Pseudo-emulsion based hollow fiber with strip dispersion pertraction of iron(III) using $(PJMTH^+)_2(SO_4^{2-})$ ionic liquid as carrier

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ABSTRACT

The transport of iron(III) from acidic media using pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) technology is investigated. As a carrier, $(PJMTH^+)_2(SO_4^{2-})$ ionic liquid, generated by direct reaction of the commercially available primary amine Primene JMT and sulphuric acid, is used. Several hydrodynamic conditions were investigated: concentration of iron $(0.01–1\,g\,l^{-1})$ and sulphuric acid concentration $(10^{-3}–0.5\,M)$ in the feed phase, carrier concentration $(1–30\%, v/v)$ and sulphuric acid concentration $(1–3\,M)$ in the organic and strip solutions, of the pseudo-emulsion phase. The values encountered for the membrane and feed resistances, 112 and $1000\,s/cm$, showed that the contribution of the membrane resistance is negligible, whereas the feed resistance contributes around 17% to the overall resistance value (near $5800\,s/cm$), thus, the interfacial resistances due to the extraction and stripping reactions appeared dominant. The performance of the system is also compared against other ionic liquids generated from available amine extractants (Primene 81R, Primene TOA, Amberlite LA2 and tridodecylamine) and other hollow fiber configurations.

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1. Introduction

Metals are present in our environment, both as a result of environmental pollution and because of intentional ingestion of nutritional supplements. Iron is an element that is indispensable for life because of its involvement in a number of important metabolic processes. In contrast to many other essential trace elements the body has an ability to store excess iron to be utilized in periods of increased requirements or reduced intakes. However, considering the fact that the exposure to iron that is harmless to some may be destructive to others with specific genetic changes [1], an excess of iron becomes highly toxic due to the generation of reactive oxygen intermediates that result in peroxidative damage to vital cellular structures.

Besides its toxic (or non-toxic) activities, the control of iron is of concern in the production of many metals, facing the world's hydrometallurgical industry with several million tons per year on its processing operations. Moreover, iron is present in liquid effluents, i.e. pickling liquors and rinse waters, generated in the steel industry. Thus, this element needs to be eliminated from various

processes, this elimination being carried out by different procedures, mainly precipitation, solvent extraction or ion exchange, or by combining a series of them.

Membrane technologies are playing an increasingly important role as unit operation for pollution prevention, environmental monitoring and quality control, etc. Developments in membrane technologies include the use of a hollow fiber membrane process such as pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) which affords, among other exciting features, high mass transfer rates of solutes, especially with high selectivity by the use of specific extractants. Some uses of the PEHFSD technology had been recently reviewed in the literature [2].

Despite the three above circumstances: iron (relative) toxicity, presence of iron in liquid effluents and increasing usage of membrane technologies, there is very limited information about the use of liquid membranes for the processing of iron-bearing liquid effluents [3–7].

On the other hand, ionic liquids or "green solvents" are a group of organic salts that exist as liquids at a temperature below 100 °C. Due to some specific features that they presented, these compounds have been used for several applications in many fields as well as they are proposed for separation processes of metals and other solutes [8–17].

This investigation presents data about the active transport of iron(III) using the ionic liquid $(PJMTH^+)_2(SO_4^{2-})$ or $(R–NH_3^+)_2(SO_4^{2-})$, generated by the reaction of the primary amine Primene JMT and sulphuric acid, as mobile carrier and PEHFSD liquid membrane operation. The influence of hydrodynamic condi-

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Table 1
Characteristics of the $(PJMTH^+)_2(SO_4^{2-})$/n-decanol/n-decane system.

Strip solution	Carrier (%, v/v)	n-Decanol (%, v/v)	Remarks
3 M H_2SO_4	2.5	–	Third phase formation. Unsuitable for practical use
3 M H_2SO_4	2.5	1	As above
3 M H_2SO_4	2.5	2	As above
3 M H_2SO_4	2.5	2.5	Two phases (organic and strip) formation. Suitable for practical use

Feed phase: 0.01 g l^{-1} Fe(III) and 0.1 M H_2SO_4. Feed flow: 300 cm^3 min^{-1}. Pseudo-emulsion flow: 100 cm^3 min^{-1}.

tions and chemical parameters were investigated in order to obtain efficient PEHFSD technology.

2. Materials and methods

Primary amine Primene JMT (Rohm and Haas) was used as carrier for transport experiments in the present investigation. This and other extractants: Primene 81R, Primene TOA and Amberlite LA2 (Rohm and Haas) and tridodecylamine (Merck), were used without further purification. All other chemicals used in this study were of AR grade. The organic membrane phase was prepared by dissolving the appropriate volume of Primene JMT (or extractants) in a mixture of 2.5% (v/v) n-decanol (modifier) and n-decane (diluent) to obtain organic solutions of different concentration. The ionic liquid is then generated in the same pseudo-emulsion tank by mixing this organic solution with the aqueous sulphuric acid phase; almost instantaneously, the next reaction occurs [18–20]:

$$2(R-NH_2)_{org} + H_2SO_{4aq} \rightarrow (R-NH_3^+)_2(SO_4^{2-})_{org} \qquad (1)$$
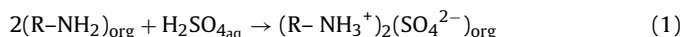
and, thus, the ionic liquid is formed. In the above equation $R-NH_2$ stands for the amine Primene JMT, and aq and org subscripts for the aqueous and organic phases in the pseudo-emulsion reservoir tank, respectively. The same reaction occurs when the above amines are used as cationic promoters for the respective ionic liquids.

The use of the modifier and in this dosage is needed in order to avoid third phase formation in the pseudo-emulsion tank reservoir after phase separation, as previous studies (details given in Table 1) had shown.

The hollow fiber device used for the investigation was manufactured by Hoechst Celanese (now Membrana): Liqui-Cel 8 cm × 28 cm 5PCG-259 contactor and 5PCS-1002 Liqui-Cel laboratory LLE and specified as in Table 2.

The hollow fiber strip dispersion process comprises a single membrane contactor, one stirred tank for preparing and used as reservoir of the pseudo-emulsion of the organic solution with 3 M sulphuric acid and one stirred tank acting as feed phase reservoir. The experimental set-up also contained two gear pumps of variable flows for both phases and flowmeters. The organic solution wet the porous wall of the fiber because of its hydrophobic nature. The interface was maintained at the pore by applying a higher pressure to the feed solution than to the pseudo-emulsion phase. The differential pressure was always kept below the break-

through pressure. In the present case, the pressure of the feed phase was 0.2 bar higher than in the pseudo-emulsion phase. A view of the PEHFSD using a single hollow fiber contactor and in the recirculation mode of the phases is shown in Fig. 1. The PEHFSD operation was carried out by passing acidic feed containing iron(III) through the tube side and pseudo-emulsion phase through the shell side in countercurrent mode. The feed reservoir tank was stirred to homogenize the solution, whereas the stirring of the pseudo-emulsion reservoir tank was needed in order to homogenize the phase and to maintain the pseudo-emulsion. Also, the characteristics of the pseudo-emulsion should be such that it should have clear and fast phase separation (organic and strip phases) when mixing is stopped. The recovery of iron from pseudo-emulsion can be accomplished (pseudo-emulsion breaks down after 15–30 s the mixing solution of the organic and strip phases stopped) and aqueous and organic phases separated automatically. Thus, the pseudo-emulsion reservoir tank somewhat acts as a mixer-settler of conventional solvent extraction operation. The volume of pseudo-emulsion phase is 800 cm^3 (400 cm^3 of the organic solution and 400 cm^3 of the strip solution), whereas the volume of the feed phase (V) is 3000 cm^3. At a predetermined time, aliquots of the feed and pseudo-emulsion tanks were taken and analyzed for iron concentration by standard AAS (Perkin Elmer 1100B spectrophotometer). The overall mass transfer coefficient was calculated from Eq. (4) (see below).

In the pseudo-emulsion based hollow fiber organic dispersion (PEHFOD) operation, the operational characteristics are similar than above except that the organic phase is dispersed into the strip phase. The main operational characteristics of non-dispersive solvent extraction (NDSX), hollow fiber supported liquid membrane (HFSLM) and hollow fiber renewal liquid membrane (HFRLM) technologies are given elsewhere [21–23].

All the experiments were performed at a temperature of 25 °C.

3. Results and discussion

The solvent extraction of iron(III) by Primene JMT had been described elsewhere [24], and the stoichiometry of the extracted

Table 2
Characteristics of the contactor and fibers.

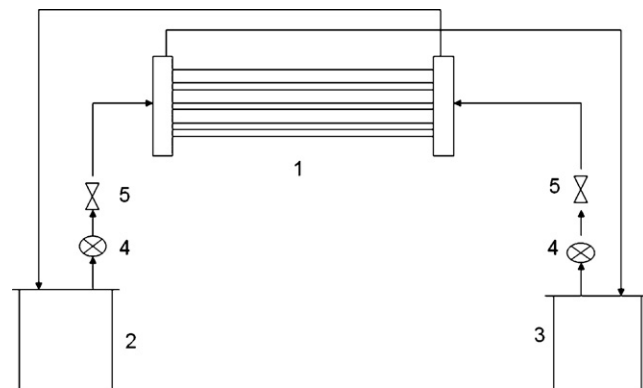|	
Contactor diameter	8 cm
Contactor length	28 cm
Active area (A)	1.4 m^2
Number of fibers (n)	10,000
Fiber internal diameter (d_i)	24 × 10^{-3} cm
Fiber outer diameter (d_o)	30 × 10^{-3} cm
Fiber wall thickness (d_{org})	3 × 10^{-3} cm
Fiber length (L)	15 cm
Porosity (ε)	30%
Tortuosity (τ)	3
Pore size	3 × 10^{-6} cm
Polymeric material	Polypropylene

Fig. 1. Schematic view of PEHFSD operated in recycling mode of the phases for separation of iron(III) from acidic media: (1) hollow fiber contactor, (2) feed solution tank reservoir, (3) pseudo-emulsion tank reservoir, (4) pumps and (5) flowmeters.
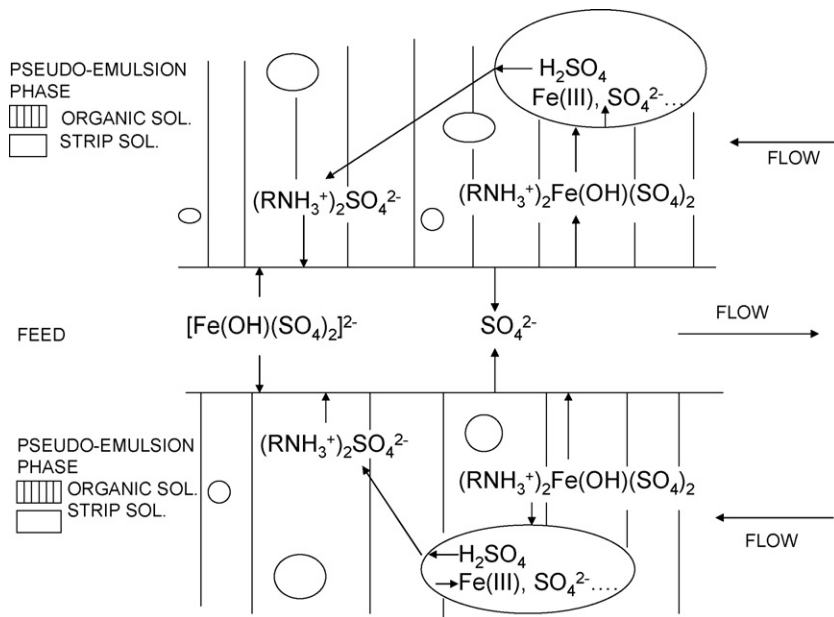
Fig. 2. Schematic view of transport mechanism of Fe(III) from sulphuric acid media with $(PJMTH^+)_2SO_4^{2-}$ ionic liquid by PEHFSD with single hollow fiber module.

species depends on the initial sulphuric acid concentration in the aqueous phase. In the 0.1 M acid concentration range, as mainly used in the present investigation, it can be better described as $(RNH_3)_2Fe(OH)(SO_4)_2$. For extraction of Fe(III) through a PEHFSD containing $(PJMTH^+)_2SO_4^{2-}$ as a mobile carrier, the concentration profile across the overall system is schematically shown in Fig. 2.

In any case, the iron(III) distribution coefficient between the loaded organic phase and the aqueous or raffinate phase can be expressed as:

$$D_F = \frac{[Fe(III)]_{org}}{[Fe(III)]_{aq}} \tag{2}$$

where $[Fe(III)]_{org}$ and $[Fe(III)]_{aq}$ represented the respective total analytical iron concentration in the above two phases.

The iron flux, J, through the hollow fiber module is given by:

$$J = K\left[[Fe]_F - \frac{D_S}{D_F}[Fe]_S\right] \tag{3}$$

where K is the overall mass transfer coefficient, $[Fe]_F$ is the iron concentration in the feed solution, $[Fe]_S$ is the iron concentration in the strip phase, D_F is the distribution coefficient of iron between the membrane phase and the feed solution at the reaction equilibrium for the feed-side interface, and D_S (which is similarly defined as D_F) is the distribution coefficient of iron between the strip and membrane phases at the reaction equilibrium for the strip-side interface. In normal practice, D_F is much greater than D_S, and the second term between the squares in the above equation can be neglected in comparison with $[Fe]_F$. Thus, the material balance on the feed solution is:

$$-V\frac{d[Fe]_F}{dt} = AK[Fe]_F \tag{4}$$

where V is the volume of the feed solution, A is the membrane area, and t is the time.

Integration of the above equation results in:

$$\ln\frac{[Fe]_F}{[Fe]_{F,0}} = -\frac{AK}{V}t \tag{5}$$

where $[Fe]_{F,0}$ is the initial concentration of iron in the feed phase.

The overall mass transfer resistance through the module is equal to the sum of all individual mass transfer resistances consisting of:

(i) the feed-side resistance,
(ii) the interfacial resistance due to the extraction reaction,
(iii) the membrane phase resistance,
(iv) the interfacial resistance due to the stripping reaction, and
(v) the strip-side resistance.

Then [25],

$$\frac{1}{K} = \frac{1}{k_a} + \frac{1}{D_F k_e} + \frac{1}{D_F k_m} + \frac{1}{D_F k_s} + \frac{1}{(D_F/D_S)k_{as}} \tag{6}$$

where k_a is the mass transfer coefficient for the aqueous feed solution, k_e is the mass transfer coefficient due to the extraction reaction, k_m is the mass transfer coefficient for the membrane phase, k_s is the mass transfer coefficient due to the stripping reaction, and k_{as} is the mass transfer coefficient for the strip phase; k_e and k_s are related to the extraction and stripping reaction rates, respectively.

3.1. Influence of feed flow

In order to achieve effective permeation of iron in a PEHFSD system, it is necessary to explore the effect of the feed phase flow on the overall mass transfer coefficient. In the present work, feed flows were vary from 75 to 400 $cm^3 min^{-1}$ (Table 3). The overall mass transfer coefficient increased for flows ranging from 75 to 300 $cm^3 min^{-1}$; this indicates that the aqueous boundary layer thickness diminished continuously with increasing feed flow and that the boundary layer is a minimum around 300 $cm^3 min^{-1}$. Further, a decrease in mass transfer coefficient at higher feed flow

Table 3
Influence of feed flow on overall mass transfer coefficient of iron(III).

Feed flow ($cm^3 min^{-1}$)	$K (\times 10^4\ cm\ s^{-1})$
75	0.34
150	0.66
300	1.2
400	0.79

Feed phase: 0.01 g l^{-1} Fe(III) and 0.1 M H$_2$SO$_4$. Pseudo-emulsion phase: 0.5% (v/v) carrier + 2.5% (v/v) n-decanol + n-decane and 3 M H$_2$SO$_4$. Pseudo-emulsion flow: 100 cm^3 min^{-1}.

Table 4
Influence of initial H_2SO_4 concentration in the feed phase on overall mass transfer coefficient of iron(III).

H_2SO_4 (M)	$K(\times 10^4 \text{ cm s}^{-1})$
0.5	0.41
0.1	2.1
10^{-2}	2.9
10^{-3}	2.9

Feed phase: 0.01 g l^{-1} Fe(III) and H_2SO_4. Feed flow: $300 \text{ cm}^3 \text{ min}^{-1}$. Pseudo-emulsion flow: $100 \text{ cm}^3 \text{ min}^{-1}$.

Table 6
Iron transport by $(PJMTH^+)_2(SO_4^{2-})$ ionic liquid at different initial iron concentrations.

Fe(III) $(g l^{-1})$	$K(\times 10^4 \text{ cm s}^{-1})$
0.01	1.6
0.1	1.3
1	0.44

Feed phase: Fe(III) and $0.1 \text{ M } H_2SO_4$. Pseudo-emulsion phase: 2.5% (v/v) carrier + 2.5% (v/v) n-decanol + n-decane and $3 \text{ M } H_2SO_4$. Feed and pseudo-emulsion flows as in Table 4.

could be due to (i) greater turbulence of feed solution which forced organic solution out of the pore, (ii) emulsion formation along the lumen side with high flow rate [26], and (iii) lower residence time, which provides insufficient time to complex iron with carrier.

Previous experiments had shown that the variation of the pseudo-emulsion flow (50–100 cm^3 min^{-1}) had not any influence on iron transport (though data are not presented here).

3.2. Influence of sulphuric acid concentration in feed phase

In order to asses the role of this variable, H_2SO_4 concentration variation studies in the range 10^{-3}–0.5 M were carried out. The pseudo-emulsion phase consisted of 3 M sulphuric acid and 5% (v/v) carrier + 2.5% (v/v) n-decanol in n-decane. It is evident from data presented in Table 4 that the overall mass transfer coefficient of iron increases with the decrease of sulphuric acid concentration from 0.5 to 10^{-2} M, though at lower acidic concentration it remained unaffected. Probably, at the highest acidic concentrations, the amine bisulphate ($R-NH_3^+ HSO_4^-$) is being formed, this species being non-reactive with respect to the extraction (transport) of iron(III).

3.3. Influence of carrier concentration on the overall mass transfer coefficient of iron

The carrier plays a decisive role in making PEHFSD system efficient and economically viable. Therefore, it is essential to evaluate the effect of carrier concentration on the transport of iron. A PEHFSD system having no carrier in the organic solution results in no transport of iron. The effect of ionic liquid concentration on K was study from 0.5 to 15% (v/v) in 2.5% (v/v) n-decanol and n-decane. As can be seen in Table 5, the overall mass transfer coefficient of iron increases with carrier concentration up to 10% (v/v) and then decreases. The maximum limiting mass transfer coefficient could be explained by assuming that diffusion in the organic membrane is negligible compared with the other terms in Eq. (6).

By assumption that the carrier concentration in the hollow fibers is constant, the next equation can be used to determine the appar-

ent diffusion coefficient for iron [27]:

$$D_o{}^a = \frac{Jd_{org}}{[\text{Primene JMT}]} \tag{7}$$

The value of $D_o{}^a$ was calculated to be $3.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ taking thickness (d_{org}) 3×10^{-3} cm and using a carrier concentration of 10% (v/v). At higher carrier concentrations (Table 5), the decrease of overall mass transfer coefficient can be explained in terms of the increase in solution viscosity that increases membrane resistance.

3.4. Influence of metal concentration on the overall mass transfer coefficient of iron

Table 6 shows the variation of the iron overall mass transfer coefficient at various iron concentrations ranging from 0.01 to 1 g l^{-1} in the feed phase. The lowest overall mass transfer coefficient was obtained for the highest concentration of iron (1 g l^{-1}). This is due to the fact that organic phase within the membrane micropores get saturated with metal complex on increasing the metal concentration in aqueous feed solution. Further, this organic complex diffuses slowly into bulk of organic solution, which in nutshell decreased the mass transfer in the organic solution. The decrease in the transport could be further enhanced either by increasing the surface area of the module or running the operation for longer time.

Concentration profiles in the three phases during the transport process are shown in Fig. 3. From the initial stages of the process, the decrease in iron concentration in the feed solution was accompanied by an increase (more notorious from 2 h) in the stripping phase concentration. It is also noted that, from near 45 min, iron(III) was being transported uphill against its concentration gradient.
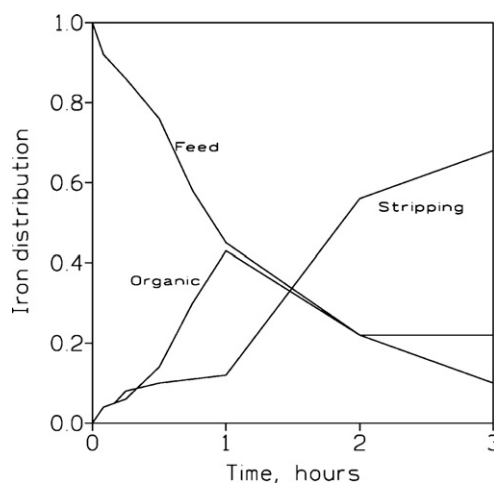
Table 5
The influence of carrier concentration on iron overall mass transfer coefficient.

Carrier (%, v/v)	$K(\times 10^4 \text{ cm s}^{-1})$
0.5	1.2
1.25	1.3
2.5	1.6
5	2.1
10	2.9
15	1.9

Feed phase: 0.01 g l^{-1} Fe(III) and $0.1 \text{ M } H_2SO_4$. Pseudo-emulsion phase: carrier + 2.5% (v/v) n-decanol + n-decane and $3 \text{ M } H_2SO_4$. Feed and pseudo-emulsion flows as in Table 4.

Fig. 3. Iron(III) concentration profiles in transport experiments. Feed phase: 1 g l^{-1} Fe(III) and $0.1 \text{ M } H_2SO_4$. Pseudo-emulsion phase: 2.5% (v/v) carrier + 2.5% (v/v) n-decanol + n-decane and $3 \text{ M } H_2SO_4$. Feed flow: $300 \text{ cm}^3 \text{ min}^{-1}$. Pseudo-emulsion flow: $100 \text{ cm}^3 \text{ min}^{-1}$.

3.5. Estimation of mass transfer coefficients

Since the reaction is instantaneous at the stripping side, and D_F is expected to be much greater than D_S, the mass transfer resistance for the strip solution is negligible in comparison with the overall mass transfer resistance. The individual feed mass transfer coefficient is dependent on the mean flow velocity of the solution (v_a) according to [28]:

$$k_a = 1.5 \frac{D_a}{d_i} \left(\frac{d_i^2 v_a}{D_a L} \right)^{1/3} \qquad (8)$$

where d_i is the inner diameter of the hollow fiber, D_a is the diffusion coefficient of iron species in the feed phase and L is the fiber length. Considering and approximate value of 10^{-5} cm^2 s^{-1} for D_a [29–31], then the k_a value calculated from the above equation, at v_a of 1.1 cm s^{-1}, was 1.0×10^{-3} cm s^{-1}. This value is in order with typical mass transfer coefficients in aqueous solutions [32], and is greater than the average overall mass transfer coefficient K value 1.7×10^{-4} cm s^{-1}, obtained from experimental data in Table 5. The fractional resistance due to the feed solution (R_a^0) to the overall process (R), can be calculated as:

$$R_a^0 = \frac{R_a}{R} \qquad (9)$$

where R_a is the mass transfer resistance due to feed phase. Under the present experimental conditions, the value of % R_a^0 was 17; this clearly indicates that this step is not the rate-controlling of the overall process.

The membrane mass transfer coefficient can be estimated from the next equation [33]:

$$k_m = \frac{D_o \varepsilon}{\tau d_{org}} \frac{d_{lm}}{d_o} \qquad (10)$$

where D_o is the diffusion coefficient in the organic phase, estimated in the 10^{-6} cm^2 s^{-1} order [34–36], and d_{lm} is the log mean diameter of the hollow fiber. Then, the calculated value of k_m is 3.0×10^{-5} cm s^{-1}, value which is in accordance with other k_m values obtained from the literature (Table 7). Taking into account the value of D_F, then the resistance due to the membrane averaged 112 s cm^{-1}, value which is insignificant in comparison with the overall mass transfer resistance.

These results indicate that the interfacial mass transfer resistances due to the extraction and/or the stripping reactions should be dominant for the present system.

3.6. Influence of strip phase composition

Stripping with sulphuric acid solutions of various concentrations for the PEHFSD with carrier was investigated. Table 8 shows

Table 7
Membrane mass transfer coefficients and operational modes.

k_m ($\times 10^5$ cm s^{-1})	Membrane technology[a]	Operational mode[b]	Reference
1.2	FSSLM	Batch	[37]
1.6	NDSX	Cocurrent	[38]
5.0	HFSLM	Feed one through, strip countercurrent	[39]
5.3	NDSX	Countercurrent	[40]
1.1	NDSX	Cocurrent	[41]
2.0	PEHFSD	Countercurrent	[42]
3.0	PEHFSD	Countercurrent	This work

[a] FSSLM: flat-sheet supported liquid membrane; NDSX: non-dispersive solvent extraction; HFSLM: hollow fiber supported liquid membrane; PEHFSD: pseudo-emulsion based hollow fiber strip dispersion.
[b] All the solutions in the recycling mode except when noted.

Table 8
Overall mass transfer coefficients and iron recovery in the strip phase.

H$_2$SO$_4$ (M)	K ($\times 10^5$ cm s^{-1})	[Fe]$_{strip}$ (g l^{-1})	% recovery$_{strip}$
0.5	1.5	1.8	46.9
1.5	2.6	4.3	82.7
3	4.4	5.1	75.6

Feed phase: 1 g l^{-1} Fe(III) and 0.1 M H$_2$SO$_4$. Pseudo-emulsion phase: 2.5% (v/v) carrier + 2.5% (v/v) n-decanol + n-decane and H$_2$SO$_4$ solutions.

the values of the overall mass transfer coefficients and the stripping results for H$_2$SO$_4$ concentrations in the strip phase ranging from 0.5 to 3 M. As shown in this table, the 3 and 1.5 M H$_2$SO$_4$ solutions stripped iron(III) much more effectively than the 0.5 M H$_2$SO$_4$ stripping solution. At the same time, this stripping difference affects the iron removal results significantly, decreasing the value of the overall mass transfer coefficient as the acid concentration in the strip phase decreases. Thus, these results suggest that the interfacial mass transfer resistance due to the stripping reaction becomes dominant at higher H$_2$SO$_4$ concentrations in the strip phase.

3.7. Iron(III) transport using amines as carriers: a comparison

The performance of the system carrier + n-decanol + n-decane on iron transport has been compared against other ionic liquids obtained from commercially available amines (Table 9) using the same experimental conditions. This same table shows the results of this study. It can be seen that the ionic liquid generated from Primene JMT gives the best iron transport, whereas a tentative transport order can be established as carriers generated from: primary amine > secondary amine > tertiary amine, being the ionic liquid promoted from Primene TOA the exception to the rule, as the overall mass transfer coefficient obtained with this carrier is of the same magnitude order than the K value obtained with the one promoted from Amberlite LA2.

3.8. Iron(III) transport using various hollow fiber module operational modes: a comparison

The transport of iron(III), using the pseudo-emulsion phase of 0.5% (v/v) Primene JMT in 2.5% (v/v) n-decanol and n-decane and 3 M sulphuric acid, had been investigated in various operational modes of the hollow fiber contactor. These various operational modes were summarized in Table 10 together with the results, in the form of the overall mass transfer coefficient K, derived from this investigation. It can be seen that best results are obtained when ordinary pseudo-emulsion based hollow fiber strip dispersion in countercurrent mode is used, though when this technology is employed with the organic phase dispersed into the strip solution, the overall mass transfer coefficient differs not too much with the value obtained before. This is not the case of using PEHFSD technology in the counter or cocurrent modes, being the iron trans-

Table 9
Amines (as precursors of the cationic group of the corresponding ionic liquids) and results in the transport of iron(III).

Precursor of cationic group	Active group	Carbon atoms (aliphatic chains)	K (cm s^{-1})
Primene JMT	(RNH$_3^+$)	R: C$_{16}$–C$_{22}$	1.3×10^{-4}
Primene 81R	(RNH$_3^+$)	R: C$_8$–C$_{12}$	6.9×10^{-5}
Primene TOA	(RNH$_3^+$)	R: C$_8$	2.6×10^{-6}
Amberlite LA2	(R′R″NH$_2^+$)	R′: C$_{12}$	2.8×10^{-6}
		R″: C$_{10}$	
Tridodecylamine	(R$_3$NH$^+$)	R: C$_{12}$	9.9×10^{-7}

Feed phase: 0.01 g l^{-1} Fe(III) and 0.1 M H$_2$SO$_4$. Pseudo-emulsion: 1.25% (v/v) carrier + 2.5% n-decanol + n-decane and 3 M H$_2$SO$_4$. Feed and pseudo-emulsion flows as in Table 4.

Table 10
Iron transport with various hollow fiber module operational modes.

Mode	Phase flow	Pseudo-emulsion	K (cm s^{-1})
PEHFSD	Countercurrent Feed: tube Pseudo-emulsion: shell	Strip dispersed into organic	1.2×10^{-4}
PEHFOD	Countercurrent Feed: tube Pseudo-emulsion: shell	Organic dispersed into strip	9.9×10^{-5}
PEHFSD	Cocurrent Feed: tube Pseudo-emulsion: shell	Strip dispersed into organic	5.4×10^{-5}
HFRLM	Countercurrent Feed: shell Pseudo-emulsion: tube	Organic dispersed into strip	7.5×10^{-5}
NDSX	Countercurrent: Feed: tube Organic phase: shell	No emulsion formed	7.5×10^{-5}
HFSLM	Countercurrent Feed: tube Strip phase: shell	No emulsion formed	8.6×10^{-5}

Feed phase: 0.01 g l^{-1} Fe(III) and 0.1 M H$_2$SO$_4$. Pseudo-emulsion or organic and strip phases: 0.5% (v/v) carrier + 2.5% (v/v) n-decanol + n-decane and 3 M H$_2$SO$_4$. PEHFSD: pseudo-emulsion based hollow fiber strip dispersion; PEHFOD: pseudo-emulsion based hollow fiber organic dispersion; HFRLM: hollow fiber renewal liquid membrane; NDSX: non-dispersive solvent extraction; HFSLM: hollow fiber supported liquid membrane. All the phases in the recycling mode except in HFSLM in which the organic phase is stationary in the pores of the fibers. In PEHFSD, PEHFOD and HFRLM, feed flow: 300 cm^3 min^{-1} and pseudo-emulsion flow: 100 cm^3 min^{-1}. In NDSX, feed flow: 300 cm^3 min^{-1} and organic flow: 100 cm^3 min^{-1}. In HFSLM, feed flow: 300 cm^3 min^{-1} and strip phase flow: 100 cm^3 min^{-1}.

port favoured using the first of the modes. On the other hand, working with the feed phase flowing in the tube side gives a relative better performance of the system if compared when this phase flows into the shell side of the module (PEHFOD against HFRLM technologies). Lastly, it should be mentioned here that the non-dispersive solvent extraction (NDSX) technology had been investigated using only a single module for extraction, very probably the performance of the system can be improve if an integrated membrane process, with two hollow fiber contactors (extraction and stripping performed together but separately on each module), is used.

4. Conclusions

Of the ionic liquids used as membrane carriers, the one generated from Primene JMT is most efficient for iron(III) transport using PEHFSD technology and under the present experimental conditions. The overall mass transfer coefficient results indicate that the mass transfer resistance for the membrane phase is negligible in comparison with the overall mass transfer resistance, whereas the feed mass transfer resistance contributes with a near 17% to the overall resistance. Thus, the interfacial mass transfer resistances due to the extraction and stripping reactions are dominant and apparently, that due to the stripping reaction seemed most dominant at higher sulphuric acid concentration in the strip solution. The PEHFSD operation was evaluated and performed well against other hollow fiber technologies.

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