Targeting the Removal of Pyridine Herbicides from an Aqueous Environment using Polymer Inclusion Membranes

Submitted by

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Summary

The beneficial use of herbicides on pastures to increase crop yields is offset by associated risks from chemical runoff contaminating environmental waters. Most commonly used methods to remove residues from environmental waters are ineffective, while some produce degradation by-products which can also affect the environment. The successful use of polymer inclusion membranes (PIMs) as a simple remediation method to remove pyridine herbicides, such as picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), and related herbicides from an aqueous environment was reported. An optimum PIM composition of 25 wt% CTA, 30 wt% Aliquat 336 and 45 wt% NPOE was used to transport picloram with an initial flux of 294 (± 14) × 10^{-8} mol.m^{-2}.s^{-1} and transport efficiency of 95 ± 1%. The PIM was reused in five consecutive transport cycles with a negligible change in flux during later cycles. The results indicate that PIMs provide a potential alternate method for the removal of troublesome herbicides from environmental waters.

Degradation products from herbicides are considered emerging contaminants and studies on effective removal methods from environmental waters are limited. The successful transport of 4-amino-2-chloropyridine (ACP) as a model degradation product of pyridine-based herbicides using PIMs was demonstrated. An optimal membrane composition of 20 wt% CTA, 40 wt% Aliquat and 40 wt% NPOE producing an initial flux of 413 (± 7) × 10^{-8} mol.m^{-2}.s^{-1} and 98 ± 1% transport efficiency was identified. Preferential transport of ACP, involving the formation of aggregates with the carrier, over picloram was noted. The results indicate the opportunity for future investigations of the extraction and transport of degradation products of pyridine-based herbicides using PIMs.

The use of natural compounds from plants as active chemicals for various applications is regarded as a "green chemistry approach" because of the reduced risk of contaminating the environment. However, there are limited investigations on the use of

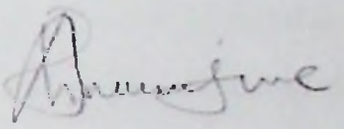
plant-based compounds as components in PIMs. Anacardic acid (AA) derived from cashew nut shell liquid was investigated as a "green cationic carrier" for some representative organic compounds. An optimal membrane composition of 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol and 40 wt% NPOE producing an initial flux of 364 (± 16) $\times 10^{-8}$ mol.m^{-2}.s^{-1} and transport efficiency of 98 ± 1% for the transport of ACP as a model compound was demonstrated. The results were comparable with using a commercial carrier, bis-(2-ethylhexyl) phosphoric acid. The membrane also displayed effective competitive transport of ACP, paraquat and diquat with an average transport efficiency of 97 ± 1%. Therefore, the potential use of plant derived natural compounds as "green chemicals" in membranes is an exciting novel development and worthy of further investigations.

PIMs have emerged as a powerful tool for the pre-treatment of samples because of their versatility and easy fabrication. The optimal membranes were tested for the pre-concentration of picloram, ACP, paraquat and diquat as representative compounds from a low initial concentration of 500 µg/L in samples of natural water. The effective pre-concentration of the compounds was indicated by the significant increase in HPLC signal intensities of the post-concentrated samples. The results indicate the suitability of PIMs as an alternate method of sample pre-treatment and the potential for fabrication and application in passive sampling devices.

The results from this thesis indicate the potential of PIMs as a viable method to remove and measure problematic herbicides and degradation products from natural waters using commercial and "green" carriers. However, more investigations simulating real-world conditions, such as long-term use of similar membrane chemistry in hollow fibre extractors and passive sampling devices, are needed to fully demonstrate this exciting potential.

Statement of Authorship

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis accepted for the award of any other degree or diploma. No other person's work has been used without acknowledgment in the main text of the thesis. This thesis has not been submitted for the award of any degree or diploma in any other tertiary institution.



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Dedication

This thesis is dedicated to the memory of my beloved father, Joel Anania Mwakalesi who passed away on 24, March of 2017. He always wanted me to be hard worker and determined. His wisdom is still useful for my life to date and has greatly shaped me. I believe without his enormous personal sacrifice and unconditional love, I would never become the person I am today.

Chapter 1: General introduction.

1.1. Introduction

As the demand for food production continues to increase worldwide, an inevitable demand for using pesticides in agriculture also increases. Consequently, a wide range of modern agricultural practices are currently associated with an extensive application of pesticides to fulfil higher yield requirements. It has been estimated that about two million tonnes of pesticides are used all over the world annually [1]. Despite undeniable benefits of using pesticides or herbicides in agriculture, they are often associated with impacts on non-target organisms. It has been revealed that less than 0.1% of applied pesticides or herbicides reaches the target organisms. The remaining pesticide leaches through runoff from treated soils and plants and affects untargeted organisms in the environment [2]. As a consequence, it has been estimated that as many as 25 million agricultural workers worldwide experience unintentional poisoning resulting from pesticide exposure each year [3].

The control of resistant weeds in most cases requires repeated applications of herbicides which considerably increases production costs. However, the use of persistent herbicides has economic benefits because they stay active in the environment for a long time, thus, avoiding the need for repeated applications. Pyridine herbicides are chemicals intended to remain active in the environment for a long time. They are resistant to the usual degradation processes caused by natural or metabolic reactions in plants or animals. As a result, they are continuously recycled through the decomposition of organisms [4]. Due to this property, these herbicides are considered more preferably than other more commonly used herbicides, such as 2,4-dicholorophenoxy acetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). However, the increased use of pyridine herbicides has heightened concerns over their accumulation in the environment, which is likely to affect the growth of desirable plant species. Their exposure to non-target species can even be difficult

to control due to their high-water mobility and leaching potential. For this reason, it is deemed necessary to find low cost and efficient ways to remove pyridine herbicides and their potential degradation by-products from the environment as an alternative approach to natural degradation.

Herbicides are chemicals designed to kill unwanted plants by inhibiting or disrupting essential biochemical pathways. However, the broad application of herbicides can express similar effects in non-target organisms [2]. Consequently, a decline in plant diversity and abundance due to the extensive use of pesticides has been reported [5]. Herbicides can also affect animals due to bioaccumulation caused by their solubility in lipids. In this context, the organisms that are at the top of the food chain are normally at the most risk because a concentration of herbicides is magnified at each step. The World Health Organisation (WHO) reports that more than three million people every year are exposed to unacceptable amounts of herbicide due to their wide-spread use [6].

Degradation is an essential strategy for the removal of the herbicides from the environment [7]. However, some herbicides are persistent to degradation and their concentrations in the environment are magnified by repeated applications. Unfortunately, micro-organisms are ineffective at degrading some herbicides in the environment [8], for example, some chlorinated hydrocarbon herbicides, such as dichlorodiphenyltrichloroethane (DDT) and dichlorodiphenyldichloroethylene (DDE) are persistent and have been detected in environmental waters at significant distances from the application sites [2]. The persistence of chemicals usually depends on the chemical structure which influences the physicochemical properties. The presence of polar functional groups, such as OH, COOH and NH_2, provides sites for microbial attack and, thus, reduces the persistence of herbicides in the environment. On the other hand, the presence of chlorine atom(s) in the chemical structure can significantly increase the persistence of a herbicide [9]. The degradation of some persistent herbicides results into the formation of various intermediate products which

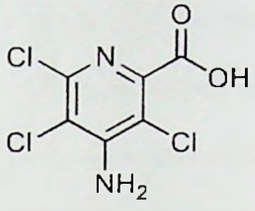
themselves can pose a threat to the ecosystem [10]. Pyridine herbicides are typical example of potential persistent herbicides in use today and thus their removal from the environment is quite important.

Polymer inclusion membranes (PIMs) have been extensively used for the extraction and transport of various metal species, in particular those with a high commercial demand [11]. The similar use of PIMs for organic compounds has recently gained attention, but, their commercial demand is not the main motivating factor. This study contributes to the growing field of PIM research by investigating the extraction and transport of pyridine herbicides and related compounds. Additionally, the potential use of anacardic acid derived from the cashew nut shell liquid (CNSL) as a low cost and environmentally friendly carrier has been explored. It is expected that the use of this compound for extraction and transport of organic compounds could reduce costs and, therefore, make the use of PIMs more economically feasible. Finally, the PIMs will be also used for the pre-concentration of selected target compounds from a complex matrix of natural water samples. It is anticipated that the work described in this thesis will provide an affordable solution and practical alternative(s) to remove pyridine herbicides and related troublesome organic compounds from an aqueous environment.

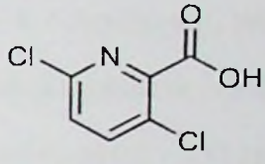
1.2. Pyridine herbicides

Pyridine herbicides are growth regulators that cause abnormal and uncontrolled growth in plants, mimicking plant growth hormones known as auxins [12]. They are designed to control a wide range of broadleaf weeds and remain active in the environment for a long time. Most pyridine herbicides are not readily metabolised and, thus, remain in their active form and are, subsequently, released to the environment during plant decomposition [13]. The effects of these herbicides to inhibit the growth of some desirable

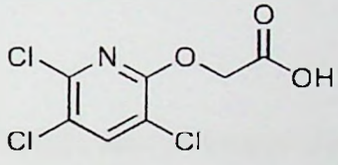
plants have been reported [14]. Some representative pyridine herbicides are: picloram (4-amino-3,5,6-trichloro-2-pyridincarboxylic acid), clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) and triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid), structures as shown in **Fig. 1.1**. For the purpose of this study, discussions are particularly focused on picloram as the most persistent member of this herbicide family.



4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid
(picloram, pK_a 2.3)



3,6-dichloro-2-pyridinecarboxylic acid
(clopyralid, pK_a 2.3)



3,5,6-trichloro-2-pyridinyloxyacetic acid
(triclopyr, pK_a 2.7)

Fig. 1.1. Chemical structures of picloram, clopyralid and triclopyr (pyridine herbicides).

1.2.1. Picloram

1.2.1.1. Use and mode of action Introduction

Picloram is a systematic herbicide mainly used to control a wide range of deep-rooted herbaceous weeds and woody plants. It is the most persistent herbicides in the chloropyridine family and stays active in the environment for a long period of time with a half-life of 2 – 4 months in clay soils with a high organic content [16]. Consequently,

residues of picloram are also useful at controlling weeds in subsequent seasons. These attributes make picloram an effective replacement for 2,4-D and 2,4,5-T. However, for some particular applications to control persistent perennial weeds, a mixture of picloram and 2,4-D is still useful. The negative animal physiological effects, such as miscarriage, birth defects and cancer, as a result of exposure to 2,4,5-T was another reason for its complete replacement [15]. Picloram residues can potentially have a negative impact on the environment as predicted by its physicochemical properties such as high water solubility, melting point and slow decomposition rate as shown in **Table 1.1**. Consequently, picloram is classified as a herbicide with high leaching potential and presents a significant risk for water contamination. It has been detected in fresh waters at concentrations of 0.3 – 437 μg/L [17]; just below the maximum permissible level of 500 μg/L in drinking water established by some regulatory agencies [18].

Table 1.1. Physical and chemical properties of picloram [19-21]

Parameter	Value(s) and conditions
Melting point	Decomposes at 215 °C
Solubility in water	0.52 g/L at 20 °C
Octanol/water partition coefficient	log P_{ow} = 1.83 at 25 °C, pH 1 log P_{ow} = 0.63 at 25 °C, pH 3 log P_{ow} = -2.01 at 25 °C, pH 7 log P_{ow} = -2.21 at 25 °C, pH 9
Hydrolysis characteristics	Half-life > 1 year at room temperature at pH 5, 7, 9
Dissociation characteristics	pK_a = 2.3
Solubility in organic solvents	26.46 g/L Methanol at 20 ± 0.5 °C <0.71 g/L n-hexane at 20 ± 0.5 °C 4.47 g/L n-octanol at 20 ± 0.5 °C

The chemical structure of picloram resembles the natural auxin hormone indole-3-acetic acid (**Fig. 1.2**). Consequently, it functions similarly to auxin by promoting normal plant growth at low concentrations, but uncontrolled growth leading to a plant death at high concentrations [22]. Plants exposed to picloram display a wide range of morphological

responses, including: stunting of leaves, twisting of stems and growth inhibition of shots and roots. These responses are subsequently followed by accelerated and localised tissue death.

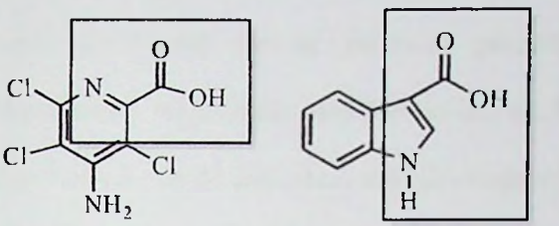


Fig. 1.2. Structural similarities of picloram and indole-3-acetic acid.

1.2.1.2. Degradation of Picloram in the Environment

Picloram undergoes incomplete degradation with a half-life of 2.6 days when exposed to sunlight in surface water or on the surface of soil and plant foliage [23]. The degradation occurs faster in flowing water and is slower on the surface of soil [24]. Degradation induced by other chemicals in the environment is very slow and usually occurs with a half-life of 9 - 116 years [25]. The resistance of picloram to degradation is mainly attributed to the type and number of substituents on the pyridine ring [26]. However, the reported biodegradation of pyridine to ammonia provides evidence that the complete biodegradation of pyridine-based herbicides is possible, once the initial resistance is overcome [26-28]. Picloram does not readily vaporise in the environment because of its low vapour pressure of 6.16×10^{-7} mm Hg at 35 °C [29]. Thus, the main way to remove picloram from the environment is through microbial degradation which in most cases is an incomplete and slow process [30].

1.2.1.3. Non-target Effects of Picloram

The slow degradation of picloram in the environment is of great concern because the residues can accumulate in soils and have subsequent effects on sensitive crops [31, 32]. Therefore, the extensive agricultural use of picloram presents potential hazardous consequences to the environment, food chains, and human health. Residual effects such as growth inhibition, reduced plant height and abnormal development of leaves have been reported [14]. A combination of residues from picloram and 2,4-D produces synergistic effects of genotoxicity, mortality and neurotoxicity in *Rhinella arenarum* tadpoles [33]. Picloram also induces carcinogenic outcomes in mice and rats and is, therefore, listed as a potential endocrine disruptor [34, 35]. As a consequence, it was previously banned due to its negative impacts in water and on non-target plants, however, it was re-registered for restricted use in 1995 [36]. Despite the negative impacts, picloram is still one of the most widely used herbicides because of its unmatched efficacy and residual activity on common and troublesome weeds. The negative effects caused by accumulation of picloram in the environment are expected to increase due to its high persistence, water solubility and mobility [37-40]. Consequently, no practical use restriction is expected to prevent picloram from contaminating the environment surrounding the target site. Therefore, the removal of picloram and related herbicides from the environment is of paramount significance.

1.3. Technologies for removal of herbicides

Several methods and techniques for the removal of herbicide residues from the contaminated environment have been successful, including: heterogeneous photo-catalysis, chemical oxidation (zero-valent metals), electrochemical advanced oxidation and microbial degradation [41-44]. Nevertheless, most of these techniques produce degradation by-products with some having properties, such as: toxicity, mobility and resistance to

degradation, different from parent compounds. Therefore, there is a demand for efficient and cost-effective methods to remove these residues from the environment without leading to the formation of other chemical products.

Solvent extraction is one of potential simple and reliable techniques/methods for the removal of herbicides from the environment. Applications of the solvent extraction in various fields, such as: petroleum refining, hydrometallurgical engineering and pharmaceutical manufacturing have been known [45]. As a separation process, it has advantages of simplicity, speed and applicability to both micro and macro amounts of solutes [46]. Solvent extraction involves a transfer of solute between two completely or partially immiscible solvents which in most cases are organic and aqueous phases. The solubility of a solute in the two phases is a critical condition for a successful separation process. The performance of solvent extraction is measured by the distribution coefficient (K_D) as defined in Eqn. 1.1. The distribution coefficient and the selectivity of the separation process can be improved by addition of an extractant to the organic phase that reacts selectively and reversibly with a target solute. However, stability of complex formed between the extractant and target solute is significantly influenced by the physical properties of the organic solvent, such as: viscosity, density and surface tension [45].

$$K_D = \frac{\text{total concentration of solute in organic phase}}{\text{total concentration of solute in aqueous phase}} \qquad \text{(Eqn. 1.1)}$$

Some disadvantages of solvent extraction are that it typically uses large amount of organic solvents, and extraction and back extraction are conducted in two distinct stages. This ultimately increase costs of chemicals, labour and time involved in the separation process. Thus, an avenue of research challenge has opened to investigate the development of alternative separation techniques. Consequently, the use of liquid membranes represents a

most promising variety of separation techniques to replace solvent extraction due to numerous advantages, in terms of energy consumption, efficiency, selectivity, and operational costs [47-49].

1.4. Liquid Membranes

Principles used in solvent extraction provide a useful guide for the design and operation of a liquid membrane [50]. Therefore, a liquid membrane can be considered as a modification of solvent extraction where an organic phase containing an extractant is used to separate aqueous feed and receiving solutions. This configuration permits the extraction and back-extraction processes, occurring in two distinct stages in the solvent extraction, to occur at the same time. Consequently, a separation involving a liquid membrane is a non-equilibrium dependent process that can yield a high separation factor [51]. Additionally, the amount of solute extracted does not depend on the amount of organic solvent in the system. This significantly reduces the volume of solvents required in the separation process compared to solvent extraction [11]. These attributes make liquid membrane a preferable separation technique in industries dealing with textile, food, hydrometallurgy, medicine, biotechnology and environmental protection [52]. Some common categories of liquid membranes based on configuration are: bulk liquid membranes, emulsion liquid membranes, supported liquid membranes, and polymer inclusion membrane; each is briefly described in sections 1.4.1 – 1.4.4 [11].

1.4.1. Bulk Liquid Membrane (BLM)

A bulk liquid membrane (BLM) is a simple non-supported membrane comprising bulk aqueous feed and stripping solutions separated by an organic phase (membrane) as

shown in **Fig. 1.3**. The membrane resembles conventional solvent extraction by contacting a source aqueous solution with a liquid organic phase. However, the U-shape allows the organic phase to also contact an aqueous receiving solution. The BLM configuration offers several advantages, such as: simplicity in construction, visual observation during experiments, and measurement of solute concentration in all three phases [53]. Consequently, a BLM is useful for a wide range of preliminary laboratory studies, such as kinetics of mass transfer processes and reaction mechanisms [47, 53]. Unfortunately, this membrane process has a relatively low mass transfer and separation efficiency due to a decreased contact area compared to solvent extraction [54].

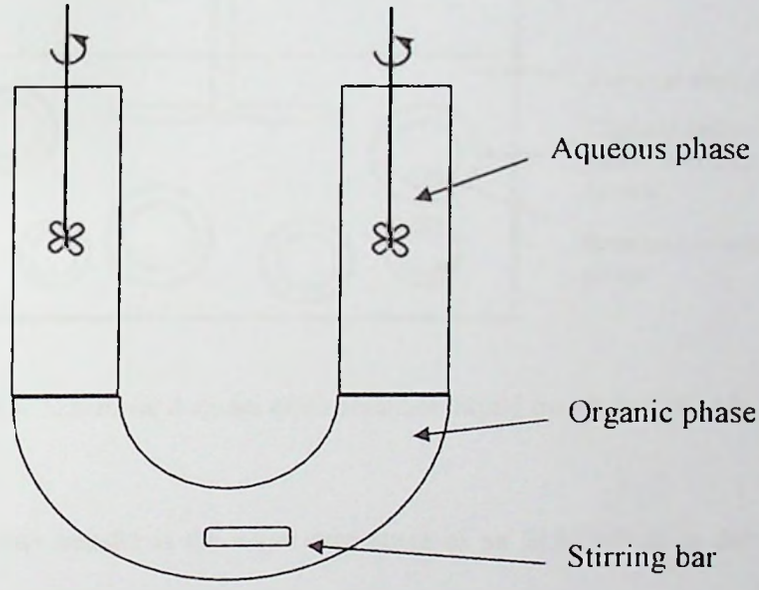


Fig. 1.3. Schematic diagram of a bulk liquid membrane (BLM) in U-tube configuration.

1.4.2. Emulsion Liquid Membrane (ELM)

Emulsion liquid membranes (ELMs) were primarily developed for the separation of hydrocarbons from aqueous wastes with a high separation efficiency due to an increased contact surface area compared to BLMs [55]. An ELM consists of three phases, namely: an innermost phase which is usually aqueous, an intermediate organic phase which is normally an organic solvent, and an outer aqueous phase as shown in **Fig. 1.4**. This type of membrane

is more complex compared to a BLM because of the complex processes of emulsification and de-emulsification. The aqueous insoluble membrane phase is comprised of a carrier, diluent and surfactant. Therefore, this membrane phase acts as a thin shell that encapsulates a stripping agent by an emulsification process. Thus, an application of this membrane type involves its dispersion into a feed solution by agitation which is a factor that affects its performance.

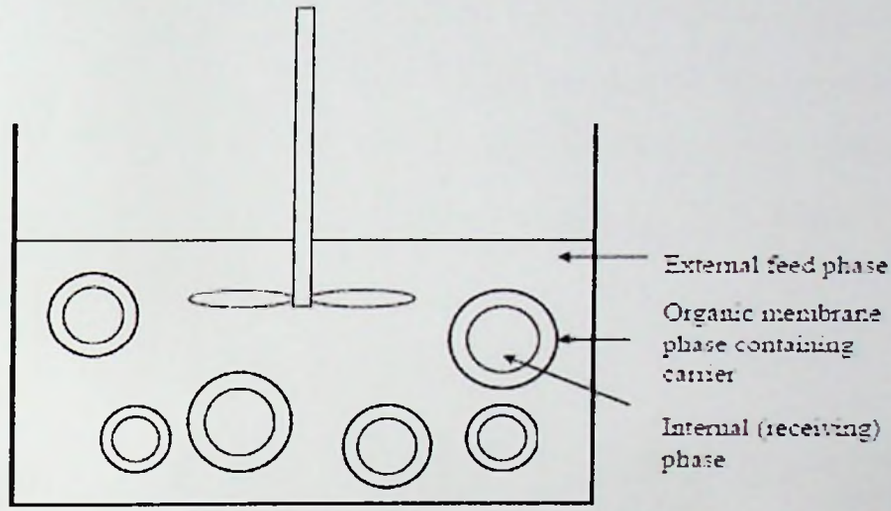


Fig. 1.4. Schematic diagram of an emulsion liquid membrane (ELM).

A high mass transfer is the major advantage of an ELM which is due to its high surface area and thin diffusion layer [54]. However, a decrease in transport performance can occur due to rapture of emulsions by an increased dispersion speed and operation time is the main disadvantage [56]. The stability can be, thus, improved by controlling these experimental conditions.

1.4.3. Supported Liquid Membrane (SLM)

A supported liquid membrane (SLM) is sometimes referred to as an immobilised liquid membrane because an organic phase containing a carrier is immobilised in micropores

of an inert polymeric material by weak capillary forces as shown in **Fig. 1.5** [47]. Commonly used polymeric supporting materials to prepare SLMs include: polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyether sulfone (PES), and Celgard®2500 [57-59]. This type of liquid membrane significantly differs from the previous types in terms of stability and the volume of organic solvents required. The former is improved due to the presence of the supporting polymeric material which provides mechanical support for the liquid membrane phase. The latter is decreased and as a result a smaller amount of carrier is required which, therefore, permits the use of expensive carriers when necessary. The membrane is also thinner compared to the other types of membrane. This improves mass transfer due to a decreased distance the target solute needs to travel from a feed to receiving solutions [54].

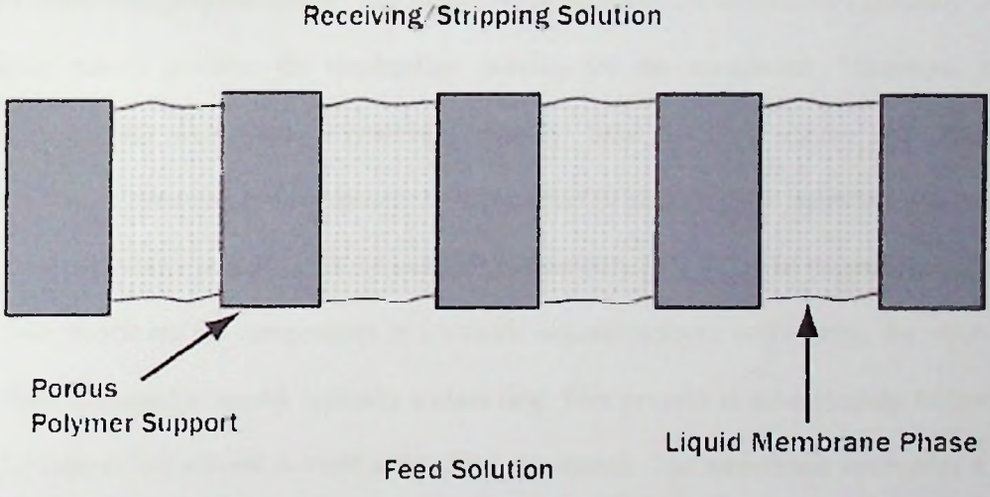


Fig. 1.5. Schematic diagram of a supported liquid membrane (SLM).

On the other hand, the application of this type of membrane for large scale operations is limited by poor stability due to solubilisation and progressive loss of the organic phase from the membrane pores [60-62]. Other causes of instability include progressive wetting of pores in the membrane by the aqueous phase, osmotic difference

across the membrane, and blockage of membrane pores by the precipitation of a solute-carrier complex and emulsion formation of the membrane [63-66]. Several approaches have been employed to improve the stability of SLMs including: online re-immobilisation of the liquid membrane, use of ionic liquid carriers with a high boiling point, and careful selection of porous support materials [67-69]. However, the instability caused by dilation of pores due to structural changes resulting from prolonged use of the membrane has led to the birth of another type of membrane called a polymer inclusion membrane [70].

1.4.4. Polymer Inclusion Membrane (PIM)

A polymer inclusion membrane (PIM) contains a liquid phase, normally composed of a plasticiser and carrier, encapsulated in a polymer matrix by entanglement and chemical interactions with polymer chains. The liquid phase provides the extraction capability and the polymer matrix provides the mechanical stability for the membrane. Therefore, a PIM usually contains three main components, namely: base polymer, carrier and plasticiser. Sometimes, a chemical reagent known as a modifier is added to the membrane to increase solubility of solutes and/or affect the extraction chemistry [11, 71]. The preparation of a PIM involves dissolving the components in a volatile organic solvent and casting the solution as thin film in a suitable mould, typically a glass ring. This process is subsequently followed by evaporation of the solvent to yield a thin film membrane. The membrane resembles a SLM except that in a PIM the organic liquid phase (liquid membrane) is entrapped by entanglement within polymer chains instead of capillary forces [72]. This entrapment makes the membrane relatively more stable compared to a SLM due to a reduced loss of chemical components. Consequently, a PIM can maintain a steady extraction performance in repetitive cycles and has the potential to be reused [73-75]. On the other hand, PIMs are regarded as exhibiting poorer extraction performance because of a high diffusive resistance produced by the polymer matrix compared to other types of liquid membranes. Additionally, the liquid

phase in the membrane is, typically, more viscous and, thus, the diffusion of solutes is slower. However, the mass transfer can be improved by making thinner membranes which reduces the distance the solutes need to travel from the feed to receiving solutions [11]. Consequently, polymer inclusion membranes can achieve a higher flux to comparable SLMs for the same process [76, 77].

1.4.4.1. Base polymer

A base polymer forms a polymer matrix encapsulating a liquid membrane through intermolecular attractions and entanglement within polymer chains, while also providing mechanical support to the membrane. The strong intermolecular forces, such as hydrogen bonds, between polymer chains produce membranes of higher mechanical strength compared to weak intermolecular forces such as dispersion forces. The entanglement significantly depends on the length of the polymer chains which must exceed a critical length for the entanglement to improve the mechanical strength [11]. Polymers with a molecular weight greater than the critical molecular weight result in significant entanglement and produce very stable membranes even if significant covalent interactions between polymer chains are absent. Polyvinyl chloride (PVC) and cellulose triacetate (CTA) are the most commonly used base polymers for PIMs because of their compatibility with many other chemicals used as carrier, plasticiser and modifier components in the membrane.

1.4.4.1.1. Polyvinyl chloride

Polyvinyl chloride is a common polymer used to make various polymeric materials due to its low cost and desirable physical and mechanical properties [78]. PVC is normally synthesised by a polymerisation reaction of vinyl chloride monomers (**Fig. 1.6**). The polymers produced from PVC exhibit unique characteristics, such as: high inertness,

mechanical resistance and light-weight, while also being compatible with numerous plasticisers [79]. Additionally, PVC polymers are amorphous because of non-specific dispersion intermolecular forces between polymer chains caused by the polar nature of the C-Cl bond. This non-regular structure enables the addition of liquid plasticisers to form channels within the PVC membranes that can transport solutes by a simple diffusion mechanism. Consequently, PVC membranes have been successfully used for the extraction/transport and sensing of numerous chemical species [79-82].

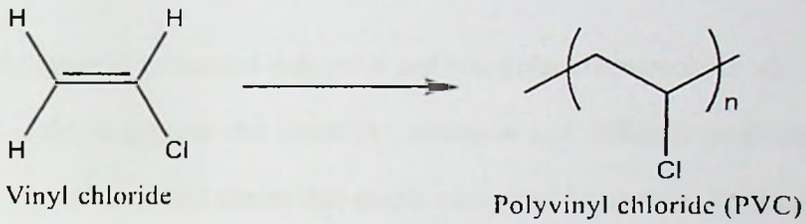


Fig. 1.6. Synthesis of polyvinyl chloride.

1.4.4.1.2. Cellulose triacetate (CTA)

Cellulose triacetate (CTA) is another common polymer routinely used to prepare PIMs. It is synthesised by acetylating cellulose using acetic anhydride as a source of acetic esters (**Fig. 1.7**). Cellulose triacetate polymers have a crystalline structure because of a high level of cross-linking between polymer chains due to the presence of hydroxyl and acetyl groups having the capability to form hydrogen bonds [83]. In addition, the membranes prepared from CTA have a homogeneous structure, excellent mechanical strength, and highly infusibility [84]. The chemical resilience of CTA over a wide range of pH make membranes suitable for a variety of applications. However, some care in choosing operating conditions is necessary because the ester linkages in the polymer can be readily hydrolysed under extremely acidic or basic conditions [11].

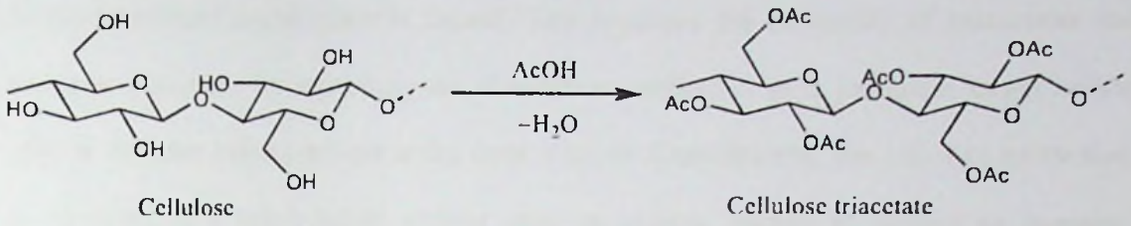


Fig. 1.7. Synthesis of cellulose triacetate.

1.4.4.2. Plasticiser

A plasticiser is a chemical with polar and non-polar characteristics which is added to polymers in order to improve the flexibility, retention and diffusion properties. A typical plasticiser contains long alkyl chains that enable non-polar interactions with polymer chains and polar groups that can polarise groups along the polymer chains. The plasticiser acts by forming secondary molecular interactions with polymer chains which increases the distance between them and diminish their entanglement. Consequently, a. plasticiser reduces brittleness, volume resistivity, hardness and viscosity of polymers while also improving elongation of polymer chains and the dielectric constant of the polymer material [85, 86]. A plasticiser also occupies and provides "free volume" in a polymer matrix which functions as a solvent to dissolve other necessary membrane components for a particular application. As a result, a plasticiser needs to have a relatively high capacity to dissolve the other components. Low viscosity and high dielectric constant are other important attributes of a plasticiser required to enhance the diffusion of solutes through membranes [11].

1.4.4.3. Carrier

A carrier is a chemical reagent that is used to bind a target solute at the feed solution/membrane interface and transport it by diffusion across a membrane [87]. As a

result of this binding, a lipophilic complex or ion-pair compound is formed which is soluble in the membrane liquid phase is formed. This improves the selectivity of extraction and transport processes by increasing the distribution coefficient of a particular target solute relative to other solutes present in the same solution. Consequently, the selective extraction or transport of a target solute without using an organic solvent to contact an aqueous solution, which improves the durability of membranes by decreasing the loss of liquid components is achieved [11].

The durability of a membrane is normally decreased by the loss of carrier which, in most cases, is associated with its water-solubility in the aqueous solutions in contact with the membrane [88, 89]. The loss can be decreased by using a carrier that is sufficiently lipophilic to remain soluble in the membrane phase, but which is insoluble in water. However, most carriers contain a hydrophilic associated with the binding site which increases water solubility. For this reason, overcoming the decrease in stability of PIMs caused by the solubility of carrier in aqueous solutions has been a common challenge [90, 91]. The membrane stability can be improved by saturating the adjacent aqueous solutions with a carrier to minimise its loss from the membrane [90]. Alternatively, an effective encapsulation of carrier into a highly cross-linked polymer can minimise the carrier loss and improve the membrane stability [91].

Many types of carriers, including: carboxylic, phosphoric and sulfonic acids, amines and crown-ethers, have been successfully used in SLMs and PIMs [92-94]. More recently, amine forms of ionic liquids have been used for extraction and transport of charged chemical species [95, 96]. Ionic liquids are recognised as having intrinsic properties, such as: low melting point, flammability and vapour pressure, which potentially decrease the risk of contaminating the environment from their use. However, there are now emerging concerns about the adverse effects of ionic liquids on the ecosystem [97]. Therefore, the use of natural compounds derived from plants as available alternatives to potentially toxic carriers is a way

forward for the development of "green polymer inclusion membranes". The development and selection of a suitable carrier depends on the transport mechanism involved.

1.5. Transport mechanisms in polymer inclusion membranes

The transport of solutes across the membranes can be through passive or carrier facilitated diffusion. These main transport mechanisms are briefly described in sections 1.5.1 - 1.5.2.

1.5.1. Passive transport

Passive transport is a mechanism where a target solute partitions between a membrane and feed aqueous solution and, subsequently, diffuses to a receiving solution. A concentration gradient of the target solute across the membrane, from the feed to receiving solution, serves as the main driving force for transport. This type of mechanism is useful for the transport of organic acids and bases. Here, a pH difference across the membrane serves as a molecular switch between the neutral and charged forms of the species, allowing the concentration of a solute against the concentration gradient. However, the selectivity for a particular solute is difficult to achieve by a passive mechanism because all solutes that are affected by the stripping process will be transported from the feed solution.

1.5.2. Carrier-facilitated transport

In some cases, the diffusion of a target solute is unachievable even if effective stripping is possible because the solute does not readily partition to the liquid membrane phase. In these cases, a carrier that can reversibly interact with the target solute to form a complex which is only soluble in the liquid membrane phase is required [98]. A carrier-

facilitated process for neutral or charged chemical species can be achieved and involves either a counter-coupled and co-coupled transport mechanism.

1.5.2.1. Counter-coupled transport

A counter-coupled transport mechanism involves the transport of a target solute ion (M^- or M^+) which is coupled by the reverse transport of a counter-ion (X^- or X^+) as shown in **Fig. 1.8**. At the feed solution/membrane interface, the target ion is loaded into the membrane to form an ion-pair complex with the carrier and a counter-ion is released into the feed solution. The ion-pair complex containing target-ion and carrier (C^+M^- or C^-M^+) diffuses across the membrane to the receiver interface where the target ion is released into the receiving solution and the carrier takes up a counter ion and is regenerated for subsequent transport cycles. The concentration gradient of the counter-ion across the membrane from a low to a high in the feed and receiving solutions, respectively, acts as the main driving force for the transport of the target ion against its concentration gradient.

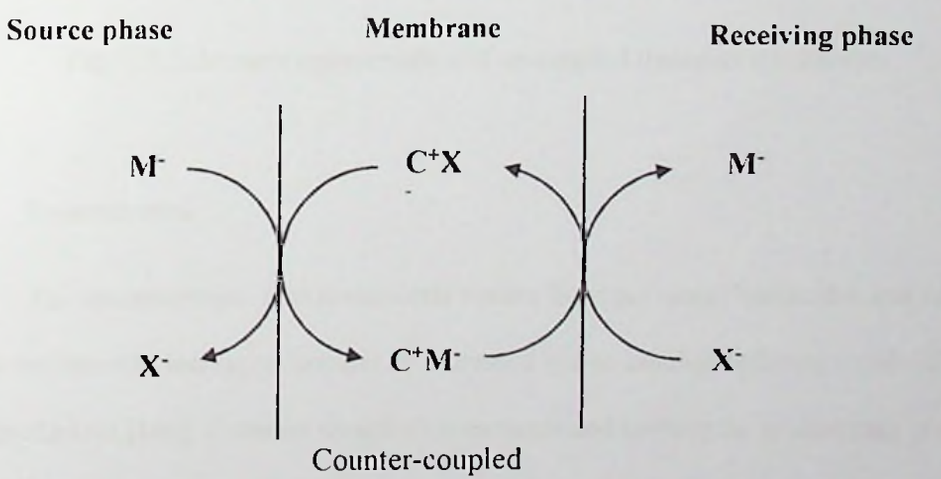


Fig. 1.8. Schematic representation of a counter-coupled transport mechanism.

1.5.2.2. Co-coupled transport

A co-coupled transport mechanism involves the transport of two oppositely charged chemical species from a feed to a receiving solution through a membrane to maintain an overall charge balance throughout the process as shown in **Fig. 1.9**. In this case, the concentration gradient of the co-coupled ion (X^+) from a high to a low concentration in the feed and receiving solutions, respectively, acts as the main driving force for the transport of target solute ion (M^-).

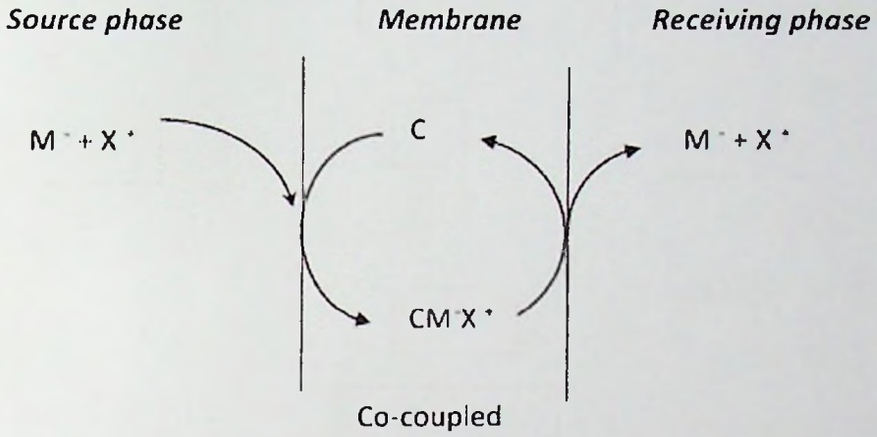


Fig. 1.9. Schematic representation of co-coupled transport mechanism.

1.6. Research aims

The contamination of environmental waters from persistent herbicides and resulting effects are recently increasing because of increased use to combat resistant weeds affecting food production [106]. Common remediation methods and techniques to eliminate persistent herbicide residues from the environment, such as biological and chemical degradation, are mostly effective but produce less active degradation products of different toxicities. Consequently, alternate methods/techniques to remove herbicides from the environment are required. The use of polymer inclusion membranes (PIMs) for this purpose is anticipated to

be an environmentally friendly method that does not produce other potentially toxic compounds during the process. Therefore, the major aim of this research is to develop PIMs for the purpose of removing pyridine herbicides from an aqueous environment.

Currently, many herbicides are considered Persistent Organic Pollutants (POPs) and their degradation by-products are also now considered to be an emerging group of environmental contaminants [107]. Most of these degradation compounds are not available as commercial products which limit the testing of their harmful effects. As a result, no standard permissible levels have been established. Therefore, studies and associated data about their removal from the environment are limited and, for this reason, further studies are deemed necessary. The second aim of the current study is to investigate using PIMs to remove potential degradation products from pyridine herbicides in water.

Research associated with the use of polymer inclusion membranes for the extraction and transport of organic compounds has not been as intensive compared to metal species [108]. The reasons for this are that the extraction chemistry of organics is not always as straightforward or selective, and the recovery of organics does not present the same commercial bonus as the recovery of some metal species. Much of the recent use of PIMs involves the use of commercial carriers that are relatively expensive [11]. Plants are a source of natural compounds that could be used as inexpensive carriers in PIMs to reduce costs. This project also investigates the use of anacardic acid sourced from cashew nut shell liquid as a cheap and environmentally friendly carrier for use in PIMs.

1.7. Thesis outline

Chapter 1 presents a summary and evaluates the current literature mainly associated with persistent herbicides and methods to remove these herbicides from the environment.

The particular focus is the research associated with the development and use of polymer inclusion membranes.

Chapter 2 informs on the extraction and transport of picloram as a representative compound of pyridine-based herbicides using polymer inclusion membranes. Membrane and transport parameters, such as: ratio of polymer to plasticiser, amounts of carrier and concentration, and type of a stripping agent are reported. The feasibility of the optimal membrane composition for practical and commercial applications was tested. Finally, the membranes were used for the competitive transport of a mixture containing picloram and other related compounds.

Chapter 3 reports on the extraction and transport of 4-amino-2-chloropyridine (ACP) as a model compound of potential decomposition products from pyridine-based herbicides. Similarly, the transport parameters influencing the transport such as carrier concentration, receiving solution pH were investigated. The suitability of the optimal membrane for practical commercial uses was also tested as well.

Chapter 4 informs on the potential use of anacardic acid from cashew nut shell liquid (CNSL) as a cheap and eco-friendly carrier in polymer inclusion membranes. The performance of anacardic acid mixture, containing closely related compounds, compared with anacardic acid isolated from CNSL on the transport of ACP was evaluated. The use of the optimal membranes containing anacardic acid to transport a mixture of ACP, paraquat and diquat was also studied.

Chapter 5 reports on the applications of the optimal membranes for the extraction and transport of target solutes from real samples of natural water. In addition, the use of the membranes for the pre-concentration of selected solutes from a complex matrix of natural water is presented.

Chapter 6 briefly presents concluding remarks drawn from the research described in this thesis. It also highlights recommendations for future research based on successes and challenges from the current study.

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2.1. Introduction

Polymer inclusion membranes (PIMs) are useful for the extraction of solute from a solution similar to solvent extraction processes [1]. The extraction is normally performed by immersion of a membrane into a solution containing a target solute, as routinely described in the existing literature [2-4]. The membranes can also be applied for the transport of a target solute from a feed phase to a receiving phase which allows extraction and back-extraction to simultaneously occur on opposite sides of the membrane. The two processes depend on the distribution coefficient of the target solute between the membrane and the feed and receiving aqueous solutions. A high distribution coefficient is required at the feed solution/membrane interface to favour extraction of a target solute into the membrane, whereas a low distribution coefficient is needed at the receiving solution/membrane interface to favour the back-extraction. Therefore, a combination of these interfacial processes allows the transport of a target solute from a feed solution to a receiving solution, without significant accumulation in the membrane phase as shown in **Fig. 2.1**. This allows continuous processing of species of interest, rather than separated extraction and back-extraction cycles that are common with other separation methods, such as solvent extraction.

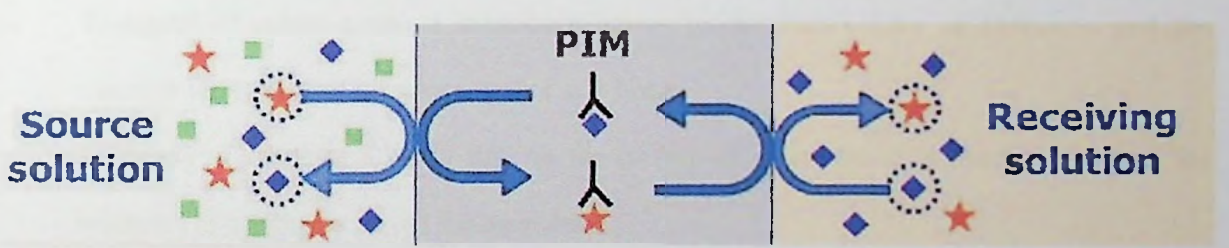


Fig. 2.1. Schematic diagram of membrane transport [5].

The application of PIMs for various purposes has gained a significant recent attention [6, 7]. They are recognised as an environmentally friendly alternative compared to other extraction techniques, such as solvent extraction and other types of liquid membranes, because of their reusability, reduced use of and exposure to organic chemicals, and a lesser risk of chemicals leaking

into the environment [8]. Moreover, versatility, ease of preparation and increased selectivity make them even more preferable [9]. Most studies involving potential use of membranes includes mathematical modelling as a crucial tool to assess the viability to any future scale-up of separation processes [10].

2.1.1. Mathematical modelling of membrane transport

Mathematical modelling involves the use of equations to describe relationships between variables in a system. It is a tool that provides deep understanding of the transport mechanism, cost estimation and design control of separation processes [10]. The simplified mathematical model for the membrane extraction/transport is often developed based on assumptions i - vi as outlined below [11].

i. Rate of reaction on the surface of a membrane is high enough to assume equilibrium of the system.

ii. Concentration of a transported solute in a membrane is very small compared to the concentration of carrier; consequently, the concentration of free carrier in a membrane is constant.

iii. Concentration of a solute-carrier complex at the membrane-receiving interface is negligible relative to the concentration at the membrane/feed interface.

iv. Transport of solute across a membrane agrees to the Fick's Law of Diffusion and the concentration gradient across a membrane is linear.

v. Diffusion of solute in a liquid film on the surface of a membrane is much faster than the diffusion of a complex across the membrane.

vi. Feeding and receiving solutions are thoroughly stirred.

Based on these assumptions, the kinetics for membrane transport processes can be described by the first-order rate equation presented in Eqn. 2.1 [11].

$$\ln\left(\frac{C}{C_0}\right) = -kt = -\frac{P}{V}At \qquad \text{(Eqn. 2.1)}$$

Where,

C = analyte concentration at a given time in a feed solution (mg/L).

C_0 = initial analyte concentration in a feed phase (mg/L).

k = rate constant (s^{-1})

t = time of transport (s)

P = permeability (m/s)

V = volume of feed solution (m^3)

A = effective surface area of membrane (m^2)

The permeability of a membrane (P), which measures the amount of solute transported through a specific distance of membrane in a unit time is determined from a rate constant (k) (Eqn. 2.1). The latter is calculated from the gradient of a plot of the natural logarithm for a change in concentration of a target solute in a feed solution ($\ln (C/C_0)$) versus time. In most cases, the performance of a membrane depends on the initial concentration of target solute, thus giving a flux (J_i), as a product of permeability and initial solute concentration (Eqn. 2.2).

$$J_i = PC_0 \qquad \text{(Eqn. 2.2)}$$

However, sometimes, not all target solute extracted into a membrane, as indicated by permeability or flux, reaches the receiving solution as some can remain in the membrane phase. As a result, another important and useful parameter of membrane performance is the transport efficiency (TE) which measures the amount of solute present in a receiving solution (C_s) compared to the initial amount in a feed solution (C_0) (Eqn. 2.3). TE_{24} and TE_{48} represent the transport efficiency after 24 and 48 hours, respectively.

$$TE = \left(\frac{C_S}{C_0} \right) \times 100 \qquad \text{(Eqn. 2.3)}$$

2.1.2. Extraction and transport of organic compounds using liquid membranes

The following brief literature review describes some highlights on previous research on the transport or extraction of organic compounds using membrane technology. It includes examples of other types of liquid membranes apart from PIMs because studies involving membranes for the extraction and transport of organic compounds are limited [12]. However, results from other types of membrane provide a useful guide to the expected extraction and transport mechanisms of organics when using PIMs under experimental conditions.

The extraction and transport of phenol using PIMs has been studied because it is a commonly found environmental pollutant [13-15]. These studies used polyeugenol, N,N-di(1-methylheptyl) acetamide and Cyanex 923 as carriers for phenol transport from acidic feed to basic receiving solutions. Thus, phenol interacted through hydrogen bonding with the carriers and stripping was achieved as the phenoxide. The pH gradient established between phenol and phenoxide in the feed and receiving solution provided the driving force for the transport process. Optimal membrane permeabilities of 880×10^{-7} m/s and 662×10^{-8} m/s were recorded for polyeugenol and N,N-di(1-methylheptyl) acetamide, respectively [14, 15].

Another study demonstrated the extraction and transport of 5-aminosalicyclic acid through a bulk liquid membrane containing Aliquat 336 prepared in chloroform [16]. The target compound contains carboxylic acid and amine functional groups and the transport was performed from a basic feed to an acidic receiving solution. The influence of amount of carrier and stripping agent (HCl) was evaluated. The results showed that an increase in the concentration of carrier improved both the extraction and back-extraction reaction rates, presumably due to an increase in the amount of ion-pair complex formed. Additionally, the membrane permeability increased with increasing concentration of HCl in the receiving solution due to the increase in the chloride concentration gradient and protonation of the amine functional group which was the main driving force. Therefore, the extraction of 5-aminosalicyclic acid involved the formation of an ion-pair complex between negatively charged

5-aminosalicyclate and Aliquat, whereas the back-extraction was triggered by ion-exchange and protonation of the amine functional group. This demonstrated the possibility of a facilitated transport mechanism by exploiting two different functional groups for extraction and back-extraction.

The transport of amino acids through a polymer inclusion membrane containing cellulose triacetate (CTA), 2-nitrophenyl octyl ether (NPOE) and Aliquat 336 carrier has also been reported [17]. The findings indicated that the initial flux improved with increasing carrier concentration, but a rapid increase in flux was noted for carrier concentrations above 20 wt%. A carrier concentration equivalent to 20 wt% was identified as a percolation threshold, above which charged sites of carrier in the membrane are close enough to permit "jumping" of the amino acid molecules from one carrier site to another as shown in **Fig. 2.2**. Below the percolation threshold concentration, the transport of amino acids is mainly by passive diffusion. Consequently, it was concluded that a mixed transport mechanism was involved in the transport of amino acids across the membrane [17-19]. The involvement of a counter-coupled facilitated mechanism was confirmed by substitution of chloride with a lipophilic counter-ion (bis(2-ethylhexyl) phosphate), which caused a significant 30% drop in flux.

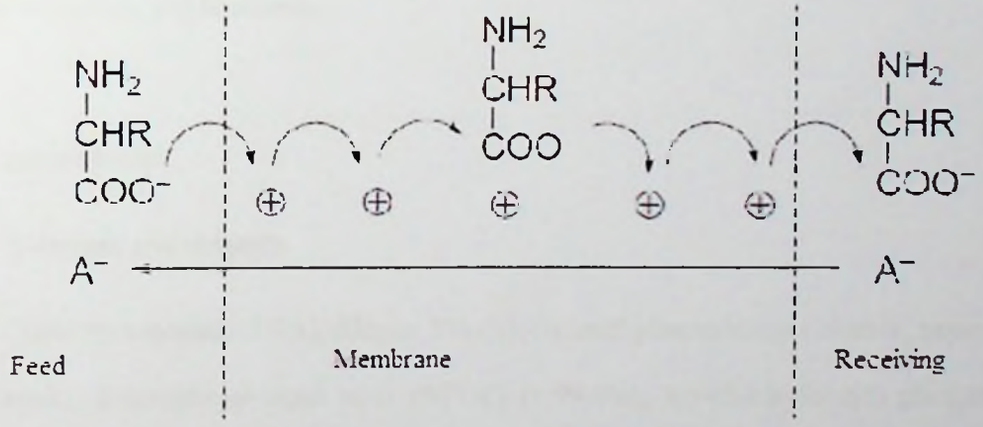


Fig. 2.2. Fixed sites jumping mechanism.

The competitive extraction and transport of a mixture of antibiotics (tetracycline and sulphonamide) using PIMs composed of 30 wt% CTA, 26 wt% Aliquat 336 and 44 wt% NPOE was investigated [20]. The mixture contained compounds having both basic and acidic functional groups and the influence of membrane composition and stripping agent concentration on the transport process at pH 7 and 9 was evaluated. It was found that the extraction efficiency increased with increasing amount of NPOE in the membrane. This result is normally associated with a decrease in the resistance of passage of solute due to the enhanced formation of liquid micro-voids in a membrane [10]. The extraction efficiency also increased with increasing stripping agent (NaCl) concentration, indicating that the transport involved a facilitated counter-coupled transport mechanism. Therefore, the chloride concentration gradient was the main driving force for the "uphill" transport of antibiotics against their concentration gradient. This demonstrated the possibility of carrying out the extraction or transport of more than one target solute at the same time.

The aim of experiments in this chapter is to study the extraction and transport of picloram, as a typical pyridine-based herbicide, and related compounds using PIMs containing CTA, Aliquat 336 (Aliquat) and NPOE. Experiment conditions, namely compositions of membrane, feed and receiving solutions, will be optimised. Additionally, membrane performance to extract and transport other pyridine herbicides will be assessed.

2.2. Experimental

2.2.1. Chemicals and reagents

Cellulose triacetate (CTA), Aliquat 336 (trioctylmethylammonium chloride, named as Aliquat in this work), 2-nitrophenyl octyl ether (NPOE) (≥ 99.0%), tris-(2-ethylhexyl) phosphate (TEHP) (97%), dioctyl phthalate (DOP) (≥ 99.5%), picloram (4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid) (BioReagent), pyridine-2-carboxylic acid (picolinic acid) ReagentPlus®, (99%) 2,4-D (2,4-Dichlorophonoxyacetic acid) (97%), triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) (PESTANAL®, analytical reagent, 99.9%), sodium monohydrogen phosphate dihydrate (98 –

101.0%), sodium dihydrogen phosphate dihydrate (98 – 100.5%) and methanol (99.9 %, HPLC grade), tris-(2-ethylhexyl) phosphate (TEHP) (97%), dioctyl phthalate (DOP) (≥ 99.5%), sodium thiocyanate (≥ 98%), sodium sulphate (99%) and sodium chlorate (≥ 99%) were purchased from Sigma-Aldrich. Clopyralid (95%) was obtained from AK scientific, Inc., USA, dichloromethane (99.8%) and sodium chloride (99.7%) from Chem Supply, Australia. Reagents and solvents were of an analytical grade and used as received. Deionised water (18.2 MΩ cm) was used for the preparation of solutions used in this work.

2.2.2. Preparation of membranes

CTA membranes were prepared by the casting method as reported elsewhere [21, 22]. Briefly, the polymer components: CTA, Aliquat and NPOE totalling 300 mg were dissolved in dichloromethane (20 mL). The mixture was vigorously stirred to obtain a homogeneous solution and concentrated to about 10 mL. The solution was poured into a glass petri dish (90 mm diameter) and loosely covered to allow the slow evaporation of solvent overnight at room temperature. The membrane was carefully peeled from the glass plate and allowed to dry to constant mass. It was then trimmed by using a circular metal cutter to remove the thick edges to give a 53 mm diameter membrane with a uniform thickness of 28 ± 2 μm and average mass of 50 ± 3 mg. A membrane containing 25 wt% CTA, 30 wt% Aliquat and 45 wt% NPOE is referred as a standard membrane and used in many experiments. Except for the stability experiments, a new and different membrane was used for each experiment.

2.2.3. Membrane thickness measurement

The membrane thickness was measured using a LEICA M125 optical microscopy. The membranes were rapidly broken after immersion in liquid nitrogen and segments obtained were sandwiched between two glass microscope slides with their edges exceeding edges of the slides and

the average thickness was determined from ten measurements taken from different regions of membranes.

2.2.4. Membrane transport experiments

A permeation cell (**Fig. 2.3**) similar to the one described by elsewhere [23] was used for all transport experiments. The membrane segment separated feed and receiving solutions of equal volumes (100 mL) by completely exposing a surface of 34 mm diameter to each solution. The two solutions were stirred at rotation speed of 300 rpm using magnetic stirrers. The start of transport process was marked by simultaneously switching one of the stirrers in both phases. The transport dynamics were monitored by measuring concentrations of a target solute in feed and receiving solutions at certain time intervals. The solutions were replaced with the appropriate initial solutions to maintain a constant volume throughout the experiments. All transport experiments were performed at room temperature (25 ± 1 °C), a pH 7 feed solution containing100 mg/L of picloram and a pH 7 receiving solution containing 0.25 M NaCl which is referred to as standard transport conditions unless stated otherwise. The feed and receiving solutions were prepared using a pH 7 buffer solution made by mixing 50:50 of 100 mM monobasic: dibasic phosphate.

F-feed solution, **M**-membrane and **R**-receiving solution

Fig. 2.3. Permeation cell used for transport studies.

2.2.5. Sample analysis

The concentration of picloram, picolinic acid, clopyralid and triclopyr was determined by UV-Vis spectroscopy using a Cary 300Bio UV-Vis spectrophotometer at absorption maxima of 223, 264, 221 and 233 nm, respectively, in non-competitive experiments. Standard solutions (0.25 – 10 mg/L) of each analyte were prepared using pH 7 phosphate buffer to construct an analytical calibration graph. Samples (250 μL) from the feed and receiving solutions were diluted to 5 mL using pH 7 phosphate buffer for measurement. A MEP Instruments Metrohm 827 pH Lab pH meter and a MEP Instruments Metrohm 6.0228.010 pH electrode were used for pH measurements.

The concentration of herbicides in solution during competitive experiments was determined using a Shimadzu LC-20AT High Performance Liquid Chromatography (HPLC) equipped with an Apollo™ C18, 5 μ, 150 mm x 4.6 m ID column and a dual-wavelength UV detector (λ = 225 and 280 nm) [24]. An isocratic mobile phase of 50:50 vol% methanol and pH 2 phosphate buffer solution was used at a flow rate of 0.7 mL/min to elute a sample of 20 μL. Salicylic acid was added as an internal standard to all samples and standard solutions (0 – 2.5 mg/L) were used for quantification.

The limit of detection (LOD) and limit of quantification (LOQ) for picloram by UV-Vis spectrophotometer and HPLC were determined and reported in **Table 2.1**.

Table 2.1. LOD and LOQ for picloram by UV-Vis spectrophotomter and HPLC.

	LOD (mg/L)	LOQ (mg/L)
Uv-Vis spectrophotometer	0.1	0.3
HPLC	0.02	0.08

2.2.6. Optimisation of membrane composition

2.2.6.1. Plasticiser-to-polymer ratio

Membranes containing a fixed amount of carrier (20 wt%) and different ratios of polymer (CTA) to plasticiser (NPOE) as shown in **Table 2.2** were used to optimise a polymer to plasticiser ratio required for the transport of picloram using standard transport conditions.

Table 2.2. Membrane compositions for CTA: NPOE ratio optimisation.

CTA (wt%)	Aliquat (wt%)	NPOE (wt%)
80	20	0
70	20	10
60	20	20
50	20	30
40	20	40
30	20	50
20	20	60

2.2.6.2. Carrier concentration

Membranes of similar initial mass containing a constant 5:3 ratio of NPOE-to-CTA and different amounts of the carrier in a range of 0 – 50 wt% were used in the transport of picloram using standard transport conditions.

2.2.6.3. Choice of plasticiser

The suitability of plasticiser for the transport of picloram was evaluated using standard transport conditions and a membrane containing 25 wt% CTA, 30 wt% Aliquat and 45 wt% plasticiser. The plasticisers used in this experiment were NPOE, dioctyl phthalate (DOP) and tris-(2-ethylhexyl) phosphate (TEHP).

2.2.7. Stripping process

The influence of chloride at 0.0 - 0.5 M on the transport of picloram was investigated using a feed solution of 100 mg/L, a standard membrane and receiving solution composed of NaCl.

The influence of 0.25 M of different salts, namely: $NaNO_3$, Na_2SO_4, NaCl, NaSCN, and $NaClO_4$, as stripping reagents was also evaluated using a standard membrane. In this case, analysis of picloram was determined by HPLC as described in **Section 2.2.5**. The stripping effectiveness was evaluated based on the transport efficiency and initial flux.

2.2.8. Membrane stability studies

The stability of a standard membrane was evaluated using standard transport conditions. In this case, the transport of picloram was performed in five successive transport cycles of 24 hours each using fresh feed and receiving solutions without changing the membrane. The initial mass of the membrane was also measured after each transport cycle.

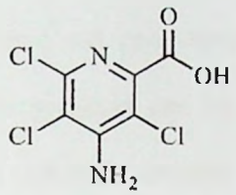
2.2.9. Non-competitive transport

Non-competitive transport was performed using a standard membrane, a pH 7 feed solution comprised of pyridine-2-carboxylic acid (picolinic acid), 3,6-dichloropyridine-2-carboxylic acid (clopyralid), and 6-chloropyridine-2-carboxylic acid (triclopyr) of 100 mg/L and a 0.25 M NaCl receiving solution both prepared at pH 7. The concentration of the compounds in feed and receiving

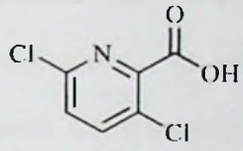
solutions was determined by a UV-Vis spectrophotometer at different maximal wavelengths using procedures described in **Section 2.2.5**

2.2.10. Competitive transport

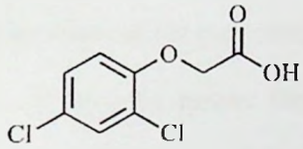
The competitive transport was performed using a pH 7 feed solution containing a mixture with equal amount (100 mg/L) of picloram, clopyralid, triclopyr and 2,4-D herbicides (**Fig. 2.4**) a 0.25 M NaCl receiving solution at pH 7and a standard membrane. The concentration of the herbicides in the mixture was determined using a Shimadzu LC-20AT High Performance Liquid Chromatography (HPLC) using salicylic acid as an internal standard as described in **Section 2.2.5.**



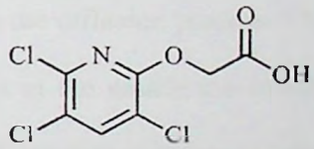
4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid
(picloram, pK_a 2.3)



3,6-Dichloro-2-pyridinecarboxylic acid
(clopyralid, pK_a 2.32)



2,4-Dichlorophenoxyacetic acid
(2,4-D, pK_a 2.60)



3,5,6-Trichloro-2-pyridinyloxyacetic acid
(triclopyr, pK_a 2.68)

Fig. 2.4. Chemical structures of picloram, clopyralid, 2,4-D and triclopyr.

2.2.11. Scanning Electron Microscopy (SEM)

Surface and cross-section of membranes were characterised by a scanning electron microscopy (SEM, JEOL JSM-840) equipped with an energy dispersive spectrometry unit (EDS, Oxford Link GEM). The membranes were rapidly broken after immersion in a liquid nitrogen and resulting segments dried under vacuum for 24 hours. The samples were then coated with gold

under vacuum (1 to 10 mbar) for 2 minutes at a deposition current of 20 mA in the presence of argon using K 950 turbo evaporator attached to K 350 sputter. The membrane samples were vertically mounted on a sample holder for cross-sectional images.

2.3. Results and Discussion

2.3.1. Introduction

The transport of picloram combines extraction and back-extraction occurring on opposite sides of a membrane. The formation of Aliquat-picloram complex takes place at the feed solution/membrane interface whereas the dissociation of the complex occurs at the receiver/membrane interface. To complete a transport cycle, the interfacial reactions are accompanied by the diffusion of the Aliquat-picloram ion pair complex through the membrane from feed to receiving solution. Consequently, the transport can be improved by optimising kinetics of interfacial reactions and diffusion of the ion-pair complex across the membranes. Consequently, the optimisation of parameters such as the composition of membranes, feed and receiving solutions is very useful. The membranes used for the transport of picloram composed an anion-exchanger carrier (Aliquat 336) to facilitate a formation of ion-pair complex, which enhances the diffusion process. The optimisation of the diffusion of aqueous species through a stagnant layer at the membrane-solution interface also improves the transport. This can be done by increasing bulk solution agitation to reduce a thickness of stagnant layer which ultimately decreases a time spent by aqueous species to diffuse through the layer. As a result, both feed and receiving solutions were stirred at a speed of 300 rpm, which is similar to previous reports [14].

Apart from chemical considerations, the Fick's Law of Diffusion indicates that the rate of transport of species through the membrane is directly proportional to the concentration gradient and inversely proportional to the thickness (Eqn. 2.4). Thus, the obvious way to improve the diffusion is by increasing the concentration gradient and decreasing membrane thickness. In this study, the concentration gradient between feed and receiving solution was optimised whereas the membranes made thin with an approximate thickness of around 30 μm. The surface area of membrane exposed

to solutions as another parameter influencing the diffusion was kept constant to allow other important parameters to be investigated.

$$J_i = -D_i\left(\frac{\partial C_0}{\partial x}\right) \qquad \text{(Eqn. 2.4)}$$

Where J_i is the molar flux for a solute i (mol.m^{-2}.s^{-1}), D_i is the diffusion coefficient (m^2.s^{-1}), C_0 is the concentration of solute i (mol.m^{-3}) and x is a distance (thickness) in meters.

2.3.2. Optimisation of membrane composition

2.3.2.1. Plasticiser-to-polymer ratio

A base polymer is used to form a polymer matrix to provide the mechanical support and encapsulate a liquid phase composed of, typically, a carrier and plasticiser when preparing a PIM. Cellulose triacetate (CTA) is a widely used base polymer and is particularly useful for applications involving polar solutes. A membrane made from CTA is normally characterised by strong intermolecular attractions (van der Waals forces and hydrogen bonds) between polymer chains, resulting in the formation of a rigid membrane structure, which produces very poor diffusive fluxes for species introduced in the membrane. Consequently, a plasticiser that can penetrate between polymer chains and diminish the associated intermolecular forces is a vital component, resulting in liquid voids in the membrane that improves the diffusion of solutes. For this reason, the ratio of polymer-to-plasticiser was optimised, prior to considering the carrier concentration in this study. Because the transport of picloram does not occur in the absence of carrier, a preliminary 20 wt% of Aliquat 336 (hereafter referred to as Aliquat) was initially used along with amounts of 2-nitrophenyl octyl ether (NPOE) and CTA required to prepare stable membranes.

The results in **Fig. 2.5** and **Table 2.3** show that the initial flux improved with increasing amounts of NPOE up to 50 wt%, however, a decreased flux was noted at 60 wt%. The improvement in flux is associated with an increase in micro-voids in the membrane. This occurs due to a greater distance between polymer chains caused by the polarising effects of increased amounts of plasticiser

at the expense of less polymer in the membrane. The micro-voids form channels through which the ion-pair complex can readily diffuse and, thus, decreases the obstruction caused by entangled polymer chains [10, 25]. A similar enhancement of flux with an increased ratio of NPOE-to-CTA for the transport of potassium has been reported [25]. As the amount of plasticiser increases above 50 wt% it is no longer readily retained in the membrane because it cannot form sufficient intermolecular interactions, presumably through hydrogen bonding, with the polymer backbone of CTA. Consequently, the plasticiser exudes to the membrane surface where it forms a 'stagnant' film exposed at the membrane/aqueous interface. This inhibits the ready uptake and diffusion of ions as indicated by the decrease in flux at 60 wt% NPOE. Membranes with more than 60 wt% NPOE were not included in this study because in preliminary experiments they exhibited poor mechanical strength attributed to the excessive amount of plasticiser, making them unsuitable for practical applications [10].

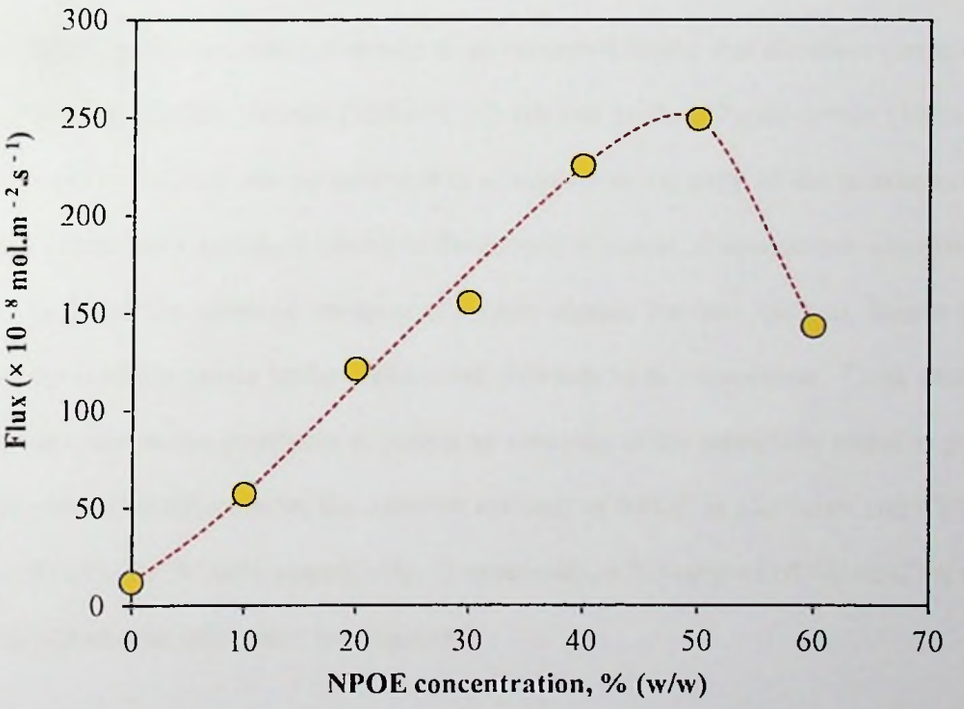


Fig. 2.5. Effect of amounts of NPOE (plasticiser) on initial flux of picloram. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 20 wt% Aliquat, 0 - 60 wt% NPOE, and remainder 20 – 80 wt% CTA.

Table 2.3. Effect of amounts of NPOE (plasticiser) on initial flux of picloram.

NPOE (wt%)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})
0	0.3	12
10	1.4	57
20	2.9	121
30	3.7	155
40	5.4	225
50	6.0	249
60	3.4	143

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 20 wt% Aliquat, 0 - 60 wt% NPOE, and remainder 20 – 80 wt% CTA.

The NPOE plasticiser which also acts as an entrapped liquid that dissolves carrier-picloram ion pairs is significantly less viscous (12.8 cP [26]) relative to the Aliquat carrier (1450 cP [27]). Thus, the increase in flux can also be attributed to a decrease in viscosity of the membrane phase as the amount of plasticiser is increased relative to the amount of carrier. A less viscous membrane phase is important as it enables enhanced transport of a large organic ion-pair, such as Aliquat-picloram, facilitating improved ion uptake at the surface and diffusion in the membrane. These observations confirm that diffusion in the membrane is limited by viscosity of the membrane phase as previously reported [28]. Based on these results, the optimum amounts of NPOE as plasticiser and CTA as base polymer are 50 wt% and 30 wt%, respectively. Consequently, a 5:3 ratio of NPOE-to-CTA was used to prepare membranes for subsequent investigations.

2.3.2.2. Carrier concentration

The concentration of carrier plays an essential role in the transport process by influencing the amount of target solute that can be loaded into a membrane. Consequently, an increase in carrier

concentration usually results in better extraction and/or transport of a target solute at the membrane/source interface. Additionally, some carriers, such as Aliquat, also have recognised plasticizing properties. In these cases, the increased carrier content also enhances the plasticizing effect leading to possible enhanced diffusion of complex or ion-pair across a membrane [29]. The influence of carrier concentration over 0 – 50 wt% on the transport of picloram was optimised while maintaining a constant 5:3 ratio of NPOE-to-CTA in membranes of a similar initial mass.

The results in **Fig. 2.6** and **Table 2.4** show that no transport occurred for membranes without carrier, which indicates that a cation-based carrier (Aliquat) is required to facilitate the extraction of picloram anion through the formation of a hydrophobic Aliquat-picloram ion-pair complex that readily partitions to the membrane phase. The initial flux improved with increased amounts of carrier up to 30 wt% as expected because more carrier was available for transport. However, the flux decreased at amounts of 40 and 50 wt% carrier due to the increased viscosity of the membrane liquid phase and formation of more picloram-Aliquat complexes, which both increase the diffusional resistance of the membrane phase. A similar profile of extraction versus Aliquat concentration is known for acetaminophen using an emulsion liquid membrane [30]. In the current work, the experiment using 30 wt% Aliquat and a 5:3 ratio of NPOE-to-CTA was conducted in triplicate to confirm the optimal membrane composition of 25 wt% CTA, 30 wt% Aliquat and 45% wt% NPOE for use in subsequent experiments.

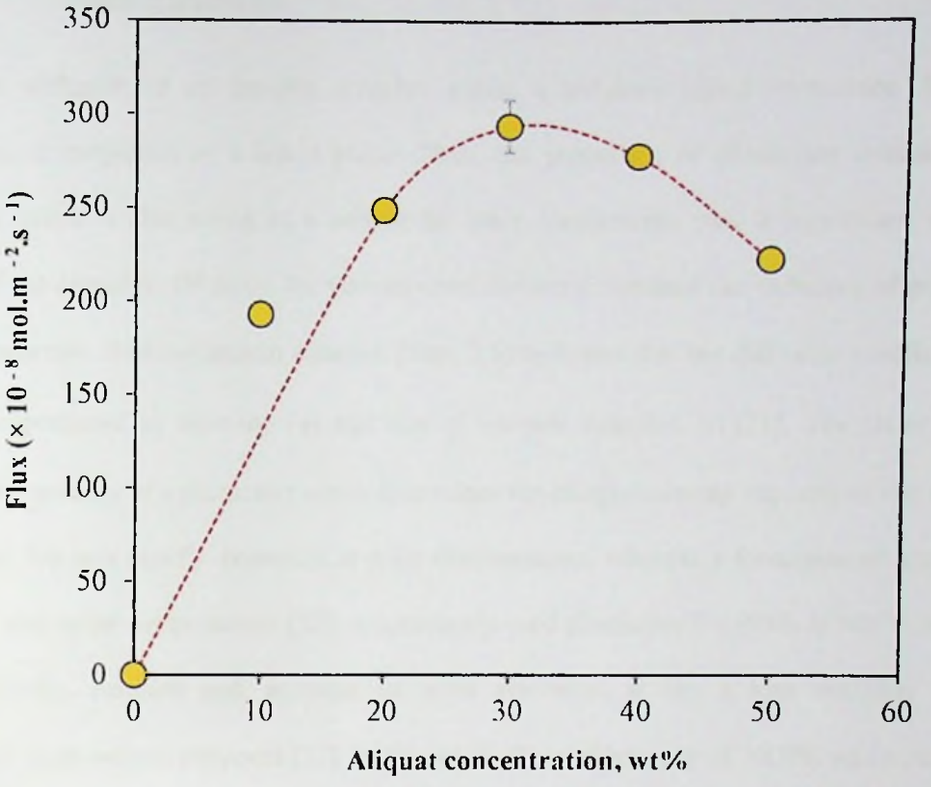


Fig. 2.6. Influence of carrier concentration on the flux of picloram. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 0 - 50 wt% Aliquat and 5:3 ratio of NPOE-to-CTA. Error bars represent a standard deviation of measurements for n = 3 experiments at 30 wt%.

Table 2.4. Influence of carrier concentration on the flux of picloram.

Aliquat (wt%)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})
0	0	0
10	4.7	193
20	6.0	249
30	7.1	294
40	6.7	278
50	5.4	223

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 0 – 50 wt% Aliquat and 5:3 ratio of NPOE-to-CTA.

2.3.2.3. Choice of plasticiser

The diffusion of an ion-pair complex across a polymer liquid membrane depends on physiochemical properties of a liquid phase. Thus, the properties of plasticiser contained in the membranes which is also acting as a solvent for other components play a significant role in the diffusion of the complex. Of these, the viscosity and dielectric constant (an indicator of polarity) are the most important. Stokes-Einstein equation (Eqn. 2.5) indicates that the diffusion coefficient (D) is inversely proportional to viscosity (η) and size of ion-pair complex (r) [31]. The latter is mainly influenced by polarity of a plasticiser which determines the charge-carrying capacity of the membrane liquid phase. Ion-pair rapidly dissociate in polar environments, whereas a formation of aggregates is common in non-polar environments [32]. A commonly used plasticiser for PIMs is NPOE because of a high dielectric constant and, amongst its other attributes, it has a low volatility and high compatibility with various polymers [33]. In this work, the performance of NOPE was evaluated and compared with two other common plasticisers, namely DOP & TEHP. These plasticisers have somewhat different viscosities and dielectric constants as indicated in **Table 2.5**.

$$D = {kT}/{6\pi r\eta} \qquad \text{(Eqn. 2.5)}$$

Where D = Diffusion coefficient

k = Boltzmann constant

T = Absolute temperature

r = Radius of complex

η = Viscosity of plasticiser

The results in **Table 2.5** show that a better initial flux and transport efficiency was achieved with a plasticiser having a high dielectric constant. Both membrane performance indicators increased in the order, TEHP < DOP < NPOE. The high transport efficiency and initial flux for NPOE is due to its substantially higher dielectric constant than DOP and TEHP. A high dielectric constant promotes

increased associations between the polar plasticiser and the Aliquat-picloram ion pairs which decreases their tendency to aggregate in the membrane. As a result, diffusion of the ion-pair is enhanced [34]. The low transport efficiency for TEHP is likely due to its loss from the membrane during conditioning and use (**Fig. 2.7**). The reduced amount of TEHP substantially changes the physiochemical properties of the membrane, consequently, making it more lipophilic which decreases the distribution of ion-pairs in the membrane.

Table 2.5. Correlation of viscosity and dielectric constant values of NPOE, DOP and TEHP with initial flux and transport efficiency for the transport of picloram.

Plasticiser	**Viscosity (cP) [10]**	**Dielectric constant [10]**	**Initial flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})**	**TE (%)**
NPOE	11	24.8	294	95
DOP	18	5.0	190	90
TEHP	13	4.8	147	55

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% Plasticiser.

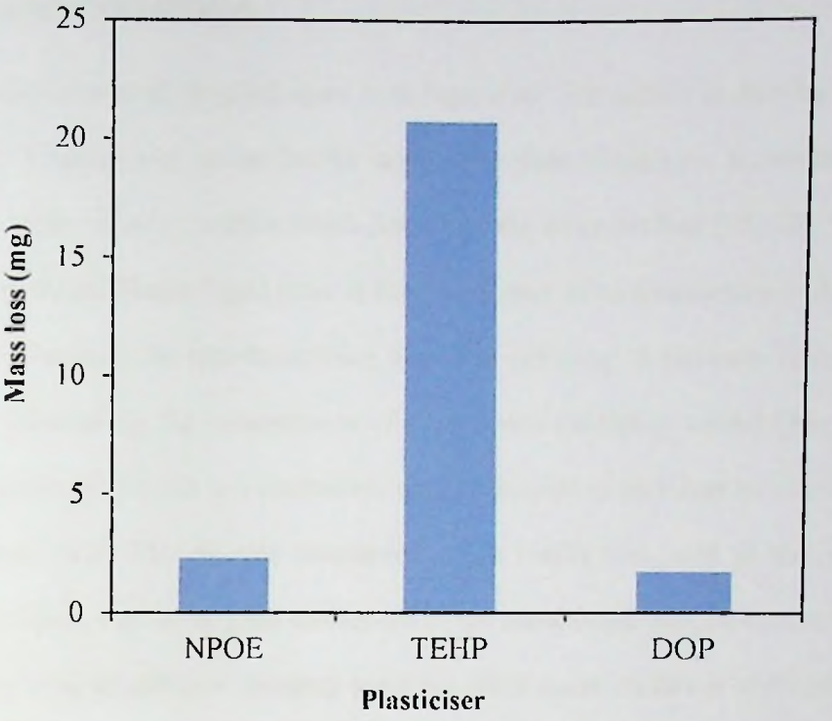


Fig. 2.7. Mass loss from membranes (50 mg. initial mass) containing a different plasticiser after conditioning in a pH 7 phosphate buffer solution for 24 hours.

The improved flux is likely due to the reduced tendency of Aliquat-picloram ion pair aggregations in the membrane as previously explained. This simplifies the dissociation of the ion-pair complex at the receiving-membrane interface. This makes free carrier more readily available and, consequently, the flux is improved. The difference in dielectric constant of DOP and TEHP is negligible and is, therefore, unlikely to reliably influence the observed difference in flux. In this instance, it is more likely that the difference in viscosity between the plasticisers is significant. However, the observed significant difference in flux between these two plasticisers and NPOE provides evidence that the dielectric constant is the essential factor which determines the choice of plasticiser for transport experiments. Therefore, NPOE was selected as the most suitable plasticiser and used to prepare membranes for subsequent investigations of the transport of picloram in this study.

2.3.3. Stripping agent concentration

The main function of stripping agent is to regenerate free carrier molecules for subsequent transport cycles. Consequently, an ineffective stripping process triggers an accumulation of solute-carrier complex at the receiver interface which diminishes the transport flux [35, 36]. When diffusion of the complex in the membrane liquid phase is faster compared to its dissociation at the interface, the stripping process becomes the rate-determining step. The stripping of picloram is an ion-exchange process that is affected by the concentration of counter-ion (stripping agent) (**Fig. 2.8**). For this reason, the influence of chloride as a counter-ion on the transport of picloram was investigated using the optimum membrane. The chloride counter-ion (from NaCl) was used as the stripping agent because it is consistent with the original counter-ion of the commercial Aliquat carrier. Also, chloride has been shown to be an effective stripping agent for other anion exchange applications involving Aliquat [20]. The stripping effectiveness was evaluated based on the transport efficiency and flux.

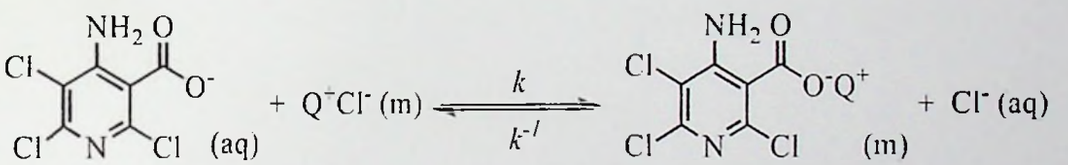


Fig. 2.8. Interfacial reactions of picloram for extraction and back-extraction processes. Where Q is Aliquat, aq and m are aqueous and membrane phases, respectively, and k and k^{-1} are forward and reverse rate constants, respectively.

The results **Fig. 2.9** and **Table 2.6** show that the transport efficiency improved with increasing concentration of the chloride counter-ion in the receiving solution. The low transport efficiencies observed at less than 0.25 M NaCl indicate that the Aliquat-picloram ion-pair accumulates at the membrane/receiving solution interface. Thus, the stripping process becomes the rate determining step ($k^{-1} < k$) for the transport process. This occurs when the diffusion of the ion-pair complex is faster compared to its dissociation at the receiving interface due to the absence or a low concentration of effective stripping agent. Therefore, the stripping and associated transport efficiency of picloram improves as the concentration of chloride counter-ion in the receiving solution increases.

Similar findings were reported for the transport of acetaminophen using an emulsion liquid membrane containing Aliquat as carrier and chloride as stripping agent [30]. The maximum transport efficiency of 95% occurred at 0.25 & 0.5 M NaCl. Notably, even at high chloride concentrations, not all solute extracted from the feed is transported to the receiving solution, some remains loaded in the membrane. This is why the transport efficiency is also included as a measure of stripping efficiency. The optimal chloride concentration was identified as 0.25 M, and above this concentration the stripping process at the receiving interface is no longer the rate determining step ($k^{-1} > k$). Consequently, increases in chloride concentration beyond 0.25 M had no significant effect on transport efficiency. A transport efficiency of 50% was observed in the absence of chloride indicating the system attained equilibrium ($k \approx k^{-1}$) with equal concentrations of picloram in the feed and receiving solutions. This provides evidence that a chloride concentration gradient across the membrane is essential to provide the necessary driving force for the "uphill" transport of picloram against its concentration gradient.

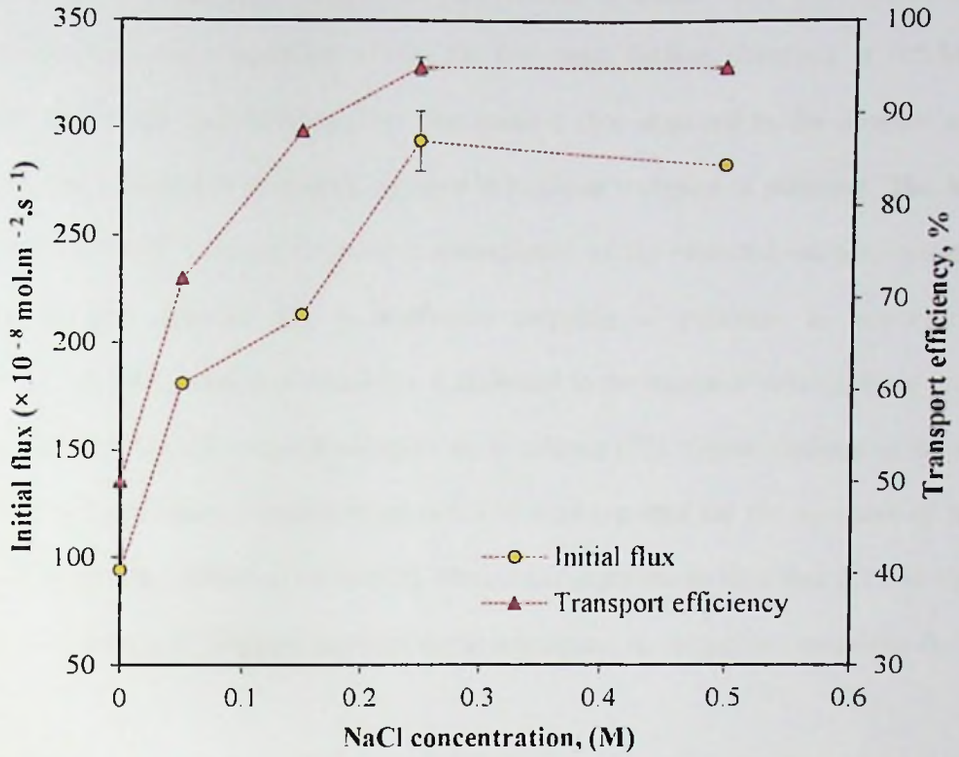


Fig. 2.9. Influence of NaCl concentration as stripping agent on the transport efficiency and flux of picloram. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.05 – 0.5 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments at 0.25 M NaCl.

Table 2.6. Effect of NaCl concentration as stripping agent on the transport efficiency and flux of picloram.

[NaCl] M	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
0.00	2.3	94	50
0.05	4.4	181	72
0.15	5.1	213	88
0.25	7.1	294	95
0.50	6.8	283	95

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.05 – 0.5 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

The results in **Fig. 2.9** and **Table 2.6** also indicate a higher flux with increased chloride concentrations, reaching a maximum at 0.25 M. The small decline observed at 0.5 M is likely insignificant and within experimental error. The minimal flux observed in the absence of chloride indicates the need for an effective stripping agent to facilitate transport of picloram. The low flux at 0.05 and 0.15 M NaCl is due to the possible accumulation of the extracted ion-pair complex at the receiving-membrane interface due to ineffective stripping of picloram as explained earlier. Consequently, the improvement in initial flux is attributed to the increased driving force provided by the larger chloride concentration gradient across the membrane [37]. Similar findings of an increase in permeability with chloride concentration up to 0.1 M were reported for the transport of lactic acid using a PIM containing Aliquat as carrier [38]. The current experiments identified 0.25 M NaCl as the optimum concentration of stripping agent for use in subsequent investigations involving the transport of picloram.

The increase in transport efficiency and flux as the concentration of NaCl increases indicates that a facilitated counter-coupled transport mechanism is involved in the transport of picloram as shown in **Fig. 2.10**. At the feed/membrane interface, the picloram anion (P^-) undergoes an anion exchange with the chloride of Aliquat (Q^+Cl^-) forming an Aliquat-picloram ion-pair (Q^+P^-) which permeates and diffuses through the membrane. The reverse ion-exchange process (stripping) occurs at the receiving/membrane interface and is driven by the 'high concentration' of chloride in the receiving solution. Consequently, the original carrier (Q^+Cl^-) is replenished and diffuses back across the membrane to the feed/membrane interface for another transport cycle. In this manner, the transport of picloram against its concentration gradient is achieved and driven by the chloride concentration gradient between the feed and receiving solutions.

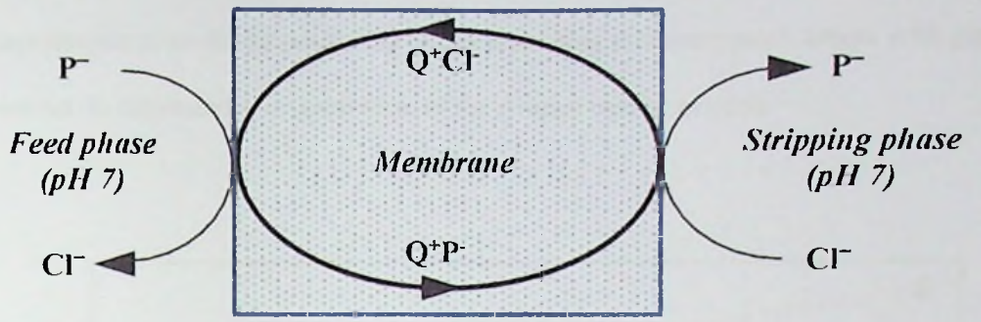


Fig. 2.10. Facilitated counter-coupled transport mechanism of picloram anion (P^-) across a PIM containing Aliquat (Q^+Cl^-) as carrier.

2.3.3.1. Stripping agent type

The significance of the stripping agent concentration on the transport of picloram is detailed in **2.3.3**. However, the type of stripping agent participating in the transport process can also influence the transport performance of the membrane [39]. Consequently, the influence of anionic stripping agents with different chemical properties, namely the Na salts of NO_3^-, Cl^-, SCN^-, ClO_4^- and SO_4^{2-}, on the transport of picloram was investigated. The results in **Fig. 2.11** show that the transport efficiency increases in the order of $ClO_4^- < SCN^- < SO_4^{2-} < NO_3^- \approx Cl^-$. With exception of SO_4^{2-}, the observed trend agrees with the Hofmeister series of lipophilicity of the counter ions. The moderately hydrophilic counter ions NO_3^- and Cl^- show a reasonably high transport efficiency compared to the other more lipophilic counter ions. This is associated with their higher diffusional mobility in the membrane. The lower transport efficiency observed for SO_4^{2-}, the most hydrophilic counter ion in the series, is due to its divalent nature requiring it to pair with two units of the cationic carrier. The resultant bulky ion-pair complex is more readily entangled within the polymer network resulting in reduced mobility in the membrane [40]. On the other hand, the decrease in transport efficiency of the lipophilic counter ions, SCN^- and ClO_4^-, is related to accumulation of their Aliquat salts in the membrane due to preferential hydrophobic interactions. Aliquat salts of these counter ions are known to decrease the loss of Aliquat as a carrier from a PVC membrane due to increased hydrophobicity [41]. The current findings demonstrate that NO_3^- and Cl^- are both effective stripping

agents for the transport of picloram. We decided to use chloride as the stripping agent for subsequent transport experiments to avoid the possibility of contaminating environmental waters with nitrate and, to a lesser extent, to maintain the original form of the Aliquat carrier as used.

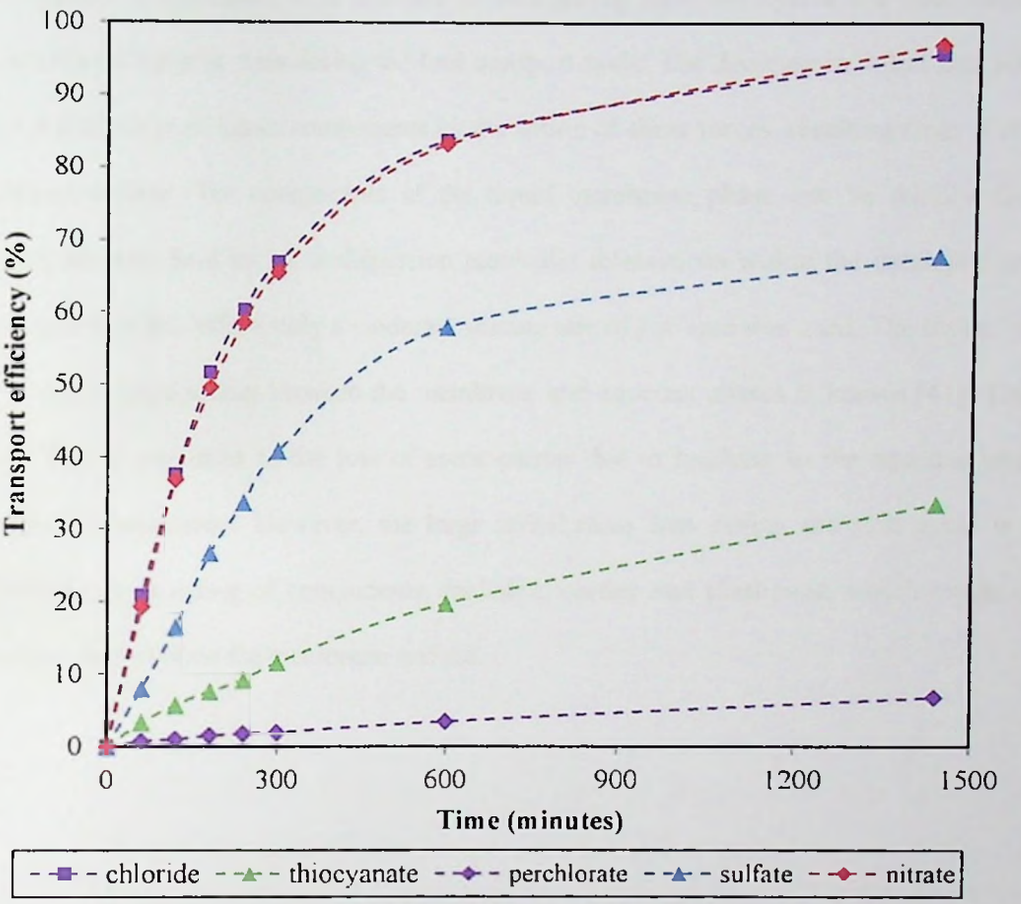


Fig. 2.11. Influence of stripping agent type on the transport of picloram. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M of NaCl, NaSCN, $NaClO_4$, Na_2SO_4, $NaNO_3$, at pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

2.3.4. Stability studies

The stability of PIMs in repeat experiments is an important consideration for their development and use for possible practical or commercial applications. The liquid components, such as carrier and plasticiser, of a PIM are usually encapsulated and protected within the polymer matrix [10]. Consequently, the potential loss to the local environment of liquid components resulting from the

action of shear forces at the membrane surface is significantly reduced compared to other membrane types, such as supported liquid membranes (SLMs) [10]. The likely enhanced stability of PIMs offers potential for repeated use in extraction cycles with an insignificant loss in performance. In this study, the stability was evaluated by flux and membrane mass measurements. The results in **Fig. 2.12** and **Table 2.7** indicate a significant 26% decrease of flux during transport cycles 1-3 and, similarly, a substantial 24% decrease in mass during the first transport cycle. The decrease in initial flux and mass indicates the likely loss of liquid components by the action of shear forces, resulting from stirring, on the membrane surface. The components of the liquid membrane phase can be readily displaced because they are only held by weak dispersion molecular interactions within the entangled polymer chains. To minimize this effect, only a moderate stirring rate of 300 rpm was used. The loss of Aliquat from PIMs due to partitioning between the membrane and aqueous phases is known [41]. Thus, the decrease in flux is attributed to the loss of some carrier due to leaching to the aqueous phases in contact with the membrane. However, the large initial mass loss during the first cycle is likely explained based on washing of components, including carrier and plasticiser, which exude during curing and are deposited on the membrane surface.

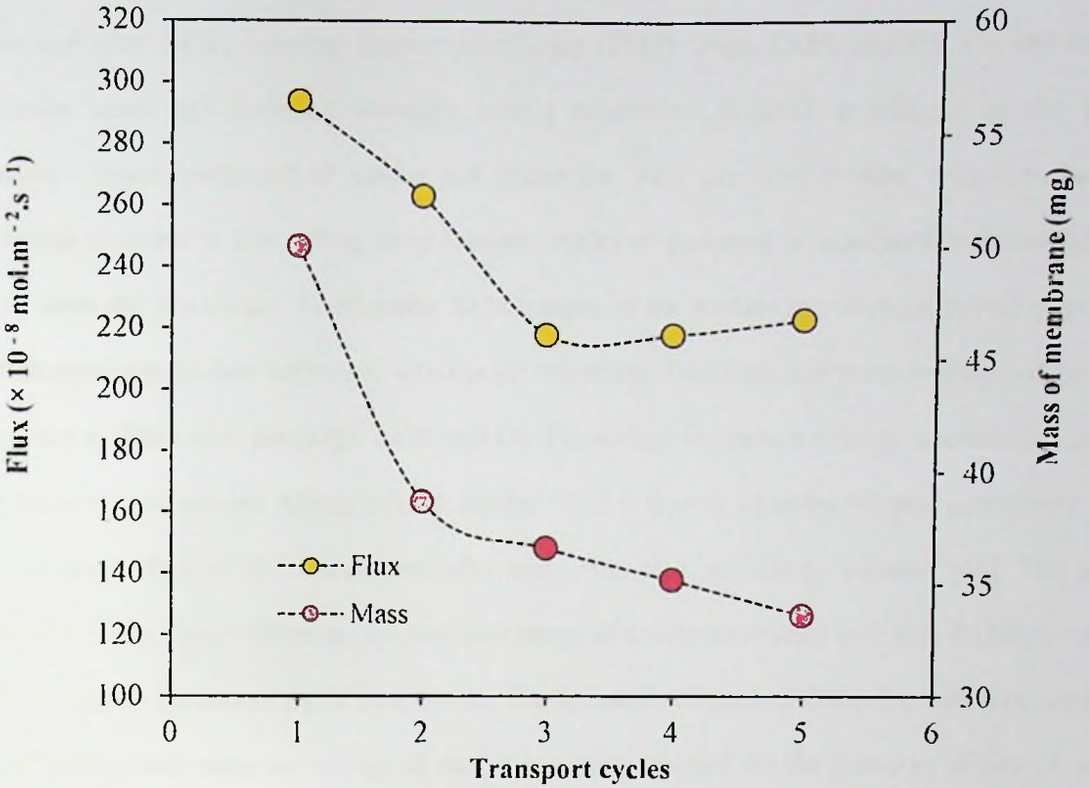


Fig. 2.12. Membrane stability as indicated by flux and membrane mass during repeated use for transport of picloram. Experiment conditions: feed solution 100 mg/L picloram, pH 7: receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

Table 2.7. Membrane stability as indicated by flux, transport efficiency and initial mass during repeated use for transport of picloram.

Transport cycle	Initial mass (mg)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
1	50.0	7.1	294	95
2	38.7	6.4	263	98
3	36.6	5.3	218	98
4	35.2	5.3	218	97
5	33.6	5.5	223	96

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

As well as mass loss, the membrane thickness was also investigated after the first and last transport cycles and a substantial decrease from 30 μm to about 20 μm, respectively, was measured.

The decreased membrane thickness is clearly visible in cross-section images of a membrane taken before and after use by scanning electron microscopy (SEM) (**Figs. 2.13A** and **B**). The decrease in membrane mass and thickness correlates with a substantial decrease in volume of the liquid membrane phase composed of carrier and plasticiser. This provides further evidence that the substantial decrease in flux during early transport cycles of picloram is associated with the loss of carrier from the membrane. Additionally, SEM images of the surface morphology reveal a smooth and homogeneous surface before use, whereas the formation of deposits and pores is observed on both membrane surfaces after use (**Figs. 2.13C** and **D**). The surface deposits are likely associated with the adsorption of hydrophobic Aliquat salts. A similar effect is known whereby Aliquat perchlorate salts form on the surface of PVC membranes after immersion in a perchlorate solution [41]. The pores which are clearly observable in the cross-section image of a membrane after use (**Fig. 2.13B**) are most likely formed by the loss of liquid components. The formation of pores and the deposition of particles on the surface, indicating the leakage of carrier, has been reported for the transport of phenol using PIMs containing copoly(eugenol-divinylbenzene) as carrier [42]. In this case, the addition of $NaNO_3$ to the feed solution caused particles to be deposited on the membrane surface due to a salting-out effect, whereby the particles enclose the surface pores and decrease further leakage of membrane components. Similarly, in the current investigation, the decrease in mass loss during the latter transport cycles is associated with the formation of surface particles, which we infer are likely to block the further leakage of carrier. Thus, the often-observed significant decline in flux and loss of membrane mass during early transport cycles need not be a major cause for alarm. As in some cases, the leakage of carrier is likely to be associated with the formation of lipophilic ion-pair species on the membrane surface which can be linked to improved stability. The mass loss of 24% after two transport cycles indicates that 23 wt% Aliquat remains in the membrane, assuming the loss is mostly associated with carrier. However, the related decrease in flux to 218×10^{-8} mol.m^{-2}.s^{-1} corresponds to an equivalent Aliquat concentration of only 15 wt%. The observed higher decrease in flux relative to that expected with the amount of Aliquat still remaining in the membrane provides evidence for blockage of some pores due to the surface deposition of Aliquat-picloram salt.

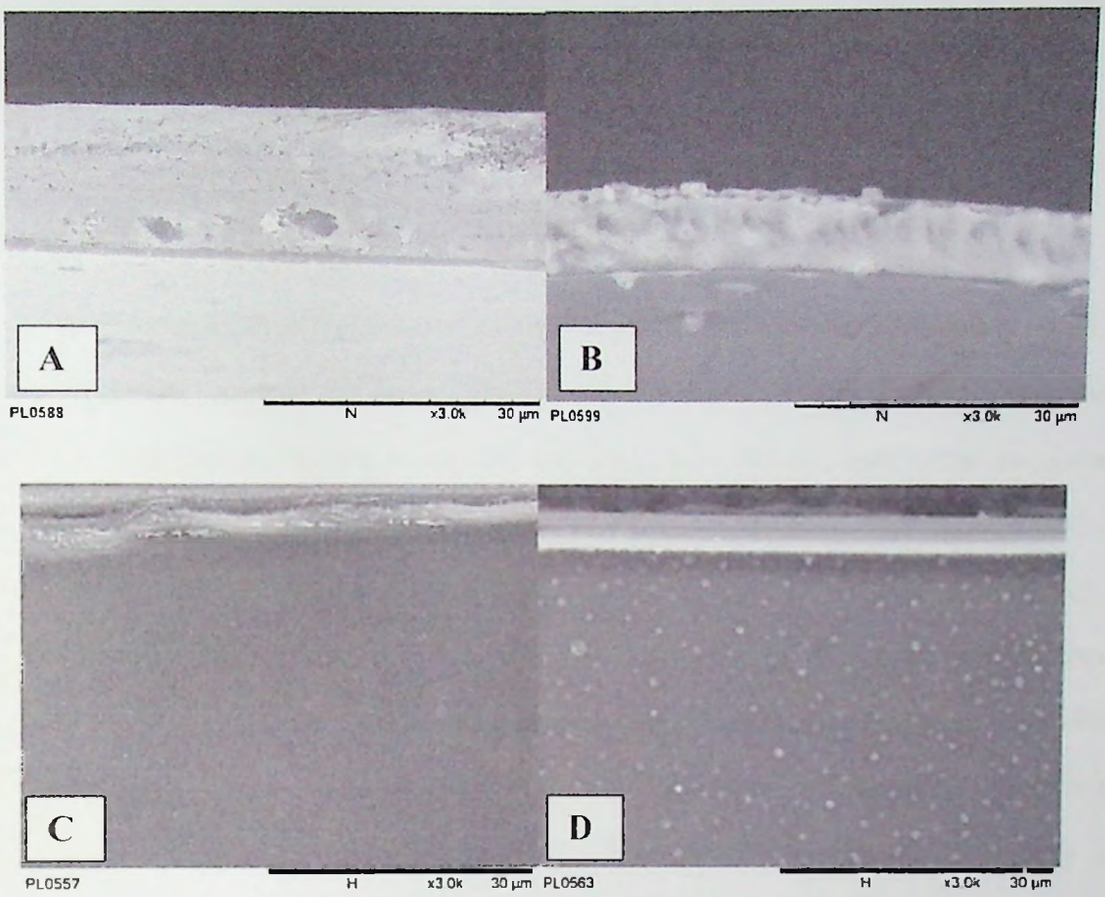


Fig. 2.13. SEM images showing cross-section (**A** & **B**) and surface (**C** & **D**) morphologies of PIM before and after use.

The decrease in flux, mass and thickness of the membranes observed in the current study indicates that the performance of PIMs is very sensitive to the loss of liquid components including carrier. This is likely caused by a presence of a small amount of liquid phase in the membranes compared to other types of liquid membranes. Therefore, the experimental design used in the current stability studies might be regarded as a harsh treatment of membranes because of the regular replacement of aqueous phases, which maximises the potential loss of carrier. When membranes are continuously exposed to the same solutions, the amount of carrier leaching from the membranes eventually saturates the adjacent aqueous solutions due to the low water solubility of the carrier. Consequently, the continual leakage of carrier from the membrane is minimised. The saturation of aqueous solutions with Aliquat when membranes are immersed in aqueous solutions for 3 hours has

been reported [41]. Despite the use of these harsh conditions, the findings show that the membranes can be used to effectively separate picloram even after four cycles of reuse. This indicates that the membrane is of reasonable stability for practical and commercial applications.

2.3.5. Transport kinetics

An understanding of the reaction kinetics is essential to provide information about the potential throughput capabilities of the membrane technology on a larger scale if used for commercial applications. Therefore, the kinetics for the transport of picloram was evaluated using the optimum membrane. The transient concentration profiles of picloram in the feed and receiving solutions as a function of time are presented in **Fig. 2.13**. The results show that the transport performance, as indicated by the slope of the transport profiles, decreases with time as the concentration of picloram in the receiving solution increases. The concentration of picloram rapidly decreased in the feed while, almost concurrently, sharply increasing in the receiving phase, reaching an equivalent concentration of 50 mg/L in both phases in less than 180 minutes. Equilibrium concentrations of 10 mg/L and 90 mg/L in the feed and receiving phases, respectively, took about 600 minutes; indicating a reasonably effective transport process. The time to reach equilibrium, in this case, is faster than the 1800 minutes for the transport of phenol using PIMs containing N,N-di(1methylheptyl) acetamide as carrier [14]. As the concentration of the relatively lipophilic picloram increases in the receiving solution, the competition between picloram and chloride for ion pairing with the carrier also increases. This slows the rate of dissociation of the picloram-Aliquat ion-pair at the receiving/membrane interface and, consequently, decreases the transport performance. This explains the decrease in transport performance with increasing concentration of picloram in the receiving solution for which a similar effect with phenol is known [14]. The steep gradient of the transient transport profiles for both solutions in the early stages is further evidence that the transport process involves a facilitated mechanism.

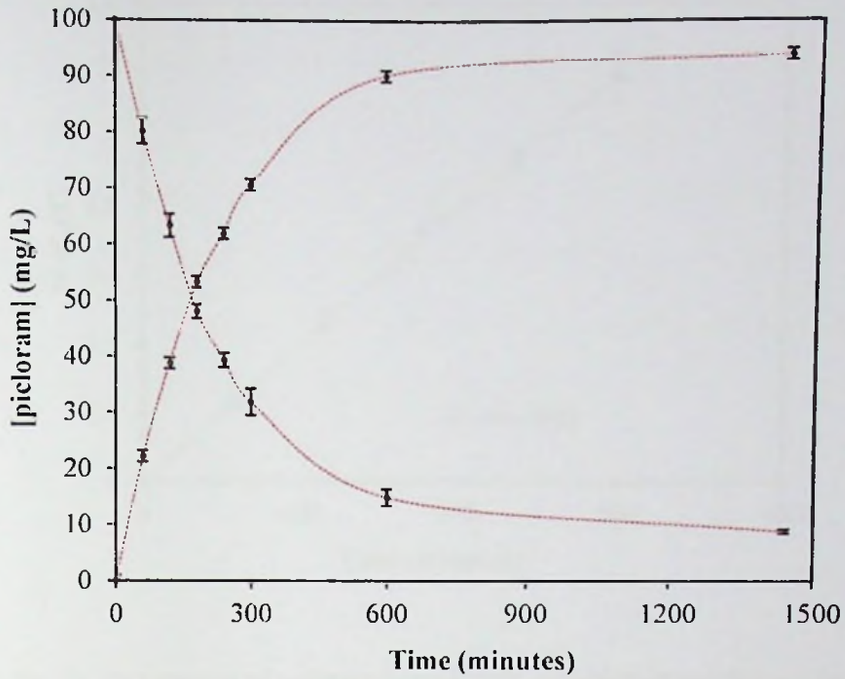


Fig. 2.13: Transient concentration profiles of picloram in feed and receiving solutions as a function of time. Experiment conditions: feed solution 100 mg/L picloram, pH 7: receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments.

The transport of picloram follows the model for mass transfer in membranes, whereby the rate is dependent on the picloram concentration as described by the integrated rate law for a first-order reaction (Eqn. 2.1) and plotted in **Fig. 2.14**. The gradient of the plot shows a strong linear relationship with a high correlation coefficient ($R^2 \geq 0.99$) which confirms first-order kinetics and from which a rate constant (k) of 6.45×10^{-5} s^{-1} was determined. An optimum permeability of 710 ($\pm$ 35) $\times$ 10^{-8} m/s for picloram was determined which is comparable to the 662 $\times$ 10^{-8} m/s reported for phenoxide using a PIM containing *N,N*-di(1-methylheptyl) acetamide as carrier [14].

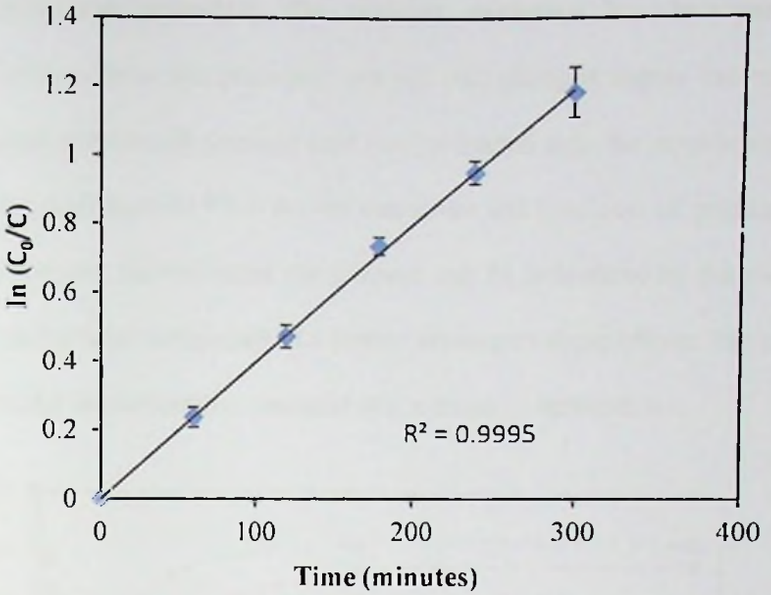


Fig. 2.14. Kinetic plot for the transport of picloram using a PIM. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments.

2.3.6. Non-competitive transport

The goal is to use the membranes to target pyridine-based herbicides from aqueous solutions. To assess this capability, applications of the optimal membrane for the extraction and transport of other pyridine compounds was also investigated. The compounds selected for non-competitive transport contain a pyridine ring attached to a carboxylic acid group to facilitate formation of ion-pair complexes with the Aliquat carrier.

The results in **Fig. 2.15** and **Table 2.8** indicate that picolinic acid, clopyralid and triclopyr were all successfully transported which indicates a similar carrier-facilitated transport mechanism involving formation and involvement of an ion-pair complex. The transient transport profile shows that equilibrium concentrations of more than 50 mg/L in the receiving solution were achieved, indicating a transport efficiency of more than 50% for each compound. The order of membrane permeability is picolinic acid < clopyralid < triclopyr. The better permeability for triclopyr is due to increased lipophilicity as indicated by Log K_{ow} values (**Table 2.8**). Picolinic acid has a comparatively low permeability because it can form a zwitterion at pH≤ 8.5 with opposite charges at the pyridine ring

nitrogen and carboxylic acid group [43]. The resultant zwitterion has decreased electrostatic interactions with Aliquat because the positively charged ring-nitrogen repels the cationic carrier. Consequently, decreased amounts of picolinic acid can be loaded into the membrane. The current results demonstrate the usefulness of PIMs for the extraction and transport of pyridine compounds related to picloram. However, the membrane performance can be influenced by the electrostatic and lipophilic properties of the target compounds. To further investigate these effects, the membrane was subsequently evaluated for the competitive transport of a mixture of herbicides.

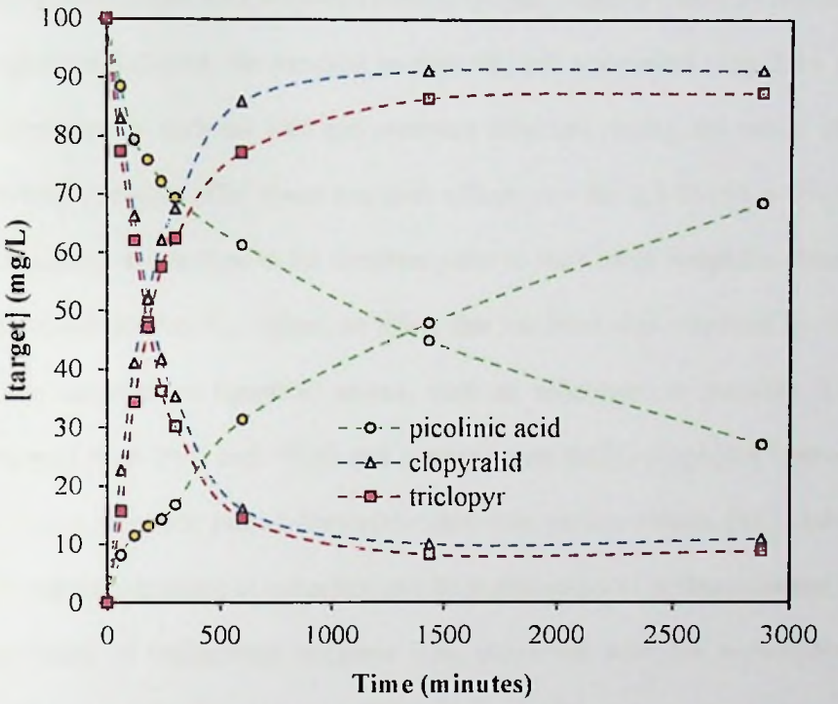


Fig. 2.15. Transport profiles of feed and receiving solutions of picolinic acid, clopyralid and triclopyr. Experiment conditions: feed solutions 100 mg/L compound, pH 7; receiving solutions 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

2.3.7. Competitive transport

Commercial herbicides often contain a mixture of active compounds. Picloram can be applied alone or in combination with other common herbicides, such as 2,4-D, triclopyr or clopyralid, to increase the effectiveness for particular applications. For example, Tordon™ is a mixture of picloram and 2,4-D, whereas Grazon™ is a mixture of picloram and triclopyr. Consequently, the potential for

herbicide runoff means that picloram can be found in combination with other herbicides in the environment. Thus, it was prudent to evaluate the membrane performance for the competitive transport of a mixture containing commonly used herbicides, namely: picloram, 2,4-D, triclopyr and clopyralid.

The results in **Table 2.8** indicate that picloram, 2,4 D, triclopyr and clopyralid were all transported with good efficiencies of 84 – 97%. The herbicides have pKa values $\leq$ 2.7, consequently, similar ion-pair chemistry is likely to involve in the membrane extraction and transport processes, whereby the anionic herbicides are transported using a counter-coupled transport mechanism. Similar to the non-competitive transport, the transport profiles of each compound (**Fig. 2.16**) show a rapid change in concentration in both the feed and receiving solutions during the initial stages which is typical of facilitated transport. The lower transport efficiencies for 2,4-D (84 $\pm$ 6%) and triclopyr (89 $\pm$ 5%) are attributed to retention in the membrane due to their more lipophilic chemical nature as indicated by the associated log K_{ow} values; an effect that has been also observed by others [32, 33]. For example, the retention of lipophilic anions, such as salicylate, as possible interferences in membranes prepared from PVC and NPOE and containing an In(III)-porphyrin hydrophobic carrier for chloride-selective electrode pulsed chronopotentiometric measurements [44]. Additionally, See and Hauser [39] report a decrease in extraction and back-extraction of octanesulfonate relative to the increased lipophilicity of background inorganic ions, consistent with the well-known Hofmeister series, using a PIM of 60 wt% CTA, 20 wt% NPOE & 20 wt% Aliquat.

Table 2.8. Permeability and transport efficiency (TE) of picloram and related compounds during non-competitive[1] and competitive transport[2].

Compound	pK_a	Log K_{ow}	Permeability ($\times 10^{-8}$ m/s) (± SD)	TE ± (SD) (%)
Picloram	2.30	0.30	710 (±35)[1]	95 (±1)
			520 (± 34)[2]	97 (± 5)
Clopyralid	2.32	1.06	649[1]	91
			471 (± 12)[2]	98 (± 3)
Triclopyr	2.68	2.53	749[1]	87
			629 (± 16)[2]	89 (± 5)
2,4-D	2.60	2.81	611 (± 33)[2]	84 (± 6)
Picolinic acid	5.50	0.72	253[1]	67

SD- standard deviation for triplicate measurements.

Experiment conditions: feed solution 100 mg/L, pH 7, receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

The permeability of picloram, clopyralid and triclopyr significantly decreased by more than 16% during competitive compared to non-competitive transport. This is consistent with increased competition between the various herbicide anions for the available amounts of carrier at the feed/membrane interface. Additionally, 2,4-D and triclopyr show better permeability, compared to picloram and clopyralid, because they are more lipophilic which results in preferential extraction. The similar permeability for pairs of herbicides (2,4-D and triclopyr, and picloram and clopyralid) having similar log K_{ow} provides further evidence that the chemical properties of individual herbicides have a significant influence on membrane extraction and transport processes. Thus, although herbicides with a high lipophilicity are initially extracted faster, they are retained in the membrane and, consequently, this results in a reduced transport efficiency. These observations are consistent with previous results linking the significant dependence of membrane extraction and back-extraction with the lipophilicity of targeted organic solutes [39]. The results in the current study demonstrate that PIMs can transport picloram and other common herbicides from aqueous solutions with reasonable efficiency.

Application of the membrane for the extraction and transport of picloram from samples of natural water is evaluated in subsequent experiments.

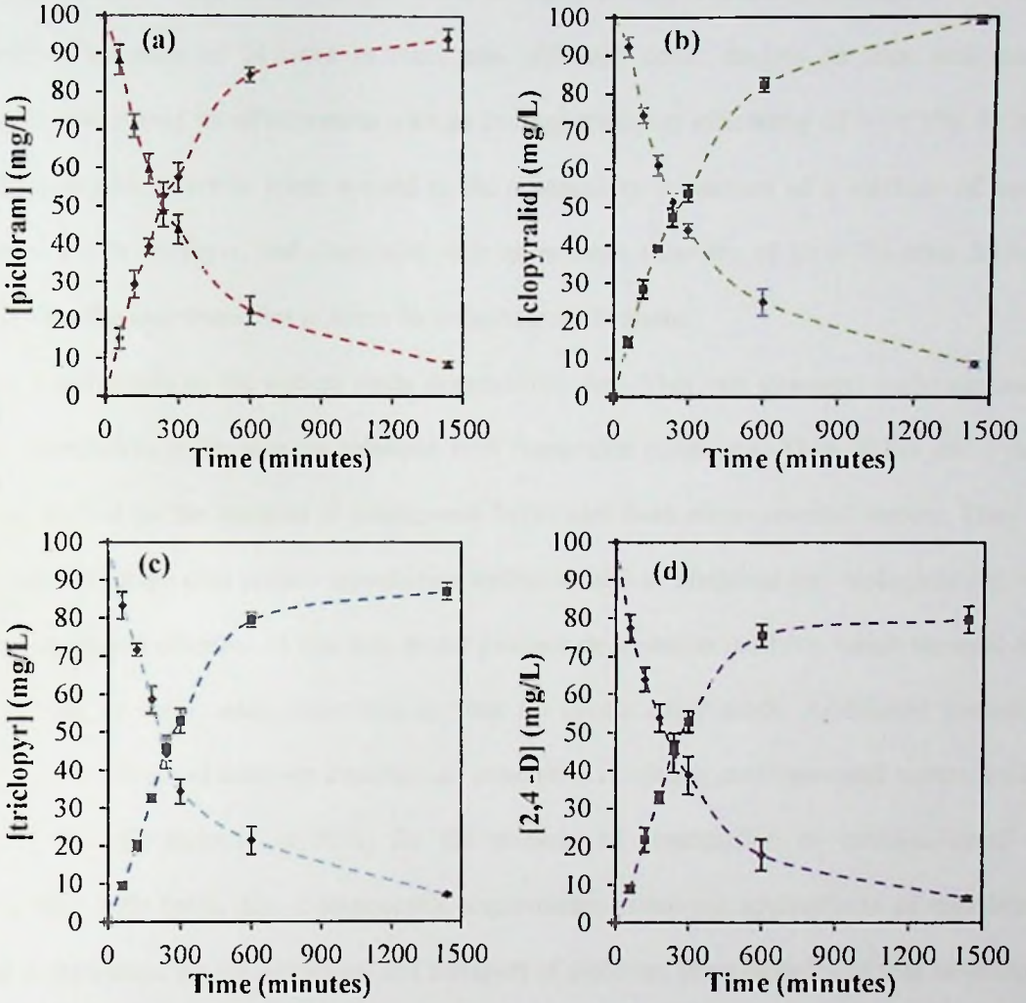


Fig. 2.16. Transient concentration profiles of feed and receiving solutions for competitive transport of picloram (a), clopyralid (b), triclopyr (c) and 2,4-D (d). Experiment conditions: feed solution 100 mg/L compound, pH 7; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments.

2.4. Conclusion

In the present work, the development of a PIM for the extraction of picloram and related herbicides from aqueous solutions was demonstrated. The extraction and transport performance of

various membrane formulations were evaluated to determine an optimum composition of 25 wt% CTA, 30 wt% Aliquat and 45% wt% NPOE which was used in subsequent experiments. The transport of picloram was evaluated and a flux of 294 (± 14) × 10^{-8} $mol.m^{-2}.s^{-1}$ was achieved.

The performance and stability of the PIM to extract picloram was tested through five consecutive transport cycles each of 24 hours or more and, although some decline in flux was noted, the membrane maintained its effectiveness with an average transport efficiency of 97 ± 1%. In addition, the PIM was also effective when applied to the competitive extraction of a mixture of herbicides (picloram, 2,4-D, triclopyr, and clopyralid) with an average recovery of 93 ± 7% after 24 hrs. This signified that the membrane has promise for industrial applications.

The experiments in the current study demonstrate that PIMs can transport picloram and other common herbicides from aqueous solutions with reasonable efficiency. Thus, PIMs are a potential alternate method for the removal of troublesome herbicides from environmental waters. They offer a significant advantage over present remediation methods, such as chemical and biological degradation that are considered effective, in that they do not produce degradation products which themselves have different and, in some cases, more toxicity than the parent compounds. Additional investigations involving extraction and transport from harsher conditions involving environmental waters are needed to assess the effectiveness of PIMs for the purpose of remediation of environmental waters contaminated with herbicides. Consequently, experiments involving applications of membranes of optimal composition for the extraction and transport of picloram from samples of real environmental water are assessed in Chapter 5.

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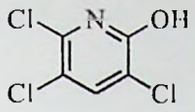
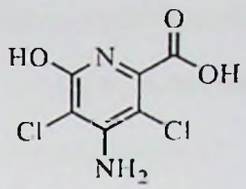
Chapter 3: Transport of potential degradation products of pyridine-based herbicides.

3.1. Introduction

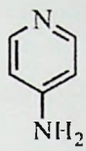
Degradation is a process through which many chemical substances, such as herbicides, decompose into smaller compounds and eventually to water, carbon dioxide and methane through photochemical, chemical or biological reactions [1]. As such, degradation is considered to be one of the safest and most cost-effective methods of removing herbicides and other toxic substances from the environment [2, 3]. However, some herbicides commonly degrade to transformation products which have their own chemical properties with regards to toxicity, adsorption capacity and resistance to the further degradation. In some instances, these degradation by-products can be more toxic than their parent compounds in the environment [4]. Detection of degradation products in the absence or, in some cases, at higher concentrations than the application rates of the parent compounds has been reported [5, 6]. Consequently, degradation by-products are now considered to be an emerging class of contaminants for which, for some, the permissible levels in the environment to protect humans and wildlife are difficult to establish [4, 7, 8]. The increased environmental accumulation of products resulting from incomplete degradation and increased use of some pyridine-based herbicides has been reported [9, 10]. Presently, the potential major transformation products of concern are: 4-amino-3,5-dicloro-6-hydroxypicolinic acid from picloram; and, 3,5,6-trichloropyridinol from triclopyr (**Fig. 3.1**) [11-13].



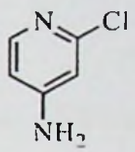
3,5,6-trichloropyridinol



4-amino-3,5-dichloro-6-hydroxypicolinic acid



4-aminopyridine



4-amino-2-chloropyridine

Fig. 3.1. Some potential transformation products of picloram and triclopyr (both pyridine-based herbicides).

3.1.1. Degradation of pyridine-based herbicides

Despite the fact that biodegradation is the main method/approach to remove and ameliorate the use of pyridine-based herbicides it is mostly ineffective, because most of these herbicides are persistent and remain intact or as transformation products in the environment. A study on the degradation of picloram in soils has revealed that the intact herbicide remains in significant amounts, and the presence of 4-amino-2,3,5-trichloropyridine and 4-amino-3,5-dichloro-6-hydroxypicolinic acid as the two major degradation products [14]. Other studies have also indicated these products during the catalytic photolytic decomposition of picloram [15-17]. Triclopyr is another pyridine-based herbicide that undergoes incomplete decomposition to produce two main products, namely: 3,5,6-trichloromethoxypyridine and 3,5,6-trichloropyridinol [11, 18, 19]. Other pyridine-based herbicides such as clopyralid and aminopyralid have been reported to undergo rapid microbial-degradation over 90 days, however, the degradation products were not identified [20].

Some of the herbicides or degradation products, such as 4-amino-3,5-dichloro-6-hydroxypicolinic acid and 3,5,6-trichloropyridinol, contain an ionisable acidic group that permits their extraction and transport to be performed in a similar manner to the pyridine-based herbicides such as picloram as reported in Chapter 2. However, the extraction and transport of degradation products

containing an amine functional group in the absence of an ionisable acidic group presents a challenge that requires immediate attention. Consequently, the discussion in this chapter is mainly limited to 4-amino-2,3,5-trichloropyridine and 3,5,6-trichloro-2-methoxypyridine.

3.1.2. Potential toxicity of degradation by-products

The toxic effects of 4-amino-2,3,5-trichloropyridine and 3,5,6-trichloro-2-methoxypyridine as degradation products in the environment have not been extensively studied. However, a related compound, 4-aminopyridine, was originally registered under the trade name Avitrol™ in the USA for controlling nuisance birds [21, 22]. This pesticide is known for its toxic effects on the nervous system, affecting most vertebrates by blocking potassium channels and enhancing the release of some neurotransmitters [23]. The microbial decomposition of the compound is reported to be relatively slow with a half-life ranging from 3 to more than 22 months [24, 25]. Consequently, the pesticide and its transformation products accumulate in the environment and affect non-target organisms, including humans. The toxicity of 4-aminopyridine is a likely indicator of the potential properties of the degradation by-products of pyridine-based herbicides in the environment. However, the presence of chlorine in the chemical structures of these degradation products is expected to increase the persistence as well as subsequent toxicity effects [26]. Therefore, the development of a simple and reliable technique to extract or transport these compounds is quite essential.

3.1.3. Extraction of aromatic amines by liquid membranes

The extraction or transport of aromatic amines using polymer inclusion membranes (PIMs) has not been extensively studied, although, a similar study using an emulsion liquid membrane has been reported [27]. The transport of these compounds often takes place by a simple diffusion mechanism, whereby the main driving force is a concentration gradient which is established by the protonation of amines at the receiving/membrane interface. Previous studies have indicated that a pH gradient is required for the transport of aromatic amines, however, the rate-determining step was not

experimentally established. The findings showed that permeability was independent of the membrane thickness and pK_a values of amines, suggesting that neither diffusion nor protonation was involved in the rate-determining step. As a result, a rate-determining step involving the migration of arylammonium cations from the membrane-receiving interface to a receiving solution was postulated [27]. This indicates that transport of amines through a liquid membrane depends importantly on a pH gradient, whereby the pH of the receiving solution is less than the pK_a of the aromatic amine.

The influence of pH and the amount of carrier on the transport of neutral aliphatic and aromatic amines through a liquid membrane from a basic feed solution to an acidic receiving solution using a macrocyclic ligand carrier has been investigated [28, 29]. The membrane permeability improved with increasing amounts of carrier, thus, demonstrating an association between amines and carrier to form aggregates which assisted the transport process. Additionally, the permeability was observed to increase with decreasing pH of the receiving solution, suggesting that a pH gradient between the feed and receiving solutions provides the driving force for the transport process. The rate determining step was determined to be the diffusion of neutral amines and associated complex aggregates through the membrane [28]. Additionally, the ability to separate aliphatic and aromatic amines was also demonstrated [29]. The selectivity for extraction of particular amines from a mixture was influenced by changing the pH with reference to the difference in pK_a of the target and non-target solutes. The interaction between amines and carrier was relatively weak and involved hydrogen bonding. The ability to perform selective separation of amines based on differences in pK_a by adjusting the pH of the receiving solution was demonstrated.

The aim of the current study is to use PIMs as simple available materials to explore the extraction and transport of potential degradation by-products of pyridine-based herbicides from aqueous solutions. Most of the intermediate degradation compounds are, unfortunately, not commercially available. Consequently, this study uses 4-amino-2-chloropyridine (ACP) as a model compound because of its structural similarity to the potential transformation products.

3.2. Experimental

3.2.1. Chemicals and reagents

Some additional chemicals and reagents to those previously reported in **Section 2.2.1** were used. Orthophosphoric acid (85%) and 4-amino-2-chloropyridine (ACP) (97%) were purchased from Sigma-Aldrich, Australia. Deionised water was used for the preparation of solutions. The pH 5 and pH 7 buffer solutions were prepared from a mixture of sodium mono-hydrogen phosphate (100 mM) and sodium dihydrogen phosphate (100 mM), and the pH 2 buffer solution was prepared using a mixture of phosphoric acid (100 mM) and sodium mono-hydrogen phosphate (100 mM). Reagents and solvents were of an analytical grade and used without further purification.

3.2.2. Preparation of polymer inclusion membranes

Polymer inclusion membranes were prepared according to the procedure described in **Section 2.4.2**. A membrane containing 20 wt% CTA, 40 wt% Aliquat and 40 wt% NPOE is referred to as a standard membrane and used in many experiments. Except for the stability experiments, a new and different membrane was used for each experiment.

3.2.3. Transport experiments

Transport experiments were performed in the same manner as described in **Section 2.4.3**. All transport experiments involved a feed solution composed of 100 mg/L of ACP at pH 7, and a 0.1 M NaCl receiving solution of prepared in 100 mM phosphate buffer solution at pH 2 which is referred to as standard transport conditions unless indicated otherwise. Concentrations of ACP were measured using a UV-Vis spectrophotometer (245 nm) at regular time intervals.

3.2.4. Determination of ACP concentration

Concentrations of ACP in aqueous solutions from all transport experiments were determined by the UV-Vis spectrophotometer at the absorption maximal of 245 nm. The samples (250 µL) from each phase were diluted with a phosphate buffer solution (pH 7) to 5 mL prior to their measurement. A calibration curve was prepared using ACP standard solutions in the range of 2.5 – 10 mg/L. Concentrations of ACP were calculated from a linear equation obtained from a calibration curve.

3.2.5. Optimisation of carrier concentration

Membranes containing a mixture of cellulose triacetate (CTA) as polymer and 2-nitrophenyl octyl ether (NPOE) as plasticiser in a fixed ratio of 5:3, and different amounts of Aliquat (Aliquat 336) as carrier. A control membrane without carrier was also studied for the purpose of comparison.

3.2.6. Influence of different plasticisers

Membranes containing 20 wt% CTA, 40 wt% Aliquat and 40 wt% plasticiser were prepared using 2-nitrophenyl octyl ether (NPOE), tris(2-ethylhexyl) phosphate (TEHP) and dioctyl phthalate (DOP) as plasticisers.

3.2.7. Optimisation of receiving solution pH

The influence of pH 2, 5 and 7 of the 0.1 M NaCl receiving solution on the transport of ACP was tested using a standard membrane.

3.2.8. Analysis of ACP species

A 250 µL aliquot of a solution containing 100 mg/L ACP at pH 7 was diluted to 5 mL using phosphate buffer solution at pH 2, 5 or 7. The resulting solutions were scanned over a wavelength range of 200 – 800 nm using a UV-Vis spectrophotometer. Spectra obtained were used to identify the changes in the ACP species that are associated with a different pH.

3.2.9. Influence of NaCl concentration

The influence of NaCl concentration in the range 0.0 – 0.2 M of a receiving solution at pH 2 on the transport of ACP was performed using a standard membrane. The feed solution composed of ACP 100 mg/L at pH 7, while the receiving solution was composed of different concentrations from 0.0 – 0.2 M NaCl at pH 2. The concentrations of the amine in the two solutions were determined using UV-Vis spectrophotometer and plotted against time. Additionally, the pH of the two solutions was also monitored and plotted against time.

3.2.10. Membrane stability studies

A standard membrane was subjected to five successive transport cycles using standard transport experiment conditions. The feed and receiver solutions were replaced by fresh solutions after each transport cycle of 48 hours without changing the membrane.

3.2.11. Influence of temperature

The influence of temperature in a range of 10 – 30°C on the transport of ACP was evaluated using a jacketed permeation cell containing two compartments of 150 mL each. A standard membrane and standard transport conditions were used. The two solutions were stirred by magnetic stirrers at 300 rpm and the beginning of the transport was marked by switching on the magnetic stirrers. A sample of 250 µL each was taken from each side at regular time intervals and replaced with fresh

amounts of initial solution. The transient concentration of ACP in each solution was determined as described in **Section 3.2.8**.

3.2.12. Transport of picloram

The transport of picloram was investigated using a standard membrane. The feed solution contained 100 mg/L picloram at pH 7, and the receiving solution contained 0.1 or 0.25 M NaCl at pH 2. The transient concentration of picloram in the both solutions was determined by UV-Vis spectrophotometry at 223 nm as described in **Section 2.2.5**.

3.3. Results and Discussion

3.3.1. Introduction

Aliquat 336 contains an electron-deficient nitrogen that permits cation-anion displacement or ion-dipole interactions with other chemical compounds. This salt depends on the stability of delocalised partial charges brought about by differences in electronegativity between atoms involved in bonds in neighbouring chemical species to enhance the ion-dipole interaction. For this matter, the electronegativity (χ) difference between hydrogen (χ 2.1) and oxygen (χ 3.5) in the carboxylic functional group normally creates partial charges that form ion-dipole interactions between organic acids and Aliquat, as shown in **Fig. 3.2**. This type of chemical interaction has been exploited for the reactive extraction of garlic acid using butyl phosphate, trioctylamine and Aliquat [30].

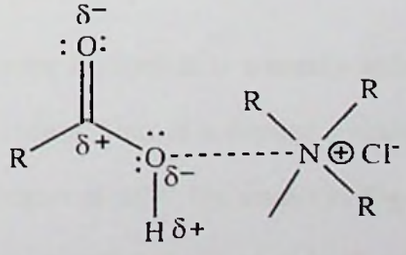


Fig. 3.2. Dipole-ion interaction between organic acid and Aliquat

Similarly, the difference in electronegativity between hydrogen (χ 2.1) and nitrogen (χ 3.0) in the amine functional group facilitates the formation of partial charges [28]. Consequently, a compound containing the amine functional group can also interact with other chemical compounds by dipole-ion interactions. This fact has been demonstrated by the transport of aliphatic and aromatic amines using a bulk liquid membrane containing macrocyclic ligand carriers [28]. Therefore, the following interfacial reactions between amine containing compounds and Aliquat for the extraction (Eqn. 3.1) and back-extraction (Eqn. 3.2) can be proposed.

$$m(RNH_2) + (R_4NCl)_p.(H_2O)_x \rightleftharpoons (RNH_2)_m.(R_4NCl)_p.(H_2O)_{x-m} + m(H_2O) \quad \text{(Eqn. 3.1)}$$

$$(RNH_2)_m.(R_4NCl)_p.(H_2O)_{x-m} + mH^{\oplus} \rightleftharpoons m(RNH_3^{\oplus}) + (R_4NCl)_p.(H_2O)_x \quad \text{(Eqn. 3.2)}$$

The most common methods for the transport of compounds containing amine functional group across liquid membranes are passive and carrier diffusion. The former involves diffusion of free amine molecules, whereas the latter is a stepwise process, in which amines associate with a carrier to form a complex as proposed in Eqn. 3.1. As a result, carrier facilitated diffusion usually improves membrane permeability and selectivity. The facilitated transport of ACP using a PIM containing Aliquat as carrier, and the parameters, such as carrier concentration and the pH of the receiving solution, which can influence the transport are investigated in this chapter.

3.3.2. Optimisation of carrier concentration

A carrier-facilitated diffusion mechanism is normally influenced by the amount of carrier contained in the membrane liquid phase. Thus, it is deemed necessary to investigate the influence of the amount of Aliquat on the transport of ACP. The results in **Fig. 3.3** and **Table 3.1** show that the initial flux improved with increasing amounts of Aliquat up to 40 wt% and, thereafter, an insignificant change in flux was observed at 50 wt% (The measurement at 50 wt% was conducted in triplicate to confirm the result). The findings also show the small initial flux of 134×10^{-8} mol.m^{-2}.s^{-1} in the

absence of the carrier (0 wt% of carrier). This indicates that passive diffusion has occurred, whereby ACP partitions into the membrane due to its lipophilic nature. A similar mechanism has been reported for the transport of aromatic amines across an emulsion liquid membrane without a carrier [27, 31, 32]. Extrapolation of the straight-line section of **Fig. 3.3** to low Aliquat concentration indicates a minimum of about 6 - 7 wt% is required for carrier facilitated diffusion to actively dominate the transport. As a result, a significant improvement in the initial flux occurred in the range 10 – 40 wt% with an optimal flux of 413 ± (7) × 10^{-8} mol.m^{-2}.s^{-1} at 40 wt% Aliquat.

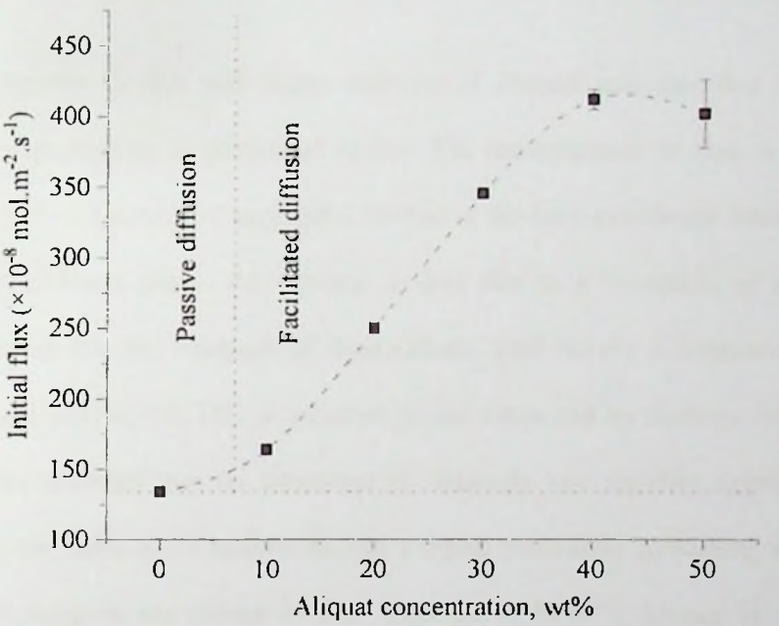


Fig. 3.3. Influence of Aliquat concentration on transport as indicated by the initial flux of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: composed of 3:5 ratio of CTA-to-NPOE, and 0 – 50 wt% Aliquat. Error bars represent a standard deviation of measurements from n = 3 experiments at 40 and 50 wt%.

Table 3.1. Influence of Aliquat concentration on transport as indicated by the initial flux of ACP.

Aliquat (wt%)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})
0	1.7	134
10	2.1	164
20	3.2	250
30	4.4	346
40	5.3	413
50	5.2	403

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: composed of 3.5 ratio of CTA-to-NPOE, and 0 – 50 wt% Aliquat.

The observed increase in flux with higher amounts of Aliquat indicates that ACP associates with Aliquat to form aggregates, as postulated earlier. The improvement in flux is likely to be largely attributed to increased amounts of aggregates formed at the feed-membrane interface which can then diffuse in the membrane phase. An increase in flux due to a formation of aggregates has been previously reported for the transport of hydrochloric acid across a supported liquid membrane containing Aliquat carrier [33]. This proposition is also supported by findings from a previous study, where it was demonstrated that the formation of relatively low stability aggregates resulted in an improvement in the transport of amines through a liquid membrane containing a macrocyclic ligand carrier [29]. The insignificant change in flux observed at 50 wt% Aliquat is a likely outcome of reduced migration of aggregates due to increased viscosity caused by higher amount of Aliquat in the membrane. A similar decrease in flux due to increased viscosity caused by high amount of Aliquat in a membrane has been previously reported in the transport of HCl [33]. Based on these findings, these experiments have identified an optimum membrane composition of 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE as suitable for use in subsequent transport experiments. Therefore, membranes of this composition are designated and referred to as the optimum membrane in subsequent discussions.

3.3.3. Influence of different plasticisers

The choice of plasticiser can significantly affect the transport of a particular solute. An investigation of the influence of the nature of some plasticisers on the transport of ACP was investigated using three common plasticisers, namely NPOE, DOP & TEHP, to prepare membranes of composition 20 wt% CTA, 40 wt% Aliquat & 40 wt% plasticiser. These plasticisers have somewhat different viscosities and dielectric constants (refer **Table 3.2**).

The results in **Table 3.2** show that the initial flux increased in the order of DOP < NPOE < TEHP. This trend shows that even plasticisers with a comparable viscosity have a significant effect on flux outcomes because of different dielectric constants, with TEHP which has the lower dielectric constant producing a 10% higher initial flux (458×10^{-8} mol.m^{-2}.s^{-1}) compared to NPOE (413×10^{-8} mol.m^{-2}.s^{-1}). This result is likely caused by the nature of the chemical interaction between ACP and the Aliquat carrier, involving the formation of aggregates which is normally favoured by a low dielectric constant environment [34]. A similar observation has been reported where the addition of a polar solvent (water) was found to decrease the aggregation of phenol-amine by increasing the association of phenol with water molecules [34]. Additionally, other researchers have reported a disruption of intermolecular hydrogen bonds in organic compounds in favour of solute-solvent intermolecular interactions in the presence of polar aprotic solvents [35]. The current observation that the plasticiser with the lowest dielectric constant produced the highest flux provides evidence that the formation of aggregates is involved in the transport process. Additionally, the plasticiser (DOP) with the highest viscosity but similar dielectric constant to TEHP showed the lowest initial flux (356×10^{-8} mol.m^{-2}.s^{-1}). This effect is associated with a slow migration of aggregates in the membrane phase due to the increased viscosity [36].

Table 3.2. Correlation of viscosity and dielectric constant values of different plasticisers with initial fluxes and transport efficiencies for the transport of ACP.

Plasticizer	Viscosity (cP) [37]	Dielectric constant [38]	Initial flux 10^{-8} mol.m.$^{-2}$.s^{-1}	TE (%)
NPOE	11	24.8	413	98
DOP	18	5.0	356	98
TEHP	13	4.8	458	82

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% Plasticiser.

The transport efficiency is another important parameter to evaluate the performance of the transport process. The results in **Table 3.2** also indicate the highest transport efficiency (98%) for NPOE and DOP, while a reduced transport efficiency (82%) resulted using TEHP. The observed higher transport efficiency for NPOE and DOP is likely to be associated with the ability of these plasticisers to be more strongly retained in the membrane compared to TEHP. Therefore, the lower transport efficiency shown by membranes containing TEHP is linked to its loss from the membrane phase, as discussed earlier in Chapter 2. The decrease in the amount of a retained plasticiser reduces the amount of liquid phase trapped in the membrane. This normally decreases the distribution coefficient of the solute, which in turn diminishes the diffusion process.

The findings indicate that TEHP produces the highest flux but is associated with the lowest transport efficiency and loss from the membrane. Whereas, NPOE produced a comparatively lower flux to TEHP but had the equal highest transport efficiency. The plasticiser DOP produced a similar transport efficiency, but a lower initial flux compared to NPOE. Therefore, based on these results, NPOE was chosen as the most suitable plasticiser to prepare membranes for the transport of ACP.

3.3.4. Influence of receiving solution pH

The high partition of solute between a feed phase and membrane, which is subsequently followed by a fast stripping process at the receiving/membrane interface, is a critical requirement for

effective mass transfer. To achieve this, it can be asserted that the partition or distribution coefficient at the receiving/membrane interface should be low to facilitate a rapid stripping process. Thus, the distribution coefficient of amines at the receiver interface can be decreased by protonation of the amine functional group, increasing the hydrophilicity of the solutes and improving the back extraction [39]. Based on this information, the effect of different pH of the receiving solution was investigated to optimise the transport of ACP. The results presented in the **Table 3.3** show that the highest initial flux occurred for a receiving solution at pH 2, while a similar lower flux was noted at pH 5 and 7. The better flux at pH 2 indicates that a pH gradient across the membrane is essential for the effective transport of ACP, and that the stripping process is inefficient at pH 5 and 7.

In a similar manner, the results showed the highest transport efficiency of 98% for the receiving solution at pH 2. However, moderate transport efficiencies of 55% and 50% were reported at pH 5 and 7, respectively. These observations support the proposition that the protonation of ACP at the receiving/membrane interface is crucial for effective back-extraction. The establishment of equilibrium between the protonated and non-protonated forms of ACP at pH 5 and 7 results in its ineffective trapping in the receiving solution. Therefore, transport likely occurs by a facilitated mechanism, however, the driving force at higher pH is insufficient to facilitate the uphill transport against the concentration gradient of the amine. A previous study on the influence of the receiving solution pH, where amines were partially trapped, revealed that the extraction efficiency decreased with time [40]. This was explained as being due to the partial protonation of amines at the receiver interface which facilitates their back diffusion, consequently, decreasing the efficiency. Thus, an optimal extraction efficiency was suppressed due to the difference in the partition coefficient between feed and receiving aqueous solutions [40].

Table 3.3. Influence of receiving solution pH on transport of ACP.

Stripping pH	Rate constant $\times 10^{-5}$ s^{-1}	Permeability $\times 10^{-8}$ m/s	Initial flux $\times 10^{-8}$ $mol.m^{-2}.s^{-1}$	TE (%)
2	4.8	531	413	98
5	2.3	254	198	55
7	2.1	231	180	50

Experiment conditions: feed solution 100 mg ACP, pH 7; receiving solution 0.1 M NaCl, pH 2, 5 and 7; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE.

In the current experiments, it was observed that an increased amount of protonated ACP at lower pH resulted in a decreased distribution coefficient between the membrane and receiving solution. This circumstance prevents the amine from re-entering the membrane phase which enhances the back extraction. Others reported accelerated back diffusion of pyridines in an absence of effective trapping when the extraction of pyridine derivatives from human urine using an electro-membrane was investigated [41] Another study established that the complete trapping of amines required that the pH of the receiving solution to be at least 3.3 units below the pK_a value of the target amine [42]. The outcomes from the current experiments have shown that the use of a pH 2 receiving solution results in the best transport efficiency and initial flux. Therefore, a pH 2 of the stripping solution was identified as being the most effective and, subsequently, used for the transport of ACP.

Based on findings in **Table 3.3**, the transport mechanism for ACP can be proposed as shown in **Fig. 3.4**. At the feed-membrane interface, ACP reacts with Aliquat to form an Aliquat-ACP complex, which diffuses through the membrane. The complex dissociates at the membrane-receiving interface to release ACP into the receiving solution and the carrier is released to diffuse back to the feed solution for another transport cycle. Therefore, the pH gradient between feed and receiving solutions is the main driving force for this transport. A similar mechanism was reported in the transport and separation of aminic compounds through a liquid membrane [28].

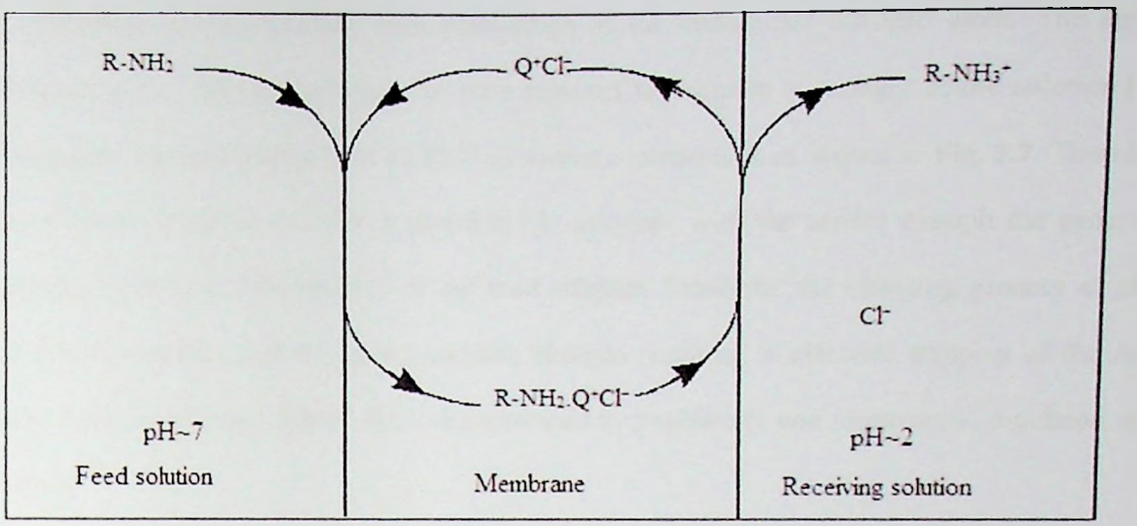


Fig. 3.4. Proposed transport mechanism for ACP from a feed solution of pH 7 to a receiving solution of pH 2.

3.3.5. Speciation of ACP

The transport of ACP depends on the nature of the chemical species present in the feed and receiving solutions. Any change in the species of this compound caused by a change in pH usually creates a concentration gradient, which provides the driving force for the transport process. Therefore, an investigation of the ACP species present in aqueous solution at pH 2, 5 and 7 was conducted to identify the species involved at the membrane interfaces during the transport process. The UV spectra of ACP ($pK_a \sim 9$) at pH 2, 5 and 7 are shown in **Fig. 3.5** and show changes associated with the different chemical species. The two maximal absorptions observed at 245 and 264 nm are associated with the monocation and dication ACP species, respectively [43]. The findings show that an aqueous solution at pH 7 contains significant amounts of the monocation species. However, the amount of monocation species decreased at lower pH and a dication species due to a second protonation is indicated by an increase in the absorbance at 264 nm. Finally, a substantial amount of dication species is indicated at pH 2. The aminopyridine contains exocyclic and endocyclic nitrogens and the latter is more basic compared to the former due to resonance stabilisation as shown in **Fig. 3.6** [44, 45]. The observations indicate that ACP in an aqueous solution at pH 7 exists in equilibrium between a neutral

and monocation species resulting from protonation of the endocyclic nitrogen atom. The second protonation at the exocyclic nitrogen has been reported to occur in a strongly acidic solution [43]. Consequently, the protonation order of ACP in aqueous solutions is as shown in **Fig. 3.7**. Therefore, based on these observations, ACP is postulated to associate with the carrier through the exocyclic nitrogen in its neutral form at pH 7 of the feed solution. Similarly, the stripping process at pH 2 involves the protonation of the same exocyclic nitrogen resulting in effective trapping of the ACP dication in the receiving solution due to its increased hydrophilicity and electrostatic repulsion with the carrier.

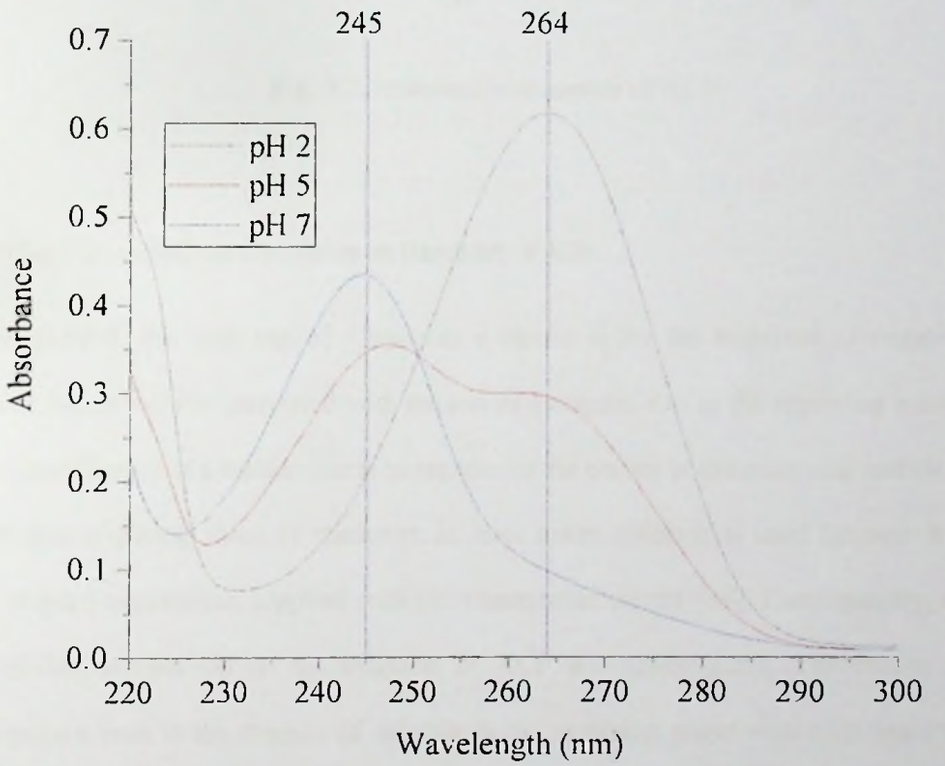


Fig. 3.5. UV - Vis absorption spectra of ACP at pH 2, 5 and 7.

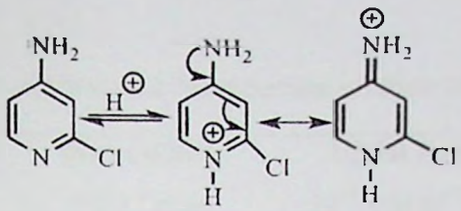


Fig. 3.6. Resonance stabilisation of mono-protonated ACP.

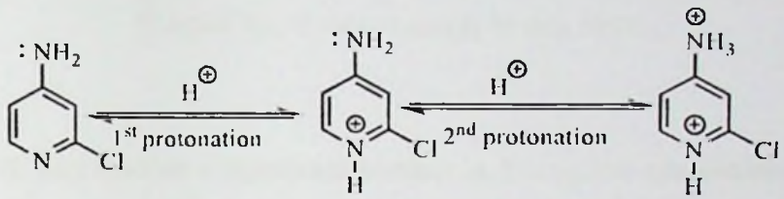


Fig. 3.7. Protonation sequence of ACP.

3.3.6. Influence of NaCl concentration on transport of ACP

In general, the main use of Aliquat as a carrier is for the transport of negatively charged species and this process is associated with the use of a counter-ion in the receiving solution. In these cases, the significance of a counter-ion is to regenerate the carrier at the receiving-membrane interface and to provide a driving force for transport. In most cases, chloride is used because it is consistent with the original counter-ion supplied with the commercial carrier [46]. Consequently, the influence of the chloride counter-ion on the transport of ACP was investigated. The results indicate that transport occurs even in the absence of chloride in the receiving phase with a transport efficiency of 98%, similar to when chloride is used (**Table 3.4**). This indicates that a chloride counter-ion is not acting as an effective stripping agent for this transport process. For a counter-ion facilitated process, such as the transport of picloram in Chapter 2, the transport efficiency improves with increasing chloride concentration in the receiving phase and only 50% transport efficiency occurred in the absence of chloride counter-ion. Therefore, the observed findings in the current study provide further evidence that a pH gradient is the main driving force.

Table 3.4. Influence of NaCl concentration in the receiving solution on transport of ACP.

[NaCl] M	Rate constant ($\times 10^{-5}$ s^{-1})	Permeability ($\times 10^{-8}$ m/s)	Initial flux ($\times 10^{-8}$ mol m^{-2} s^{-1})	TE (%)
0.0	4.1	451	352	98
0.1	4.8	531	413	98
0.2	5.0	550	430	98

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.0 – 0.2 M NaCl, pH 2. PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE.

The results also indicate a significant increase in flux as the concentration of the chloride counter-ion is increased from 0.0 to 0.1 M. However, an additional increase in the concentration of chloride to 0.2 M produced an insignificant change in flux (**Table 3.4**). The low flux in the absence of chloride is the likely direct consequence of phosphate counter-ions ($H_2PO_4^-$) from the buffer being involved in the transport process. Therefore, in the absence of chloride counter-ions, phosphate ions undergo an ion-exchange with chloride from the carrier to maintain electroneutrality as shown in **Fig. 3.8**. The reduced flux is a possible outcome of the increased hydrodynamic size of phosphate aggregates resulting in lower mobility in the membrane phase [47-50]. This observation is consistent with the well-established mobility order of counter-ions in a membrane phase as predicted by the Hofmeister series [51].

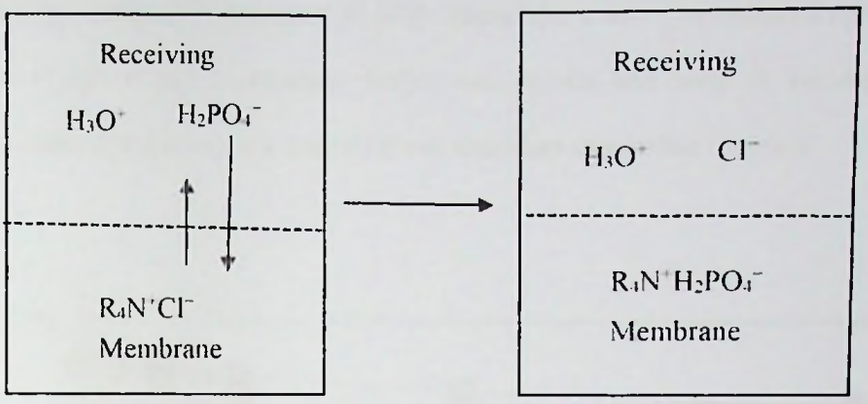


Fig. 3.8. Proposed interfacial ion-exchange process between chloride and phosphate ions at membrane-receiving solution interface.

The involvement of phosphate in the transport process is likely to affect the pH of the system because it is a major component of the buffer solution used in the feed and receiving solutions. To assess this, the pH of both the feed and receiving solutions was monitored during the transport process. The results shown in **Fig. 3.9** indicate only a slight change in the pH of the feed and receiving solutions in the presence of 0.1 & 0.2 M chloride. However, a significant change was observed in the absence of chloride which provides evidence for the transport of phosphate as a counter-ion, sourced from the buffer used in the experiments. Others have reported a similar change in pH involving the transport of phosphate ions from an aqueous solution by Donnan dialysis with an anion-exchange membrane [52]. The results also indicate that the involvement of phosphate ions in the transport is likely to decrease with increasing concentration of the chloride counter-ion. This same effect is indicated in the current experiments by the decrease in pH change as the chloride concentration is increased from 0.1 to 0.2 M. Only a small change in pH occurred at 0.2 M chloride when the concentration of the counter-ions is higher than the 0.1 M phosphate ions in the buffer solution. At this concentration, the ion-exchange with chloride is preferred and protonation of the amine that consumes protons from the receiving solution is minimised. The results substantiate that the presence of chloride is important to maintain the pH of the transport process. However, the

reduced pH change which occurred when the chloride concentration was increased from 0.1 to 0.2 M did not significantly improve the transport of ACP. Therefore, a less concentrated receiving solution containing 0.1 M NaCl in pH 2 phosphate buffer was chosen and used in subsequent transport experiments as it should enhance mass transfer at the receiving-membrane interface.

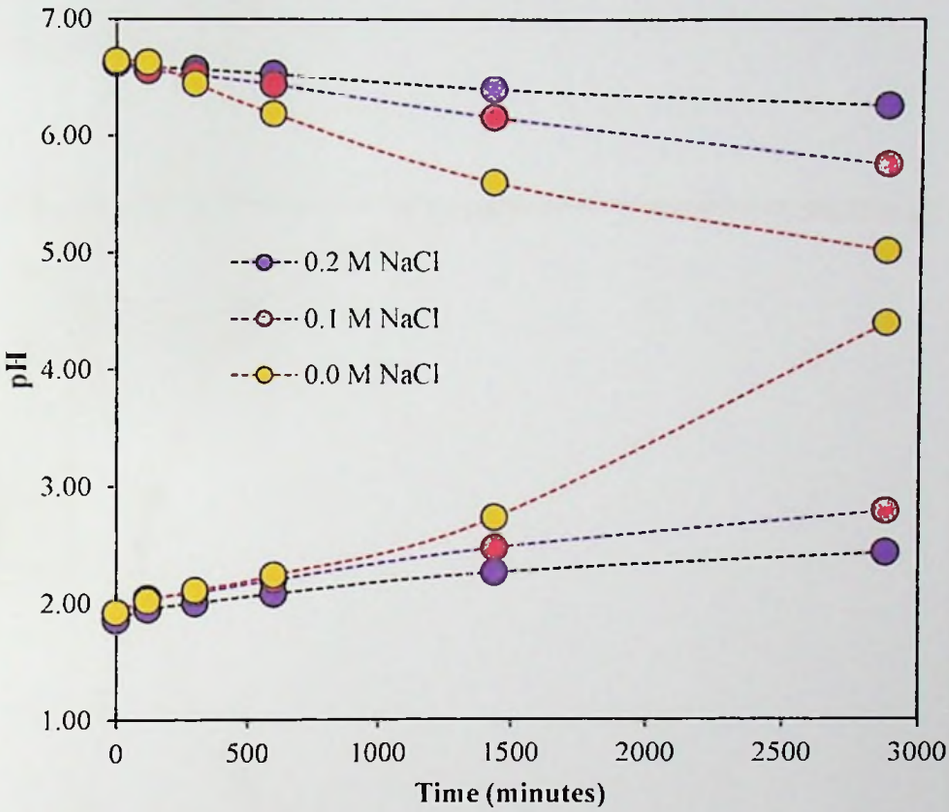


Fig. 3.9. Influence of NaCl concentration on pH for transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.0, 0.1 or 0.2 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE.

3.3.7. Transport kinetics

The transport profiles for both the feed and receiving solutions are presented in **Fig. 3.10**. The transport rate, as indicated by the gradient of the transient concentration profiles, is efficient and linear for both the feed and receiving solutions during the first 600 minutes. The result is attributed to the

electrostatic repulsion between the carrier and the now protonated ACP at the receiving-membrane interface, which limits back-diffusion into the membrane. Additionally, the protonation makes ACP highly hydrophilic, which also enhances its effective trapping in the receiving solution. This result is different to that reported earlier for the transport of picloram, where the transport rate decreased with time and a lower overall transport efficiency was noted. In this case, the picloram anions that accumulate in the receiving solution compete with chloride to form ion-pairs with the carrier that can diffuse into the membrane.

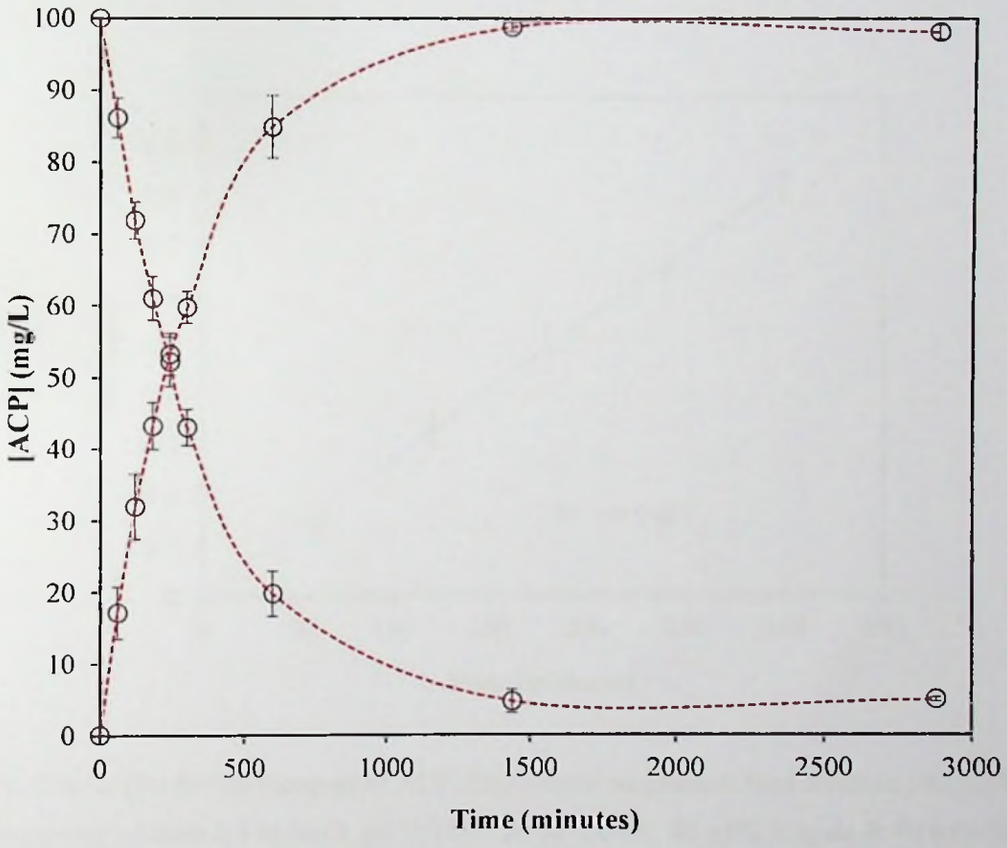


Fig. 3.10. Transient concentration profiles of ACP in feed and receiving solutions as a function of time. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments.

The kinetic plot in **Fig. 3.11** shows a linear relationship of $\ln(C/C_o)$ with time, indicating the transport is a first-order kinetic process. Similar kinetics have been reported for the transport of phenoxide through a PIM containing *N,N*-di(1-methylheptyl) acetamide as carrier [53]. In the current work, an optimum permeability of 531 ± (9) × 10^{-8} m/s was calculated. This permeability is almost an order of magnitude higher than the 49 × 10^{-8} m/s reported for the recovery of aniline from an aqueous solution using a membrane recovery system [54]. Therefore, it can be asserted, the membrane and experiment conditions used in the current study is likely to offer a potential alternative for the improved transport of compounds, such as aniline, having similar chemical properties to ACP.

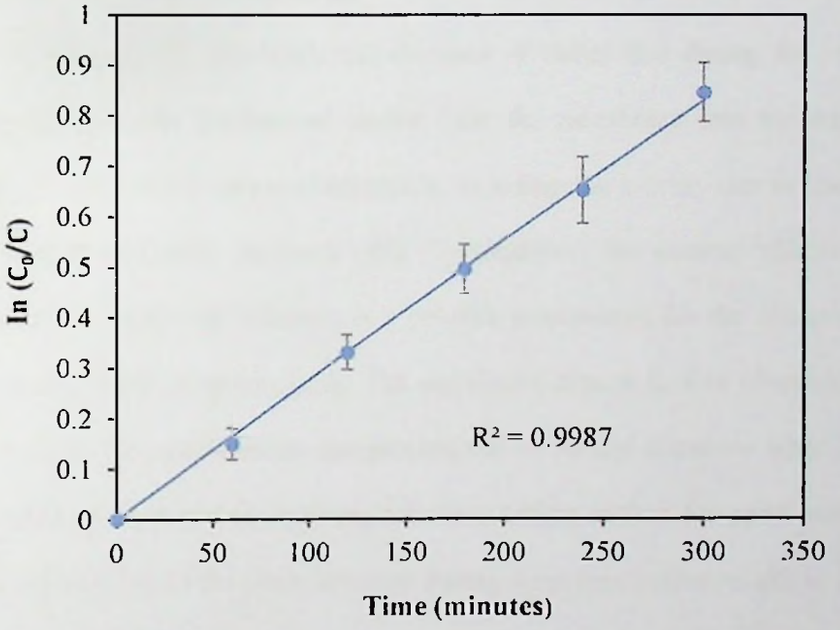


Fig. 3.11. Kinetic plot for the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments.

3.3.8. Membrane stability studies

The long-term stability of a membrane is an important factor to indicate the feasibility of a particular separation process for practical and commercial applications. A suitable membrane must

have adequate stability so that it can be reused for numerous cycles with only a negligible decline in performance; reducing costs associated with its periodic replacement. In most cases, the stability is assessed by the capacity of a membrane to retain its structural integrity and maintain performance. These indicators are commonly associated with the ability of the membrane to retain the liquid phase including a carrier originally encapsulated in the polymer matrix. In the current work, the stability of the optimum membrane was evaluated by its ability to maintain its performance over numerous transport cycles.

The findings shown in **Fig. 3.12** and reported in **Table 3.5** show that the initial flux remarkably decreased by 18% from 413 to 337 × 10^{-8} mol.m^{-2}.s^{-1} during the first and second transport cycles, respectively. Thereafter, during cycles 3 – 5, the flux remained nearly constant at an average of 320 ± (6) × 10^{-8} mol.m^{-2}.s^{-1}. The substantial decrease of initial flux during the second transport cycle has been linked to the leaching of carrier from the membrane into the adjacent aqueous phases [49, 55]. The loss of membrane components, including the carrier, due to leaching normally results in a decreased membrane thickness [56]. Consequently, the counter effects of the loss of carrier and decrease in membrane thickness is a possible explanation for the observed insignificant change in flux during latter transport cycles. The significant change in flux observed in the current experiments is because the conditions are unrepresentative of typical situations when membranes are used without replacing the feed and receiving solutions before each subsequent transport cycle. In these cases, the repeated use of the same solutions during numerous cycles results in them becoming saturated with carrier, and other leachable components, consequently, diminishing further loss from the membrane. Using tributyl phosphate as carrier to saturate aqueous solutions in contact with a membrane was shown to be an effective method to decrease carrier loss from the membrane [57]. The average 22% decrease in flux over the five transport cycles indicates that the PIM is relatively durable, and it is expected to have a reasonable life-span in commercial and practical applications. Additionally, the similar transport efficiency of about 98% in all five transport cycles provides further evidence of the viability of the membranes.

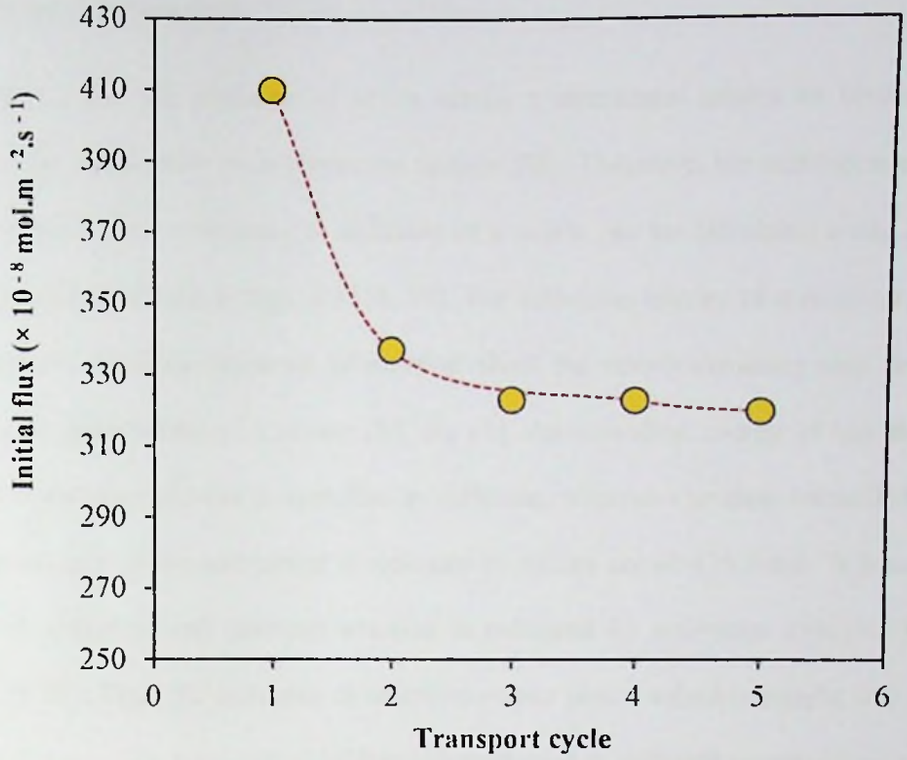


Fig. 3.12. Membrane stability as indicated by flux during repeated use for the transport of ACP. Experiment conditions, feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE.

Table 3.5. Membrane stability as indicated by flux and transport efficiency during repeated use for the transport of ACP.

Transport cycle	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
1	5.3	413	98
2	4.3	337	98
3	4.2	323	99
4	4.2	323	98
5	4.1	320	97

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE. Fresh solutions were used for each transport cycle.

3.3.9. Influence of temperature

In most cases, the diffusion of solute across a membrane relates to viscosity, which is influenced by the temperature in an Arrhenius fashion [58]. Therefore, the activation energy of self-diffusion or viscous flow correlating to diffusion of a solute can be calculated using a form of the Arrhenius equation as shown in Eqn. 3.3 [53, 59]. The activation energy of a reaction involved in a separation process provides important information about the rate-determining step that affects the overall transport performance of a system [53, 60, 61]. An activation energy of less than 20 kJ/mol indicates that a transport process is controlled by diffusion, whereas a process controlled by chemical interaction between a solute and carrier is indicated by values above 42 kJ/mol. A transport process involving both diffusion and chemical reaction is indicated by activation energies between 20 - 42 kJ/mol [59, 62]. Thus, the influence of temperature can give a valuable insight into the nature of the transport process. The transport of ACP was investigated at different temperatures as a means to better understand the nature of the transport process.

$$\log J_i = \frac{-E_a}{2.303RT} + B \qquad \text{(Eqn. 3.3)}$$

Where J_i is initial flux ($mol.m^{-2}.s^{-1}$), E_a is the activation energy of the transport process (kJ/mol), R is the gas constant (8.314 kJ/mol), T is temperature (K) and B is a constant.

The results in **Fig. 3.13** and **Table 3.6** show that the flux improved with increasing temperature which is expected and, most likely, due to a decrease in viscosity of the membrane phase. Similarly, an increase in the flux of triazole fungicides has been shown to be related to decreased viscosity of the liquid membrane phase at higher temperatures [63]. The increase in flux at elevated temperatures can also be explained due to the increased motion of polymer chains, which increases the free volume within the membrane that, in turn, promotes diffusion of solute across the membrane [54]. The findings also show that the transport efficiency is insignificantly affected by increasing temperature, which indicates that temperature affects the transport kinetics but not the overall amount of solute to be transported.

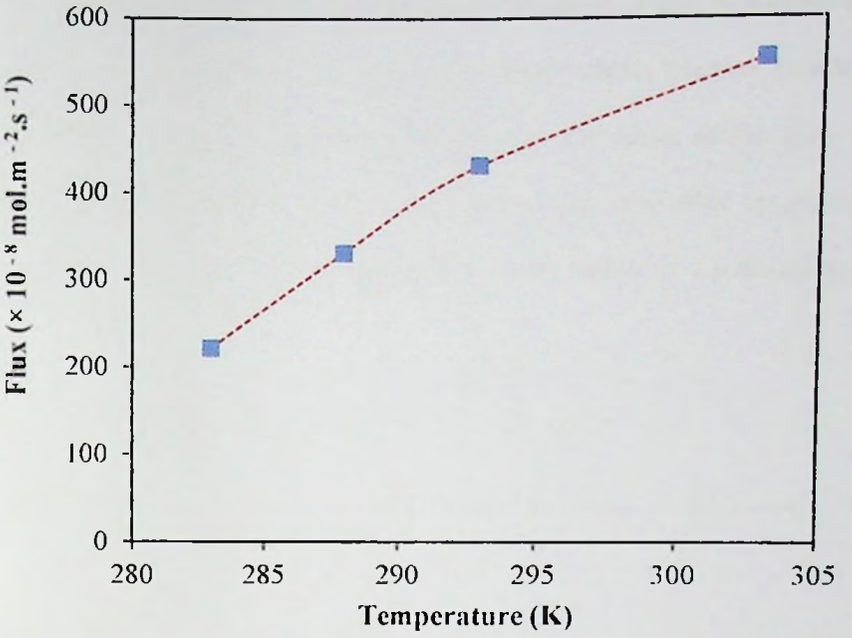


Fig. 3.13. Influence of temperature on initial flux for transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE; temperature 283 - 303 K.

Table 3.6. Influence of temperature on initial flux and efficiency for the transport of ACP.

Temperature (K)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
283	2.9	222	99
288	4.3	331	97
293	5.5	431	99
303	7.1	554	97

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution 0.1 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE; temperature 283 - 303 K.

In the current study, the activation energy was calculated using the Arrhenius equation (Eqn. 3.3) and the gradient from the Arrhenius plots is presented in the **Fig. 3.14**. A single linear line-of-best fit does not match well with all the data points, however, there are low and high temperature

regions where a straight line can be fitted. The calculated values of 24 and 46 kJ/mol for the activation energy indicates that passive diffusion dominates at low temperature, whereas facilitated diffusion is the dominating process at elevated temperature. The average activation energy over the temperature range of 35 kJ/mol indicates the transport of ACP, is not simply controlled by passive or facilitated diffusion involving the formation of aggregates but, more likely, a combination of both these processes.

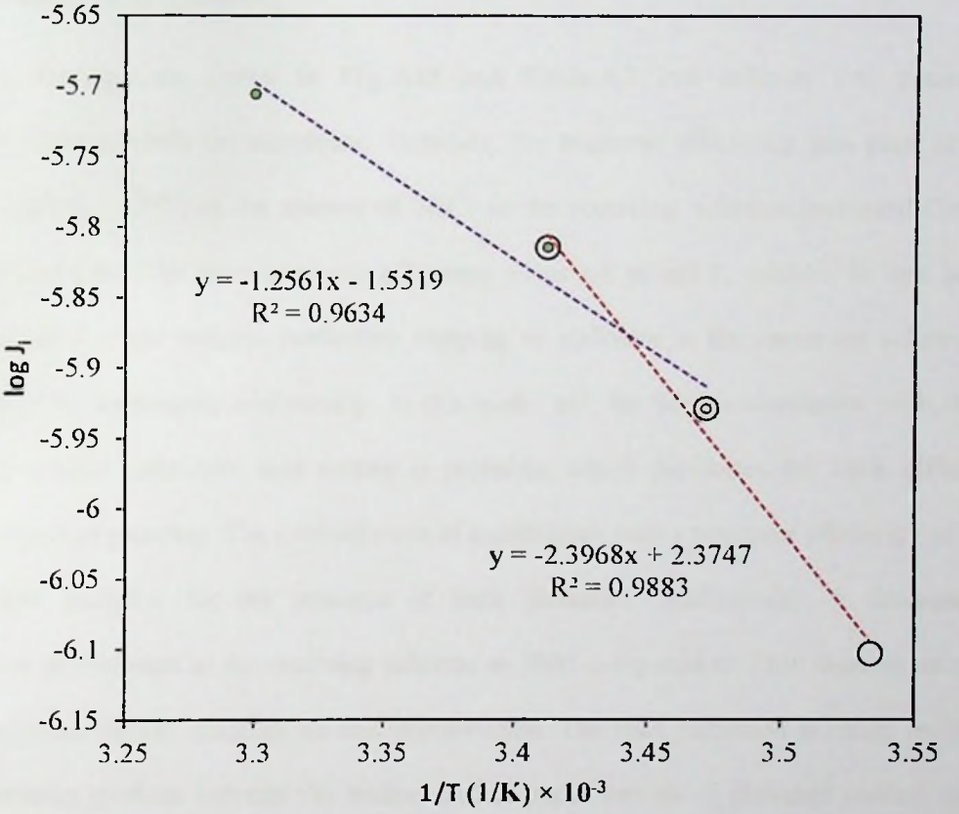


Fig. 3.14. Arrhenius plot showing influence of temperature on the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP at pH 7; receiving solution 0.1 M NaCl at pH 2; PIM: 20 wt% CTA, Aliquat 40 wt% & 40 wt% NPOE; temperature 283 - 303 K.

3.3.10. Transport of picloram

The membrane of a similar composition was also used to transport picloram using feed and receiving solutions at pH 7, as reported in Chapter 2, whereas the effective transport of ACP used an acidic (pH 2) receiving solution. Transport of a solute containing dual functionality has been reported for 5-aminosalicyclic acid across a bulk liquid membrane, involving the carboxylic acid group for extraction and protonation of the amine moiety for back extraction [64]. As picloram contains both carboxylic acid and amine functional groups, it was prudent to also study the effects of using a pH 2 receiving solution on its transport.

The findings are shown in **Fig. 3.15** and **Table 3.7** and indicate that picloram was successfully extracted into the membrane. However, the transport efficiency was poor at 47% but improved slightly to 55% as the amount of NaCl in the receiving solution increased from 0.1 to 0.25 M, respectively. The poor transport efficiency observed at pH 2, relative to that previously observed at pH 7, could indicate ineffective trapping of picloram in the receiving solution due to protonation of the carboxylic acid moiety. At this acidic pH, the hetero-association with the carrier through the neutral carboxylic acid moiety is probable, which facilitates the back diffusion and reverse transport of picloram. The establishment of equilibrium with a transport efficiency of less than 60% provides evidence for the presence of back diffusion. Additionally, a decrease in the concentration of picloram in the receiving solution at 2880 compared to 1440 minutes as shown in **Fig. 3.15** provides further evidence for this phenomenon. The back diffusion is likely facilitated by the concentration gradient between the neutral and charged species of picloram caused by the pH difference between the feed and receiving solutions.

The protonation of the amine moiety of picloram at pH 3 was previously reported [65]. Thus, the pH 2 was adequate to facilitate the back-extraction of picloram through protonation of the amine moiety as for ACP. However, the improved transport efficiency and initial flux in the presence of an increased concentration of chloride as a counter-ion indicates that effective stripping involves an ion-exchange process as previously reported [66]. This supports the previous assertion that protonation of the carboxylic acid moiety limits effective trapping of picloram. Thus, the experimental conditions,

specifically, a pH 2 receiving solution, used in this chapter is advantageous for the transport of ACP over picloram. This could form the basis for the preferential extraction of picloram degradation products from a feed solution still containing the active herbicide.

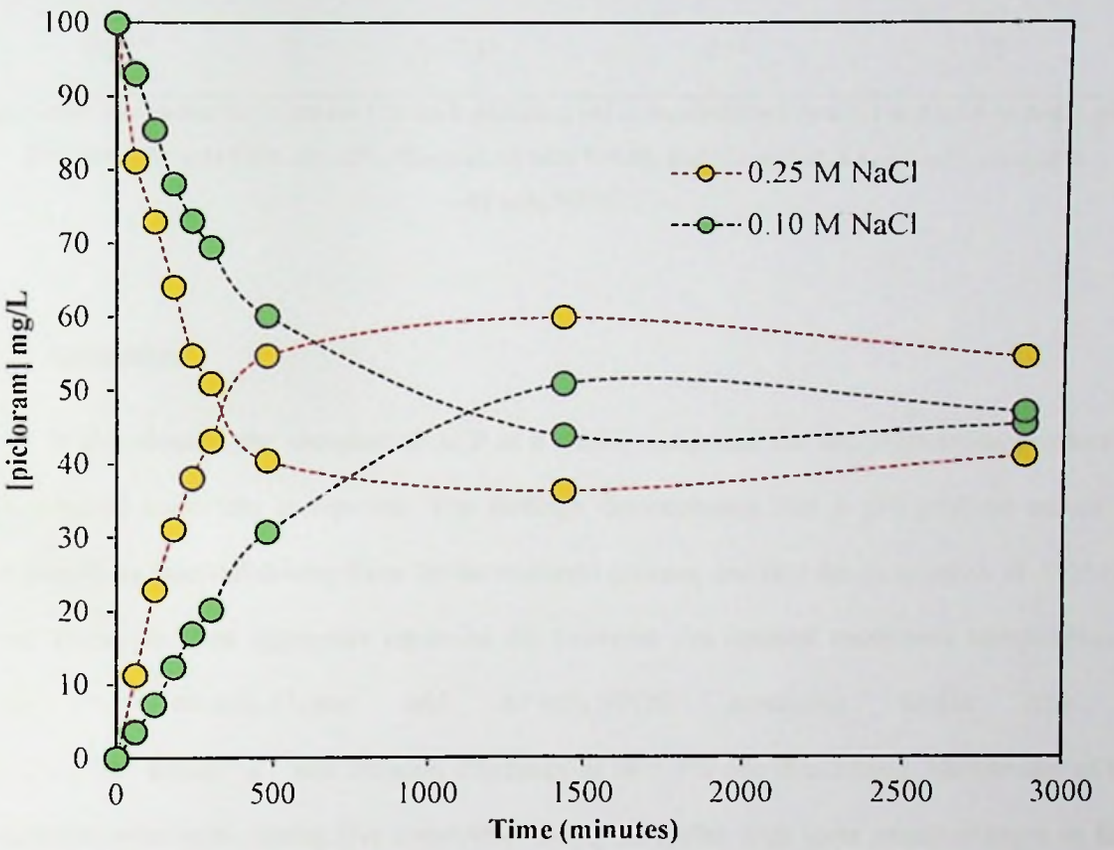


Fig. 3.15. Transport of picloram across the PIM. Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.10 and 0.25 M NaCl, pH 2; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE.

Table 3.7. Membrane performance indicators for transport of picloram across PIM.

[NaCl] M	Receiving solution pH	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
0.10	2	2.3	97	47
0.25	2	4.4	183	55
0.25*	7	7.11	294	95

Experiment conditions: feed solution 100 mg/L picloram, pH 7; receiving solution 0.1 and 0.25 M NaCl, pH 2 & 7; PIM: 20 wt% CTA, 40 wt% Aliquat & 40 wt% NPOE, and *25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

3.4. Conclusion

In this chapter, the transport of ACP as a model compound for the degradation products of pyridine-based herbicides is reported. The findings demonstrated that a pH gradient across the membrane is an essential driving force for the transport process, and that the association of ACP with Aliquat carrier to form aggregates improved the transport. An optimal membrane composition of 20 wt% CTA, 40 wt% Aliquat and 40 wt% NPOE producing initial flux of $413 \pm (7) \times 10^{-8}$ mol.m^{-2}.s^{-1} and transport efficiency of 98 ± 1% was determined. Membranes of this composition were stable during five consecutive transport cycles with some minor changes in flux, but maintained a similar high transport efficiency.

The influence of physicochemical properties of different plasticisers on transport of ACP was investigated. Plasticisers of comparable viscosity (NPOE and TEHP) displayed different effects with the plasticiser having the lower dielectric constant (NPOE) producing the highest initial flux. Additionally, the plasticiser with the highest viscosity (DOP) produced the lowest initial flux.

Influence of temperature on the transport of ACP demonstrated that the initial flux improved with increasing temperature, whereas the efficiency was insignificantly affected. An average activation energy of 35 kJ/mol was determined for the transport process. This indicated both the

passive and facilitated diffusion involving the formation and diffusion of aggregates across the membrane are as the rate-determining steps.

The aminopyridine studied was shown to exist as a cation with the charge on the endocyclic nitrogen at pH 7. Under these conditions, extraction involves the interaction of the uncharged exocyclic nitrogen of the amine with Aliquat. Effective stripping at pH 2 involved protonation of the exocyclic nitrogen to minimise back diffusion and facilitate trapping in the receiving solution. The observation that ACP exists as a cation at pH 7 led to the subsequent investigation of its extraction and transport using anacardic acid as a cationic carrier in Chapter 4.

A preliminary investigation of the extraction and transport of potential transformation products from the decomposition of pyridine-based herbicides using PIMs was presented in this chapter. The findings demonstrate that a model product can be effectively transported, however, actual transformation products were not studied because most are not readily commercially available, and their synthesis was outside the scope of this study. The current findings serve as a starting point for future investigations of the extraction and transport of degradation products of pyridine-based herbicides using polymer inclusion membranes.

3.5. References

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Chapter 4: Potential use of anacardic acid as a cheap and environmentally friendly carrier for applications of polymer inclusion membranes.

4.1. Introduction

There are several undeniable advantages, such as cost reduction compared to solvent extraction, associated with using polymer inclusion membranes (PIMs) as a separation method. However, their applications have, in most cases, been challenged by leakage of carrier from the membrane [1, 2]. The carrier is normally entrapped by chemical attractions and entanglement within the polymer matrix which also imposes a diffusive resistance to solutes. The addition of a plasticiser, or carrier that can also function as a plasticiser, normally results in the formation of micro-channels which improves diffusion of solutes across the membrane. However, these channels can also contribute to the leakage of carrier from the membrane which often results in diminished performance. As a result, the acceptability of PIMs for environmental applications is limited because of the toxicity of some carriers. For instance, some ionic liquids which are used as carriers are known to cause adverse effects on ecosystems [3]. Furthermore, the products as a result of photolytic and photochemical decomposition of imidazolium-based ionic liquids are more toxic, whereas other ionic liquids are very stable and can accumulate in the environment [4]. Therefore, studies on the development of alternate carriers that are less harmful to the environment are necessary to improve the applicability of PIMs.

The cost of carriers is an important factor in determining the economic feasibility of a separation process [5]. Most PIM applications use commercially available carriers which require some synthesis and are relatively expensive [6]. Currently, the use of PIMs is mainly devoted to the extraction and transport of metallic species, such as gold and copper, which have a relatively high commercial value [6]. Applications of PIMs for organic compounds

has not been as widely investigated and is an area that requires significant attention [7]. The use of compounds that originate or are derived from plants can be appropriate candidates as carriers because they are comparatively cheap and readily available. Additionally, the use of renewable resources for the preparation of commercial products has captured recent attention [8].

Cashew nut shell liquid (CNSL) is a processing by-product that used as a raw material to source and produce chemicals that does not create any pressure on the supply of edible oils. Thus, the use of compounds derived from CNSL for PIM applications is an attractive proposal because of the associated low manufacturing cost, abundant availability, and diverse chemical nature of the components [9].

4.1.1. Cashew tree

The cashew tree (*Anacardium Occidentale L.*) which originated from eastern Brazil has spread to many tropical areas including Vietnam, India and Tanzania [10]. The plant usually takes 3 - 4 years from planting to fruiting and can live for 40 years or more. The fruit known as an apple has a kidney-shaped structure with a nut attached to an end of fleshly pulp as shown in **Fig. 4.1**.

Fig. 4.1. Cashew nut and its apple

The nut contains a curved edible seed housed in a honeycomb like shell known as a cashew nut fruit. The fruit comprises a kernel which is encapsulated by an outer and inner shell. The soft honeycomb matrix situated between the outer and inner shells is a good source of the dark brown cashew nut shell liquid (CNSL). The liquid is regarded as a sustainable resource due to the increased production of cashew nut as shown in **Fig. 4.2**.

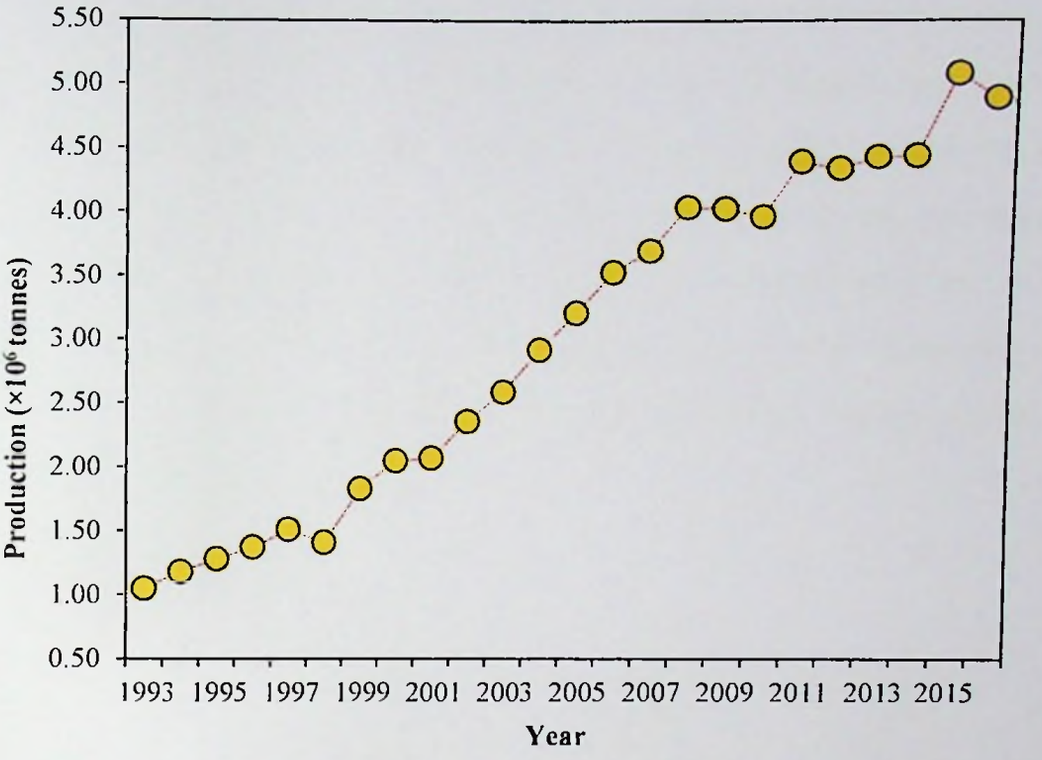


Fig. 4.2. World production of cashew nuts from 1993 to 2016 [11, 12].

4.1.2. Cashew Nut Shell Liquid (CNSL)

The cashew nut shell liquid (CNSL) represents about 25% of cashew weight and 30% - 35% of nut shell weight [13]. It is a waste by-product of cashew nut processing which has limited economic use and, thus, creates a problem for disposal [14, 15]. The liquid is a good source of numerous phenolic compounds which are suitable for the production of chemicals useful in various applications such as insulating varnishes, oil- and acid-proof cold setting cements, industrial floor tiles, and automobile brake linings [16]. Additionally, biologically active compounds, such as antifungal, antitumor and antioxidants, have also been derived from CNSL [17, 18].

The chemical composition of CNSL depends on the extraction method used. The liquid obtained by solvent extraction contains a high proportion of anacardic acid (60 - 65%) together with cardol (15 - 20%), cardanol (10%), and traces of 2-methyl cardanol (**Fig. 4.3**). Whereas, technical grade CNSL which is normally extracted by roasting the shells at elevated temperature contains substantially more cardanol (up to 84%) due to the decarboxylation of anacardic acid to cardanol at higher temperatures [20]. Consequently, the composition of technical CNSL can be varied to include different cardanol content by changing the actual roasting temperature [14].

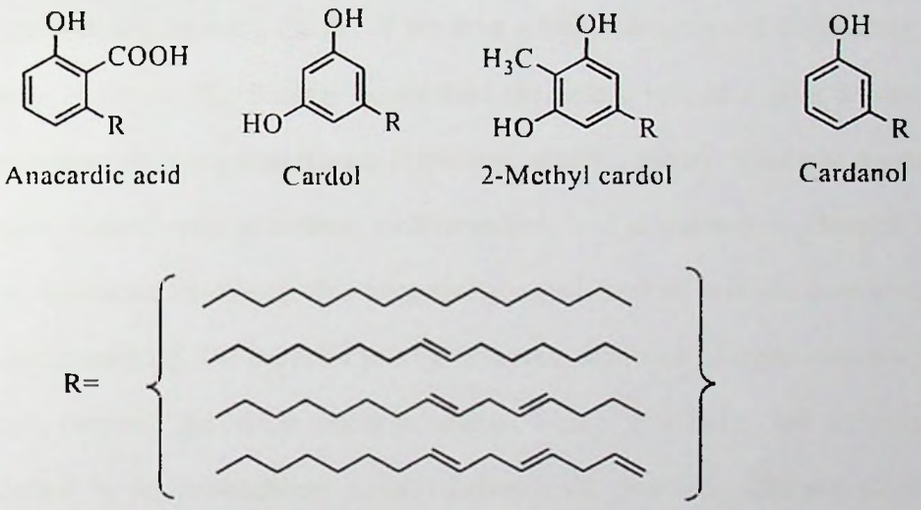


Fig. 4.3. Chemical structure of typical chemical constituents of CNSL.

4.1.3. Transport of positively charged organic compounds

The transport of organics is typically more problematic than inorganics. Most organics can exist as neutral or charged species depending on the solution pH. Whereas, inorganics typically exist as charged species in solution and transport involves an ion-

exchange process. The transport of bipyridinium herbicides and aromatic amines through hydrophobic liquid and ion exchange membranes respectively was previously reported [21, 22]. The influence of carrier concentration, and pH of feed and receiving solutions on the transport of bipyridinium herbicides (diquat and paraquat) across a hydrophobic liquid membrane containing di-(2-ethylhexyl) phosphoric acid as a carrier was investigated [21]. The improved extraction efficiency as the amount of the carrier increased up to 40 vol% was linked with enhanced formation of complex between the carrier and target solutes. However, at 50 and 60 vol% of carrier the diffusion of the solutes was inhibited due to the increased viscosity of the membrane phase. The efficiency also increased as the pH of the receiving solution decreased due to a larger pH gradient across the membrane, whereas lowering the pH of the feed solution decreased the efficiency due to protonation of carrier. The findings demonstrate the crucial role of a pH gradient for the transport process involving a membrane containing an acidic carrier. Similarly, the transport of aromatic amines, such as aniline, *p*-chloroaniline, and *p*-nitroaniline, through an ion-exchange membrane containing fixed negative charged sites of sulfonic acid groups has been investigated [22]. The transport process involved positively charged aromatic amines "jumping" between the fixed negative charged sites. Similarly, the stripping was accomplished by an ion-exchange process between the positively charged amines and protons at the receiver/membrane interface.

The presence of an acidic hydrogen in anacardic acid and its structural similarity to other acidic carriers, such as di-(2-ethylhexyl) phosphoric acid, indicates its possible use as an effective carrier for positively charged species in liquid membranes [24]. Also, importantly, anacardic acid can undergo biodegradation in the environment which supports the growing interest in using green materials in polymers [28, 29].

The experiments in this chapter explore the potential use of anacardic acid as a cost-effective and eco-friendly carrier for extraction and transport of organic compounds. Preliminary experiments used 4-amino-2-chloropyridine (ACP) as a model compound and subsequent experiments used paraquat and diquat as representative cationic herbicides to assess membrane performance.

4.2. Experimental

4.2.1. Chemicals and reagents

Some additional chemicals and reagents to those previously reported in **Sections 2.2.1** and **3.2.1** were used. Petroleum ether (≥95%), ethanol (96%), palladium catalyst (Pd-C, 10 wt%), ethyl acetate (99.8%), calcium hydroxide (≥95.0%), *N,N'*-dimethyl-4,4'-bipyridinium dichloride (paraquat) (98%), 1,1'-ethylene-2,2'- bipyridinium dibromide (diquat) (PESTANAL®, analytical reagent) (95 – 105%), sodium 1-heptanesulfonate(≥99.9%) and bis-(2-ethylhexyl) phosphoric acid (97%) were all purchased from Sigma-Aldrich.

4.2.2. Preparation of polymer inclusion membranes

Polymer inclusion membranes were prepared as described in **Section 2.2.2.** Anacardic acid and dodecanol were used as carrier and modifier, respectively.

4.2.3. Transport experiments

Transport experiments were performed as described in **Section 2.2.4.** Most experiments used a feed solution containing 100 mg/L ACP at pH 7, and a receiving solution

of 100 mM pH 2 phosphate buffer; referred to as standard transport conditions unless indicated otherwise. Except for the stability experiments, a new and different membrane was used for each experiment.

4.2.4. Measurement of ACP concentration

Concentrations of ACP in all experiments were determined using UV-Vis spectrophotometry at 245 nm as described in **Section 3.2.4**, unless stated otherwise.

4.2.5. Preparation of anacardic acid mixture (AAM)

Standard methods of extraction, isolation and purification of phenolic compounds from the CNSL were used as described [30]. The CNSL was extracted from cashew shells by soaking (1500 g) in petroleum ether (2.5 L) for 3 days. The solution was concentrated using a rotary evaporator under vacuum at 40 °C to yield the crude CNSL (400 g).

Anacardic acid was isolated by dissolving crude CNSL (100 g) in 5% aqueous methanol (400 mL) followed by addition of a slurry of $Ca(OH)_2$ (150 g) in 5% methanol at 60 °C. The precipitated calcium anacardate was thoroughly washed with 5% aqueous methanol using Buchner filtration. The anacardate (100 g) was suspended in ice cold water (300 mL) and the resulting solution adjusted to pH 2 by the addition of 6 N HCl while stirring for 30 minutes. The aqueous solution was extracted with ethyl acetate (150 mL × 2) and washed with water. The organic solution was dried using anhydrous sodium sulphate and then concentrated using a rotary evaporator under vacuum at 40 °C to obtain a mixture of anacardic acid as a deep brown liquid (60 g).

4.2.5.1. Preliminary investigation - anacardic acid mixture

A membrane containing 30 wt% CTA and 70 wt% AAM was used to transport ACP under standard transport conditions. Similar experiments using membranes containing 30 wt% CTA, 20 wt% AAM and 50 wt% NPOE were also performed.

4.2.5.2. Optimisation of carrier concentration

Membranes containing CTA as a base polymer, NPOE as plasticiser in a fixed ratio of 5:3, and 0 – 50 wt% of anacardic acid mixture were used under standard transport conditions.

4.2.5.3. Membrane stability studies

A membrane containing 25 wt% CTA, 30 wt% AAM and 45 wt% NPOE was used for five successive days under standard transport conditions. The feed and receiving solutions were changed after each transport cycle without changing the membrane. The mass of the membrane was also measured after each transport cycle.

4.2.6. Hydrogenation of anacardic acid (AA)

The anacardic acid mixture (20 g, 58.42 mmol) was dissolved in ethanol (200 mL) in a 250 mL three-necked round bottomed flask and palladium catalyst on activated carbon (0.4 g, Pd - C, 10 wt%) was added (**Fig. 4.4**). The flask was placed on a hydrogenation setup and hydrogen gas was passed through the solution while stirring for 2 hrs. The reaction mixture was filtered through a Celite bed using vacuum filtration and washed with ethanol (100 mL). The resulting solution was concentrated using a rotary evaporator under vacuum

at 40 °C and the precipitate collected. The precipitate was re-crystallized from petroleum ether to yield pure 2-hydroxy-6-pentadecylbenzoic acid (referred to as anacardic acid (AA)) as off-white crystals (12.5 g).

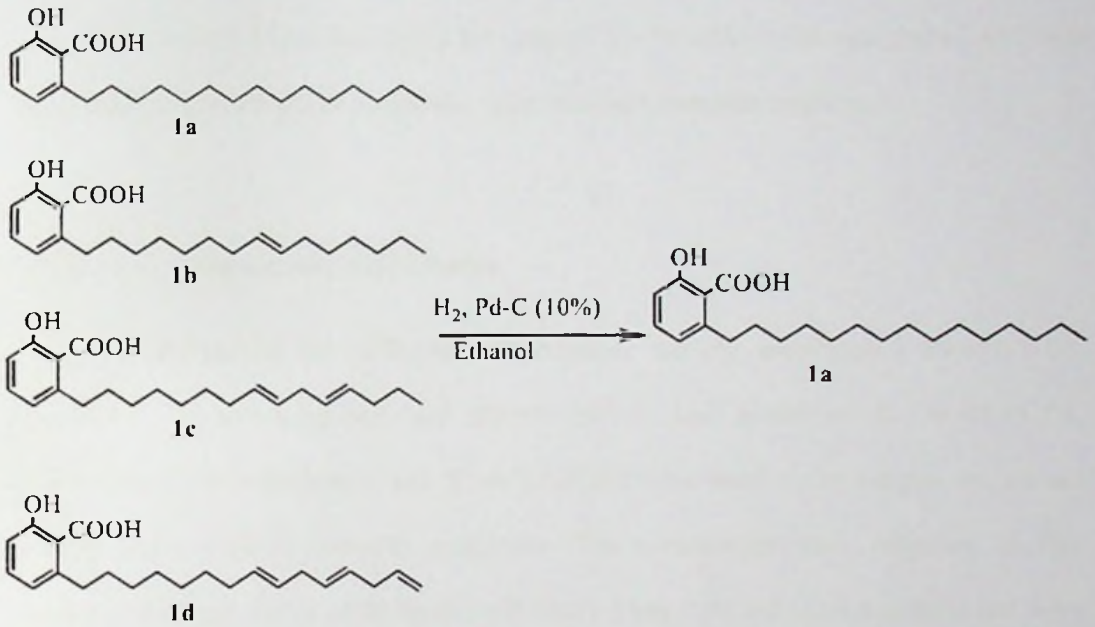


Fig. 4.4. Catalytic hydrogenation of AAM. **1a**. saturated chain and **1b - 1d** unsaturated chain.

4.2.6.1. Preliminary investigations using AA

Membranes containing different amounts of AA (5 - 40 wt%) were prepared for preliminary investigations. A small amount (5 - 20 wt%) of dodecanol was added to some membranes as a modifier to improve the solubility of anacardic acid. The membranes were evaluated for clarity and homogeneity based on a visual inspection. Transparent membranes were regarded as containing miscible amounts of carrier and a homogeneous distribution indicated the absence of significant aggregation of components. Additionally, membranes

that were successfully removed from the glass petri-dish without observable deformations or liquid residues were considered to be stable.

4.2.6.2. Influence of carrier concentration

The amount of AA (carrier) in the range of 5 - 20 wt% on the transport of ACP was investigated using two sets of membrane under standard transport conditions.

4.2.6.3. Membrane stability studies

Membranes of two different compositions, namely membrane 1: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol and 40 wt% NPOE and membrane 2: 30 wt% CTA, 10 wt% AA, 10 wt% dodecanol and 50 wt% NPOE, were used to investigate membrane stability under standard transport conditions. The membranes were subjected to five successive transport cycles of 48 hours each where fresh feed and receiving solutions were used after each cycle without changing the membrane.

4.2.6.4. Optimisation of feed and receiving pH

Membrane 1 was used to investigate the influence of pH on the transport of ACP using feed solutions at pH 2, 5 and 7, and a pH 2 receiving solution.

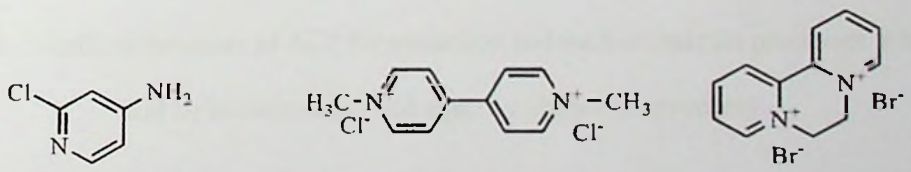
Similarly, the influence of pH of the receiving solution at pH 2, 5 and 7 on the transport of ACP was evaluated using a feed solution of 100 mg/L ACP at pH 7 and membrane 1.

4.2.6.5. Transport of picloram

Transport was performed using the membrane 1, a feed solution containing 100 mg/L of picloram at pH 7 and a receiving solution of (100 mM phosphate buffer, pH 2).

4.2.6.6. Competitive transport

Competitive transport was assessed using a feed solution containing a mixture of ACP, paraquat and diquat shown in **Fig. 4.5** (100 mg/L of each, pH 7), a receiving solution (100 mM phosphate buffer, pH 2) and membrane 1. Concentrations of each target solute in the feed and receiving solutions were determined using a previously reported procedure [31]. Briefly, the concentration of analytes was measured by High-Performance Liquid Chromatography using a Shimadzu LC-20AT equipped with a C18 column (Apollo™ 15 cm ×5 µm) and a dual wavelength UV detector (265 and 310 nm). A mixture prepared from orthophosphoric acid (11.2 mL, 0.2 mol), diethyl amine (10.2 mL, 0.1 mol) and sodium heptanesulfonate (2 g, 0.01 mol) diluted to 1.0 L with aqueous methanol (25 vol%) was used as the mobile phase for isocratic elution at a flow rate of 0.6 mL/min. A sample volume of 20 µL was used for analysis.



4-amino-2-chloropyridine (ACP) paraquat diquat

Fig. 4.5. Chemical structures of ACP, paraquat and diquat.

4.3. Results and discussion

4.3.1. Introduction

The transport of positively charged ACP across a liquid membrane containing an acidic carrier is postulated to involve a cation exchange process (**Fig. 4.6**) similar to that reported for amino acids [32-35]. The protonated amines exchange with protons from the carrier at the feed solution/membrane interface forming an ion-pair complex which diffuses across the membrane. Subsequently, the ion-pair complex dissociates at the receiving solution/membrane interface to release the amines into the receiving solution while the carrier accepts protons and is regenerated for another transport cycle. A proton concentration gradient across the membrane acts as the main driving force for the transport process [35]. Therefore, the pH of feed and receiving solutions was investigated to optimise conditions for the deprotonation and protonation of ACP and the carrier. The concentration of the carrier was also optimised in this work.

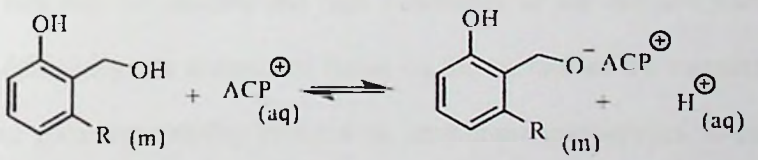
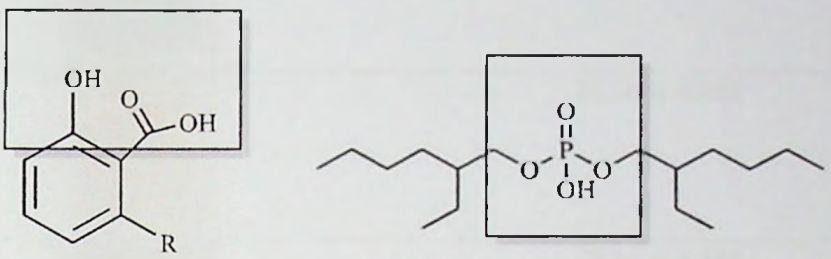


Fig. 4.6. Interfacial reactions of ACP for extraction and back-extraction processes. where m and aq are membrane and aqueous phases, respectively.

4.3.2. Anacardic acid mixture as a carrier-preliminary investigation

The chemical structure of anacardic acid has some similarity to the acidic carrier di-(2-ethylhexyl) phosphoric acid which is also recognised for its plasticising properties [36]. Both contain features of some common plasticisers, namely non-polar groups and, importantly, a polar grouping of hydroxyl and double bonded oxygen which can interact

with polar regions in the polymer backbone and, thus, decrease the entanglement of polymer chains (**Fig. 4.7**). Thus, it is likely that anacardic acid mixture can also act as a plasticiser.



Anacardic acid Di-(2-ethylhexyl) phosphoric acid

Fig. 4.7. Chemical structure of anacardic acid and di-(2-ethylhexyl) phosphoric acid.

The influence of anacardic acid mixture (AAM) as both a carrier and plasticiser at different amounts in CTA-based membranes (**Table 4.1**) was evaluated. Observations showed that the membranes were flexible and homogeneous even at high amounts of AAM. The mechanical flexibility indicates that AAM can act as a plasticiser, whereas the homogeneity indicates the uniform and high miscibility of the mixture with CTA in the membrane. Additionally, the absence of liquid on the surface of the membrane is further confirmation of good compatibility between the membrane components. These preliminary investigations indicate the usefulness of AAM as both a carrier and plasticiser to prepare PIMs for extraction and transport applications.

Table 4.1. PIMs containing different amounts of AAM.

Image	Composition
	0 wt% AAM
	20 wt% AAM
	30 wt% AAM
	40 wt% AAM
	50 wt% AAM
	60 wt% AAM
	70 wt% AAM
	80 wt% AAM

A membrane containing 30 wt% CTA and 70 wt% AAM was used in a preliminary experiment for the transport of ACP and the transient concentration profiles are shown in

Fig 4.8. The results indicate that ACP was transported slowly through the membrane with a linear change in concentration in both the feed and receiving solutions. This indicates passive diffusion rather than facilitated diffusion which is normally characterised by rapid changes in the concentration of a target solute in both solutions during the initial stages of the transport process [37]. Additionally, there was a substantial lag (>180 minutes) for ACP to be clearly detected in the receiving solution. This is associated with resistance at the boundary layer and in the membrane to the diffusion of the ion-pair complex [38]. Further evidence for poor membrane performance was the water insoluble deposits on the feed side of the used membrane as shown in **Fig. 4.9**. The presence of the hydrophobic deposits and indicators of passive diffusion provides good evidence that the ion-pair complex is insoluble in the current membrane liquid phase. Thus, even though AAM can plasticise CTA-based membranes, it is an ineffective solvent for the ion-pair complex. Therefore, the ability of AAM to also act as a plasticiser, as well as a carrier, was not further considered in this study. Consequently, an additional plasticiser is needed to improve solubility and diffusion of the ion-pair in the membrane.

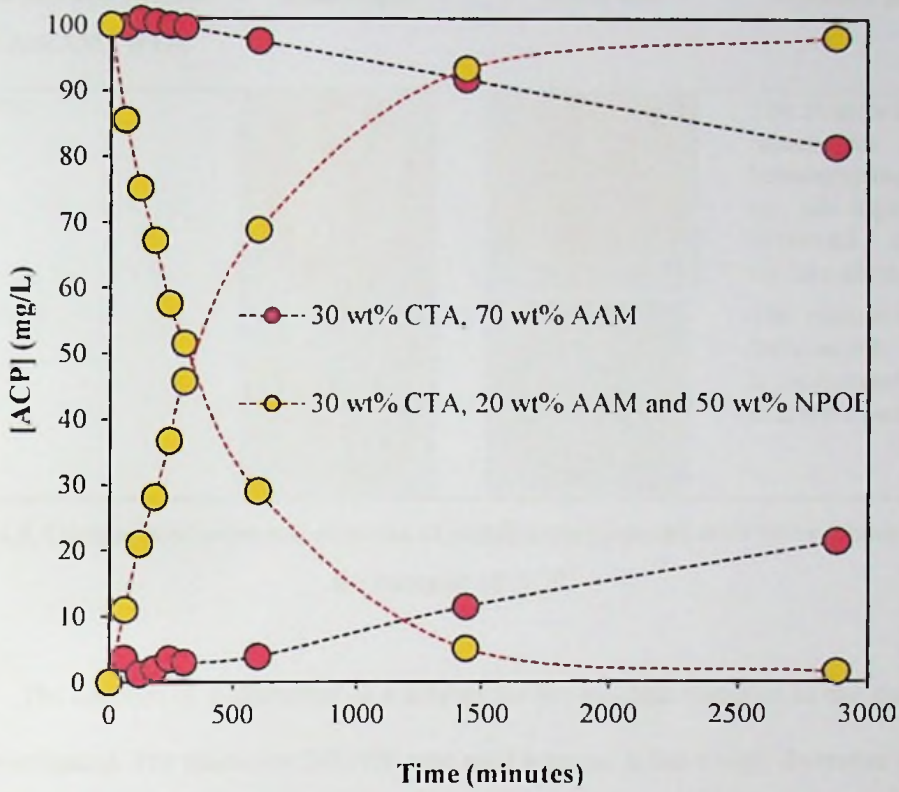


Fig. 4.8. Transport of ACP using anacardic acid mixture as a carrier. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 70 wt% AAM, & 30 wt% CTA, 20 wt% AAM & 50 w% NPOE.

Composition (wt%) CTA:AAM:NPOE	Before use	After use	Observation
30:70:0			The membrane was transparent and homogeneous, but an oil liquid was observed on the surface after use
30:20:50			The membrane was transparent and homogenous before and after use

Fig. 4.9. Comparison before and after use of membranes prepared with and without NPOE for transport of ACP.

The addition of a plasticiser as a solvent for the ion-pair complex in the membrane was investigated. The plasticiser 2-NPOE was used because it has a high dielectric constant for compatibility with CTA, and low viscosity to facilitate the rapid diffusion of solutes across similar membranes as seen for picloram and ACP in chapter 2 and 3, respectively. The findings show that a composition of 30 wt% CTA, 20 wt% AAM and 50 wt% NPOE produced a transparent homogeneous membrane (**Fig. 4.9**), indicating good miscibility and uniform distribution of carrier and plasticiser. The transient concentration profiles of both the feed and receiving solutions were now characterised by rapid changes at the initial stages of the transport process as indicated in **Fig. 4.8**. This provides strong evidence that facilitated transport now occurs. No oil residue was observed on the surface which indicates that the ion-pair complex is now soluble in the membrane (**Fig. 4.9**). Consequently, membranes containing NPOE were used for all subsequent transport experiments.

4.3.2.1. Optimisation of carrier concentration

The findings from preliminary investigations demonstrated that AAM can facilitate the transport of ACP. The membrane performance is influenced by the carrier content which determines the amount of target solute that can be loaded. For this reason, the amount of AAM required for the optimal transport of ACP was explored using PIMs containing a ratio of 3:5 of CTA-to-NPOE.

The results in **Fig. 4.10** and **Table 4.2** show the flux increased as the amount of AAM in the membrane increased up to 30 wt% and thereafter, a decrease in flux was observed at a higher carrier concentration. The flux increase is due to the increased amount of the ion-pair complex formed at the feed/membrane interface. However, the solubility of the total amount of complex in the membrane is limited by the available amount of plasticiser relative to the amount of carrier. Above the optimal carrier concentration of 30 wt% there is insufficient plasticiser to dissolve further amounts of complex, as indicated at the end of experiments using 40 & 50 wt% carrier by the oily droplets on the membrane surface exposed to the feed. Similar deposits of lipophilic ion-pair complexes, in this case containing Aliquat, on the surface of PVC membranes have been reported [39].

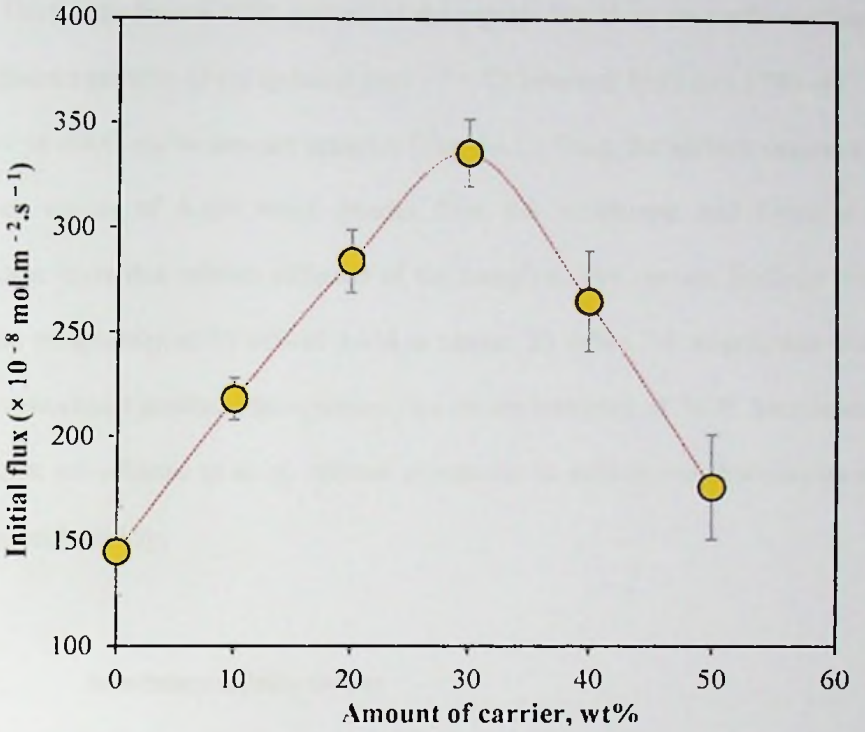


Fig. 4.10. Influence of amount of anacardic acid mixture as carrier on the transport of ACP as indicated by the initial flux. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 3:5 ratio of CTA-to-NPOE, and 0 – 50 wt% AAM. Error bars represent a standard deviation of measurements from n = 3 experiments.

Table 4.2. Influence of amount of AAM as carrier on transport of ACP as indicated by the initial flux.

Carrier (wt%)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})
0	1.9	145
10	2.8	218
20	3.6	284
30	4.3	336
40	3.4	265
50	2.3	176

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM 3:5 ratio of CTA-to-NPOE, and 0 – 50 wt% anacardic mixture.

The results from a FTIR analysis of the organic liquid on the surface of membranes show a distinct splitting of the carbonyl peak (C = O) between 1630 and 1740 cm^{-1} which is indicative of AAM and/or ion-pair complex (**Fig. A4.1**). Thus, the surface organics could be due to an excess of AAM which exudes from the membrane and forms a stagnant hydrophobic layer that inhibits diffusion of the complex. The current findings identified a membrane composition of 30 wt% of AAM as carrier, 25 wt% CTA as polymer and 45 wt% NPOE as plasticiser produced the optimum flux for the transport of ACP. Membranes of this composition are referred to as an optimal membrane in subsequent discussions involving anacardic acid mixture.

4.3.2.2. Membrane stability studies

The suitability of a membrane for commercial and practical applications is determined by its capacity to maintain performance over repeated use. To assess this capability, stability studies over five transport cycles were performed using an optimal membrane. The results show a remarkable 30% drop in the initial flux after the first cycle and a further 10% decline during the third transport cycle. Thereafter, the initial flux remained mostly constant for transport cycles 4 & 5 (**Fig. 4.11**).

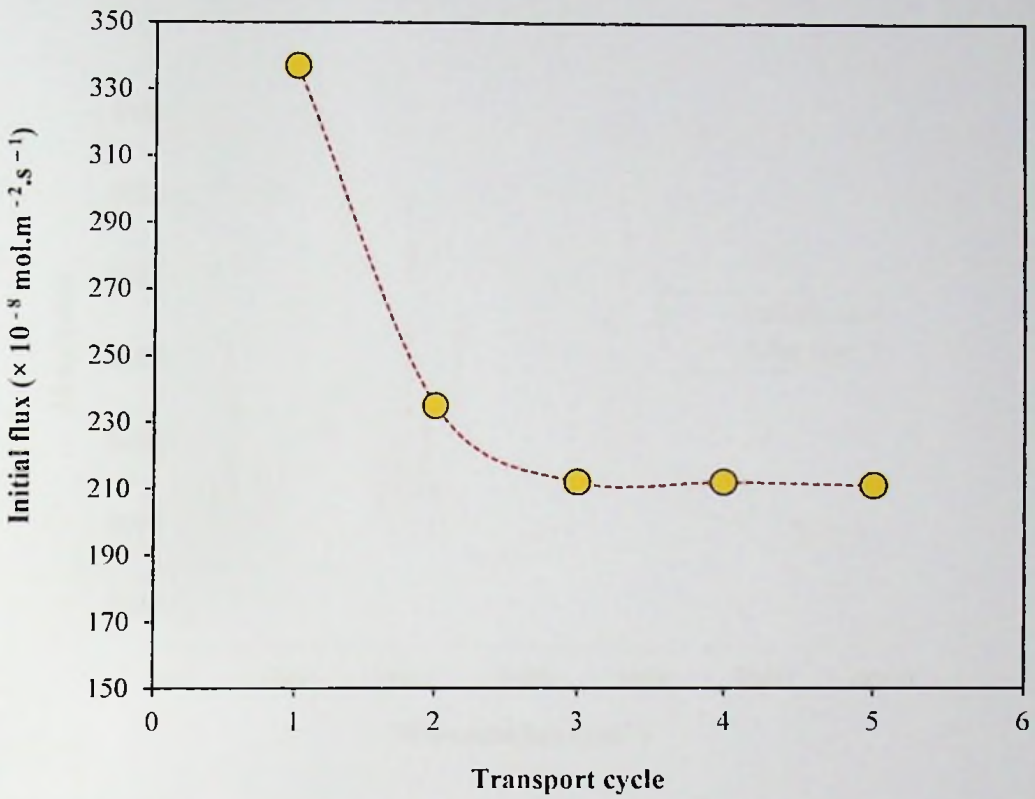


Fig. 4.11. Membrane stability as indicated by flux during repeated use for the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 25 wt% CTA, 30 wt% AAM & 45 wt% NPOE.

The initial substantial decrease in flux is caused by the loss of some liquid components which were observed to desorb to the surface of the membrane after use. The loss of carrier was indicated by a relative decrease compared to CTA of associated infrared peak intensities in spectra of PIMs before and after use as shown in **Fig. 4.12**. The loss of liquid components, including carrier, is normally associated with a decrease in membrane thickness as reported in previous chapters. The observed insignificant change in the initial flux during latter transport cycles is likely caused by the counteracting effects of loss of carrier and decrease in membrane thickness.

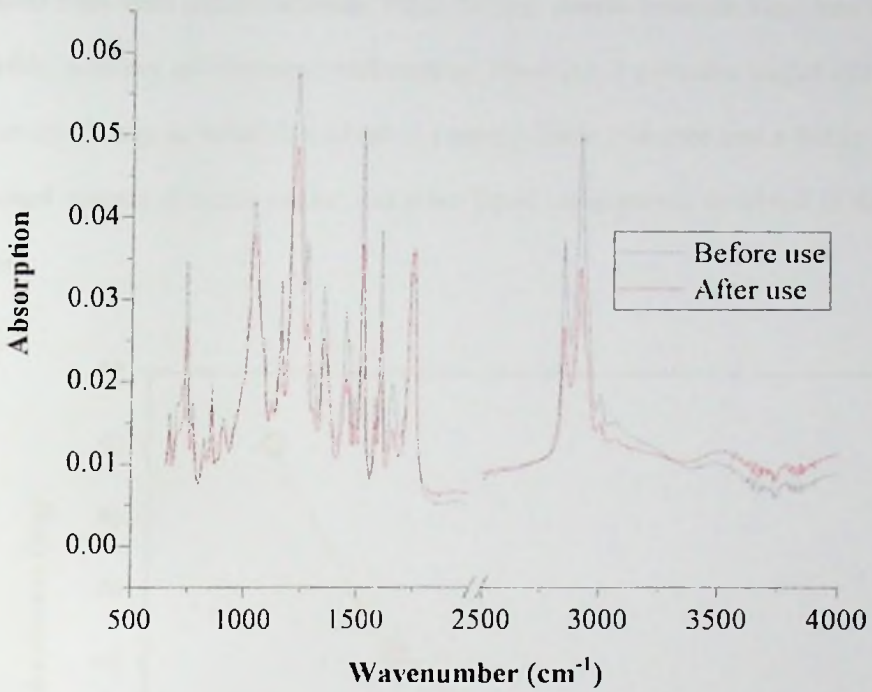


Fig. 4.12. FTIR spectra for an optimal membrane before use (black) and after use (red).

Mass loss is another important indicator of membrane stability and, for this reason, the initial and final mass of the membrane was measured for each transport cycle. The results as indicated in **Fig. 4.13** show that a significant 12% mass loss occurred during the first transport cycle, whereas in later cycles the loss was less and on average only 2 (± 1)%. The high initial mass loss is likely caused by washing of components that exude, due to limited solubility in the entrapped liquid phase, and form a surface layer during the curing stage of membrane preparation. A small amount of brown liquid droplets were observed on the surface of the membrane during latter cycles. This liquid is most likely AAM and the associated small mass loss indicates its limited solubility in aqueous solutions. The observed mass loss, in this case, is likely to underestimate the actual loss of components from the liquid membrane phase because some remains adsorbed on the membrane surface. Thus, the

actual amount of active carrier in the membrane could be significantly less than that indicated from mass loss calculations. These findings demonstrate the mass loss alone is not a reliable indicator of membrane performance. However, it provides useful information to support the change in initial flux which is a more reliable indicator and a better measure of the actual amount of active carrier, and other liquid components, involved in the transport process.

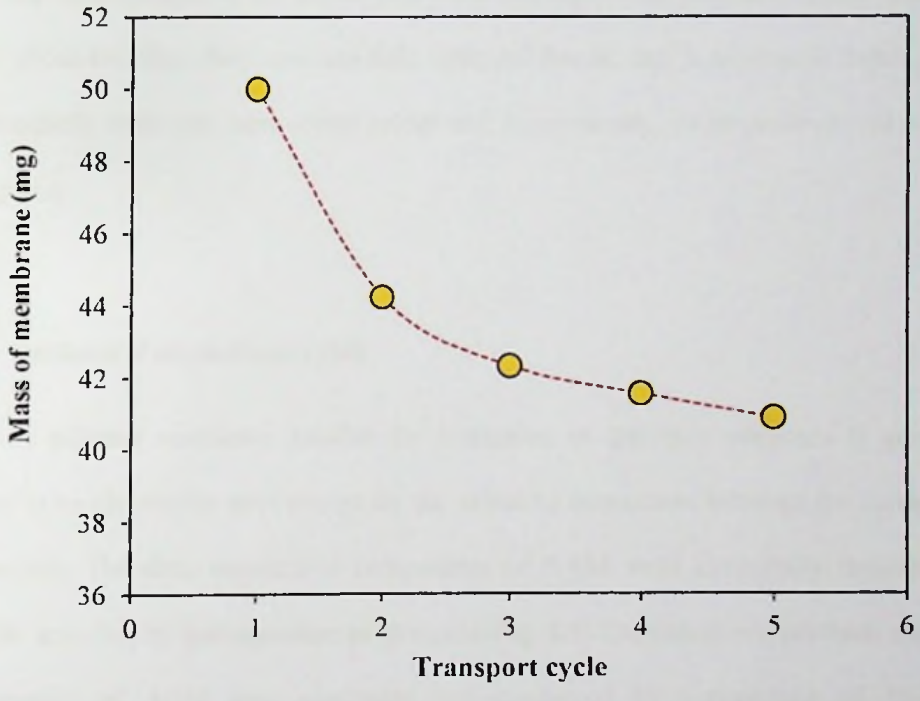


Fig. 4.13. Membrane stability as indicated by membrane mass during repeated use for the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 25 wt% CTA, 30 wt% AAM & 45 wt% NPOE.

The loss of liquid components limits the use of PIMs for commercial applications and also presents a potential risk to the environment because some of the chemicals are toxic. Importantly, the loss of AAM from membranes is, in this case, a matter of less

concern because of the environmentally benign chemical nature of the plant sourced carrier compared to other synthetic carriers.

The results from the use of AAM demonstrate that it is a useful carrier for the transport of ACP. However, the presence of reactive functional groups (double bonds) in some constituents of the mixture could limit its widespread use. In practical applications, some samples might contain chemicals that could react with the unsaturated alkene bonds to reduce the effectiveness of the carrier and yield decomposition products. Thus, anacardic acid in which the alkyl chain contains fully saturated bonds, that is no double bonds, could be a potentially better and more robust carrier and, consequently, its preparation and use was investigated.

4.3.3. Synthesis of anacardic acid (AA)

A polymer membrane suitable for extraction or transport purposes is generally required to be chemically inert except for the selective interaction between the carrier and target solute. The three unsaturated components of AAM were chemically converted to anacardic acid (**1a**) by hydrogenation as shown in **Fig. 4.5**. The extent and products from the hydrogenation of AAM were monitored and confirmed by comparison of ^{1}H-NMR spectroscopy. Typical ^{1}H-NMR spectra before and after hydrogenation are shown in **Figs. 4.14** and **4.15**, respectively. The spectrum (**Fig. 4.15**) of the product isolated after hydrogenation shows no peaks due to alkyl double bonds between 3 – 6 ppm which are readily apparent in **Fig. 4.14**. This is good evidence for the success of the hydrogenation reactions and the conversion of the unsaturated compounds to 2-hydro-6-pentadecyl benzoic acid (**1a**), which is referred to as anacardic acid in this work. The presence of a single compound is also indicated by sharper peaks in **Fig. 4.15** compared to **Fig. 4.14**.

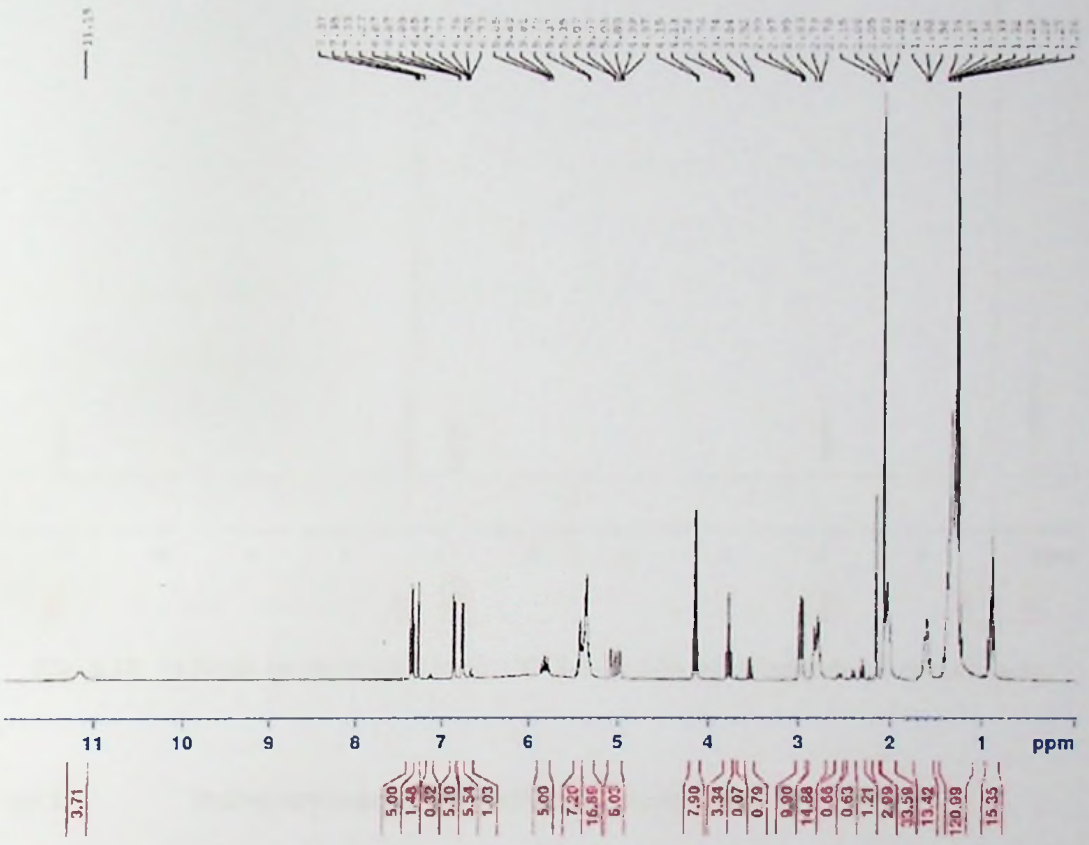


Fig. 4.14. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) for a mixture of anacardic acids.

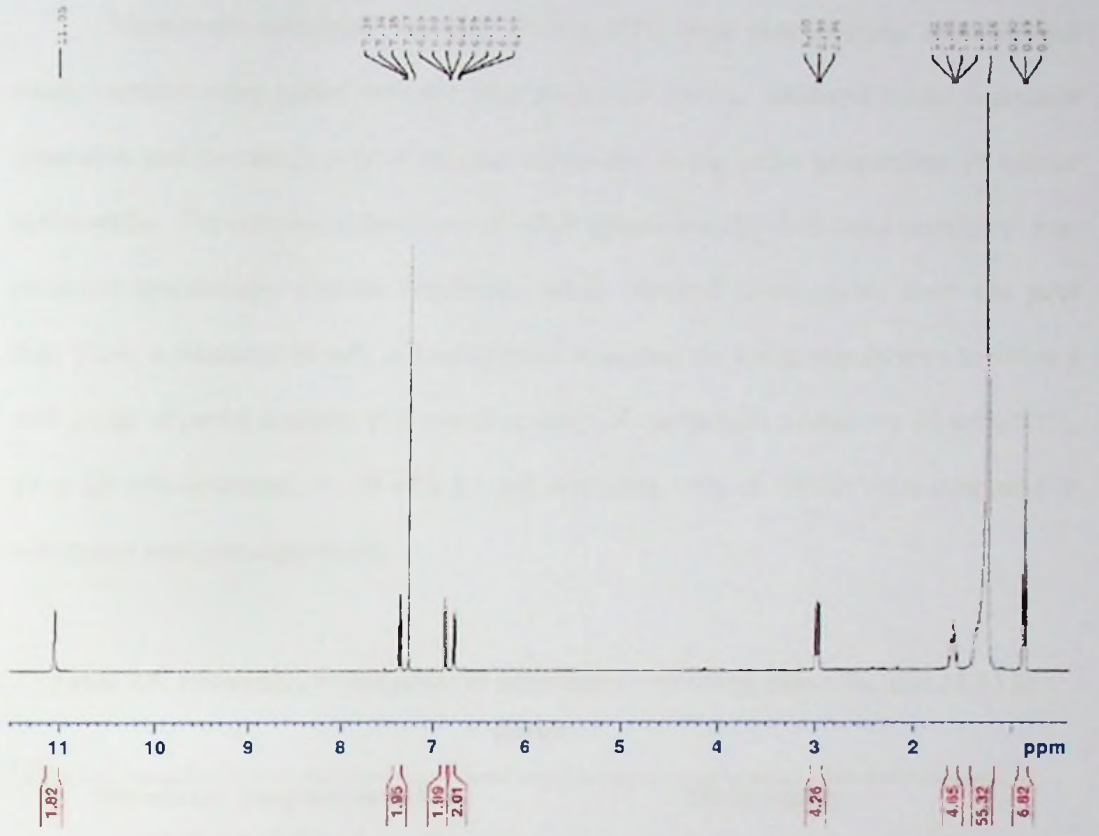


Fig. 4.15. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) for 2-hydro-6-pentadecyl benzoic acid.

4.3.3.1. Preliminary investigations with anacardic acid (AA)

Membranes were prepared with anacardic acid (AA) and a fixed 5:3 ratio of CTA-to-NPOE. Observations about the physical nature of the PIMs are reported in **Table 4.3** and show that 5 wt% AA produced clear, stable and homogeneous membranes. However, an insoluble white residue was obvious in membranes containing more than 5 wt% AA, indicating that AA is only sparingly soluble in NPOE. Anacardic acid is soluble in dodecanol and, consequently, small amounts were added as a modifier to the PIM formulation to improve the solubility of the acid in the membrane liquid phase. Membranes containing 5 wt% dodecanol proved useful for low amounts of 5 & 10 wt% AA, however, 10 or 20 wt% dodecanol was needed to dissolve larger amounts up to 20 wt% AA to produce transparent and homogenous membranes.

Membranes containing less than 30 wt% CTA were mechanically unstable and easily ruptured when peeled from the glass petri dish. This is attributed to the increased separation and disentanglement of polymer chains due to the larger proportions of carrier and modifier. The complete replacement of NPOE (plasticiser) by dodecanol (modifier) also produced mechanically unstable membranes which ruptured when peeled from the petri dish. Thus, a minimum 30 wt% of base polymer is needed for stable membranes to allow a wide range of carrier amounts to be tested. A series of membranes containing 30 wt% CTA, 10 or 20 wt% dodecanol, 5 – 20 wt% AA and remaining wt% of NPOE were evaluated in subsequent transport experiments.

Table 4.3. Preliminary investigation of membranes containing anacardic acid (AA) as carrier.

Membrane composition (wt%) CTA:AA:NPOE:Dodecanol	**Observation**
35:5:60:0	Transparent and flexible
34:10:56:0	Some ppt was observed
30:20:50:0	ppt was observed
34:10:51:5	Transparent and flexible
30:20:45:5	ppt
34:10:46:10	Transparent and stable
30:20:40:10	Transparent and stable
26:30:34:10	ppt and ruptured
34:10:26:20	Transparent and stable
30:20:30:20	Transparent and stable
26:30:24:20	ppt and ruptured
23:40:28:10	ppt and ruptured
34:10:0:56*	Ruptured
30:20:0:50*	Ruptured
26:30:0:44*	Ruptured

Where CTA, cellulose triacetate; NPOE, 2-nitrophenyl octyl ether; ppt, precipitates; *, membranes without NPOE.

4.3.3.2. Influence of amount of AA

The amount of AA in the range 5 – 20 wt% required for the transport of ACP was optimised. The findings as shown in **Fig. 4.16** and **Table 4.4** indicate that the initial flux improved with increasing amount of carrier up to 10 wt% and then decreased at 15 & 20 wt%. The initial flux improvement is associated with the formation of more ion-pair complex at the feed/membrane interface as the amount of carrier is increased. However, subsequent further increases in amounts of carrier results in decreased mobility of the carrier-solute complex in the membrane as indicated by the diminished flux at 15 & 20 wt% carrier. The higher flux for membranes containing 20 wt% compared to 10 wt% dodecanol at 15 and 20 wt% carrier indicates a likely improved solubility of carrier. A similar decrease in flux due to the precipitation of oxyethylate carrier on the membrane surface to form a layer that increased diffusional resistance for the transport of citric acid has been reported [40]. The current experiments indicate that 10 wt% AA is the optimal carrier amount in membranes also containing 10 or 20 wt% dodecanol as modifier. Therefore, the following "best" compositions were used in subsequent experiments to assess membrane stability and performance; PIM1: 30 wt% CTA, 10 wt% AA, 10 wt% dodecanol and 50 wt% NPOE; and PIM2: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol and 40 w% NPOE.

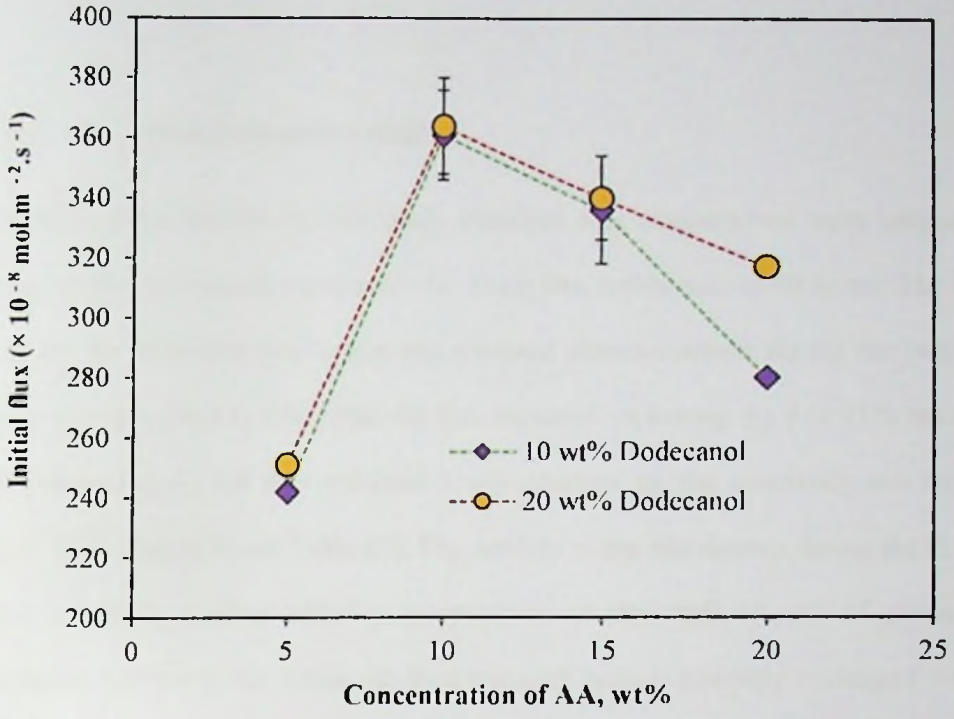


Fig. 4.16. Influence of carrier and modifier concentrations on the transport of ACP as indicated by the initial flux for two different PIMs, one with 10 wt% and other 20 wt% dodecanol. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2. Error bars represent a standard deviation of measurements from n = 3 experiments at 10 and 15 wt%.

Table 4.4. Influence of carrier and modifier concentrations on transport of ACP as indicated by the initial flux.

	10 wt% dodecanol		20 wt% dodecanol	
Carrier (wt%)	**Permeability ($\times 10^{-6}$ m.s^{-1})**	**Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})**	**Permeability ($\times 10^{-6}$ m.s^{-1})**	**Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})**
5	3.1	242	3.2	251
10	4.6	362	4.7	364
15	4.3	336	4.4	340
20	3.6	280	4.1	317

Experiment conditions: feed solution: 100 mg/L ACP, pH 7; receiving solution: phosphate buffer, pH 2.

4.3.3.3. Membrane stability studies

Membranes prepared from the previously identified best compositions were subjected to stability studies in transport experiments involving five cycles each of 48 hours. The results show that the initial flux was similar and remained almost constant during the two initial transport cycles (1 and 2). Thereafter, the flux decreased on average by 9 (± 2) % during the third transport cycle and then remained nearly constant for the remaining two transport cycles (4 - 5) (**Fig. 4.17** and **Table 4.5**). The stability of the membranes during the first two cycles is a likely result of effective encapsulation of the small 10 wt% of carrier. The subsequent decrease in flux during the third transport cycle is probably associated with the partitioning of dodecanol to the adjacent aqueous solutions which is known to occur [41, 42]. The dodecanol loss was more noticeable for PVC membranes that were found to be suitable for only one transport cycle [42], whereas membrane instability was significantly less for CTA membranes where only a 16% mass loss after eight transport cycles was noted [41]. Thus, the use of CTA polymer in the current study might have minimised the loss of dodecanol. The findings from the current study demonstrate that a membrane of composition 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol and 40 wt% NPOE is relatively stable and, thus, suitable for use in subsequent investigations. Membranes of this composition are referred to as optimal membranes in the following discussions.

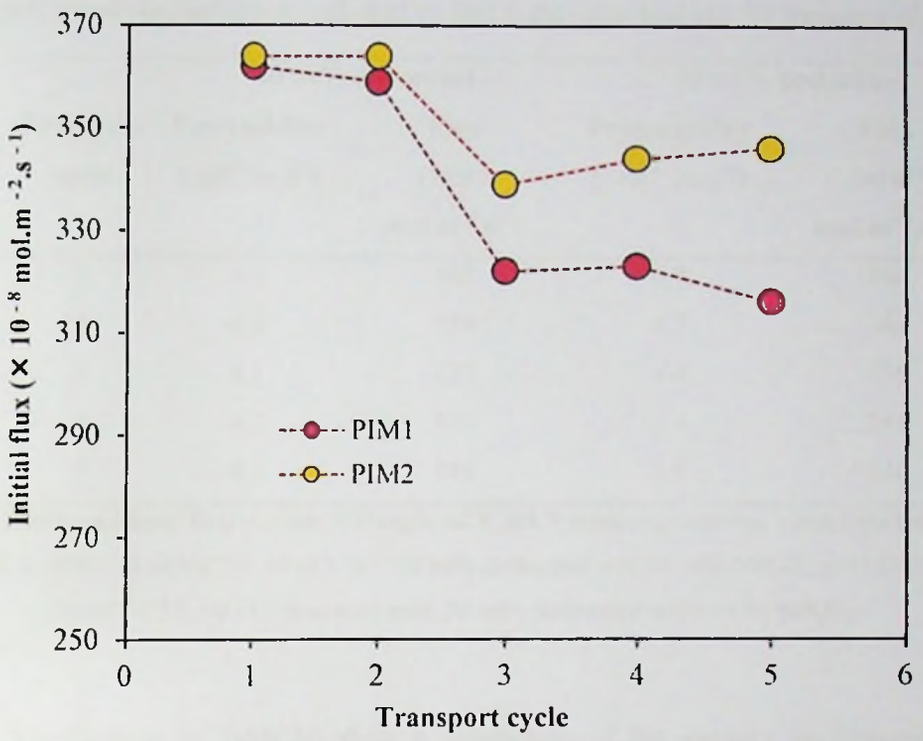


Fig. 4.17. Membrane stability as indicated by flux during repeated use for the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM1: 30 wt% CTA, 10 wt% AA, 10 wt% dodecanol & 50 wt% NPOE; and PIM2: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 w% NPOE.

Table 4.5. Membrane stability as indicated by flux during repeated use for transport of ACP.

	10 wt% dodecanol		20 wt% dodecanol	
Transport cycle	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})
1	4.6	362	4.7	364
2	4.6	359	4.7	364
3	4.1	322	4.4	339
4	4.2	323	4.4	344
5	4.1	316	4.5	346

Experiment conditions: feed solution: 100 mg/L ACP, pH 7; receiving solution: phosphate buffer, pH 2; PIM1: 30 wt% CTA, 10 wt% AA, 10 wt% dodecanol and 50 wt% NPOE, and PIM2: 30 wt% CTA, 10 wt% anacardic acid, 20 wt% dodecanol and 40 w% NPOE

The findings in **Table 4.6** show a comparison of the stability performance for membranes of optimal composition containing AAM or AA. The results indicate that regardless of the observed small changes in initial mass and flux, both membranes produce a high transport efficiency of around 97% during all five transport cycles. This observation demonstrates the potential suitability of the carriers for practical and commercial applications. In common, both carriers are eco-friendly, renewable and abundantly available because they are naturally produced by cashew plants. Consequently, other factors such as flux and chemical environments to which membranes are to be subjected could dictate the preference of one compound over the other.

Table 4.6. Comparison of stability for optimal membranes containing AAM or AA.

Carrier type	Cycle	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	Initial mass (mg)	TE (%)
AAM	1	337	50	99
	2	235	44	98
	3	212	42	97
	4	212	42	97
	5	211	41	95
AA	1	364	50	99
	2	364	46	97
	3	339	45	99
	4	344	44	99
	5	346	42	99

4.3.3.4. Optimisation of feed and receiving pH

The transport of ACP from a feed to receiving solution involves the counter-coupled transport of hydrogen ions (H^+). At the membrane/feed interface, the protonated amines are loaded into the membrane through the electrostatic attractions with the carrier as shown in Eqn. 4.1. The effectiveness of extraction significantly depends on the pH of the feed solution, whereby anacardic acid is deprotonated enabling formation of significant amounts of ion-pair complex at the membrane/feed interface. This improves the loading capacity in the membrane and, as a result, enhances the flux.

$$RCOO^{-}H^{+}(m) + Q^{+}(aq) \underset{k^{-1}}{\overset{k^{1}}{\rightleftharpoons}} RCOO^{-}Q^{+}(m) + H^{+}(aq) \qquad \text{(Eqn. 4.1)}$$

Where Q^{+} is ACP cation, $RCOO^{-}H^{+}$ anacardic acid, aq and m are solution and membrane phases, respectively.

On the other hand, at the receiving solution/membrane interface, hydrogen ions are loaded into the membrane when protonated amine molecules are released into the receiving solution by an ion-exchange process. Therefore, changes to the acidity of the receiving solution will affect the transport of the amine in a Fickian manner (concentration gradient), as well as changing the driving force of the chemical reaction at the interface. Thus, experiments using different pH of the feed and receiving solutions were performed to determine the optimal conditions for the extraction, back-extraction and transport of ACP.

Unsurprisingly, the results in **Fig. 4.18** and **Table 4.7** show that facilitated transport does not occur for a feed solution at pH 2, because anacardic acid ($pK_a \approx 5.8$ [43]) is not deprotonated and, as a result, cannot function as a cation carrier, even if the target is protonated. Significant transport occurs using a feed solution of pH 5 or 7 with a similar transport efficiency of 98%, however, the flux was significantly better, three times greater, at pH 7 (**Table 4.7**). The pH of the feed solution affects the form of the carrier and target at the membrane/feed interface which, consequently, determines the loading capacity of the carrier-target ion-pair in the membrane. This significantly affects the transport kinetics, but not the total amount of solute eventually transported. The observed improved flux at pH 7, which is at least one unit greater than the pK_a of anacardic acid, is associated with increased amounts of deprotonated carrier, resulting in an optimal flux of 364×10^{-8} $mol.m^{-2}.s^{-1}$.

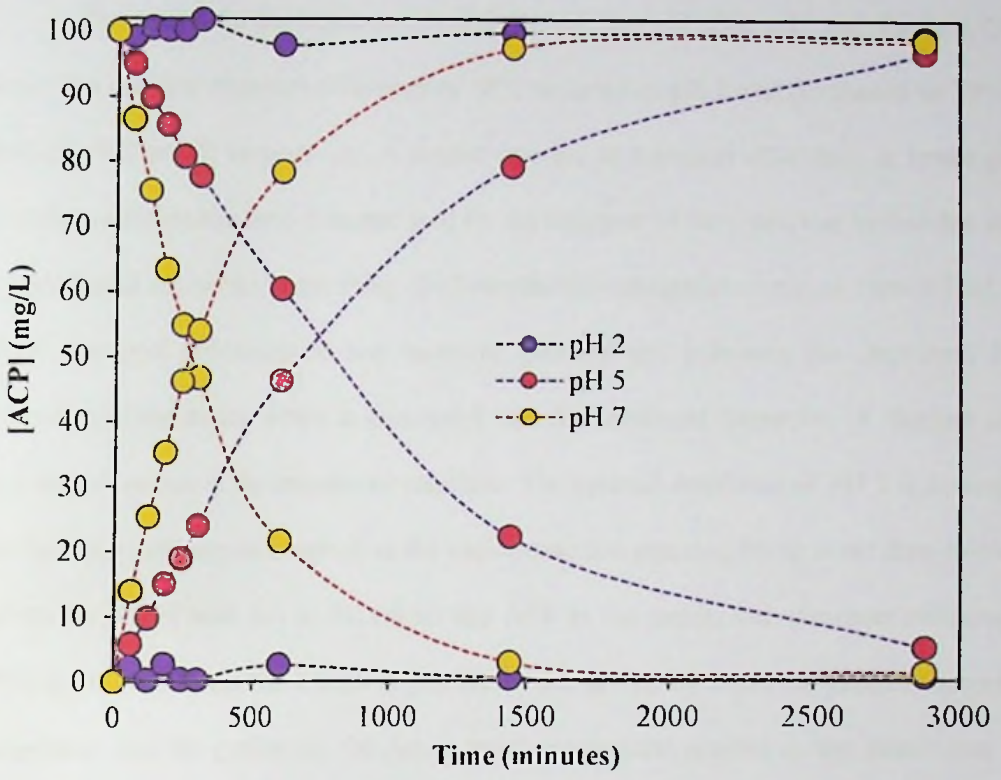


Fig. 4.18. Influence of the pH of the feed solution on the transport of ACP. Experiment conditions: feed solution 100 mg/L ACP at pH 2, 5 and 7; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE.

Table 4.7. Influence of feed and receiving solution pH on transport of ACP.

Feed pH	Receiving pH	Initial flux $\times 10^{-8}$ mol.m^{-2}.s^{-1}	TE_{48} (%)
7	2	364	98
7	5	170	79
7	7	130	50
5	2	123	98
2	2	0	0

Experiment conditions: feed solution 100 mg/L ACP at pH 7; receiving solution phosphate buffer at pH 2, 5 and 7; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE.

The results for the influence of receiving solution pH (**Fig. 4.19** and **Table 4.7**) also show that the best transport efficiency of 98% occurred at pH 2 and decreased to 79% and 50% at pH 5 and 7, respectively. A similar increase in transport efficiency at lower pH of receiving solution has been demonstrated for the transport of bipyridinium herbicides across a bulk liquid membrane containing di-(2-ethylhexyl) phosphoric acid as carrier [31]. The better transport efficiency at low receiving solution pH indicates the improved back-extraction of the amine which is associated with the enhanced formation of charged amine and neutral carrier at the membrane interface. The optimal condition of pH 2 is synergistic for the chemical species involved in the back-extraction process, being more than two units below the pK_a of both AA as the carrier and ACP as the target. The transport efficiency of 79% at pH 5 indicates the transport process is still driven by a proton gradient across the membrane, and the preference for AA to exist as a neutral species in the membrane. The absence of a proton gradient at pH 7 for both the receiving and feed solutions explains the 50% transport efficiency, whereby an equilibrium concentration of ACP is established in both.

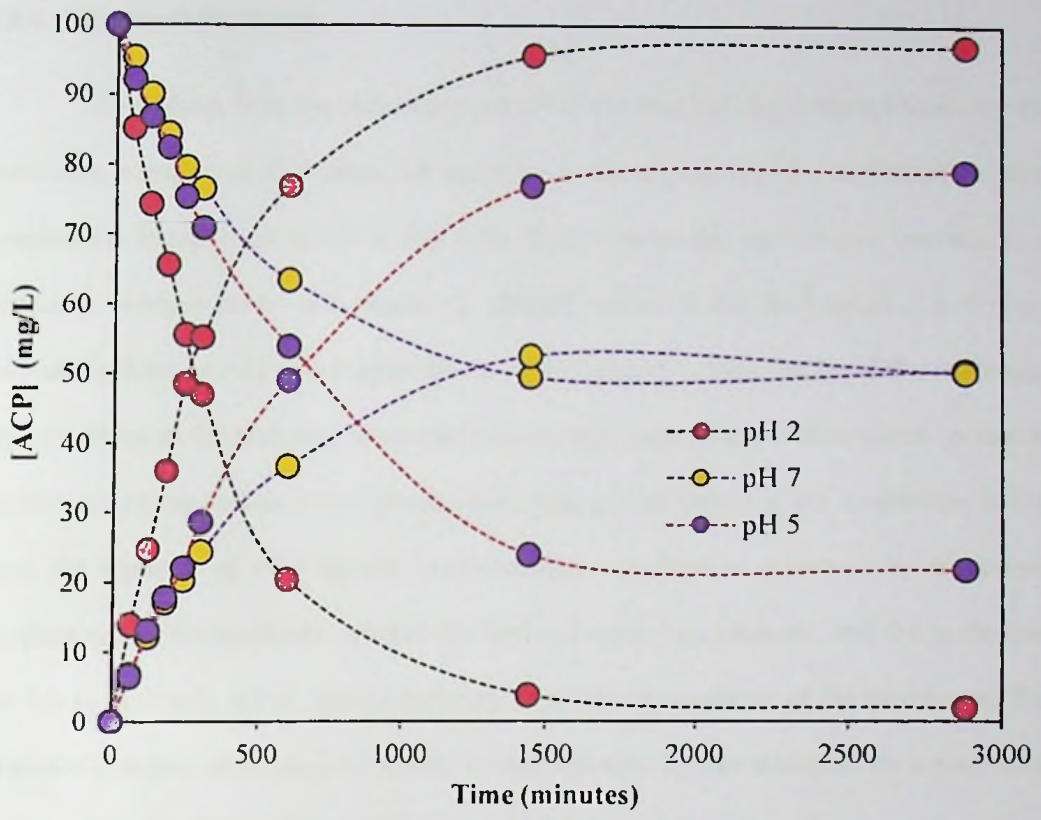


Fig. 4.19. Influence of pH of the receiving solution on transport of ACP. Experiment conditions: feed solution 100 mg/L ACP at pH 7; receiving solution phosphate buffer at pH 2, 5 or 7; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE.

Similarly, the initial flux as shown in **Table 4.3** also increased in the order of pH 7 < pH 5 < pH 2 of the receiving solution, with this trend conforming to the observed increase in the pH gradient across the membrane. This provides further evidence that the pH gradient is essential for the transport process as has been previously demonstrated for other positively charged amines [44]. Therefore, a receiving solution of pH 2 and a feed solution of pH 7 are indicated from the current investigations as conditions that produce the optimal transport efficiency and flux. Thus, these conditions are suitable for subsequent investigations involving the transport of ACP.

4.3.4. Transport mechanism

The findings from the optimisation of pH of the feed and receiving solutions for the membrane transport of ACP using AA as carrier permit a proposal of a facilitated counter-coupled ion transport as shown in **Fig. 4.20**. This involves the electrostatic interaction of positively charged amine with negatively charged carrier at the feed solution/membrane interface to form an ACP-AA ion-pair complex. Subsequently, the complex diffuses through the membrane to the receiving solution/membrane interface, where it dissociates to release amine via a cation exchange with protons that forms neutral carrier in the membrane. In this case, the transport of ACP against its concentration gradient is governed by the proton gradient across the membrane between the feed and receiving solutions, and the preference for AA to exist as a neutral species in the hydrophobic environment of the membrane. The proposed transport mechanism is similar to that reported for the transport of amino acids across liquid membranes containing di-(2-ethylhexyl) phosphoric acid as a carrier [25, 31, 34, 45].

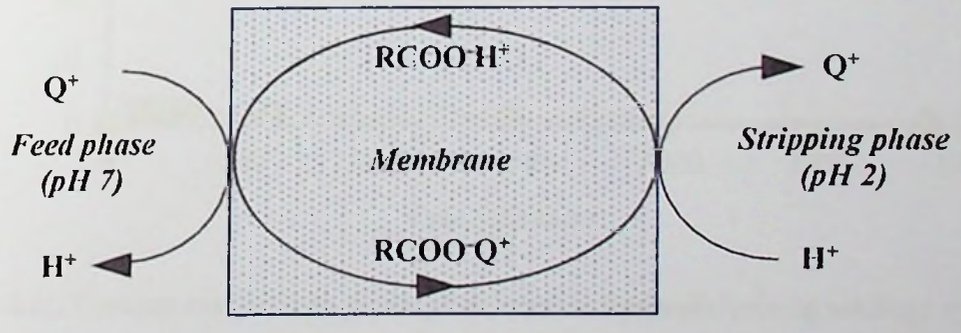


Fig. 4.20. Generalised facilitated counter-coupled transport mechanism of positively charged ACP (Q^+) across a polymer inclusion membrane containing AA ($RCOO^-H^+$) as carrier from a feed solution of pH 7 to a receiving solution of pH 2.

The existence of AA in the negatively charged form at the feed-membrane interface was further investigated using the same conditions by the transport of picloram ($pK_a \approx 2.30$)

which would exist as an anion in the feed solution at pH 7. The results (**Fig. 4.21**) are consistent with expectations and show that no transport occurred involving either facilitated or passive diffusion of picloram across the membrane. This is because at the membrane interface at pH 7 both picloram and AA have a negative charge, resulting in electrostatic repulsion between the chemical species. This provides supporting evidence that AA functions as a cation exchange carrier in the transport of ACP.

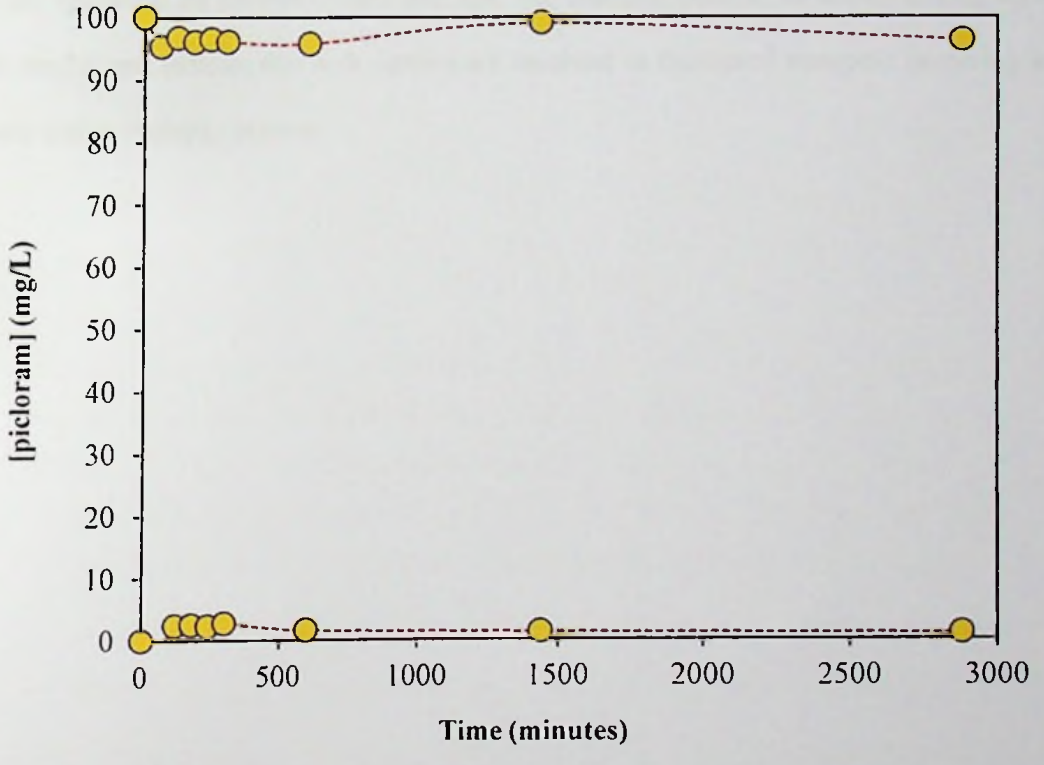


Fig. 4.21. Transient concentration profile of picloram in feed and receiving solutions as a function of time. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE.

4.3.5. Transport kinetics

The transport of ACP across a membrane containing anacardic acid as carrier has been shown to involve a cation exchange process similar to that of other acidic carriers [31]. Thus, it was prudent to evaluate the transport kinetics under the same conditions using the "novel" AA compared to a "familiar" acidic carrier. The carrier chosen for this purpose was bis-(2-ethylhexyl) phosphoric acid (DEHPA) ($pK_a \approx 3.24$ [46]). The pK_a of DEHPA is more than two units below the pH of the feed, indicating that it should similarly form and exist as a base species at the feed/membrane interface. The transport profiles as shown in **Fig. 4.22** are similar and indicate that both carriers are involved in facilitated transport involving a likely cation exchange process.

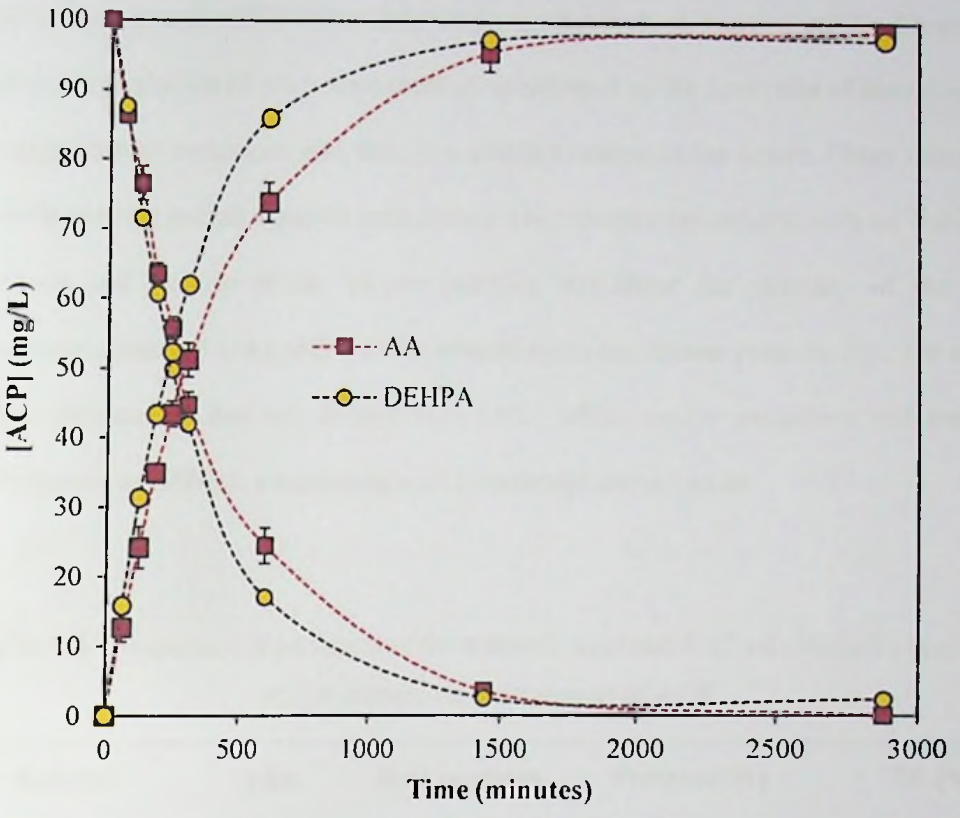


Fig. 4.22. Transient concentration profiles of ACP in feed and receiving solutions as a function of time using AA or DEHPA as carrier. Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% carrier, 20 wt% dodecanol & 40 wt% NPOE. Error bars represent a standard deviation of measurements from n = 3 experiments for anacardic acid as carrier.

The performance of each carrier was similar as indicated by permeability and transport efficiency data as reported in **Table 4.8**. Specifically, the similar permeability values of 525 and 468 ($\times 10^{-8}$ m/s) for di-(2-ethylhexyl) phosphoric acid and anacardic acid, respectively, are a strong indicator that both carriers are involved in the same type of transport mechanism, namely a cation exchange process. The small difference in the permeability is likely associated with the amounts of each deprotonated carrier species involved in the transport process due to the different pK_a values. At pH 7, anacardic acid ($pK_a \approx 5.8$) does not fully exist as a base, whereas DEHPA ($pK_a \approx 3.24$) exists primarily as a

deprotonated species and is able to function more effectively as a cation carrier. However, a significant proportion of AA is deprotonated, as indicated by the 16:1 ratio of base-to-acid at the experimental conditions, and, thus, is available to transport the amine. Other factors can contribute to the overall transport performance when comparing carriers, such as: the carrier viscosity and the size of the ion-pair complex that affect the viscosity of the liquid membrane phase and permeability of the ion-pair in the membrane, respectively. The current results demonstrate that AA derived from CNSL offers similar extraction and transport performance to DEHPA, a commonly used commercial cation carrier.

Table 4.8. Comparison of performance for anacardic acid and di-(2-ethylhexyl) phosphoric acid as carriers for the transport of ACP.

Carrier	pKa	Rate constant ($\times 10^{-5}$ s^{-1})	Permeability ($\times 10^{-8}$ m/s)	TE (%)
AA	5.8 [43]	4.25	468	98
DEHPA	3.24 [46]	4.77	525	98

Experiment conditions: feed solution 100 mg/L ACP, pH 7; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% carrier, 20 wt% dodecanol & 40 wt% NPOE.

4.3.6. Competitive transport

Many contaminants of various chemical forms are normally found in environmental water samples with the broad range of compounds loosely categorised on the basis of their physicochemical properties. Consequently, a membrane applied to real environmental samples containing agricultural chemicals from water runoff is likely to involve the competitive transport of more than one compound. Thus, an understanding of how a membrane performs during competitive transport is important in determining the potential

feasibility for applications involving real environmental samples. As a result, the competitive transport of a sample containing a mixture of ACP, and paraquat and diquat as examples of heterocyclic herbicides was performed.

The transport results are summarised in **Table 4.9** and **Fig. 4.23** and indicate that AA is an effective carrier for all three compounds because each had a similar transport efficiency of greater than 97%. The neutral pH of the feed solution represents almost optimum environmental water conditions, and at this pH the three compounds are present as cations. Therefore, the base of AA formed at the membrane interface is able to function as an effective cation carrier and form ion-pair complexes. Consequently, the transport process involves the facilitated diffusion of carrier-solute ion-pair complexes as shown by the indicative rapid change in the concentration of each solute during the initial stages and shown in **Fig. 4.23**

Table 4.9. Permeability, transport efficiency and lipophilicity of ACP, paraquat and diquat.

Compound	Log K_{ow}	Permeability ($\times 10^{-8}$ m/s)	TE (%)
ACP	1.21	331 ± 22	98 ± 3
Paraquat	- 4.5	308 ± 32	98 ± 2
Diquat	- 4.6	276 ± 12	97 ± 2

Experiment conditions: feed solution 100 mg/L ACP, paraquat and diquat, pH 7; receiving solution phosphate buffer solution, pH 2; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE.

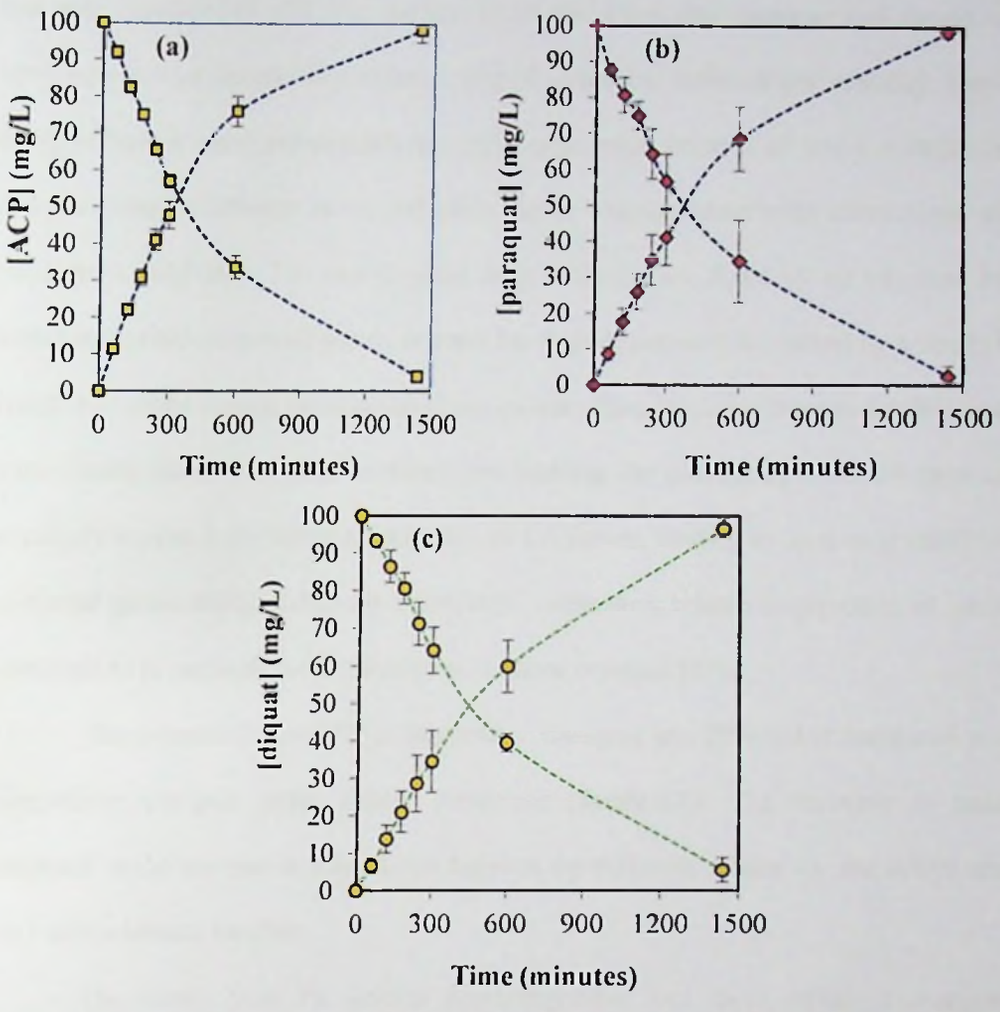


Fig. 4.23. Transient concentration profiles of ACP (**a**), paraquat (**b**) and diquat (**c**) in feed and receiving solutions as a function of time. Experiment conditions: feed solution 100 mg/L ACP, paraquat, and diquat, pH 7; receiving solution phosphate buffer solution, pH 2; PIM: 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol & 40 wt% NPOE. Error bars represent a standard deviation of measurement for n = 3 experiments.

The membrane permeability for each compound is similar and increased in the order of ACP > paraquat > diquat which is consistent with the lipophilicity as indicated by the octanol-water partition coefficient (log K_{ow}) and displayed in **Table 4.9**. A similar preferential extraction indicated by a higher flux of lipophilic compared to hydrophilic amino compounds into liquid membranes containing di-(2-ethylhexyl)phosphoric as carrier

has been reported [47, 48]. The current results also show that paraquat and diquat which have very similar lipophilicity values displayed somewhat different permeability. Diquat is likely to have a lower permeability compared to paraquat because of lower stability of the ion-pair complex between carrier and solute due to weaker electrostatic interactions arising from steric hindrance. The two pyridine rings in diquat are fixed by an ethylene bridge which makes the compound planar, whereas the rings in paraquat are joined by a single bond and free to rotate making the compound non-planar. Thus, paraquat is more flexible and can more readily adopt a structural configuration enabling the cationic pyridine nitrogen atoms to closely approach the active anionic sites of the carrier, leading to increased stability and improved permeability. Enhanced electrostatic interaction related to structure of paraquat compared to diquat with humic substances has been reported [49].

The permeability of ACP in competitive transport was 20% lower compared to non-competitive transport under similar conditions (**Table 4.8**). The decrease is possibly attributed to the increase in competition between the different solutes for the active sites at the feed/membrane interface.

The results from the current non-competitive and more stringent competitive transport experiments has demonstrated that AA is a suitable carrier for extraction and transport applications of organics that can be protonated at or about pH 7, or which commonly exist as cationic compounds. Accordingly, AA should be further investigated as a useful "green" carrier for other compounds, such as inorganic and bioinorganic compounds, which can also exist as cations

4.4. Conclusion

The experiments reported in this chapter explored the use of anacardic acid derived from CNSL as a cheap and eco-friendly carrier for applications using polymer inclusion

membranes. To the best of our knowledge, this is the first report of a carrier derived from plants for use with PIMs. An optimal membrane composition of 30 wt% CTA, 10 wt% AA, 20 wt% dodecanol and 40 wt% NPOE producing flux $364 \pm (16) \times 10^{-8}$ mol.m^{-2}.s^{-1} and transport efficiency 98 ± 1% for the transport of ACP as a model compound was identified. No significant difference in membrane performance was apparent using either "raw" anacardic acid containing a mixture of closely related compounds, or "pure" anacardic acid prepared from the raw material and containing only saturated anacardic acid. Therefore, the economic benefit of using the raw product outweighs the small performance benefit associated with the purified product for single or small repeat use applications. The use of purified anacardic acid could be beneficial in applications involving complicated sample matrices in which some compounds might react with components of raw anacardic acid containing unsaturated sites. Optimising the solution conditions, namely a pH of 7 and 2 for the feed and receiving solutions, respectively, resulted in almost complete (98%) transport of ACP.

A comparison of anacardic acid with DEHPA, a commercial cation carrier, gave remarkably similar and good transport performance as indicated by permeability and transport efficiency. The stability of the optimal membrane composition was demonstrated with some loss of flux noted during the first two cycles, whereas a transport efficiency of 99 ± 1% was mostly unaffected over the five consecutive transport cycles. Some mass loss from the membrane was noted during stability studies. However, any loss associated with anacardic acid is of less concern because it is readily degraded in the environment to less toxic compounds, compared to similar mass loss and degradation involving some commercial carriers. Overall, the observed stability is similar to other PIMs which indicates suitability for short-term practical and commercial applications.

The optimal membrane was tested for the competitive transport of a mixture of ACP, paraquat and diquat, and returned an average transport efficiency of 97 ± 1%. This demonstrates the potential application to other organic solutes that can be protonated or exist as cations at or about pH 7. Additionally, no transport of negatively charged organics was observed when using picloram as a representative compound. This indicates the potential of using similar PIMs for samples of environmental water which, in many cases, are affected by the formation of a fouling layer on the membrane surface due to adsorption of negatively charged humic substances. However, in the current work, only synthetic solutions made from phosphate buffer were used. Consequently, an investigation using PIMs containing anacardic acid for environmental water applications is warranted and this will be addressed in subsequent work in chapter 5.

The current study was limited to the extraction and transport of organic compounds. However, anacardic acid, like many other cation carriers, could also be applied to the transport and recovery of inorganic and bioinorganic species. Therefore, future investigations should explore the use of anacardic acid for metals and other inorganic species. The current findings demonstrate that replacing commercially available carriers, such as DEHPA, with "green" carriers derived from plants is feasible. Any subsequent widespread or large-scale use of "green" carriers to replace current commercial carriers could return both economic benefits from lower chemical costs, and environmental benefits from a lessened risk of harm from using less toxic and more readily degraded chemicals. Thus, further investigations are needed to explore the use of anacardic acid and similarly sourced compounds for extraction and transport purposes of a variety of chemical species. The results from which could open a new direction for the application of PIMs and the extraction industry.

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Chapter 5: Applications of polymer inclusion membranes for environmental waters.

5.1. Introduction

The accumulation of herbicide residues and degradation by-products in the environment is increasing due to global and intensified applications of persistent herbicides for increased food production. Consequently, there is an ongoing need for the analysis of herbicide residues and by-products from environmental waters to measure levels and limit the likely impact on the ecosystem. However, the direct analysis of chemicals from environmental samples is, in most cases, impracticable due to low concentrations and matrix interference effects [1, 2]. As a consequence, an effective analysis often requires the pre-treatment of samples in order to increase the concentration of analytes to quantifiable levels and remove potential matrix interferences. The process of gathering solutes from a large to small volume or surface area as a method to increase concentration to measurable levels is known as pre-concentration [3].

Solvent extraction techniques are widely used, efficient and reliable for the removal (separation) of interferences and pre-concentration of target solutes [4]. However, these techniques are not easily automated and often require significant amounts of time, labour and reagents [5]. Therefore, the development and use of alternative techniques for particular applications is worthwhile. Solid phase extraction involving the partition of solutes between a solid and liquid phase offers method simplicity, high separation factor and minimised use of reagents [6]. However, the requirement of separate extraction and back-extraction stages is time consuming and limiting for high-throughput sampling. Thus, separation techniques, such as liquid membranes, that integrate extraction and back-extraction in a continuous process are very convenient. A type of liquid membranes called polymer inclusion membranes (PIMs) have become popular due to enhanced stability and versatility compared to other types of liquid membranes [7]. As a result, PIMs have emerged as a powerful tool for sample preparation including pre-concentration [8].

5.1.1. Applications of PIMs for sample preparations

The use of PIMs for sample preparation is generally categorised into two methods either passive or facilitated diffusion, depending on the nature of the driving force. Passive diffusion does not involve the use of an external driving force whereas facilitated diffusion uses an external driving force, such as an electric-field in electro-membrane extraction [9]. The diffusion process can be performed online where samples are directly injected and off-line involving manual collection of samples for analysis. Some representative examples of applications using PIMs for sample preparation are presented in **Table 5.1**.

Table 5.1. Some examples showing applications of PIMs for preparation of samples.

Target species	PIM composition (wt%)	Media	References
Antibiotics	26% Aliquat 336 44% NPOE 30% CTA	Well and river water	[10]
Oxytetracycline	6% Cyanex 11% NPOE 83% CA	Milk samples	[11]
GLYP and AMPA	20% Aliquat 336 20% NPOE 60% CTA	Spiked river water	[12]
Drugs abuse	35% D2EHPA 13% TEHP 52% CTA	Human plasma	[13]
Cationic herbicides	32% D2EHPA 14% TEHP 54% CTA	River water	[14]
Anionic herbicides	4.5% Aliquat 336 19.1% TEHP 76.4% CTA	River water	[14]
Non-steroidal anti-inflammatory drugs and highly polar acidic drugs	29% CTA 71% Aliquat 336	Human urine samples	[15]
Chlorpyrifos, diazinon and cyprodinil	70% CTA 30% NPOE	River water	[16]

Where AMPA, aminomethylphosphoric acid; CTA, cellulose triacetate; GLYP, glyphopshate; NPOE, 2-nitrophenyloctyl ether; TEHP, tris(2-ethylhexyl) phosphate; CA, cellulose acetate; D2EHPA, di(2-ethylhexyl) phosphoric acid. Membrane compositions are in mass percentages (wt%).

The aim of experiments in this chapter is to assess the feasibility of the optimal PIMs, previously identified for extraction and transport of selected representative target compounds, as a sample pre-concentration method for environmental waters.

5.2. Experimental

5.2.1. Chemicals and reagents

Some additional chemicals and reagents to those previously reported in **Sections 2.2.1, 3.2.1** and **4.2.1** were used. Sodium carbonate (99.9%), Merck Pty. Ltd, Australia, and sodium sulphate (99.0%), sodium hydrogen carbonate (99.7 - 100.3%), sodium nitrate (99.0%), Acetone (99.9%) all Ajax chemicals, Australia.

5.2.2. Sample collection

An environmental water sample was collected in November 2017 from the moat system at the Bundoora campus of La Trobe University. The moat system collects run-off water from neighbouring residential and recreational areas, and the university agricultural and wildlife reserves. The sample was filtered through a 0.45-micron filter before use.

5.2.3. Water analysis

Concentrations of common anions in environmental water namely, chloride, phosphate, sulphate and nitrate were determined using a Metrohm Basic 83 Ion-chromatograph with a Metrosep A Supp 5e150/4.0 anion separation column. An eluent of 4 mmol/L Na_2CO_3 and 1 mmol/L $NaHCO_3$ in 10% acetone was used. Standards and quality control solutions were prepared from 1 g/L stock solutions of dried analytical grade salts.

5.2.4. Transport experiments

Transport experiments were conducted using the permeation cell as previously described in **Section 2.2.3**. The experiments were performed using the experimental conditions presented in **Table 5.2**. Concentrations of target solutes were determined using a UV-Vis spectrophotometer as previously described in **Sections 2.2.5** and **3.2.4**, respectively. Except for the stability experiments, a new and different membrane was used for each experiment.

Table 5.2. Experimental condition for the transport of picloram and 4-amino-2-chloropyridine (ACP) from environmental water.

Feed solution (100 mg/L)	Receiving solution	Membrane composition
Picloram	0.25 M NaCl, pH 7	25 wt%, CTA, 30 wt% Aliquat 45 wt% NPOE
ACP	0.1 M phosphate buffer, pH 2	30 wt% CTA, 10 wt% anacardic acid 20 wt% dodecanol 40 wt% NPOE

5.2.5. Membrane stability studies

The stability studies were performed using the experimental conditions similar to those described in **Section 5.2.4**. However, the experiments were performed in five consecutive transport cycles using fresh feed and receiving solutions in each cycle without changing the membrane.

5.2.6. Pre-concentration experiments

Pre-concentration experiments were performed using a membrane-based device made according to the reported procedure [10, 17]. The device is made of an open glass tube with a PIM held at the bottom using a screw cap as shown in **Fig. 5.1**. A surface area of 1.26×10^{-3} m^2 was exposed to a source solution. The tube containing the membrane was then partially submerged into a

mechanically stirred feed solution (250 mL) containing 500 µg/L of the target solutes. A receiving solution (10 mL) of 0.25 M NaCl, pH 7 for picloram and 100 mM pH 2 phosphate buffer for a mixture of ACP, paraquat and diquat was used. All the pre-concentration experiments were conducted at room temperature (25 ± 1 °C) and concentrations of target solutes were measured using a Shimadzu LC-20AT High-Performance Liquid Chromatography containing a Apollo™ C18, 5 µ, 150 mm x 4.6 m ID column and a UV detector. For picloram, the determination was made using an isocratic mobile phase of 70:30 (v/v%) methanol and pH 2 phosphate buffer mixture at a flow rate of 0.5 mL/min, whereas for the mixture of ACP, paraquat and diquat the measurement was performed as described in **Section 4.2.6.6**.

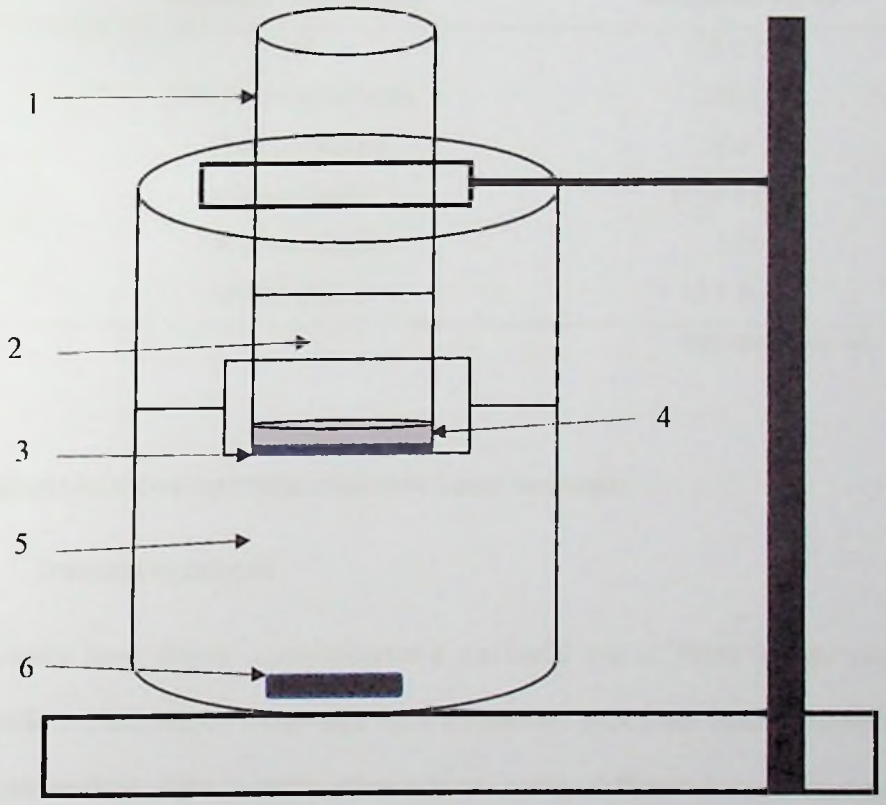

Fig. 5.1. PIM-based device for pre-concentration (1- device, 2- receiving solution, 3- O-ring, 4- PIM, 5- feed solution, 6- magnetic stirrer).

5.3. Results and discussion

5.3.1. Waters analysis

Natural water can contain a variety of dissolved and suspended compounds that could interfere with extraction and transport processes. In particular, other anions can form ion-pairs with the quaternary ammonium carrier because it is non-selective and this could limit its effectiveness for the task. Therefore, the chemical parameters of pH, conductivity and common inorganic anions of the water sample were evaluated and determined to be within normal expectations as shown in **Table 5.3**.

Table 5.3. Chemical parameters for environmental water.

Chemical parameters	Measured value
pH	7.8 ± 0.2
Conductivity (μS/cm)	224 ± 5
Chloride (mg/L)	20 ± 3
Nitrate (mg/L)	0.72 ± 0.30
Phosphate (mg/L)	ND
Sulfate (mg/L)	12.3 ± 3.5

ND-not detected

5.3.2. Transport and pre-concentration of pyridine-based herbicides

5.3.2.1. Transport of picloram

The results from chapter 2 demonstrated a successful use of PIMs for the extraction and transport of picloram and related compounds from a synthetic phosphate buffer solution. However, the chemical composition of the synthetic solution is reasonably different from environmental water. In addition to other inorganic anions, environmental water can contain humic substances which could exist as anions at this pH and this could have a significant adverse effect because of similar extraction chemistry. For this reason, it was deemed necessary to investigate the transport of picloram as a model compound for negatively charged organic anions from environmental water. The chloride concentration of 20 mg/L (**Table 5.3**) in the moat water used as the feed solution is significantly

lower than in the receiving solution (0.25 M, 8900 mg/L). Consequently, a similar chloride concentration gradient across the membrane, as in earlier experiments, was used to provide the necessary driving force for the "uphill" transport of picloram.

The results in **Fig. 5.2** show that picloram was successfully transported from environmental water with an efficiency of 97% which is similar to earlier experiments using a phosphate solution. However, rather surprisingly, the observed initial flux of 329×10^{-8} mol.m^{-2}.s^{-1} is 12% higher than that noted in earlier non-competitive experiments. We infer that the better flux is due to increased mobility of picloram in solution due to electrostatic repulsion with negatively charged humic substances; as has been proposed to explain the high-water mobility of the herbicide in the environment [18]. Additionally, the improved initial flux is also a likely result of the larger hydrodynamic size of the humic substances, containing many polar functional groups, compared to the smaller herbicides (**Fig. 5.3**) [19]. This slows their effective mobility in solution and, consequently, reduces their ability to compete with picloram. We also envision that the bulky size of ion-pairs of Aliquat with anionic humic substances would significantly limit their permeability. Any such ion pairs are likely restricted to the membrane surface where the humic anions could undergo ion exchange with more mobile anions. Consequently, the transport profile for the fifth transport cycle indicates that the transport process is likely to be dominated by-passive diffusion as shown by linear change in the concentration of picloram in both feed and receiving solutions throughout the transport cycle (**Fig. 5.2**).

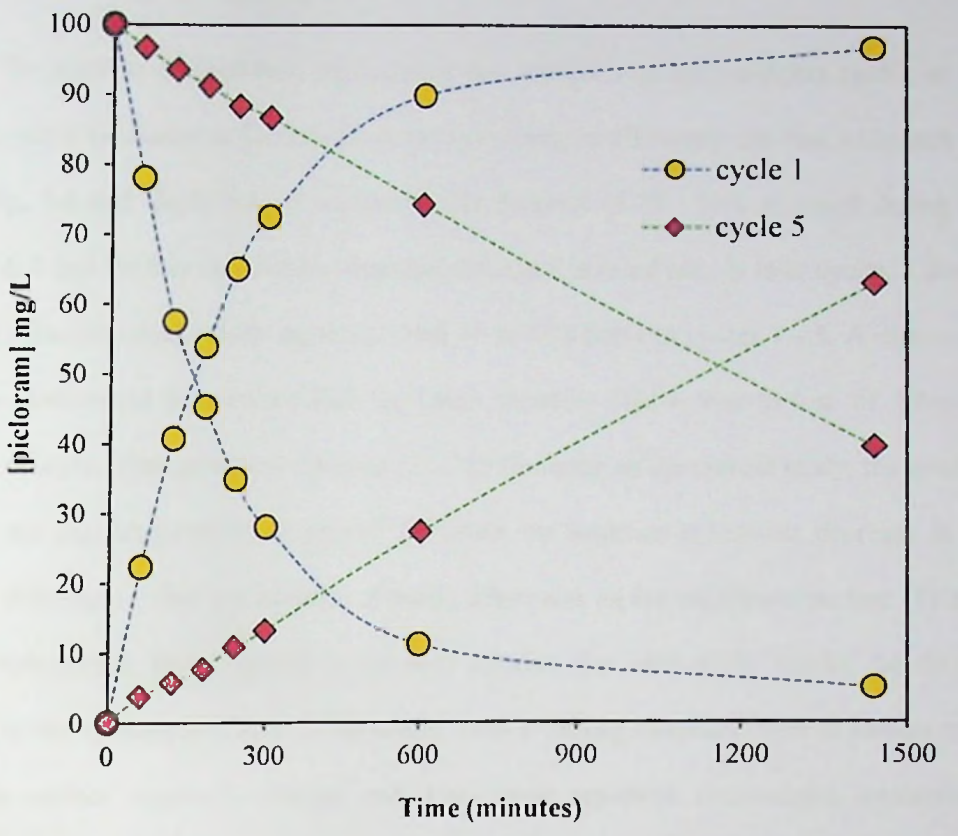

Fig. 5.2. Transient extraction profiles for the transport of picloram from environmental water in repeat experiments using the same PIM. Experiment conditions: feed solution 100 mg/L picloram, pH 8; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

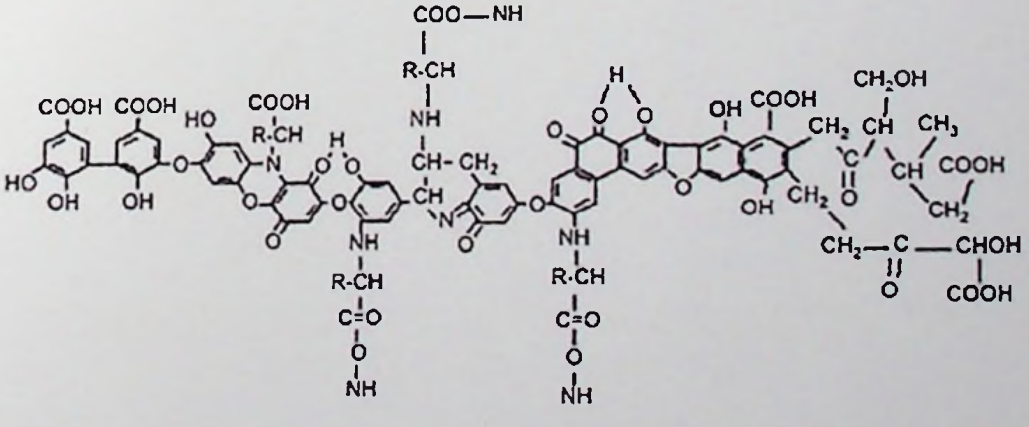

Fig. 5.3. Molecular structure of humic acid [20].

5.3.2.2. Membrane stability studies

The stability of membrane performance was studied over five transport cycles of picloram using the same membrane and revealed a decrease in transport efficiency and flux with each transport cycle (**Fig. 5.4 and Table 5.4**). A substantial flux decrease of 25 – 30% occurred during transport cycles 2 & 3 and the flux continued to decrease, albeit at a reduced rate, in later cycles. Likewise, the transport efficiency dramatically decreased from 97 to 63% between cycles 1 - 5. A decrease in flux was also observed in later cycles from the buffer solution. This is due to loss of Aliquat to the adjacent aqueous solutions which is known [21, 22]. However, in the current study, the general trend was that the flux progressively decreased. Therefore, the assertion is that the decrease in flux and transport efficiency is due to adsorption of humic substances on the membrane surface. This forms a fouling hydrophobic layer exposed to the feed solution that effectively blocks the diffusion of picloram to the membrane surface. Additionally, such a fouling boundary layer is known to make a membrane surface negatively charged and, thus, cause repulsive electrostatic interactions with negatively charged solutes like picloram at this pH [23].

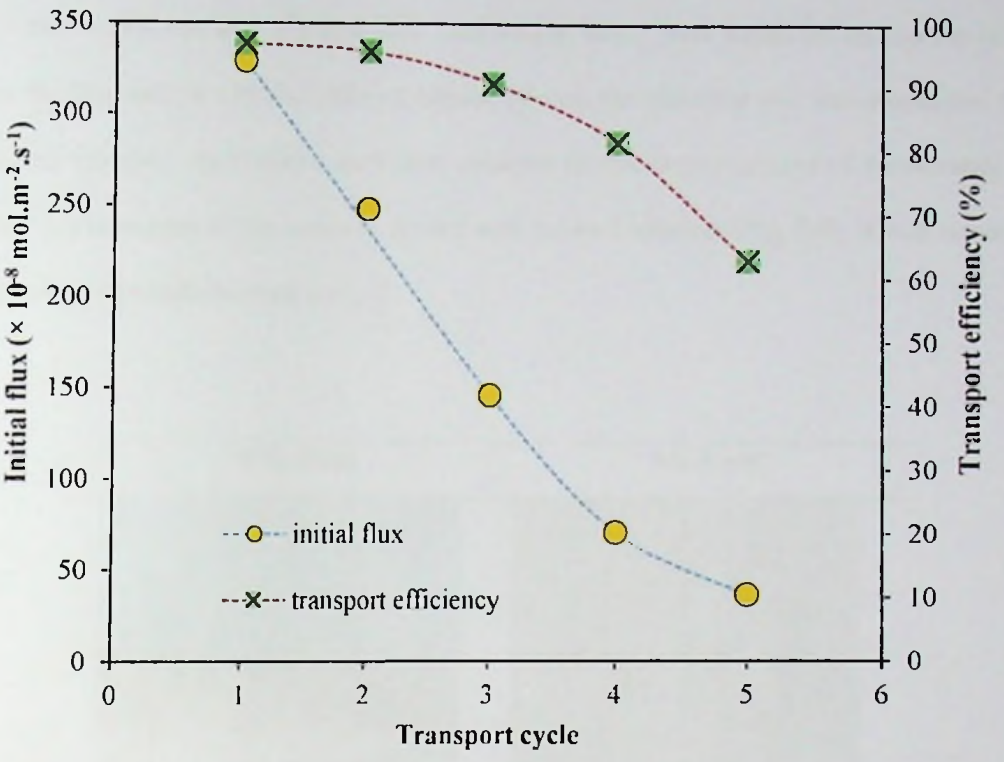

Fig. 5.4. Membrane stability as indicated by transport efficiency and flux for the transport of picloram from environmental water. Experiment conditions: feed solution 100 mg/L, pH 8; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

Table 5.4. Membrane performance as indicated by flux, transport efficiency and initial mass for the transport of picloram from environmental water.

Transport cycle	Initial mass (mg)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
1	50.0	8.0	329	97
2	36.1	6.0	248	96
3	33.2	3.5	146	91
4	32.6	1.7	70.7	82
5	30.6	0.9	36.5	63

Experiment conditions: feed solution 100 mg/L, pH 8; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

As mentioned earlier, the adsorption of humic acid to the membrane surface is likely due to the large hydrodynamic size of ion-pairs Aliquat-humic acid which limits their diffusion in the

membrane. Significantly slower diffusion of Aliquat-humic acid compared to Aliquat-fluvic acid ion-pairs across a PIM has been reported [24]. Additionally, others have noted the adsorption of humic acid on the feed side of a PIM containing Aliquat, whereas the receiving side was unaffected [25]. In the current transport experiments, qualitative evidence for the humic content of membranes comes from the brown colour of the region in contact with the feed solution (**Fig. 5.5**); which is consistent with previous reported observations [24].

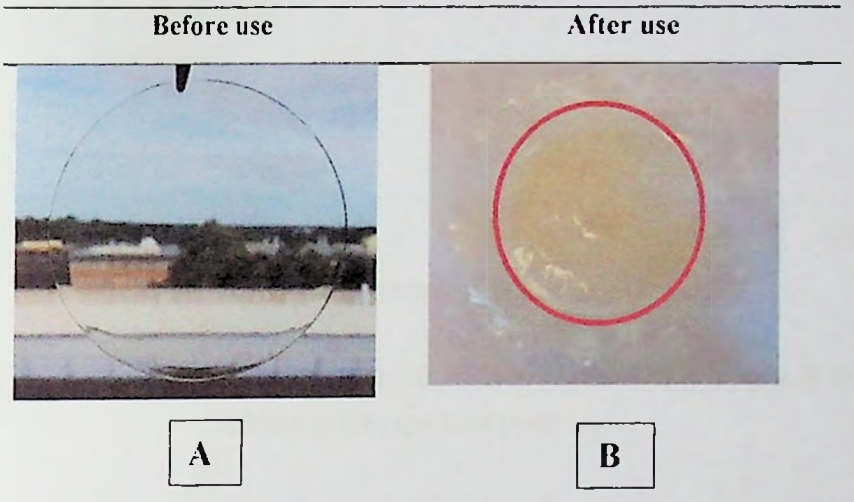

Fig. 5.5. Comparison of membrane containing 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE before **(A)** and after **(B)** transport experiments.

Although, the FTIR spectrum (**Fig. 5.6**) of a membrane after use is still dominated by signals due to CTA and NPOE, there is evidence of increased intensity of the broad band in the region 3000 - 3600 cm^{-1}. This indicates an increase in the number of hydroxyl groups involved in hydrogen bonding which is consistent with humic substances. Additionally, the increase in peak intensity at 1750 cm^{-1} assigned to C = O indicates the presence of other compounds containing a carboxylic acid functionality, such as humic acid. This qualitative infrared information indicates the likelihood that humic substances have been adsorbed to the membrane surface. Similar infrared observations due to the adsorption of humic substances to the surface of a PIM containing Aliquat are known [24].

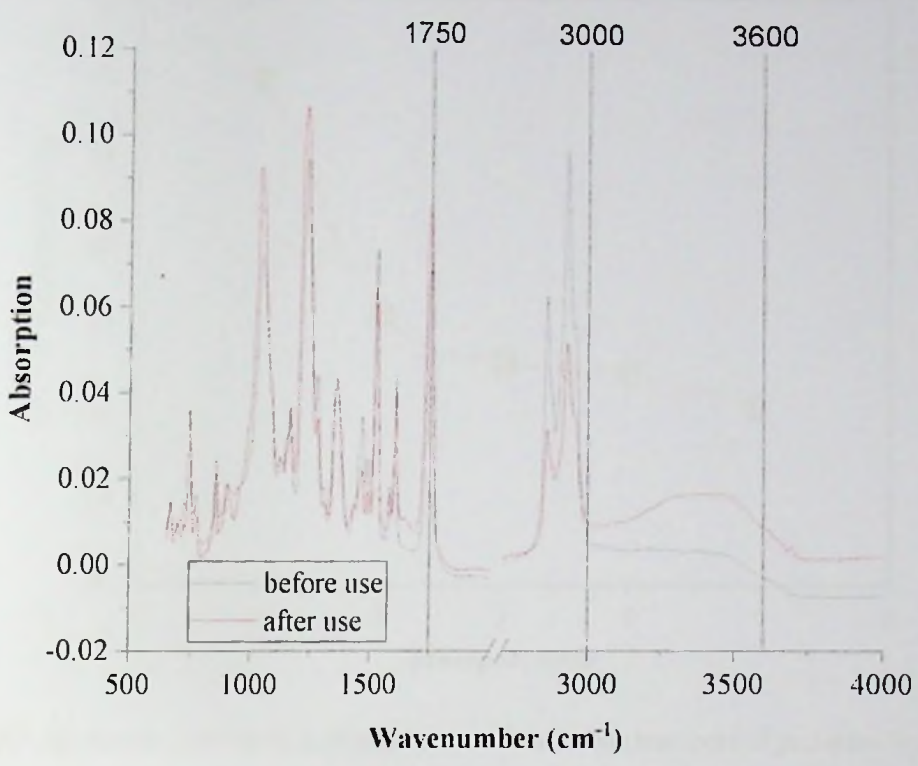

Fig. 5.6. FTIR spectra for the membrane containing 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE before (**black**) and after (**red**) use.

Another indicator of membrane instability is a loss of mass and a decrease of 26% in the first transport cycle was observed which was subsequently followed by a insignificant loss in latter transport cycles (**Fig. 5.7** and **Table 5.4**). The significant decrease in mass in the first cycle is likely caused by the washing of membrane components which are exuded and deposited on the surface during curing (Refer chapters 3 & 4). However, the loss of the membrane liquid phase due to partitioning into adjacent aqueous phases as reported in chapter two cannot be ruled out. The membrane is affected by the loss of liquid phase and adsorption of humic substances which decrease and increase, respectively, the final mass. Consequently, the insignificant mass loss observed in latter transport cycles is likely to be associated with the counter effect of the two processes.

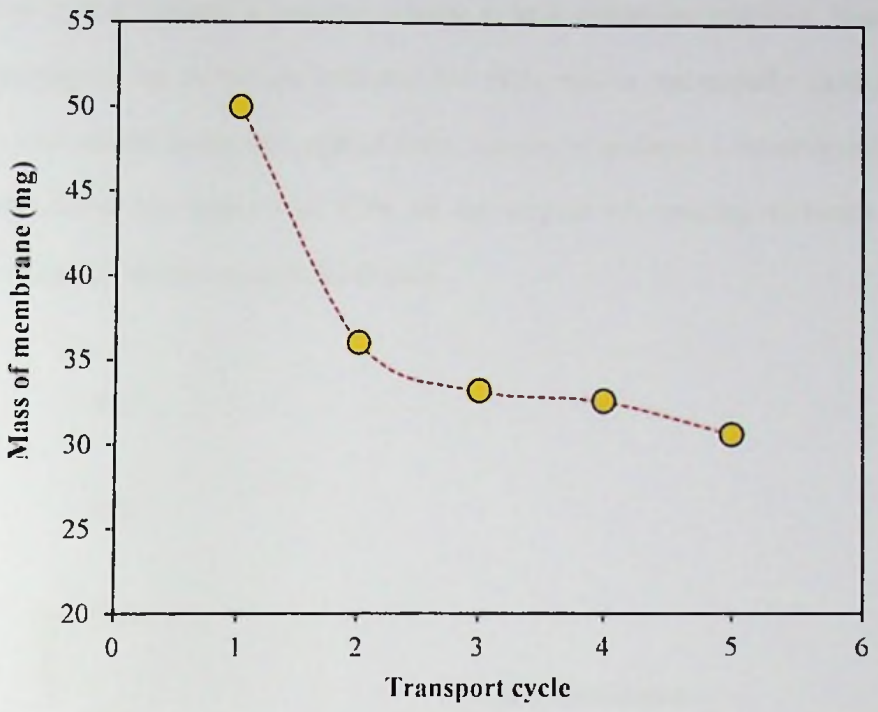

Fig. 5.7. Membrane stability as indicated by mass loss for the transport of picloram from the environmental water. Experiment conditions: feed solution 100 mg/L picloram, pH 8; receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

5.3.2.3. Pre-concentration of picloram

The membranes were also used for the pre-concentration of picloram as a representative pyridine-based herbicide. The results in **Fig. 5.8** show that picloram was successfully extracted with a significant improvement in signal intensity by a ratio of 1:20 relative to pre- and post-concentration. A recovered concentration of 10 mg/L and a transport efficiency of about 80% was demonstrated after 24 hours. However, it is acknowledged that 24 hours is a too long for routine sample preparation. Nevertheless, a significant improvement in signal intensity after 24 hours which enabled the measurement of picloram above the usual limit of detection of 0.5 ppb by HPLC methods was also noted [26]. A reduced time needed for pre-concentration to a suitable measurable level would make this a more viable sample preparation method. An alternate sample preparation and pre-concentration method using PIMs could use a membrane optimised for extraction. In this case, the membrane would be exposed to the sample solution for a pre-determined time to extract the analyte/s, and then removed

and placed in a small volume of receiving solution to back-extract the analyte/s. Nonetheless, the current investigation has further demonstrated that PIMs can be successfully used as a sample preparation method and, in this case, applied to the recovery of picloram from environmental water. As such, the further development of PIMs for the purpose of sampling picloram and related compounds from real world samples is worthwhile.

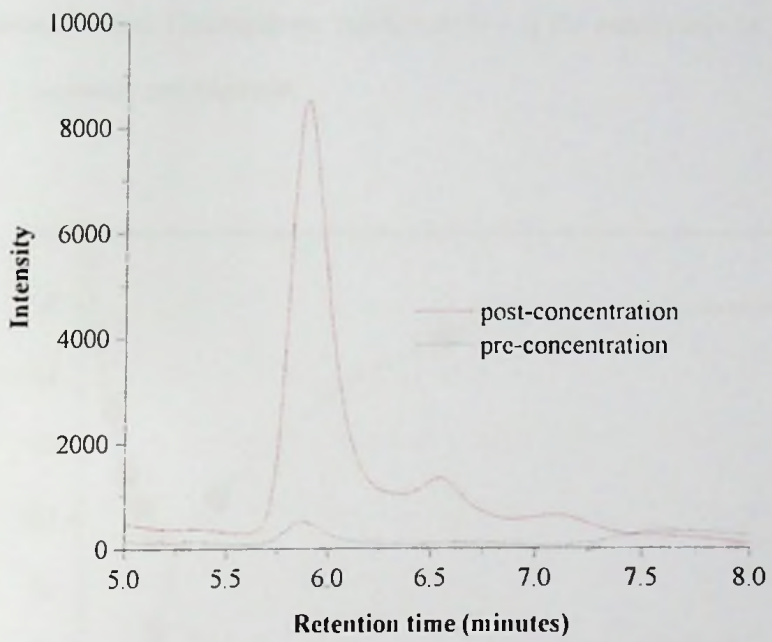

Fig. 5.8. HPLC-UV-chromatogram of picloram for pre-concentration (**black**) and post-concentration (**red**) after 24 hrs (Reconstructed from HPLC data). Experiment conditions: 250 mL feed solution 500 µg/L picloram, pH 8; 10 mL receiving solution 0.25 M NaCl, pH 7; PIM: 25 wt% CTA, 30 wt% Aliquat & 45 wt% NPOE.

5.3.3. Transport and pre-concentration of pyridine-based transformation products

5.3.3.1. Transport of ACP

The transport of ACP from environmental water using a membrane containing anacardic acid as a naturally occurring compound was investigated. The transport profiles are shown in **Fig. 5.9** and the results indicate a flux of 294×10^{-8} mol.m^{-2}.s^{-1} which is 20% lower compared to the 364×10^{-8} mol.m^{-2}.s^{-1} from a similar experiment with a buffer solution. Similarly, the transport efficiency

decreased from 99 to 90% with buffer and environmental water, respectively. The decrease in flux and transport efficiency is possibly attributed to the encapsulation of protonated ACP by humic substances due to the electrostatic attractions caused by a difference in charges. A similar encapsulation of proteins by humic substances over a pH 5 - 7 due to electrostatic attractions has been reported [27]. Regardless of the notable decrease in flux and transport efficiency, the findings demonstrate that the membranes could be useful for the extraction or transport of target compounds from environmental water. Consequently, stability studies of the membranes in environmental water were deemed a necessary consideration.

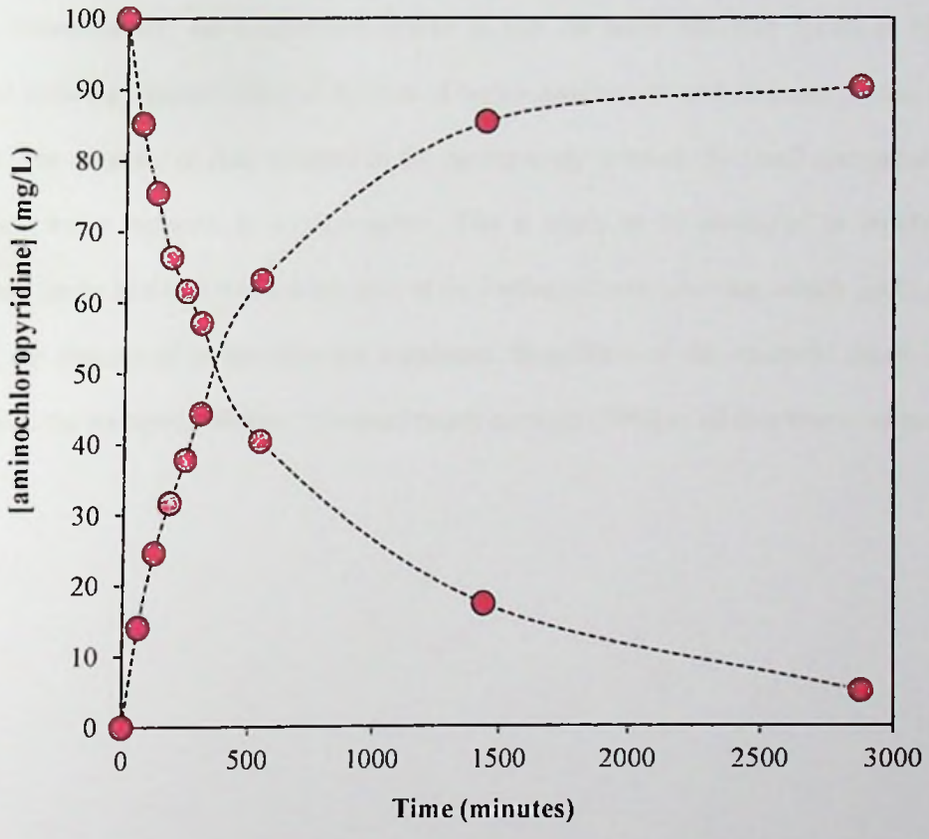

Fig. 5.9. Transport of ACP across PIM from environmental water. Experiment conditions: feed solution 100 mg/L ACP, pH 8; receiving solution phosphate buffer solution, pH 2; PIM: 30 wt% CTA, 10 wt% Anacardic acid, 20 wt% dodecanol & 40 wt% NPOE.

5.3.3.2. Membrane stability studies

The membranes were subjected to stability studies during five transport cycles of ACP to determine the feasibility/robustness for practical and commercial applications. The findings show that the initial flux remained very similar at 293 (±2) × 10^{-8} mol.m^{-2}.s^{-1} for the first three cycles and then decreased to about 199 × 10^{-8} mol.m^{-2}.s^{-1} in the remaining two cycles (**Fig. 5.10 and Table 5.5**). The observed decrease in flux is associated with the loss of the liquid components, ie. plasticiser and modifier, from the membrane as previously explained. The loss of these components is likely to be progressive due to the renewal of the feed and receiving solutions after each transport cycle. The loss of components is normally associated with a decrease in the membrane thickness as reported in earlier chapters. Consequently, the insignificant change in flux for latter transport cycles is likely to be associated with the counter-effect of the loss of liquid components and decrease in the membrane thickness. The decrease in flux observed in the current study is relatively small compared to similar experiments using picloram as a target solute. This is likely to be attributed to repulsive forces between anacardic acid and humic substances at the feed/membrane interface, which could potentially minimise the leakage of carrier from the membrane. Regardless of the observed small loss of the components, the transport efficiency remained nearly constant (90%) in all five transport cycles.

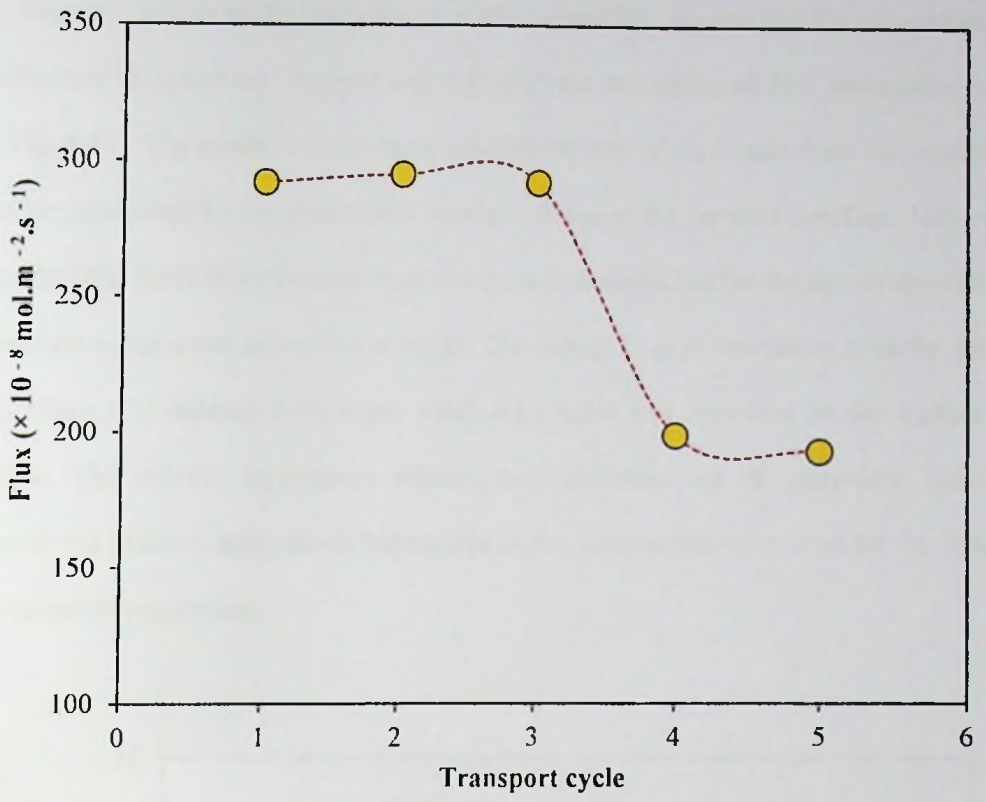

Fig. 5.10. Membrane stability as indicated by flux for the transport of ACP from the environmental water. Experiment conditions: feed solution 100 mg/L ACP, pH 8; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% anacardic acid, 20 wt% dodecanol & 40 wt% NPOE.

Table 5.5. Membrane stability as indicated by flux, efficiency and initial mass for the transport of ACP from environmental water.

Transport cycle	Initial mass (mg)	Permeability ($\times 10^{-6}$ m.s^{-1})	Flux ($\times 10^{-8}$ mol.m^{-2}.s^{-1})	TE (%)
1	50.0	3.7	292	90
2	50.0	3.9	295	90
3	47.9	3.8	292	91
4	45.4	2.6	199	90
5	45.2	2.5	193	90

Experiment conditions: feed solution 100 mg/L ACP, pH 8; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% anacardic acid, 20 wt% dodecanol and 40 wt% NPOE.

The mass loss, as another indicator of membrane stability, showed that the mass decreased by about 10% over all cycles but remained within 47 (± 2) mg throughout all five consecutive transport cycles (**Fig. 5.11**). The mostly constant mass indicates the loss of the carrier from the membranes is likely to be minimised by the electrostatic repulsive forces at the receiver interface. However, the FTIR results (**Fig. 5.12**) showed a significant change in peak intensities for the signals associated with the membrane components before and after use. The change in peak intensities is likely due to the washing effect of membrane components which are exuded and deposited on the surface during preparation. The stability experiments indicate the membranes are of acceptable stability for commercial and practical applications. Membranes of this composition were used for the subsequent pre-concentration experiments.

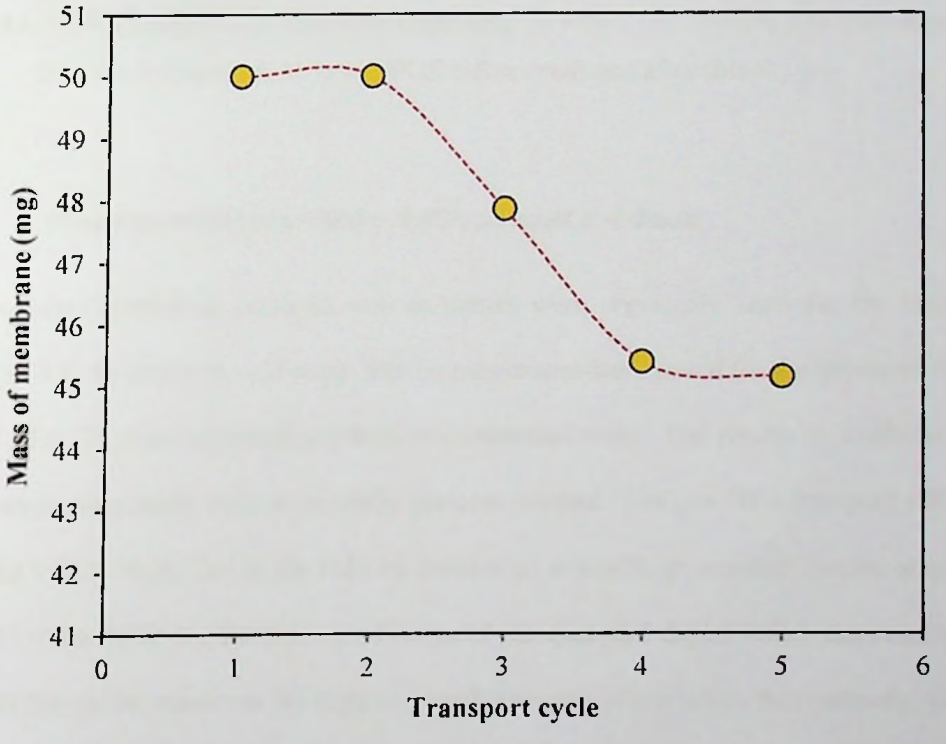

Fig. 5.11. Membrane stability as indicated by mass for the transport of ACP from the environmental water. Experiment conditions: feed solution 100 mg/L ACP, pH 8; receiving solution phosphate buffer, pH 2; PIM: 30 wt% CTA, 10 wt% anacardic acid, 20 wt% dodecanol & 40 wt% NPOE.

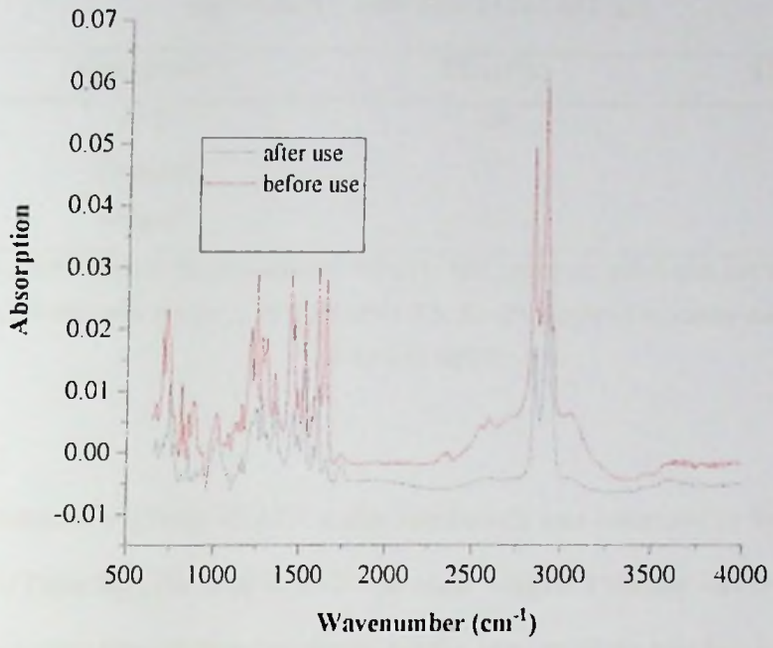

Fig. 5.12. FTIR spectra for the membrane containing 30 wt% CTA, 10 wt% anacardic acid, 20 wt% dodecanol & 40 wt% NPOE before (**red**) and after (**black**) use.

5.3.3.3. Pre-concentration of a mixture of ACP, paraquat and diquat

Membranes containing anacardic acid as carrier were previously used for the successful transport of ACP from environmental water. Similar membranes were tested for the pre-concentration of a mixture of ACP, paraquat and diquat from environmental water. The results in **Table 5.6** show that all the target compounds were successfully pre-concentrated. The low 90% transport efficiency for ACP (pKa ≈ 9) is likely due to the reduced amount of available protonated species at pH 8 in environmental water. Whereas, the protonated forms of paraquat and diquat which can readily form ion-pairs with the carrier results in the high observed transport efficiencies. Alternatively, the low transport efficiency for ACP could be associated with electrostatic interaction and encapsulation with humic substances in environmental water. A similar encapsulation of amino acids by humic substances has been previously documented [27].

Table 5.6. Transport efficiencies (TE) for pre-concentration of ACP, paraquat and diquat from spiked environmental water after 24 and 48 hours.

Compound	TE_{24} (%)	TE_{48} (%)
ACP	48	90
Paraquat	72	100
Diquat	85	100

Experiment conditions: 250 mL feed solution 500 µg/L ACP, paraquat, and diquat, pH 8; 10 mL receiving solution 100 mM buffer solution, pH 2; PIM: 30 wt% CTA, 10 wt% saturated anacardic acid, 20 wt% dodecanol & 40 wt% NPOE.

The transport efficiency of ACP is also significantly less compared to the other test solutes after 24 hours (**Table 5.6**), the trend is: ACP < paraquat < diquat. Paraquat was complexed by humic compounds in greater amounts than was diquat, but the amounts of the two herbicides complexed by humic acid were higher than those complexed by fulvic acid [28]. This indicates that the charge and structure of solutes has an important effect on interaction with humic substances. The lower transport efficiency for ACP, containing only a single positively charged nitrogen, indicates a more favourable interaction and subsequent encapsulation, that is less sterically hindered, on humic substances compared to paraquat and diquat.

The observed effective transport of all available paraquat and diquat after 48 hours is comparable to results reported from an electro-membrane extraction using di-(2-ethylhexyl)phosphoric acid as a carrier [14]. This indicates that anacardic acid performs as effectively as a commonly used carrier. The significant improvement in HPLC peak intensities for post-concentration compared to pre-concentration of all test solutes as shown in **Fig. 5.13** provides further evidence of the extraction ability of the carrier. The preliminary results on the use of anacardic acid as a "green" carrier are encouraging. However, more studies are necessary to further demonstrate its suitability as an effective carrier for particular applications.

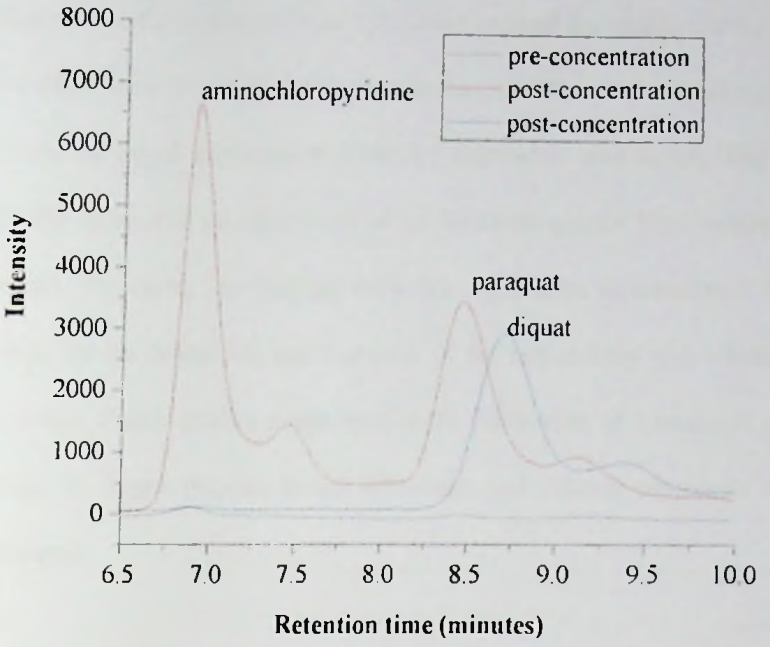

Fig. 5.13. HPLC-UV chromatograms of ACP, paraquat and diquat for pre-concentration (500 µg/L each) (**black**) and post-concentration (ACP and paraquat (**red**), and diquat (**blue**)) after 24 hrs. Measurements for (ACP + paraquat) and diquat were taken at 265 and 310 nm, respectively (Reconstructed from HPLC data).

5.4. Conclusion

In the current work, the application of the optimal PIMs for the transport and extraction of picloram and ACP, diquat and paraquat as representative target compounds from environmental water is reported. The membranes displayed the successful extraction and transport of the compounds from feed solutions of environmental water. For the first transport cycle, the humic substances present in the water were postulated to increase the initial flux for the transport of picloram due to electrostatic repulsion. However, the initial flux decreased for the transport of ACP, which was postulated to be attributed to its encapsulation by humic substances as a result of electrostatic attractions.

Stability studies revealed that membranes containing Aliquat as carrier were relatively stable for the transport of picloram. However, a remarkable decrease in the membrane performance due to a fouling effect caused by the accumulation of humic substances on the surface of membranes was

observed. Consequently, the transport efficiency and flux declined with increased number of transport cycles. Membranes containing anacardic acid as carrier showed acceptable stability of almost 90% for the transport of ACP. However, a slight decrease in the initial flux and transport efficiency associated with a small loss of liquid components from the membrane was noted. The application of the membranes for the successful pre-concentration of the target solutes from environmental water was also demonstrated. Therefore, the findings from this work have demonstrated that the membranes could be suitable for the extraction and transport of the test solutes and related compounds from environmental water. Future studies might involve the fabrication of membrane extractor or passive sampling devices to target pyridine-based herbicides and related chemicals from contaminated environmental waters.

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Chapter 6: Conclusion and recommendations.

6.1. Introduction

Polymer inclusion membranes (PIMs) to target pyridine-based herbicides and their potential degradation by-products from an aqueous solution are reported in this thesis. The use of particular compounds derived from cashew nut shell liquid (CNSL) as a "green carrier" for the extraction and transport of organic compounds using PIMs is also discussed. The main conclusions from the research reported in this thesis and suggested future works are summarised in sections 6.2 and 6.3, respectively.

6.2. Conclusion

The development of PIMs as a simple and reliable remediation method for the removal of pyridine-based herbicides from aqueous solutions was investigated. The transport of picloram as a representative pyridine-based herbicide using CTA-based membranes containing Aliquat 336 as an anionic carrier showed an acceptable transport efficiency of 95 ± 1%. The use of different anionic stripping agents produced a significant influence on the transport performance, with chloride and nitrate giving the optimal performance. The chloride ion was subsequently used as a suitable stripping agent for most transport experiments in order to avoid the possible contamination of water with nitrates; a useful consideration if the membranes are to be used for commercial and practical purposes. The membranes also demonstrated an appreciable performance of 84 - 97% for the transport of other compounds related to picloram, namely triclopyr, clopyralid and 2,4-D. The lipophilic properties of the target compounds were shown to significantly influence the extraction and transport efficiency.

In an extension of this study, the PIMs were also used for the extraction and transport of 4-amino-2-chloropyridine (ACP) as a model compound of the degradation by-products of pyridine-based herbicides. The preliminary results indicated that ACP was mainly transported through the

membrane by a combination of passive and facilitated diffusion involving a pH gradient between the feed and receiving solutions. It was postulated that the carrier interacts with the target compound to form a hetero-conjugate complex. This resulted in improved transport in the presence of an Aliquat carrier as indicated by initial flux which increased with temperature, whereas the transport efficiency was unaffected. Additionally, the preferential transport of ACP over picloram was demonstrated.

The use of anacardic acid compounds from CNSL as cheap and readily available cationic carriers of organic compounds in PIMs was also assessed. Membranes containing anacardic acid at pH 7 indicated the successful transport of ACP and the cationic herbicides paraquat and diquat. A transport efficiency of greater than 96% for all three compounds using anacardic acid was observed which was similar to results using a commercial carrier, bis-(2-ethylhexyl) phosphoric acid.

The application of PIMs as a simple, robust and low-cost method for the pre-concentration of pyridine-based herbicides and their degradation by-products from environmental water was studied. Membranes containing Aliquat or anacardic acid were successfully applied for the pre-concentration from environmental water of picloram, ACP, paraquat and diquat as selected representative compounds. A significant improvement in HPLC peak intensities of each analyte was noted after pre-concentration. However, the prolonged use of membranes containing Aliquat as carrier for the pre-concentration of picloram was significantly affected by a fouling effect caused by the accumulation of humic substances. A similar effect was not observed for the extraction and transport of ACP, paraquat and diquat using membranes containing anacardic acid as carrier. In this case, the encapsulation of the positively charged solutes by humic substances in the feed solution due to electrostatic interactions was postulated to influence the membrane performance of some solutes.

The achievements of this work are expected to contribute to the available knowledge on the use of PIMs for the transport of organics which has been less widely studied than inorganic species. The use of Aliquat as carrier for the transport of neutral and organic anions associated with picloram could serve as a potential benchmark for future investigations on the preferential extraction and transport of similar organic compounds. Additionally, the use of anacardic acid from CNSL as a natural carrier has highlighted a new direction of research. This is expected to facilitate further

investigations on using cheap, abundant, and readily available renewable chemicals as active membrane components. The use of natural compounds in PIMs could reduce associated costs and enhance their acceptance as a viable alternate extraction method for, in particular, environmental applications.

6.3. Recommendations for future work

The membranes used for all experiments in this thesis were made with CTA as the base polymer and, thus, the use of different base polymers to prepare PIMs is a topic for further investigations. This could identify methods to improve the transport of pyridine-based herbicides because the associated hydrophilic nature of different polymers could affect permeability [1].

The preferential transport of ACP over picloram for membranes with Aliquat as carrier was mainly based on altering the conditions of the receiving solution. However, it is known that compounds with different properties, such as hydrophilicity and lipophilicity, show different permeability in membranes [2]. Thus, the use of a broad range of target compounds having different chemical properties could be a useful method to demonstrate the potential of PIMs for wider applications to target individual or a class of closely related compounds. In particular, the effective conditions for the transport of degradation by-products of pyridine-based and other herbicides would be a useful future investigation.

The current work investigated compounds from plants as a source of a "green carrier" for organic compounds in PIMs. Notably, there are many reports that most of the plasticisers used in the polymer industry are potentially toxic to the environment [3]. Therefore, the current work could be extended to investigate other natural compounds derived from plants as potential "green plasticisers" to replace existing toxic plasticisers. This could make a significance contribution to the current efforts to use environmentally friendly compounds in the polymer industry [4].

The pre-concentration results reported in this work involved the use of membranes in the form of flat sheets as a convenient experimental method to investigate optimal conditions. However,

the use of membranes in the form of hollow-fibres for the pre-concentration of environmental samples is a convenient way to increase surface area and, consequently, improve the efficiency of the process for real-world applications [5]. Thus, the construction and use of a hollow-fibre membrane extractor as a passive sampling device should be investigated as a potential beneficial method to improve pre-concentration efficiency.

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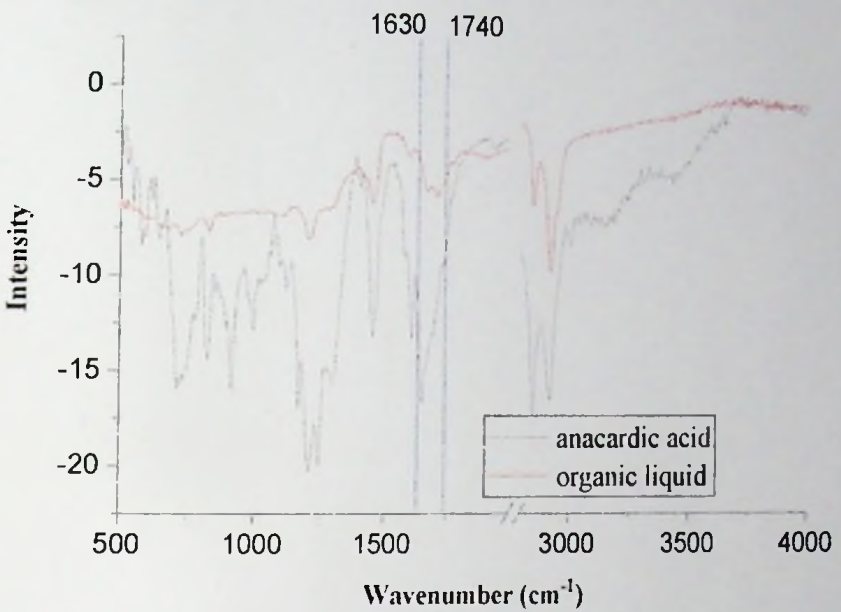

Fig. A4.1. FTIR spectra of AAM and organic liquid on the surface of some membranes.