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On the potential of a poly(vinylidenefluoride-*co*-hexafluoropropylene) polymer inclusion membrane containing Aliquat® 336 and dibutyl phthalate for V(V) extraction from sulfate solutions

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Abstract: A polymer inclusion membrane (PIM) composed of 50 wt% poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) as its base polymer, 40 wt% Aliquat® 336 as its extractant and 10 wt% dibutyl phthalate (DBP) as plasticizer provided efficient extraction of vanadium(V) from its sulfate solutions adjusted to pH 2.5. It was suggested that V(V) was extracted as $VO_2SO_4^-$ via an anion exchange mechanism. Quantitative back-extraction was achieved in a sulfuric acid solution (6 mol L^{-1}) containing 1 v/v% of hydrogen peroxide. It was assumed that the back-extraction process involved the oxidation of VO_2^+ to $VO(O_2)^+$ by hydrogen peroxide. The newly developed PIM with the optimized composition mentioned above exhibited excellent selectivity for V(V) in the presence of metallic species present in digests of spent alumina hydrodesulfurization catalysts (i.e., Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II)). The co-extraction of Mo(VI) with V(V) was eliminated by its selective extraction at pH 1.1. The optimized PIM was characterized by contact angle measurements, atomic-force microscopy (AFM), energy dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA)/derivatives thermogravimetric analysis (DTGA), and the stress-strain measurements.

Keywords: Polymer inclusion membrane (PIM); Poly(vinylidenefluoride-*co*-hexafluoropropylene); Vanadium(V); Extraction; Aliquat® 336

1. Introduction

Vanadium with some unique properties including hardness, fatigue resistance, tensile strength, good corrosion resistance at low temperature and high melting point [1], is a valuable metal used extensively in a variety of industries such as electronic equipment, automobile fabrication, nuclear reactor construction, glass coating processes, and catalyst production [2,3]. It is estimated that vanadium forms 0.019% of the Earth's crust (18th among the most abundant elements) [4]. Nevertheless, the great amount of industrial needs and the increasing consumption of this element, on one hand, and the depletion of the corresponding mineral resources, on the other hand, require the development of efficient methods for the recovery of vanadium from the second-hand sources and

industrial residuals [5]. Moreover, vanadium is considered as a serious contaminant [6] similarly to mercury, lead, and arsenic [7]. The International Agency for Research on Cancer reported that vanadium is possibly carcinogenic to humans [8]. Among the vanadium species with different oxidation states, its pentavalent oxidation state is more noxious than the others [6]. Thus, vanadium pollution of water sources, due to discharging of improperly managed industrial wastes, is of considerable environmental concern which together with the associated economic benefits justifies the recovery of vanadium from industrial wastes [9] and its clean-up from contaminated water sources [10].

Though solid phase extraction of vanadium using metal oxides [11] and modified chitosan [12] as adsorbents has shown some success in vanadium clean-up of contaminated waters, solvent extraction has evolved as the most popular technique for the recovery of vanadium [13,14]. This separation technique is relatively simple to execute, rapid, applicable for large-scale separation processes, highly selective, and does not require sophisticated equipment [15]. However, industrial solvent extraction uses large volumes of volatile, flammable and toxic diluents and significant amount of energy which is of considerable safety and environmental concern [16].

Separation based on the use of liquid membranes offers an attractive alternative to solvent extraction applications in both chemical analysis and industrial production [17]. Bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs) have been studied extensively for their potential in industrial separation and water treatment [18]. The limited interfacial surface area and slow mass transfer rates are the main disadvantages of separation based on bulk liquid membranes. The limitations in the use of emulsion liquid membranes are caused mainly by difficulties associated with the formation and breakdown of the double emulsion used. Relatively poor long-term stability caused by leaking of the extractant solution into the adjacent aqueous phases is the main drawback of SLMs [19].

Polymer inclusion membranes (PIMs) are a relatively new type of liquid membranes which are composed of a base polymer and an extractant, often referred to as carrier [20]. In some cases, a plasticizer/modifier may also be present in the PIM composition. Although the introduction of PIMs as the sensing membranes in ion-selective electrode dates back more than 50 years, PIM applications in industrial and analytical separation have attracted significant interest only for the past decade [21]. PIMs are visibly similar to SLMs, but they have a different structure, i.e., the extractant is located within a network of nanometre size channels in PIMs while it is retained by capillary forces within micrometer size pores of SLMs thus leading to poorer long-term stability [19].

Aliquat® 336, an ionic liquid, is a mixture of quaternary alkylammonium chlorides in which the main component is trioctylmethylammonium chloride (called also tricaprylmethylammonium chloride). The potential of Aliquat® 336 as an anionic extractant has been utilised in a variety of separation techniques, including solvent extraction methods [22], and those based on the use of bulk liquid membranes [23], emulsion liquid membranes [24], supported liquid membranes [25], and polymer inclusion membranes [26].

Although the suitability of Aliquat® 336 for the extraction-based separation of V(V) has been already demonstrated [27,28], to the best of the author's knowledge the use of this extractant in polymer inclusion membranes for the extraction of V(V) has not been reported. In fact, there is just one published study of a PIM application for the separation of V(V) [29], which describes the potential of a PIM composed of poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) as its base polymer, trihexyltetradecylphosphonium chloride (Cyphos® IL 101) as its extractant and 2-nitrophenyloctyl ether (NPOE) as its plasticizer for the separation of V(V) from its sulfate solutions.

This paper reports on the development of a method for the separation of V(V) from its sulfate solutions using a PVDF-HFP based PIM containing Aliquat® 336 as its extractant and dibutyl phthalate as its plasticizer.

2. Experimental

2.1. Reagents

Aliquat® 336 (≥ 98%, Aldrich, USA), PVDF-HFP (Aldrich, USA), HPLC grade tetrahydrofuran (THF) (99.9%, Samchun, South Korea), 2-nitrophenyloctyl ether (NPOE) (> 99%, Fluka, Switzerland), tributylphosphate (TBP) (> 98%, Merck, Germany), tris(2-ethylhexyl)phosphate (TEHP) (≥ 98%, Merck, Germany), dibutyl phthalate (DBP) (99%, Merck, Germany), reduced graphene oxide nanoplatelets (rGONPs) (Green Nanoscale Technology, Iran) were used in the PIM preparation. Sodium orthovanadate (99.98%, Sigma-Aldrich, USA), hydrogen peroxide (36%, Dr. Mojallali, Iran), barium chloride dihydrate (≥ 99%, Merck, Germany), sodium carbonate (≥ 99.9%, Merck, Germany), sodium sulfate anhydrous (≥ 99%, Dr. Mojallali, Iran), sulfuric acid (98%, Merck, Germany), hydrochloric acid (37%, Dr. Mojallali, Iran), nitric acid (65%, Merck, Germany), and sodium hydroxide (≥ 95%, Dr. Mojallali, Iran) were utilized in the preparation of the solutions employed in the extraction and back-extraction experiments. Aluminium chloride (≥ 98%, Merck, Germany), manganese(II) nitrate tetrahydrate (≥ 98.5%, Merck, Germany), nickel(II) nitrate hexahydrate (≥ 96%, Fluka, Switzerland), copper(II) nitrate trihydrate (≥ 99.5%, Merck, Germany), iron(III) nitrate (≥ 99%, Merck, Germany), cobalt(II) nitrate hexahydrate (≥ 99%, Merck, Germany), and sodium molybdate(VI) dihydrate (≥ 99%, Acros, USA) were used in investigating PIM selectivity. Xylenol orange (Merck, Germany), used as the colorimetric reagent for the analysis of V(V), was dissolved in an acetate buffer solution. The buffer solution was prepared by using glacial acetic acid (≥ 99.8%, Dr. Mojallali, Iran). Deionized water (resistivity ≥ 18.2 MΩ cm, Zolalan, m-uv-3⁺, Iran) was used for the preparation of all aqueous solutions.

2.2. Instrumentation

A circulating water bath fitted with a digital thermoregulator (Org Mp-5, Julabo, Germany) was used for keeping the temperature constant during the dissolution of the PIM components in THF. Membrane casting solutions were stirred using a magnetic stirrer (IKA, Germany). A platform orbital shaker (PIT 10 LO, PIT, Iran) was employed for shaking the source and back-extraction solutions during the extraction and back-

extraction experiments. The pH measurements were done with a glass electrode (Metrohm, Switzerland) connected to a pH meter (780, Metrohm, Switzerland). A UV–visible spectrophotometer (DR5000, Hach, USA) was used for the detection of the V(V)-xylenol orange complex. Flame atomic absorption spectrometry (FAAS) with nitrous oxide/acetylene flame (novAA 350, Analytic Jena, Germany) was employed for the analysis of vanadium in the cases that the chemical composition of the samples prohibited the determination of V(V) by the spectrophotometric method mentioned above. Membrane thickness measurements were made using a caliper (SL-M, Insize, China). The homogeneity of the PIMs was characterized by energy dispersive X-ray spectroscopy (TESCAN mira3, Czech Republic). An atomic force microscope (AFM) (Nano Vac, Ara Research Company, Iran), operated in contact mode, was used for studying membrane surface morphology. Thermogravimetric analysis (TGA) and derivatives thermogravimetric analysis (DTGA) were done by using a STA 409 PC/PG analyser (Netzsch, Germany). A contact angle goniometer (CAG-10, Jikan, Iran) was employed for the contact angle measurements. The stress-strain behaviour of the PIMs was followed by using a force digital gauge (STM-5 Cap. 5 kN, Santam, Iran) connected to a personal computer. The samples studied were 1 cm in width and 5 cm in length. All the measurements were performed at a strength rate of 50 mm min^{-1}.

2.3. Membrane preparation

PIMs were prepared by dissolving 1.0 g PVDF-HFP, Aliquat® 336 and plasticizer in 10 mL of THF (10 mL of THF per 1 g of the polymer PVDF-HFP). The mixture was magnetically stirred for 2 h at room temperature (22±1 °C), followed by a further 2 h of stirring at 40 °C. The solution was poured into a homemade Teflon casting knife [30], placed on a glass plate. The casting knife was then displaced athwart the glass plate to form a thin layer of the membrane casting solution. The glass plate was covered with an aluminium tray to allow slow evaporation of THF for 24 h. Circular membrane segments were cut from the casted PIM (using a 3.5 cm diameter steel punch) and used in the extraction and back-extraction experiments. The membrane with an optimal composition (i.e., 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP) had an average mass of 0.057 ± 0.005 g and the thickness of 46 ± 6 μm, respectively.

2.4. Extraction and back-extraction experiments

In the extraction experiments, circular PIM segments (3.5 cm in diameter) were immersed in 50 mL of solutions containing 9.8×10^{-4} mol L^{-1} (50 mg L^{-1}) V(V) and 0.2 mol L^{-1} sulfate. The pH of these solutions was adjusted to 2.5 by adding sulfuric acid or sodium hydroxide solutions. The solutions containing the PIM were agitated on a platform orbital shaker (200 rpm). Sampling was performed by withdrawing 0.2 mL of solution at predetermined times during the experiments. The samples were diluted and analysed either spectrophotometrically at 522 nm for the determination of V(V) with the complexing reagent xylenol orange or by FAAS.

2.5. Eliminating the co-extraction Mo(VI) with V(V)

A two-step procedure developed in an earlier study [29] was applied for the removal of Mo(VI) which otherwise would be co-extracted with V(V). The first step involved the adjustment of the aqueous 0.2 mol L^{-1} sulfate solution, containing V(V), Mo(VI) Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) (50 mg L^{-1} each), to pH 1.1 and immersing an optimized PIM in this solution for 24 h under shaking. The PIM was then removed from the solution and immersed in 50 mL of 6 mol L^{-1} H_2SO_4 containing 1 v/v% H_2O_2 for the recovery of the extracted metallic species. In the second step of the approach, the solution pH was increased to 2.5 and a fresh 3.5 cm circular PIM was immersed in it for 24 h under shaking. This was followed by withdrawing the PIM from the solution, rinsing it with deionized water and immersing it in 50 mL of 6 mol L^{-1} H_2SO_4 solution containing 1 v/v% of H_2O_2.

3. Results and discussion

3.1 Preliminary extraction experiments

The variation of the extraction percentage of V(V) as a function of the aqueous source solution pH was investigated by performing a series of extraction experiments using the PIMs composed of 70 wt% of PVDF-HFP and 30 wt% Aliquat® 336. In these experiments, a circular PIM with 3.5 cm diameter was immersed in 50 mL of 0.2 mol L^{-1} sulfate solution containing 50 mg L^{-1} V(V) ions. The pH of the aqueous solutions was adjusted to 1.5, 1.8, 2.1, 2.3, or 2.7, and the extraction percentage of V(V) after 8 h was measured (Figure 1).
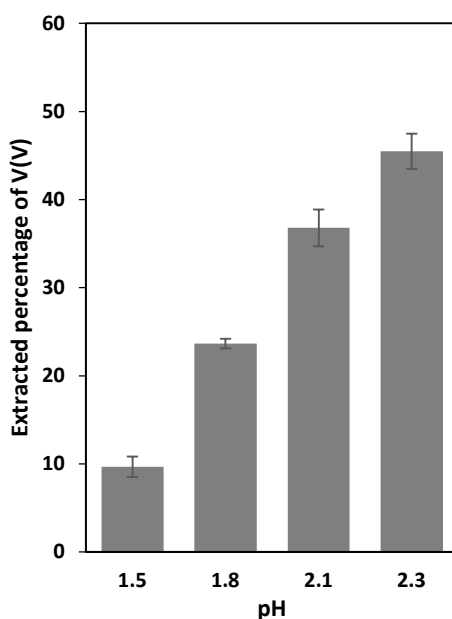

Figure 1. Effect of the aqueous source solution pH on the extraction of V(V) (initial concentration 50 mg L^{-1}) from 0.2 mol L^{-1} sulfate solutions into PVDF-HFP-based PIMs containing 30 wt% Aliquat® 336. PIMs/aqueous source solution contact time and temperature were 8 h and 22±1 °C, respectively. Error bars = ± standard deviation (SD).

As expected, the extraction of V(V) was found to be pH-dependent. The PIM in contact with the solution adjusted to pH 1.5 was colorless and transparent. Under such conditions, the extraction percentage of V(V) was lower than 10%. When the solution pH was increased to 1.8 and 2.1, the PIMs became brown but remained transparent. The extraction percentages of V(V) from such solutions were around 24% and 37%, respectively. The transparency of the PIMs at the pH mentioned above at equilibration indicated that the membranes were homogeneous and thus compatible with the extracted complex.

By increasing the pH to 2.3, the increase in the extraction percentage of V(V) caused the opaqueness of the PIMs. This observation attributed to low solubility of the extracted V(V)- Aliquat® 336 adduct in the PIM liquid phase. A further increase in pH to 2.7 resulted in the formation of yellow-colored sediment on the surface of the PIMs which was most likley polyoxovanadate [3].

3.2. Selection of a plasticizer/modifier

The improvement of the compatibility of the membrane components and/or improvement in the solubility of the extracted adduct into the membrane liquid phase are the main roles attributed to the plasticizer/modifier in a PIM [31]. Therefore, the effect of several plasticizers/modifiers including NPOE, DBP, TEHP, and TBP on reducing/eliminating the incompatibility issues mentioned above was studied and the results are presented in Figure 2.
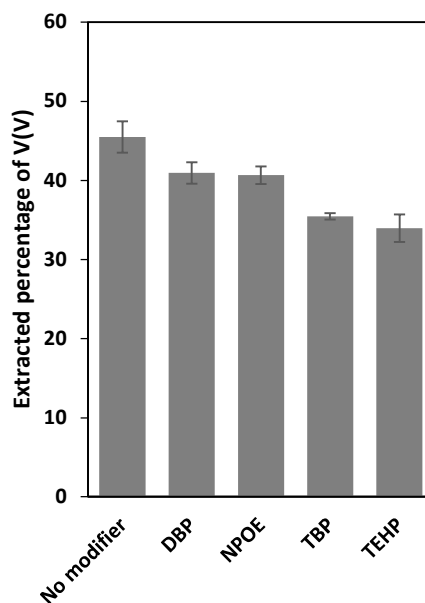

Figure 2. Effect of the modifier on the extraction of V(V) from aqueous 0.2 mol L^{-1} sulfate solutions adjusted to pH 2.3 and containing initially 50 mg L^{-1} V(V) into PVDF-HFP-based PIMs either 30 wt% Aliquat® 336 and no modifier or 25 wt% Aliquat® 336 and 5 wt% modifier (DBP, NPOE, TBP, or TEHP). PIMs/aqueous source solution contact time and temperature were 8 h and 22±1 °C, respectively. Error bars = ± SD.

The results revealed that all 4 modifiers eliminated the limited solubility of the V(V)-Aliquat® 336 adduct in the corresponding PIMs. The higher extraction percentage of V(V)

by the modifier free PIM compared to that of 4 modifier containing PIMs (Figure 2) was attributed to their lower concentration of Aliquat® 336, i.e., 25 wt% as opposed to 30 wt% in the modifier free PIMs. The results showed also that the extraction percentage of V(V) in the PIMs containing a modifier decreased in the order DBP ≈ NPOE > TBP > TEHP. Taking into account the similar extraction results for the PIMs containing NPOE or DBP and the higher cost of NPOE, DBP was selected as the PIM modifier for the subsequent experiments.

3.3. Optimization of the PIMs composition

To determine the optimal PIM composition, a series of PIMs with different concentrations of their components were prepared. These PIMs covered the ranges of 50–90 wt% PVDF-HFP, 10–50 wt% Aliquat® 336, and 0-20 wt% DBP. It was found that PIMs containing more than 15 wt% DBP were sticky and mechanically weak. In addition, PIMs with the extractant and polymer concentrations greater than 40 wt% and 55wt%, respectively, were also discarded because while being initially transparent, they became cloudy and opaque when used in a single extraction experiment. The PIMs which were transparent, homogeneous, flexible, and mechanically stable (Table. 1) were deemed as successful and were examined in the extraction experiments.

Table 1. Comparison of the extraction percentages of the successful PIMs.[a]

PIM	PVDF-HFP (wt%)	Aliquat® 336 (wt%)	DBP (wt%)	Extracted V(V) ± SD (%)
1	50	35	15	61.41 ± 0.82
2	55	35	10	61.48 ± 1.06
3	55	40	5	62.19 ± 0.49
4	50	40	10	63.80 ± 0.42

[a] The remaining experimental conditions are outlined in Figure 2.

All 4 successful PIMs did not change their physical properties as a result of the extraction experiments. Therefore, the PIM with the composition of 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP was selected as the best performing PIM for the subsequent experiments.

3.4. Effect of the aqueous solution pH on the extraction rate of V(V)

Based on the results obtained in the preliminary experiments, the pH of the source solution was varied between 1 and 2.5. Figure 3 shows its effect on the extraction of V(V) by the PIM composed of 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP. The results confirmed that the extracted amount of V(V) for 24 h, increased from 11.6% to 76.3% as the solution pH was raised from 1 to 2.5, respectively. For pH values above 2.5 the V(V)-Aliquat® 336 started precipitating. Therefore, pH 2.5 was selected as the optimal pH for the source solution. It should be noted that $VO_2SO_4^-$ is the dominant vanadium species in the source solution under the experimental conditions (i.e., pH 1-3 and V(V) concentration of the order of 10^{-4} mol L^{-1}) [3].
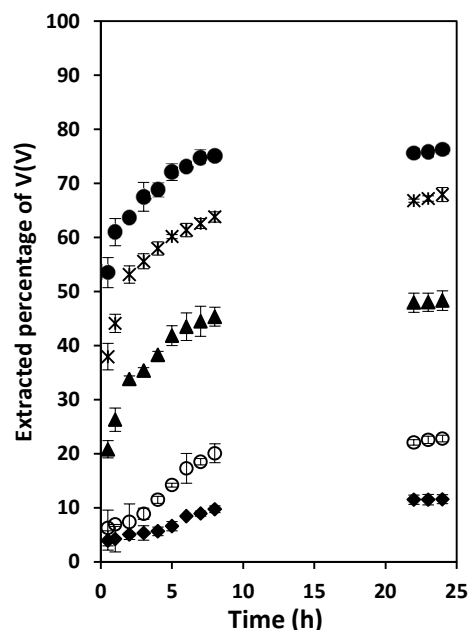
Figure 3. Variation of the extraction percentage of V(V) during extraction from aqueous solutions adjusted to pH 1 ◆, 1.5 ○, 2.0 ▲, 2.3 ✶, or 2.5 ●. Experimental conditions: aqueous solution composition - 50 mg L⁻¹ V(V) and 0.2 mol L⁻¹ sulfate; PIM composition – 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP; PIMs/aqueous source solution contact time and solution temperature - 24 h and 22±1 °C, respectively. Error bars = ± SD.

3.5. Effect of the sulfate ion concentration and characterization of the extracted species

Since $VO_2SO_4^-$ is the dominant V(V) species present in the aqueous source solution under the selected experimental conditions, it is expected that the extraction of the V(V) follows the anion exchange mechanism described by Equation (1) [32], [33], [29].

$$VO_2SO_4^-\,_{(aq)} + R_3R'N^+Cl^-\,_{(PIM)} \leftrightarrows [R_3R'N^+\bullet VO_2SO_4^-]_{(PIM)} + Cl^-\,_{(aq)} \qquad (1)$$
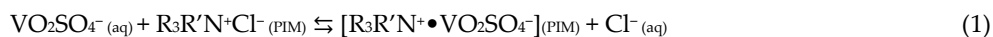
where $R_3R'N^+Cl^-$ denotes Aliquat® 336.

As the sulfate anion is involved in the extraction of V(V), its effect was evaluated by varying its source solution concentration (i.e., 0.03, 0.05, 0.1, 0.2, and 0.3 mol L⁻¹). A yellow precipitate was formed on the surface of the PIMs when the sulfate concentration was lower than 0.1 mol L⁻¹. The yellow precipitate has been most likely the result of polyoxovanadates formation at these low concentrations of the sulfate ion. The extraction of V(V) was found to be independent of the sulfate concentration when it was higher than 0.1 mol L⁻¹ which was in agreement with the results of an earlier study [29]. Therefore, the subsequent extraction experiments were carried out by adjusting the sulfate ion concentration and the pH of the aqueous solutions to 0.2 mol L⁻¹ and 2.5, respectively.

The stoichiometry of the extracted V(V) adduct (Equation (1)) was confirmed by performing a series of extraction experiments of V(V) from source solutions adjusted to pH 2.5 and containing V(V) in the concentration range 30-110 mg L⁻¹ and 0.2 mol L⁻¹ sulfate. The results presented in Figure 4 indicated that the PIM was saturated with V(V)

when the mole ratio V(V)/Aliquat® 336 approached 1 which was in agreement with Equation (1). The PIM capacity was calculated as 56 mg V(V) per 1 g of PIM.
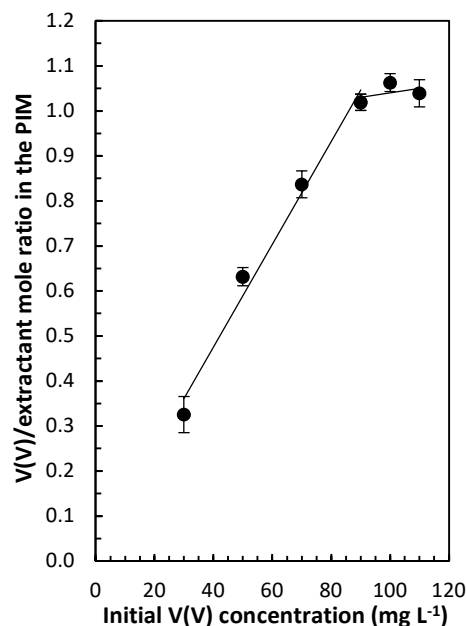

Figure 4. The variation of V(V)/Aliquat® 336 mole ratio in the PIM studied (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP) as a function of the initial V(V) concentration in the aqueous source solution containing 0.2 mol L^{-1} sodium sulfate and adjusted to pH 2.5. PIMs/aqueous source solution contact time and temperature were 24 h and 22±1 °C, respectively. Error bars = ± SD.

3.7. Back-extraction studies

The average percentage of V(V) extracted after 24 h into the best performing PIM (#4, Table 1) from aqueous source solutions containing 50 mg L^{-1} V(V) and adjusted to pH 2.5 was determined to be 76.3 ± 0.5% which corresponded to 60% saturation with respect to the moles of extractant in the PIM. A back-extraction study in which loaded with V(V) PIMs were immersing for 24 h into 1 mol L^{-1} solutions of hydrochloric acid, nitric acid or sulfuric acid under shaking produced back-extraction percentages of 44.6 ± 0.9%, 44.4 ± 0.8% and 56.1 ± 1.1%, respectively. Although the back-extraction of V(V) was relatively more successful by using the sulfuric acid solution, none of the tested stripping reagents were able to provide a quantitative V(V) back-extraction. Therefore, back-extraction experiments with higher concentrations of sulfuric acid were conducted which demonstrated that an increase in the sulfuric acid concentration increased both the back-extraction percentage and its rate (Figure 5). However, quantitative back-extraction of V(V) could not be achieved even in the case when a 6 mol L^{-1} sulfuric acid solution was used.
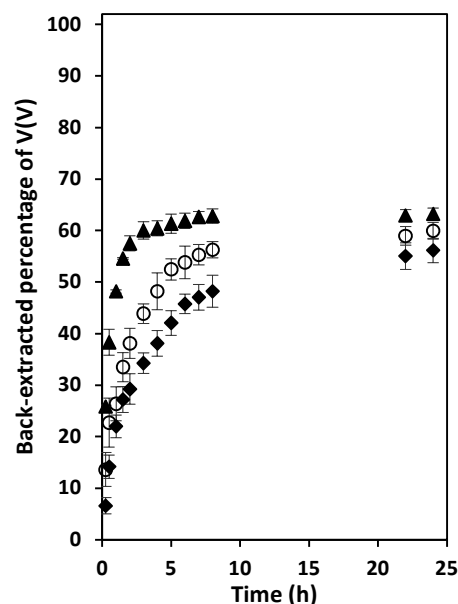
Figure 5. Back-extraction percentage of V(V) from loaded PIMs (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP; 33.5 mg V(V)/g PIM) in solutions containing 1.0 (◆), 3.0 (○), or 6.0 (▲) mol L^{-1} sulfuric acid under shaking as a function of time. PIMs/aqueous back-extraction solution contact time and temperature were 24 h and 22±1 °C, respectively. Error bars = ± SD.

The possibility of improving the efficiency of back-extraction by converting the back-extracted VO_2^+ species to the oxoperoxo species $VO(O_2)^+$ in the presence of H_2O_2 (Equation (2), [34]) was explored by adding H_2O_2 to the sulfuric acid back-extraction solution.

$$VO_2^+ + H_2O_2 \rightarrow VO(O_2)^+ + H_2O \qquad (K = 3.5 \times 10^4 \text{ at } 25 \text{ °C}) \tag{2}$$
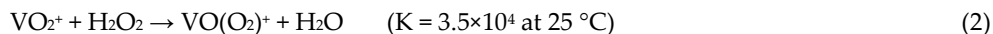
The overall back-extraction process in this case can be described by Equation (3).

$$VO_2SO_4^-{}_{(PIM)} + H^+{}_{(aq)} + H_2O_2{}_{(aq)} \rightarrow VO(O_2)^+{}_{aq} + HSO_4^-{}_{(PIM)} + H_2O_{(aq)} \tag{3}$$
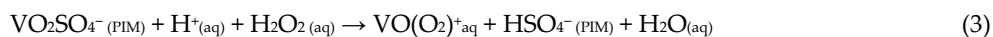
where the subscripts "aq" and "PIM" denote "aqueous" or "PIM", respectively.

The results when the back-extraction solution contained 1 mol L^{-1} sulfuric acid 1 v/v% H_2O_2 showed that the presence of hydrogen peroxide increased the V(V) back-extraction percentage from 56.1 ± 0.4% to 71.1 ± 0.4%. Increasing the concentration of sulfuric acid to 3 and 6 mol L^{-1} while maintaining the H_2O_2 concentration at 1 v/v% further enhanced back-extraction efficiency, reaching complete back-extraction at 6 mol L^{-1} (Figure 6).
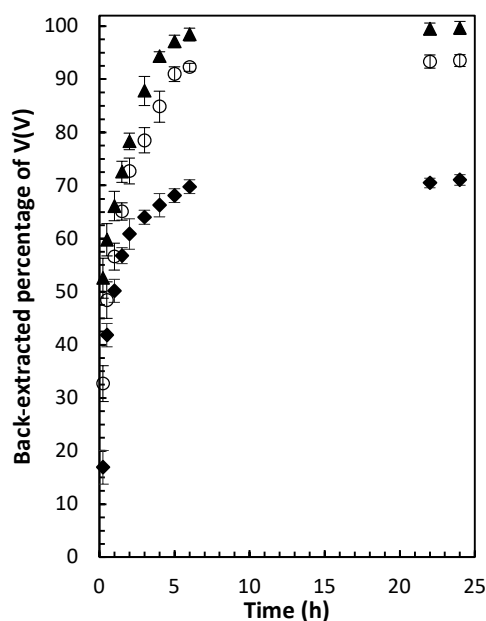
Figure 6. Back-extracted percentage of V(V) from PIMs (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP, 33.5 mg V(V)/g PIM) using sulfuric acid solutions (1.0 ◆, 3.0 ○, and 6.0 ▲ mol L^{-1}) containing 1 v/v% H_2O_2 as a function of time. PIMs/aqueous back-extraction solution contact time and temperature were 24 h and 22±1 °C, respectively. Error bars = ± SD.

It should be noted that the back-extraction solution was reddish-brown (Figure 7) thus confirming the presence of the $VO(O_2)^+$ species [35]. To confirm the presence of the sulfate ion in the PIM as a result of the back-extraction process described by Equation (3), a back-extracted PIM was washed with deionized water and then immersed in a dilute solution of $BaCl_2$. The formation of the white $BaSO_4$ precipitate on the PIM surface indicated the presence of sulfate species in the PIM which were exchanged for the chloride ions of the $BaCl_2$ reagent.
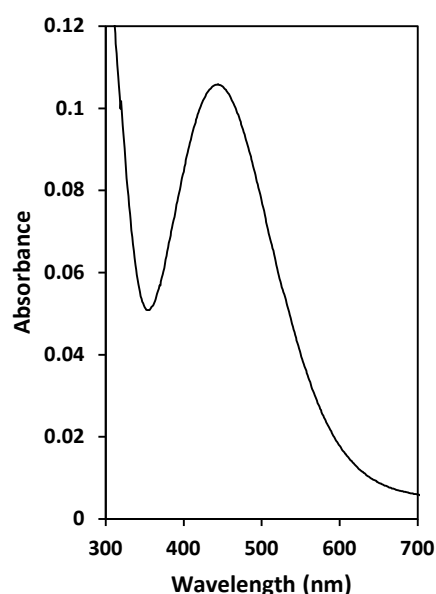
Figure 7. UV-Vis spectrum of the back-extraction solution (6 mol L^{-1} H$_2$SO$_4$ + 1 v/v% H$_2$O$_2$) confirms the presence of the VO(O$_2$)$^+$ species [35].

3.8. PIM selectivity

The optimized PIM (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP) was assessed for its selectivity in the extraction of V(V) from solutions containing Mo(VI), Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) species, usually present in digests of spent hydrodesulfurization catalysts. Experiments involving the extraction of V(V) from solutions containing only one or all of these metallic species showed that except for Mo(VI), the newly developed PIM was highly selective for V(V) (Table 2). These results are in agreement with those of a previous study where a PIM composed of PVDF-HFP, Cyphos® IL 101 (trihexyltetradecylphosphonium chloride) and NPOE, as the base polymer, extractant, and plasticizer, respectively, was applied to the extraction of V(V) from solutions of similar composition [29].

Table 2. Extraction and back-extraction percentages of V(V) from its solutions containing other metallic species.[a,b]

Solution	Metallic species	Extraction (%)	Back-extraction (%)
1	V(V)	76.3 ± 0.6	76.1 ± 0.6
2	V(V)	52.2 ± 2.1	51.7 ± 1.5
	Mo(VI)	98.6 ± 2.6	20.0 ± 2.0
3	V(V)	72.3 ± 0.7	71.4 ± 0.4
	Al(III)	2.6 ± 0.9	ND
4	V(V)	73.9 ± 1.1	73.6 ± 1.3
	Co(II)	0.6 ± 2.0	ND
5	V(V)	74.4 ± 1.9	74.0 ± 0.7
	Cu(II)	ND	ND

6	V(V)	75.2 ± 2.1	75.0 ± 1.8
	Fe(III)	ND	ND
7	V(V)	76.1 ± 1.6	76.0 ± 1.8
	Mn(II)	ND	ND
8	V(V)	73.2 ± 2.2	72.9 ± 1.3
	Ni(II)	ND	ND
9	V(V)	50.4 ± 1.3	49.6 ± 0.5
	Mo(VI)	99.3 ± 2.6	19.8 ± 2.1
	Al(III)	ND	ND
	Co(II)	ND	ND
	Cu(II)	ND	ND
	Fe(III)	ND	ND
	Mn(II)	ND	ND
	Ni(II)	ND	ND

[a]PIMs: 3.5 cm diameter circular segments containing 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP. Extraction: initial aqueous source solution: 50 mL V(V) alone or with other ions (each 50 mg L^{-1}) adjusted to 0.2 mol L^{-1} sulfate and pH 2.5, extraction time 24 h. Back-extraction: 50 mL 6 mol L^{-1} sulfuric acid and 1 v/v% hydrogen peroxide, back-extraction time 24 h. [b]ND - not detectable.

The co-extraction of Mo(VI) from Solution 2 decreased the extraction percentage of V(V) by approximately 24%. Therefore, under the selected experimental conditions, the PIM could only be directly applied for the separation of V(V) from samples which did not contain Mo(VI). Therefore, it was necessary to remove Mo(VI) from the solution before using the PIM for the extraction of V(V). A two-step procedure developed in an earlier study [29] and outlined earlier was applied. The first step resulted in the quantitative removal of Mo(VI) while V(V) was selectively extracted in the second step. The results, presented in Table 3 indicate that the two-step procedure allowed the selective separation of V(V) from the initial solution containing Mo(VI), Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II).

Table 3. Results of a two-step extraction/back-extraction procedure for the selective PIM-based separation of V(V) from a source solution containing Mo(VI), Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) (50 mg L^{-1} each).[a,b]

Ionic Species	pH 1.1 (Step I)		pH 2.5 (Step II)	
	Extraction (%)	Back-extraction (%)	Extraction (%)	Back-extraction (%)
V(V)	ND	ND	74.2 ± 1.9	73.7 ± 1.4
Mo(VI)	96.4 ± 1.2	19.6 ± 2.6	ND	ND
Al(III)	ND	ND	ND	ND
Co(II)	ND	ND	ND	ND
Cu(II)	ND	ND	ND	ND
Fe(III)	ND	ND	ND	ND
Mn(II)	ND	ND	ND	ND
Ni(II)	ND	ND	ND	ND

[a]Experimental conditions: aqueous source solution - 50 mL, back-extraction solution: 50 mL, 6 mol L^{-1} H_2SO_4 and 1 v/v% H_2O_2, PIM composition: 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP, extraction and back-extraction time 24 h. [b]ND - not detectable.

3.9. PIM reusability and stability

The reusability of the newly developed PIM was evaluated by conducting five consecutive extraction/back-extraction cycles (24 h each) (Figure 9a). It was observed that the extraction efficiency of the PIM used in the second extraction/back-extraction cycle dropped ~24% with respect to its extraction efficiency in the first cycle. The extraction efficiency further decreased with each subsequent extraction/back-extraction cycle. The most likely reason for this effect was the leaching of the membrane liquid phase into the aqueous solutions in contact with the PIM, observed in other studies [36], which was confirmed by the membrane mass loss after each extraction/back-extraction cycle (Figure 8).
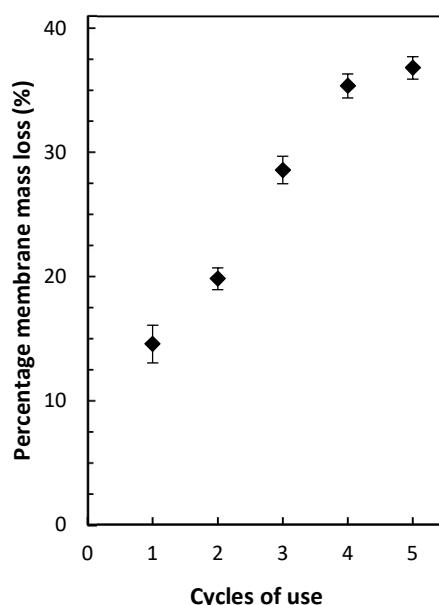

Figure 8. Percentage mass loss of PIMs containing PVDF-HFP/Aliquat® 336/DBP 50/40/10 wt% after each extraction/back-extraction cycle. Error bars = ± SD.

By assuming that the plasticizer influences the PIMs characteristics [37], DBP in the investigated PIM was replaced by NPOE to prepare a PIM composed of PVDF-HFP/Aliquat® 336/NPOE (50/40/10 wt%). Since it has been reported that the presence of reduced graphene oxide nanoparticles (rGONPs) may improve the stability of PIMs [38], PIMs containing PVDF-HFP/Aliquat® 336/DBP/rGONPs (49/40/10/1 wt%) were also prepared. The reusability of these PIMs was compared with that of the original DBP-based PIM. The results presented in Figures. 9a - 9c revealed that the replacement of DBP by NPOE improved to some extent the stability of the PIM unlike the addition of rGONPs. Comparison of these results with those reported on the extraction of V(V) by a PIM containing Cyphos® IL 101 [29] showed better stability for the Cyphos® IL 101 - based PIM due to the lower water solubility of Cyphos® IL 101 compared to Aliquat® 336.
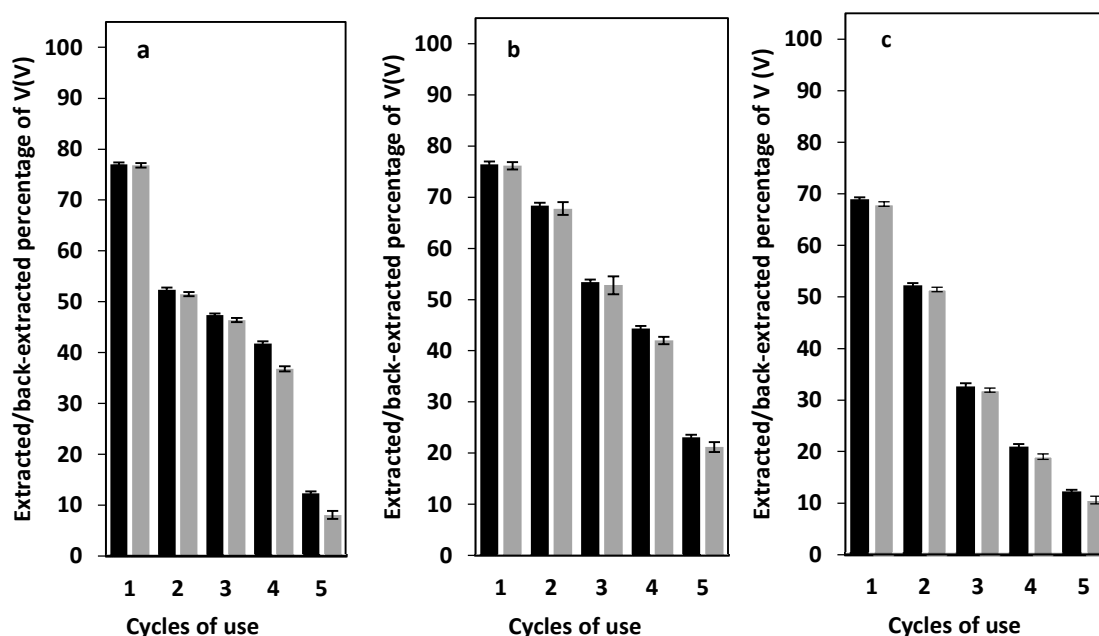
Figure 9. Extraction (black bars)/back-extraction (grey bars) percentage of V(V) in the case of PIMs containing (a) 50/40/10 wt% of PVDF-HFP/Aliquat® 336/DBP, (b) 50/40/10 wt% of PVDF-HFP/Aliquat® 336/NPOE, or (c) 49/40/10/1 wt% of PVDF-HFP/Aliquat® 336/DBP/rGONPs. Experimental conditions: aqueous source solution 50 mL of 50 mg L^{-1} V(V) and 0.2 mol L^{-1} sulfate ion (pH 2.5), back-extraction solution 50 mL of 6 mol L^{-1} H$_2$SO$_4$ and 1 V/V% H$_2$O$_2$. PIMs/aqueous solutions shaking time in both the extraction and back-extraction processes 24 h.

3.10. PIM's characterization

To evaluate the hydrophobicity of the optimized PIM, its contact angle was measured and compared with that of a blank PVDF-HFP film. The contact angle of the blank PVDF-HFP film (94°) was considerably higher than that of the PVDF-HFP/Aliquat® 336/DBP 50/40/10 wt% PIM (28°). The higher hydrophilicity of the optimized PIM could be attributed to the polar groups in both Aliquat® 336 and DBP. The contact angle values agree with the results obtained in the AFM study of the optimized PIM and the blank PVDF-HFP film, where it was found that the roughness of the former (3.82 nm) was lower than that of the latter (19.8 nm) (Figure 10). It is reported that rougher surfaces are characterised by higher contact angles [39]. The decreased roughness of the optimized PIM compared to that of the blank PVDF-HFP film can be attributed to the presence of the membrane liquid phase [40].
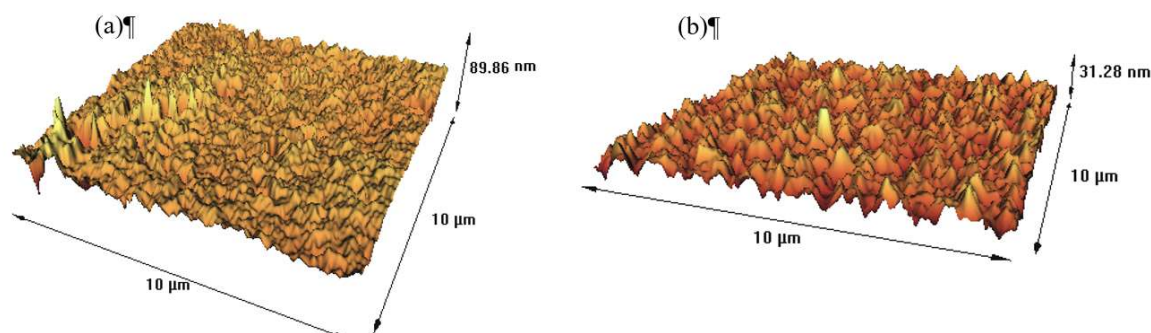
Figure 10. AFM three dimensional topographic images of the surface of (a) the blank PVD-HFP film and (b) the optimized PIM consisting of 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP.

Energy dispersive X-ray spectroscopy (EDS) can provide information about the uniformity of distribution of the extractant within the PIM. Figure 11, presenting an EDS image of the optimum PIM, indicates uniform distribution of nitrogen and chlorine, as two main constituent elements of Aliquat® 336 which are not encountered in the other membrane components.
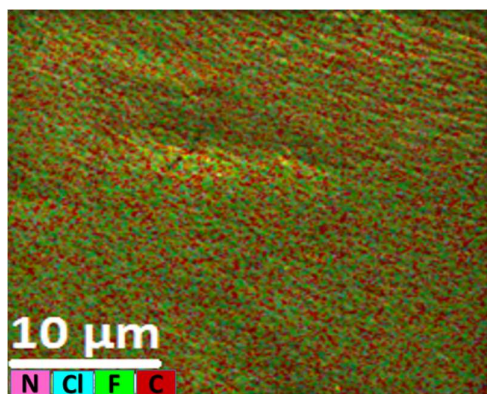

Figure 11. EDS-layered image and compositional map of the optimized PIM (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP).

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) results for the PVDF-HFP film and the optimized PIMs, presented in Figure 12, revealed that the blank PVDF-HFP underwent thermal decomposition under 450 °C in one single step with 91.0% mass loss (Figure 12a). However, the thermal decomposition of the optimized PIM proceeded in two main steps (Figure 12b). The first step, starting at approximately 170 °C, resulted in 48.0% mass loss and was attributed to the loss of both extractant and plasticizer. The second step, starting at 330 °C, led to 31.6% mass loss and corresponded to the decomposition of the base polymer. The shift of the PVDF-HFP decomposition to lower temperatures for the optimized PIM compared to the blank PVDF-HFP film was most likely caused by interactions between the PIM components [41].
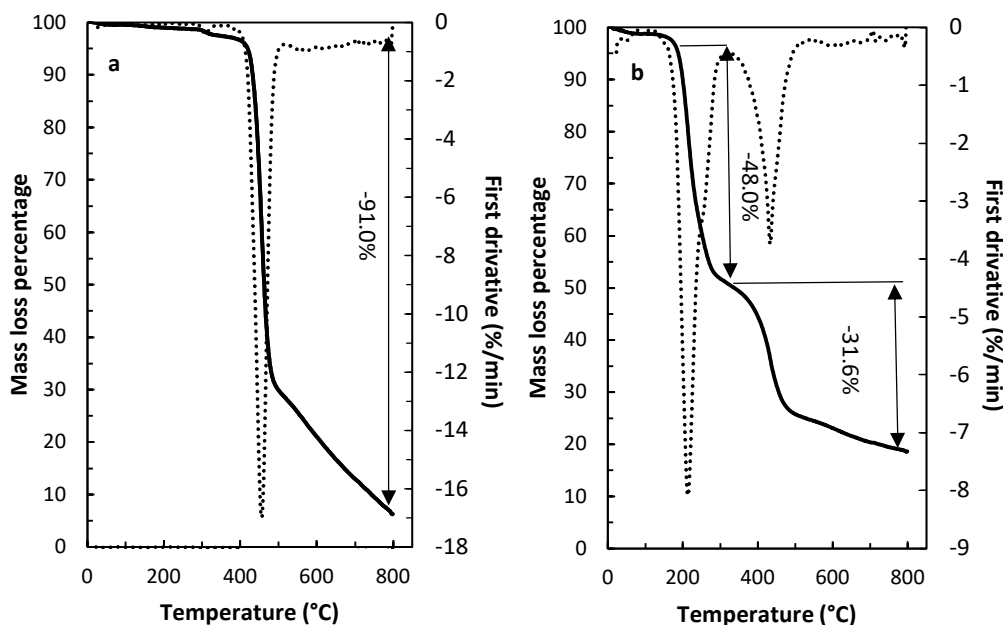
Figure 12. TGA and DTGA thermograms of (a) the PVDF-HFP film and (b) the optimized PIM (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP) under N₂ atmosphere.

The stress-strain curves of the blank PVDF-HFP film and the the optimized PIM (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP) (Figure 13) showed that the presence of the membrane liquid phase in the optimized PIM led to drastic reduction in tensile stress, i.e., from 33.2 to 5.2 MPa in the peak point. More importantly, the addition of extractant and plasticizer resulted in significant increase in flexibility, reaching a maximum at around 500% of elongation.
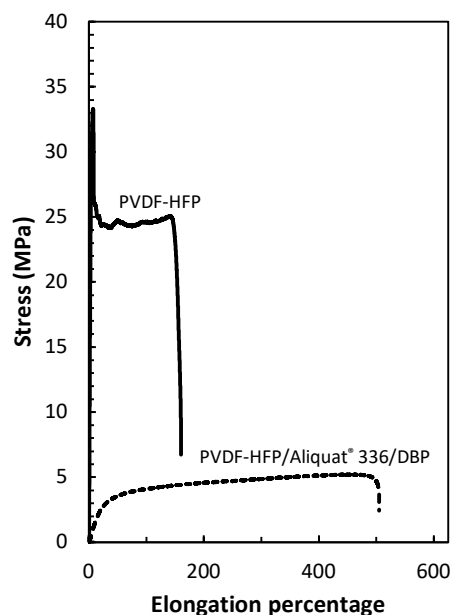

Figure 13. Stress-strain diagrams for the PVDF–HFP film and the optimized PIM (50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP).

4. Conclusions

The present study showed that a PIM composed of 50 wt% PVDF-HFP, 40 wt% Aliquat® 336 and 10 wt% DBP was suitable for the selective extraction of V(V) from its sulfate solutions in the presence of Al(III), Co(II), Cu(II), Fe(III), Mn(II), and Ni(II), often encountered in digests of spent alumina hydrodesulfurization catalysts. The co-extraction of Mo(VI) was eliminated in a two-step process where Mo(VI) was extracted first into a PIM at higher acidity. Quantitative back-extraction of V(V) was achieved in a back-extracting solution containing 6 mol L^{-1} H_2SO_4 and 1 v/v% H_2O_2. The extraction of V(V) was suggested to be based on the exchange of the Aliquat® 336 chloride anions with $VO_2SO_4^-$, while the formation of the $VO(O_2)^+$ in the back-extraction process as a result of the oxidation of VO_2^+ to $VO(O_2)^+$ by H_2O_2 was assumed to playa a key role in the qutaitative back-extarction of V(V).

Author Contributions:

Salar Bahrami: Investigation, Formal Analysis, Writing original draft. **Leila Dolatyari:** Investigation, Validation, Formal analysis, Writing original draft. **Hassan Shayani-Jam:** Investigation, Validation, Formal analysis, Writing original draft. **Mohammad Reza Yaftian**: Conceptualization, Project administration, Methodology, Resources, Supervision, Writing - review & editing. **Spas D. Kolev**: Conceptualization, Project administration, Supervision, Writing - review & editing.

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