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## The Performance and Characterization of Polymeric Inclusion Membranes (PIMs) Containing 2-Nitro Phenyl Octyl Ether as Plasticizer on Phosphate Transport

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### Abstract

Polymer Inclusion Membranes (PIMs) have been fabricated for diffusive passive sample layers. A study of various concentrations of plasticizers and characterization of PIM performance on phosphate transport has been carried out. The composition of PIM consisted of cellulose triacetate (CTA) as the base polymer, Aliquot 336-Cl as a carrier, and 2-Nitro phenyl octyl ether (2-NPOE) as a plasticizer. The plasticizer concentration varied between 0 and 10% (w/w). The performance of PIM on phosphate transport was studied with a passive sampler filled with 15 mL 0.1 M NaCl as the internal phase. The passive samplers were deployed into the bulk phase of a phosphate solution of 0.6 mg/L for 0-48 hours. The phosphate concentration in the passive sampler was determined using the visible spectrophotometry method at 691 nm (in the bulk phase) and 710 nm (in the internal phase). PIMs were characterized for stress-strain, contact angle, surface morphology, and cross-section. The sampling rate of phosphate, phosphate time-weighted concentration (CTWA), and accuracy of phosphate measurement was also determined. The results showed that PIM A (0% w/w 2-NPOE) resulted in a sampling rate of  $0.0005 \pm 0.0002$  (L/hour), CTWA 0.09 mg/L, and an accuracy of 28.38%. PIMs B (10% w/w 2-NPOE) resulted in a sampling rate of  $0.0003 \pm 0.0001$  (L/hour), CTWA 0.18 mg/L, and an accuracy of 52.15%. PIMs A and B have a contact angle of  $17.02^\circ$  and  $18.71^\circ$ , respectively. It means that these PIMs are hydrophilic membranes. In addition, PIMs B was more elastic than PIMs A, showed by the tensile strength of PIMs B was 31.05 MPa compared with PIMs A's tensile strength (29.01 MPa). PIMs A and B have no pores, as shown by surface morphology using SEM. However, based on the cross-section area, PIMs A showed a break section instead of PIMs B, which indicates that PIMs B is more elastic than PIMs A.

**Keywords:** 2-nitro phenyl octyl ether, phosphate transport, polymeric inclusion membranes (PIMs).

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### 1. INTRODUCTION

Phosphate is one of the essential nutrients that are useful for plants (Jiao *et al.*, 2012). Phosphate has two forms in water, namely 90% in organic phosphate and 10% in inorganic phosphate (Bennett & Schipanski, 2013). One form of dissolved inorganic phosphate is orthophosphate with the species of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{PO}_4^-$ , which depend on the pH of the water. Orthophosphate is one of the nutrients that cause algae blooms or eutrophication (Feng *et al.*, 2018). It is indicated by high phosphate concentration in

aquatic. Eutrophication is when a water body undergoes an excess of nutrients, causing plants to bloom (Tan *et al.*, 2020). One of the negative impacts of eutrophication is algae blooms causing hypoxia in aquatic organisms (Godoy *et al.*, 2019). Therefore, a device is needed for monitoring phosphate concentration in the water systems as one of the eutrophication prevention periodically.

Phosphate measurement can be carried out by spot sampling. The measurement of this method can only determine the phosphate concentration at that time. Therefore, spot

sampling provides less representative investigation due to the fluctuation of phosphate concentration during measurement (Wilson *et al.*, 2022). On the other hand, using the passive sampling method Time-Weighted Average Concentration (CTWA) of phosphate can be measured. This method can be carried out by deploying passive samplers in the water system for several hours (Cristóvão *et al.*, 2021). During deployment, phosphate will be transferred from the bulk to the internal phase inside a passive sampler (Górecki & Namienik, 2002). Passive samplers based on membranes have been developed for analytes measurements, such as semipermeable membrane device (SPMD) (Lima *et al.*, 2019), polar organic chemical integrative sampler (POCIS) (Jeong, 2020), Chemcatcher (Garnier *et al.*, 2020), polyethylene (PE) (McKay *et al.*, 2020), diffusion gradient in thin (DGT) (Kreuzeder *et al.*, 2015) and Polymeric Inclusion Membrane (PIM) (Maiphetho *et al.*, 2021). Polymeric inclusion membranes (PIMs) have been used for a diffusive layer of passive samplers to measure metal ions (Ni, Co, Zn) (Keskin *et al.*, 2021), ammonia (Almeida *et al.*, 2016), pesticides (Mwakalesi & Potter, 2021). The advantages of PIMs are simple synthesis, efficient carrier immobilization, adaptability, and high mechanical characteristics (Rodríguez de San Miguel, 2022).

PIM is the development of SLM (supported liquid membranes). Unlike SLM, where weak capillary forces hold the liquid phase within the micro pores of the hydrophobic microporous membrane, PIM integrates the membrane liquid phase into the entangled chains of the base polymer to the adjacent aqueous phase. Therefore, PIM is much more stable and robust than SLM (Almeida *et al.*, 2017). PIM consists of the base polymer, plasticizer, and carrier. Base polymers frequently used are polyvinyl chloride (PVC) (Keskin *et al.*, 2021) and cellulose triacetate (CTA) (Ait Khaldoun *et al.*, 2018). Base polymer holds the carrier as a liquid phase and gives strength to the membrane (Nitti, Cendana *et al.*, 2021). 2-nitro phenyl octyl ether (2-NPOE) is a plasticizer commonly used with CTA base polymer instead of tris(2-ethylhexyl) phosphate (TEHP) and dibutyl phthalate (DBP) (Wang *et al.*, 2016). The suitable plasticizer has to present a high dielectric constant because the dielectric constant will affect the ion transport through

the PIM-containing amines group in the carrier (Monroy-Barreto *et al.*, 2021). Both TEHP and DBP show lower dielectric constant than 2-NPOE. PIM also contains a carrier that facilitates molecule or ion transport through PIM. Keskin *et al.* (2021) reported that aliquot 336-Cl as the carrier could be used to monitor metal ions.

PIM formed will be thin, flexible, and transparent. Some research presented PIM can be used to determine ammonia (Almeida *et al.*, 2016), metal ions (Keskin *et al.*, 2021), and sulfamethoxazole (Garcia-Rodríguez *et al.*, 2016). Phosphate transport has been studied using PIMs consisting of PVC/Aliquat 336-Cl/1-decanol (Rumhayati *et al.*, 2021), where the sampling rate of this PIM containing 55:15:30 (% w/w) was  $8 \times 10^{-5}$  L/minutes. However, PIM that is consisted of CTA/Aliquat 336-Cl/2-NPO has not been investigated for phosphate measurement. Therefore, in this study, we purposed to determine the performance and characteristics of PIMs containing CTA/Aliquat 336-Cl/2-NPOE for phosphate transport.

## 2. MATERIALS AND METHODS

### Materials

Chemicals needed to fabricate PIM were cellulose triacetate (CTA) (Merck), 2-nitro phenyl octyl ether (2-NPOE) (Merck), Chloroform Gr (Merck), and Aliquot 336-Cl (Merck). Phosphate solution stock could be prepared by dissolving potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , Sigma) in demineralized water. The internal phase inside the PIM passive sampler was Sodium Chloride (NaCl) solution 0.1 M. These reagents were applied to analyze phosphate were ammonium heptamolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ) (Sigma), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (98%, Merck), glycerol (Merck), and Tin(II) chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) (Merck).

### Instrumentation

VTSYIQI Ultrasonic Thickness Gauge Tester was used to measure the thickness of the membrane. Genesys 10 Spectrophotometer UV-Vis was used to detect phosphate concentration. Scanning electron microscopy (SEM, FEI Inspect-S50) was used to observe the surface section and cross-section of PIMs. The contact angle was measured by the instrument of OCA 15EC with a video system. The mechanical measurement of PIMs was

carried out by digital force gauge push-pull gauge with RS232 output (BAOSHISHAN ZP-50N).

## Procedure

### PIM Preparation and Characterization

This study produced PIMs with two different compositions, as shown in **Table 1**, based on the variation of plasticizers. The total weight of the composition was 300 mg (Rumhayati *et al.*, 2021). PIMs solution was prepared by diluting some CTA in 10 mL chloroform. Afterwards, Aliquot 336-Cl and 2-NPOE were added and stirred thoroughly for 2-3 hours to dilute the compounds well. The membrane solution resulted was 15.2 g. The solution was then put into a 6 cm diameter molded glass. The molded glass was covered with filter paper and watch glass to evaporate the chloroform gradually at room temperature. After 24 hours, the membrane could be peeled out of the molded glass.

**Table 1.** Compositions of PIMs

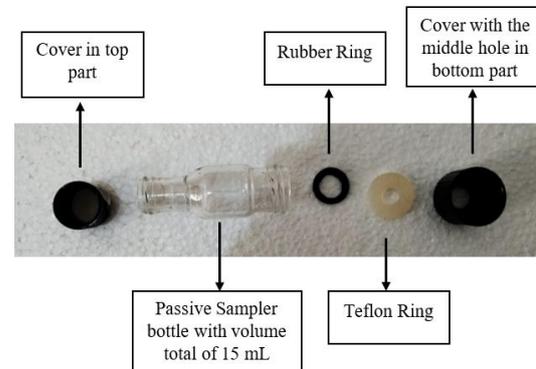
Membrane	CTA (%) w/w	2-NPOE (%) w/w	Aliquot 336-Cl (%) w/w
PIM A	80	0	20
PIM B	70	10	20

The thickness and weight of membranes were then measured using VTSYIQI Ultrasonic Thickness Gauge Tester, and the elasticity of PIMs was determined based on the tensile strength value. The characteristic of hydrophobicity-hydrophilicity was tested based on the contact angle measurement. The surface morphology and cross-section were determined using SEM. All the produce membranes were kept in sealed plastic before being used as a diffusive layer of passive samplers.

### PIM Passive Sampler Assemble

PIM passive sampler devices used in this research have been shown in Figure 1. The device consists of a Teflon ring, rubber ring, cover in the top part, cover with the middle hole in the bottom part, and passive sampler bottle with a volume total of 15 ml. The membrane was cut with a diameter of 2.2 cm and placed between a rubber ring and a Teflon ring (Rumhayati *et al.*, 2021).

The assembled sandwich was then positioned at the bottom opening of the passive sampler device and closed tightly. Then, the bottle of the passive sampler was filled with 15 mL of NaCl solution 0.1 M as an internal phase before it was closed tightly. The possibility of leakage should be checked and avoided before using the device for phosphate measurement.



**Figure 1.** Parts of passive sampler (Rumhayati *et al.*, 2021)

### The Effect of Plasticizer Concentration on the Phosphate Sampling Rate

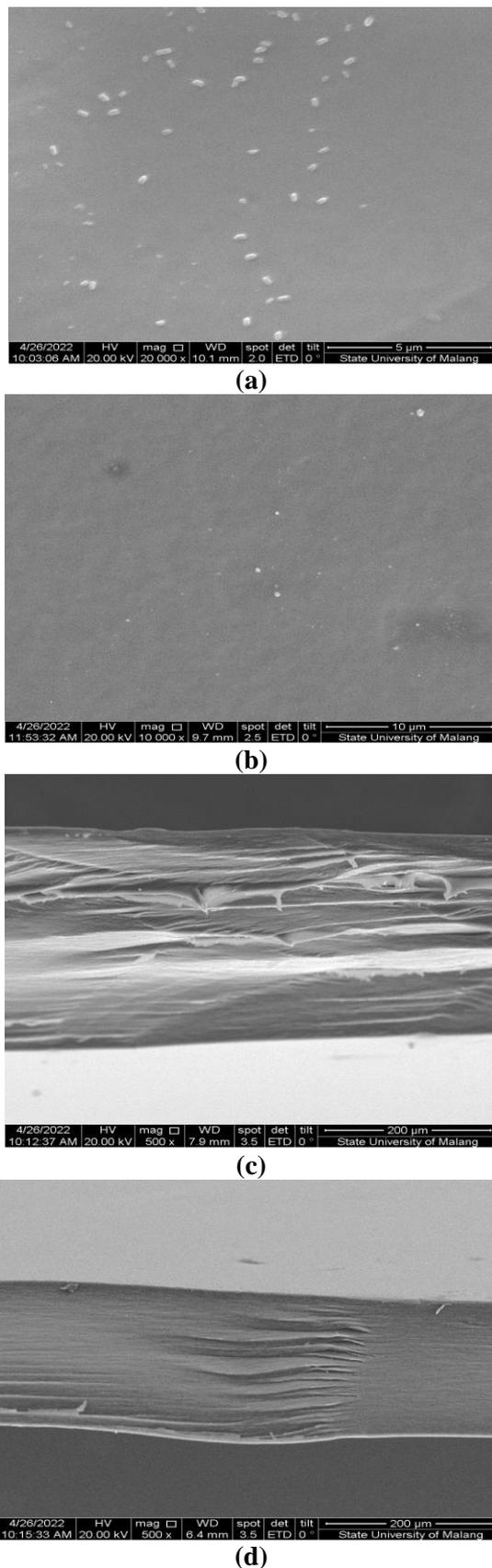
The sampling rate ( $R_s$ ) determines the equivalent phosphate volume transported ( $V_{eq}$ ) through PIM during experiment time ( $t$ ). It becomes a specific characteristic of a PIM as a passive sampler device's diffusive layer. For the experiment in this section, a tank of water was filled with 1 L of phosphate solution of 0.6 mg/L. The solution was bubbled using an aquarium bubble pump overnight to ensure homogeneity. PIM at specific composition was positioned inside passive samplers. The devices filled with 15 mL of NaCl 0.1 M were placed floatingly with the PIM part faced inside the bulk solution. 5 mL of bulk solution and 5 mL of internal phase were pipetted out at 0 - 48 hours from each device. Then, the concentrations of phosphate in the bulk phase and internal phase were detected. All experiments were conducted three times for replication. The sampling rate ( $R_s$ ) was then obtained from the slope value of the straight-line equation between equivalent volume ( $V_{eq}$ ) and time ( $t$ ), as shown in Eq. 1 below

$$V_{eq} = R_s \cdot t \dots\dots\dots (1)$$

### Performance of PIM Passive Sampler for Phosphate Measurement

In this research, the phosphate measurement was conducted using a passive





**Figure 4.** SEM images: the surface section of (a) PIM A: 80% CTA + 0% 2-NPOE + 20% Aliquot 336-Cl, (b) PIM B: 70% CTA + 10% 2-NPOE + 20% Aliquot 336-Cl; and the cross section of (c) PIM A, (d) PIM B

PIM A and PIM B, as shown in Figure 3, had thicknesses of 174 and 159.67  $\mu\text{m}$ , respectively. The weight of PIMs was relatively the same, i.e.,  $0.440 \pm 0.009$  grams. Their homogenous, transparent elasticity and hydrophilicity – hydrophobicity specified the PIMs (Nitti *et al.*, 2021; Govindappa *et al.*, 2022)). Visually, both membranes did not have a significant difference in either the surface or transparency. The homogenous PIM depends on the compatibility of plasticizer binding between the base polymer and carrier used (Bonggotgetsakul *et al.*, 2015). 2-NPOE can penetrate the polymer strands and neutralize the polar groups of CTA (Nitti *et al.*, 2021) by greasing the section motions of the polymer, which will give the flexibility of membrane (Casadellà *et al.*, 2016).

SEM can study the surface and cross-section morphology. SEM pictures of the surface and cross-sections were taken to examine the effect of the membrane composition on the morphology (Sellami *et al.*, 2019). Figure 4 depicts the morphology of PIM by comparing the surface section and the cross-section. PIM A and PIM B were no pores, similar to those studied in another research (Ait Khaldoun *et al.*, 2018). It can be seen that PIMs A has a break section compared to PIMs B. In addition, PIMs B was more homogeneous than PIMs A. Those showed that the more increase of 2-NPOE as a plasticizer, the more decrease in the roughness of the membrane (Wang *et al.*, 2016). However, the membrane can be rigid and brittle with low plasticizer concentration. Comparing the plasticizer and base polymer determines the minimum plasticizer concentration, and a plasticizer varied predisposes the distinguish in membrane pores (Kiswandono *et al.*, 2013). Furthermore, PIMs based on CTA were compact and homogenous (Xu *et al.*, 2022).

### Hydrophilicity-Hydrophobicity

The hydrophilic or hydrophobic properties of the membrane can be assigned from the contact angle. The higher contact angle of the membrane ( $> 90^\circ$ ) shows the hydrophobic membrane, whereas the lower contact angle of the membrane ( $< 90^\circ$ ) presents the hydrophilic (Soo *et al.*, 2021). The contact angles of PIM A and PIM B were observed, and those membranes were hydrophilic (Table 2). There was an increase in contact angle, but it was still classified as hydrophilic

membranes. In addition, Aliquot 336-Cl as a carrier determines the hydrophilicity characteristic of membranes. Aliquot 336-Cl has aliphatic chains (with eight carbons) oriented upward (in the air) and is deposited on the surface of the membrane. The aliphatic chains will prevent the membrane from interacting with water (Benosmane *et al.*, 2022).

**Table 2.** Contact angle of PIMs

Sample	Angle (°)
PIM A	17.02
PIM B	18.71

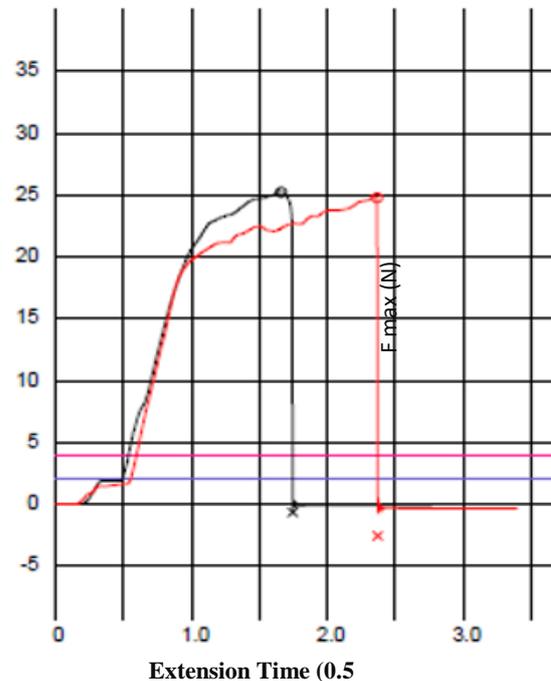
However, the presence of the charged quaternary ammonium groups in Aliquot 336-Cl induces hydrophilicity in the membrane (Sellami *et al.*, 2019). The membrane with high hydrophilicity will have higher wettability and higher tendencies of water uptake (Soo *et al.*, 2021). On the other hand, adding plasticizer also increases surface hydrophobicity because of the aromatic ring and alkyl groups (Sedkaoui *et al.*, 2021). Hence, PIM B is better than PIM A because PIM B is more hydrophobic than PIM A, with 10% NPOE as a plasticizer.

**Tensile Strength**

PIM's mechanical properties like tensile strength, elongation, modulus young are essential to determine (Kotsilkova *et al.*, 2018). Tensile strength is used to assess membrane mechanical properties by measuring deformation resistance, where mechanical properties depend on the base polymer (Upitis *et al.*, 2009). The tensile mechanical strength of the tested membrane is highly dependent on its quality and structural homogeneity (Kotsilkova *et al.*, 2018). Furthermore, this tensile strength test is also used to identify the elasticity of the membrane measured by modulus young. The tensile strength can be seen from the compositions of the membrane, for instance, the plasticizer (Upitis *et al.*, 2009).

Figure 5 shows that the maximum force of PIM A and PIM B was 25.24 N and 24.79 N. The modulus of young of PIM A and PIM B were 2.90 MPa, and 1.86 MPa were obtained from the division between stress and strain. The tensile strength showed that PIM B was higher than PIM A because the addition of

plasticizer will increase the membrane's tensile strength and physical strength (Kiswandono *et al.*, 2013). The modulus young is used to indicate the elasticity of the membrane, where the higher the modulus young, the higher film's stiffness (Hazrati *et al.*, 2021).



**Figure 5.** Tensile strength of PIM A (black) and PIM B (red)

**Table 3.** Tensile strength and Modulus Young of PIMs

Membrane	Thickness (µm)	Tensile Strength (MPa)	Modulus Young (MPa)
PIM A	174 ± 21	29.01	2.90
PIM B	160 ± 7.57	31.05	1.86

The modulus young of PIM A is more significant than PIM B, resulting in PIM A being more rigid than PIM B. If the resulting membrane is stiffer, it will be more easily broken if it is subjected to continuous pressure (Souisa, 2011). The addition of plasticizer causes strong hydrogen bonds produced by intermolecular activity, so the PIM B with plasticizer is more elastic than PIM A without plasticizer, indicating the comparison of modulus young. Furthermore, the tensile strength also depends on the membrane's quality and structural homogeneity (Sanyang *et al.*, 2015). It can be concluded that PIM B was better than PIM A for elasticity, so PIM B

showed that the membrane applied would not be easily ruptured.

### The Effect of PIM Plasticizer on Phosphate Sampling Rate.

The intramolecular forces included in PIM are mostly Van der Waals forces (Rumhayati *et al.*, 2021). Polymers composed of cellulose units, such as CTA, form crystalline films where polymer chains do not follow a systematic order, increasing the distance between polymer chains. Therefore, water molecules in the CTA film accumulate in the amorphous regions (larger spaces), leading to hydrogen bonding between CTA and water so that voids in the structure are reduced (Casadellà *et al.*, 2016).

Accordingly, the plasticizer is added because plasticizer can reduce van der Waals and hydrogen bonds between polymer and water molecules. Polar groups in plasticizers are essential for good compatibility. When plasticizer molecules are presented into the polymer mass, the polymer chains are separated by small liquid molecules that can align dipoles with polymer dipoles. Dipoles aligned in this way are a compelling force of attraction. Liquid molecules can have polarizable ring structures that form points of mutual attraction. Polymer chains that are separated in this way are more mobile relative to each other than polymer chains that are tightly bound (Marcilla & Beltrán, 2012).

The plasticizer is one of the membrane components that also influences membrane stability and plays a role in condensing or hardening the membrane. PIM contained by plasticizers is more flexible, and there is an increase in substance transport (Keskin *et al.*, 2021).

The effect of the base polymer and plasticizer on the phosphate transport rate is shown in Table 4. It can be seen that phosphate has good transport through PIM B with a sampling rate was  $0.0003 \pm 0.0001$  L/hour. PIM-containing plasticizers will increase the ability of ion transport because PIMs are not rigid and easily damaged (Gibbons & Kusy, 1998).

That is concluded that the plasticizer influenced ion transport (Djamila *et al.*, 2011). Nevertheless, the excessive plasticizer will interrupt ion transport (Kiswandono *et al.*,

2013) and become a barrier because the membrane forms a film on the surface of the membrane (Kiswandono *et al.*, 2013). The base polymer in PIM A became dominant because no addition of the plasticizer increased the membrane's ability to transport ions.

**Table 4.** The sampling rate (Rs) of phosphate determined used PIM-passive sampler

Membrane	CTA : 2-NPOE : Aliquot 336-Cl (%w/w)	Rs (L/hour)
PIM A	80:0:20	$5 \pm 2 (10^{-4})$
PIM B	70:10:20	$3 \pm 1 (10^{-4})$

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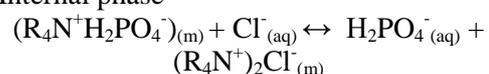
### Performance of PIM Passive Sampler for Phosphate Measurement

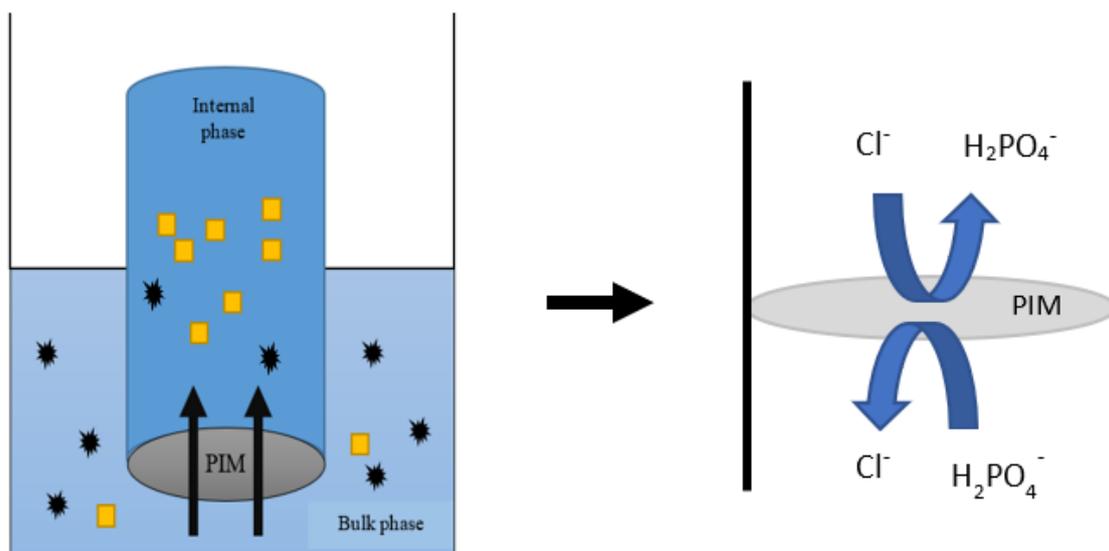
Transport of phosphate through PIM assisted by Aliquot 336-Cl ( $R_4N^+Cl^-$ ) as the carrier that exchanged ions and formed an ion pair.  $Cl^-$  ion in the internal phase will assist the ion-exchanged so phosphate can be measured as below:

#### a. Bulk phase



#### b. Internal phase





**Figure 6.** Analyte transport through PIM

The carrier in PIM binds the target analyte forming either an anion or cation. Figure 6 shows that the bulk phase released  $H_2PO_4^-$  while  $Cl^-$  was released in the internal phase. The bubbling process during the deployment of the passive sampler will reduce the second diffusion layer in front of the PIMs so phosphate transport will not be influenced. The concentration of the internal phase has to be higher than the bulk phase because the difference in the driving force of ion transport from the bulk phase to the internal phase was also against the existing concentration gradient (Almeida et al., 2017).

**Table 5.**  $C_{TWA}$  and accuracy of PIMs

Membrane	$C_{TWA}$ (mg/L)	Accuracy (% v/v)
PIM A	0.09	28.38
PIM B	0.18	52.15

Transport of phosphate through PIMs B is more accurate than through PIMs A (Table 5). Accuracy was obtained by dividing the  $C_{TWA}$  and phosphate concentration in the bulk phase. However, both PIMs showed low accuracy, where the accuracy of PIM A was 28.38 % (v/v), and PIM B was 52.15% (v/v). That is because CTA is a polar polymer (Maiphethlo *et al.*, 2021) than PVC, where the carboxyl group of CTA binds with the ammonium group of aliquot 336-Cl strongly (Sellami *et al.*, 2019). On the other hand, the research conducted by Benavente *et al.* (2018) showed that membranes containing Aliquot-Cl/CTA have a low amount of Cl ion, and

phosphate ion exchange with  $Cl^-$  is minimal, resulting in low phosphate transport accuracy.

#### 4. CONCLUSIONS

The transport of phosphate into a passive sampler containing PIMs as the diffusive layer is affected by the performance and characteristics of PIMs themselves. PIMs containing plasticizer (10% w/w 2-NPOE) showed good agreement for a diffusive layer. The PIMs have no pores, no break section, and homogeneous membranes that can transport phosphate. PIMs B was more elastic and hydrophobic than PIMs A. Phosphate was more easily transported through PIMs B, indicated by the high sampling rate of  $0.0003 \pm 0.0001$  L/hour. Even if the transport is low, the PIM passive sampler could be used to measure phosphate with an accuracy of 52.15%. This low accuracy was due to membranes containing Aliquot-Cl/CTA having a low amount of  $Cl^-$  ion; this causes low phosphate ion exchange with  $Cl^-$  ion.

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