



The first comparison of the effectiveness of phosphonium ionic liquids in classical solvent extraction and in polymer inclusion membranes for Hg(II) removal

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Received 1 June 2023; Accepted 18 October 2023

ABSTRACT

This paper presents the results of the removal of mercury(II) ions from acidic aqueous solutions. Toxic ions were separated using compounds from the Cyphos group. Six types of ionic liquids were used as extractants in classical solvent extraction, while results showed that Cyphos IL 101 and Cyphos IL 102 presented the highest efficiency for binding mercury(II) ions in given conditions. Therefore, these two compounds were further utilised as ion carriers in studies of transport across polymer inclusion membranes. Membranes were obtained from widely available poly(vinyl chloride) and biodegradable poly(lactide) with the addition of an appropriate plasticizer dedicated to polymer: bis(2-ethylhexyl) adipate or 2-nitrophenyl octyl ether. Moreover, the characterisation of the surfaces of the investigated pure membranes was performed using the Fourier-transform infrared spectroscopy-attenuated total reflectance method and the sessile drop method. Additionally, the membranes, after the processes of mercury(II) ions transport were analysed using Wavelength-dispersive X-ray fluorescence spectroscopy.

Keywords: Mercury(II) ions; Polymer inclusion membrane; Cyphos phosphonium ionic liquids; Poly(vinyl chloride); Poly(lactide)

1. Introduction

Mercury, which is considered one of the most toxic metals, is present in the natural environment in small amounts as a result of natural processes, for example, related to volcanic and geothermal activity. However, the dynamic development of various industries, for example, those related to the combustion of fossil fuels or mining and processing of metal ores, has contributed to an increase in the amount of mercury and its compounds in the soil, water, air and, consequently, also in the tissues of plants and animals. The impact of toxic mercury, which is non-degradable and bioaccumulative, on living organisms depends on many factors, including, for example, the speciation of the metal and environmental conditions [1]. For example, the Hg⁰ form found

in soil is less toxic than the Hg²⁺ form, which can form various organic complexes and is more bioavailable to plants [2]. Moreover, Hg²⁺ easily combines with organic substances in sediments found at the bottom of water reservoirs, which is why such sediments are the “storehouses” of that element [3]. Hg²⁺, under the right conditions, can also be converted by bacteria into neurotoxic methylmercury, which can enter the human body, for example, with consumed fish, in whose tissues it has bioaccumulated [2,4]. Often, due to complex environmental factors, determining the effects of mercury present in an ecosystem on living organisms is not easy and requires advanced research over a long period of time. It has been shown that mercury not only has direct negative effects on the functioning of various organs in animals

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Presented at the XIV Scientific Conference Membranes and Membrane Processes in Environmental Protection – MEMPEP 2023, 21–24 June 2023, Zakopane, Poland

and humans but the exposure to mercury of some organisms for a long time, for example, of birds, may contribute to changes affecting their reproductive performance [5].

Considering the threat posed by mercury to the environment, many methods have been developed to remove it, for example, from aqueous solutions such as contaminated surface water, groundwater or sewage. The group of techniques enabling the removal of various metal ions, including mercury(II), from aquatic media, includes chemical precipitation, adsorption, ion exchange, methods based on the use of microorganisms, solvent extraction, membrane processes, etc.; the well-known methods are modified to increase their efficiency, adapt to specific conditions, reduce costs, energy consumption and limit their negative impact on the environment [6–9]. For solvent extraction (SE), based on exploiting the difference in the solubility of the components of the mixture in two immiscible liquids, the so-called ionic liquids (ILs), which consist only of ions, are more and more often used instead of classic organic solvents and extractants. ILs are various anion–cation compositions, non-volatile and chemically stable, characterised by high performance in the SE processes and are considered to be safer for the environment than organic solvents [10–12]. Ionic liquids with the proven ability to bind metal ions from aqueous solutions are also used as carriers in polymer membranes [13]. One of the types of membranes are polymer inclusion membranes (PIMs), which consist of a metal ion carrier, a polymer matrix and, usually, a plasticizer. PIMs have many advantages, including the possibility of simultaneous extraction and re-extraction of metal ions; moreover, to produce the membranes a relatively small amount of chemical reagents is required. The use of PIM instead of SE also makes it possible to significantly reduce the amount of used organic solvents, which has a positive environmental and economic impact [14]. Among ILs, also called “green solvents” due to their properties, phosphonium ionic liquids, such as Cyphos IL 101, 102, 104, are very popular [15]. Those compounds have been successfully used many times to remove various metal ions from aqueous solutions, both in SE processes and in membrane separation using PIMs [16–19]. Mercury(II) ions have also been removed from aqueous solutions using polymer inclusion membranes, but with the use of different carriers. For example, Zawierucha et al. [20] performed separation of mercury(II) ions from industrial wastewater through PIM with calix[4]pyrrole derivative as a carrier and reported high removal efficiency of Hg(II) and great repeatability. Elias et al. [21] used two different ILs based on the same trioctylmethylammonium cation but bearing the anion thio-salicylate (TOMATS) or salicylate (TOMAS) as carriers in PIMs for mercury(II) preconcentration in aquatic mediums, and reported that PIM-based system allowed the transport of Hg(II) at low concentration levels in different types of natural waters (rivers, groundwater, seawater) without any previous treatment. The possibility of using ionic liquids to modify sorption materials intended to remove Hg(II) ions from aqueous solutions is also being studied, for example, TOMATS and Cyphos IL 104 were used to modify the properties of silicon dioxide at a nanoparticle range with cellulose powder at a microparticle range and activated carbon from mixed recyclable waste, respectively [22,23].

Recently, polymer inclusion membranes with different phosphonium ionic liquids carriers have been successfully used in various studies, for example, for the removal of Cr(VI) ions from model aqueous solutions, for the separation of Ce(III) ions from La(III), Cu(II), Co(II) and Ni(II) containing solutions, for the recovery of Cu(II), Zn(II) and Ni(II) ions from leachates of jewellery waste or for the simultaneous recovery of precious and heavy metal ions from leachates of electronic waste [17, 24–26]. A combination of PIM and phosphonium IL (Cyphos IL 104) has also been used to probe biofilm zinc accumulation [27]. Despite the fairly wide use of polymer inclusion membranes containing phosphonium ionic liquids as carriers for the removal or recovery of various metal ions from aqueous solutions, the potential of these methods has not been fully exploited in relation to mercury(II) ions so far.

Therefore, in this study we present the results of the first comparison of the effectiveness of a range of phosphonium ILs (Cyphos IL 101, 102, 103, 104, 105 and 109, respectively) as extractants in classical solvent extraction and as carriers in polymer inclusion membranes designed to remove mercury(II) ions from model aqueous solutions. The SE processes were carried out with the use of all tested phosphonium ionic liquids, while the membrane processes were performed with the use of ILs most effective in solvent extraction (i.e., Cyphos IL 101 and 102). To assess the influence of the type of polymer and plasticizer on the membrane processes, the separation of Hg(II) ions was done using four membranes with a different composition, that is, containing, apart from a carrier (Cyphos IL 101 or Cyphos IL 102), a polymer matrix made of poly(vinyl chloride) and the plasticizer bis(2-ethylhexyl) adipate (PVC/ADO), or containing biodegradable poly(lactide) and the plasticizer 2-nitrophenyl octyl ether (PLA/NPOE). Based on the obtained results, the most effective carrier with respect to mercury(II) ions is Cyphos IL 102 and its use in both types of PIMs (with PVC/ADO and PLA/NPOE) after 24 h of transport processes made it possible to remove more than 99% of Hg(II) ions.

2. Materials and methods

2.1. Reagents

The nitrate standard solutions of Hg(II) ions with a concentration of 1,000 mg/L were of analytical grade and were purchased from Sigma-Aldrich (St. Louis, MO, USA). The phosphonium ionic liquids:

- Cyphos IL 101 (triethyl(tetradecyl)phosphonium chloride, CIL 101),
- Cyphos IL 102 (triethyl(tetradecyl)phosphonium bromide, CIL 102),
- Cyphos IL 103 (triethyl(tetradecyl)phosphonium decanoate, CIL 103),
- Cyphos IL 104 (triethyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate CIL 104),
- Cyphos IL 105 (triethyl(tetradecyl)phosphonium dicyanamide, CIL 105),
- Cyphos IL 109 (triethyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide, CIL 109)

were purchased from Sigma-Aldrich (St. Louis, MO, USA). The poly(vinyl chloride) (PVC) was purchased from Anwil (Włocławek, Poland) and the poly(lactide) (PLA) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The analytical grade plasticizers (bis(2-ethylhexyl) adipate (ADO) and 2-nitrophenyl octyl ether (NPOE)) and solvents (tetrahydrofuran and dichloromethane) were sourced from Avantor (Gliwice, Poland) and used without further purification.

The formulas of the used reagents are presented in Fig. 1.

2.2. Classic solvent extraction

The mercury(II) ions were separated from the aqueous solution using solvent extraction. The studies were run at $25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$, at a fixed ionic strength (0.5 mol/L) maintained in the aqueous phase with KNO_3 . The organic phase contained one of the tested extractants (the selected Cyphos IL) diluted in dichloromethane. The concentration of mercury(II) ions in the aqueous solution was constant at 1,000 mg/L, while the concentration of each Cyphos IL in organic phases was adjusted in such a way as to obtain the metal to ligand molar ratio of 1:2.

The same volumes of both phases (aqueous and organic phase) were added to calibrated test tubes. The prepared samples were then shaken for 1 h. The equilibrium was established after approximately 15 min by visual observation. It was checked if any changes in the phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured. The concentration of metal ions in aqueous phases before and after the process was determined using graphite furnace atomic absorption spectroscopy (GF-AAS) by PerkinElmer AAnalyst 300 (Norwalk, Connecticut, USA). The pH meter utilised in the performed experiments was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) with a pH of 2.00, 4.01, 7.00 and 10.00.

The classic solvent extraction of mercury(II) ions from aqueous solutions was described and calculated using extraction efficiency (%E) [28].

2.3. Transport of metal ions across polymer inclusion membrane

The transport of mercury(II) ions from nitrate solution was carried out in a permeation module cell, in which one of the obtained polymer inclusion membranes (with an active surface of 2.2 cm^2) described in paragraph 2.3.1 – Preparation of PIMs was placed between two cell compartments, which contained the feed and stripping aqueous phases. Both phases were mechanically agitated at 800 rpm. PIM transport experiments were performed at $25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. Examples of the feed and stripping phases were sampled periodically and analysed using GF-AAS by PerkinElmer AAnalyst 300 (Norwalk, Connecticut, USA) to determine the concentration of mercury(II) ions.

2.3.1. Preparation of PIMs

Four different polymer inclusion membranes were obtained (Table 1). Membranes PLA/CIL 101 and PLA/CIL 102 were obtained from a dichloromethane solution

of PLA used as a polymer matrix, NPOE used as a plasticizer, and ion carrier Cyphos IL 101 or Cyphos IL 102, respectively. PIMs PVC/CIL 101 and PVC/CIL 102, on the other hand, were obtained from a tetrahydrofuran solution of PVC used as a support, ADO used as a plasticizer, and CIL 101 or CIL 102, respectively. All membranes contained 60 wt.% of polymer matrix, 20 wt.% of ion carrier, and 20 wt.% of plasticizer.

2.3.2. Feed solution

The feed phase of about 45 mL contained a standard solution of Hg(II) ions with a concentration of 1,000 mg/L. The pH of the feed phase was kept constant (at approx. 2.5) and controlled using a pH meter (SevenCompact S210, Mettler Toledo), with a combination pH electrode (ERH-13-6, Hydromet, Poland).

2.3.3. Stripping solution

The stripping phase was a 1.0 mol/L HNO_3 solution with a volume of about 45 mL.

2.3.4. Characterization of the surface of the investigated PIMs

2.3.4.1. Fourier-transform infrared spectroscopy-attenuated total reflectance analysis of PIMs

The structures of obtained pure PIMs were confirmed using the Fourier-transform infrared spectroscopy-attenuated total reflectance method (FTIR-ATR). The FTIR-ATR spectra were recorded using a Bruker Alpha-PFT-IR device with a diamond attenuated total reflectance (ATR) accessory at a wavenumber range of $360\text{--}2,000\text{ cm}^{-1}$ for each membrane.

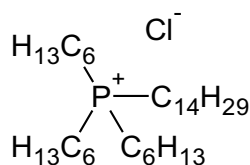
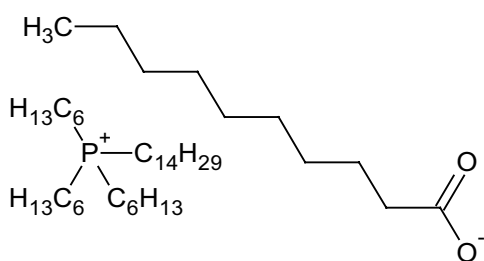
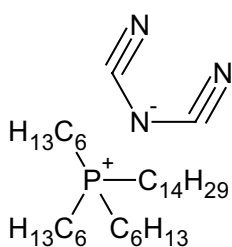
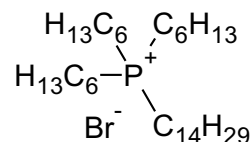
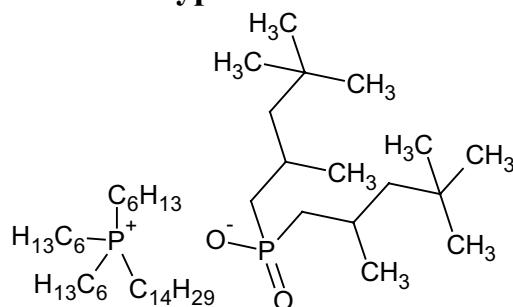
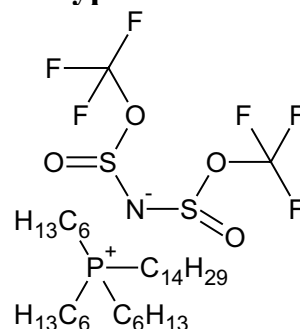
2.3.4.2. Wettability of PIMs

The static water contact angles on the surfaces of prepared polymer inclusion membranes were measured using the sessile drop method at the ambient temperature (23°C) using a contact angle goniometer (T-1, DSA100E - Drop Shape Analyzer, Krüss). A PIM sample was washed thoroughly with distilled water and wiped with filter paper to remove the moisture content prior to contact angle (CA) measurements. A $5\text{ }\mu\text{L}$ droplet of deionised water was placed on the membrane surface and, within 3 s of the addition of the water drop, the CA was measured. The CA was measured at three random locations for each sample and the average value was reported.

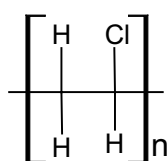
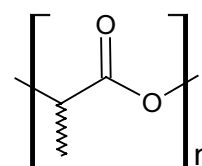
2.3.4.3. Wavelength-dispersive X-ray fluorescence spectroscopy analysis of PIMs

The chemical composition of the polymer membranes was determined using wavelength-dispersive X-ray fluorescence spectroscopy (WD-XRF). This analysis of PIMs was the only analysis carried out after, instead of before, the transport of mercury(II) ions from aqueous solutions. This at the same time enabled an assessment of the correct composition of the membranes, in relation to the substrates

Extractants / Ion Carriers

Cyphos IL 101**Cyphos IL 103****Cyphos IL 105****Cyphos IL 102****Cyphos IL 104****Cyphos IL 109**

Polymers

PVC**PLA**

Plasticizers

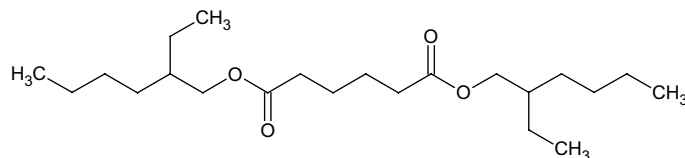
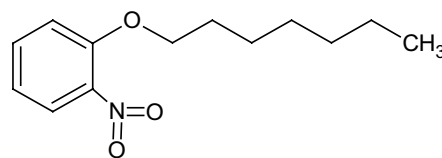
ADO**NPOE**

 Fig. 1. Formulas of reagents used both during solvent extraction processes and transport across polymer inclusion membranes.

used in obtaining them, but also the identification of any potential permanent retention of mercury(II) ions in membrane structures. A qualitative analysis of the spectrum was performed by identifying spectral lines and indicating their possible coincidence. On this basis, analytical

lines were selected. Semi-quantitative analysis was developed using the SQX Calculation Programme (fundamental parameter method). The analysis was performed in the fluorine-uranium (F-U) range and the content of the identified elements was normalised to 100% using CH as balance.

3. Results and discussion

3.1. Classic solvent extraction results

In order to describe the process of extraction of mercury(II) ions from the simple model solution using the selected compounds from the Cyphos IL group, further calculations were conducted. In the beginning, the distribution ratios (D_M) were calculated according to Eq. (1):

$$D_M = \frac{C_{M(\text{org})}}{C_{M(\text{aq})}} = \frac{C_M^0 - C_M}{C_M} \quad (1)$$

where C_M^0 and C_M are analytical mercury(II) ion concentrations in the aqueous phase before and after attaining a partition equilibrium (mol/L), respectively.

After that, the percentage of metal ions extraction (%E) was calculated [Eq. (2)]:

$$\%E = \frac{D_M \cdot 100\%}{D_M + \frac{V_{\text{aq}}}{V_{\text{org}}}} \quad (2)$$

where V_{aq} and V_{org} are the same volumes of aqueous and organic phases, respectively ($V_{\text{aq}}/V_{\text{org}} = 1$).

The results of parameters described in classic solvent extraction (D_M and %E) are presented in Table 2.

The highest distribution ratio ($D_M = 3.23$) and percentage of extraction (%E = 76.37%) was obtained using Cyphos IL 102 in given conditions. In the case of Cyphos IL 101, the efficiency of the process decreases by more than half (%E = 35.59%) with a value of D_M equal to 0.55. For other

extractants, the values of %E are very low and decrease in the following order: 16.24% > 15.78% > 15.27% > 11.84% for CIL 103 > CIL 104 > CIL 109 > CIL 105, respectively. The obtained efficiencies also correspond to the values of distribution ratios in those processes. These results show that classic solvent extraction of mercury(II) ions in selected conditions is effective with CIL 102, but for other extractants is not very efficient.

3.2. Characterisation of PIMs

Taking into account the results obtained during classic solvent extraction, only CIL 101 and CIL 102 were used for PIM experiments.

3.2.1. FTIR-ATR analysis

The obtained polymer inclusion membranes (Fig. 2) were investigated using FTIR-ATR spectroscopy.

The FTIR-ATR analyses of PIMs were made before the transport experiments. The recorded spectra are presented in Fig. 3.

The interpretation of infrared spectra was conducted using IRPal 2.0 programme and based on the literature data [29–31].

Fig. 3a shows the FTIR-ATR spectrum of the PLA/CIL 101 polymer inclusion membrane consisting of PLA as polymer support, Cyphos IL 101 as ion carrier, and NPOE as a plasticizer. In turn, Fig. 3b presents the spectrum of

Table 1
Composition of tested polymer inclusion membranes

Membrane symbol	Polymer	Plasticizer	Carrier
PLA/CIL 101	PLA	NPOE	Cyphos IL 101
PLA/CIL 102	PLA	NPOE	Cyphos IL 102
PVC/CIL 101	PVC	ADO	Cyphos IL 101
PVC/CIL 102	PVC	ADO	Cyphos IL 102

Table 2
Values of distribution ratios (D_M) and the percentage of mercury(II) ions extraction (%E) using Cyphos IL compounds

Extractant	D_M	%E (%)
Cyphos IL 101	0.55	35.59
Cyphos IL 102	3.23	76.37
Cyphos IL 103	0.19	16.24
Cyphos IL 104	0.19	15.78
Cyphos IL 105	0.13	11.84
Cyphos IL 109	0.18	15.27

Values of D_M and %E given with tolerance ± 0.01 .

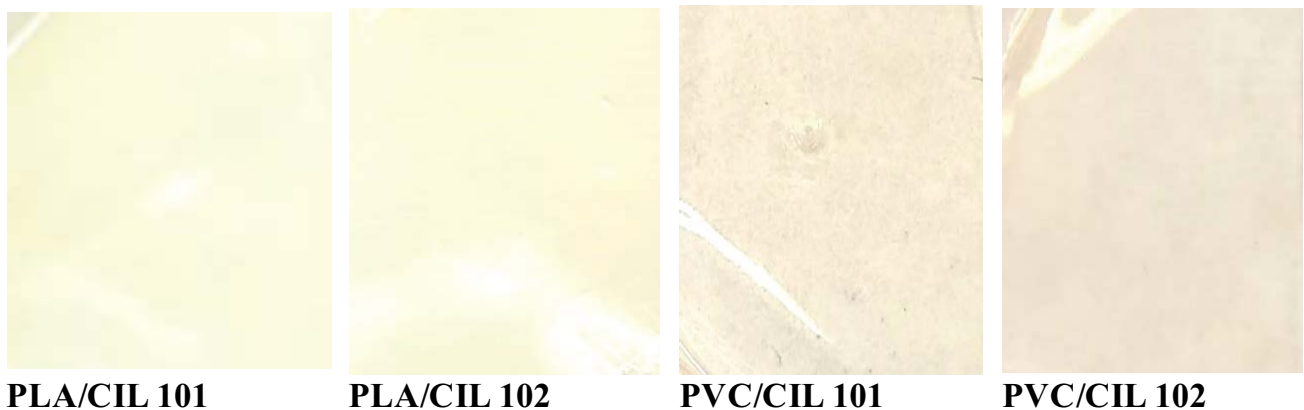


Fig. 2. Fragments of polymer membranes whose composition was analysed using FTIR-ATR spectroscopy.

PLA/CIL 102 membrane, which differs from the previous membrane in that it contains Cyphos IL 102 instead of Cyphos IL 101. In both spectra, peaks characteristic of groups from the polymer matrix can be seen. The spectra show the characteristic peaks that appears at 1,754 and 1,756 cm^{-1} related to the stretching vibration of the carbonyl group (C=O) present in PLA structure. Moreover, a series of peaks in the range of 1,550–1,610 cm^{-1} are visible and correspond to C–O bonds. The characteristic bands near to 2,925 cm^{-1} present at all spectra (Fig. 3) are related to CH_2 and CH_3 groups, which are present in all compounds used for the formation of PIMs. The presence of groups from NPOE ether is confirmed by the bands in the range of 1,290–1,360 cm^{-1} and 1,475–1,550 cm^{-1} which correspond to the stretching modes of N–O groups in nitro compounds, but also by the peak at 745 cm^{-1} related to C–H bonds and bands in the range of 1,400–1,500 cm^{-1} which correspond to C–C bond in aromatic compounds. Halides such as Cl and Br from CIL 101 and CIL 102 are confirmed by the presence of a band in the range 500–680 cm^{-1} , whereas the peak at 1,454 cm^{-1} is responsible for the C–P bond.

In the case of the PIMs: PVC/CIL 101 (Fig. 3c) and PVC/CIL 102 (Fig. 3d), characteristic peaks at 2,925 and 1,728 cm^{-1} are visible and correspond to the alkyl (CH_2 and CH_3) and C=O groups, respectively. Carbonyl groups in the mentioned membranes are related to plasticizer ADO. The peaks from halides are also present on the spectra (500–680 cm^{-1}). Cl atoms are present in PVC and in the Cyphos IL 101 molecules, whereas Br atoms are in Cyphos IL 102 molecules. Moreover, the peak at 1,434 cm^{-1} is attributed to the stretching vibrations of the C–P group of CIL 101 and CIL 102.

All of the characteristic bands visible in the above FTIR-ATR spectra (Fig. 3) confirmed the presence of individual components in the tested polymer inclusion membranes: PLA or PVC as a polymer matrix, NPOE or ADO as plasticizers, and CIL 101 or CIL 102 as ion carriers. Between components, probably only van der Waals or hydrogen bonds are present.

3.2.2. Contact angle measurement of PIMs

The determination of the contact angle of polymer inclusion membranes makes it possible to determine their

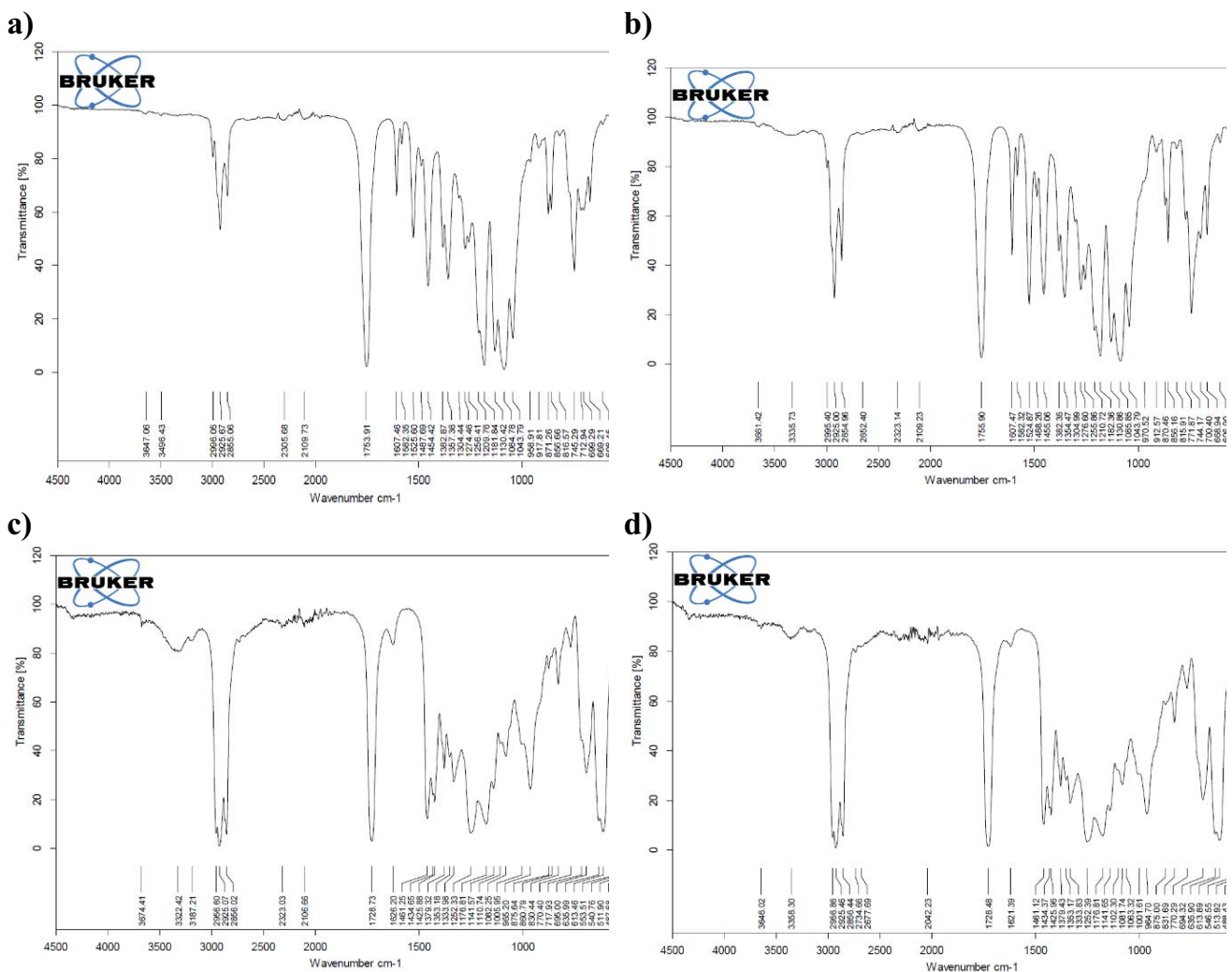


Fig. 3. FTIR-ATR spectra of polymer inclusion membranes recorded before the transport experiments: (a) PLA/CIL 101, (b) PLA/CIL 102, (c) PVC/CIL 101, and (d) PVC/CIL 102.

physical properties. The surface is hydrophobic when its static water contact angle is $>90^\circ$ and is hydrophilic when CA is $<90^\circ$ [32]. Fig. 4 presents the contact angle for the tested PIMs. The results of CA for polymer membranes containing PLA used as a matrix were 41.03° and 49.27° for the PLA/CIL 101 and PLA/CIL 102 membranes, respectively. In turn, for membranes with PVC, they were 45.23° and 50.1° for the PVC/CIL 101 and PVC/CIL 102 membranes, respectively. The values of CA for the tested membranes are similar and indicate that all of the surfaces are hydrophilic. Materials that exhibit hydrophilic properties have found application in separation processes [33], so the resulting polymer membranes have been used to remove mercury ions from acidic aqueous solutions.

3.3. Transport of mercury(II) ions across tested PIMs

As already noted, for the experiments on the transport across the tested PIMs, membranes obtained from PLA or PVC as a polymer matrix, NPOE or ADO as a plasticizer and CIL 101 or CIL 102 as a metal ion carrier (prepared according to paragraph 2.3.1) were used. Only CIL 101 and CIL 102 were selected as carriers because they exhibited the highest efficiency in binding mercury ions from an aqueous

solution in extraction processes. The study also aimed to compare the efficiency of the transfer of these ions from the feed phase to the stripping phase by two types of polymer matrices: affordable and widely available PVC and biodegradable PLA.

The kinetics of the transport processes across all of the PIMs were described using a first-order reaction concerning metal ion concentrations according to the procedure described by Zawierucha et al. [20]. The rate constant (k) values were calculated from a plot of the relationship of $\ln(c/c_0)$ vs. time (Fig. 5).

The correlations between $\ln(c/c_0)$ and time were linear, as confirmed by the high correlation coefficient (R^2) ranging from 0.9455 to 0.9952.

The kinetics parameters and recovery reached during the Hg(II) ions transport across the tested PIMs from the feed phase are summarised in Tables 3 and 4.

From Table 3 it can be seen that the highest kinetics parameters (k , P , J_i) can be observed for the PLA/CIL 102 membrane, obtained from PLA polymer and with Cyphos IL 102 used as an ion carrier. The lowest initial values of the rate constants, permeability coefficients and initial flux of the transport of Hg(II) ions were observed in case of membranes containing Cyphos IL 101 as a carrier (membranes

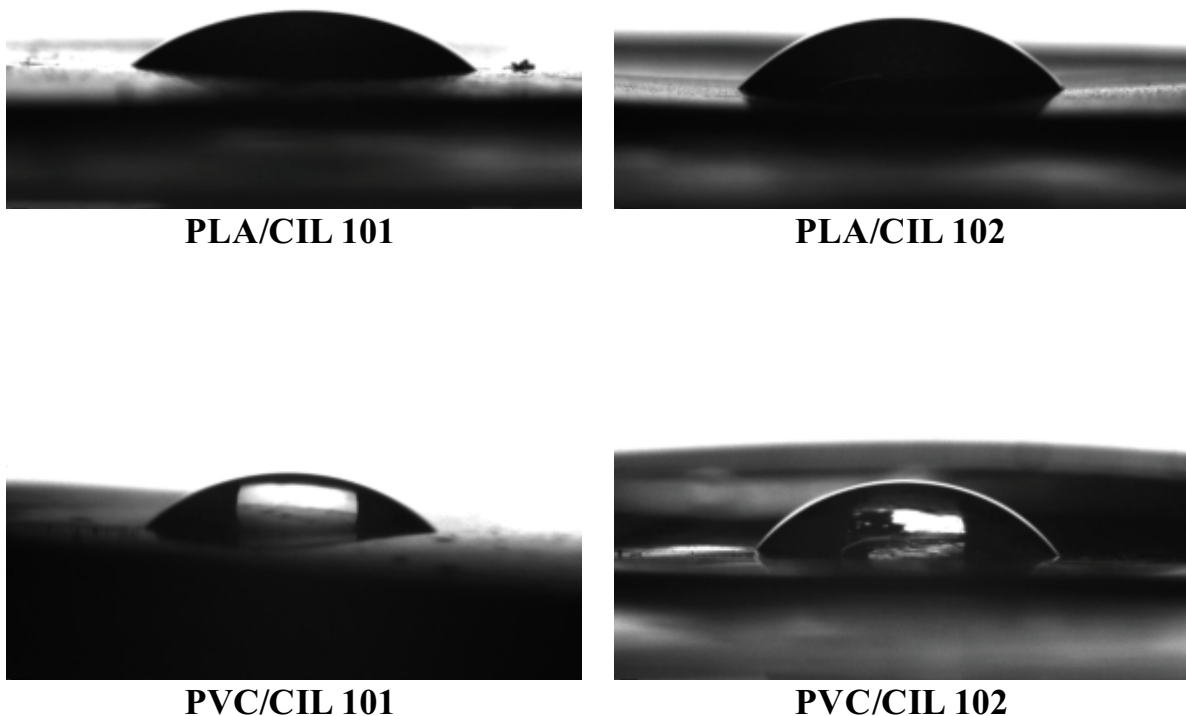


Fig. 4. The picture shows the wettability of the tested polymer inclusion membranes. Contact angle was determined using the Krüss DSA100E drop shape analyser, method T-1, 5 μL of water, 23°C .

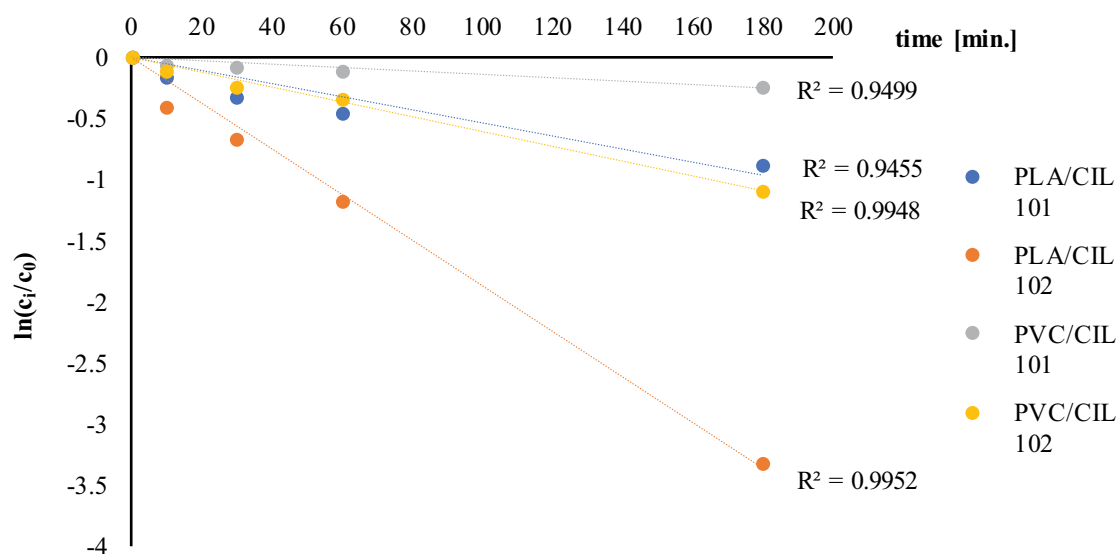


Fig. 5. The changes in the relationship of $\ln(c_t/c_0)$ vs. time for Hg(II) transport across the tested polymer inclusion membranes. Feed phase: 1,000 mg/L of Hg(II) ions; stripping phase: 1.0 mol/L HNO_3 . The values of $\ln(c_t/c_0)$ given with tolerance ± 0.001 .

Table 3

Kinetic parameters for competitive transport of Hg(II) ions across the tested polymer inclusion membranes. Conditions as in Fig. 5

k (s^{-1})	Permeability coefficient, P ($\mu\text{m/s}$)	Flux, J_i ($\mu\text{mol/m}^2\cdot\text{s}$)
PLA/CIL 101		
9.02×10^{-5}	18.45	91.96
PLA/CIL 102		
3.12×10^{-4}	63.88	318.45
PVC/CIL 101		
2.34×10^{-5}	4.78	23.84
PVC/CIL 102		
1.02×10^{-4}	20.84	103.88

Values of k given with tolerance $\pm 1 \times 10^{-5}$, and the values of P , J_i and RF given with tolerance ± 0.01 .

PLA/CIL 101 and PVC/CIL 101). Those differences can be connected with the differences in the formation and stability of the Hg(II) complexes with both of the investigated carriers.

Based on the change in Hg(II) ion concentration in the feed phase, the recovery factor (RF) was calculated (Table 4). Polymer membranes containing Cyphos IL 102, irrespective of the type of matrix, showed the highest rates of Hg(II) ion separation. The PVC/CIL 102 membrane separated the most, as much as 99.76% of Hg(II) after 24 h of the process. At the same time, 99.48% of Hg(II) ions were separated using the PLA/CIL 102 membrane. Moreover, this membrane enabled the recovery of approximately 96.37% of Hg(II) ions after only 3 h of the process. By contrast, lower recovery rates were obtained for membranes containing Cyphos IL 101 as

a carrier (PLA/CIL 101 membrane 80.40% and PVC/CIL 101 membrane 66.40% Hg(II)) after 24 h of the process.

Regardless of the metal ion carrier used, polymer membranes containing PLA as a matrix enabled faster and more efficient recovery of mercury(II) ions. This was probably due to the presence in the polymer structure of additional carbonyl groups which may also be involved in the binding of mercury(II) ions. Also, PLA, as a biodegradable polymer derived from renewable raw materials, may be an alternative to synthetic polymer membranes.

3.4. WD-XRF analysis of PIMs after Hg(II) ions transport processes

The WD-XRF spectra of the membranes used in the transport of mercury(II) ions are shown in Fig. 6.

The analysis performed confirmed the presence of the key components used to obtain polymer membranes. Moreover, the spectra show that mercury(II) ions were permanently accumulated only in the structure of membranes obtained on the basis of poly(vinyl chloride) and with the addition of ADO plasticizer. This phenomenon is not observed for biodegradable PLA membranes and could possibly be explained by the more compact structure of PVC membranes compared to PLA ones. The other elements identified in the qualitative XRF spectra above originate either from the film used during the measurements or represent minor contamination of the sample.

Therefore, when the advantages of using the tested PIMs are assessed not only in terms of the efficiency of separation of mercury(II) ions from aqueous solutions, but also in terms of the recyclability of PIMs after the transport processes of these ions, one can conclude that PLA membranes are definitely easier to dispose of. In the first place, they do not contain toxic ions after the separation processes, as proven by X-ray fluorescence studies and, secondly, they are made of an environmentally friendly and easily biodegradable polymer.

4. Conclusions

The study investigated the removal of mercury(II) ions from acidic aqueous solutions. From all the tested extractants, Cyphos IL 102 and Cyphos IL 101 showed the highest efficiency for binding mercury(II) ions in classic solvent extraction in given conditions, and in these two cases, the percentage of extraction reached 76.37% and 35.59%,

respectively. Cyphos IL 102 also turned out to be the most effective ion carrier in the tested polymer inclusion membranes. After a 24 h transport process, 99.76% of Hg(II) ions were separated across the PVC/CIL 102 membrane (obtained from poly(vinyl chloride) used as polymer matrix and bis(2-ethylhexyl) adipate used as plasticizer), and 99.48% across PLA/CIL 102 membrane (obtained from biodegradable poly(lactide) used as polymer matrix and 2-nitrophenyl

Table 4

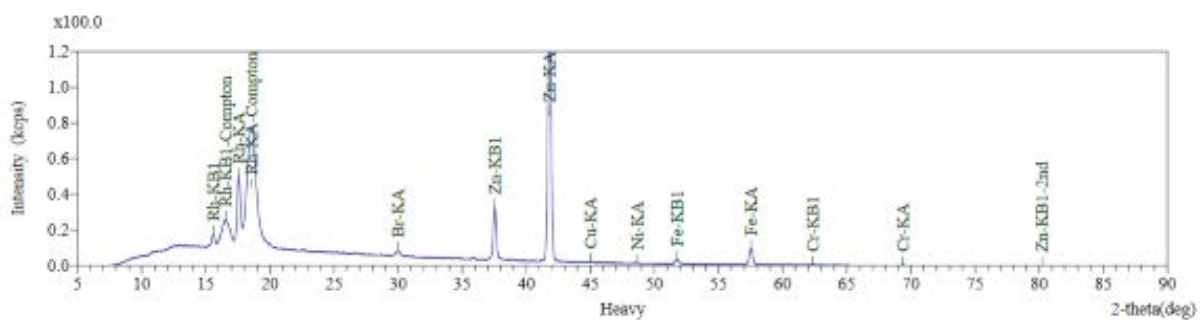
Recovery factors for competitive transport of Hg(II) ions across the tested polymer inclusion membranes. Conditions of experiments as in Fig. 5

PLA/CIL 101		PLA/CIL 102	
Time (min)	Recovery factor, RF (%)	Time (min)	Recovery factor, RF (%)
0	0	0	0
10	15.00	10	33.00
30	27.50	30	49.00
60	36.50	60	68.85
180	58.80	180	96.37
1,440	80.40	1,440	99.48

PVC/CIL 101		PVC/CIL 102	
Time (min)	Recovery factor, RF (%)	Time (min)	Recovery factor, RF (%)
0	0	0	0
10	5.75	10	26.50
30	6.99	30	22.00
60	10.12	60	29.00
180	20.94	180	66.20
1,440	66.40	1,440	99.76

Values of RF given with tolerance ± 0.01 .

PLA/CIL 101



PLA/CIL 102

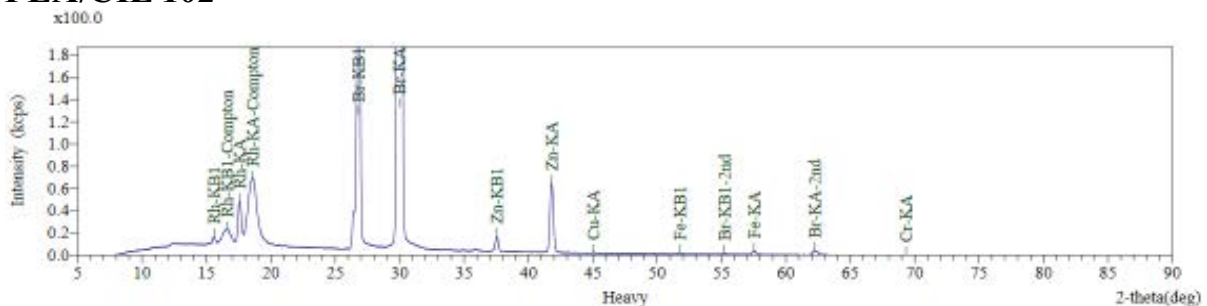
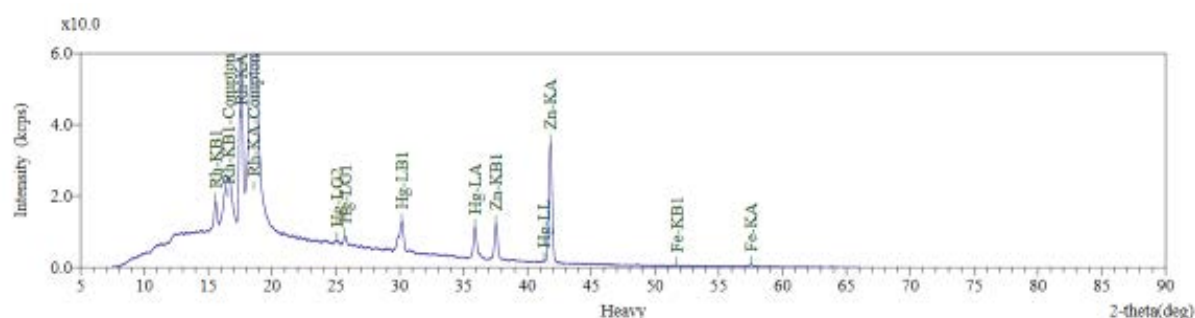


Fig. 6. (Continued)

PVC/CIL 101



PVC/CIL 102

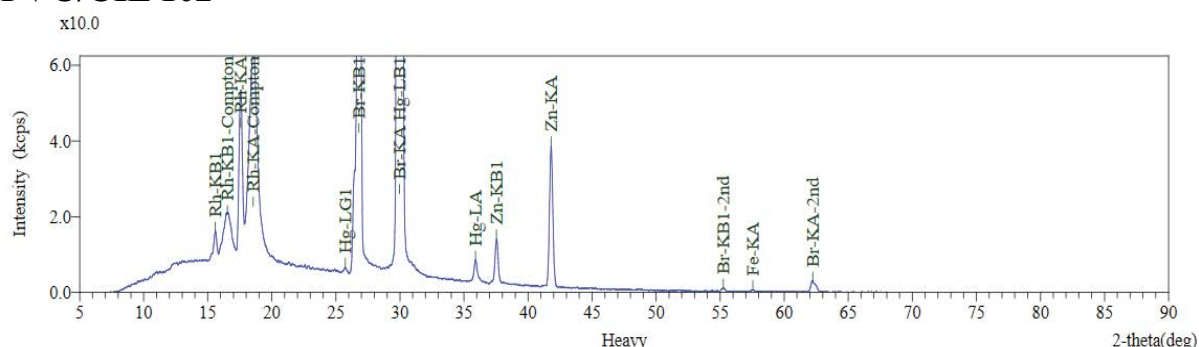


Fig. 6. The WD-XRF spectra of polymer inclusion membranes used in transport processes.

octyl ether used as plasticizer). The Fourier-transform infrared spectroscopy studies confirmed the presence of individual components in the tested pure polymer inclusion membranes: a polymer – PLA or PVC, a plasticizer – NPOE or ADO and the ion carrier – CIL 101 or CIL 102. In turn, the values of contact angles for all polymer membranes were similar and confirmed the hydrophilic character of their surfaces. The wavelength-dispersive X-ray fluorescence spectroscopy study proved that mercury(II) ions accumulate in the structure of membranes obtained from poly(vinyl chloride).

Symbols

ADO	– Bis(2-ethylhexyl) adipate
CA	– Contact angle, °
C_M^0	– Analytical mercury(II) ion concentration in the aqueous phase before attaining a partition equilibrium, mol/L
C_M	– Analytical mercury(II) ion concentration in the aqueous phase after attaining a partition equilibrium, mol/L
D_M	– Distribution ratio
%E	– Percentage of metal ions extraction, %
FTIR-ATR	– Fourier-transform infrared spectroscopy-attenuated total reflectance
GF-AAS	– Graphite furnace atomic absorption spectroscopy
ILs	– Ionic liquids
J_i	– Initial flux, $\mu\text{mol}/\text{m}^2\cdot\text{s}$
k	– Rate constant, s^{-1}
NPOE	– 2-nitrophenyl octyl ether
P	– Permeability coefficient, $\mu\text{m}/\text{s}$

PLA	– Poly(lactide)
PIMs	– Polymer inclusion membranes
PVC	– Poly(vinyl chloride)
RF	– Recovery factor, %
SE	– Solvent extraction
V_{aq}	– Volume of aqueous phase, L
V_{org}	– Volume of organic phase, L
WD-XRF	– Wavelength-dispersive X-ray fluorescence spectroscopy

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