

Effects of membrane content, feed phase, and stripping phase for palladium solution extraction by using a polymer inclusion membrane

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ABSTRACT

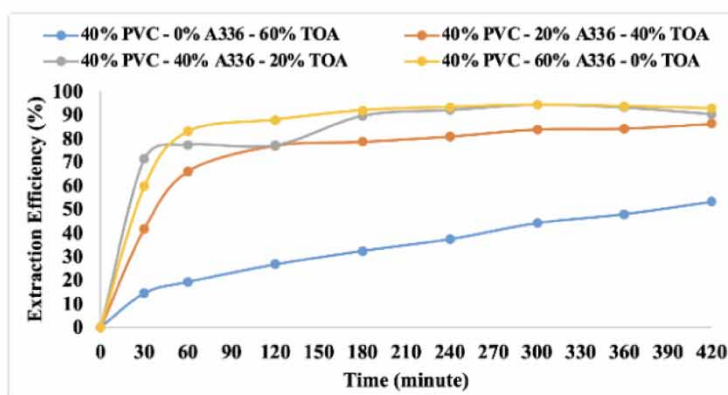
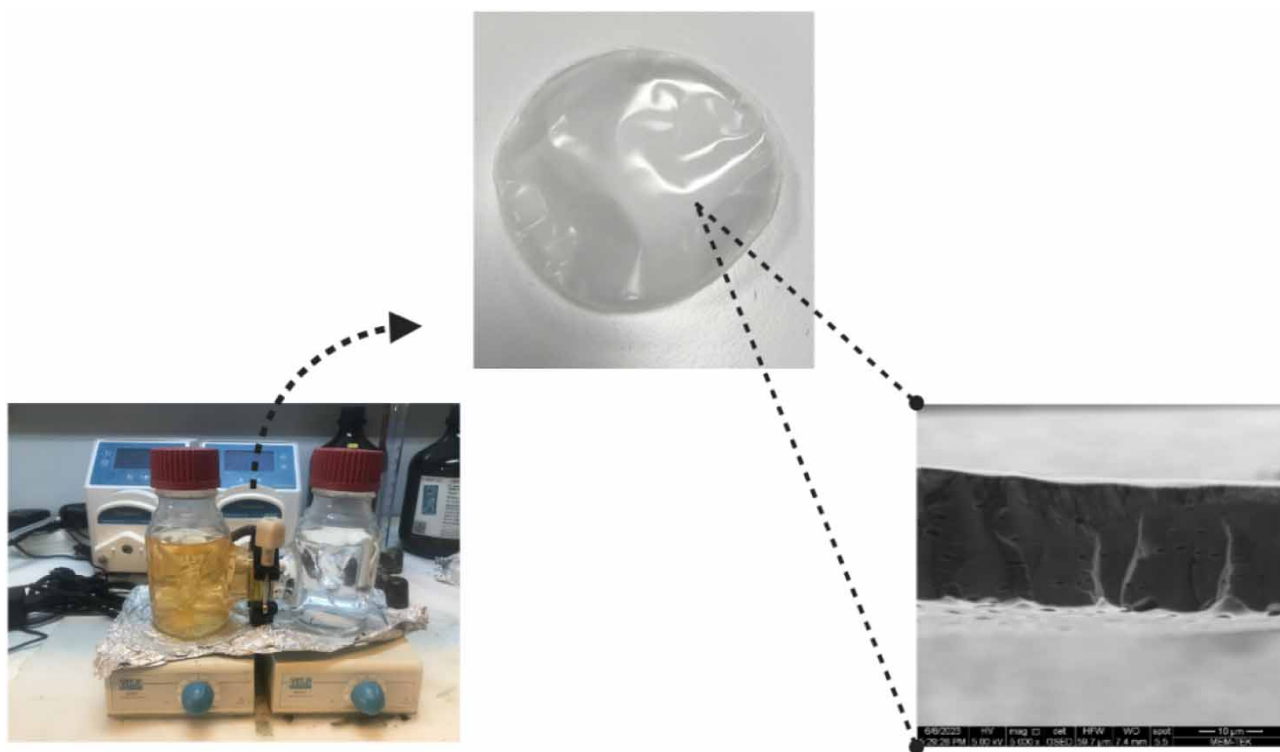
Palladium is now frequently utilized in fuel cells, electroplating, electronics, and catalysis. Due to their rarity and high cost, precious metal recovery has taken on a significant role. The extraction method frequently utilized in polymer inclusion membranes (PIMs) is both efficient and simple since it has been demonstrated that precious metal adsorption on the membrane significantly controls the mechanism of chemical adsorption. In this study, polyvinyl chloride (PVC) as a polymer, A336 as a plasticizer, and trioctylamine (TOA) as a carrier were used to produce a PIM by evaporation. After the production of PIMs, palladium extract was studied. The stripping phase, palladium concentration in the feed phase, and components of the membrane were changed to determine the optimum condition with better extraction ability. When 0.5 M of HCl was used, higher kinetic parameter results and higher than 85% extraction efficiency were achieved compared to other concentrations. When the EDX results were examined, 3.3% palladium was retained on the membrane surface. When the palladium concentration was selected at 2.5 ppm, higher kinetic parameters were observed, and the extraction efficiency was over 90%. The best membrane was the PIM containing 40% PVC–40% A336–20% TOA.

Key words: base polymer, evaporation, extraction, palladium, polymer inclusion membrane

HIGHLIGHTS

- Palladium metal recovery is very important to reduce the depletion of natural resources.
- PIMs are preferred because of their physical and chemical properties.
- The polymer inclusion membrane is the most innovative extraction method.
- PVC as a polymer can be used for the production of PIMs containing different ratios of plasticizers and carriers.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Palladium (Pd) is one of the precious metals frequently used in the jewelry, automotive, and electrical electronics industries. Since precious metals have limited resources, they must be recovered from both primary and secondary sources (Regel-Rosocka *et al.* 2015). However, their concentrations are quite small because they are found together with more than one ion. Therefore, special separation processes are required for its recovery (Reddy *et al.* 2013). While pyrometallurgical methods are generally used as the separation process, the use of hydrometallurgical methods has increased recently. It is mainly observed for the recovery of metals from aqueous chloride solutions. In addition, hydrometallurgical processes are preferred as energy-saving processes (Regel-Rosocka *et al.* 2015). Solvent extractions have many benefits, including excellent selectivity and metal purity, making them a viable approach for the extraction of precious metals from sources with low amounts of these metals (Behbahani *et al.* 2014). Polymer inclusion membranes (PIMs) provide more advantages than other processes due to their simplicity in design, ease of implementation, and high physical and chemical properties (Keskin *et al.* 2023). Transport over PIMs for the separation of metal ions and tiny organic molecules has been suggested as an alternative to these procedures by numerous researchers searching for ecologically friendly separation strategies (Regel-Rosocka *et al.* 2015).

The use of PIMs, one of the membrane processes for palladium recovery has become important, especially in recent years. As it shows a significant decrease in reagent use when compared to other methods and enables the use of potentially more expensive extractants, using PIMs is seen as an appealing green alternative to conventional extractions (López-Guerrero *et al.* 2020). PIMs are a more streamlined, reliable, and adaptable variation of liquid membranes (Kagaya *et al.* 2012). They are produced by the evaporation method. It usually consists of three materials (Gherasim *et al.* 2011). These are the base polymer, carrier, and plasticizer.

Base polymers are generally thermoplastic polymers and provide physical strength to the membrane (Nghiem *et al.* 2006). One of the base polymers commonly used in the production of PIMs is cellulose triacetate (CTA) (Kunene *et al.* 2020). Because of their crystal structure, CTA-based PIMs have outstanding physical characteristics and are widely accessible (Dahdah *et al.* 2022). The carrier delivers the target analyte to an acceptor solution by binding to it and acting as an ion exchanger or complexing agent (Almeida *et al.* 2012). Extractors can be classified according to their functional groups, such as acidic, basic, and neutral extractants (Pirom *et al.* 2017). While basic extractants successfully form complexes with anions, acidic extractants powerfully attach to cations. Chelating groups are highly effective extractants that can help liquid membrane systems separate better (Pirom *et al.* 2017). Aliquat 336, which is a blend of tri octyl- and decyl-ammonium chloride, has a constant positive charge and may form complexes with anions over a wide pH range. Ion-pair creation leads to extraction (Cho *et al.* 2018). Some ionic liquids, such as Aliquat 336, can act as both carriers and plasticizers at room temperature; in such cases, it is not necessary to add a plasticizer (Bonggotgetsakul *et al.* 2016). The plasticizer softens the membrane and increases its flexibility (Almeida *et al.* 2014). By switching between the chains of the polymer, they separate from one another more and exert fewer intermolecular pressures. The increased plasticizing characteristics of the plasticizer depend on the optimal balance between its polar and non-polar groups. In addition, compatibility with the base polymer, low cost, toxicity, viscosity, and volatility are also important for a good plasticizer (Cristea & Bourceanu 2011).

When studies in the literature were examined, the performance of PIMs was examined using different carriers, plasticizers, and base polymers for palladium extraction. Cyphos IL-101 and IL-104 were used in the study by Cieszyńska and Wiśniewski. As a result of the study, the effects of HCl concentration and temperature on performance were explained. When IL-101 was used, 97% palladium was recovered and when IL-104 was used, 96% palladium was recovered (Cieszyńska & Wisniewski 2010). In addition, in the study conducted by Regel-Rosocka *et al.*, Cyphos IL-102 was used and palladium recovery was observed to be between 84 and 90% (Regel-Rosocka *et al.* 2015). Fajar *et al.* produced membranes containing another ionic liquid, tri octyl (dodecyl) phosphonium chloride (P88812Cl), to examine palladium separation and the performance after consecutive use. The recovery of palladium(II) after the seventh cycle was calculated to be 96% (Fajar *et al.* 2019). Also, since the diversity of carriers also affects membrane performance, the performances were examined depending on both carrier concentration and HCl concentration when Cyanex 471X (triisobutylphosphine sulfide) was used in the studies. Under optimum conditions, the highest recovery was observed above 91% (Shao *et al.* 2020).

As is known, it has been observed in the literature that PIMs are effective and promising in the removal of different heavy metal ions, but the research in the literature on the recovery of precious metals with the help of PIMs is still very new.

The primary goal of this study is to develop a new technique for the removal of palladium using a laboratory-scale system. Palladium extraction performance was evaluated using polyvinyl chloride (PVC), Aliquat 336, and trioctylamine (TOA) for membrane production. The unique aspects of this study are that the palladium extraction efficiency has not been examined with these materials before and the system is innovative. To detail this performance, the concentrations of both the feed phase, the receiver phase, and the materials in the membrane were changed. As a result of this study, it was determined that the most suitable membrane in terms of both recovery and removal efficiency is PIMs containing 40% PVC–40% A336–20% TOA.

2. MATERIALS AND METHODS

2.1. Chemicals

PVC (MW:80,000 g/mol) was used for the base polymer, which was provided by Arkema. Also, tetrahydrofuran (THF) was utilized for the solvent, which was provided by Sigma-Aldrich. As carriers and plasticizers, methyltrioctyl ammonium chloride (MW: 404.16 g/mol) and trioctylamine (MW: 353.67 g/mol) were utilized. As the experiment's transport agent, hydrochloric acid (37%) was used, which was purchased from SCI. CPA Chem provided the 1,000 mg/L solution of

palladium metal ions. The pH of aqueous solutions was calibrated using the Seven Compact pH Meter. Sigma-Aldrich also offered all the components required to produce PIMs.

2.2. Membrane preparation

Aliquat 336 and TOA were then added to the solution after the PVC base polymer had been dissolved in 10 mL of THF. The solution was mixed for 2 h at room temperature. After that, the mixture was poured into a glass ring with a 9.0 cm diameter that was resting on a flat glass plate. The membrane solution was covered with filter paper and glass, which let the solvent gradually evaporate for 24 h. The glass plate was placed in water to make peeling it off easier.

2.3. Membrane characterization

Zeta potential, contact angle, surface roughness, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), thermal gravimetry analysis (TGA), and scanning electron microscopy (SEM) were used to describe the shape and surface characteristics of PIMs. Using an electrokinetic analyzer (SurPAS, Anton Paar GmbH), the surface charge of membranes was measured as streaming potential. During the analysis, the pH value was changed between 4 and 11 to determine the pH effect. To circulate through the adjustable gap cell containing the membrane samples, 500 mL of a 1.0 mM KCl solution was made. KSV Attention–Theta model contact angle equipment was used to assess the surface hydrophilicity of PIMs. Within the first 5 s of the droplet's droop on the PIM's surface, the contact angle is determined using this method. The topology and surface roughness of all membranes were explored by applying the Zygo NewView 7100 model profilometer. To understand the chemical functional groups of every PIM produced, the ATR-FTIR procedure was used. TGA is a thermal analysis technique in which weight changes in material are measured under programmed heating conditions. To ascertain the surface morphologies of PIMs, an SEM (FEI – Quanta FEG 250 model) investigation was carried out. The content of Pd in the samples was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, 7000 DV; Perkin Elmer, USA).

2.4. Extraction device setup

The extraction mechanism of the membrane was used to observe the effect of the stripping phase, feed phase, and contents of membranes on palladium extraction.

The feeding phase and the stripping phase are the two sections of this system. In the feed phase, 250 mL of a 10 ppm palladium standard solution was prepared for the extraction of palladium. In addition, the hydrochloric acid solution (0.1, 0.5, 1.0, and 2.0 M) (250 mL) was placed in the stripping phase. The palladium ions were retained in identical volumes (250 mL) and mixed at the same speed in both phases to ensure that they passed from the feed phase to the stripping phase uniformly (400 rpm). At the beginning of the experiment, samples from both phases were obtained every 30 min for a total of 7 h.

2.5. Transport experiment

The change in HCl molarity, the change in palladium concentration, and the change in membrane content affected the membrane performance. Because of that reason, first of all, the molarity of HCl was changed between 0.1 and 2 M. During the experiments, a 15-mL sample was taken from both phases at room temperature at 400 rpm, and adsorption was performed. The optimum molarity of HCl was selected and the effect of palladium concentration was changed between 2.5 and 15 ppm. According to these experiments, both the molarity of HCl and the palladium concentration were selected, and the different contents of the membrane were used to find the optimum results. In the experimental setup that was described and given in detail elsewhere, transport measurements were carried out (Keskin & Koyuncu 2023). The kinetics of palladium ion movement through the PIM may be predicted using the following equation (Pospiech 2018):

$$\ln \frac{C}{C_i} = -k \times t \quad (1)$$

where the constant of rate is k (s^{-1}), the transport time is t (s), the palladium concentration is C (M) in the feed phase at a specific time, and the initial palladium concentration in the feed phase is C_i . The rate constant (k) was calculated using the

$\ln(C/C_i)$ vs. time plot. The permeability coefficient (P) was then calculated using the following equation (Pospiech 2018):

$$P = \frac{V}{A} \times k \quad (2)$$

where V is the volume of the aqueous feed phase and A is the membrane's effective area.

The initial flux value (J_i) was subsequently calculated using the following equation:

$$J_i = P \times C_i \quad (3)$$

Equation (4) was used to obtain the extraction efficiency (%) (Ghaderi *et al.* 2022):

$$\text{Extraction efficiency} = \left(\frac{C_i - C}{C_i} \right) \times 100\% \quad (4)$$

Equation (5) was used to obtain the recovery factor (RF %) (Ghaderi *et al.* 2022):

$$\text{Recovery factor (RF)} = \left(\frac{C \text{ stripping phase } i}{C \text{ feed phase } i} \right) \times 100\% \quad (5)$$

3. RESULTS AND DISCUSSIONS

3.1. Characterization of PIM

The contact angle, surface charge, and surface roughness of all PIMs were characterized and the results are given in Table 1.

For determining membrane surface charge, the zeta potential is a reliable and significant measure. When the pH-dependent surface charges of the membranes were examined, it was observed that the membrane surfaces were positive at the initial pH. This is because Aliquat 336 and TOA are positively charged. This is why the surface negativity decreases as the Aliquat 336 ratio increases. It was observed that the surface negativity increased toward the basic conditions where the membranes were positively charged in acidic conditions.

Membrane hydrophilicity at different plasticizers and carriers was assessed by measuring the contact angle. A membrane's hydrophilicity determines how easily it will dissolve in water and leach out the carrier; its hydrophobicity determines how easily it will become biofoul and how effectively it will extract. To prevent the carrier from leaking away and to lengthen the period the membrane surface is in contact with the feed solution, the PIM must be both hydrophobic and hydrophilic. The carrier and plasticizer added to the PIM and polymer matrix affect the water contact angle of the membrane. There are hydrophilic ammonium groups in Aliquat 336. As a result, the hydrophilicity increases, and the contact angle decreases as the Aliquat ratio increases.

In Figure 1, the surface and cross-sectional images of the PIMs produced with PVC material were examined by SEM. As a result of the examination of the surface and cross-section images, it was observed that the surface images of the a, c, and d membranes were close to each other, and the most porous membrane was the b membrane. Consistent results are obtained when the surfaces and cross-sectional images of membranes after extraction are examined and compared with the calculated values.

Table 1 | Characterization of PIM

Membrane ID	Contact angle (°)	Zeta potential at pH 3	Zeta potential at pH 8	Zeta potential at pH 11	Average RMS (μm)
0 A336-60 TOA	68.5 ± 1.2	24.7 ± 1.0	-25.5 ± 1.4	-26.2 ± 0.6	0.09 ± 0.02
20 A336-40 TOA	64.7 ± 1.6	58.2 ± 1.6	-32.2 ± 2.6	-25.5 ± 1.0	0.62 ± 0.12
40 A336-20 TOA	45.6 ± 1.4	45.0 ± 3.9	-10.3 ± 1.3	-9.5 ± 1.0	0.85 ± 0.10
60 A336-0 TOA	31.7 ± 0.8	100.1 ± 1.5	-42.1 ± 1.5	-6.6 ± 0.2	0.14 ± 0.06

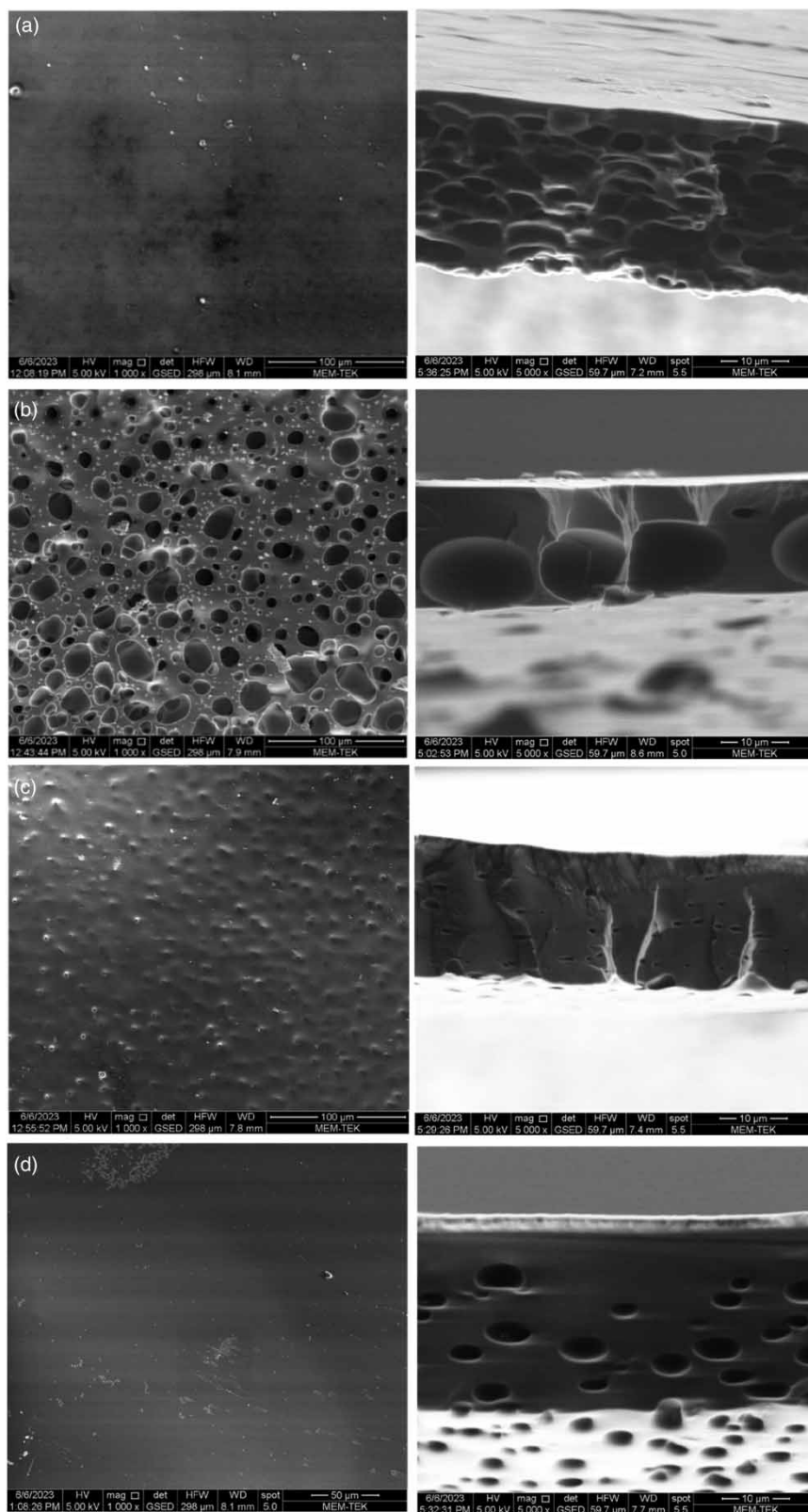


Figure 1 | SEM surface images of the membranes after extraction (on the left) and cross-sectional images of the membranes after extraction (on the right) (a) PIM containing 60% TOA, (b) PIM containing 20% A336 and 40% TOA, (c) PIM containing 40% A336 and 20% TOA, and (d) PIM containing 60% A336.

Optical profilometry was used to examine the membrane roughness (RMS). According to the RMS values, the addition of Aliquat 336 and TOA slightly affected the surface roughness of the membranes. In general, an increase in average membrane surface roughness results in an increase in membrane flow, providing a highly effective area for filtration. However, due to the retention of contaminants in the high-roughness membrane surface valleys, the membranes ability to protect against deposits decreases with an increase in membrane roughness (Figure 2).

According to FTIR analysis results, C-Cl bands between 610 and 692 cm^{-1} , C-H bonding at 1,425 cm^{-1} , and C-H stretching at 2,915 cm^{-1} are assigned to the typical characteristics of PVC base polymer. When TOA addition has an O-H bond (between 3,700 and 3,550 cm^{-1}). When Aliquat 336 was added, it was observed that there were $-\text{CH}_3$ group bonds (between 2,926 and 2,857 cm^{-1}), and ammonium group bonds (between 1,467 and 1,378 cm^{-1}) apart from these bonds.

It is necessary to ensure that the membrane material is thermodynamically stable and does not degrade under temperature conditions. The thermal stability of membranes is characterized by TGA analysis. As a result of the analysis, the first degradation temperature of the PVC membrane occurred at 200 °C and was due to the separation of the HCl molecule from the chain. The second thermal decomposition zone is around 400 °C and is due to the complete degradation and charring of the polymer chain. As a result of the addition of carrier and plasticizer, each weight loss curve is divided into three parts. The first part of the weight loss below 180 °C corresponds to the evaporation of the solvent. The next step is called weight loss relative to the added plasticizer and carrier. It has also been observed that Aliquat 336 has better thermal stability than other materials.

3.2. Transport experiments

In PIM, a carrier, either a complexing agent or an ion exchanger, performed the bulk of the transport work. Ions pass through the membrane more readily because of the complex or ion-pair formed when they come into contact with the extractant. The transfer of precious metals was aided by the carrier and plasticizer present in PIM. In our previous study (Keskin *et al.* 2023), we investigated Pd adsorption with different pH, temperature, and different carriers using membranes produced with different polymers. The membrane that gives the optimum result as a result of the study is 40% PVC–20% Aliquat–40% TOA membrane.

In this work, PVC-based PIMs with carriers and plasticizers were created. Experiments were carried out using palladium as a precious metal in the membranes. Therefore, using this membrane in extraction studies, first, the stripping phase was changed and then the palladium concentration in the feed phase was changed. After these two variables were optimized, the membrane contents were changed to the same mold ratios.

3.2.1. Effect of HCl concentration in the stripping phase

The most efficient working medium for the separation of platinum-group metals is the chloride medium (Mohdee *et al.* 2019). Using PIMs, it was possible to selectively recover palladium from HCl solutions with various concentrations.

The dominance of precious metal species varies with changing HCl concentrations, especially in strongly acidic solutions. For palladium, PdCl_4^{2-} is dominant in a 0.1 M HCl acidic solution, while for other metals, the dominant species changes at different HCl concentrations. In addition, the lower concentrations of acidic solutions ensure that the complexes of metals are more diverse.

The concentrations of 40% PVC, 20% Aliquat 336, and 40% TOA were fixed for the production of PIM. To investigate the effect of HCl concentration on the separation of the palladium, the amount of HCl in the stripping phase was increased from 0.1 to 2 M.

Figure 3 shows that the palladium in the solution was extracted in the HCl concentration range of 0.1–2 M and the extraction percentage of palladium increased steadily with the further increase of HCl concentration. However, the extraction of palladium was negligible at any HCl concentration (Nguyen *et al.* 2016).

The contributions of the produced palladium chloride species in the aqueous chloride solutions can be utilized to explain these transport experiment results. PdCl_4^{2-} is the main palladium species in concentrated chloride environments (0.1–2.0 M) (Charlesworth 1981; Nikoloski & Ang 2014). Palladium requires the release of two chloride ions from the complex to be extracted via a solvation process. Due to the ease with which chloride ligands may be released from the palladium complex compared to other precious metal complexes, palladium can be extracted selectively (Foulon *et al.* 1999).

Table 2 shows the effect of HCl concentration in the stripping phase on the value of rate constants, permeability coefficients, and recovery factors. The highest rate constant of the transport process was obtained when 0.5 M HCl was used as the source phase. The RF of palladium was the highest (above 61%) at 2 M HCl.

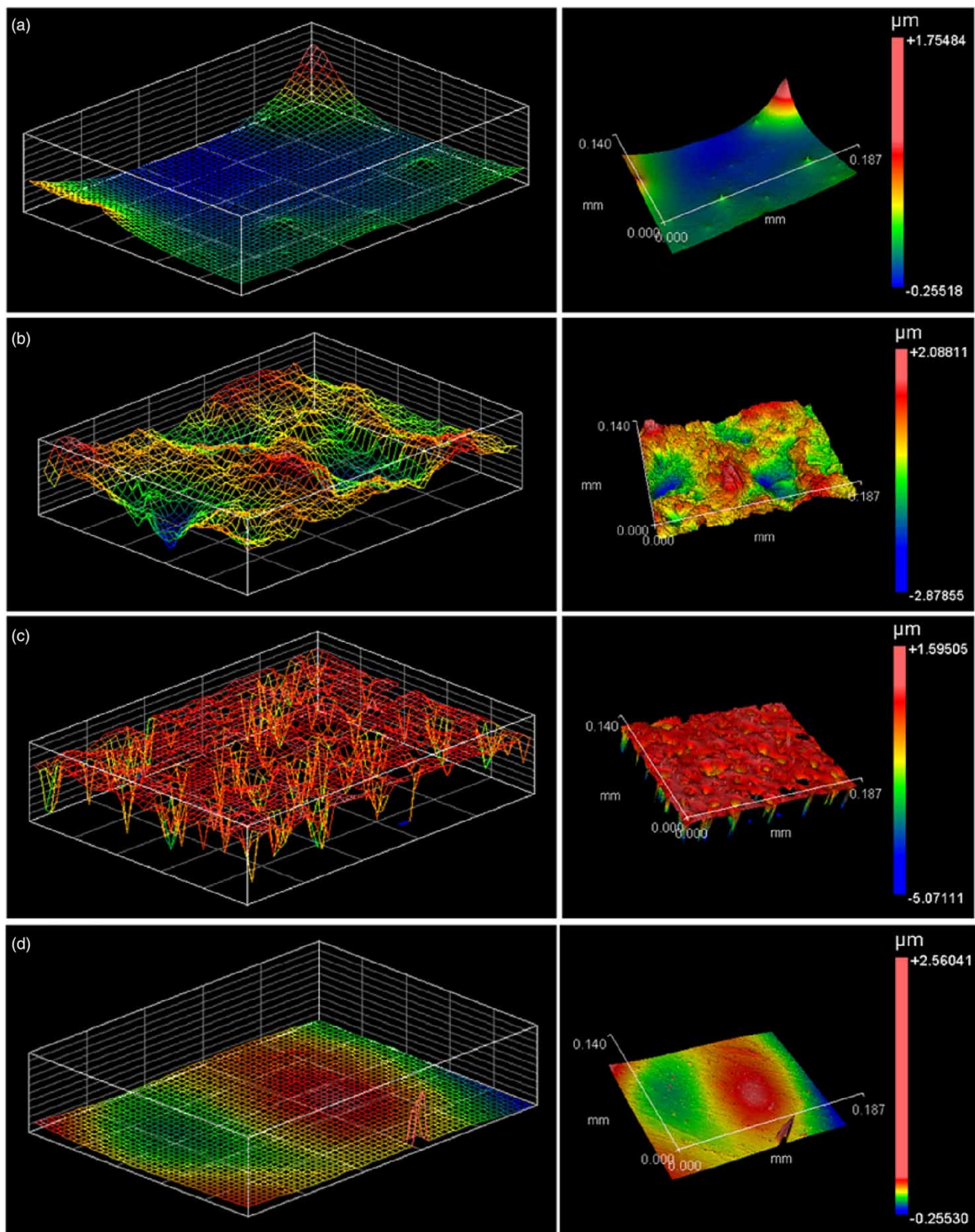


Figure 2 | The surface morphologies of membranes (a) PIM containing 60% TOA, (b) PIM containing 20% A336 and 40% TOA, (c) PIM containing 40% A336 and 20% TOA, and (d) PIM containing 60% A336.

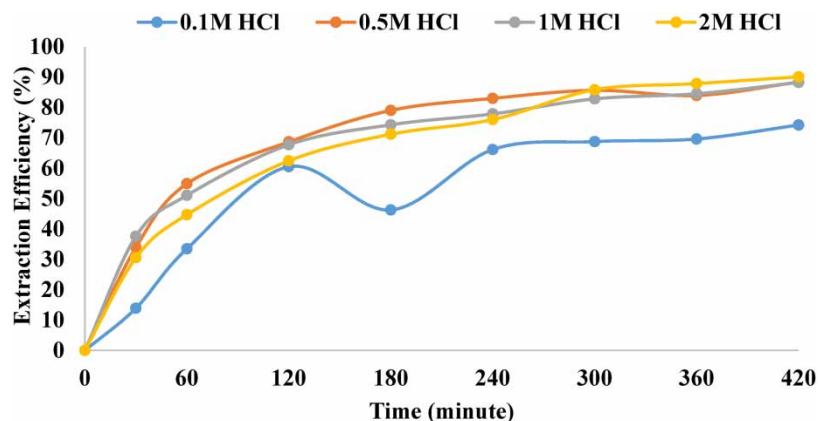


Figure 3 | Effect of the receiving phase on the extraction of palladium.

Table 2 | Effect of HCl concentration on kinetic parameters of palladium

Receiving phase	Rate constant k (h^{-1})	Permeability coefficient (m/h)	Recovery factor (%)
0.1 M HCl	0.0047	0.0008	0.04
0.5 M HCl	0.0087	0.0015	6.11
1.0 M HCl	0.0084	0.0014	40.98
2.0 M HCl	0.0076	0.0013	61.74

In hydrometallurgical procedures, a concentrated HCl solution is used to dissolve the palladium in the resources in the presence of oxidizing chemicals (Jha *et al.* 2014; Pospiech 2018). It may be anticipated that the palladium ion may be recovered using any hydrochloric acid concentration since the palladium and extractant combination react with protons in the recovery solution (Sunsandee *et al.* 2021). When the energy dispersive X-ray analyser (EDX) results of the membranes used in studies from 0.1 M HCl to 2 M HCl concentrations were examined, palladium concentrations were observed as 2.6, 3.3, 2, and 2.6 wt% by weight, respectively. This is also confirmed by the ICP results. As a result, the HCl content of the palladium solution was set at 0.5 M, and further tests were conducted using these solutions.

3.2.2. Effect of palladium concentration in the feed phase

Varying the palladium concentration in the feed phase from 2.5 to 15 ppm transported more than 85% of palladium in all cases except for 15 ppm palladium (Figure 4).

Similar results are obtained at palladium concentrations in the feed solution up to 15 ppm, indicating the retention and permeation capacity of the membrane. In studies conducted in the literature, it has been observed that the extraction efficiency of precious metal solutions is better up to a maximum of 10 ppm, but at high concentrations, the capacity of the membrane is not sufficient, and therefore the results decrease with increasing concentration. When the kinetic parameters were examined, it was observed that the excess concentration remained in the feed and could not pass to the receiving part, and in addition, it reduced other parameters, including the rate constant and permeability coefficient.

Since the concentration of the metal in this concentration range does not affect the extraction of palladium, only mono-nuclear species are present in the feed phase, and the permeability has thus stabilized (Monroy-Barreto *et al.* 2021). The palladium concentration of the feed solution was fixed at 2.5 ppm and further experiments were done with these solutions.

When the EDX results of the membranes used in studies from 2.5 to 15 ppm palladium concentrations were examined, palladium concentrations were observed as 1.1, 1.3, 2.3, and 2.7 wt% by weight, respectively. This is also confirmed by the ICP results.

3.2.3. Effect of membrane type

The extraction of target metal ions is greatly influenced by the concentration of an extractant. The concentration of the extractant is also one of the most important variables that affects the extraction process while studying theoretical phenomena

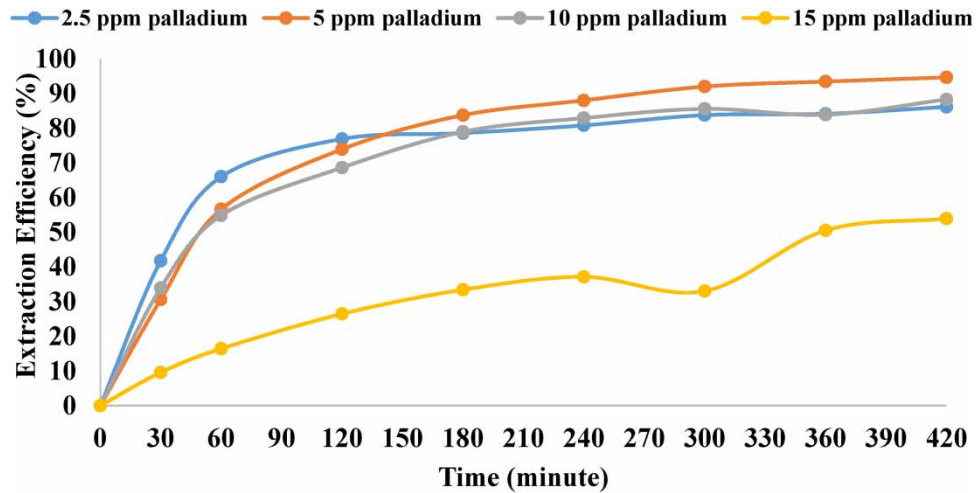


Figure 4 | Effect of palladium concentration in the feed phase on the extraction of palladium.

(Mohdee *et al.* 2019). In this section, the effects of both Aliquat 336 and TOA on the kinetic parameters of palladium ions were investigated (Table 3).

Figure 5 shows that palladium in the solution was extracted by using PIMs. Further increases in carrier concentration in the membrane phase resulted in decreased metal ion flux, probably due to the limited solubility of the carrier. This effect can also be attributed to membrane saturation by the metal ion transporter complex (Pospiech 2015). However, the rate of separation increased when the Aliquat 336 concentration reached. This can be explained by the fact that the viscosity of the liquid

Table 3 | Effect of palladium concentration in feed phase on kinetic parameters of palladium

Feed phase	Rate constant k (h^{-1})	Permeability coefficient (m/h^{-1})	Recovery factor (%)
2.5 ppm	0.0100	0.0017	12.84
5 ppm	0.0099	0.0016	8.72
10 ppm	0.0087	0.0015	6.11
15 ppm	0.0023	0.0004	0.24

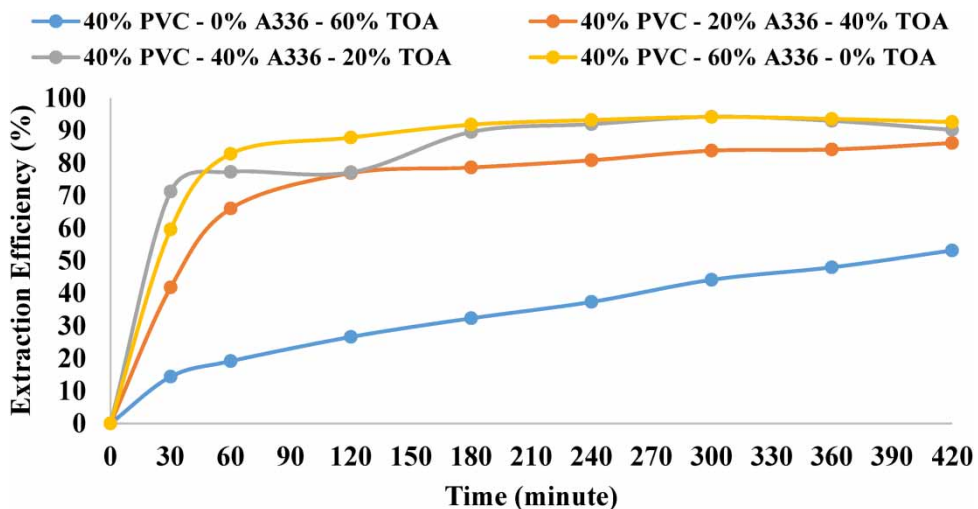


Figure 5 | Effect of membrane contents on the extraction of palladium.

membrane phase decreases (Pirom *et al.* 2017; Sunsandee *et al.* 2021). The decreasing tendency of liquid membrane viscosity causes high diffusivity and obstructs the mass transfer of palladium, which ultimately increases the extraction and recovery percentages of palladium (Pirom *et al.* 2017). Consequently, the 40% PVC–40% A336–20% TOA membrane was accepted as the best membrane content for extraction (Wannachod *et al.* 2016).

Table 4 shows the effect of membrane content on the value of the initial flux (J_i) and other kinetic parameters such as rate constants, permeability coefficients, and recovery factors. The highest rate constant and recovery factory of the transport process was obtained when a membrane containing 40%PVC–40% A336–20%TOA PIM was used. The RF of palladium was the highest (above 24%) by using a membrane containing 40%PVC–40% A336–20%TOA.

Transport in PIMs is accomplished by a carrier, either a complexing agent or an ion exchanger. That is why the carrier itself and its presence are very important. Carriers are divided into basic, acidic, and solvent categories (Nghiem *et al.* 2006). The molecular structure of the carriers used significantly affected the transport rate (Argiropoulos *et al.* 1998). In this study, Aliquat 336 was used because of its chemical structure and compatibility with PVC polymers. In the studies conducted in the literature, it was observed that as the Aliquat 336 ratio increased, the flux increased and the precious metal retention in the feed solution increased (Fontàs *et al.* 2005). In addition, it has been observed that as TOA concentration increases, the flux increases, and TOA concentration must be high for TOA and PVC to be highly compatible in the literature. It was observed that the membrane surface was smooth by using a TOA mixture without Aliquat 336, but the surface roughness increased when the plasticizer was added to the membrane solution (Nghiem *et al.* 2006).

The differences that occur as a result of the change in membrane contents depend on the viscosities of the carrier and plasticizer. When the viscosities alone are examined, TOA is 7.94 mPa.s and Aliquat 336 is 1,176.5 mPa.s. Increases or decreases in kinetic parameters occurred due to viscosity changes in mixed-produced membranes (Burgé *et al.* 2016). Chakrabarty *et al.* reported a decrease in diffusion coefficient and flux, in the presence of an excess amount of carrier concentration. This was also due to the high viscosity during the liquid membrane phase (Chakrabarty *et al.* 2008).

On the other hand, the increase in the concentration of the extractant also promotes permeation swelling, which dilutes the aqueous receiving phase and decreases the efficiency of the process (Kumbasar 2010).

The increase in carrier ion concentration in the membrane phase also caused an increase in the thickness of the membrane, which affected the transport rates. The obtained membranes had different thicknesses; the permeability coefficient increased as the thickness increased. In the literature, the effect of membranes produced using different Aliquat 336 concentrations on the transport of palladium ions has been investigated. As a result, it was observed that the permeability coefficient increased as the carrier concentration increased.

4. CONCLUSION

In this study, membranes containing PVC, Aliquat 336, and TOA were produced and characterized by using zeta potential, contact angle, surface roughness, and SEM.

The main aim is the examination of the removal performance of palladium. For this, the effect of the receiving phase, palladium concentration in the feed phase, and membrane contents were examined. The effect of the receiving phase was investigated. In the research part, the molarity of the receiving phase was changed from 0.1 to 2 M HCl. According to this experiment, the optimum concentration was determined to be 0.5 M HCl. After the receiving phase was decided, the palladium concentrations were determined. According to the extraction analysis, the concentration of palladium was selected at 2.5 ppm for the feed phase. The last step is about membrane contents. The concentrations of base polymer, plasticizer, and carrier were changed for extraction experiments. Since the 7-h removal efficiency results of all membranes containing Aliquat

Table 4 | Effect of membrane content on kinetic parameters of palladium

Membrane contents	Rate constant k (h^{-1})	Permeability coefficient (m/h^{-1})	Initial flux ($\text{mg}/\text{m}^{-2}\text{h}^{-1}$)	Recovery factor (%) after 7 h
0 A336–60 TOA	0.0026	0.0005	0.0011	1.56
20 A336–40 TOA	0.0100	0.0017	0.0055	12.84
40 A336–20 TOA	0.0154	0.0027	0.0076	24.64
60 A336–0 TOA	0.0157	0.0027	0.0081	3.52

336 were almost equal, the recovery rates were examined. As a result of this, the membrane with 40% PVC–40% A336–20% TOA was selected.

Some studies have been conducted in the literature using different membranes for palladium recovery. It was aimed to recovering palladium from water containing 1,000 mg/L palladium at pH 1 using an anion exchange membrane, and a 90% recovery rate was achieved after 4 h (Tekinalp *et al.* 2024). In another study, 90% recovery was achieved by using a liquid surfactant membrane and applying a voltage of 10 kV (Kakoi *et al.* 1996). Furthermore, by using a double-layer adsorptive membrane, an adsorption capacity of 61.5 mg/g was obtained at the end of 6 h when the pH was 2 (Zhang *et al.* 2024). So, when the results of the study in this article are compared with the studies in the literature, it is observed that higher amounts of palladium are retained and recovered with PIM membranes without requiring larger volumes of energy. The study may potentially be focused on developing PIMs with a higher extraction rate and improved stability.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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