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Preliminary Study on the Stability of Self Plasticised Thin-Flat PIM for the Extraction of 2-(4-Isobutylphenyl) Propanoic Acid (Ibuprofen)

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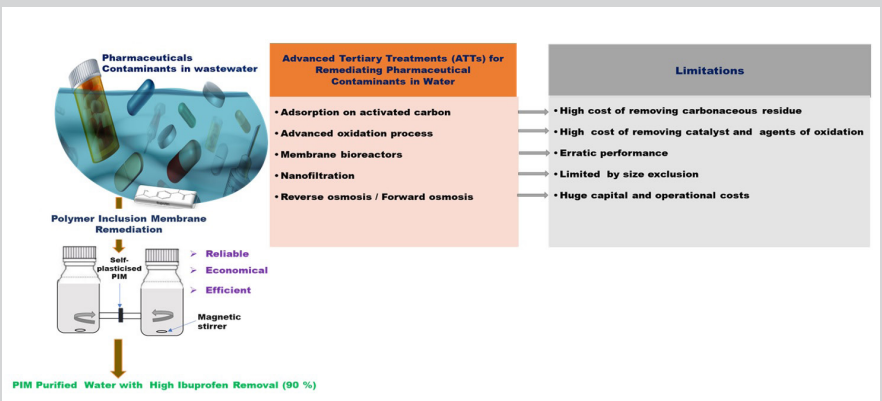
Highlights

- Application of PIM for the extraction of organic pharmaceutical microcontaminants is emerging.
- Unplasticised PIM effectively remediated low concentration Ibuprofen model.
- Bioaccumulation of the ubiquitous Ibuprofen in water is potentially harmful.
- Aliquat 336 as a carrier effectively plasticized PVC-PIM for Ibuprofen remediation.

Graphical abstract



Abstract

Advanced tertiary treatments (ATTs) have been embraced as alternative technologies to prevent the harmful health influence of pharmaceutical contaminants such as 2-(4-Isobutylphenyl) propanoic acid (Ibuprofen, Ibup.) in living beings. However, some significant drawbacks of these techniques necessitated a compelling desire to investigate alternative techniques to remediate emerging pharmaceutical compounds from water. Hence, Polymer inclusion membranes (PIMs) are currently being investigated as potentially efficient, reliable, and affordable alternative treatments. A self-plasticised PIMs containing tri-caprylmethylammonium chloride (Aliquat 336) embedded as the carrier and PVC base polymer was synthesized to remediate low Ibuprofen concentration. In a preliminary investigation, fabricated PIMs were examined by Fourier transforms infrared spectroscopy (FTIR), SEM, water uptake, contact angle (CA), chemical and physical stabilities. In addition, the PIMs were evaluated for the removal efficiency of low Ibuprofen concentration in an aqueous solution. The results showed that the self-plasticised thin-PIM could effectively extract low concentration Ibuprofen from a simulated aqueous Ibuprofen model up to ~ 90% at optimum conditions. However, a drop in removal efficiency to ~ 67% after prolonged usage stability based on continuous extraction studies (over 280 h) of three cycles indicates the limited stability of the PIM.

1. Introduction

Previously, the Drinking water inspectorate, saddled with regulating public water supplies in England and Wales, assumed that granular activated carbon (GAC) and ozone treatments were sufficient to free tap water supplies from pesticides and other traces of organic pharmaceuticals [1]. However, recent

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studies and reports have shown that several drugs are resistant to conventional wastewater treatment techniques (WWTTs) because of their high hydrophilicity and low biodegradability [2–5]. As a result, advanced tertiary treatments (ATTs) have been embraced as alternative technologies to prevent the potential harmful health effects of pharmaceutical contaminants such as the 2-(4-Isobutylphenyl) propanoic acid (Ibuprofen, Ibup.) in a living organism [6,7] Therefore, the application of advanced oxidation process (AOP), membrane separation process (MSP), and adsorption on activated carbon (AAC) in wastewater treatment have been investigated over the past three decades to meet the stringent minimum quality standard by environmental regulators [8–12]. However, some significant drawbacks of these techniques, especially the high maintenance and installation costs, are well enumerated by Olasupo and Suah [13] and Taheran et al. [14]. Furthermore, a systematic review of Scopus indexed published articles on the frequency of different Advanced tertiary water treatment techniques for removal of pharmaceutically active compounds in an aquatic system revealed that the use of Polymer Inclusion membranes (PIMs) is the least explored technique (1.8%) [13]. Hence, there is a compelling desire to investigate alternative efficient, reliable, and affordable techniques such as the limitedly explored Polymer Inclusion Membrane (PIM) to remediate pharmaceutical compounds from water.

Polymer Inclusion Membranes (PIMs) are physically transparent, flexible, and homogeneous membranes containing appropriate carrier extractants. They have highly rigid backbone structures commonly provided by a base polymer such as the frequently used polyvinyl chloride (PVC), cellulose triacetate (CTA), or, more recently, Polyvinylidene hexafluoropropylene (PVDF-Co-HFP). In addition, the base polymer provides diffusive resistance, while the carrier is required as a complexing agent or ion exchanger to transport the species of interest across the PIM selectively [15]. Aliquat 336 and D2EHPA are the two most popular commercial extractants, with the added economic advantage of plasticising the resultant membrane [16,17]. The concentration of the ubiquitous Ibuprofen in the aqueous environment is currently relatively low (10 ng / L - 209 µg / L), and the short-term exposure to anti-inflammatory drugs may be considered to be of minor concern; however, there is potential long-term exposure bioaccumulation harm of these compounds, particularly at the increasing administration of the popular over-the-counter medicine. The adverse health impacts of Ibuprofen on humans and animals are due to its high partition coefficient (log Kow = 3.79), which readily accumulates in organism tissues and obstructs human and animal endocrine activities [7,8,18–23].

The excellent properties and performance of PIMs containing no additional Plasticisers were reported perhaps for the first time by Benosmane et al. using calix[4]resorcinarenes as a carrier [24] and followed by Gherasim et al. using bis-(2-Ethylhexyl) phosphoric acid (D2EHPA) as a carrier [25]. The use of self-plasticized PIM has since been identified as a research direction of interest for the studies of PIM remediation capacities [26,27]. In addition, environmentalists have recently expressed safety concerns and biodegradability issues related to conventional Plasticisers used in PIM fabrication, particularly at the industrial level [30,31]. Besides these concerns, significant reduction in PIM production cost, reduced dope solution viscosity, increased space for more carrier embedment (the major components needed for transportation), and promotion of green technology are additional benefits of self-plasticised PIMs. A self-plasticised PIM containing DHEPA/Aliquat 336 as a carrier was successfully employed to remove metallic contaminants [24,26,27] and organic compounds [28,29]. Furthermore, Aliquat 336 carrier embedded in PVC-based PIM has successfully produced flexible and transparent structure membranes at increased Aliquat 336 content [32].

To the best of the author's knowledge, studies of self-plasticised PIMs containing Aliquat 336 for organic pharmaceutical compounds' remediation are emerging green technology that has not been sufficiently investigated. Although in our recent publication, we successfully used self-plasticised Aliquat-PVC PIM doped with graphene oxide to extract 10 mg/L Ibuprofen in an aquatic solution [33]. The addition of graphene oxide improved the physical stability of the PIMs compared to the control graphene oxide-free PIM containing only Aliquat 336 carrier, which was observed to be physically brittle. However, the relatively small amount of Aliquat 336 carrier (33.3%) employed in fabricating the graphene-free PIM may be considered insufficient to achieve the desired plasticizing effect and Ibuprofen extractability. A high carrier concentration is required to create intramembrane pathways, enabling the formed complex to transport low analytes effectively [24]. Moreover, the presence of graphene oxide in the GO-doped PIM contributed to its instability due to the hydrophilic nature of graphene oxide. Hence, the present study investigates the removal efficiency and prolonged usage stability of Self plasticised PVC-based flat sheet PIMs embedded with a varied amount of Aliquat 336 as an ionic carrier to remove the low concentration of modeled Ibuprofen wastewater.

2. Materials and Methods

2.1. Materials and reagents

Ibuprofen drug, Ibup. (Purity ≥ 99.0%) (Sigma–Aldrich, St. Louis, MO, USA) (Fig. 1a) was prepared as a modeled aqueous IBP pollutant. Polyvinylchloride (PVC) (Mw~43000) as base Polymers, Tetrahydrofuran (THF) (99.9%) (Darmstadt, Germany) employed as solvent was purchased from Sigma–Aldrich. The cationic Aliquat 336 TG carrier (Heysham, Lancashire, UK) was purchased from Alfa Aesar Thermofisher Scientific (Fig. 1b). The analytical standard reagents used include 0.1M Hydrochloric acid as the receiving phase (Merck, Darmstadt, Germany) (37% purity) and 0.1M Sodium hydroxide (Sigma Aldrich) (≥99% purity). Deionized water (Milli-Q Water System, Millipore, resistivity=18.2 MΩ/cm at 25 °C) was used throughout this study.

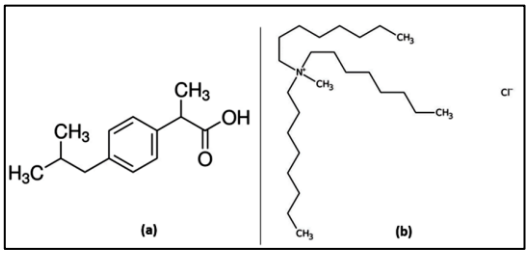

Fig. 1. Chemical; structure of (a) Ibuprofen drug, IBP and (b) Aliquat® 336 TG

2.2. Membrane fabrication

The dope solution was prepared based on fixed 20% wt PVC and varied amounts of Aliquat 336 carrier (0, 10, 20, 30, 40, and 50wt.%) dissolved in an appropriate quantity of THF solvent to obtain a dope solution (Table 1). First, the dope solution was continuously stirred on a magnetic stirrer at 65 °C. The resulting homogeneous dope solution was then sonicated to remove any air bubbles. Next, the PIM was fabricated by pouring the bubble-free dope solution on a glass plate at 30 µm pre-set thickness on a K4340 Automatic filmograph Applicator, Elcometer (Manchester, UK). The formed thin film of the membrane was allowed to evaporate at room temperature to remove the THF solvent for 24 h. Then, the partially dried film was carefully peeled off the glass plate and allowed for further THF evaporation at 25.9 ± 1 °C beyond 48 h (Fig. 2). Each fabricated PIM was first screened based on its physical stability and transparency (Table 1). However, the PIM AF contains 71.43 wt.% Aliquat 336 carrier and 28.57wt.% PVC polymer became flaccid and sticky; hence, it could not be further characterized for lack of good physical stability.

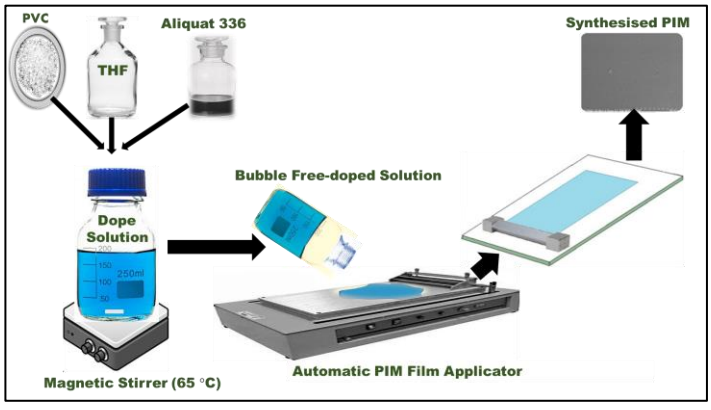

Fig. 2. A synthesis scheme of the fabricated PVC-Aliquat PIM

2.3. PIM Characterization

In the current preliminary investigation, all the fabricated PIMs except PIM AF were examined by Fourier transforms infrared spectroscopy (FTIR), water uptake, contact angle (CA), and chemical and physical stabilities. However, further characterizations were not done because only a small area of the PIM membrane samples sandwiched between 250 ml identical diffusion bottles were employed under atmospheric operating pressures and room temperature [34].

Table 1.

Fractional weight composition of the dope solution, PVC: Aliquat carrier, water uptake, and description of the resulting PIMs

Dope solution	AA	AB	AC	AD	AE	AF
Aliquat 336 (%)	0	10	20	30	40	50
THF (%)	80	70	60	50	40	30
PVC (%)	20	20	20	20	20	20
Synthesized PIM						
Aliquat 336 (%)	0	33.33	50	60	66.66	71.43
PVC (%)	100	66.66	50	40	33.33	28.57
Physical stability	Transparent but brittle	Transparent but brittle	Transparent and flexible	Transparent and flexible	Transparent and flexible	Flaccid and sticky
Water Uptake (%)	4.992 ± 0.929	13.269 ± 2.0420	23.428± 1.869	25.325± 1.560	19.306 ± 1.843	-
Remark	Slightly hydrophobic	Slightly hydrophilic	Hydrophilic	Hydrophilic	Slightly hydrophilic	-

2.3.1. Fourier transform infrared (FTIR) spectroscopy

Fourier transform–infrared spectroscopy (FTIR) was conducted to identify the interrelations among PIMs constituents. 32 scans were collected for each PIM measurement over 4000–500 cm^{-1} spectral range by FTIR spectrometry (Thermo Scientific, Nicolet 10, Waltham, MA, USA). All the FTIR spectra were analyzed using Omnic software (version 5.2a).

2.3.2. Scanning microscopy (SEM) analysis

The previously gold-plated PIM's morphological structures using Quorum SC7620 (Laughton, East Sussex, USA) were examined by SEM imaging. The membrane surface was observed at × 200 magnification while its cross-section was examined at ×1000 magnification by scanning electron microscopy (SEM) Hitachi (TM3000) Tokyo, Japan.

2.3.3. Contact angle measurements

The membranes' water contact angle (θ) was measured using an image-processing software equipped with goniometer contact angle equipment (Rame-Hart 250-FI USA) via deionized water sessile drop method on the PIM surface at ambient temperature (24 ± 1°C) with the aid of a microsyringe and droplet volume of 6 µL. An average of five (5) randomly analyzed spots were taken as the average contact angle value for each PIM to minimize experimental errors.

2.3.4. Water uptake

Water uptake was conducted to assess the hydrophilicity of the fabricated PIMs. A circular piece of each pre-weight fabricated PIMs (AA-AE) (⌀ = 30 mm) was wholly immersed in water and allowed to stand at room temperature (25.9 ± 1 °C) for 24 h. The soaked PIMs were removed using forceps, and adhering surficial water was mopped up carefully. The wet membrane was weighed and placed in a vacuum oven at 60 °C until a constant dry weight was obtained [35,36]. Equation (1) was employed to determine the percentage of water uptake. The analysis was done in duplicates to minimize experimental errors. The average values were reported as the percentage of water uptake (U).

$$\text{Water uptake (U)}\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

W_{wet} represents the weight of the wet membrane, and W_{dry} represents the constant weight of the dry membrane.

2.3.5. Membrane physical and chemical stability studies

2.3.5.1 PIM's physical stability

The physically stable PIMs were evaluated by manually bending and squeezing a sizeable portion of the PIM membrane to observe structural deformation or tears resulting from moderate hand stretching [37].

2.3.5.2. Stability based on mass change of PIMs containing Aliquat 336

The chemical stability of PIM is a helpful tool for assessing the membrane's stability for practical application in specified environmental conditions of interest because the mass loss of PIM in specific aquatic environments indicates its resilience, strength, and reusability [37,38]. Furthermore, a relationship between carrier loss due to leaching and membrane mass loss has been reported by Kagaya et al. in a detailed investigation of changes in the mass of PIMs containing PVC-Aliquat 336 carrier where the concentrations of Cl^-, NO_3^-, and SO_4^{2-} in the resulting aliquots solution of the immersed PIM were determined by ion chromatography. It was reported that the mass loss in the PIM correlates almost directly to the exact amount of Aliquat 336 leaching out of the membrane. The loss in the membrane mass was, therefore, a function of the anion exchange equilibrium between the membrane components and the type of immersed solution, which is also related to the leakage of Aliquat 336 from the PIM [39]. Hence, to preliminarily assess the loss of Aliquat 336 carrier embedded in PVC-based self-plasticised PIMs, the mass change of PIMs containing varying concentrations (0, 33.33, 50, 60, 66.67% (w/w) of Aliquat 336 carrier) immersed in deionized water and of the optimum PIM in 0.1 M NaOH solution (pH~10) and 0.1 M HCL solution (pH~1) were investigated. Each 2 x 2 cm of the Aliquat 336 embedded PIMs was immersed in freshly collected 50 mL deionized water **(**18.2 MΩ/cm and pH = ~ 6.7**)** in a 100 ml glass vial tightly capped and shaken at 400 rpm using an orbital mixer incubator (Protech Model SI-1000) at 27.9 ± 1 °C For 24 h. Similarly, the optimum PIM AD of mass 0.0455 - 0.0400 g size was immersed in a 50 ml 0.1 M NaOH for the alkalinity stability and 0.1 M HCL solution for the acidity stability test and stirred in an orbital shaker at 200 rpm for 6 hr. Subsequently, the PIMs were removed from the solution, allowed to dry at room temperature for more than 24 h, and then weighed to obtain a constant dry weight [39]. The percentage mass loss of the membranes in each media was calculated using Equation 2: All measurements were conducted in duplicates.

$$\text{Mass loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100 \quad (2)$$

Where W_o is the initial weight of the Fresh PIM, and W_t is the dry PIM's constant weight.

2.3.5.3. PIM's stability based on repeated cycles for Ibuprofen extraction

The stability and reusability of polymer inclusion membranes are critical for their commercial application. The measure of PIM's instability due to loss of the membrane liquid phase resulting in a gross mass loss of the PIM correlates to the membrane reusability. Therefore, the stability and durability of a membrane can be accessed by its reusability [40]. The stability of the optimum PIM AD containing 60% (w/w) Aliquat 336 and 40% (w/w) PVC based on repeated cycles for Ibuprofen extraction was investigated during the prolonged batch experiments (288 h). The same membrane was used in three consecutive cycles to evaluate its stability while the feed and receiving phases were renewed with an appropriate fresh supply for each cycle [41,42].

2.4. Ibuprofen Extraction Studies

A 10 mg/L of model Ibuprofen was prepared to study the rate of Ibuprofen removal from the feed compartment. The 10 mg/L model Ibuprofen solution was filled into the feed phase of two identical compartments (250 mL) with the PIM sandwiched on Teflon support between the two glass diffusion cells, while 0.1 M HCL was filled into the receiving phase of the identical bottles. The tested PIM has an approximate diffusing area (*A)* of ~7.07 cm^2, and both phases were simultaneously and continuously stirred at 400 rpm [43]. The moderate stirring speed of 400 rpm in both the feed and receiving phases was maintained throughout the study as a compromise between a decreased aqueous boundary layer thickness and high turbulence[23]. The pH of the feed solution has been reported as one of the most critical factors in evaluating solutes' integrity and extraction efficiency using carrier-embedded PIM [44,45]. Ibuprofen is considered a weak-acid pharmaceutical drug with an optimum acid dissociation constant (pKa) value of 4.91 [4,46]. The removal efficiency of Ibuprofen is strongly pH-dependent, and the extraction of Ibuprofen is enhanced at higher pH, where it is deprotonated and forms an ion pair with the cationic Aliquat

336 carrier (diffusion of the ion-carrier complex in the PIMs membranes) as previously demonstrated by Ahmad et al., and Wang & Yang, [33,48]. However, it is well established that PVC-based PIMs are better stable in an acidic medium than in an alkaline medium [49]. Hence the current preliminary experiment was conducted in a mildly acidic solution (pH = 6) but at a higher Ibuprofen pKa (4.91). All experiments were performed in duplicates and at room temperature (25.9 ±1 °C). First, the simulated stock solution of Ibuprofen was prepared by dissolving the appropriate quantity of Ibuprofen in deionized water. Subsequently, experimental solutions were prepared freshly to obtain the desired Ibuprofen concentration by serial dilution from the prepared simulated stock solution. Finally, samples were taken every 24 h in a quartz cuvette to measure the concentration of Ibuprofen at 222.5 nm using a direct UV–Vis spectrometer (Spectroquant Pharo 300, Merck, Darmstadt, Germany) [23]. The removal efficiency of Ibuprofen was evaluated using equation 3.

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Where C_o and C_t represent the solute concentration in the feed at a time 0, and at a time t, respectively.

3. Results and Discussion

3.1. FTIR analysis

Fourier transforms–infrared spectroscopy (FT–IR) measurement is a technique for identifying the organic composition, types of bonds, chemical bonds, and organic content differences among fabricated PIM membranes [50]. The FTIR spectrum of the pristine PIM AA peaks signifies the specific chemical groups of pure PVC, such as the carbon-hydrogen (C−H) bond and carbon-chlorine (C−Cl) bond, presented in Table 2. The C−H stretching mode corresponds to 2850, 2910, and 2970 cm^{-1}, while peaks 1430-1440 and 684 cm^{-1} correspond to the aliphatic C−H bending. The peak at 1250 cm^{-1} is attributed to the bending bond of C−H near Cl. [51,52]. Finally, a broad peak at 1630 cm^{-1}, PIM, has been well-established to correspond to the bending vibration of water [53]. The peaks at 1060 and 832 cm^{-1} correspond to the C−O−C stretch coordinated bands of residual THF solvent on the PIMs [51]. The unique uniform FTIR spectra of the Aliquat 336 embedded PIMs typified by Fresh PIM AD are presented in Table 2 and Fig. 3a. It is observed that besides the identical typical peaks in the fresh and Aliquat carrier embedded PIMs, there is a new distinct O−H stretch broad peak at 3380 $cm^{-1,}$ which was observed to stretch increasingly in proportion to the amount of Aliquat 336 embedded. This new peak could be attributed to the water, octanol, and decanol content of the added Aliquat 336 [54,55]. Aliquat 336 in the embedded PIM is also observed on strong peaks at 2920 and 2850 cm^{-1}. Although these peaks are identical to the less intense ones on the pure PVC PIM, the strongly stretched new peaks of 2920 and 2850 cm^{-1} observed on the Aliquat embedded PIM represent the C-H stretching of Aliquat 336 aliphatic CH group or the CH_3–N and CH_2–N groups, respectively [44,51]. After the Ibuprofen extraction using PIM AD, an entirely new distinct carbonyl stretching of the iso-propionic acid group observed at a peak at 1720 cm^{-1} is recognized as well-defined bands characteristic of pure Ibuprofen (Fig. 3b) [56]. Similarly, the distinctive peak peaks at 1617-1639 cm^{-1} are assigned to ring C−C characteristic aromatic absorptions stretch of a benzene ring, indicating the physical presence of Ibuprofen in the membrane [57–59]. A complimentary study conducted to investigate the effect of Ibuprofen concentration on the intensity of the peculiar Ibuprofen peaks on the membrane shows that the intensity of the peaks at 1710-1723 cm^{-1} and 1617-1639 cm^{-1} (Fig. 3c), which are attributed to the iso-propionic acid group and pharmaceutical excipients contain aromatic groups of the Ibuprofen drug respectively, increases as the concentration of Ibuprofen increase from 5 to 50 ppm.

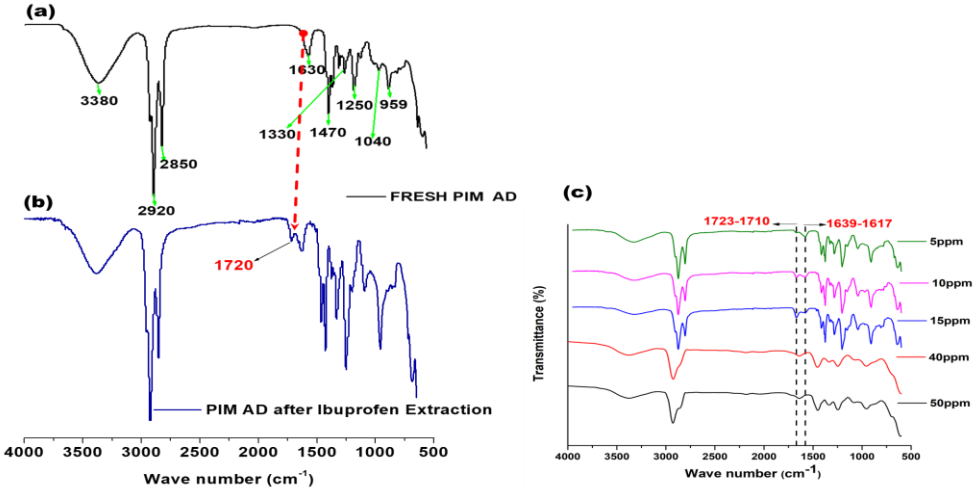

Fig. 3. FTIR spectra of (a) Fresh PIM AD, (b) PIM AD post-Ibuprofen, and (c) PIM AD soaked in a varied concentration of Ibuprofen

Table 2.

Absorbance peaks, corresponding functional group, and assignments of fabricated PIMs

Membrane	Wave number (cm^{-1})	Functional group	Assignment	Source
Pristine membrane (PIM AA)	2910- 2970	C-H stretching	alkene	PVC
	2850 / 956 - 959	C-H stretching	alkane	PVC
	1060 and 832	C-O-C stretch	alkyl-substituted ether	Residual THF
	1250	C-Cl bending	C−H near Cl	PVC
	1330	C–H deformation mode	alkane	PVC
	1430-1440 and 684	C-H bending	alkene	PVC
	1630	O-H stretch	water	PVC
Aliquat embedded membrane (PIM AD)	3380	O-H stretch	water, octanol, decanol	Aliquat 336
	2920-2850	C-H (CH2) extensive stretch	aliphatic CH group	Aliquat 336
Post Ibuprofen extraction (PIM AD)	1720	carbonyl stretching	isopropionic acid group	Ibuprofen
PIM AD at varied Ibuprofen concentration	1617-1639	aromatic stretching	pharmaceutical excipient	Ibuprofen

3.2. Physical stability and Morphological structure of the Fabricated PIMs

The successfully fabricated membranes were transparently homogenous, as pictorially depicted in Fig. 4c. The pure PVC PIMs without Aliquat 336 (PIM AA) were rigid but became more flexible with the increasing amount of Aliquat 336 carrier embedded into the film, which was confirmed by bending and writhing the optimum membranes (PIM AD) without any permanent deformation or tearing, as shown pictorially n Fig. 4c. It has been reported that an increase in the hydrophilicity of Aliquat embedded- PVC-based PIMs shows the excellent plasticizing ability of the carrier and correlates well to its mechanical stability [17,27,37,60]. Membrane morphology is a critical parameter in evaluating the properties of PIMs [41]. The homogeneous symmetric dense microstructure of the thin PIM surface indicates a uniform interfacial interaction of the PVC/Aliquat 336 carrier in the PVC polymer matrix [61]. As observed from the SEM images in Fig. 4a, at nil Aliquat 336 wt.% (AA) and 33.3 Aliquat 336 wt.% (AB), the PIM's surface had no apparent pores, but at higher Aliquat concentration, few apparent tiny pores were observed (PIMs AC-AE), which are not easily perceptible due to the limitation of the SEM acquisitions. In addition, obvious wrinkles were observed on the PIM with 66.7 Aliquat 336 wt.% (AE) [61,62]. Furthermore, visually homogenous PIMs that are transparent and free of any extractant droplets were most times assumed to be chemically homogenous; however, it has been observed that despite the transparency and homogeneity of Supported liquid membranes (SLM), its microstructure is filled with organic liquids in their pores hence, the chemical homogeneity of a PIM cannot always be deduced by mere visual homogeneity [61].

3.3. *Membrane formation mechanism for different concentrations of Aliquat 336 embedded PIMs*

The SEM surface and cross-section images obtained in this study are presented in Fig. 4a and b. The results of the obtained image show that the PIM surface's internal morphology is affected by the quantity of Aliquat 336 carrier embedded to the extent of the membrane homogeneity and its interior structure [61,62]. For example, the SEM captured membrane surface and cross-section morphology of PIMs AA and AB with nil and 33.3% Aliquat 336 carrier, respectively, appeared to be microscopically homogenous with no apparent pores or micro-channeling; however, PIMs AD containing 60/40 Aliquat 336 /PVC weight% carrier shows they are microscopically densely homogenous with some microscopically apparent pores and the existence of micro-channels filled with Aliquat 336 in the PIM, as opined by Xu et al. [61,62]. It has been reported that the state of distribution of Aliquat 336 in the PVC-based PIM depends on the number of embedded carriers in the membrane. Aliquat 33 molecules are believed to be entangled with the PVC polymer in a PIM consisting of 30 - 40% Aliquat 336 carrier, thereby acting as a plasticiser while it forms an aggregate in the membrane bulk at higher concentration. [62,63]. The phase morphology of the resulting PIM is determined by PIM thickness and evaporation rate of THF during the phase separation of the solution of Aliquat 336 and PVC [32]. However, using the automatic film casting technique employed in the current study rather than the commonly employed method of pouring the dope solution into a petri dish or glass ring on a flat glass plate [37,45,64,65]. PIMs containing higher Aliquat 336 carriers (60 and 66.7%) were successfully fabricated using the automatic film casting technique in the current study. Hence, future studies will investigate and characterize, using higher resolution instrumentation, the morphological properties of PIM-containing carriers above the 55% critical level.

According to Nurul Syazana Abdul-Halim et al. [32], the phase morphology of PIM is determined not only by its composition but also by the fabrication techniques employed. The latter authors have quantitatively demonstrated using thermal analysis that PIMs membranes containing 20 - 70 wt.% Aliquat 336 exists in a two-phase structure of a discrete Aliquat 336 rich phase and a discrete PVC rich phase, although the actual form in which the Aliquat 336 rich phase exists (either as in a continuous or in closed pores) and the spatial dimensions of the phases could not be clarified by the employed technique. The observed wrinkles in the PIM containing a high Aliqaut 336 carrier (66.7%), similar to what was observed by Syazana & Halim [51,61], suggest the formation of two separate domains in its microstructures. Perhaps the wrinkles contain viscous liquid formed underneath when the THF solvent evaporates alongside a smaller volume of the viscous liquid, which causes the surface to compress and buckle. Indeed, there is a relationship between the concentration of the Aliqaut 336 carrier and its intrusion mechanism within the PIM's polymer matrix. However, the often-assumed PIMs' facilitated transport mechanism seems more logical speculation due to insufficient understanding of its homogeneity nature. Therefore based on available information, the possible transportation-extraction mechanism in our present study involves both continuous and semi-continuous Aliquat 336 rich phase modes but is dominated by either of the two [32,61].

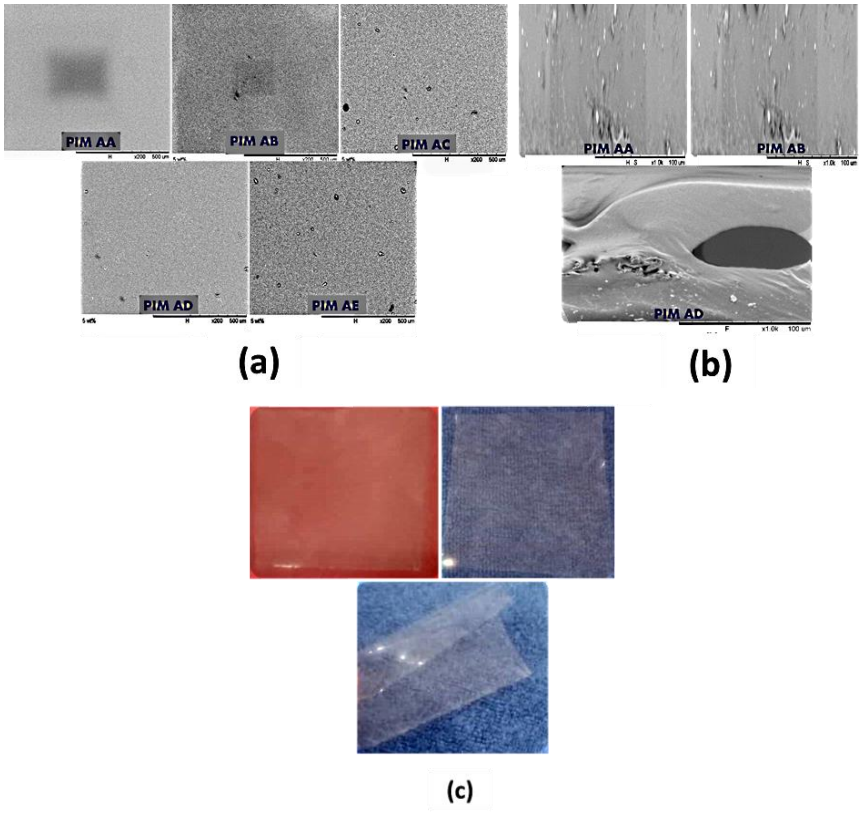

Fig. 4. (a) SEM surface images x 200 of PIMs AA-AE, (b) Cross-section images x 1000 of PIMs AA, AB, and AD, and (c) Photographic images of transparent flexible PIM AD in both flat and bent positions.

3.4. Membrane hydrophilicity assessment

The contact angle and water uptake assessments were employed to assess the hydrophilicity/hydrophobicity properties of the fabricated PIMs. The assessment determines the membrane surface chemistry, layer resistance, and solute extraction efficiency [41,66,67]. The hydrophilicity of the membranes increased significantly with increased Aliquat-336 content in the polymeric solution from PIM AA to AD, as indicated by the decreasing contact angle (Fig. 5c) and a corresponding increase in water uptake (Table 2). Hence, the quaternary amine of the Aliquat-336 carrier was able to modify the hydrophobic (ϕ 81.075 ± 0 .046) property of the pristine pure PVC - PIM to a higher hydrophilic PIMs (AB - AD) (ϕ = 75.175 ± 0.052 - 54.10 ± 2.813) and also correspondingly increase the water uptake significantly. The decreasing trend in the contact angle observed in the present study is comparable to the trend reported by [34,68,69]**.** This increase in membrane hydrophilicity can be traced to the more exposed polar functional groups of the carrier from the migration of the quaternary ammonium Aliquat 336, increasing the active sites of the embedded carrier, which provides an increased active site for water uptake due to the increase in the formation of hydrogen bonds of water molecules in what is referred to as the vehicular and Grotthuss mechanism [61,70]. The pure PVC-based PIM consisting of a nil carrier has water uptake and contact angle values of 5.27 ± 1.0% and 81.075 ± 0.046, respectively, confirming its lower water wettability and absorption capacity typical of PVC-based PIM surfaces [17,35]. However, strangely the contact angle increased slightly with the increased concentration of Aliquat carrier (66.67%) to a contact angle of 65.40 ± 2.3, while its water uptake also decreased to 19.31 ± 1.8%, signifying reduced hydrophilicity going from PIM AD to PIM AE. The decreased hydrophilicity observed in PIM AE can be attributed to the slight roughness and swelling of the polymer matrix at high Aliquat concentration attributed to the miscibility of the PVC/Aliquat 336 PIMs, which favors hydrophobicity tendency as described by Cassie's theory [34,61,72,]. High carrier concentration in PIM is also a potential additional barrier in a diffusion mass transport process due to increased solution viscosity and membrane thickness [52,73].

3.5. PIM's chemical stabilities

The loss in mass of the Aliquat embedded PIMs after 24 h immersions in 50 mL of deionized is presented in Fig. 5b. It is observed that the PIM mass decreased proportionally (2.52 ± 0.43%, 5.15 ± 1.10%, 26.82 ± 1.36%, 37.87 ± 1.32%, 43.77 ± 1.05%) to the amount of the embedded Aliquat 336 carrier [38]. A similar study by Argiropoulos et al. reported a 30 – 40% loss of Aliquat 336 extractant from PVC-based PIMs after ten (10) days of continuous immersion in unstirred deionized water. The high mass loss of the Aliquat 336 carrier has been attributed to its high solubility in a neutral aqueous solution [39,74]. A comparative study to compare the difference in the mass changes of Aliquat embedded PVC-based PIM immersed in deionized water and HCl solutions was conducted by Xu et al. [49] and Argiropoulos et al. [74]. They reported that the PIM in contact with the acidic solution was more stable than those in contact with deionized water [39]. According to Zhang et al. [75] and Kagaya et al. [39], a maximum mass loss of 35% occurred after 24 hours of immersing PVC-based PIMs (containing D2EHPA as the carrier and dioctyl phthalate as plasticizer) in deionized water. Furthermore, the latter authors stated that the immersion of PVC-Aliquat 336 as a carrier PIM in deionized water for 48 h resulted in a release of Cl expressed as Aliquat 336 in the solution aliquot, corresponding almost to the exact value of the PIM weight loss as depicted in the Equation below

$$R_3MeN^+Cl^-_{\ mem} \leftrightharpoons R_3Me\ N^+Cl^-\ aq \leftrightharpoons R_3Me\ N^+ + Cl^-\ aq \qquad (4)$$

where "mem" and "aq" refer to the membrane and aqueous solution [39].

The mass loss observed in this study is higher than the maximum mass loss of 35% reported for a PVC-based PIM containing 40% (m/m) embedded DHEPA and dioctyl phthalate (DOP) as plasticizer after 24 h in deionized water [75]. The higher mass loss in the current study can be attributed to induce mechanical stirring (400 rpm), the thinness (30 µm) of the PIMs and probable the higher hydrophilicity of Aliquat 336 compared to DHEPA. According to Moulahcene et al. [76], the mass loss of PIM increased with the agitation speed. Similarly, in line with Fick's first law of diffusion, the thickness of the membrane varies inversely to its chemical stability [77]. The result of the study of the chemical stability of the optimum PIM AD in alkaline and acidic media is presented in Fig. 5a. The result showed that the PIM was significantly more stable in the acidic medium compared to the alkaline medium, with a mass loss of approximately 8.2% and 15.8%, respectively. The mass loss of 8.2% in the acidic medium is close to the value of 7% reported by Argiropoulos et al. [74] in a 50% Aliquat 336 composite PIM immersed in a 2.5 M HCL aqueous solution.

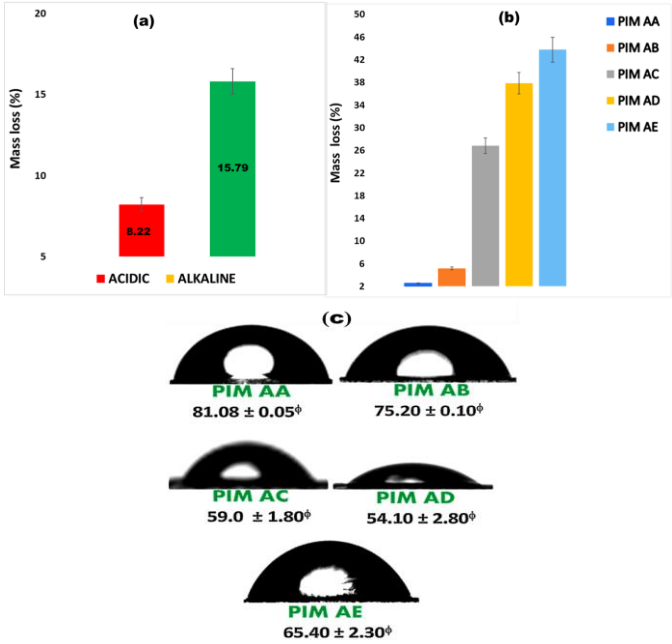

Fig. 5. (a) Mass loss in acidic and alkaline media after 6 h and shaking at 200 rpm (b) PIM's stability in deionized water (18.2 MΩ/cm) after 24 h under continuous shaking at 400 rpm and (c) Contact angle deionized water sessile drop (θ) droplet volume 6 µL measured using an image-processing software equipped with goniometer contact angle equipment at ambient temperature (24 ± 1°C) on the PIMs AA-AE surfaces.

3.6. PIM Performance Evaluation

3.6.1. Effect of PIM's carrier concentration on extraction of Ibuprofen

To study the influence of the Aliquat carrier concentration on Ibuprofen extraction efficiency. The extraction experiments were performed using PIMs AA-AE and 10 ppm Ibuprofen simulated feed solution to determine the optimal PIM composition. As presented in Fig. 6a, it is observed that Ibuprofen extraction began within the first 24 h when the concentration of Aliquat 336 reached 33.3 wt.% (AB). The highest removal efficiency (~85%) occurred with the PIM AD containing 60 Aliquat 336 wt.%. The results showed that the rate of Ibuprofen extraction increases rapidly with time as the concentration of Aliquat 336 in PVC membrane exceeded 30 wt.%; hence, a minimum Aliquat 336 carrier is required for optimum selectivity/removal of target solute [63,78]. This trend is similar to what Nurul Syazana Abdul-Halim et al. (2013) reported. The plain PVC film without Aliquat-336 has the least removal efficiency (~5%) after 96 h, which can be considered insignificant [79]. Several authors have reported that the carrier type and concentration in the PIM are the main factors affecting the type and rate of compounds transported in the membrane, which varies significantly with the carrier concentration [44,69,80]. The results of the Ibuprofen extraction in this study demonstrated that the extraction rates significantly increased with an increase in the Aliquat 336 carrier content. This observation is attributable to the kinetics of membrane extraction, which is associated with changes in the activity of Aliquat 336 molecules, and the mode of diffusion of Aliquat 336-Ibuprofen extracted complex in the membrane. At a higher Aliquat 336 carrier (60%), the carrier aggregates in the membrane probably due to de-mixing of Aliquat 336 and PVC) and interferes when the THF solvent evaporates during the formation of PVC polymer matrix resulting in the formation of microchannels-structure as observed in PIM AD (Fig. 4b). The marked increase in the Ibuprofen extraction rate observed in PIM AD compared to other PIMs containing a lesser amount of carrier can be adduced to the formation of the microstructures in the membrane film in the form of microchannels; hence the activity and diffusion coefficient of the extractant molecules, and the Ibuprofen-extractant ion-pairs are higher in those microchannels than in the polymer matrix where those channels are absent [62]. However, there is a limit to the quantity of carriers that can be embedded in a PIM to ensure its physical stability, as observed with the over-plasticized, flaccid, sticky, and physically unstable PIM AF (containing 71.43 wt.% Aliquat carriers) in this study (Table 3). Furthermore, the roughness of the membrane surface at high carrier concentration beyond a threshold limit has been demonstrated as a limiting factor to the mass transport of solute through PIM,

as observed in the reduced removal efficiency of PIM AE (containing 66.7 Aliquat 336 wt.%) [52,81]. Hence, the optimum PIM AD was further studied to evaluate the effect of feed concentration and its reusability for Ibuprofen extraction.

3.6.2. Effect of feed concentration on extraction of Ibuprofen

It is acknowledged that Ibuprofen in environmental water bodies is of low concentration (100-10^{-4} ppb); nonetheless, when it enters the system of a living organism, it remains a concern [82,83]. Therefore, to investigate the effect of low Ibuprofen concentrations on the removal efficiency using the optimum PIM AD, Ibuprofen Feed concentration of 5 ppm, 10 ppm, and 15 ppm at the optimum was prepared from the stock solution. The result showed a progressive increase in the overall extraction efficiency from 78% when the feed concentration was 5 ppm to 90% when the feed concentration was increased to 15 ppm (Fig. 6b). The increased Ibuprofen extraction efficiency with an increase in the feed concentration is related to the increase in driving force due to the increased contact between IBP and Aliquat carrier, which facilitates its extraction [23,84].

3.6.3. Reusability efficiency of optimum PIM for Ibuprofen extraction

The optimum PIM AD reusability assessment was carried out in three consecutively cycles, and the extraction efficiency for each 96-h circle (totaling 288 h) was noted. The result showed that the Ibuprofen extraction efficiency decreased with each successive repetition. The main factor affecting the stability and removal efficiency of PIMs after repeated cycles is the leaching out of ionic liquid resulting in the loss of the embedded Aliquat 336 carrier [40]. As presented in Fig. 6c, a ~ 25.6% decrease in the percentage of extracted Ibuprofen from ~90% for the first cycle to ~ 67% for the third cycle was observed, implying carrier leakage as the extraction cycle increases [17]. The observed reduction trend in this study aligned with several data from the literature, including that of Kiswandono et al., as reported by Saka et al. [40] and Nitti et al. [42], using PVC-based PIMs embedded with 30 (w/w) of Aliquat 336 carrier. The authors reported a mass loss of 33% of the Aliquat carrier from the PIM after 240 h. extraction period. Similar findings have been reported by Zhang et al [75] and Sellami et al. [41]. However, Kebiche-Senhadji et al. [85] reported a much higher reduction in its efficiency (42%) after 144 h transportation when extracting (Cr (VI)) using a PIM containing Aliquat 336 as the carrier [39]. Although, Maiphetlho et al. [17] believed that acceptable PIMs should be effectively reusable up to ten times; however, as observed by Kagaya et al. [39], both Plasticised and unplasticised PIMs also exhibit some stability problems, especially during a prolonged usage period. Therefore an acceptable general satisfactory criterion for PIM's life studies remained a subject of progressive studies because the stability of PIM compared to other liquid membranes is more relativity than absolute [39,86]. To this end, further synergistic modifications of PIM using different types and quantities of base polymers, carriers, and additives to achieve improved membrane long-term performance are currently being investigated in our laboratory [42,69,87,88].

Table 3.

Comparative performance efficiency of PIM containing PVC / Aliquat 336 carrier for the extraction of aqueous Ibuprofen

Polymer	Carrier	% Carrier (w/w)	PIM Thickness (µm)	Ibup. Conc (mg/l)	Media	Driving force	Time (h)	pH	Extraction Eff. (%)	Recovery Eff. (%)	Ref.
CTA	Aliquat®336	71	25	259	human urine	Electromembrane	1/2	4	N/A	37	[15]
PVC	Insoluble β-CD polymer	50 - 60	N/A	10	aqueous solution	Passive facilitated	6	4	~ 35	N/A	[76]
PVC	Aliquat®336	50	30	10	aqueous solution	Passive facilitated	96	10	~ 84	N/A	[33]
PVC	Aliquat®336	60	30	15	aqueous solution	Passive facilitated	96	6	~ 90	N/A	This work

N/A = Not available CTA= Cellulose triacetate Ibup = Ibuprofen Eff. = Efficiency

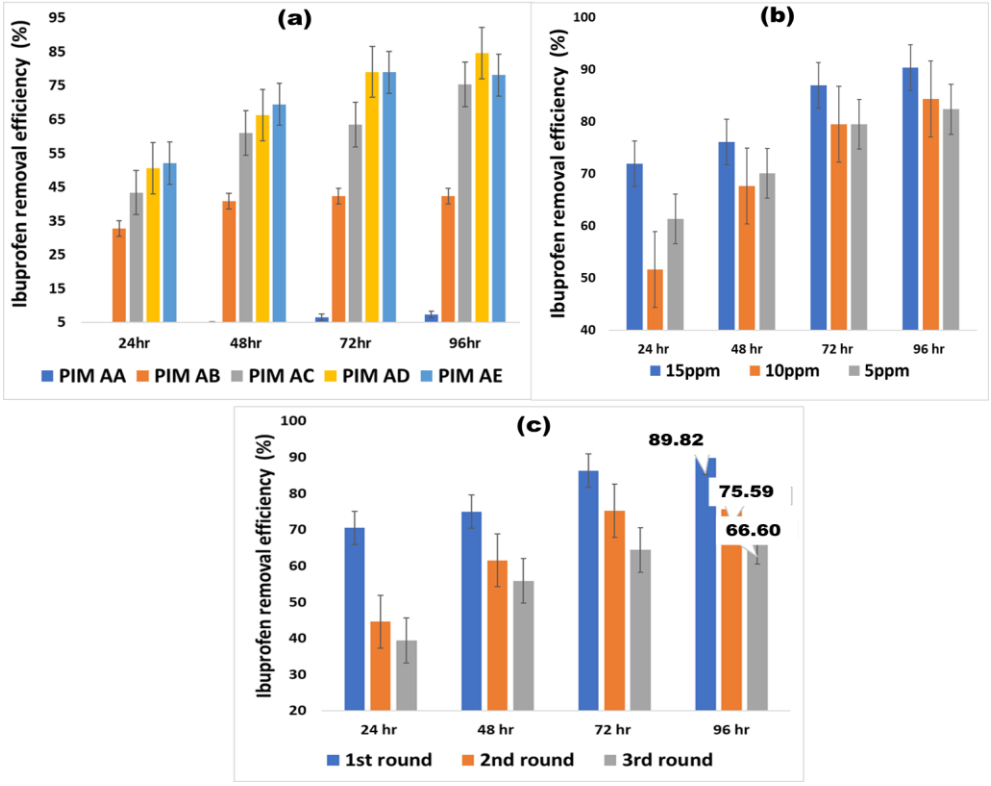

Fig. 6. (a) Effect of Aliquat 336 wt.%- carrier concentration on the removal of Ibuprofen at 10 ppm feed, (b) Effect of Ibuprofen feed concentration on extraction efficiency through PIM AD, and (c) Reusability efficiency of PIM AD on the extraction of Ibuprofen at 15ppm feed solution.

3.7. Ibuprofen Removal Mechanism

The overall transport mechanism process for all carrier types is similar; however, the complexation mechanisms depend on the feeding / receiving phases' ionic composition and the ionicity of the particular carrier employed [89]. The kinetics of the liquid membrane transport mechanism, either with or without chemical reactions, is commonly described by the solution-diffusion phenomenon; however, for a carrier-mediated transport, there is an increased drastic chemical change of solute species such as the creation of new compound, association, aggregation or dissociation of the solute [90]. Generally, the potential chemical difference initiates the first force between the membrane surface and the feed in the PIM transport behaviors. However, when the penetrated solute moves forward, the potential chemical difference between any two points in the membrane diminishes [41]. According to Casadellà et al. [91,92], the PIM transportation of metal ions in an acidic solution as receiving phase depends on the pH-driving force offered by the carrier-mediated diffusion mechanism as demonstrated by Zawierucha et and Salazar-Alvarez et al. [93,94]. Therefore, the Ibuprofen removal mechanism in the current study seems to follow the ion-carrier complex's diffusion pattern. The extraction of deprotonated Ibuprofen (at least at the initial feed pH of 6) by the cationic Aliquat 336 carrier occurs as the Aliquat 336 reacts as an ion exchanger with the deprotonated anion Ibuprofen forming a complex [61]. The ionic interaction mechanism between the cationic quaternary ammonium Aliquat carrier and the carboxylate moiety of the deprotonated Ibuprofen is illustrated in Fig. 7. The chemical reactions in extraction and transport of organic compounds using PIM are either anion exchange or the formation of hydrogen-bonded heteroconjugate anions. The ability of Ibuprofen to form hydrogen bonds in the presence of a lipophilic cation and a hydrogen bond acceptor anion such as the Aliquat 336 carrier suggests that such a mechanism is equally tentatively feasible [23,43,95,96]. However, in line with the findings of Fan et al. and Khachatryan, who demonstrated that Ibuprofen extraction efficiency using Aliquat 336 as a carrier in a bulk liquid membrane remains relatively constant at the pH below the pKa value (4.9), suggesting some form of electrostatic attraction or repulsion interaction mechanism [23,97]**.** Accordingly, therefore, the extraction and transport mechanism for organic compounds (amino acids) using Aliquat 336 is predominate by either the anion exchange or the formation of heteroconjugate anions depending on the prevailing pH of the feed solution.[95]. Indeed the extraction of organic compounds using carrier-embedded membranes is more complex than metal ions transportation, and scientific investigation involving the remediation of organic micropollutants by PIM is still evolving [98,99]. Hence, a comprehensive study is ongoing to elucidate the Ibuprofen removal mechanism in more detail by evaluating the effect of different feed pH, receiving phase types, and concentration using stability-enhanced optimum PIM.

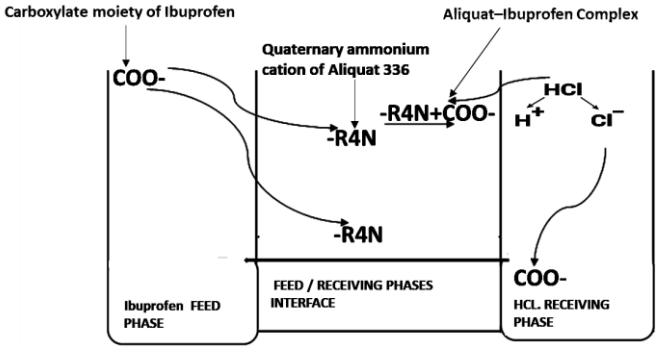

Fig. 7. Hypothetical facilitated transport interaction mechanism between the anionic Ibuprofen (2-(4-isobutylphenyl) propionic acid) and the cationic Aliquat 336 carrier

4. Conclusion

The fabricated Self-plasticized Aliquat embedded PVC PIMs in the present study successfully removed ~ 90% aqueous Ibuprofen at optimum conditions. The extraction rate of Ibuprofen was found to vary significantly with initial feed concentrations. However, the study on the chemical stability of the PIMs based on mass loss and reusability suggests that the Self-plasticised PIM is relatively unstable, with a significant loss (25.6%) in the initial removal efficiency. Therefore, further technical fabrication modification is required to enhance the reusability of self-plasticised PIM for practical application and regeneration potentials. Furthermore, to better elucidate the transport mechanism of Ibuprofen using self-plasticised Aliquat embedded- PIM, the next research aims to investigate the effect of varied feed pH and different receiving solutions on the recovery, permeability, and flux of the optimum PIM.

Credit authorship contribution statement

Idowu Ebenezer Oluwasola: Conceptualization, Investigation, Original draft. ***Abdul Latif Ahmad***: Methodology: Supervision Funding acquisition. Noor ***Fazliani Shoparwe***: Data curation: Supervision.

Declaration of competing authors' interest

The authors hereby declare that there is no known conflict of interest whatsoever.

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Data availability

This study's raw/processed data can only be shared on request as the data also forms part of an ongoing study.

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