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Extraction of zirconium from simulated acidic nitrate waste using liquid membrane in hollow fiber contactor

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ABSTRACT

Zirconium (Zr) is a valuable metal with numerous applications in refractory, nuclear and space industries. The acidic waste raffinate of zirconium purification plant contains about 2 g/L of Zr in 2 N nitric acid. The conventional solvent extraction process cannot be applied to recover Zr from this lean stream due to low distribution coefficient of Zr with tri-*n*-butyl phosphate at low acidity. An in-house synthesized ligand, mixed alkyl phosphine oxide (MAPO), was found to be suitable for recovery of Zr from the above stream. Using 0.1 M MAPO at 2 N acidity, distribution coefficient of Zr is found as 20. Batch liquid extraction studies revealed that MAPO forms 3:1 complex with Zr. The selected organic and strippant concentration from batch studies were used to investigate the applicability of dispersion liquid membrane in hollow fiber contactor for Zr recovery from simulated Zr plant raffinate feed. Hollow fiber contactor employing dispersion liquid membrane in once through mode delivers 24% transport of Zr from the aqueous feed containing 1.2 g/L Zr using 0.1 M MAPO. A mathematical model was developed to predict the transport phenomena of Zr in nitrate media through MAPO membrane in hollow fiber contactor. Predictions made from the model tie in well with the data.

Keywords: Zirconium, Dispersion liquid membrane, Pertraction

1. Introduction

Zirconium (Zr) is an important metal of numerous industrial applications. Properties of Zr such as low neutron absorption cross section, strength and high corrosion resistant makes it suitable for the cladding material of the fuel pellets and structural material for reactor components in the nuclear industry. Zr is also used in non-nuclear industries as the catalyst in organic reactions during manufacture of water repellent textiles, in dye pigment and in ceramics [1]. In nature, Zr minerals, zircon and baddeleyite contain some amount of hafnium (Hf). Solvent extraction techniques are employed on the commercial scale to extract Zr from zircon. Nuclear grade Zr should contain less than 100 ppm Hf, hence, separation of Zr and Hf is indispensable to the nuclear industry. Multiple crystallization, solvent extraction and extractive distillation are the established technologies for the Zr and Hf separation [2]. Zircon sand after caustic fusion is converted to aqueous zirconium nitrate solution and then Zr is extracted from the aqueous solution using tri-*n*-butyl phosphate (TBP). In India, Zr is produced commercially using TBP extraction technique; raffinate stream generated from this process contains some unextracted Zr in nitrate medium. The acidic waste raffinate stream of Zr purification plant contains about 2 g/L of Zr in

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about 2 N free nitric acid medium. TBP, which is the most commonly used solvent in the nuclear industry, is not suitable for Zr extraction from this lean stream. Hence investigation on extractant which can extract Zr from this raffinate stream at low acidity was crucial.

A survey of the literature shows that various neutral, acidic and basic extractants have been employed for the recovery of Zr from nitrate, chloride and sulphate media. Sato [3] investigated the extraction of Zr from nitric acid solution by TBP and Di-(2-ethylhexyl) phosphoric acid (DEHPA) at various conditions. The extraction studies showed that K_{df} increases with increase in nitric acid concentration. It has been reported that a K_{df} is nearly equal to 1 at feed acidity of 5 N using 93% v/v TBP. So, TBP cannot be used for recovery of Zr from low acidic stream due to its low distribution coefficient. Thus, there is a need to identify ligand, which gives better distribution coefficient at low acidity. Schrotterova et al. [4] investigated the extraction of Zr from sulphuric acid by primary, secondary and tertiary amines. However, application of amines for extraction of Zr from nitrate medium is not reported. Different ligands such as DEHPA, Cyanex 272 and Cyanex 925 were reported to extract Zr from chloride medium [5–7]. Taghizadeh et al. [5] studied the extraction of Zr and Hf by TBP, DEHPA and Cyanex 272. Using Cyanex 272, separation factor of 8 with respect to Hf was obtained at 2 N feed acidity. Da Silva et al. [6] studied the applicability of Cyanex 925 in chloride medium and Zr is observed to be loaded preferentially in organic phase compared with Hf resulting in good separation. Thus, it is observed that alkyl phosphine oxide ligand is capable of extracting Zr from chloride medium even at low acidity [5–7], so the applicability of such ligands in nitrate medium should be studied. Few literatures show that alkyl phosphine oxide ligands such as Cyanex 923 and Cyanex 925 are capable of extraction and separation of Zr from nitrate medium. Gupta et al. [8] developed a method for recovery of Zr from zircon using Cyanex 923. Nayl et al. [9] investigated the applicability of various Cyanex extractant for the extraction of zirconium from nitrate medium. For feed containing 0.1 g/L of metal ion in 2 N acidity, 93% extraction and separation factor of 21 was reported. Thus, alkyl phosphine oxide ligands are capable of extracting Zr from the solution of low acidity with higher efficiency.

Paramanik et al. [10] developed a novel extractant mixed alkyl phosphine oxide ligand (MAPO) similar to Cyanex 923 but not identical. They reported distribution coefficient of about 20 with 0.1 MAPO at feed conditions similar to raffinate of Zr plant. Pandey et al. [11] compared the composition of Cyanex 923 and MAPO, due to less trioctylphosphine oxide (TOPO) content in MAPO stripping is relatively easy.

Traditional methods for recovery of values viz solvent extraction and ion exchange have their own limitations. In solvent extraction, the interdependence of liquid to be contacted leads to difficulties such as emulsion formation, flooding, foaming, etc. Ion exchange suffers from problems such as resin fouling, selectivity, etc. Moreover, conventional separation processes are equilibrium limited [12]. Recently these shortcomings were overcome using membrane-based extraction methods. Liquid membrane using microporous membranes eliminates the major disadvantages of solvent extraction such as emulsification, flooding and loading limits, phase disengagement and large solvent inventory. Also, stripping and extraction can be combined in a single step in liquid membranes.

Among many configurations possible, one is dispersion liquid membrane (DLM) in which one of the phase interface is mobile while the other phase interface is immobilized. In this configuration, stability issues are overcome due to continuous replenishment of membrane liquid. This configuration can be operated in hollow fiber membrane contactor, which are shell and tube type contactors having fluid to be contacted flow on opposite sides of the membrane and the fluid/fluid interface forms at the mouth of each membrane pore. Thus, improvement in the recovery of value can be attempted by intensification of the process through the use of hollow fiber module in DLM configuration.

In the present work, efforts have been made to recover Zr from the simulated lean raffinate stream of Zr purification plant. More efficient ligand, MAPO was evaluated and potential of application of DLM in hollow fiber contactor was investigated.

2. Experimental

The literature survey shows that batch equilibrium studies on the extraction of Zr using alkyl phosphine oxide ligand has been done for the simulated pure solution of Zr in the range of 0.1 g/L. However, it is important to study and optimize extraction of Zr from a concentration range relevant to real streams which is about 1–2 g/L Zr in feed acidity of 2 N. Initially, liquid–liquid extractions were conducted in batch mode for determination of distribution coefficient (K_{df}) of Zr for extraction and stripping under various conditions for the selection of the optimum conditions. Following the successful completion of these studies, when the best reagent and other conditions for the system have been established, small-scale continuous experiments in once through mode were conducted using hollow fiber membrane contactor in DLM configuration to investigate its applicability for the desired system.

2.1. Materials and reagents

MAPO is an in-house synthesized extractant which is a mixture of four trialkyl phosphine oxides, with the general formula R_3PO (10%), $R_2R'PO$ (40%), $RR'2PO$ (40%) and R'_3PO (10%), in which R denotes *n*-octyl and R′ stands for *n*-hexyl group. Its average molecular weight is 348 g/mol. Paramanik et al. [10] describe the synthesis of MAPO. The extractant was prepared by dissolving MAPO in a mixture of *n*-dodecane and isodecanol.

Zirconium nitrate pure solution (ZNPS) was obtained by dissolving zirconium nitrate powder in nitric acid of desired morality. A typical value of Zr in raffinate stream is around 2 g/L. Oxalic acid used as the strippant was prepared by dissolving its required amount in distilled water. All chemicals used were of AR grade.

The extraction and stripping batch experiments were carried out in borosilicate conical flasks. The flasks were mechanically shaken using wrist action movement, in a DBK shaker. Phase separation was done in glass separating funnel.

Liqui-Cel® Extra Flow modules were used as membrane contactors for studies in the continuous contactor. A simulated zirconium nitrate pure solution stream which is an

aqueous solution of 2 g/L of Zr was circulated through the lumen side of the hollow fiber contactor using a gear pump, while the dispersion of extractant and strippant was circulated through the shell side in a counter-current flow by another gear pump. The dispersion was prepared externally by using a high-speed emulsifier. The pressure of the aqueous phase was maintained higher than the pressure of the organic containing phase to stabilize the interface in the pores and to avoid mixing of the phases since the hydrophobic fibers are wetted by the organic solvent. The pressure of each stream was monitored by two pressure gauges. Structural parameters of the hollow fiber modules used in this work are given in Table 1. Aqueous phase after extraction was analyzed for Zr concentration by ICP-AES.

2.2. Batch studies for equilibrium data

Aqueous feed is ZNPS in 2 N nitric acid and MAPO in 80:20 dodecane:isodecanol is used as organic feed. Preliminary studies showed that equilibrium was reached rapidly for Zr. Nevertheless, the shaking time was set at 10 min. The standard procedure was to place an equal volume of organic and aqueous phase (10 mL each) in a tightly stoppered conical flask. The flasks were shaken at room temperature for 10 min. After extraction, phase separation proceeded via separating funnel. The metal ion in the organic phase was determined by the mass balance. No variation in phase volume was observed. Metal ion concentration and extractant concentration was varied to generate distribution data.

The distribution ratio of extraction K_{df} was calculated from the relation:

$$K_{df} = \frac{C_0 - C}{C} \tag{1}$$

where C_0 and C are the metal ion concentration in the feed and raffinate obtained after extraction, respectively. For the generation of stripping data loaded organic was stirred with an equal volume of strippant. Again after phase separation, concentration of the metal ion in the aqueous phase was determined. Various strippants were tested to get a suitable strippant. The distribution coefficient for stripping (K_{ds}) is given in Eq. (2):

$$K_{ds} = \frac{C_0 - C - C_S}{C_S} \tag{2}$$

where C_s is the metal ion concentration in the aqueous phase after stripping.

Table 1
Characteristic of hollow fiber contactor

Characteristic	Value
Number of fibers (n_f)	10,000
Effective fiber length (m)	0.15
Average cartridge i.d. (m)	0.022
Average cartridge o.d. (m)	0.050
Priming volume shell side (L)	0.40
Priming volume lumen side (L)	0.15
Fiber material	Polypropylene
Fiber internal diameter (d_i, μm)	220
Fiber outer diameter (d_o, μm)	300
Fiber wall thickness (μm)	40
Effective pore size (μm)	0.05
Porosity (ε, %)	40
Tortuosity	2
Mass transfer area (=$2\pi r_i l \varepsilon n_f$) ($m^2$)	0.44

2.3. Experiments with hollow fiber contactor

Strip-organic dispersion is passed through shell side whereas aqueous feed is passed through the lumen. The dispersion of strip, 0.2 M oxalic acid and organic, MAPO in 80:20 dodecane:isodecanol is kept under constant agitation to prevent phase disengagement. Aqueous to organic ratio is kept 1:1. Parametric studies have been carried by varying carrier concentration and feed metal ion concentration to see the effect on metal transport in once through mode. Percentage ZrO^{2+} transported from feed to organic is estimated by analyzing the raffinate for Zr concentration. The ZrO^{2+} transport through the organic membrane is calculated by Eq. (3):

$$ZrO^{2+}\text{tranport}(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{3}$$

Specific extraction rate (SER) is defined as the number of moles of solute being transferred per unit time per unit mass transfer area. Mathematically SER can be expressed as

$$\text{SER} = \frac{\%E \times C_{ai} \times Q_{feed}}{a} \tag{4}$$

where $\%E$ is the percent extraction, C_{ai} denotes inlet concentration of the metal in the aqueous phase, Q_f is the flow rate of aqueous feed and a is the mass transfer area.

3. Results

3.1. Batch studies

3.1.1. Determination of stoichiometry

The 1:3 ZrO^{2+}:MAPO stoichiometry has been adopted from Nayl et al. [9]. They investigated the extraction process of alkyl phophine oxide ligand and zirconyl nitrate at 2 N feed acidity through batch extraction studies. The extraction reaction reported reveals that for extraction of one mole of ZrO^{2+}, three moles of extractant are required. Since MAPO is similar to alkyl phosphine oxide ligand which they have used, it will complex with ZrO^{2+} in a similar way. Thus, extraction equilibrium can be represented as following:

$$ZrO^{2+}(aq) + 2NO_3^-(aq) + 3MAPO(org) \xleftrightarrow{K_{eq}} ZrO(NO_3)_2.3MAPO(org) \tag{5}$$

The equilibrium constant for this reaction can be represented as:

$$K_{eq} = \frac{[ZrO(NO_3)_2.3MAPO]_{org}}{[ZrO^{2+}]_{aq}[NO_3^-]^2_{aq}[MAPO]^3_{org}} = \frac{K_{df}}{[NO_3^-]^2_{aq}[MAPO]^3_{org}} \quad (6)$$

where K_{df} is the distribution coefficient. If $[L]^0$ represents the total concentration of MAPO in the organic phase, free MAPO concentration in the organic phase after extraction can be represented by:

$$[MAPO]_{org} = [L]^0 - 3[Zr]_{org} = [L]_{org} \quad (7)$$

Eq. (6) can be rewritten as

$$K_{eq} = \frac{K_{df}}{[NO_3^-]^2_{aq}[L]^3_{org}} \quad (8)$$

$$K_{df} = K_{eq}[NO_3^-]^2_{aq}[L]^3_{org} \quad (9)$$

Thus if the logarithm of K_{df} is plotted against the logarithm of $[L]_{org}$, the resulting plot will be a straight line with slope three.

To validate the stoichiometry as given in Eq. (5), experiments were carried out at various concentrations of ZrO^{2+} in feed solutions. The concentration of Zr in aqueous feed was varied from 0.01 to 0.05 M and the K_{df} were determined for each feed concentration using 0.1 M MAPO in 80:20 dodecane:isodecanol as extractant. The concentration of free MAPO in the organic phase, $[L]_{org}$, was determined using Eq. (7). From the log–log plot of K_{df} against $[L]_{org}$ as shown in Fig. 1, we get 2.9 as the exponent of $[L]_{org}$. Thus, it can be concluded that three moles of MAPO are required for the extraction of one mole of ZrO^{2+}. The calculated stoichiometry agrees well with the reported stoichiometry as given by Eq. (5).

3.1.2. Effect of varying metal ion

The influence of initial Zr concentration on K_{df} was studied by varying the initial feed concentration from 1 to 4 g/L. 0.1 M MAPO in a mixture of dodecane and isodecanol was taken as the extractant. Fig. 2 shows the variation in distribution coefficient values. It is observed that as the feed concentration increases K_{df} decreases for the given extractant concentration. The decrease in the K_{df} with the increase in the initial metal concentration can be explained by Eq. (6). As the initial metal ion in the feed increases, free MAPO concentration in the organic phase decreases viz $[L]_{org}$. As the K_{eq} is constant for a system at a particular temperature, so K_{df} decreases to maintain constant K_{eq}.

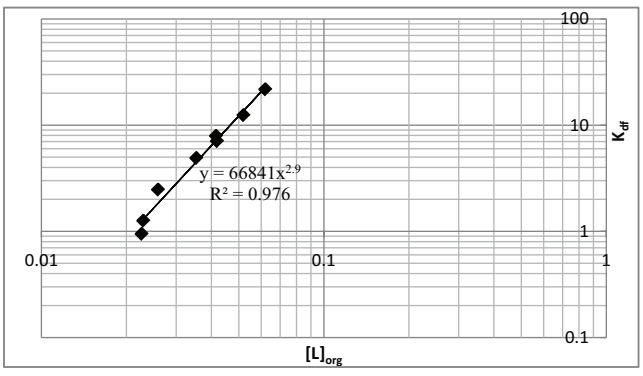

Fig. 1. Determination of stoichiometry of MAPO with ZrO^{2+} via plot of $\log(K_{df})$ vs. $\log[L]_{org}$.

3.1.3. Effect of variation of extractant concentration

The effect of variation of MAPO concentration on the extraction of Zr from 2 N nitric acid was studied by varying the MAPO concentration in the organic phase from 0.1 to 0.3 M and keeping the initial concentration of Zr in the aqueous feed as 2 g/L. It is observed from Fig. 3 that as the concentration of MAPO increases from 0.1 to 0.3 M extraction increases; this is due to the availability of more extractant molecules. It is seen that 100% extraction is achieved in a single contact with 0.3 M MAPO

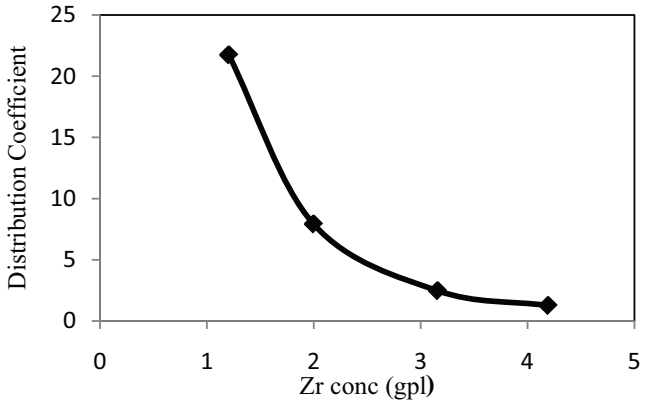

Fig. 2. Effect of varying Zr concentration in feed on extraction of Zr by 0.1 MAPO in 80:20 dodecane:isodecanol at 2 N feed acidity.

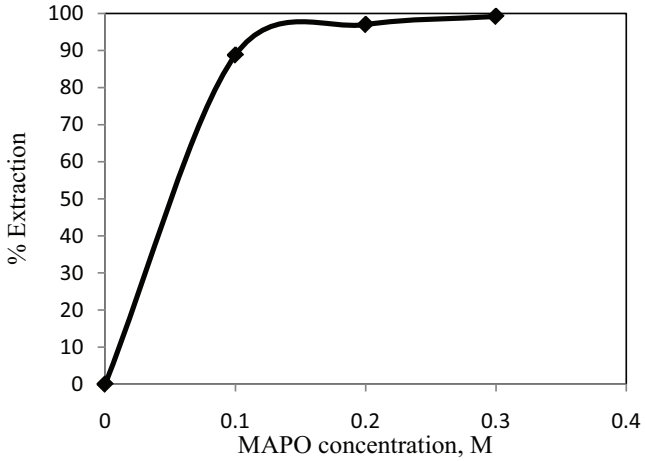

Fig. 3. Effect of varying MAPO concentration in 80:20 dodecane:isodecanol on extraction of Zr from feed containing 2 g/L Zr at 2 N feed acidity.

when the initial concentration of Zr in the aqueous feed is 2 g/L. Further increase in the extractant concentration will have no effect as 0.3 M is enough for complete extraction of Zr; therefore, it is suggested to keep the extractant concentration below 0.3 M.

3.1.4. Effect of strippant

The effect of stripping agents on the recovery of Zr from the loaded organic solution of 0.1 M MAPO in 80:20 dodecane:isodecanol was investigated. The value of K_{ds} should be less than 1 for efficient back extraction of metal from loaded organic to the aqueous phase. Various stripping agents were investigated and their K_{ds} is estimated using Eq. (2). It is seen from Table 2 that K_{ds} is lowest with 0.2 M oxalic acid; hence, it is the most effective strippant and is taken up as stripping agent in further studies. It is observed that K_{ds} is not affected by pH of stripping agent; hence, it is suggested that stripping occurs via complexation. Pandey et al. [11] also suggested complexation mechanism for stripping of Zr. As the Zr–MAPO complex is very strong, a strong complexing agent such as oxalic acid is required for back extracting the metal in aqueous solution.

$$ZrO\left(NO_3\right)_2.xL_{(org)} + C_2O_4^{2-}{}_{(aq)} \rightarrow ZrC_4O_{8(aq)} + xL_{(org)} + 2NO_3^- \quad (10)$$

3.2. Continuous extraction in hollow fiber dispersion liquid membrane

3.2.1. Effect of varying initial feed zirconium concentration

Fig. 4 shows the variation of zirconium transport for different initial feed zirconium concentrations by 0.1 MAPO in 80:20 dodecane:isodecanol. As seen from Fig. 4, 24% transport is achieved in once through using 0.1 M MAPO, when the concentration of Zr in aqueous feed is 1.2 g/L. It is observed that rate of transport decreases with the increase in feed metal ion concentration. It is not recommended to use DLM for feed having a high concentration of Zr as the Zr transport is very less using 0.1 M MAPO as extractant. High feed concentration in the feed–membrane interface leads to saturation of membrane phase.

SER is defined as the moles of ZrO^{2+} transported per unit time per unit area of mass transfer and is estimated as 2.386×10^{-5} mol m^{-2} s^{-1} using Eq. (4). The performance of hollow fiber contactor can be evaluated by specific mass transfer area, which is mass transfer area per unit contactor volume as per Table 1. For used hollow fiber contactor specific area is estimated as 1,857 m^2/m^3. Specific mass transfer area for conventional contactors used in solvent extraction lies in the range of 100–800 m^2/m^3 [13]. It can be seen that specific mass transfer area available in hollow fiber contactor is much higher than the conventional contactors used in solvent extraction.

Table 2
Effect of various stripping agent on recovery of Zr from loaded 0.1 M MAPO

Stripping agent	K_{ds}
0.05 M ammonium carbonate	32
2 M HCl	13.23
2 M H_2SO_4	4.11
1 M acetic acid	4
0.1 M oxalic acid	0.17
0.2 M oxalic acid	0.016

3.2.2. Effect of varying extractant concentration

Experiments were conducted by varying the concentration of MAPO in 80:20 dodecane:isodecanol. Fig. 5 shows the variation in percentage transport of zirconium for different extractant concentration. It is observed that for feed containing 2 g/L Zr, the % transport increased from 3.2 to 13.6 on increasing the extractant concentration from 0.1 to 0.3 M. This can be explained by the enhanced formation of ZrO^{2+}–MAPO complex at the feed–membrane interface. Thus for an

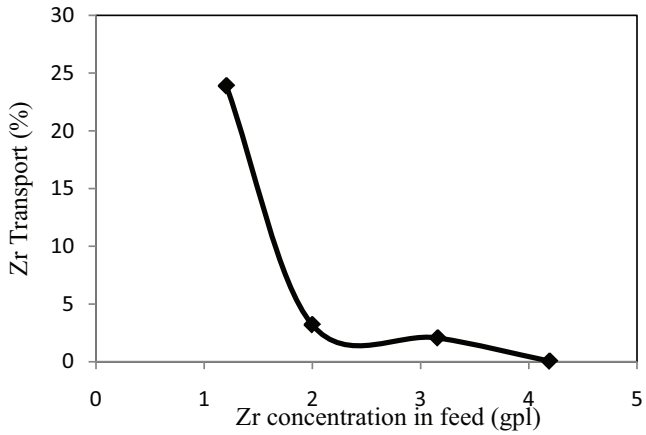

Fig. 4. Effect of varying initial feed zirconium concentration on percentage extraction in once through mode; feed Zr in 2 N nitric acid medium; dispersion:aq/org 1:1, aq 0.2 M oxalic acid, org 0.1 M MAPO in 80:20 dodecane:isodecanol.

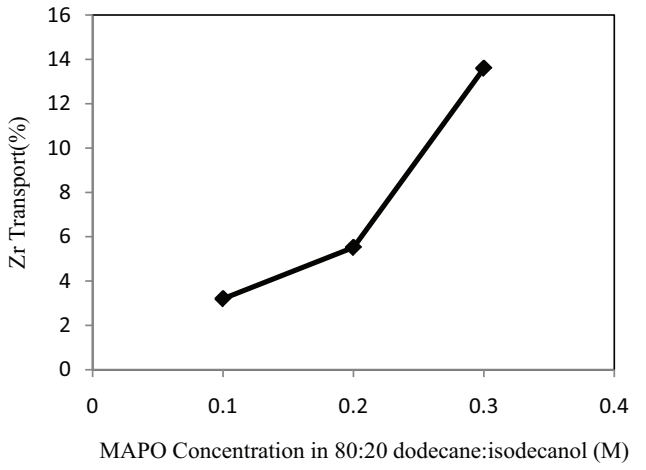

Fig. 5. Effect of varying MAPO concentration on percentage extraction in once through mode; feed 2 g/L Zr in 2 N nitric acid medium; dispersion:aq/org 1:1, aq 0.2 M oxalic acid, org MAPO in 80:20 dodecane:isodecanol.

aqueous feed containing a high concentration of Zr, DLM can be used by increasing extractant concentration.

4. Modeling and predictions

An effort has been made to model the transport phenomena of ZrO^{2+} in nitrate media through organic membrane employed in microporous hollow fibers. In carrier-facilitated transport through liquid membrane employed in hollow fiber contactor, metal cation diffuses through aqueous feed boundary layer and reacts reversibly with carrier agent at feed–membrane interface resulting in the formation of metal–carrier complex as given by Eq. (5). The complex then diffuses through the membrane due to its own concentration gradient and consequently at the membrane–strip interface, it releases metal ion. The carrier thus left over diffuses back towards feed–membrane interface and the cycle continues. Released cation diffuses through the aqueous strip film. The model predicts the rate of transport of ZrO^{2+} from feed phase to the strip phase through film diffusion and interfacial equilibrium distribution coupled with continuity equations for lumen and shell side and the mass balance of carrier agent. Details of modeling can be referred in [14]. Final equations for prediction of transport in once through mode are as follows:

$$ZrO^{2+}(aq) + 2NO_3^-(aq) + 3MAPO(org) \xleftrightarrow{K_{eq}} ZrO(NO_3)_2.3MAPO(org)$$

$$K_{eq} = \frac{\left[ZrO(NO_3)_2.3MAPO\right]_{org}}{\left[ZrO^{2+}\right]_{aq}\left[NO_3^-\right]_{aq}^{2}\left[MAPO\right]_{org}^{3}} = \frac{K_{df}}{\left[NO_3^-\right]^2\left[MAPO\right]^3} \tag{11}$$

$$\frac{dZr_f}{dz} = \left(-\frac{1}{\pi r_i^2 vl}\right)\frac{K_{df}Zr_f - K_{ds}Zr_s}{\zeta} \tag{12}$$

$$\frac{dZr_S}{dz} = \left(\frac{N}{\dot{V}_s\, l}\right)\frac{K_{df}Zr_f - K_{ds}Zr_s}{\zeta} \tag{13}$$

where $\zeta = \frac{K_{df}}{k_{aqf}a_1} + \frac{1}{k_{org}a_{lm}} + \frac{K_{ds}}{k_{aqs}a_2}$

ζ is the resistance that appears during the transport process. It constitutes three resistances. One of them is the resistance when the liquid is flowing through the hollow fiber lumen. The second resistance is due to the diffusion of the metal–ligand complex across the liquid membrane which is immobilized in the porous wall of the fiber. The third resistance is presented by the strip solution and organic interface at the outside of the fiber (shell side). Eqs. (11) and (12) form an initial value problem (IVP) in two variables Zr_f and Zr_s. This IVP can be solved to get the variation of Zr_f and Zr_s with axial distance, z along the fiber. The initial condition is taken as (Zr_{f0}, $Zr_{s0} = 0$) at $z = 0$, where, Zr_{f0} and Zr_{s0} are the initial zirconium concentration of feed and strip, respectively.

Fig. 6 shows the model prediction along with the data for the different initial concentration of zirconium in the feed solution. Distribution coefficients, K_{df} and K_{ds}, have been generated through independent liquid–liquid extraction experiments (section 3.1) and utilized for prediction.

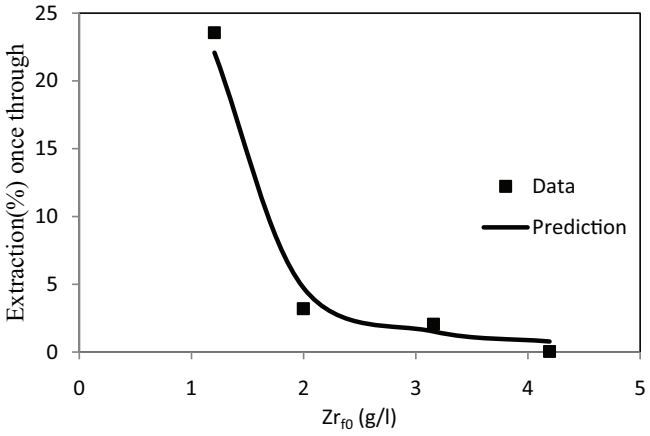

Fig. 6. Extraction (%) vs. concentration of zirconium in once through mode: feed – zirconium nitrate pure solution 2 N, carrier – 0.1 M MAPO in 80:20 dodecane:isodecanol, strip – 0.2 M oxalic acid.

Table 3
Input parameters utilized for simulation

Parameters	Value
Fiber inner diameter (cm)	220e-04
Fiber outer diameter (cm)	300e-04
Fiber thickness (cm)	40e-04
Effective length of fiber (cm)	16
Feed velocity (cm/s)	0.88
No. of fibers	10,000
Aqueous mass transfer coefficient (cm/s)	2.49e-03 [14]
Membrane mass transfer coefficient (cm/s)	4e-06 [15,16]
Feed acidity	2
Porosity, ε	0.4
Strippant flow rate (mL/min)	200
Dispersion flow rate (mL/min)	200
MAPO concentration	0.1 M
Strippant concentration	0.2 M

Distribution coefficients

Zr_{f0} (gpl)	Zr_{f0} (M)	K_{df}	K_{ds}
1.205	0.013	21.73	0.168
1.998	0.022	7.919	0.016
3.158	0.035	2.47	0.048
4.192	0.046	1.259	0.001

Parameters utilized for simulation are listed in Table 3. Prediction ties in well with the data.

Extractant concentration is taken as 0.1 M MAPO throughout the experiments unless specified.

5. Conclusions

The result obtained reveals that MAPO is an efficient ligand that can extract Zr from the lean stream at low acidity.

The study highlights the intensification of the process for recovery of Zr through the use of hollow fiber module in DLM configuration. The specific area is estimated as 1,857 m^2/m^3, which is way higher than the conventional contactors. The rate of pertraction from feed to strip has been simulated using the mathematical model. Parameters of the model have been calculated independently through separate batch studies and physical properties of the system. The developed model will be useful for the prediction of transport for the similar system with limited experiment trials.

Symbols

C_0	—	Initial metal ion concentration in feed, M
C	—	Final metal ion concentration in raffinate, M
Zr_f	—	ZrO^{2+} concentration in feed, M
Zr_s	—	ZrO^{2+} concentration in strip, M
Z	—	Length along the axis of the fiber, cm
r_i, r_o	—	Inner and outer radius of the fiber, cm
v	—	Feed linear flow velocity, cm/s
l	—	Effective length of the fiber, cm
K_{df}, K_{ds}	—	Distribution coefficient of metal ion at feed–membrane and membrane–strip interface
ε	—	Porosity of hollow fiber
N	—	Total number of hollow fibers in the contactor
$\dot{V}_s$	—	Volumetric flow rate of strippant, cm^3/s
k_{aqf}	—	Mass transfer coefficient at lumen side, cm/s
k_{org}	—	Mass transfer coefficient at organic, cm/s
a_1, a_2 and a_{lm}	—	Internal, outer and log mean area of fiber lumen, cm^2

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