Facilitated transport of germanium from acidic medium through supported liquid membrane using Cyanex 301 as mobile carrier

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Abstract: In this research, a flat sheet supported liquid membrane (FSSLM) system was used to transfer germanium from the acidic medium. The poly-tetra fluoro ethylene (PTFE) membrane filter with the hydrophobic nature and Cyanex 301 were selected as the support and the mobile carrier, respectively. The influence of various parameters being pH of the feed solution (1.5-5), germanium concentration (10-40 mg/dm³), carrier concentration in the solid membrane (10-40 vol%), and sulfuric acid concentration of the receiving phase (100-400 g/dm³) was investigated on the transport of germanium. Under the optimum condition being pH of 1.5, the germanium concentration of 40 mg/dm³, the carrier concentration of 1.18 mol/dm³, and the sulfuric acid concentration of 400 g/dm³, a mass transfer model was developed. Based on this model, the transport mechanism, diffusion of species to the feed-membrane interface, the chemical reaction of species and Cyanex 301, and diffusion of germanium-Cyanex 301 complexes across SLM were explained. According to the obtained model, the values of 6.57 and 738.6 s/cm were achieved for the aqueous and organic diffusion resistances, respectively.

Keywords: Germanium, supported liquid membrane, Cyanex 301, mass transfer model, acidic medium

1. Introduction

Germanium is strategically used in semiconductors, optical fiber, etc. (Scoyer et al., 2000). Germanium extensively dispersed in nature; however, the natural resources of this element are rare (Zhang and Xu, 2017). More than one-half of germanium is produced from secondary resources such as electronic and optical tools (Jorgenson, 2000). In some metal industries especially zinc and coal companies, germanium can be produced as a by-product from effluents (Nusen et al., 2016; Kamran Haghighi et al., 2017; Kamran Haghighi et al., 2018a). According to the literature, about 12558 t of germanium may be the reserve weight of the lithosphere. The amount of germanium in zinc sulfide ores and fly ashes are estimated to be 8049 t and 3900 t, respectively. Using the present extraction processes, it can be calculated that more than 50% of germanium cannot be recovered and transferred to tails (Licht et al., 2015). Therefore, developing highly efficient processes for the recovery of germanium is important. There are various hydrometallurgical techniques used to treat different types of aqueous solutions containing germanium. Leaching of the above-mentioned resources in acids (Kul and Topkaya, 2008) or water medium (Kamran Haghighi et al., 2018a) is an initial step bringing germanium to aqueous solutions for further processing. Since the concentration of dissolved germanium in these solutions is low, an effective separation from these solutions is vital to gain a pure product (Arroyo et al., 2009). Various types of hydrometallurgical separation procedures such as precipitation (Seifullina et al., 1973), carbon adsorption (Marco-Lozar et al., 2007), and solvent extraction (Nusen et al., 2015) were applied to separate germanium from aqueous solutions. Recently, solvent extraction has been used for the extraction of germanium from aqueous solutions. Some researchers reported disadvantages for the SX process such as the difficulty in the phase separation, extractant loss, emulsification, difficult control, etc. (Swain et al., 2007). Therefore, an alternative method can be useful for eliminating these

disadvantages. Supported liquid membrane (SLM) is such a method having some similarities to solvent extraction. This method has some advantages such as considerable selectivity, operative easiness, and low extractant consumption (Swain et al., 2007). Various SLM systems such as hollow fiber SLMs and flat sheet SLMs are a type of non-dispersive solvent extraction processes (Swain et al., 2015). The extraction and stripping processes in these systems are simultaneously carried out (Swain et al., 2006). This feature helps that the separation and the purification of the solution are carried out without the need for several mixers and settlers which are common in industrial solvent extraction processes (Pabby and Sastre, 2002; Parhi, 2012).

Since carriers have an important role in SLM systems, identification of extractant extractability toward germanium is important. Various extractants were used as mobile carriers to recover and separate germanium from aqueous solutions, among them KELEX 100 (Schepper et al., 1984), LIX 63 (Nusen et al., 2016), TOA (Arroyo and Fernández-Pereira, 2008), Ionquest 801 (Nusen et al., 2015) and Cyanex 301 (Harbuck et al., 1991). Up to now, a few studies were carried out on the transport of germanium using flat sheet supported liquid membrane. However, several types of research have investigated the separation of germanium using other types of membrane processes. Selective separation of indium and germanium from an aqueous medium was carried out using nano-filtration and SLM (Werner et al., 2015). The aim of the mentioned study was to separate germanium by nano-filtration followed by extracting indium from a solution containing Zn, Cu, Fe, As and Ge using a membrane of polypropylene and Cyanex 272 as a carrier. Germanium-catechol complex could be extracted using anion exchange systems such as an RX-1 membrane (Kuroiwa et al., 2014). In the mentioned system, germanium dissolved in an alkaline medium from solar panels was complexed with catechol followed by passing through the RX-1 membrane to adsorb germanium. In order to strip germanium, the germanium-catechol complex was eluted with HCl solution. To increase the germanium concentration, catechol was removed from the solution in a solvent extraction process by trioctylphosphine oxide (TOPO). In another study, a porous hollow-fiber membrane produced by graft polymerization could remove germanium from an aqueous solution (Ozawa et al., 2000). The separation of germanium has been done by Soylak and Yigit (2015) with the polysulfone ion exchange membrane of 0.45 μm pore size and a 47 mm diameter. The germanium(IV) transport efficiency with the polysulfone membrane filter reached 97% from a solution containing 1000 mg/L Ge at a pH of 4. A liquid membrane containing a nonionic polyamine (ECA 4360J) and sorbitan monooleate (Span 80) as surfactants, Kelex 100 as a carrier and diluents such as toluene, and Escaid 110 was used to extract germanium from a leach solution containing Zn, Cd, Co and Fe (Tutkun et al., 1999). In this system, germanium was extracted with 95% efficiency from a zinc leach solution. Finally, it was stripped using 3 mol/dm^3 NaOH. Since Kelex 100 strongly extracts germanium and copper in concentrated acidic solutions over Zn, Cd, Fe, and Co; thus, copper should be eliminated before germanium extraction. According to the literature, germanium can be extracted from a fly ash leach solution by a liquid emulsion membrane containing carbon tetrachloride, xylene and a surfactant (Gutknecht and Schuegerl, 1988). Recently, the facilitated transport of germanium through a FSSLM containing Alamine 336 diluted in kerosene has been reported by Kamran Haghighi et al. (2017). The membrane used was a polytetrafluoroethylene (PTFE) membrane with a diameter of 47 mm and a pore size of 0.45 μm. They modeled the germanium-tartrate anionic species transport using Fick's law and the extraction equilibrium reaction and calculated mass transfer and diffusion coefficients. About 90% of germanium was transported from the feed phase to the strip phase containing 1 mol/dm^3 HCl using 15 vol% Alamine 336 as a carrier during 600 min. Furthermore, germanium facilitated permeation from a solution by a PTFE membrane containing trioctylamine (TOA) has been carried out by Kamran Haghighi et al. (2018b). A mass transfer model was also used to represent the transport behavior based on Fick's law. The complete germanium transport from a feed solution with a pH of 3 by the mentioned membrane containing 40 vol% TOA toward a strip phase containing 1-3 mol/dm^3 HCl was achieved in the process. The transport of germanium using a microemulsion membrane was investigated (Liu et al., 2010). In this system, bis(2-ethylhexyl)sulfosuccinate sodium salt (AOT), n-heptane, n-butanol, Na_2SO_4 and N235 (tertiary amine) were used as a surfactant, cosurfactants, an inner solution and a carrier, respectively (Liu et al., 2010). Germanium-tartrate anionic species were transported through the microemulsion membrane with an efficiency of 95% at a pH of 6.

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In this study, for the first time, transport of germanium from a synthetic solution was carried out by an FSSLM system. In this system, the polytetrafluoro ethylene (PTFE) membrane filter and Cyanex 301 as a mobile carrier were used to transport germanium from the feed solution through the membrane containing the carrier. Several parameters such as pH, the germanium concentration of the feed solution, extractant concentration and sulfuric acid concentration of strip solution, having effects on the ion flux and the germanium transport percentage were investigated. Finally, the mechanism of the germanium transport was introduced and a mass transfer kinetic model for this transport was developed and model parameters were found.

2. Materials and methods

2.1. Chemicals

In this study, 1000 mg/dm³ of stock germanium solution from GeO_2 (Merck, Germany), prepared in various concentrations of the HNO_3 solution was used to produce synthetic solutions with various concentrations (10-40 mg/dm³). Since HNO_3 concentration affects the pH value, in the further investigation, the pH value is reported instead of HNO_3 concentration. The extractant namely bis(2,4,4-trimethylpentyl)dithiol phosphinic acid (Cyanex 301) with the purity of 85% produced by Fluka was applied as a mobile carrier without any pretreatment. The characterization of Cyanex 301 is as follows: molecular weight of 322, a viscosity 78 mPa.s at 24 °C, density of 0.95 g/cm³ at 24 °C, and solubility in water of 7 mg/dm³. Furthermore, kerosene supplied by Irannol Oil Co. was used as a diluent in the experiments.

2.2. Identification of cationic species of germanium in acidic medium

In order to identify media or solutions in which there are germanium cationic species, the distribution diagram of these species in a broad pH range was constructed in the literature (Marchon et al., 1979). According to the reported data, cationic germanium species exist at lower pHs (high acidities), as at pHs lower than 1, germanium cations in the form of Ge^{4+} are predominant species. With an enhancement of pH up to neutral values, neutral species of germanium ($Ge(OH)_4$) form in the solution.

The extraction of cationic ions from various media using Cyanex 301 has been reported in the literature (Tong et al., 2009; Miaomiao et al., 2013). Furthermore, it is supposed that nitrate ions do not participate in the transfer process. There are some works on germanium solvent extraction from sulfuric acid medium etc. (Harbuck et al., 1991; Harbuck, 1992), however, no complexation was reported between germanium and Cyanex 301. With respect to limited information about this complexation, another study (Bhattacharyya et al., 2006) on the transport of trivalent actinides and lanthanides using the FSSLM system containing Cyanex 301 was considered. Therefore, the mentioned reaction was generalized to the reaction of tetravalent germanium and Cyanex 301 as Eq. (1), and can be attributed also to transport through SLM:

$$Ge^{4+} + 4RH_{org} \rightarrow GeR_{4org} + 4H^+ \tag{1}$$

2.3. Membrane

A microporous disc hydrophobic membrane namely polytetrafluoroethylene (PTFE) supplied by Membrane Solution Co. was applied in the experiments. The used membrane had the pore size of 0.45 μm, diameter of 47 mm, and thickness of 140 μm.

2.4. Supported liquid membrane procedure

All the experiments were conducted in an apparatus manufactured for the flat sheet (FSSLM) as shown in Fig. 1. Experiments were performed in two containers with the same volume of 250 cm³ for the feed and receiving solutions. The active area of the membrane was found to be 9.62 cm². To prevent "polarization between the bulk and membrane surface solutions", the aqueous phases were stirred. To understand the performance of transport, samples were taken from the feed and receiving phases at desired times. These samples were then analyzed for the germanium concentration by ICP-MS (Varian). In order to understand the effect of various parameters on the germanium flux, the values of the pH

(1.5-5), germanium concentration of feed solution (10-40 mg/dm³), extractant concentration (10-40 vol%) and acid concentration of the receiving solution (100-400 g/dm³) were changed.
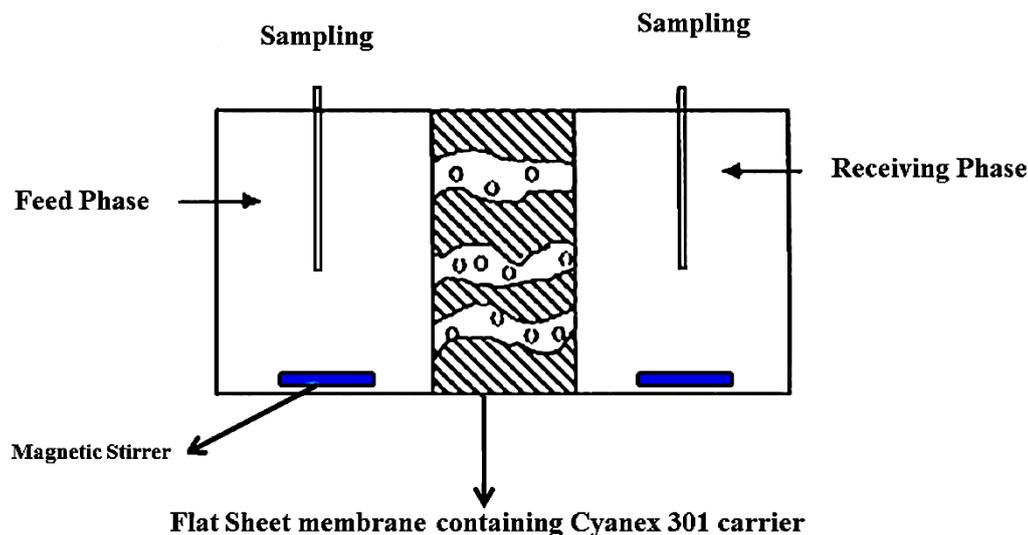
Fig. 1. Schematic of SLM used in the study

Transport process in the SLM system includes three steps: (1) diffusing to the feed-membrane interface, (2) diffusion through the membrane, and (3) diffusing to the membrane-receiving interface (Panja et al., 2014). The membrane flux *J* relates to the feed concentration C_f, by Eq. (2):

$$J = P_f C_f \; . \tag{2}$$

In this equation, P_f is the permeability coefficient in the feed phase. The flux can also be represented by Eq. (3):

$$J = -(\frac{V}{A})(\frac{[dC_f]}{dt}) \tag{3}$$

where *V* accounts for the volume of feed solution and *A* is the effective area of the membrane. By merging Eqs. (1) and (2) followed by integrating of that, Eq. (4) was obtained as follows:

$$\ln(C_f / C_{f,t}) = -\frac{APt}{V} \; . \tag{4}$$

Consequently, the flux (*J*) can be calculated at each time. Furthermore, the transport percentage (*T*) of the germanium at a desired time can be determined as Eq. (5):

$$\%T = 100 \times \frac{(C_{f,0} - C_{f,t})}{C_{f,0}} \; . \tag{5}$$

3.   Results and discussion

3.1. Effect of pH

The transport of germanium from aqueous nitrate solutions containing 40 mg/dm³ was carried out by Cyanex 301 1.18 mol/dm³ (40 vol%) in the pH range of 1.5 to 5. Furthermore, the sulfuric acid concentration of the receiving phase was kept at 200 g/dm³. The transport percentage (%*T*) against the initial pH of the feed solution was plotted as shown in Fig. 2.

Fig. 2 illustrates that germanium transport decreased from 78.4 to 10% as the initial pH of the feed solution enhanced from 1.50 to 5.00. This behavior is in agreement with Harbuks's research in which the solvent extraction percentage of germanium from a diluted acidic solution was lower than that from concentrated acidic solution (Harbuck et al., 1991). It was noted that the pH value of solutions descended during the experiment due to releasing proton from Cyanex 301. Based on results, the final pH for the solutions with initial pHs of 5, 4, 3, and 1.5 were 2, 1.5, 0.5, and below 0, respectively. Thus, with respect to the speciation diagram of germanium, predominant speacies at pHs below 0 is Ge⁴⁺

which can be extracted by Cyanex 301. At higher pHs, germanium species tend to form neutral complexes which cannot be extracted by Cyanex 301.
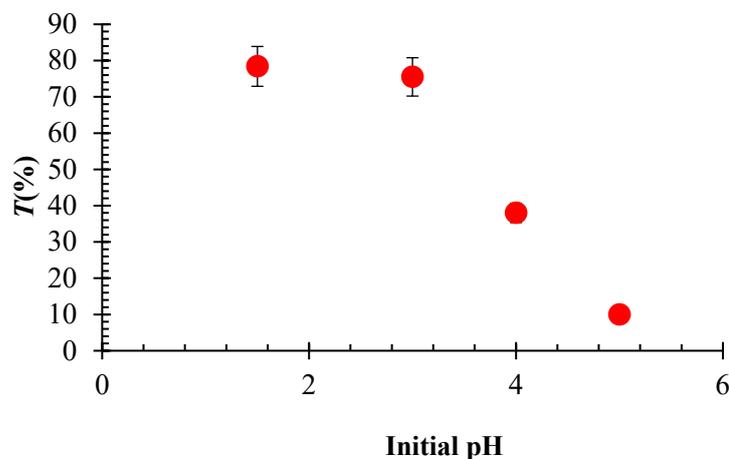
Fig. 2. The transport percentage (*T*) against pH of the feed solution (aqueous feed phase: [Ge]= 40 mg/dm³; organic phase: [Cyanex 301] = 1.18 mol/dm³ ≈ 40 vol%; stripping phase: [H₂SO₄]= 200 g/dm³ and contact time= 20 h)

3.2. Effect of extractant concentration

In order to investigate the effect of Cyanex 301 concentration as a carrier on the germanium transport (at the initial concentration of 20 ppm), various concentrations of extractant being in the range of 0 -1.18 mol/dm³ (0-40 vol%) were examined (Fig. 3). The experiments were conducted at the initial pH 1.5 and the germanium concentration of 40 mg/dm³ in the feed solution. As a result, with increasing the Cyanex 301 concentration from 0 to 1.18 mol/dm³, the transport percentage of germanium enhances gradually from 0 to 62.80%. As seen in Fig. 3, the germanium flux reached a plateau when the Cyanex 301 concentration increased up to 0.59 mol/dm³ (20 vol%). According to Eq. (1), with an increase in Cyanex 301 concentration at the feed-membrane interface, the germanium–Cyanex 301 complex formation is enhanced. Thus, the germanium flux through the membrane increased. However, at the lower Cyanex 301 concentration, the mentioned interface was not saturated by Cyanex 301 and the transport decreased. The flux of germanium (J_{Ge}) reached 4.35×10^{-7} (mol/cm²·s) at the carrier concentration of 1.18 mol/dm³ (40 vol%).
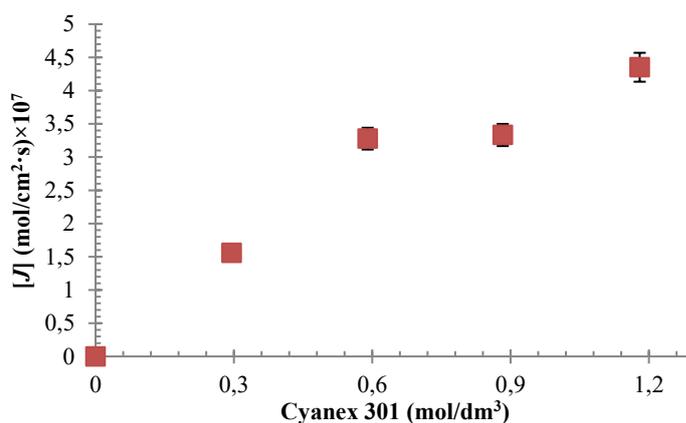
Fig. 3. Effect of Cyanex 301 concentration on the germanium flux (*J*) (aqueous feed phase: pH= 1.5, [Ge]= 40 mg/dm³; stripping phase: [H₂SO₄]= 200 g/dm³; contact time= 20 h)

3.3. Effect of germanium concentration in the feed solution

In order to investigate the effect of germanium concentration in the feed solution on the germanium transport, a set of experiments was performed in various concentrations being in the range of Ge 10-40

mg/dm^3. The experimental conditions of this set of experiments were as follows: the feed pH of 1.5, Cyanex 301 concentration of 1.18 mol/dm^3 (40 vol%) and H$_2$SO$_4$ concentration of 200 g/dm^3 in the receiving phase. Table 1 presented the results and showed that the permeation coefficient is not sensitive to the initial concentration; however, as seen in Fig. 4, the flux of germanium gradually increased by enhancing the germanium concentration of the feed solution from 1.60×10^{-7} to 10.47×10^{-7} mol/cm$^2 \cdot$s. This is in agreement with the tendency reported in the literature, in which the flux of transported species has a direct relationship with species concentration in feed solutions (Nosrati et al., 2013). This enhancement means that with increasing concentration, the germanium accessibility to the interface of the feed-membrane increased. Therefore, the chemical reaction at the interfacial level resulted in transporting germanium from the feed solution followed by formation of germanium-Cyanex 301 complexes as mentioned in Eq. (1).
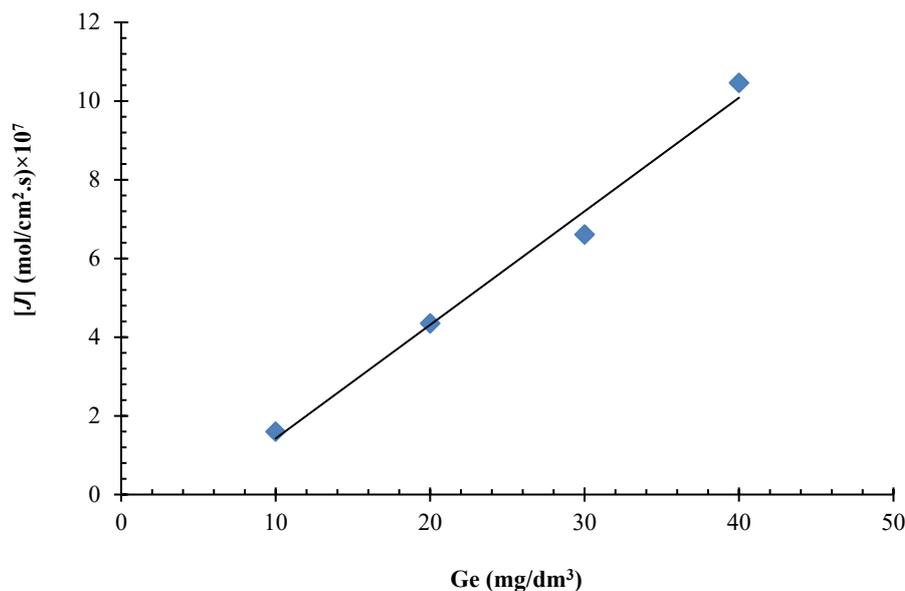
Fig. 4. Effect of germanium concentration on *J* of germanium (aqueous feed phase: pH= 1.5; stripping phase: [H$_2$SO$_4$]= 200 g/dm^3; organic phase: [Cyanex 301]= 40 vol% and contact time= 20 h)

Table 1. Effect of initial germanium concentration on permeability and flux of metal ions

[Ge(IV)], mg/dm^3	P ($\times 10^3$), cm/s	J ($\times 10^7$), mol/cm^2.s
10	1.16	1.59
20	1.58	4.35
30	1.6	6.61
40	1.9	10.5

3.4. Effect of acid concentration in the receiving solution

This reaction occurring at the interface of the membrane and the receiving solution is essential in the mobility of species from the feed solution to the receiving solution (Swain et al., 2007). Regarding this, the flux of germanium in various sulfuric acid concentrations in the receiving solution (i.e. 100-400 g/dm^3) was investigated. The experiments were conducted at an initial pH of 1.5 in the feed solution, the germanium concentration of 40 mg/dm^3, and 1.18 mol/dm^3 of Cyanex 301 concentration. Fig. 5 illustrates the plot of J_{Ge} vs. time in various H$_2$SO$_4$ concentrations. As seen in this figure, with an increase of the acid concentration, the flux of germanium increased from 100 to 400 g/dm^3. Extra enhancement in the acid concentration up to 400 g/dm^3 showed no meaningful effect on the metal ion flux because at higher acid concentrations, stripping of the extracted species persuaded by the chemical reaction at the boundary layer happens rapidly, as diffusion into the bulk of the strip solution does not depend on the acid concentration (Duan et al., 2017). The maximum value of the flux equal to 11.4×10^{-7} mol/cm$^2 \cdot$s

was obtained at 400 g/dm³ of H₂SO₄ concentration in the receiving solution. Moreover, Table 2 showed that the permeability coefficient of germanium through the membrane progressively increased from 1.43×10^{-3} to 2.58×10^{-3} cm/s because the dissociation of germanium–Cyanex 301 was gradually completed and reached an optimum condition.

Table 2. Effect of sulfuric acid concentration in the receiving solution on permeability coefficient

[H₂SO₄], (g/dm³)	Permeability coefficient, $P \times 10^3$ (cm/s)
100	1.43
200	1.90
300	2.21
400	2.58
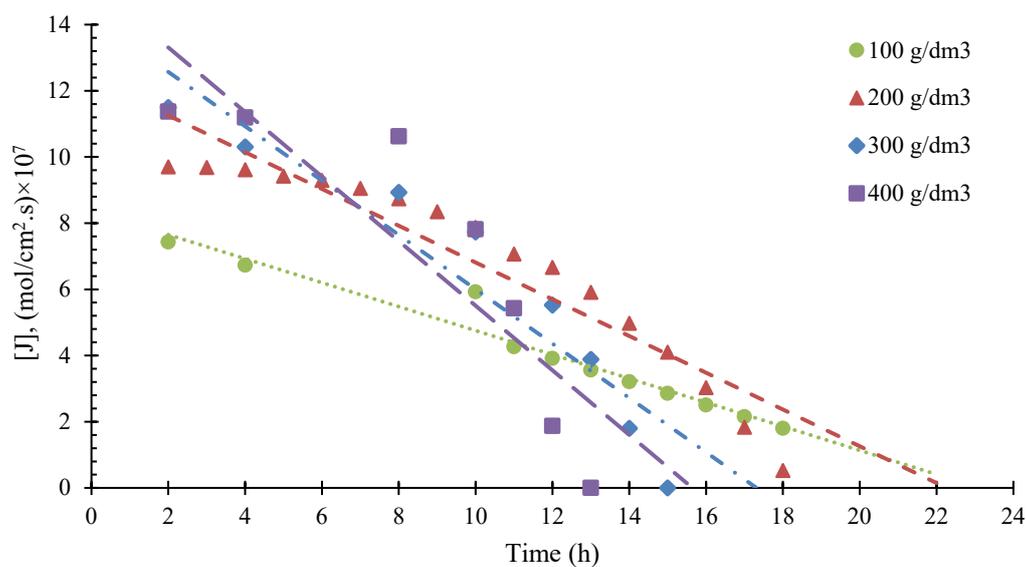
Fig. 5. Germanium(II) flux curves in SLM experiments at various concentrations of sulfuric acid (aqueous feed phase: pH= 1.5; [Ge]= 40 mg/dm³; organic phase: [Cyanex 301]= 40 vol% and contact time= 20 h)

3.5. Kinetic study

In order to investigate the effect of the operational parameters such as pH, the concentration of the carrier, and the strip solution concentration on the kinetic pertraction of germanium through the SLM system, variations of the germanium concentration in the feed and strip phases versus time were plotted. These curves are shown in Fig. 6. According to this figure, it is obvious that the plot of the concentration in the feed phase versus time is mono-exponential. Therefore, the kinetic behavior of the facilitated transport can be explained by the irreversible first order equation as Eq. (6) (Granado-Castro et al., 2008):

$$\frac{d(C_t)}{dt} = -k_1 C_t \qquad (6)$$

With integrating Eq. (6), Eq. (7) is obtained to find the rate constant:

$$\frac{C_t}{C_0} = \exp(-k_1 t) \qquad (7)$$

where C_t represents the concentration after the time of t in the feed phases, C_0 depicts the initial concentration, and k_1 is the pseudo-first apparent rate constant. According to the results illustrated in Table 3, with increasing the Cyanex 301 concentration, the Ge concentration and the acid concentration in strip solution up to 1.18 mol/dm³, 40 mg/dm³, and 400 g/dm³, the maximum rate constant (k_1) was equal to 15.2 (1/min ×10⁴). On the other hand, the maximum rate constant was obtained at pH 1.5.

Table 3. Effect of the operational parameters on the pertraction rate of germanium
with Cyanex 301 as a carrier and PTFE as a membrane

Parameter	Levels	Pertraction rate (k) ($1/\text{min}\times10^4$)
pH	1.5	12.7
	3	11.7
	4	1.72
	5	2.67
Cyanex 301 concentration (mol/dm³)	0.25	3.67
	0.59	7.67
	0.88	11.5
	1.18	12.7
Ge concentration (mg/dm³)	10	8.33
	20	10.2
	30	10.8
	40	12.7
Acid concentration (g/dm³)	100	11.2
	200	12.7
	300	14.3
	400	15.2
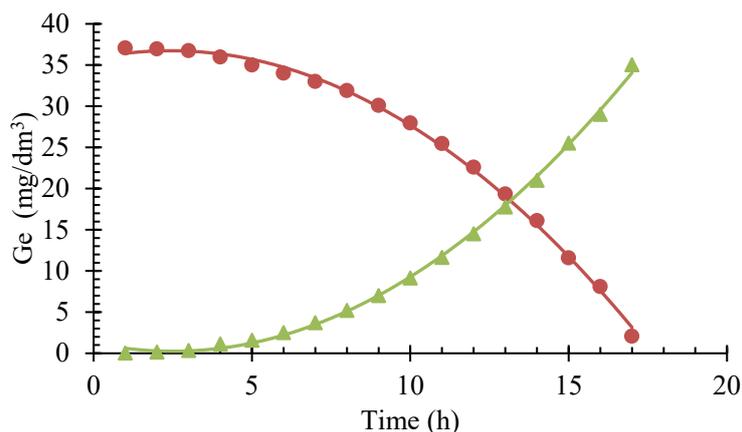
Fig. 6. Concentration of germanium versus time of the FSSLM process
(aqueous feed phase: pH= 1.5; [Ge]= 40 mg/dm³; organic phase: [Cyanex 301]= 40 vol% and contact time= 20 h)

3.6. Permeability model of SLM and evaluation of mass transfer resistances

In order to develop a model for the mass transfer of Ge(IV) through the solid membrane of this study, the following assumptions were considered: (1) the transfer of ions through the membrane was carried out by only diffusional factors, and (2) chemical reactions happen instantly in comparison with a diffusional reaction (Alonso et al., 2006). With respect to these assumptions, a model of a mass transfer is commonly obtained using the following stages:

(a) in the boundary layer of the feed phase-membrane, the metal complex of germanium diffuses to this boundary from the solution.

(b) diffusion of sulfate and nitrate ions is neglected.

(c) the diffused species and the carrier molecules meet together at the specified boundary to react and produce the hydrophobic metal-carrier complexes.

(d) these complexes diffuse from the feed phase-membrane interface layer through the membrane body and then to the membrane-receiving phase interface layer.

(e) sulfuric acid as a strippant detaches metal-carrier complexes at the membrane-receiving phase interface, and metals go to the receiving phase bulk.

(f) finally, the regenerated carrier molecules transfer inversely to the feed phase-membrane interface.

As mentioned before, the equilibrium reaction of the germanium extraction by Cyanex 301 diluted with kerosene has been described by Eq. (1) and in this study, assumes that this possible reaction has occurred. The extraction constant of this reaction can be calculated using Eq. (8):

$$K_{ex} = \frac{[Ge \cdot R_4]_{org}[H^+]_{aq}^4}{[Ge^{4+}]_{aq}[HR]_{org}^4} = 0.87 \tag{8}$$

where R depicts the extractant molecule.

The germanium diffusional flux through the membrane can be obtained using Fick's first diffusion law. The calculations were carried out according to the diffusion of ions to the diffusion layer in the feed phase and the solid membrane. Hence, the fluxes at the feed phase boundary and the membrane were called J_{aq} and J_{org}, respectively, and written as Eqs. (9) and (10):

$$J_{aq} = \frac{1}{\Delta_{aq}}([Ge(IV)]_{0,f} - [Ge(IV)]_{i,f}) \tag{9}$$

$$J_{org} = \frac{1}{\Delta_{org}}([GeR_4]_{i,f} - [GeR_4]_{i,s}) \ . \tag{10}$$

In these equations, Δ_{org} and Δ_{aq} represent the resistances occurred when ions diffused across the membrane and to the feed phase boundary, respectively. Moreover, $[Ge(IV)]_{i,f}$ is the total metal in the feed phase.

Since the concentration of germanium-carrier complex in the membrane in the receiving phase is lower than that in the feed phase, Eq. (10) was corrected and simplified as Eq. (11):

$$J_{org} = \frac{1}{\Delta_{org}}([GeR_4]_{i,f}) \ . \tag{11}$$

Considering $J_{aq} = J_{org} = J$ at the steady state, the equations above were used to find overall J as Eq. (12) showing the combination of the equilibrium and diffusivity conditions:

$$J = \frac{K[R]_{org}^4}{\Delta_{org}[H^+]^4 + \Delta_{aq}(K[R]_{org}^4)} \ . \tag{12}$$

According to the flux equation, the permeability coefficient is also written as Eq. (13):

$$P = \frac{K[R]_{org}^4}{\Delta_{org}[H^+]^4 + \Delta_{aq}(K[R]_{org}^4)} \ . \tag{13}$$

To evaluate the mass transfer resistances, Eq. (13) was converted to Eq. (14) as follows:

$$\frac{1}{P} = \Delta_{aq} + \frac{\Delta_{org}[H^+]^4}{(K[R]_{org}^4)} \ . \tag{14}$$

As seen in this equation, the intercept and the slope of the line are Δorg and Δaq which can be found by plotting $1/P$ as a function of $[H^+]^4/(K[R]^4_{org})$ (Fig. 7(a)). Thus, the values of 6.57 and 738 s/cm were found for Δ_{org} and $\Delta_{aq,}$ respectively. Then, P can be found with respect to Eq. (13) and compared to the experimental P values to see the validity of the mass transfer model. Fig. 7(b) shows this comparison in which $P \times 10^3$ (cm/s) was plotted as a function of Cyanex 301 concentration (vol%). As seen in this figure, close values of the model and experimental results show the validation of the model. According to the model curve, the permeability coefficient reached a plateau at higher concentrations of the carrier. Furthermore, using this curve, the permeability can be estimated at any carrier concentration. Table 4 compares the permeability of germanium and trivalent actinides and lanthanides transported by FSSLM with the 0.5 mol/dm³ of Cyanex 301 as the carrier. The permeability of germanium through FSSLM by TOA was also illustrated in this table. According to this table, the permeability corresponding to La³⁺, Eu³⁺, Tb³⁺, Ho³⁺, and Yb³⁺ are very low in comparison with that of Am³⁺, Cm³⁺, and Ge⁴⁺. Moreover, the permeability values of Am³⁺ and Ge⁴⁺ are close together. The permeability of germanium through the membrane with the similar characteristics to that used in the present study containing TOA is approximately 0.24×10^{-3} cm/s. This value is approximately 4 times lower than that obtained in the present study.

Table 4. Comparison of permeability values corresponding to the various elements transported
in FSSLM systems using Cyanex 301

Element	P (cm/s) $\times 10^3$	Carrier	Concentration of carrier (mol/dm³)	Ref.
La³⁺	5.26×10^{-3}	Cyanex 301	0.5	
Eu³⁺	1.01×10^{-2}	Cyanex 301	0.5	
Tb³⁺	5.62×10^{-3}	Cyanex 301	0.5	
Ho³⁺	5.44×10^{-3}	Cyanex 301	0.5	
Yb³⁺	5.35×10^{-3}	Cyanex 301	0.5	(Bhattacharyya et al., 2006)
Am³⁺	1.17	Cyanex 301	0.5	
Cm³⁺	0.26	Cyanex 301	0.5	
Ge⁴⁺	0.24	TOA	0.56	(Kamran Haghighi et al., 2018b)
Ge⁴⁺	1.07	Cyanex 301	0.5	this study
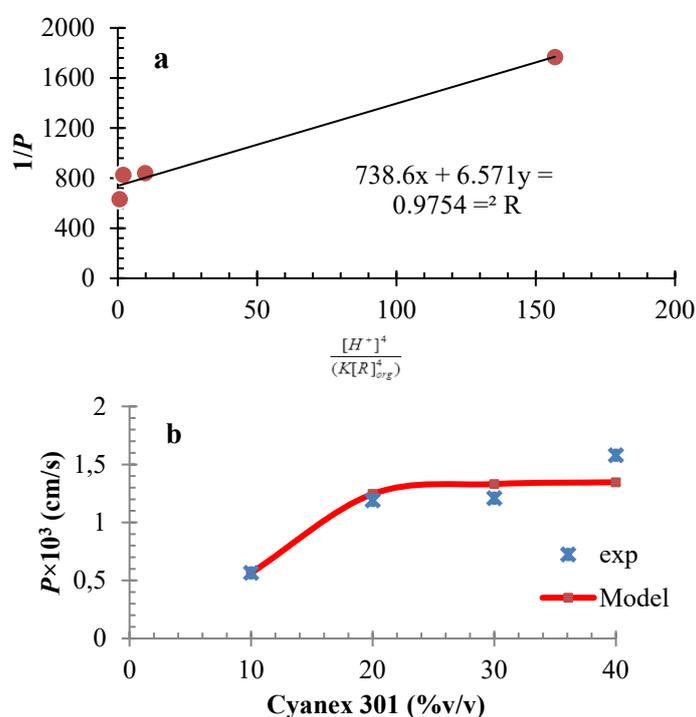
Fig. 7. (a) The plot of $1/P$ vs. $[H^+]^4/(K[R]^4_{org})$ (b) Effect of the concentration of Cyanex 301 as a carrier in the SLM system on the germanium permeability coefficient (Aqueous feed phase: pH= 1.5; Stripping phase: $[H_2SO_4]$= 400 g/dm³; and contact time= 20 h)

4.   Conclusions

In this study, the transport of germanium was carried out by the supported liquid membrane using Cyanex 301 solvent as a mobile carrier and PTFE as a solid membrane. According to the results, the germanium transport decreased with an increasing pH from 1.50 to 5.00 in the feed solution; thus, the subsequent experiments were conducted at pH 1.5. Moreover, metal transport was affected by some parameters such as carrier concentration and sulfuric acid concentration in the receiving phase. The germanium transport increased with increasing the mobile carrier concentration in the membrane phase up to 1.18 mol/dm³, and the acid concentration from 100 to 400 g/dm³. Moreover, the change in the concentration of germanium did not have a significant effect on the permeability. Therefore, under the optimum condition obtained at a pH 1.5, the germanium concentration of 40 mg/dm³, Cyanex 301 concentration of 1.18 mol/dm³, and the strip acid concentration of 400 g/dm³, the flux of Ge(IV) was found to be 11.4×10^{-7} mol/cm²·s. Under these conditions, the transport kinetics was obtained using an irreversible first-order kinetic model and the rate constant of the transport was determined to be 15.2

×10⁻⁴ (1/min). Furthermore, the reusability of the SLM system including Cyanex 301 and PTFE as a membrane for Ge transport from the acidic solution was possible. Finally, according to the mass transfer model, the values of 6.57 and 738 s/cm were found for resistances occurred when ions diffused across the membrane and to the feed phase boundary, respectively. The results showed that the obtained model had a good fit to the experimental data showing validation of the model.

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