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Th(IV) transport from nitrate media through hollow fiber renewal liquid membrane

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ABSTRACT

In this study, Th(IV) is transported through a hollow fiber renewal liquid membrane (HFRLM) in the system containing tributyl phosphate (TBP) and 0.1 mol L^{-1} HNO_3 as the carrier and the acceptor phases, respectively. The effects of operating mode, flow rates of the lumen and the shell sides and volume ratio of the organic to the aqueous phase on the mass transfer performance of HFRLM process are scrutinized. Experimental results indicate a satisfactory stability of HFRLM process during 12 h of continuous operation. Moreover, the mass transfer rate of Th(IV) in the operating mode in which a stirred mixture of feed and organic phases passes through the lumen side is higher than the mode in which a stirred mixture of the acceptor and the organic phases flows through it. In addition, the correlations used for calculation of local mass transfer coefficients of the renewal layer and the shell side are modified. Furthermore, the mass transfer rate in the HFRLM system was about twice more than that in the hollow fiber supported liquid membrane.

1. Introduction

In recent years, due to the development of nuclear energy, finding the more abundant and sustainable resources for nuclear fuels has attracted more attention all over the world. In the meantime, thorium and thorium based fuel can be considered as a suitable replacement of uranium fuels [1]. Thorium fuel cycle comprises many processes in which Th(IV) waste may be produced. One of the methods of waste treatment is the solvent extraction. Traditional processes of the solvent extraction have been carried out in various kinds of contactors such as mixer-settlers, spray columns, baffle-plate columns, perforated-plate columns, packed columns and centrifuge contactors [2,3]. These contactors suffer from some challenges in design and operation due to the formation of emulsions, foaming, flooding, unloading and high capital and operating costs [4–6]. In the past few years, in order to overcome the aforementioned difficulties, the liquid membrane technique has been developed. Some advantages of this method are non-equilibrium mass transfer, low consumption of energy and material, compact units of operation, high mass transfer rate and high selectivity [7–12].

The liquid membrane (LM) is an organic barrier consisting of an extractant in the solvent which separates the aqueous feed (donor) from the aqueous striping phase (acceptor). The liquid membrane methods can be classified as dispersion or non-dispersion methods. Bulk liquid membrane (BLM), supported liquid membrane (SLM) and liquid film pertraction (LFP) are categorized as the non-dispersion methods, while emulsion liquid membrane (ELM) is a dispersive method. Due to the small interfacial area and low mass transfer rate, BLM's applications are limited to the laboratory activities [13–15]. Furthermore, the commercial potential of ELM and SLM methods are restricted due to the low degree of stability of liquid membrane [9,16–19].

In order to improve the stability of the liquid membrane and maximize the efficiency of the process, the new integrated types of liquid membrane have been introduced. These methods include non-dispersive solvent extraction (NDSX) [20–22], hollow fiber supported liquid membrane (HFSLM) [23], pseudo-emulsion-based hollow-fiber strip dispersion (PEHFSD) [24–27], hollow fiber containing liquid membrane (HFCLM) [28–31] and hollow fiber renewal liquid membrane (HFRLM) [32–35].

Zhang et al. brought forward the hollow fiber renewal liquid membrane (HFRLM) method [32]. In HFRLM process, the liquid membrane is immobilized in the hydrophobic pores of the hollow fibers, while by passing the aqueous stream containing the dispersed phase of LM through the fibers, a thin renewal layer of LM coats the inner surface of them. In the renewal layer, repeatable peeling off the liquid membrane layer as microdroplets and

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simultaneously coalescence of these droplets could increase the mass transfer rate. Therefore, The main advantages of this method that are comparable with the other types of L/L extraction, especially with SLM system are the intensification of mass transfer rate due to the renewal effect of the liquid membrane and the high membrane surface area, the long-time stability of the liquid membrane because of the continuous replenishment of the liquid membrane trapped in the pores of the hollow fibers, creation of no secondary pollution by the emulsification due to lateral shear forces, the possibility to use the expensive solvents because of the free-surfactant process and low extractant consumption, less capital, low cost of maintenance and operation, low energy consumption and easy scale-up due to the compact and modular hollow fiber devices of the process, easy operation and wide range of operation region [36]. Hence HFRLM would have potential applications including the removal of organic pollutants, aroma recovery [37,38], pharmaceuticals extraction [39], recovery of metallic compounds from industrial wastewaters and hydrometallurgical processes [36,40–47].

In this study, the mass transfer characteristics of Th(IV) transport through HFRLM are investigated. For this purpose, the effect of various parameters such as flow rate, type of fluid in the lumen and shell side and aqueous to organic volume ratio are studied. Furthermore, a mathematical model is developed to predict the individual and overall mass transfer coefficients of HFRLM process. In addition, the mass transfer performance of HFRLM is compared with HFSLM system.

2. Materials and methods

2.1. Materials

$Th(NO_3)_4 \cdot 5H_2O$ (99.95%), HNO_3 (65%) and $NaNO_3$ ($>99\%$) were purchased from Merck company. Tributhylphosphate (TBP) and kerosene were provided by Sigma-Aldrich Company.

2.2. Apparatus

Our investigation focuses on, a hollow fiber module containing 50 polypropylene fibers which are supplied from the Persian Polymer Company, fabricated and prepared for laboratory scale usage. The main characteristics of the fabricated module are given in Table 1. In addition, a schema of HFRLM system is presented in Fig. 1. Continuous separation of Th(IV) using HFRLM process has been carried out in the single pass and countercurrent fashion.

2.3. Experimental procedure

The donor (feed) solution containing 167 mg L^{-1} of Th(IV) and 2 mol L^{-1} of $NaNO_3$ is prepared by dissolving appropriate amounts of thorium nitrate and sodium nitrate salts in deionized water. The pH of the donor phase is adjusted by adding an appropriate amount of diluted HNO_3 and NaOH solutions and using a digital pH meter (model Metrohm 691). The solution of 0.1 M HNO_3 is selected as the acceptor (stripping) phase. The liquid membrane also possesses TBP as a carrier dissolved in kerosene by the volume ratio of 30%.

In order to obtain the equilibrium curve in the donor-LM (extraction) and acceptor-LM (back extraction) systems, first, equal volumes of aqueous and organic phases are mixed together and shaken vigorously at room temperature for 4 h. After the separation of immiscible phases, Th(IV) concentration in the aqueous phase is measured by ICP-OES analyzer. The concentration of Th (IV) in the organic phase is determined from the mass balance. The concentration of Th(IV) in the donor phase varies in the range of 40–1000 mg L^{-1}. Moreover, in the back extraction process, the concentration of Th(IV) in LM (30 vol% of TBP in kerosene) is in the range of 40–200 mg L^{-1}.

Table 1
Characteristics of hollow fiber module.

Shell characteristics	
Material	Glass
Length (cm)	35
Internal diameter, $2R_i$ (cm)	0.6
Outer diameter (cm)	0.9
Fiber characteristics	
Material	PP(polypropylene)
Number of fibers in module	50
Effective length, l(cm)	30
Internal diameter, d^{int} (μm)	275
External diameter, d^{ext} (μm)	375
Effective surface area of module, A (m^2)	6.9×10^{-3}
Membrane porosity, ϵ	0.4
Membrane tortuosity, τ	2

In order to impregnate the fiber's pores with a liquid membrane, the LM passes through the fibers in the flow rate of 2.3 ml min^{-1} for 30 min. After that, the stirred mixture of the LM and the aqueous phase (donor or acceptor) at various volume ratios of the aqueous to organic phase (A/O) in the range of 5–50 is pumped through the lumen side of the module while another aqueous phase (acceptor or donor) flows through the shell side. The flow rates of the lumen and the shell sides are in the range of 2.61–26.34 and 2.42–9.64 ml min^{-1}, respectively. In order to prevent the phases from mixing together, it is necessary to build up a positive pressure on the shell side. The pressure difference between the shell and the lumen side is maintained at 0.3 bar. In order to find the steady state time, a test is conducted in which the concentration of Th(IV) across the outlet streams is measured throughout various durations.

Sampling in the other tests is carried out after reaching the steady state condition. Th(IV) concentration in the aqueous phases was measured by using an induction coupled plasma optical emission spectrometer (ICP-OES) model Liberty 220 Varian. We noted that each experiment was repeated thrice. As a matter of course, the average results are reported.

The stability of LM in HFRLM process is studied by carrying out the process for about 12 h. The mixture of the donor and LM with the volume ratio of (A/O) 20:1 passes through the lumen side, while the acceptor phase flows through the shell side.

The experimental mass transfer flux of Th(IV) from the donor to the acceptor phase through the liquid membrane is determined as follows:

$$J_{Th,Exp} = \frac{L_s \Delta C_{s,Th}}{A} \quad (1)$$

where $J_{Th,Exp}$, A, L_s and $\Delta C_{s,Th}$ are the experimental molar flux of Th (IV) (mol m^{-2} s^{-1}), the effective mass transfer area (m^2), the flow rate (m^3 s^{-1}) and the difference between thorium concentration (mol m^{-3}) in the inlet and outlet streams of the shell side, respectively.

The effective mass transfer area (A) is calculated as below:

$$A = \varepsilon \times N \times (2\pi r_o l) \quad (2)$$

where r, l, N and ε are the outer radial, effective length, number and porosity of the fibers.

3. Mathematical model

Thorium is extracted from the nitrate media using TBP. The procedure is carried out according to the following reaction [48].