Performance evaluation on vanadium transport through supported liquid membrane by TOMAC as carrier

S. Nosrati, N.S. Jayakumar, M. A. Hashim[*], Soumyadeep Mukhopadhyay

Department of Chemical Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia

Abstract

Many industries use vanadium increasingly and as a consequence, the toxic effluents cause environmental concern. Here, we study the extraction of vanadium in supported ionic liquid membrane was studied. The effect of operational conditions on the process performance such as initial feed phase concentration, pH of the feed solution, pore size of the membrane support, type of ionic liquid charged on the support and stripping agent solution was investigated. Vanadium was effectively transported from the feed phase to the stripping phase of ammonia solution using the room temperature ionic liquid, tri-*n*-octyl methyl ammonium chloride (TOMAC) embedded in the support membrane. Selective transport of vanadium from its mixture with chromium ions was carried out applying TOMAC as the carrier. It was also observed that addition of a slight amount of a second room temperature ionic liquid, 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide [BMIM][NTF$_2$], improved the vanadium extraction process considerably.

Keywords: Vanadium, Supported liquid membrane, TOMAC, [BMIM][NTF$_2$], Ionic liquid, Chromium

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[*] Corresponding author. Tel.: +603-79675296; Fax : +603-79675371
E-mail address: alihashim@um.edu.my

1. Introduction

Metal ions are one of the main water pollutants found in industrial effluent and are extremely toxic for the environment. They can be removed by the chemical precipitation, ion exchange, membrane filtration and carbon adsorption processes [1].

Vanadium is a hazardous metal belonging to the same class as lead, arsenic and mercury in terms of toxicity [2]. It can be found in the flyashes generated by power stations [3], effluents from glass, textile, metallurgy, ceramic, steel manufacturing, spent catalysts, rubber and pigments manufacturing industries [1, 4, 5]. It is a significant component in several catalysts and steel and iron and titanium alloys [6]. In the United States, the maximum exposure level of vanadium has been recommended to be 35 mg m^{-3} by National Institute for Occupational Safety and Health[7, 8].

The oxidation state decides the toxic property of a metal species. . Vanadium appears in different oxidation states in aqueous solution, and its speciation depends on pH of the solution, concentration and redox potential [1, 9]. According to Naeem et al., twelve species of vanadium can exist at the same time in a solution, and its speciation diagram reveals the dominance of cationic forms below pH3 and anionic species between pH 4 and 11[2]. In aqueous solutions, III, IV and V are dominant oxidized states of Vanadium [2]. Vanadium pentoxide is one of the most toxic forms [5], and tetravalent $VOSO_4$ has been reported to be over five times more toxic than trivalent V_2O_3 [7].

Several techniques have been proposed for the recovery of vanadium such as leaching or bioleaching followed by precipitation, ion exchange and solvent extraction [6]. Separation of

vanadium by liquid membranes are recommended for low concentration solutions [10]. Yadav et al. proposed an emulsion liquid membrane process as an alternative refinement method to the conventional extraction process for enrichment of vanadium [11].

Supported liquid membrane technique is an alternative approach to other techniques such as absorption, extraction and emulsion liquid membrane and is a proven and promising technique for the transport of vanadium. Palet et al. designed a liquid membrane system for vanadium transport by using Aliquat 336 dissolved in isopropylbenzene (cumene) or dodecane as a career [10]. Lozano et al. studied the feasibility of vanadium facilitated transport through a supported liquid membrane from diluted effluents by applying a mixture of tertiary amines, Alamine 336 and phosphine oxide Cyanex [12]. Melita et al. studied the transport of vanadium (V) and nickel (II) through activated composite membranes based on the carrier Aliquat 336, in cyclohexane and dodecane [7]. A combined single step process of extraction and stripping and a minimum liquid membrane requirement provides advantages of high separation factors, low energy requirements, possible usage of expensive carriers, easy scale-up, less capital and operating costs [13, 14].

Ionic liquids are organic salts entirely composed of organic cations and either organic or inorganic anions. Minimization of solvent loss, less exposure to hazardous vapors and low toxicity makes them attractive for industrial use. Most of them have melting points around or less than ambient temperature. So they are normally liquid at room temperatures and are called room

temperature ionic liquids (RTIL) [19]. Interaction of either the cation or anion of ionic liquid with the metal species may affect the chemical behavior of RTILs [15].

The room temperature ionic liquid carrier tri-*n*-octyl methyl ammonium chloride (TOMAC) is a typical extractant employed as a cation exchanger at low pH, and as anion exchanger at high pH values [19]. It was previously used for extraction of gold [16], transport of lactate ions in membrane contactors [17] and benzimidazole separation in an emulsion liquid membrane technique [18]. The chemical structure of TOMAC is shown in Fig. 1.
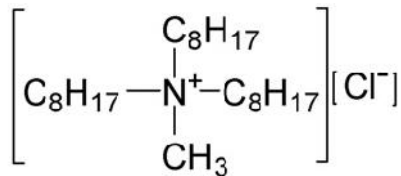

Fig. 1 Tri-*n*-octyl methyl ammonium chloride (TOMAC)

Industrial effluents contain different metal ions, and it is necessary to separate vanadium selectively. Kojima et al. [20] studied the process for selective recovery of vanadium (V) from mixture of various metal ions. They measured the selectivity of vanadium (V) over chromium (VI) for three types of membrane systems, and their applicability to metallurgical process for vanadium recovery.

The aim of this study is to investigate the vanadium extraction process using supported ionic liquid membrane technique. The conditions such as initial feed phase concentration, pH of the feed solution, pore size of the membrane support, type of ionic liquid charged on the support and stripping agent solution were varied to determine their influence on the vanadium permeability to

optimize the separation. The last objective of the present study is to investigate the selective vanadium (IV) recovery from a solution containing both vanadium (IV) and chromium (VI) ions.

2. Experimental method

2.1 Reagents and membranes

The initial aqueous solutions and the feed solution of known concentration of vanadium ions were prepared by dissolving an appropriate amount of standard vanadyl(IV) sulphate in sulphuric acid solution procured from Merck, Malaysia. Potassium dichromate ($K_2Cr_2O_7$), supplied by R&M Chemicals, was used as the source of chromium (VI) in the feed phase. Sodium hydroxide (NaOH) pellets and ammonia (NH_3) solution were provided from R&M Chemicals, Malaysia. The ionic liquids 1-Hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF_6], 1-Hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF_4], 1-Butyl-3-methylimidazolium hydrogensulfate [BMIM][HSO_4], 1-Butyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide [BMIM][NTF_2] and tri-n-octyl methyl ammonium chloride (TOMAC) were supplied by Merck, Malaysia. Deionized water was used for preparing the chemical solutions. All the chemicals were used as received. A PTFE plain supported membrane filter with a pore size of 0.45 and 65 µm thickness having 85% porosity was obtained from Membrane Solutions, China.

2.2 Preparation of supported liquid membranes

Hydrophobic microporous membranes were impregnated with a 100% solution of ionic liquids, for at least 24 hours before use. After the impregnation, the excess ionic liquid was wiped out from the surface of the membrane with a tissue paper. The cleaning procedure was performed

gently and carefully to assure that no ionic liquid was removed from the membrane pores. Then, the membrane was sandwiched in between the feed and strip cells as demonstrated in Fig. 2. A new supporting membrane was used in each experiment. The amount of ionic liquid loaded in the supporting membrane was determined by weighing the membrane before and after impregnation with the ionic liquid.
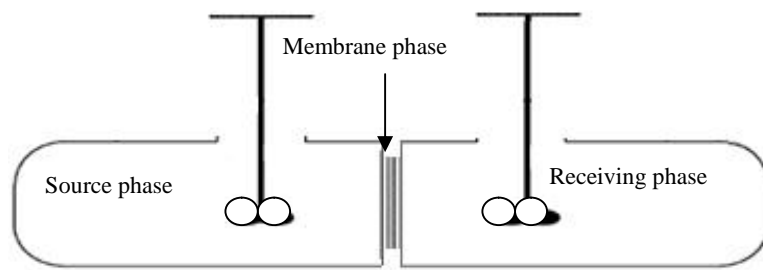

Fig. 2 Schematic illustration of the glass diffusion cell set up with two independent compartments used for experiments

2.3 Experimental setup

Vanadium removal process in the supported liquid membrane was studied at the ambient temperature using a glass diffusion cell with two separated compartments, as shown in Fig. 2. Each compartment contained 50 ml of the process solutions. The initial concentration of vanadium in feed solution was adjusted according to each experiment run. NH_3 or $NaOH$ was used as the receiving phase and the concentration was varied in each experiment run according to the requirement of each test. Both feed and receiving solutions were mechanically stirred to reach homogeneity. The sampling of the feed solution was accomplished at particular time intervals and in a defined period of time so as to observe concentration change of vanadium in the feed phase.

2.4 Transport studies

The change in solute concentration of the feed phase implies the process of vanadium transfer to the stripping phase. The percentage of vanadium removal was calculated using Eq. (1):

$$R_e \quad (\%) = \frac{c_0 - c_1}{c_0} \times 100 \tag{1}$$

where c_0 is the initial and c_1 is the final vanadium concentration in the feed compartment.

The kinetics of the transport process through a supported liquid membrane can be described by a first-order reaction involving solute concentration as in Eq. (2), [21]:

$$\ln \frac{C_t}{C_0} = -\frac{k}{V} t \tag{2}$$

where C_t is the metal ion concentration (mol dm^{-3}) in the feed phase at a given time, is the initial ion concentration in the feed solution, k is the rate constant (s^{-1}), A is the area of membrane, V is the volume of aqueous phase and t is the process time (s).

The value of k was gained by drawing a plot of ln (C_t/C_0) versus time and calculating the steep of the line in the graph. A high value of the determination coefficient was obtained. Afterward, the flux (J) was determined as Eq. 3 [22]:

$$J_i = \frac{V}{A} k C_i \tag{3}$$

2.5 Analytical methods

The concentration of each sample was measured by ICP-OES (Perkin Elmer, Optima 7000 DV). pH was measured with pH meter Cyber Scan pH300 and Rheintacho Rotaro Tachometer was

used for stirring speed determination. Solutions were stirred mechanically by IKA Lab-Egg Overhead Stirrer RW11.

3. Results and discussion

3.1 Selection of stripping agent

The solution of sodium hydroxide is a well-known alkaline stripping agent in metal ion separation processes [23]. Moreover, sodium hydroxide solution was used by Abas [24] to recover vanadium pentoxide (V_2O_5) from spent catalyst. On the other hand, ammonia was widely used for stripping vanadium from its aqueous solution [10, 12, 25]. Accordingly, in the present study sodium hydroxide and ammonia were applied in supported liquid membrane to evaluate their stripping functionality in the vanadium removal process. TOMAC was used as the carrier. Fig. 3 displays the obtained results. Ammonia, being much more efficient in stripping vanadium when compared to sodium hydroxide, was chosen for the rest of the experiments, and it maintained the required pH to strip the extracted metal throughout the process.
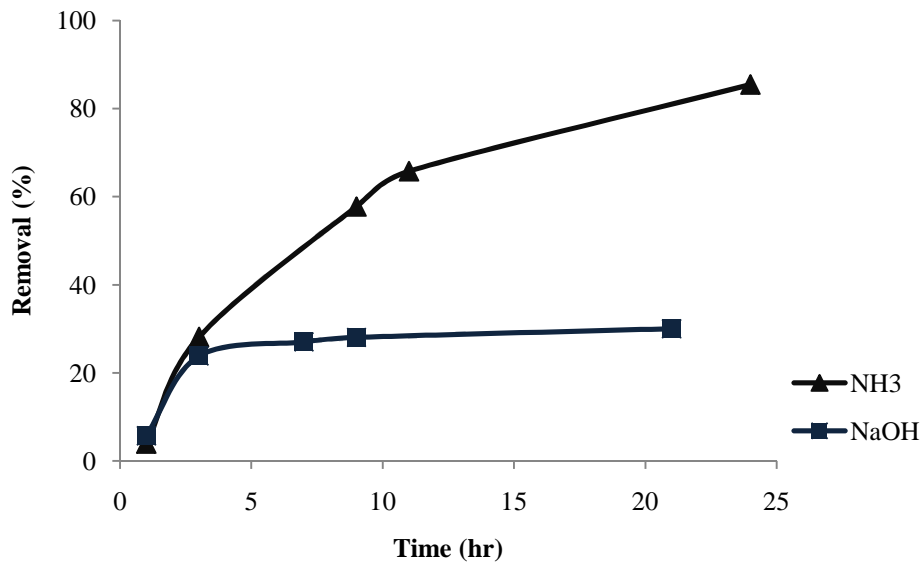
Fig. 3 Vanadium removal with different stripping agent

3.2 Effect of membrane support pore size

Thickness, pore size and hydrophobicity of the membrane support are among the main factors that contributed to the efficiency and stability of supported liquid membrane [26]. In our previous study, a PTFE membrane support with the thickness of 65 µm, having 85% porosity demonstrated better performance and stability. A thinner membrane was found to provid less mass transfer resistance and a membrane with high porosity provided more surface area. Smaller pores improved the stability of a membrane support [26]. Therefore, to enhance the effectiveness of the PTFE membrane support, another support filter with the same characteristics such as porosity and thickness but smaller in pore size was chosen. TOMAC was used as the carrier. The characteristics of the hydrophobic supports are summarized in Table 1. Fig. 4 demonstrates the evaluation result of pore size effect on vanadium removal. The support with a pore size of 22 µm accomplished better results during the initial hours of operation. However, its performance diminished with time and fell even lower than that of the support with the pore size of 45 µm.

This may be the result of lesser effective area of the transport caused by the blockage of small pores.

Table 1 Characteristics of the hydrophobic supports

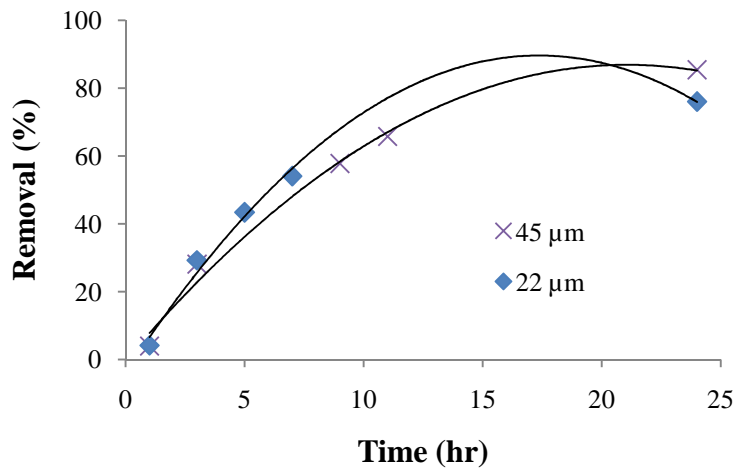| Membrane type	MS	MS
Material	PTFE	PTFE
Porosity (%)	85	85
Thickness (µm)	65	65
Pore Size (µm)	0.45	0.22

Fig. 4 The effect of pore size of the membrane support on vanadium removal

3.3 Effect of pH

The solubility of vanadium oxides changes with increasing pH. Over normal acidic pH range of wastewater, vanadium(IV) and (V) species were found to be water soluble [27]. However, highly alkaline environment does not assure complete removal of vanadium from its aqueous solution. As per Fig. 5, vanadium concentration in the solution decreased when pH was increased till 7. However, it bounced back into the solution once the pH was increased beyond 7. This signifies that any deviation from a pH of 7 will bring back vanadium in the solution. In the next step, to

investigate the influence of initial pH of the feed solution on the removal process, the vanadium solution was applied in the supported liquid membrane at different pH values. The initial pH of vanadium solution was 2.4. Two other solutions were prepared by adjusting the pH at 7 and 11. Fig. 6 shows the obtained results. The slope of ln (C_t/C_0) against time indicates the rate of ion transfer. A significant higher transfer rate of vanadium ion was observed while using a feed solution without adjusting initial pH. This confirms the idea that vanadium transport through the supported liquid membrane takes place on the basis of a pH gradient between feed and stripping solutions [25]. This is also in agreement with the results obtained by Zhang et al. [28] claiming the maximum vanadium (IV) extraction at the optimum pH of 2.
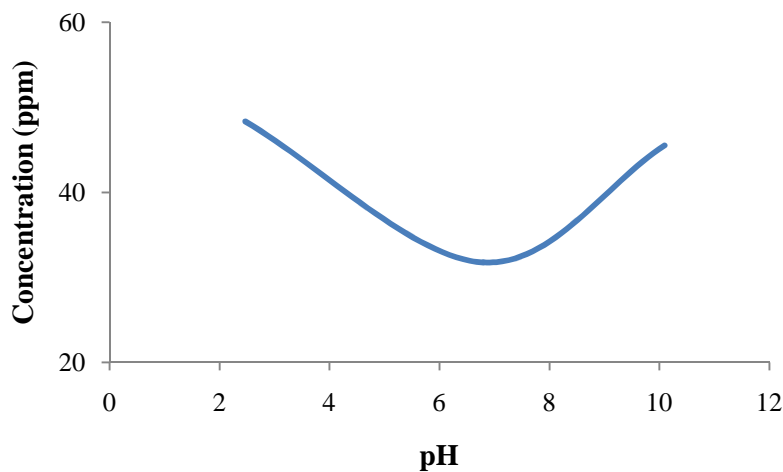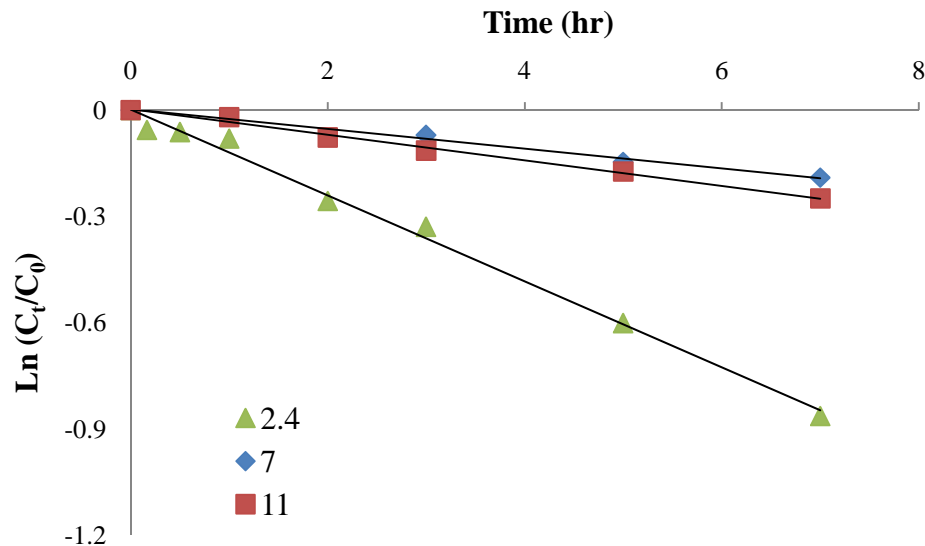
Fig. 5 pH effect on the solubility of vanadium

Fig. 6 Plot of ln (C_t/C_0) vs. operation time for vanadium transport across supported liquid membrane for observing the effect of pH at 2.4, 7 and 11.

3.4 A study on the type of ionic liquid

Fig. 7 illustrates the removal of vanadium, by using ionic liquids as the carrier in supported liquid membrane. Two salts of 1-n-alkyl-3-methylimidazoliumviz. $[C_nMIM]^+[BF4]^-$ and $[C_nMIM]^+[PF_6]^-$ were introduced as metal extractants [29]. However, they were not competent enough to offer high extraction of vanadium. The acidic ionic liquid [BMIM][HSO$_4$] also failed to extract vanadium. As already mentioned, TOMAC has earlier extracted several metal ions from aqueous solution. Correspondingly, the tetraalkylammonium cation exhibits higher extraction efficiencies and this is in agreement with de los Rios et al. [30]. Although, TOMAC carried out the vanadium extraction successfully, it was observed that adding a slight amount of the RTIL composed of bis[(trifluoromethyl)sulfonyl] imide anion and 1-butyl-3-methylimidazolium (bmim) cation considerably improved the extraction process . It can be inferred that owing to hydrophobic characteristics, NTF$_2$ has a tendency to form metal ion complexes and then transfer them to the organic phase at one pH and to the aqueous phase at

another pH. In fact, this behavior helped the TOMAC in forming complex. According to Williams et al. [15], this can be attributed to the stabilized monomeric ligand-deficient transition–metal complexes. Their findings disclosed that NTF_2 anions stabilize the metal complexes by means of four different binding modes: monodentate nitrogen or oxygen coordination and/or bidentate oxygen–oxygen´ or nitrogen–oxygen coordination. While working with different kinds of metals, they found out that the binding modes depended upon the electronic and steric demands of the metal centre [15].
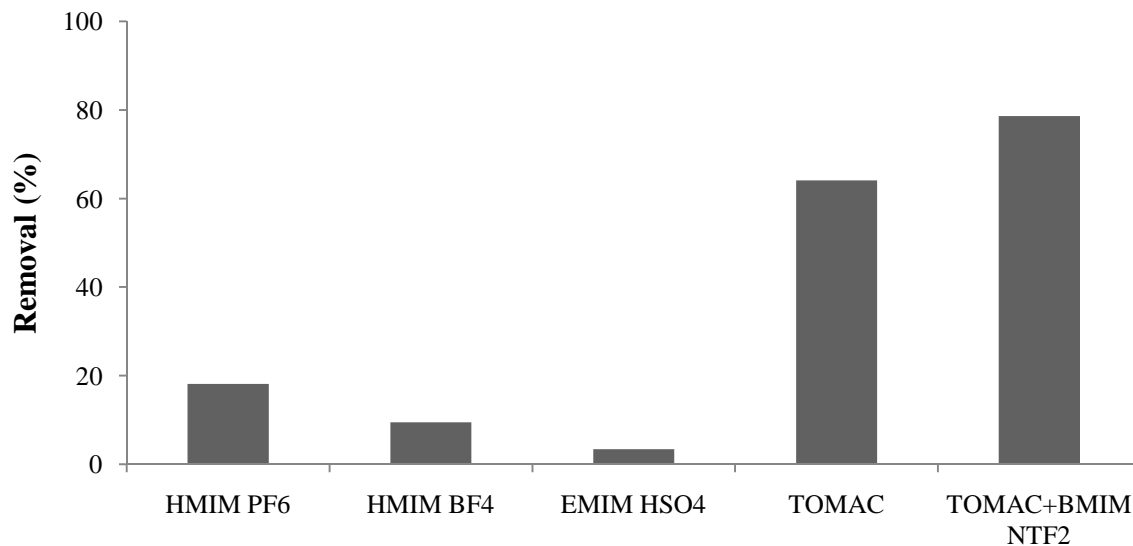

Fig. 7 Vanadium removal using ionic liquids as carrier in supported liquid membrane

3.5 Effect of initial concentration of vanadium on the permeability

The effect of initial vanadium concentration on the flux is illustrated in Fig. 8. The vanadium concentration varied from 0.1 to 1.1 mmol dm^{-3}. The results revealed that the flux was dependent on the initial vanadium concentration in the feed phase which was partly in agreement with the anticipated trend as per Eq. (3), i.e. the flux changes proportionately with the metal concentration. The flux tended to decline defying the trend beyond the initial concentration of

0.8 mmol dm^{-3}, apparently caused firstly, by membrane saturation and a lower effective membrane area in the supported liquid membrane and secondly, due to saturation of the membrane pores with metal carrier species and build-up of the carrier layer on the membrane interface, enhancing the retention of the separating constituent on the entry side and thus causing the permeability flux to reach a constant value [31].
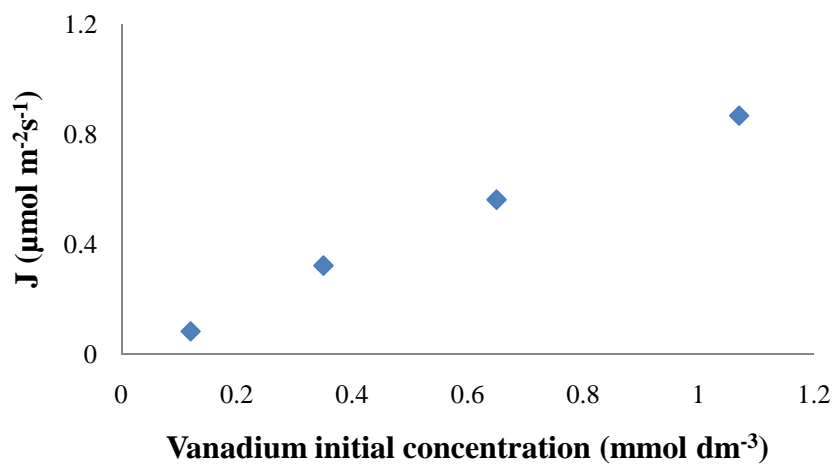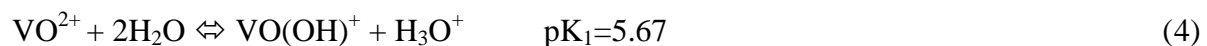

Fig. 8 The effect of initial vanadium concentration on the flux

3.6 *The transport mechanism of vanadium across the supported liquid membrane*

As already mentioned, vanadium forms different hydrolyzed species in aqueous solution and the distribution of the vanadium (IV) species varies dependent upon the pH and total vanadium concentration. The primary hydrolyzed vanadium (IV) species are distributed as [32]:

$$VO^{2+} + 2H_2O \Leftrightarrow VO(OH)^+ + H_3O^+ \qquad pK_1=5.67 \qquad (4)$$

$$2VO^{2+} + 4H_2O \Leftrightarrow (VO)_2(OH)_2{}^{2+} + 2H_3O^+ \qquad pK_2=6.67 \qquad (5)$$

According to Bhatnagar, et al. [1], vanadium forms cations below pH value of 3 and in the pH range of 4-11, the anions are dominant. In this study, for the extraction of vanadium (IV) the feed

contained vanadyl sulphate ($VOSO_4 . xH_2O$) and the tetravalent vanadium in the form of oxo-complex VO^{2+} is the dominating cationic species. Color inspection confirms the existence of vanadium(IV) species throughout the conducted experiments. In the feed-supported liquid membrane interface, the vanadium that exists as VO^{2+} ion, forms a neutral complex VOL (L represents the Ligand carrier). At the supported liquid membrane-receiving phase interface, vanadium is extracted from the organic phase [33]. The mechanism of the ion pair mediated transport is given in Fig. 9. At the interface between feed and membrane, metal ion pair forms complex with ligand and the [VO L] complex diffuses through the membrane. At the interface between membrane and stripping phase, i.e. in alkaline condition, the complex collapses releasing the carrier thereby liberating the metal ion into the receiving phase. Finally, the ligand carrier diffuses back across the membrane aqueous boundary layers to the feed solution-membrane interface where the cycle starts again [34, 35].
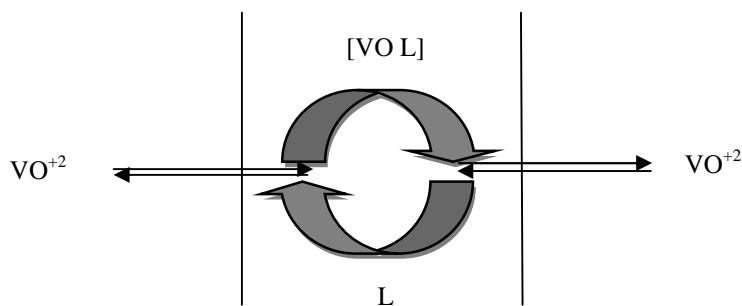

Fig. 9 Mechanism of ion-pair intervened transport through supported liquid membrane

3.7 Selectivity tests

In a previous study [23], the extractant Cyanex 923 was applied as a carrier to remove chromium from aqueous solution. In this study, its performance has been compared to TOMAC, as shown in Fig. 10. The permeation rate for TOMAC is obviously higher than that of Cyanex 923.

Consequently, TOMAC emerged to be a prospective extractant for chromium. The selectivity of TOMAC- based supported liquid membrane towards vanadium (IV) and chromium (VI) ions was assessed. A solution of identical concentrations of chromium (VI) and vanadium (V) was used in the feed compartment. The stripping cell contained sodium hydroxide solution. The concentration change in the feed phase was measured in order to determine the selectivity. Fig. 11 shows that the selectivity of chromium over vanadium was as high as 2.6. In the next step, the removal process was carried out using ammonia solution as the stripping agent. It is worth noting that the selectivity dramatically changed towards the vanadium ion over chromium, as illustrated in Fig. 12. This achievement confirms that the selectivity of vanadium (V) over chromium (VI) depends strongly on the nature of the stripping agent.
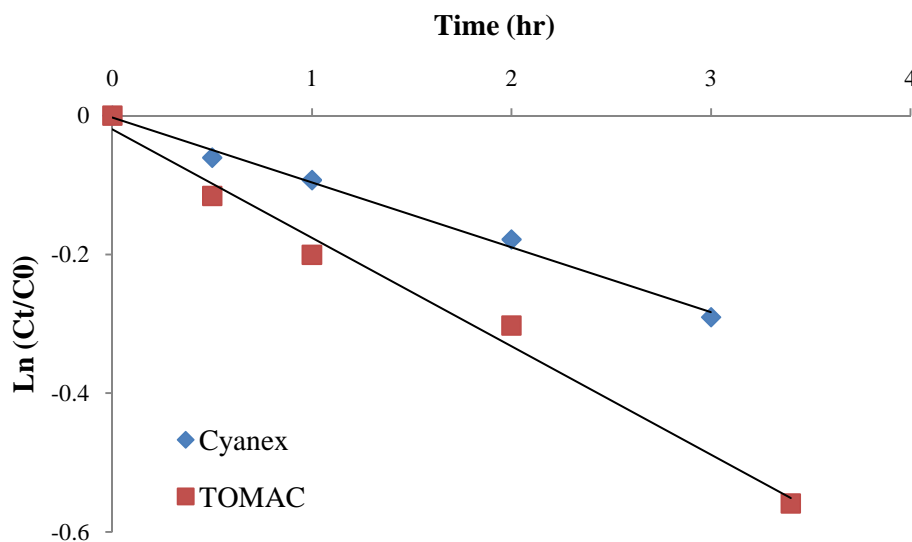

Fig. 10 A comparison of chromium removal between the metal extractant Cyanex 923 and TOMAC.
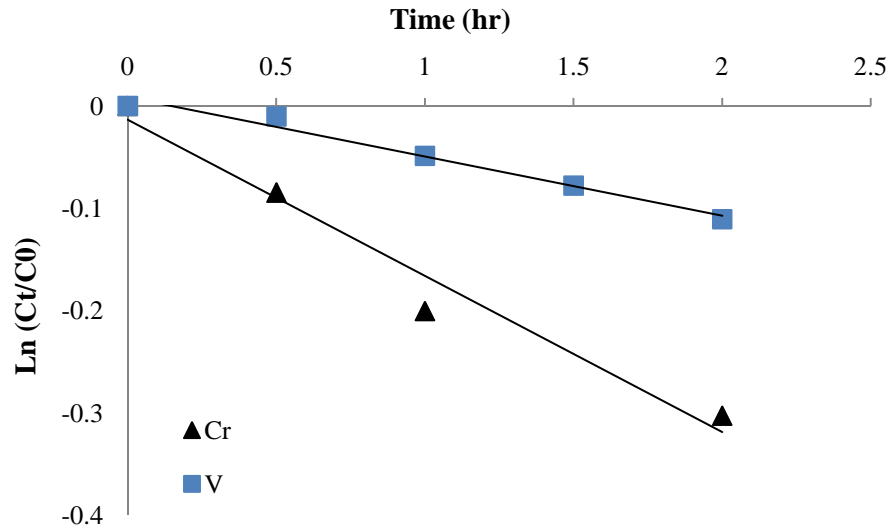
Fig. 11 Plot of ln (C_t/C_0) vs. operation time for vanadium and chromium transport across supported liquid membrane using sodium hydroxide as stripping agent
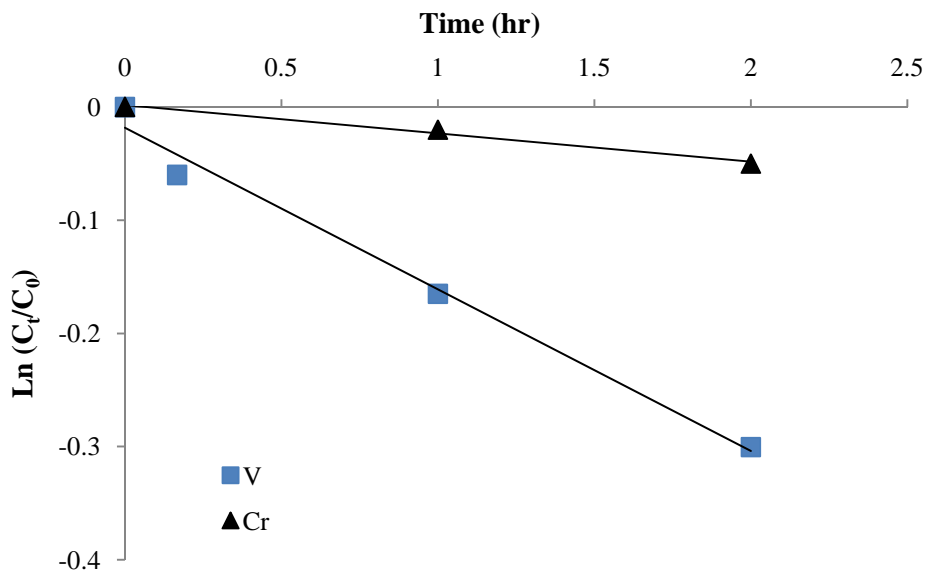

Fig. 12 Plot of ln (C_t/C_0) vs. operation time for vanadium and chromium transport across supported liquid membrane using ammonia as stripping agent

4. Conclusion

Vanadium was effectively transported from the feed phase to the stripping phase of ammonia solution using the room temperature ionic liquid, TOMAC, impregnated in the PTFE support

membrane. A significant higher transfer rate of vanadium ion was observed while using an acidic feed solution without adjusting initial pH. Moreover, it was observed that adding a slight amount of a second room temperature ionic liquid, [BMIM][NTF$_2$], improves the extraction process remarkably. Selective transport of vanadium from its mixture with chromium ions was also carried out applying TOMAC as the carrier. The selectivity of vanadium (V) over chromium (VI) depended strongly on the nature of the stripping agent.

Acknowledgements

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