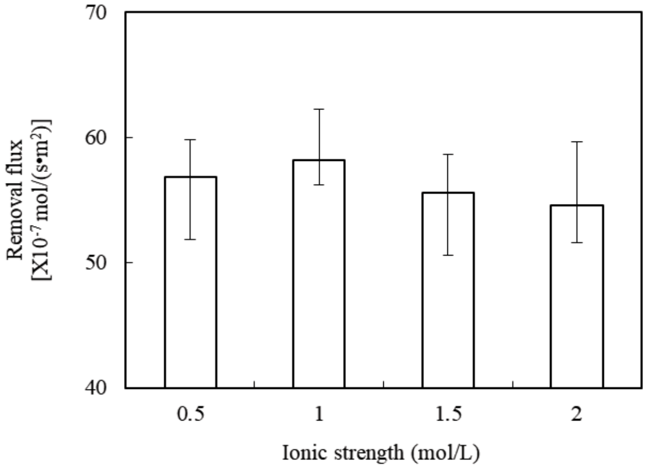

Fig. 12. Effect of ionic strengths on removal of neodymium(III).

can be reused for many times before re-removal with strong acid after each experiment. In the four experiments, the organic phosphonic acid solution in UFCR can be reused for many times, and the variation trend of removal rate is stable. After four experiments, the removal rate of neodymium(III) decreased gradual

4.11. Reuse of microtubes

The reuse of microtubes was studied under the optimum conditions. The organic phosphonic acid solution was reused only four times. In the fifth experiment, we used a new organic phosphonic acid solution or the organic phosphonic acid solution purified by strong acid stripping. The results are shown in Fig. 14. In 9 experiments, UFCR microtubes with enrichment part can be reused for many times, and the variation trend of removal rate is stable. However, when there was no organic phosphonic acid in the UFCR enrichment part, the variation trend of removal rate was unstable, and the removal rate gradually decreased after two experiments. In this study, we can also conclude that the stability of UFCR system is better when the enrichment part increases the organic phosphoric acid solution.

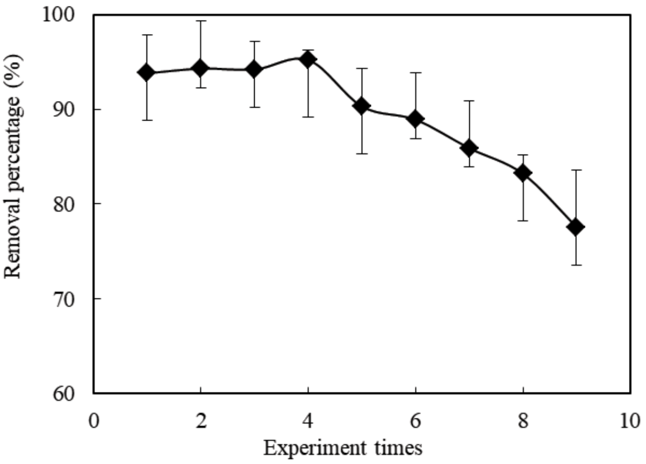

Fig. 13. Reuse of organic phosphonic acid solution.

4.12. Retention in microtubes and stripping effects

Under the optimum conditions, the retention in microtubes and stripping effects were studied. Adjust the pH value to 4.50, and the cinit of neodymium(III) in the wastewater was 1.420 × 10^{-4} mol L^{-1}, the volume ratio (O/W) was adjusted to 0.50, and the concentration of nitric acid solution in the concentrated part was also adjusted to 4.00 mol L^{-1}. Adjust the concentration of organic phosphoric acid to 0.150 mol L^{-1}. According to the concentration of neodymium(III) in wastewater and stripping stage, the concentration of neodymium(III) in microtube can be obtained, and then the stripping effect of enrichment part and the retention phenomenon of microtube can be obtained. The results are shown in Fig. 15. We can conclude that the retention rate of neodymium(III) in microtubes gradually decreases with the extension of time, because the stripping speed in the removal process is faster than the complexation speed.

4.13. Effect of structural parameters of PAN ultrafiltration microtubes

The effects of microtube structure parameters (tube inner diameter, tube thickness and porosity) on mass transfer performance of neodymium(III) removal by UFCR were also studied. Six polyacrylonitrile (PAN) microtubes were selected, and additional information on these modules is listed in Table 2.

4.13.1. Effect of microtube thickness

The microtube thickness will affect the thickness of organic phosphonic acid interface layer in UFCR module and the removal rate of neodymium(III) complex. Microtube modules L1, L2 and L3 were selected to study the effect of microtube thickness on neodymium(III) removal under the optimal removal conditions. The results are shown in Fig. 16. We can conclude that the thicker the microtube, the lower the removal rate of neodymium(III). The main reason may be that the thicker the microtube, the lower the removal rate of neodymium(III) complex.

4.13.2. Effect of microtube inner diameter

The inner diameter of microtube will affect the flow state of liquid and the removal rate of neodymium(III) in UFCR system. The effect of microtube inner diameter on the removal of neodymium(III) was studied under the optimum removal conditions. The results are shown in Fig. 17. The results showed that the larger the inner diameter of microtubes, the higher the removal rate of neodymium(III). The main reason may be that the larger the inner diameter of microtube, the more organic phosphoric acid solution of microtube system. Therefore, more organic phosphoric acid solution can make the stripping and complexation reaction more effective.

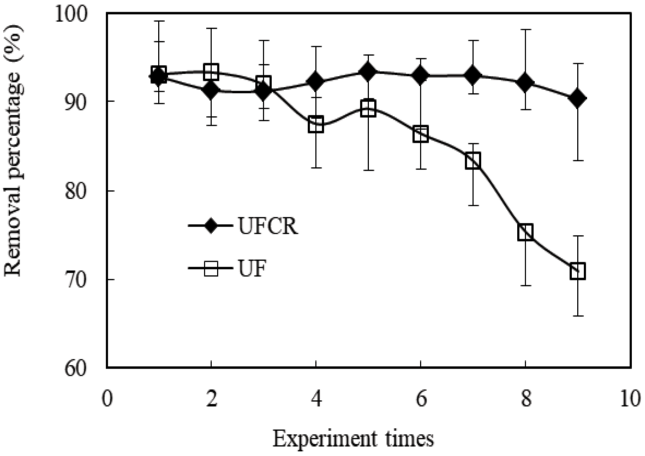

Fig. 14. Reuse effect of microtubules.

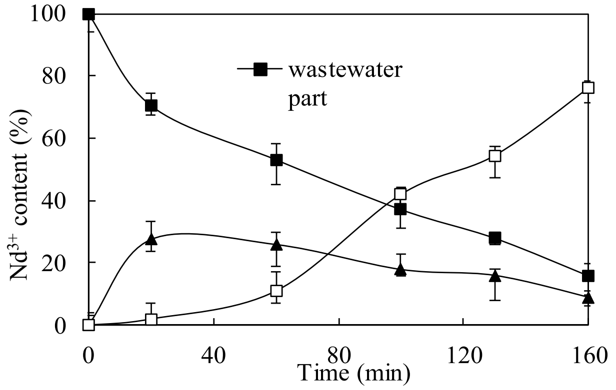

Fig. 15. Retention in microtubes and stripping effects.

4.13.3. Effect of microtube porosity

The porosity of microtubes has an important effect on the removal rate of neodymium(III) complexes. Microtube modules L1 and L6 were selected to study the effect of microtube porosity on the removal of neodymium(III) under the optimal removal conditions. The results are shown in Fig. 18. We can conclude that the larger the porosity of microtubes, the higher the removal rate of neodymium(III). The main reason may be that the larger the porosity of microtubes, the larger the effective removal area of microtubes.

5. Conclusions

It has been found that UFCR systems using organophosphates on rare-earth metals can selectively separate neodymium(III) from acidic media. We can draw the following conclusions: the optimum removal conditions of neodymium(III) in UFCR system were as follows: the concentration of nitric acid solution was 4.00 mol L^{-1}, the volume ratio (O/W) of organic phosphoric acid solution to acid solution was 0.50, the concentration of organic phosphoric

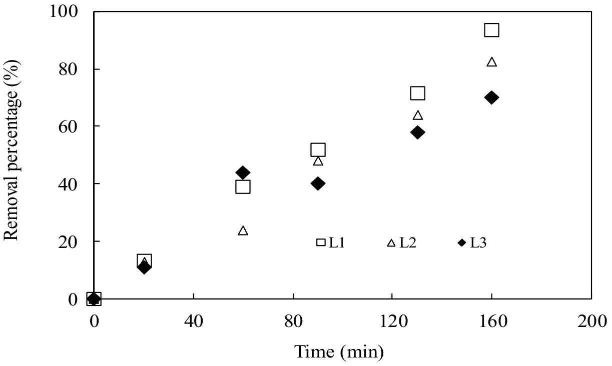

Fig. 16. Effect of microtubule thickness.

Table 2
Structure parameters of membrane and membrane module

No.	PAN microtube structure parameters				
	Effective length of microtube, *L*/(m)	Porosity	Number of microtubes	Inner diameter of microtube, d_i/(mm)	Thickness of microtube, d_m/(mm)
L1	0.25	63%	20	2.88	0.27
L2	0.25	63%	22	2.88	0.51
L3	0.25	63%	20	2.88	0.58
L4	0.25	63%	22	2.08	0.5
L5	0.25	63%	20	1.43	0.4
L6	0.25	22%	23	2.88	0.28

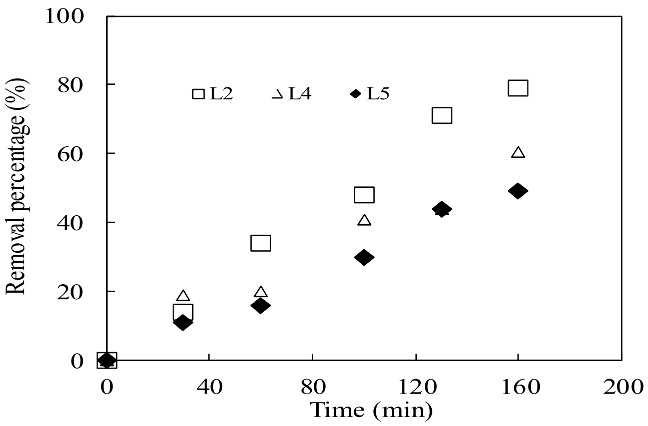

Fig. 17. Effect of microtubule inner diameter.

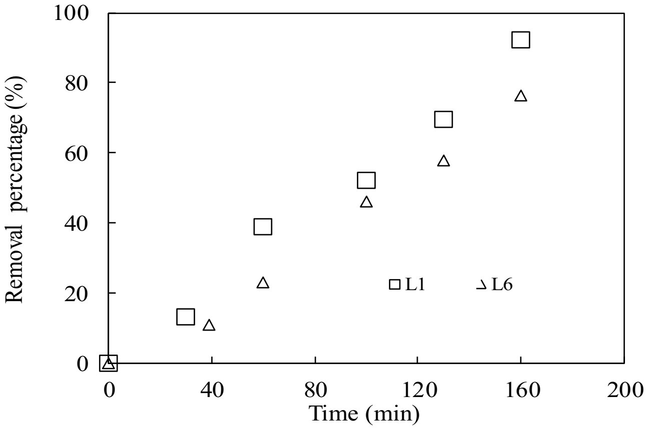

Fig. 18. Effect of microtubule porosity.

acid in the enrichment part was 0.150 mol L^{-1}, and the pH value of wastewater part was 4.50. When the initial concentration was 1.42 × 10^{-4} mol L^{-1}, the removal effect of neodymium(III) was very obvious under the best conditions. In the removal time of 150 min, the removal rate of neodymium(III) reached 93.5%.

The stability of UFCR is better than that of traditional supported liquid membrane. The outer wall solution velocity of microtube had little effect on the removal rate of neodymium(III), and the wastewater velocity in microtube had little effect on the removal rate of neodymium(III). The organic phosphoric acid solution in UFCR can be reused for more than 4 times after re-removal with strong acid after each experiment. In 9 experiments, the UFCR module with enrichment part can be reused for many times, and the variation trend of removal rate was stable. With the extension of time, the retention rate of neodymium(III) in microtubes decreased gradually. The removal rate of neodymium(III) increased with the decrease of film thickness, the increase of microtube inner diameter and the increase of microtube porosity, respectively.

This study attempted to explore the method of neodymium removal. It provided theoretical support for the purification of neodymium wastewater in the future. The research direction in the future is the industrial application of this technology. We also need to expand the device for pilot research, but the premise is to reduce the price of membrane materials. This requires our country to support in many aspects, such as research on membrane materials, supporting policies, and the development of environmental protection projects.

Acknowledgements

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Symbols

A — Effective area of microtubes, m^2
c_f — Concentration of metal ion in the wastewater part, mol L^{-1}
c_{fi} — Concentration of metal ion in the diffusion layer in wastewater part, mol L^{-1}
c^0_{mf} — Concentration of metal ion in the microtubes near wastewater part, mol L^{-1}
c^0_{ms} — Concentration of metal ion in the microtubes near enrichment part, mol L^{-1}
$c_{f(0)}$ — Concentration of metal ion in the wastewater part when time = 0, mol L^{-1}
$c_{f(t)}$ — Concentration of metal ion in the wastewater part when time = t, mol L^{-1}
d_f — Thickness of diffusion layer between the wastewater part and microtubes, m
d — Inner diameter of microtube, mm
d_m — Thickness of the microtube, m
D_f — Diffusion coefficient of metal ion in the wastewater part, m^2 s^{-1}
D^0_m — Diffusion coefficient of metal ion in the microtubes, m^2 s^{-1}
[HR] — Concentration of organic phosphoric acid solution, mol L^{-1}
$(\mathrm{HR})_2$ — Extractant/organic phosphoric acid solution
[H$^+$] — Concentration of H$^+$, mol L^{-1}
J — Microtube flux, mol m^{-2} s^{-1}
K_1 — Forward reaction percentage constant at the left interface of the microtube
K_{-1} — Backward reaction percentage constant at the left interface of the microtube
K_2 — Forward reaction percentage constant at the right interface of the microtube
K_{-2} — Backward reaction percentage constant at the right interface of the microtube
K_{ex} — Removal equilibrium constant
K_d — Distribution ratio of metal ion
L — Effective length of module, m
P_C — Permeability coefficient of metal ion, m s^{-1}
NdR$_3$·3HR — Neodymium-organic phosphoric acid complex
V_f — Volume of the wastewater part, m^3

Greek letter

ε — Porosity of the microtubes

τ — Tortuosity of the microtubes

η — Removal percentage of neodymium(III) (%)

Δf — Removal resistance due to diffusion by aqueous feed boundary layer, s m^{-1}

Δm — Removal resistance due to diffusion through the microtubes, s m^{-1}

Subscripts

f — Wastewater part

m — Microtube and organic phosphoric acid solution

org — Organic phosphoric acid solution

s — Enrichment part

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