Advancements in Polymer Inclusion Membranes for Metal Ion and Organic Compound Transport: A Post - 2017 Review

Sourabh Muktibodh[1], Aditi Kumawat[2], Aaradhana Yadav[3]

[1]Head & Professor, Department of Chemistry, Mata Jijabai Govt. Girls. P. G. College (Affiliated to D. A. V. V. University), 452007, India
Email: *sourabhmuktibodh[at]gmail.com*

[2]Research Scholar, Mata Jijabai Govt. Girls. P. G. College (Affiliated to D. A. V. V. University), 452007, India
Email: *aditikumawat132[at]gmail.com*
Corresponding Author Email: *aditikumawat132[at]gmail.com*

[3]Research Scholar, Mata Jijabai Govt. Girls. P. G. College (Affiliated to D. A. V. V. University), 452007, India
Email: *aaradhanayadav4[at]gmail.com*

Abstract: ***Author of this article has given a review on this subject earlier[1] indicating developments till 2017. Many other review articles of similar nature are also available[2] specially i. e., S. D. Kolev and Co - workers. An exhaustive review in 2006[3] by the same authors drew attention of many researchers in the field. Mathematical models have been proposed and recovery of various metal ions including precious metal ions like gold (Au) [4] have been successfully achieved by PIM experiments. There has been a rapid growth in the field and new applications of PIM are constantly appearing in the scientific text. Different carriers, plasticizers and membrane materials have been used to develop PIM that offers flexibility, stability and effective separation. This makes the field attractive, fascinating and addresses many environmental issues. Present article critically reviews all such parameters after 2017 till date.***

Keywords: transport, polymer inclusion membrane, carrier, polymer, plasticizer

Abbreviations:
BLM, Bulk liquid membrane; SLM, Supported liquid membrane; ELM, Emulsified liquid membrane; PIM, Polymer inclusion membrane; CTA, Cellulose tri acetate; PVC, Poly vinyl chloride; PVDF - HFP, Poly (vinylidene fluoride - co - hexafluoropropylene); PBAT, Poly (butylene adipate - co - terephthalate); 2 - NPOE, 2 - Nitrophenyl octyl ether; DOP, Dioctyl phthalate; o - NPPE, o - Nitrophenyl pentyl ether; o - NPOE, o - Nitrophenyl octyl ether; Aliquat 336, Ionic liquid methyl trioctylammonium chloride; IL, Phosphonium ionic liquids; D2EHAG, N - [N, N - di (2 - ethyl hexyl) amino carbonyl - ethyl] glycine; HTTA, (2 - thenoyltrifluoro acetone); PC - 88A, 2 - ethylhexylphosphoric acid mono - 2 - ethyl hexyl ester; D2EHAF, N - [N, N - di (2 - ethyl hexyl amino carbonyl ethyl) phenylalanine; Cyphos IL (101), trihexyl (tetradecyl) phosphonium chloride; Versatic - 10, neodecanoic acid; KP1, methyl; KP2, Carboxyl group; TOPO, Trioctylphosphine oxide; D2EHPA, bis (2 - ethylhexyl) phosphoric acid; TBP, Tributylphosphate; EDAB - acac, ethylene diamine bis - acetylacetone matrix; P_{88812} Cl, trioctyl (dodecylphosphonium chloride); Cyphos IL (104), trihexyltetradecylphosphonium bis - (2, 4, 4 - trimethylpentyl) phosphinate; RIL, Reactive ionic liquids, RILC1Br, 3 - (1, 3 - diethoxy - 1, 3 dioxopropan - 2 - yl) methylimidazolium bromide; RILC4 - Br, 3 - (1, 3 - diethoxy - 1, 3 - dioxopropan - 2 - yl) - 1 - ethylimidazolium bromide; RILC8 - Br, 3 - (1, 3 - diethoxyl - 1, 3 - dioxopropan - 2 - yl) - 1 - octylimidazolium bromide; FT - IR, Fourier - Transform infraredspectroscopy; XRD, X - ray diffraction; DSC, Differential scanning colorimetry; AFM, Atomic force microscopy; SEM, Scanning electron microscopy; ICP - AES, Inductively coupled plasma atomic emission spectroscopy; ICP - OES, Inductively coupled plasma optical emission spectrometry; AAS, Atomic absorption spectroscopy; WD - XRF, X - ray fluorescence with wave dispersion; TG, Thermal gravimetry; REM, Rare earth metal ions; FIA, Flow injection analysis; β - CD, Cyclodextrin; PVDF, Poly (vinylidene fluoride);

1. Introduction

Membrane based processes have fascinated substantial attention as an invaluable technology for many industries in current years[5]. This involves BLMs, ELMs, SLMs. Due to the certain limitations such as poor stability, low interfacial surface area and emulsion breakage, these membranes are impractical for use in large scale application. To overcome these limitations, a novel type of liquid membranes, commonly called Polymer Inclusion Membranes have developed. Due to their special superiority, for instance easy synthesis, effective carrier, adaptability and good mechanical properties, they are proved to be a great substitute to supported liquid membrane[5]. Polymer Inclusion Membrane is a kind of liquid membrane where liquid segment is occupied inside the polymer linkage of base polymer. PIMs are generally made of a base polymer (commonly P. V. C. (Poly Vinyl Chloride)), C. T. A. (Cellulose triacetate), plasticizer or modifier and an extractant (Carrier). The base polymer gives the mechanical strength and the plasticizer offers elasticity and flexibility. The function of Carrier is to ties with the species of interest and carriages it across the membrane. Polymer Inclusion Membrane is superior because it proposes an effective separation method, utilizes negligible solvent, offers fast mass transfer and high selectivity. This can also be used for sensing especially Electrochemical Sensing. As it offers high selectivity. Therefore, it can be used for making ion selective electrodes and come to be a part of industries[6].

It is astonishing that P. V. C and C. T. A. have been the only two main polymers used for most of the P. I. M. researches governed so far because both P. V. C. and C. T. A. are compatible with most of the carriers such as D2EHPA and Aliquat 336, easily available and easy to handle. P. V. C. is broadlyused polymer because it has high strength and flexibility andit shows firmnessin both acidic and basic solutions. Those having membranes with low M. W. provides easier transport. This is because both P. V. C. and C. T. A. can be used to prepare a thin film of membrane with a comparatively simple practice depends on dissolution in an organic solvent. Polymers which are used in P. I. M. are thermoplastic[7] because theycomprise of linear polymer fibers and there are no cross - linkage between these fibers, making them soluble in an organic solvent, where the polymer fibers become separated. As a result, a very stable thin film can be formed, in spite of the absence of any intermolecular covalent bonds although it should be noticed that there is a disentanglement process happening over a very long - time scale. It is still essential that the M. W. (molecular weight) of the polymer used is larger than the critical entanglement molecular weight (M. Wc) of that polymer[7].

C. T. A. that is capable of forming highly oriented hydrogen bonding contains a large number of acetyl and hydroxyl groups. On the other hand, the C - Cl group in P. V. C. is comparatively polar and non - specific dispersion forces dominate the intermolecular interactions. As a result, P. V. C. is an amorphous polymer with a small degree of crystallinity and C. T. A. is usually highly crystalline. Additionally, C. T. A. can be slightly hydrated, P. V. C. is not. The hydration characteristics of C. T. A. and other cellulose derivatives makes them vulnerable to hydrolysis, especially in an acidic environment[8].

Table 1: Properties of three polymers most frequently used in PIMs

Polymer	M. W. used in PIMs (KDa)	M. Wc (KDa)	Tg (^{0}C)	Tm (^{0}C)	Polymer Characteristics
Poly Vinyl Chloride (P. V. C.)	90 - 180	12.7	80	-	Slightly crystalline, mostly amorphous
Cellulose triacetate (C. T. A.)	72 - 74	17.3	-	302	Infusible, high degree of crystallinity, excellent strength
Cellulose tributyrate (C. T. B.)	120	47.4	-	207	Infusible, high degree of crystallinity, excellent strength

Source: "Extraction and transport of metal ions and small organic compounds using Polymer Inclusion Membranes" by Long D. Nghiem

All investigation on PIMs has been governed on a laboratory scale until now. Beaker experiments have been used for extraction studies where the PIM is submerged in a solution of the target species and experiments of the solution are taken at different time intervals for evaluation. A two - partition transport cell with a similar architecture to the one used in a normal SLM experiment has also been utilized to convey some extraction operations.

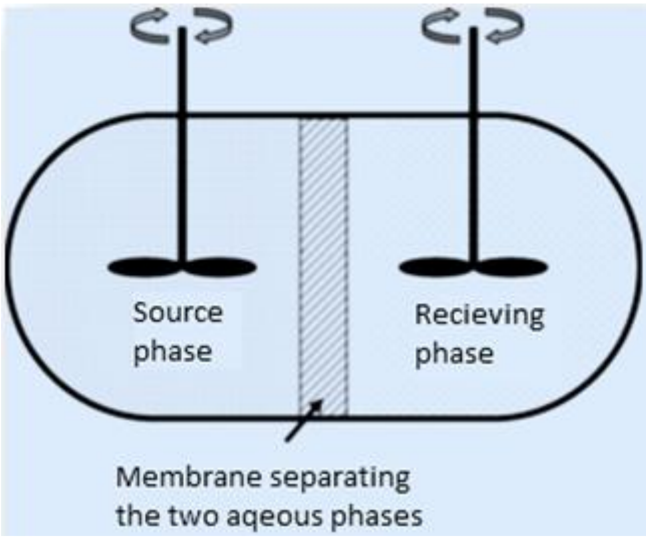

Figure 1: A typical PIM or SLM experiment set up

Although research on transport employ this kind of cell more frequently. All different kinds of carriers go through a similar transport process. Ionic species are exchanged between these two compartments along the membrane phase separating them as part of the transport mechanism via PIMs. With the right ionic composition in the source and receiving compartments, the desired solute can be transported through the membrane[9].

Important components of P. I. M. transport modelare -
1) Polymer Inclusion Membrane
2) Feed Phase (metal solution)
3) Receiving Phase (acid solution)
4) Stirring Magnets
5) Water Bath
6) Magnetic Stirrer

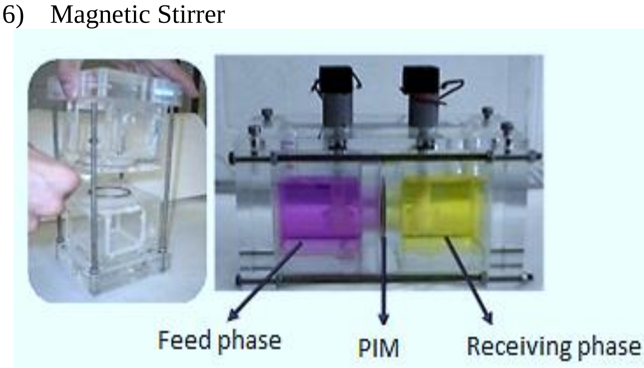

Figure 2: PIM Fabrication Model

The nature of the target solute, membrane composition, temperature, physiochemical characteristics of the carrier, PH, and nature of the source (feed phase) and stripping phase all play a role in the actual transport mechanism in PIM, which can be highly complex. To fully comprehend the intricate connections between these elements, more study is required[10].

For membranes with crystalline structures, the mechanism is based on the ion jumping between the subsequent carriers present in the layer of the membrane, which results in consecutive complexation and decomplexation from the feed to the strip compartment[11].

2. Transport Studies

For the extraction of various metal ions and small organic solutes, this review aims at giving an exhaustive concise of the recent knowledge pertinent to PIMs.

Work of Ruben Vera et. al (2018) [12]indicates that a PIM containing the Aliquat 336 as the extractant has been used satisfactorily for the preconcentration of arsenate found in groundwater samples, permitting its determination through an easy colorimetric approach. Interestingly, the delivery of As (V) was not affected by the material used in PIM (CTA or PVC) nor the thickness of the membrane. A mathematical model needs to be developed. Recoveries from 79% to 124% after only 5h of contact time has been reported in this work. Work of Monica Baczy#ska et. al (2018) [13] signifies that a PIM containing Phosphonium ionic liquids as a carrier and CTA, PVC as a polymer has been used for the transport of Zn (II). To show the impact of PIM morphology on the efficacy of ZnII) transport, commonly used techniques were employed. The stability of PIM was investigated after five cycles of transport processes. Differences in the morphology and structure of the membrane material finally affects the transport study. The membrane made up of C. T. A. is capable of transporting Zn (II) to the receiving phase up to 90% while P. V. C. membranes are unable to transport Zn (II) ions and results obtained through are negligible.

The work of Fukiko Kubota et. al (2018) [14]was focused on the selective separation and restoration of gold ions from leachates of rejected mobile phones using PIM transportation system and liquid - liquid extraction using 2 - NPOE as a plasticizer and D2EHAG as an extractant. The examination of the results confirmed that mobile phone scrap has 397g/ton of gold. Recovery of 96% of the Au (III) ions into the receiving solution of the transport cell leaving all other metal ions inside the leachate has been reported. Focus on the separation of other ions is also an interesting area. In other interesting work of Wataru Yoshida et. al (2018) [15]selective separation of Sc from other REM ions using CTA as a polymer, 2 - NPOE, DOP as a plasticizer and HTTA, PC - 88A, D2EHAG, D2EHAF as a carrier has been investigated. Interestingly, the authors examined that the newly advanced PIMcontaining D2EHAF exhibited wonderful firmness in five cycles of extraction and back - extraction of Sc (III) with unimportant deterioration in its performance. Results indicate that the molecular structure of the carrier has strong impact on membrane stability. It was observed that the carrier molecule with the introduction of the phenyl group shows substantial stability development.

In other publication Mohammad Reza Yaftian et. al (2018) [16]reported the separation of V (V) from sulfate solutions in a presence of variety of cations and anions using 2 - NPOE as a plasticizer, Cyphos IL (101) as a carrier was used in PVDF - HFP based membrane. Off line extraction method was used to eliminate the interference of molybdenum (VI) using the same PIM. A FIA system was conducted for the determination of V (V) in water. Relatively low sampling rate of $4h^{-1}$ is the drawback of FIA Method. It was suggested that drawback can be improved by using thinner PIMs with suitable mechanical strength.

In the recent work of Maha Sharaf et. al (2018) [17]reported the selected separation of Sc from other rare earth metals using PIM prepared with PC - 88A as a carrier and DOP, 2 - NPOE as a plasticizer. The membrane organized with PC - 88A showed high extractability but the weak back - extraction of the extracted Sc^{+3} ions did not permit the transport of those ions to the receiving solution of a membrane transport apparatus. To conquer this hassle, a novel technique was developed using a mixture of the carriers PC - 88A and Versatic - 10 and DOP as a plasticizer. The PIM made with these materials shows interestingly the selective recovery of Sc^{+3} ions from other REM ions in nitrate media. Work of Lamia Moulahcene et. al (2019) [18]indicates a PIM carrying insoluble β - CD polymer as an extractant, PVC as a polymer and DBP as a plasticizer in different proportions has been used for the removal of pharmaceutical pollutant from waste water. This work can be delivered to industries for environmental cleanup of contaminated water. FT - IR investigation found that DBP was inserted among those polymer chains through non - covalent interactions. This brought about a spacing of PVC /poly (β - CD) chains producing a better approach of guest molecules to PIM cyclodextrins. PIMs containing β - CD polymer became unsteady in basic conditions and was extra powerful at acidic P^H. Authors of this article further reported that the proportion of β - CD polymer and waste water agitation had a favorable impact on drug extraction at 10ppm. Those preliminary effects exhibit the excessive capacity for drug extraction of this polymer.

The work of Anna Nowik - Zajac et. al (2019) [19]for the separation of Ag (I) in PIM interestingly demonstrated the use of the o - NPPE as a plasticizer. CTA as a polymer and derivatives of calixpyrroles with methyl (KP1) and carboxyl (KP2) groups as ion carriers. Various factors such as P^H of the source phase, metal and plasticizer etc. on the efficiency of Ag (I) transport is presented in his work. It was confirmed from the results that transport of silver ions through PIM follows the first order reaction kinetics and by altering the composition of source phase values of initial Ag (I) ions transport fluxes increase with an increasing p^H from 2 to 4. CTA proves to be a best polymer in comparison to PVC. PVC is less efficient, which results in lower values of Ag (I) ions transport flux. Another work appeared in 2019[20]by Wataru Yoshida et. al where the membrane composition is investigated using PIM containing variety of carriers like D2EHAG, D2EHAF, Versatic - 10, TOPO and 2 - NPOE as a plasticizer for the separation and recovery of scandium from $0.1moldm^{-3}$ sulfate solutions. The PIM composition with the use of two amino acid extractants D2EHAG and D2EHAF indicates easier extraction of Sc (III) instead of using industrial extractants such as Versatic - 10, TOPO has been demonstrated in his study. Sc (III) was completely separated thermodynamically from mixture of metal ions and partially separated from Fe (III) kinetically using a PIM containing D2EHAF as a carrier. It was observed that the initial flux value for Sc (III) was two times higher than that of Fe (III).

Adam Makowka et. al (2019) [21]reported the separation of La (III) using PIM containing CTA as a polymer matrix and 2 - NPOE as a plasticizer. D2EHPA, TBP are used as a carrier. Results have shown that the metal ions were transported from the source phase into 2M H_2SO_4 as a receiving phase. The use of D2EHPA as the ion carrier has been considered to be more effective for removal of La (III). Samples were tested using a plasma emission spectrophotometer.

The authors (Nurul Syazana Abdul - Halim et. al (2019)) [22]have developed a PIM containing Aliquat 336 as an extractant and CTA as a base polymer. It was observed that the metal ions adsorption uptake increased with increasing Aliquat 336 concentration. The PIM composed of CTA and Aliquat 336 gave the excessive removal productivity for ion metal Cd (II) compared to Zn (II) and Fe (II). Using Legergren first order kinetics model the kinetic studies were performed. Interestingly, it was shown that there is no metal uptake in CTA - Aliquat 336PIMs in the absence of Aliquat 336. Kinetical data gave useful information of adsorbtion rate.

Work of Hona Pyzska et. al (2020) [23] indicates that a new PIM with EDAB - acac matrix has been used for the separation of Zn (II) from solutions containing nonferrous metal ions (Co (II), Ni (II), Cu (II), Cd (II)). Studies show that the stability constants increase in series Ni (II) < Cu (II) < Co (II) < Cd (II) < Zn (II), and their logarithms are 8.85, 10.61, 12.73, 14.50, 16.84 respectively. The PIMs show following series of transport selectivity Zn (II) > Cd (II) > Co (II) > Cu (II) > Ni (II). The initiated stability constants of the complexes also decrease in this order. Highest recovery factor (90 - 98.0%) for Zn (II) ions has been reported in his work. The recovery factors for Cd, Co, Cu are also high. Healing issue of every ion relies upon at the composition of aggregate.

Another work appeared in 2020 by Anna Nowik - Zajac et. al[24]where CTA based PIM with diverse concentrations of calixpyrrole ester as the carrier were studied to decide their potential to move Ag (I) from aqueous nitrate solutions. The prepared membranes have been found to be noticeably permeable. The initial fluxes had been determined at diverse temperatures. Results have shown that when the metal concentration in the source aqueous phase was below 10^{-3} M, the process was very fast and effective. Authors reported that excessive quantity of plasticizer lead to increase in membrane viscosity and highest rate of Ag (I) transport beyond the membrane was found with 0.05M of the carrier. The association constant values can be a reason for the fast transport rate. The authors (Piotr Szczepanski) 2020 et. al[25]have developed a PIM containing CTA as a polymer, D2EHPA as a carrier and NPOE as a plasticizer for the separation of Zn, Cd, Cu, Pb. In this paper, two kinetic models are suggested for the explanation of metal ion transport in PIM. The models have ben suited to the actual experimental statistics of Zn (II), Cd (II), Cu (II), and Pb (II). The consequences indicated that initial fluxes (from $2X10^{-11}$upto $9X10^{-10}$mol/cm^{2}s) are much like the values found by other authors in systems working underneath similar conditions. It was observed that one of the most frequently applied models based on equation similar to the first - order chemical reaction equation.

The authors (Ferhat Sellami) 2020 et. al[26]of this paper describe the enhanced removal of Cr (VI) by PIM based on PVDF and Aliquat 336. The plasticizer 2 - NPOE was also used. It was observed from the results that the PIM with only 20 wt% of Aliquat 336 is suitable for the complete transport of Cr (VI) ions from the donor to acceptor phase. Furthermore, plasticizer addition of 5 wt% increases the transport flux. PVDF based PIMs were found to be highly stable and highly durable in his study and because of such qualities they are suitable for long term application. Recovery of 97% Cr (VI) from a mixture containing other heavy metal ions (Cd (II), Pb (II), Fe (II), Zn (II), Cu (II), Ni (II), Co (II)) has been reported.

Phumlile Kunene (2020) [27]and co - workers found that polysulfone was investigate as an alternative base - polymer for PIM's. In this work of Phumlile and co - workers, Polysulfone based PIMs were successfully synthesized using the solvent evaporation technique. The PIMs did not contain plasticizer. This PIMs found stable in both acidic and basic mediums as well as chemically stable at as high as 180^0C. PSF based PIMs had a significantly lower extraction efficiency for Cr (VI) when compared to the PVC based PIMs. The result obtained in this study indicate that polysulfone can effectively be used as a base polymer for PIMs and the absence of plasticizer makes the polysulfone based PIM more cost effective to synthesis.

Takafumi Hanada (2020) [28] and co - workers observed the efficient and selective transport of rhodium (III) across a polymer inclusion membrane (PIM) from a 0.1 mol dm^{-3} HCl feed solution also containing iron (III) to a receiving solution containing 0.1 mol dm^{-3} HCl and 4.9 mol dm^{-3} NH_4Cl was achieved using a $P_{88812}Cl$ as the metal ion carrier. It was indicated from the results that the concentration difference of the chloride ion between the feed and the receiving solutions is the driving force for the Rh (III) transport and the transport performance was emphasized by decreasing the membrane thickness.

Work of Nauman Ali et. al. (2020) [29]indicates a selective transportation of molybdenum from model and ore through polymer inclusion membrane using PVC as a polymer and Aliquat 336 as a carrier. PVC is used as uphold for tricaprylymethyl ammonium chloride a basic carrier and which depends on the extractant concentration in organic phase. It was concluded that PIM was quite more stable and 99% of Mo (VI) was extracted through PIM. The results indicate that maximum flux value was obtained at 0.16M Aliquat - 336. Increase in H_3PO_4 concentration from 0.05 to 1.5 M results into an increase in molybdenum ions. The maximum flux of 3.00×10^{-6} mol/m^{2}s through PIM was found at 1.5M H_3PO_4.

Tania C. F. Ribas et. al. (2020) [30] reported the use of polymer inclusion membrane and a chelating resin for the flow based sequential determination of copper (II) and Zinc (II) in natural waters and soil leachates using PVC as a base polymer and D2EHPA as a carrier. To retain copper (II) at P^H 2.0, chelex 100 was used as a polymeric material. Zinc (II) was not retained at this P^H, thus permitting for its quantification to be executed free of copper (II) interference.

Work of Elzbieta Radzyminska – Lenarcik et. al (2020) [31] indicates a transport of cadmium (II) and lead (II) through polymer inclusion membrane using O - NPOE as a plasticizer and alkylimidazole as a carrier and CTA as a base polymer.

Cadmium (II) ions can be effectively separated from equimolar aqueous solutions of lead (II) nitrates by using transport across PIMs with 1 – alkylimidazole as well as in solvent extraction. The initial fluxes of cadmium (II) and lead (II) ions increase with an increase in the basicity of carrier molecules. It can be assumed that more hydrophobic 1– alkylimidazole can be more effective in the separation of cd and lead ions in membrane techniques.

Enriqueta Antico (2021) [32]and co - workers prepared a nanoparticle – doped polymer inclusion membranes and characterized as new materials for the removal of arsenate and phosphate from waters using CTA as a base polymer.

They have used the ionic liquid (Aliquat 336) as the extractant. For the extraction inorganic nanoparticles such as ferrite (Fe_3O_4), SiO_2, TiO_2 and multiwalled carbon nanotubes, were blended with the extractant mixture.

Since Aliquat 336 acts as an anion exchanger, the nanoparticle – doped polymer inclusion membranes have been explored in different applications (i) as a sorbent material for extraction of arsenate & phosphate anions. (ii) as an organic phase for separation of arsenate and phosphate in a three - phase system. It was found that the presence of the nanoparticle has no effect in mass loss results.

Work of Joanna Konczck et. al. (2021) [33]indicates a facilitated transport of Pb (II) through polymer inclusion membrane containing O - NPOE, O - NPPE as a plasticizer and calixresorcin [4]arenes as an extractant.

The highest Pb (II) ions removal efficiency was obtained for the membrane with tetrathiophosphorylated heptyl – calixresorcin [4]arene as an ion carrier. The activation energy value suggests that the transport process is controllable both by diffusion and chemical reaction.

The obtained study results indicate that the efficiency of the tested ions transport by means of non - functionalized resorcin [4] arenes with heptyl chains is lower than for the derivatives functionalized with phosphoryl, triphosphoryl or ester group, where by tetrathiophosphorylated resorcin [4] arene is the most efficient carrier of Pb (II) ions.

In the paper Ferhat Sellami (2021) [34] and his team observed that the extraction of Cr (VI) ions can be done by PIM containing ionic liquid Aliquat 336 as carrier.

The FT – IR analysis revealed the presence of interactions between the negatively charged carboxyl group of CTA and the positively charged ammonium groups of Aliquat 336 and between the hydroxyl group of CTA and the carboxyl groups of PBAT. It was observed that PIMs containing PBAT prepared in this study were more effective regarding the transport of Cr (VI) ions from the feed solution to the stripping solution. The membrane based on CTA accumulation in the membrane phase decreases and the recovery factor increases. It was determined that the transport of Cr (VI) was the highest when the membrane contained 35 wt% PBAT, 35% wt% CTA and 30% Aliquate 336.

The paper reports on the first application of a PIM for the extraction of bismuth (III) ion using D2EHPA as an extractant and PVC as a base polymer[35]. A plasticizer – free PVC based PIM containing the extractant D2E4PA in 50% concentration was found to extract with high selectivity Bi (III) from its 0.2 mol l^{-1} sulfate feed solutions adjusted to P^H 1.3 and containing other common base metal ions such as Cu (II), Zn (II), Mn (II), Co (III), Ni (II), Cd (II), Al (III), Mo (VI), Cr (III). The co - extraction of Fe was readily eliminated by the addition of sodium fluoride. It was established that Bi (III) is extracted via a cation exchange mechanism. It involves the formation of BiL_3 $(HL)_3$ adduct where HL stands for D2EHPA.

Bosirul Hoque et. al. (2021) [36]signifies a cross linked PIM for enhanced gold recovery from electronic waste using variety of polymers, NPOE as a plasticizer and cyphod IL 104 as a carrier. This membrane was developed for the first time for the enhanced Au (III) recovery from aqua regia digests of electronic waste (discarded mobile phones) CTA, PVC, PVDF – HFP were examined as base polymer.

In aqua regia feed solutions (6 mol L^{-1} acidity) only the cross - linked PIM containing triarylsulfonium hexafluorophosphate was able to achieve complete Au (III) recovery.

The authors (Piotr Szczepanski et. al. (2021) [37] have developed a PIM containing O - NPOE as a plasticizer, reactive ionic liquids and Aliquat 336 as an extractant and CTA as a base polymer to transport and separation of Cd (II), Cu (II), Pb (II), Zn (II) ions from chloride aqueous solutions. Studies found that three ionic liquids based on the imidazole derivatives were synthesized. The effect of alkyl chain length in the imidazolium cation of RILs on transport and separation properties were evaluated. From among three synthesized RILs only the RIL with longest alkyl chain (RIL_8 –Br) can be successfully applied as the carrier for Cd (II). In the investigated feed solution concentration range the selectivity order was found to be Cd (II) > Zn (II) > Pb (II) > Cu (II) and it was independent of experimental conditions.

The study of Salar Bahrami et. al. (2022) [38] showed that PIM composed of 50% PVDF - HFP 40 wt%, Aliquat 336 and 10wt% DBP was suitable for the selective extraction of V (V) from sulphate solution in presence of Al (III), Co (II), Cu (II), Fe (III), Mn (II) and Ni (II). Quantitative back - extraction of V (V) was achieved in a back - extracting solution containing 6M H_2SO_4 / 1 v/v % of H_2O_2. The extraction of V (V) was suggested to be based on the exchange of the Aliquate 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 play a key role in the quantitative back - extraction of V (V). Co - extraction of MO (VI) with V (V) was eliminated by its selective extraction at P^H 1.

Table 2: Review Table

S. No.	Membrane base polymer	Plasticizer	Carrier	Target ions / Molecules	Morphology	Remarks
1.	CTA, PVC	-	Aliquat 336	As (v)	UV - Visible Spectrophotometer	Ruben Vera et. al. (2018)
2.	CTA, PVC	NPOE	Phosphonium Ionic Liquids (IL)	Zn (II)	FT - IR, XRD, DSC, AFM, SEM	Monica Baczy#ska et. al. (2018)
3.	PVC	2 - NPOE	D2EHAG	Au (III)	ICP - AES	Fukiko Kubota et. al. (2018)
4.	CTA	2 - NPOE, DOP	HTTA, PC - 88A, D2EHAG, D2EHAF	Sc (III)	Contact angle measurements, ICP - AES	Wataru Yoshida et. al. (2018)
5.	PVDF - HFP	2 - NPOE	Cyphos IL (101)	V (V)	ICP - OES	Mohammad Reza Yaftian et. al. (2018)
6.	CTA	2 - NPOE, DOP	PC - 88A, Versatic 10	Sc (III)	ICP - AES, SEM	Maha Sharaf et. al. (2018)
7.	PVC	DBP	βCyclodextrin	Ibuprofen, Progesterone	FT - IR, SEM, Thermogravimetric analysis	Lamia Moulahcene et. al. (2019)
8.	CTA	O - NPPE	Derivatives of Calixpyrroles with methyl (KP1) and carboxyl (KP2) groups	Ag (I)	SEM, AFM	Anna Nowik – Zajac et. al. (2019)
9.	CTA	2 - NPOE	D2EHAG, D2EHAF, Versatic 10, TOPO	Sc (III)	ICP - OES	Wataru Yoshida et. al. (2019)
10.	CTA	NPOE	D2EHPA, TBP	La (III)	Plasma aemission Spectrometer	Adam Makowka et. al. (2019)
11.	CTA	-	Aliquat 336	Cd (II), Zn (II), Fe (II)	AAS	Nurul Syazana Abdul - Halim et. al. (2019)
12.	CTA	O - NPPE	EDAB - acac	Zn (II)	AAS	Hona Pyzska et. al. (2020)
13.	CTA	O - NPPE	Calix [4] pyrrole ester	Ag (I)	SEM	Anna Nowik – Zajac et. al. (2020)
14.	CTA	NPOE	D2EHPA	Zn (II), Cd (II), Cu (II), Pb (II)	SEM	Piotr Szczepanski (2020)
15.	PVDF	2 - NPOE	Aliquat 336	Cr (VI)	SEM	Ferhat Sellami et. al. (2020)
16.	Polysulphone	-	Aliquat 336	Cr (VI)	FT - IR	Phumlile Kunene et. al. (2020)
17.	PVDF - HFP	2 - NPOE	$P_{88812}Cl$	Rh (III)	SEM	Takafumi Hanada et. al. (2020)
18.	PVC	-	Aliquat 336	Mo (VI)	UV - Visible Spectrophotometer, SEM	Nauman Ali et. al. (2020)
19.	PVC	-	D2EHPA	Cu (II), Zn (II)	ICP - OES	Tania C. F. Ribas et. al. (2020)
20.	CTA	O - NPOE	Alkylimidazole	Cd (II), Pb (II)	AFM	Elzbieta Radzyminska - Lenarcik et. al. (2020)
21.	CTA	-	Aliquat 336	As (V), phosphate	SEM, FT - IR, Contact angle measurements	Enriqueta Antico et. al. (2021)
22.	CTA	O - NPOE, O - NPPE, bis (2 - ethyl hexyl) adipate	Calixresorcin [4]arenes	Pb (II)	WD - XRF, SEM, AFM, TG	Joanna Konczck et. al. (2021)
23.	CTA, PBAT	-	Aliquat 336	Cr (VI)	FT - IR, Tensile tests, Contact angle measurements, SEM, DSC, TGA, X - ray diffraction studies	Ferhat Sellami et. al. (2021)
24.	PVC	-	D2EHPA	Bi (III)	FT - IR, SEM, AFM, TGA, Contact angle measurements, Stress - strain analysis	Davood Kazemi et. al. (2021)
25.	PVDF - HFP, PVC, CTA	NPOE	Cyphos IL 104	Au (III)	ICP - OES, AFM	Bosirul Hoque et. al. (2021)
26.	CTA	O - NPOE	Reactive Ionic Liquids (RILC1 - Br), (RILC4 - Br), (RILC8 - Br), Aliquat 336	CdII), Cu (II), Pb (II), Zn (II)	SEM, AFM	Pioyr Szczepanski et. al. (2021)
27.	PVDF - HFP	DBP, 2 - NPOE	Aliquat 336	V (V)	AFM, Contact angle measurements, TGA, Energy dispersive X - ray spectroscopy, Stress - strain measurements	Salar Bahrami et. al. (2022)

3. Conclusion

One of the major goals of this review is to display the variation of materials (plasticizer, carrier, base polymer) used in the preparation of Polymer Inclusion Membranes and the inputs of different authors to the literature. Studying the literature, the correct composition of the membrane material is very essential because it affects both the performance and quality of the membrane. Commonly, the composition with 40% base polymer, 40% carrier, and 20% plasticizer were used in the literature for membrane production[39]. Among various plasticizers, the most usually used are NPOE and NPPE because membranes made with these plasticizers gave the best flux results. In most of the studies conducted until now, Aliquat 336 and D2EHPA have been favored as extractants due to its availability and versatility[39]. We need more research to find new types of carriers and plasticizers. Considering the studies, it must be admitted that there are many publications available in literature related to P. I. M. and number of these publications is slowly progressively. Nevertheless, it is considered that PIMs can displace traditional systems and perform major role chiefly in metal removal and recovery. It is superior because PIMs are both recyclable and can be reconstructed[40].

Water monitoring has also been done by P. I. M. experiments. PIMs can be useful in distinct analytical advances like sensing, passive sampling, sample pre - treatment employing partition and pre - concentration for the resolution of a various types of environmental water contaminants[41]. PIMs proved to be useful in the separation of certain heavy metal (As) found in ground water[42]. Due to the toxicity of arsenic, separating it from ground water has proved to be really important research in this field. Recently, the most common heavy metal contaminants such as cadmium, chromium, copper, lead, mercury have been separated by different authors using P. I. M. Not only these, selective separation and restoration of gold ions from the leachates of rejected mobile phones using P. I. M. transportation system have been performed by Fukiko Kubota et. al. (2018). This is the great achievement of the authors in this field to save our environment from the garbage of electronic scrap.

References

[1] Muktibodh S & Mishra P, *Int J Sci Res*, 7 (2018) 800 - 808.
[2] Almeida M I G S, Cattrall R W & Kolev S D, *AnalChim Acta*, 987 (2017) 1 - 14.
[3] Nghiem L D, Mornane P, Potter I D, Perera J M, Cattrall R W & Kolev S D, *J Membr Sci*, 281 (2006) 7 - 41.
[4] Kubota F, Kono R, Yoshida W, Sharaf M, Kolev S D, Goto M, *Sep PurifTechnol*, 214 (2018) 1 - 32.
[5] Gyves J D & Miguel E R D S, *Ind Eng Chem Res*, 38 (1999) 2182 - 2202.
[6] Almeida M I G S, Cattrall R W & Kolev S D, *J MembrSci*, 415 - 416 (2012) 9 - 23.
[7] Rais J, Mason C V & Abney K D, *Sep Sci Technol*, 32 (2006) 959 - 969.
[8] Gardner J S, Walker J O & Lamb J D, *J Membr Sci*, 229 (2003) 87 - 93.
[9] Nghiem L D, Mornane P, Potter I D, Perera J M, Cattrall R W, Kolev S D, *JMembr Sci*, 281 (2006) 7 - 41.
[10] Sastre A M, Kumar A, Shukla J P &Singh R K, *Sep purif Meth*, 27 (1998) 213 - 298.
[11] Arous O, Amara M & Kerdjoudj H, *Arab J Sci Eng*, 35 (2009) 79 - 93.
[12] Vera R, Antico E & Fontas C, *Water*, 10 (2018) 1 - 10.
[13] Baczy#ska M, Waszak M, Nowicki M, Prz#dka D, Borysiak S & Rosocka M R, *Ind Eng Chem Res*, 57 (2018) 1 - 57.
[14] Kubota F, Kono R, Yoshida W, Sharaf M, Kolev S D & Goto M, *Sep PurifTechnol*, 214 (2018) 1 - 32.
[15] Yoshida W, Baba Y, Kobuta F, Kolev S D & Goto M, *J Membr Sci*, 572 (2018) 291 - 299.
[16] Yaftian M R, M I G S Almeida, Cattrall R W & Kolev S D, *Talanta*, 181 (2018) 385 - 391.
[17] Sharaf M, Yoshida W, Kubota F, Kolev S D & Goto M, *RSC Adv*, 16 (2018) 8631 - 3637.
[18] Moulahcene L, Skiba M, Bounoure F, Benanamor M, Milon N, Hallouard F & Skiba M L, *Int J Environ Res Public Health*, 16 (2019) 1 - 12.
[19] Zajac A N, Zawierucha I & Kozlowski C, *RSC Adv*, 9 (2019) 31122 - 31132.
[20] Yoshida W, Kubota F, Baba Y, Kolev S D & Goto M, *ACS Omega*, 4 (2019) 21122 - 21130.
[21] Makowka A &Pospiech B, *Autex Res J*, 19 (2019) 288 - 292.
[22] Halim N S A, Shoparwe N F, Weng S K, Zulkefeli N S W, *In proceedings ofInternational Conference on Environmental (ICENV)*, pp.020014 - 1 - 020014 - 7 (2019).
[23] Pyszka H & Lenarcik E R, *Membr*, 10 (2020) 1 - 14.
[24] Zajac A N, Zawierucha I& Kozlowski C, *Int J Mol Sci*, 21 (2020) 2 - 17.
[25] Szczepanski P, *Membr*, 10 (2020) 1 - 11.
[26] Sellami F, Senhadji O K, Marias S, Colasse L & Fatyeyeva K, *Sep PurifTechnol*, 248 (2020) 1 - 12.
[27] Kunene P, Akinbami O, Motsoane N, Tutu H, Chimuka L &Richards H, *J Membr Sci Res*, 6 (2020) 203 - 206.
[28] Hanada T, Firmansyah M L, Yoshida W, Kubota F, Kolev S D & Goto M, *ACS Omega*, 5 (2020) 12989 - 12995.
[29] Ali N, Naz N, Shah Z, Shah A, Khan A & Hawaz R, *Bull Chem Soc Ethiop*, 34 (2020) 93 - 102.
[30] Ribas T C F, Croft C F, Almeida M I G S, Mesquita R B R, Kolev S D & Rangel A O S S, *Molecules*, 25 (2020) 1 - 24.
[31] Lenarcik E R, Pyszka I & Urbaniak W, *DesalinWater Treat*, 214 (2021) 56 - 62.
[32] Antico E, Vera R, Vazquer F, Fontas C, Lu C & Ros J, *Materials*, 14 (2021) 2 - 14.
[33] Konczyk J & Ciesielski W, *Membr*, 11 (2021) 1 - 17.
[34] Sellami F, Senhadji O K, Marias S, Couvrat N & Fatyeyeva K, *React FunctPolym*, 139 (2021) 121 - 132.
[35] Kazemi D, Yaftian M R & Kolev S D, *React Funct Polym*, 16 (2021) 1 - 10.

[36] Hoque B, Kolev S D, Cattrall R W, Gopakumar T G & Almeida M I G S, *Waste Management*, 124 (2021) 54 - 61.
[37] Szczepanski P, Guo H, Dzieszkowski K, Rafinski Z, Wolan A, Fatyeyeva K, Kujawa J &Kujawski W, *J Membr Sci*, 638 (2021) 1 - 13.
[38] Bahrami S, Dolatyari L, Jam H S, Yaftian M R & Kolev S D, *Membr*, 12 (2022) 1.
[39] Keskin B, Gokoglu B Z & Koyuncu I, *Chemosphere*, 279 (2021) 7 - 10.
[40] Keskin B, Gokoglu B Z & Koyuncu I, *Chemosphere*, 279 (2021) 7 - 10.
[41] Kuswandi B, Nitti F, Almeida M I G S & Kolev S D, *Environ Chem Lett*, 18 (2019) 129 - 132.
[42] Vera R, Antico E & Fontas C, *Water*, 10 (2018) 1 - 10.