PREPARATION AND CHARACTERIZATION OF CATION SELECTIVE PERMEABLE MEMBRANE

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Abstract

Heavy metals are used in many industrial processes and their cations are either valuable or environmentally harmful to discharge in wastewater. Thus, it is necessary to separate heavy metals in wastewater treatment. Amongst several technical methods of separation, use of permeable membranes is an important one. For separation processes, membranes can be selective towards a target heavy metal cation either against mono-valent common cations or against other similar heavy metal cations.

Synthesis of selective permeable membranes for separation purposes is an area of continuous research to meet specific needs in different applications. One of the common applications of selective separation by a permeable membrane is cation/anion separation processes using cation exchange and anion exchange membranes. Another application of selective permeable membranes is the separation of mono-valent cations from other higher valence cations.

Some researchers have focused on specific selective separation of heavy metal cation from other heavy metal cations having the same valent charge. Some use chelating particulates dispersed in a neutral polymeric membrane matrix and others applied a thin chelating film on the surface of a commercial cation exchange membrane.

In this work, the synthesis of novel permeable selective membranes and their use for selective separation between two di-valent heavy metal cations is presented. Three different sets of membranes were prepared in non-imprinted and imprinted forms. The ion imprinted membranes form is prepared by pre-reacting the target metal ion with the selective chelating monomer before applying *in situ* polymerization step, and in the non-imprinted membranes form this step is not considered. Their morphological and chemical structures were determined and their separation performances were investigated using a diffusion dialysis technique.

The first membrane (non-imprinted polyvinylidene fluoride-divinylbenzyl-triethylenetetramine (PVDF/diVB-TETA) and Cu-imprinted PVDF/diVB-TETA-Cu forms) was prepared by *in situ* polymerization of the chelating monomer divinylbenzyl-triethylenetetramine diVB-TETA (or diVB-TETA-Cu) within a PVDF substrate, using a divinylbenzene cross-linker. Fourier transform infrared FT-IR spectroscopy showed the successful *in situ* polymerization of the chelating monomer within the PVDF texture. The permeation study showed that the ion-imprinted membrane has a Cu^{2+} selectivity factor of 3.78, while the non-imprinted membrane has a Cu^{2+} selectivity factor of 1.65. In addition the Cu^{2+} permeation flux in the imprinted membrane is 3.9 time that in the non-imprinted membrane

For the second membrane, the synthesis is similar to the first membrane for both non-imprinted and imprinted forms (polyvinylidene fluoride-divinylbenzyl-triethylenetetramine-N,N'-methylenebis(acrylamide) (PVDF/diVB-TETA-N) and PVDF/diVB-TETA-N-Cu respectively), except that the used cross-linker was N,N'-methylenebis(acrylamide). In addition, sodium 4-vinylbenzyl sulfonate was added in selected percentages, (5-15% mol), to enhance the permeation flux. FT-IR spectroscopy analysis of the prepared membranes confirmed the chemical structure of diVB-TETA-N and sulfonate group into PVDF. Permeation and selective separation

studies for the prepared membranes showed that the ion-imprinted membrane has a higher selectivity for copper permeation over the non-imprinted membrane. However imprinted membrane showed a lower flux for the permeated cations than that of the non-imprinted membranes The addition of the sulfonate groups to the prepared membranes enhanced the flux of the permeated cations, but the copper selective permeation decreased for both types (non-imprinted and ion-imprinted). Moreover, the ion-imprinted membrane PVDF/diVB-TETA-N-Cu showed a lower flux for the permeated cations than that of the non-imprinted membranes PVDF/diVB-TETA-N. Selective separation factors decreased to unity when the content of the sulfonate groups increased to 15% mol. Ion imprinted membrane prepared with 10% of sulfonate group showed optimum copper selectivity factor ($\alpha = 30304$) and permeation flux for copper (0.4949 μmol cm^{-2} h^{-1})

The third membrane (non-imprinted Selemion TM cation exchange membrane-divinylbenzyl-triethylenetetramine (CMV-S/diVB-TETA) and ion-imprinted CMV-S/diVb-TETA-Cu forms) was prepared by *in situ* polymerization of the chelating monomer, diVB-TETA (or diVB-TETA-Cu), on the surface of the commercial cation exchange membrane, Selemion, using divinylbenzene as cross-linker. FT-IR spectroscopy confirmed the chemical structure of the chelating polymer on the CMV-S membrane surface. Permeation study showed that ion-imprinted CMV-S/diVB-TETA-Cu membrane reached high separation factor ($\alpha = 17$), yet the flux is low (0.0391 μmol cm^{-2} h^{-1}). Non-imprinted CMV-S/diVB-TETA membrane of thickness (0.115±0.005 mm) using cross-linker (10% DVB) showed reasonable copper selectivity factor ($\alpha = 2.723$) and permeation flux (0.433 μmol cm^{-2} h^{-1})

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Preface

This thesis has been prepared according to McMaster University regulations of theses consisting of work prepared for publication in peer-reviewed journals. Chapter 1 is an introduction to the thesis. Chapter 2 consists of literature review. Chapters 3, 4 and 5 consist of material previously prepared for publication as journal articles.

As such, the material in Chapters 3, 4 and 5 had multiple authors. The original contributions made by the thesis author to the material in each of these chapters are outlined below:

Chapter 3

Title: Preparation and Characterization of Ion Selective Membrane and its Application for Cu^{2+} Removal

Authors: Mohamed M. K. Mohamed, Sarah E. Dickson, Younggy Kim and Waleed Mekky.

The idea for these experiments came from Mohamed M. K. Mohamed, Sarah E. Dickson and Younggy Kim. The experiments were designed and conducted by Mohamed M. K. Mohamed. All aspects of testing membrane preparation and characterization of the tested membrane were conducted by Mohamed M. K. Mohamed. The analysis of the results was conducted by Mohamed M. K. Mohamed in consultation with Sarah E. Dickson, Younggy Kim, Jim Dickson and Waleed Mekky. The text was written by Mohamed M. K. Mohamed and edited by Sarah E. Dickson, Younggy Kim, and Waleed Mekky.

Chapter 4

Title: Copper Selective Facilitated Transport through Chelating Composite Based Membrane

Authors: Mohamed M. K. Mohamed., Sarah E. Dickson, Younggy Kim, and Waleed Mekky.

The idea for these experiments came from Mohamed M. K. Mohamed, Sarah E. Dickson and Younggy Kim. The experiments were designed and conducted by Mohamed M. K. Mohamed. All aspects of testing membrane preparation and characterization of the tested membrane were conducted by Mohamed M. K. Mohamed. The analysis of the results was conducted by Mohamed M. K. Mohamed. in consultation with Sarah E. Dickson, Younggy Kim, Jim Dickson and Waleed Mekky. The text was written by Mohamed M. K. Mohamed and edited by Sarah E. Dickson, Younggy Kim, and Waleed Mekky.

Chapter 5

Title: A Modified Cation Exchange Membrane by Surface Coating to Enhance Copper Ion Selective Separation from other Di-valent Heavy metal Cation Solution Mixture

Authors: Mohamed M. K. Mohamed, Sarah E. Dickson, Younggy Kim, and Waleed Mekky.

The design of the experiment and its parameters was designed by Mohamed M. K. Mohamed, Sarah E. Dickson, Younggy Kim, and were conducted by Mohamed M. K. Mohamed. The preparation of the modified cation exchange membranes and their characterization using FT-IR, as well as the SEM and separation using diffusion dialysis were conducted by Mohamed M. K. Mohamed. The analysis of the results was conducted by Mohamed M. K. Mohamed. in consultation with Sarah E. Dickson, Younggy Kim, and Waleed Mekky. The text was written by Mohamed M. K. Mohamed and edited by Sarah E. Dickson, Younggy Kim, and Waleed Mekky.

Glossary

Abbreviations

AAc	Acrylic acid
AIBN	2,2-azobis(2-methyl propionitrile)
AEM	Anion exchange membrane
BPO	Benzoyl peroxide
CEMs	Cation exchange membranes
CMC	Carboxymethyl cellulose
CMV-S	Cation exchange membrane (Selemion)
^{13}C-NMR	Carbon-13 nuclear magnetic resonance
DENBT	Dendritic benzoylthiourea functionalized polyamide
diVB-TETA	Divinylbenzyl triethylenetetramine monomer
diVB-TETA-Cu	Copper complex divinylbenzyl triethylenetetramine monomer
DMS	Dimethyl sulfoxide
DVB	Divinylbenzene
ED	Electro dialysis
FCMs	Fixed site carrier membranes
FT-IR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
HEMA	2-hydroxyethyl methacrylate
^{1}H-NMR	Proton nuclear magnetic resonance
ICP	Ion coupled plazma
IEC	Ion exchange capacity
IEMs	Ion exchange membranes
IIPs	Ion imprinted polymers
LDPE	Low density polyethylene substrate
MBAC	N,N'-methylenebis (acrylamide)
MIPs	Molecular imprinted polymers
NSERC	Natural Sciences and Engineering Research Council of Canada

PAH	Poly(allylamine)
PAMAM	Polyamide-amine
PANI	Polyaniline
PAP	Polyaminophenylene
PDCMAA	Poly[(N,N0-dicarboxymethyl) allylamine]
PEC	Pectin
PEI	Polyethyleneimine
pGMT	Poly(glycidylmethacrylate-co-trimethylacrylate)
PNF	Polyolefin nonwoven fabric
PPy	Polypyrrole
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
SEM-EDS	Scanning electron microscope coupled with Energy dispersive X-ray spectroscopy
SPES	Sulfonated poly(ether sulfone)
SSS	Sodium styrenesulfonate
Sty/Man	Styrene/maleic anhydride
TETA	Triethylenetetramine
THF	Tetrahydrofuran
TRIM	(2-ethyl-2-(hydroxymethyl) propane-1,3-diol trimethacrylate)
VBC	Vinylbenzyl chloride
VBTAC	Vinyl benzene triethylammonium chloride

Symbols

A	Membrane effective area (cm^2)
b	Langmuir constant (L.mg^{-1})
C_o	Initial concentrations(mg.L^{-1})
C_e	Equilibrium concentrations (mg.L^{-1})
J	Ion flux (μmol cm^{-2} h^{-1})
K_F	Freundlich constant
$\mathrm{K_{Cu\text{-}TETA}}$	Stability constant of copper with TETA
$\mathrm{K_{Ni\text{-}TETA}}$	Stability constant of nickel with TETA
m_f	Mass of the dried sample membrane (g)
m_o	Mass of the dried substrate PVDF (g)
m	Membrane mass (g)
$\mathrm{M_{NaOH}}$	Equivalent concentration of NaOH solution
$\mathrm{M_{HCl}}$	Equivalent concentration of HCl solution
N	Heterogeneity factor of Freundlich isotherm
Q_{exp}	The experimental equilibrium adsorption amounts of for Cu^{2+} and Ni^{2+} (mg.g^{-1})
Q_o	Maximum adsorption capacity of the membrane (mg. g^{-1})
q_{exp}	Adsorption amount at equilibrium (mg.g^{-1})
q_t	(mg.g^{-1}) the adsorption amount at time (h)
$\mathrm{V_{NaOH}}$	NaOH solution volume (mL)
$\mathrm{V_{HCl}}$	HCl titrant volume (mL)
V	The volume of solution (mL)
W_{wet}	Mass of the membrane for the wet form (g)
W_{dry}	Mass of the membrane for the dried form (g)
W	Weight of the dried sample membrane (g)
α	Selectivity factor
α'	Selectivity ratio
ΔC	Concentration of the permeated ion (μmol/L)
Δt	Ion permeation elapsed time (s)

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Chapter 1

Introduction

1.1 Background

Membrane is a selective media barrier that is used in separation and purification processes. Industries such as metal finishing, batteries manufacture, electrical cables manufacture and electronic microchip manufacturing produce a large amount of wastewater containing heavy metal ions such as copper, nickel, cobalt, zinc, cadmium and lead (Abu and Moussab, 2004; Chakrabarty et al. 2013; Cojocaru et al., 2009; Rahmanian et al., 2010). These metals are valuable resources from industry point of view but when discharged, they are considered as toxic contaminants. Hence, efficient separation processes are required to separate heavy metals from wastewater.

Conventional methods such as chemical precipitation, coagulation, flocculation, filtration, adsorption and ion exchange are well known methods for the removal of heavy metal ions from wastewater and sometimes for the metal recovery and recycling (Li et al. 2009; Boricha and Murthy, 2010; Rahmanian et al. 2011). Use of ion selective permeable membranes is another promising technique for the removal and recovery of heavy metal ions especially when combined with dialysis and electrodialysis processes (Lambert et al. 2006; Marty et al., 2000).

A common application of ion exchange membranes is the ion separation using electrodialysis. Electrodialysis can also be used to separate cations of different valences, e.g. di-valent cations from mono-valent ones. In addition, separation of a specific mono-valent cation (elements of group I) has been demonstrated. However, separation of a specific multivalent metal ion from a mixture of multiple metal ions of the same valence has not been extensively investigated (Lambert et al. 2006; Davis et al., 1997; Gohil et al. 2006; Le et al. 2010; Yao et al. 2013).

Recently, some studies showed improved selectivity to a specific ion using existing membranes or preparing new membranes. Some researchers developed cation selective chelating membranes by using chelating agent-loaded particles into a polyvinyl alcohol (PVA) matrix. However, the membrane lakes homogeneity and potentially loses the chelating particles. In another study, chelating cation selective membrane was prepared by blending chelating polymers with suitable elastomer and then casting the mixture to produce the membrane, however, this method showed a limited homogeneity of the prepared membrane.

This research focused on developing preparation methods for new cation chelating selective membranes. The preparation considers the followings: (i) the simplicity of synthesis, (ii) the homogenous distribution of chelating active sites, (iii) the ability to produce chelating matrix in different forms, and (iv) the ability to change chelating compound for a different targeted cation. The simplicity, homogeneity and different forms can be achieved by directly *in situ* polymerizing chelating monomers within the texture or on the surface of commercial porous membranes or cation exchange membranes such as Polyvinylidene fluoride (PVDF) and Selemion membranes. The selected chelating compound can be replaced by similar chelating agents that have affinities to other target cations.

The following criteria need to be considered for the selection of the chelating agent:

1- The chelating agent must have a substantially higher stability constant with a targeted cation than with other competing cations.

2- The chelating agent has the ability to be converted into a monomer form with at least two polymerizing positions.

3- When polymerized, the chelating agent must show high affinity, i.e. affinity does not change to guarantee the aimed selectivity preference.

4- It is preferred to be of a linear form to simplify the cation-site-recognition when the ion-imprinting technique is applied. By imprinting, linear structure can easily attain the geometrical shape of the target metal cation during chelation and can preserve this geometrical shape by *in situ* polymerization.

5- A low molecular weight (as low as possible) is preferred to increase the amount of the chelating agent in the structure of the prepared membrane.

1.2 Thesis Objectives

The aim of the research is to develop preparation methods for a novel type of membrane that can selectively separate a di-valent heavy metal cation from other di-valent heavy metal cations. Such selective separation is feasible because a chelating compound that has a higher affinity towards a targeted cation over other competing ones is integrated in the membrane preparation. Thus, proper selection of the chelating compound is crucial for effective separation of a target ion.

The following objectives are designated to achieve the stated aim:

1- Synthesis of new cation chelating selective permeable membranes that have permeation selectivity due to chelation affinity difference to different di-valent heavy metal cations.
2- Using PVDF and Selemion cation exchange membranes as neutral and active substrate respectively.
3- Enhancing the flux of the permeated selected cation by adding sulfonic acid functional group.
4- Investigation of the success of synthesis process to guarantee the good implementation of the chemical design.
5- Evaluation of synthesized new membranes for selective separation of a target di-valent cation from another cation of the same valence.

In this study, Cu(II) was selected as the targeted cation to separate. Copper is a valuable heavy metal for various industries. Ni(II) was selected as the competing cation against Cu(II). These cations are very similar as they have the same valence charge and similar ionic radius. PVDF and Selemion were selected as membrane substrates within or on which modification by chelate-polymerization was carried out. The first was chosen due to its neutrality towards both competing cations. This neutrality means that competitive separation is expected to be dependent only on chelating sites. The second was chosen due to its cation exchange behaviour that is expected to enhance ionic flux. To increase the selectivity to Cu(II), triethylenetetramine (TETA) was selected as the chelating compound for cation complex formation as it meets the above mentioned requirements.

1.3 Thesis Overview

This thesis consists of 6 chapters. Chapter 2 describes an extensive literature review on ion selective permeable membranes and recent developments for enhancing its selectivity. Chapter 3 is an independent research article for journal submission on the synthesis of a chelate cation selective membrane by bulk modification of a PVDF membrane by in-situ polymerization of TETA using divinylbenzene as a cross-linker. Chapter 4 is another research article that describes the bulk modification of PDVF by *in situ* polymerization TETA using N,N'-methylenebis(acrylamide) (MBAC) as a cross-linker. In this chapter, membranes prepared with a hydrophilic component (sulfonate functional group) were also examined. Chapter 5 includes the third research article that describes the surface modification of a commercial cation exchange membrane (Selemion) by *in situ* polymerization of TETA using divinylbenzene as a cross-linker. The ion-imprinted technique and non-imprinted method were consistently applied in membrane preparation and compared to study. Prepared membranes were characterized and their performance for selective separation was examined in diffusion dialysis and adsorption experiments. Chapter 6 presents conclusions of the three independent research articles.

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Chapter 2

Literature Review

2.1 Introduction

The removal of heavy metals is an essential process to ensure the safety of wastewater prior to its discharge. In many industries, a separation process is an important step to retrieve valuable metals for reuse. The removal and separation processes of heavy metals can be achieved by technological methods, such as adsorption, coagulation, flocculation, precipitation and membrane technology (Fu and Wang, 2011).

Ion exchange membranes are the most common ion selective membranes. They contain ionic exchange functional groups that have the ability to pass charged ions. The cation exchange membranes separate cations from anions and anion exchange membranes separate anions from cations. Ion exchange membranes are found in many applications for wastewater treatment, desalination, heavy metal removal and fuel cells (Strathmann, 2004; Nagarale et al. 2006; Savari et al., 2008; Choi et al., 2007). While ion exchange membranes can separate ions of the same type (e.g., cations or anions) they cannot be used for selective separation of sepcific ions from the same type (e.g., Cu^{2+} from other cations), and this is a limitation in some industrial processes.

Some reseachers attempted to prepare ion selective membranes with a specific selectivity to a target ion such as membranes for the selective separtion of mono-valent ions from multivalent ions as well as membranes for the competitive separation of ions of the same charge. Chemistry of the ion selective membranes, their preparation methods and the factors that affect membranes selectivity are discussed in the following sections.

2.2 Ion selective membranes

Most ion selective membranes such as ion exchange membranes are prepared from organic polymers that contain fixed functional groups that are covalently bonded to the polymer. These polymers are usually styrene/divinylbenzene copolymers or perflorinated copolymers. The divinylbenzene ring in styrene/divinylbenzene copolymers increases the degree of cross-linking of the polymer. As a result, the membrane has good mechanical properties (i.e. increased tensile strength and hardness and reduced swelling) (Davis et al., 1997).

One method of synthesis is the copolymerization of functionalized alkenes containing ionic groups with unsubstituted alkene. Another method comprises the polymerization of alkenes and subsequent introduction of ionic functional groups (Davis et al., 1997). The preparation of ion selective membranes follows technical methods such as radiation graft copolymerization, casting and pore filling. The following section discusses these methods with examples.

2.2.1 Methods of ion selective membrane preparation

(a) Graft copolymerization (radiation)

Graft coploymerization (radiation) is a process whereby a functionalized monomer starts the polymerization process over a porous polymer substrate using radiation. The substrate has to be cut into rectangular or square pieces and pretreated (by immersion in a solvent such as acetone), dried (by vacuum) and then immersed in a solution of the co-monomer. The substrate pieces can then be exposed to direct radiation to start the copolymerization process. The grafted copolymer on the substrate has to be washed with acetone to remove any residuals monomers and homopolymers, and then the membrane has to be dried under vacuum (Abd El-Rehim et al., 2000). Figure 2.1 shows the grafting of polyethylene (PE) sheets with sulfochlorination and amination reaction as an example. (Nagarale et al., 2006).

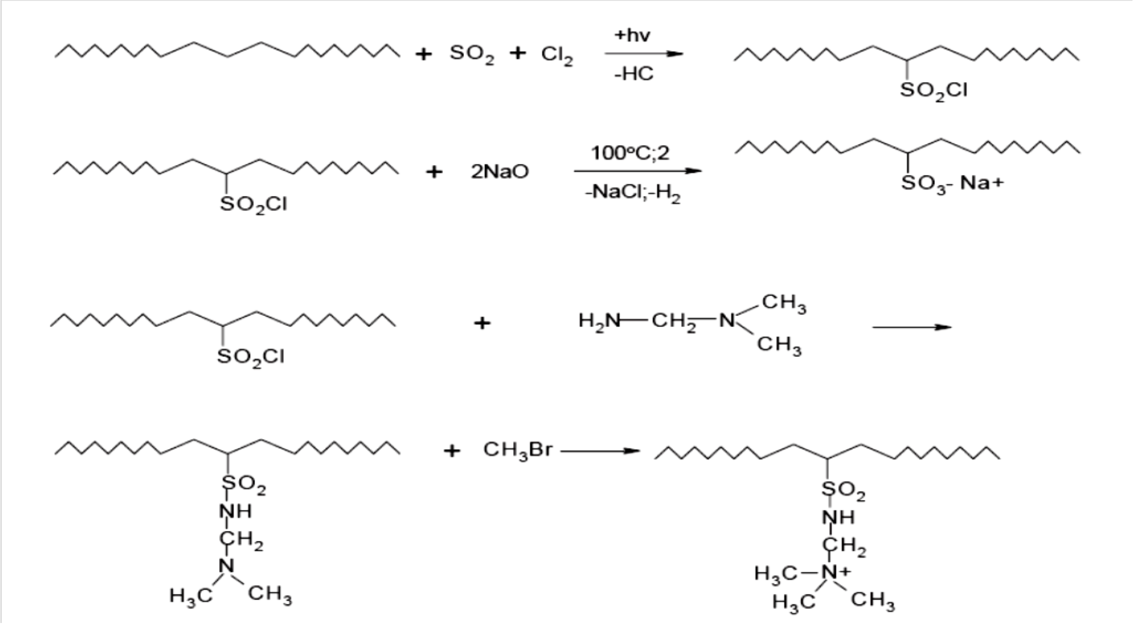

Figure 2.1 Sulfonation and amination of PE to produce an ion exchange membrane (Nagarale et al., 2006).

For the graft polymerization using radiation, most previous studies focused on introducing a weak acid or base functional groups onto a base film by grafting acrylic and 4-vinyl pyridine to the film. However, strong acid and base functional groups, such as sulfonic acid or trimethyl ammonium groups, are required to be attached to the base film for practical applications under a wide range of pH conditions. The main problem of introducing monomers that contain strong acidic or basic functional groups is the large hydration ion size of these monomers which are incompatible with the hydrophobic nature of these polymers where they are not immobilized within the film base.

Tsuneda et al. (1995) developed a method for the preparation cation and anion exchange membranes. The PE base film is pre-irradiated to ensure its readinessfor the introducion of monomers through the grafting polymerization process. Sulfonic acid (SO_3H) and triethyl ammonium ($N(CH_3)_3$) groups were introduced onto the PE substrate through the radiation induced graft copolymerization of sodium styrenesulfonate (SSS) with acrylic acid (AAc) for the cation exchange membrane and vinyl benzene triethylammonium chloride (VBTAC) with 2-hydroxyethyl methacrylate (HEMA) for the anion exchange membrane (Tsuneda et al., 1995).

Choi et al. (2001) demonstrated the introdction of glycidy methacrylate (GMA) into polyolefin nonwoven fabric (PNF) by radiation induced grafting and then modified the product with triethylamine [$-N(CH_2CH_3)_3$] and phosphoric acid ($-PO_3H$), where these functional groups are selective for the heavy metal ions (Choi et al. 2001; Oh et al. 2007).

In another study, Lee et al. (2002) used poly alkene non-woven fabrics (PNF) as a base material for the preparation of three cation exchange membranes with carboxylic acid, phosphoric acid, and sulfonic acid groups. These acids were mixed with PNF to introduce their functional groups through the radiation induced grafting technique (Lee et al., 2002).

(b) Casting

In the casting technique, Membrane is prepared by dispersion of a selective precursor in a polymer solution. Subsequently, the solution is casted onto a glass surface to form a thin film where its thickness is controlled using a spacer or thin surgery knife. The glass plate is immersed in water at room temperature to separate the membrane from the glass plate. Finally, the membrane is washed with deionized water to remove any unattached funcrional groups or solvent residue (Hosseini et al., 2010; Denizli et al., 2000).

Hosseini et al. (2010) prepared a heterogeneous cation exchange membrane using casting technique whereby a cation exchange resin is dispersed in a polymer binder solution (poly carbonate in THF solvent). The study revealed that an increase in the resin content caused an increase in water content, hydrophlicity, fixed ionic groups and ion exchange capacity. Moreover, the electrical resistance decreased. However, voids and cracks increased, resulting in poor mechanical properties of the membrane.

The increment in the resin content shows a high selectivity towards mono-valent ions over di-valent ions (Hosseini et al., 2010).

(c) Pore filled membranes

There are many materials that have a high degree of selectivity for specific ions such as hydrogels, complexing agent and polyelectrolytes. These selective materials have not been employed for membrane synthesis. the pore filling technique is a helpful way to produce ion selective membranes with good mechanical properties by introducing these selective materials into pores of a polymer substrate of good mechanical properties. Yamaguchi et al. (2002) expalined the technique asdepicted in Figure 2.2. Pore filling materials are anchored into the substrate pores by different methods such as physical adsorption, grafting, thin layer protection, entanglement and polymer chain cross-linking (Yamaguchi et al., 2002; Jiang, 1999).

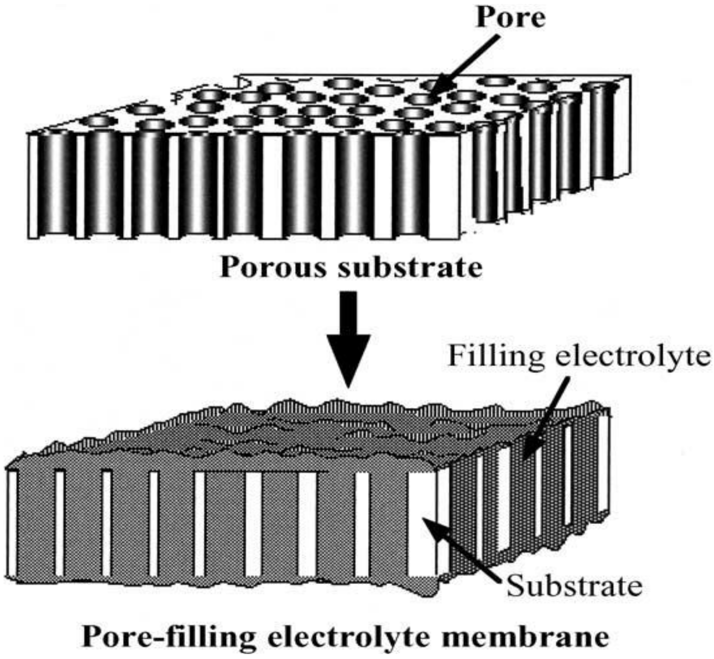

Figure 2.2 Pore filling electrolyte membrane (Yamaguchi et al., 2002).

The most durable pore filled membrane is the one prepared by applying a cross-linking and entanglement approach. Figure 2.3 shows an example where divinyl benzene (DVB) was used as a cross-linking agent to 4-vinylpyridine (4-VP) during the polymerization process to produce a pore filled membrane (Jiang, 1999).

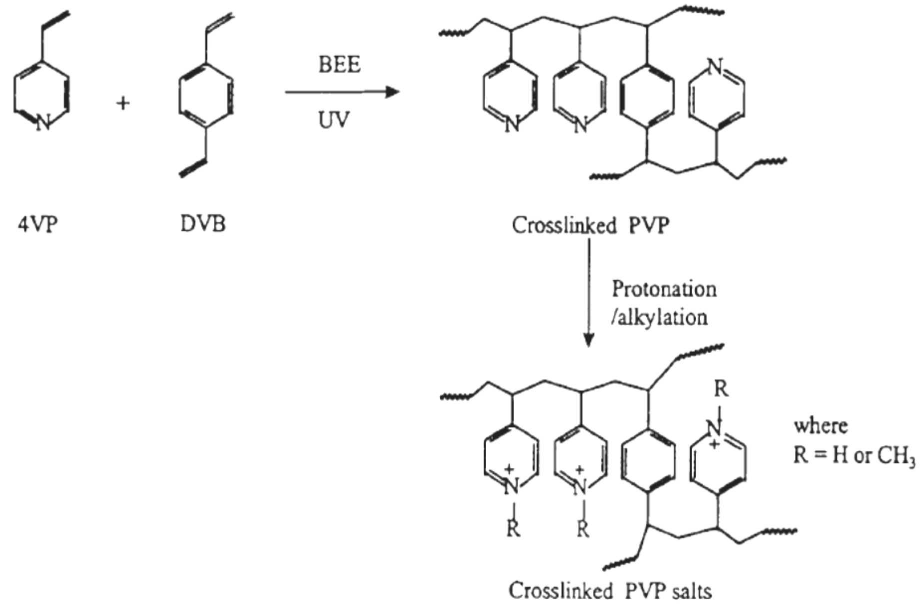

Figure 2.3 Preparation of crosslinked PVP (Jiang, 1999).

Polyelectrolyte pore filled membranes are used for ion exchange membrane production. The cross-linked polyelectrolyte swells to a certain degree and does not dissolve in water because it is caged in the host polymer network through cross-linking. As the degree of cross-linking increases, therfore, the swelling decreases.

T.Vasudevan et al. (2009) prepared pore filled a poly(proplyene) membrane substrate with ethylene glycol methacrylate phosphate groups as fixed sites for the selective separation of europium (III) in a dialysis process (Vasudevan et al., 2009).

The casting technique has some drawbacks: the preparation conditions are difficult to control and the dispersion of the ion exchange resin in the polymer solution may produce a membrane with poor mechanical properties. It can be inferred that pore filling and radiation grafting are more reliable methods for the preparation of ion exchange membranes.

There are important properties that govern the application of the membranes. These properties are: conductivity, stability, fouling resistance and selectivity. For separation and removal appplications, selectivity is of prime importance. Selectivity is determined by the type of fixed ionic groups that is functionalized in the membrane matrix.

2.2.2 Factors affecting membrane selectivity

Chemical composition and structure are main factors affect that membrane selectivity. The membrane backbone structure, fixed functional groups, length of side chains, molecular weight, degree of cross-linking, water content and solvation of ions are also important factors affecting selectivity. For example, increasing the number of hydrophilic fixed ionic groups in the membrane increases the hydrophilic degree of the membrane so that the selectivity of the transportation of ions through the membrane will decrease (Caprarescu et al., 2012; Davis et al., 1997). Hence, controlling the degree of hydrophilicity is important.

The physical structures, including thickness, porosity and polymer supporting material are important to consider for each specific application: the thinner the membrane is, the greater the permeation. The larger the pores the higher the flux, but, at the same time, larger pores cause the polymer's selectivity to decrease (Davis et al., 1997). For example, sulfonated polyether sulfone SPES-based CEMs was prepared by using the dry and wet phase inversion method to control the pore size and structure. The membranes that had interconnected pores showed poor selectivity while the membranes with dense structures and small pores were more selective (Klaysom et al., 2011). Figure 2.4 shows the effect of the membrane structure (porosity) on selectivity.

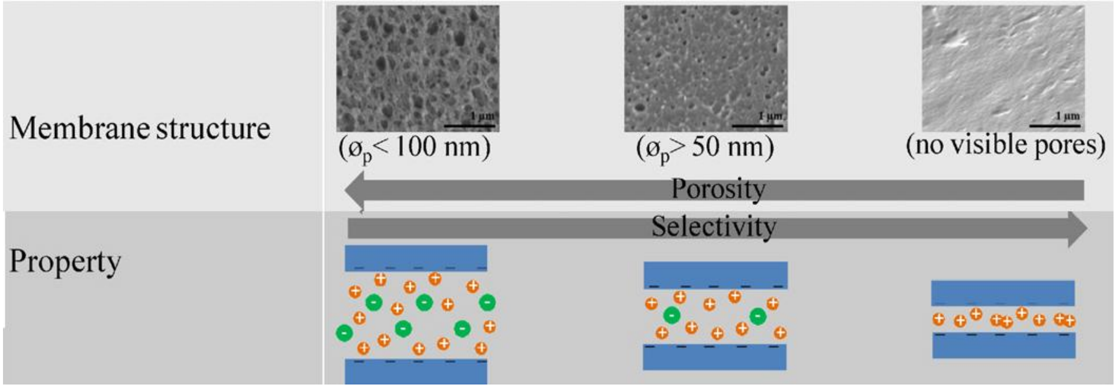

Figure 2.4 Effect of preparation conditions on the membrane structure, properties and stability (Klaysom et al., 2011).

Some of the membranes designed for selective separation processes take advantage of the above considerations and present some useful ideas. Some are given in the following sections.

For specific selectivity, such as the separation of mono-valent from multivalent ions and the competitive separation of ions of the same charge, the design of prepared membrane should take into account some different aspects (Davis et al., 1997). several proposed mechanisms were investigated based on IEM surface modifications such as electrostatic repulsion, cross-linkage, and effect of charge (Nagarale et al., 2006). The setric effect (due to cross-linking density of the membrane, charge and size of the ions) determines the mobility of ions. Counter-ions with a high charge and small hydrated ions show high permeability in the ion exchange membranes. For large hydrated ions, the predominant rule in selectivity is the sieving action rule (Strathmann, 2004; Caprarescu et al., 2012). Additionally, introducing certain functional site groups (where are more selective to certain ions) and imprinting (which provides more cation recognition) help the polymer to meet certain application purposes. The following two sections present membranes with more specific selectivity.

2.2.3 Membranes for selective separation of mono-valent from multi-valent cations

The separation of mono-valent cations from multivalent cations can be achieved by applying charge repelling polymers to ion exchange membrane surfaces. One study, for example, used a styrene/divinyl benzene copolymer poly(vinyl chloride) based membrane that was surface-coated with a thin film of a polymer containing a positive charge that repelled the multivalent cations and permeated mono-valent ones (Strathmann, 2004).

The surface coating process was achieved by treating the membrane surface with an aqueous solution of an amine to form amide groups with positive charges. Figure 2.5 shows this technique which produces ®Neosepta membranes (Davis et al., 1997).

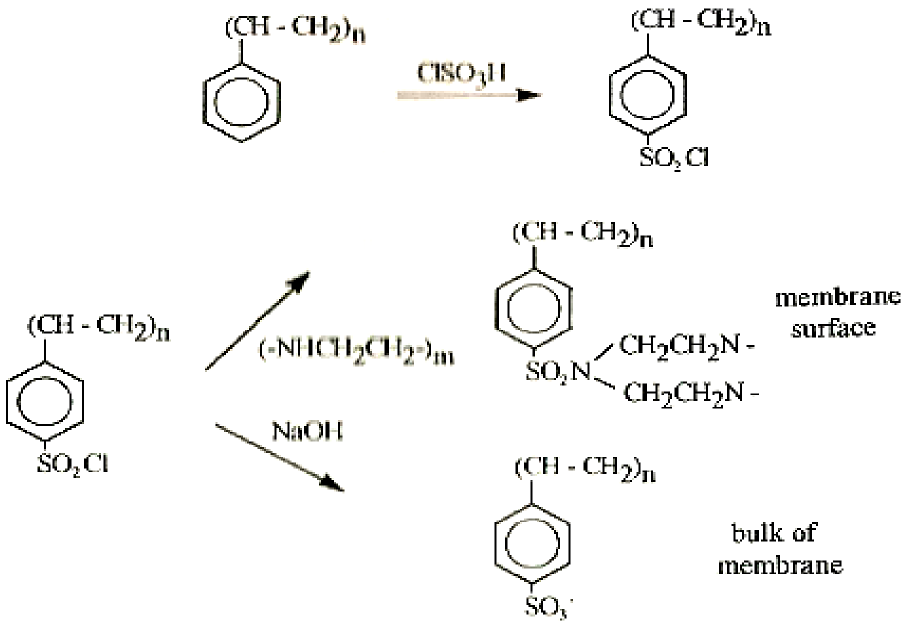

Figure 2.5 The production of ®Neopesta membranes (Davis et al., 1997).

Lambert et al. (2006) prepared a cation selective membrane to separate sodium ions (mono-valent) from tri-valent chromium ions by electrodialysis (ED) as shown in Figure 2.6. The membrane was prepared by electrodeposition of an electrolyte polyethyleneimine layer on the membrane surface (®Nafion 324) using ED where the polyelectrolyte polyethylenimine (PEI) is fully protonated in the solution as PEI-H^+. Under the applied potential, PEI-H^+ ions migrate to the cation exchange membrane where they are deposited on its surface to form a thin film. This positively charged layer repels the multivalent ions (Lambert et al., 2006).

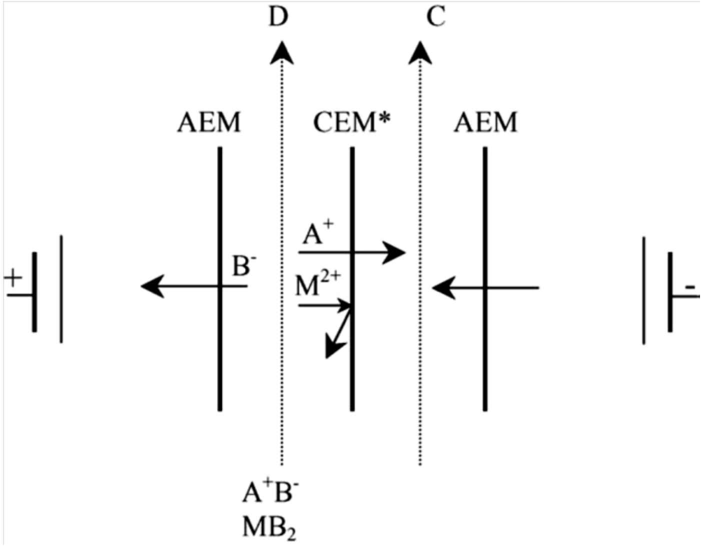

Figure 2.6 Separation of mono-valent from di-valent using ED, CEM*: mono-valent cation selective membrane, AEM: anion-exchange membrane, D: dilute, C: concentrate, electrolyte contains AB and MB_2 (Lambert et al., 2006).

Gohil et al. (2006) prepared a mono-valent ion selective composite membrane. Their method was to coat CEM and AEM with a thin layer of the conductive polymer polypyrrole. These ion exchange membranes are mainly interpolymer of polyethylene and styrene divinylbenzene copolymer. The conductivity of the composite membrane increased and the selectivity of mono-valent ions became higher as the polypyrrole film hindered the migration of the di-valent ions (Gohil et al., 2006).

In another study, a mono-valent selective CEM was modified to enhance its selectivity by grafting a thin layer of polyaniline to its surface. The modification was performed by catalytic reduction of p-phenylendemine on the CEM surface as shown in Figure 2.7 (Le et al., 2010). Polyaniline (PANI) and polypyrrole (PPy) are usually applied to enhance the selectivity of mono-valent cations because of their conductivity and the simplicity of their preparation (Cui et al., 2012).

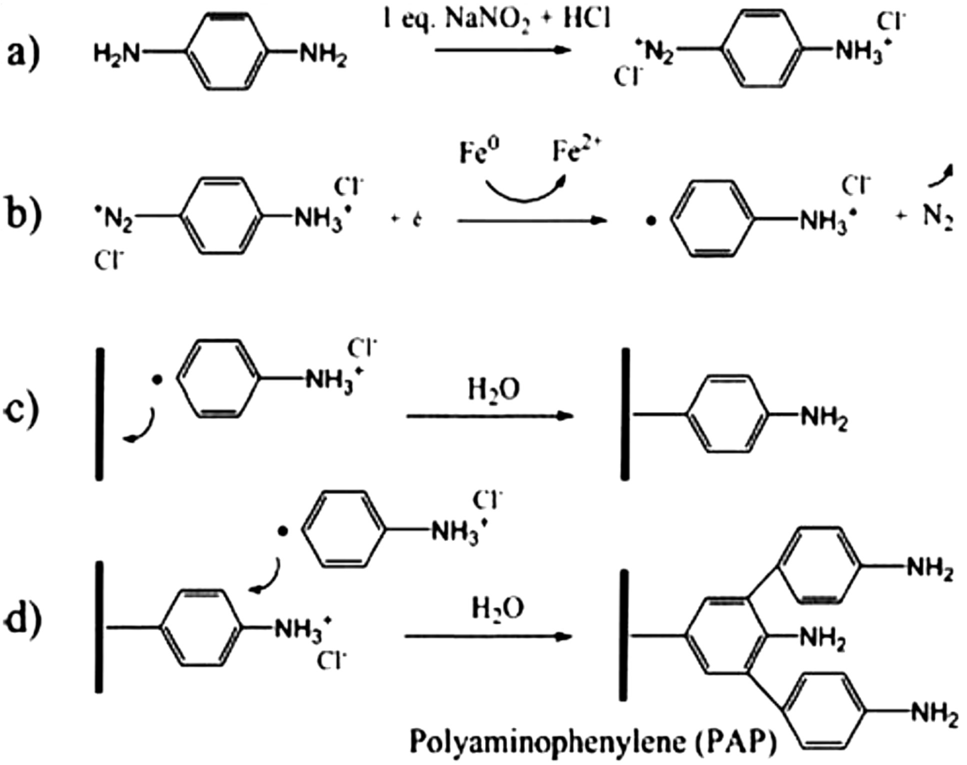

Figure 2.7 Polyaminophenylene (PAP) grafting onto CEM surface (Le et al., 2010).

Some sophisticated attempts were carried out to separate selected cations of the same valence. This is described in the next section.

2.2.4 Membranes for selective separation of cation from same valent cations

Attempts to enhance the selectivity of membranes make use from the selectivity of chelating polymers. A chelating polymer can be applied to an ion exchange membrane or blended in the polymeric matrix. Ion-imprinted technique can also be used to enhance the selectivity of the chelating polymer incorperated into ion exchange membranes. The next subsections provide explanation of the ion-imprinting technique and preraration of ion-imprinted membranes for ion selective separation processes as well as discussion of the chelating polymers, which have selectivity towards metal ions, and their applications as cation selective membranes for selective separation processes.

2.2.4.1 Ion-imprinted membranes

Ion-imprinting was developed to produce selective polymers for specific metal molecules (i.e molecular imprinting polymers MIPs) or metal ions (i.e ion imprinting polymers IIPs). Generally IIPs preparation is based on three main steps: (1) complexing metal to a polymerizable ligand, (2) polymerization of this complex, and (3) removal of the metal ion as shown in Figure 2.8 (Branger et al., 2013) .

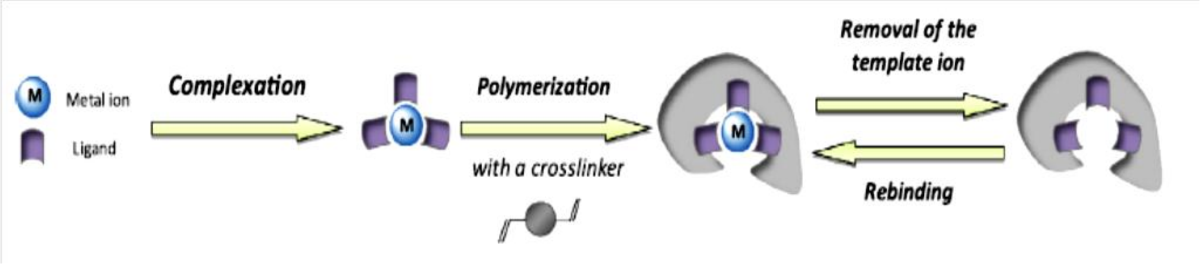

Figure. 2.8 IIPs preparation steps (Branger et al., 2013)

Polymerizable ligands contain both, a chelating function and a vinyl function, so they are called bi-function reagents. The polymerization mainly occurs by free radical polymerization of the vinyl group. The selectivity of the IIPs depends on the ligand affinity towards the imprinted metal and on the shape and size of the produced cavities. Cross-linking can maintain the complex geometry so that the cavities will suit the template metal ion. Ease of preparation and low expense are the biggest advantages of IIPS. Figure 2.9 depicts different methods for IIP preparation (Branger et al., 2013).

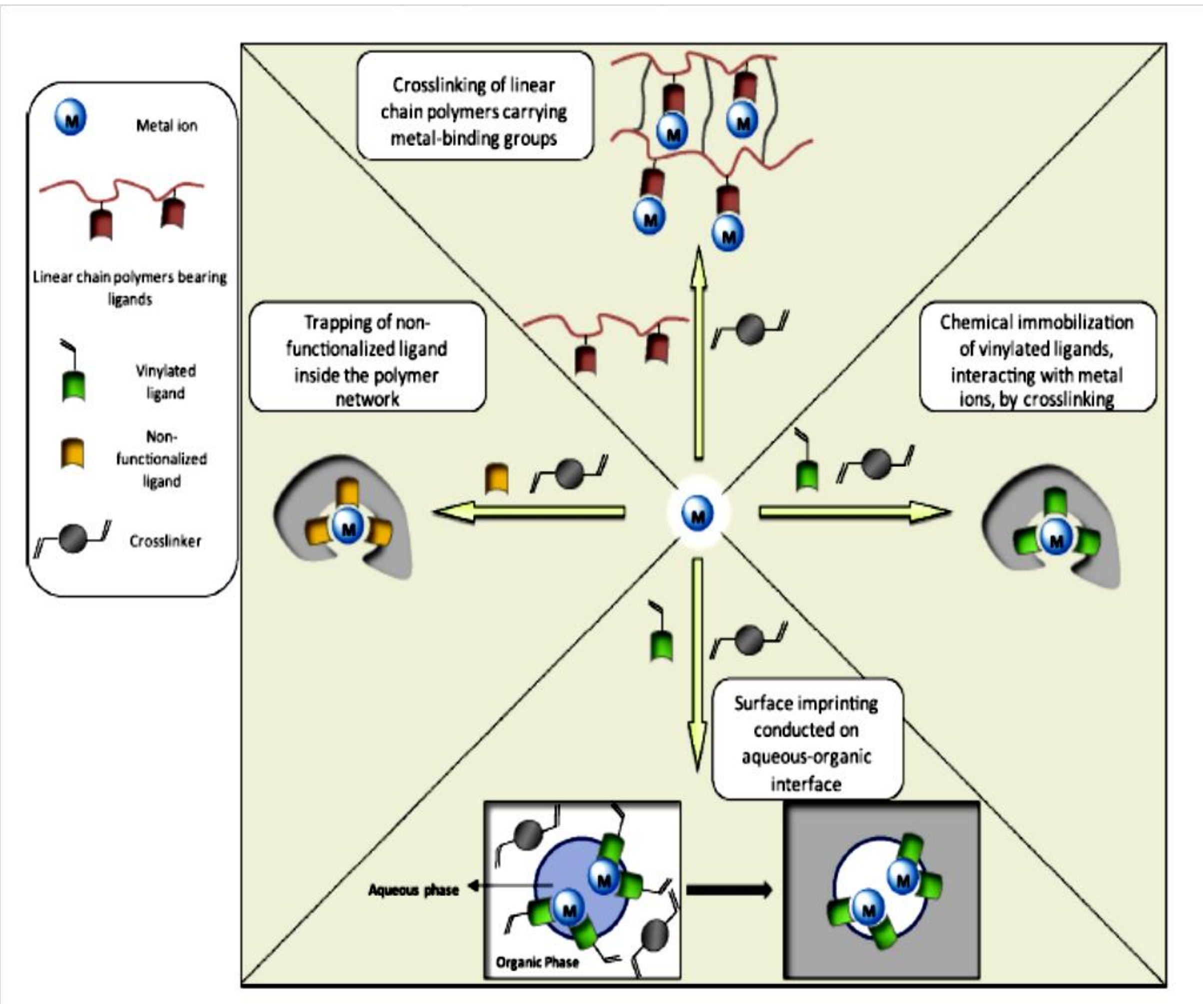

Figure 2.9 Different method for IIP preparation (Branger et al., 2013).

Zheng et al. (2012) prepared ion-imprinted micro-porous polypropylene membrane by graft polymerization that is followed by chemical treatment to be selective for copper (see Figure 2.10). The selective permeation of copper occurs by binding the imprinted sites onto the membrane surface (Zheng et al., 2012).

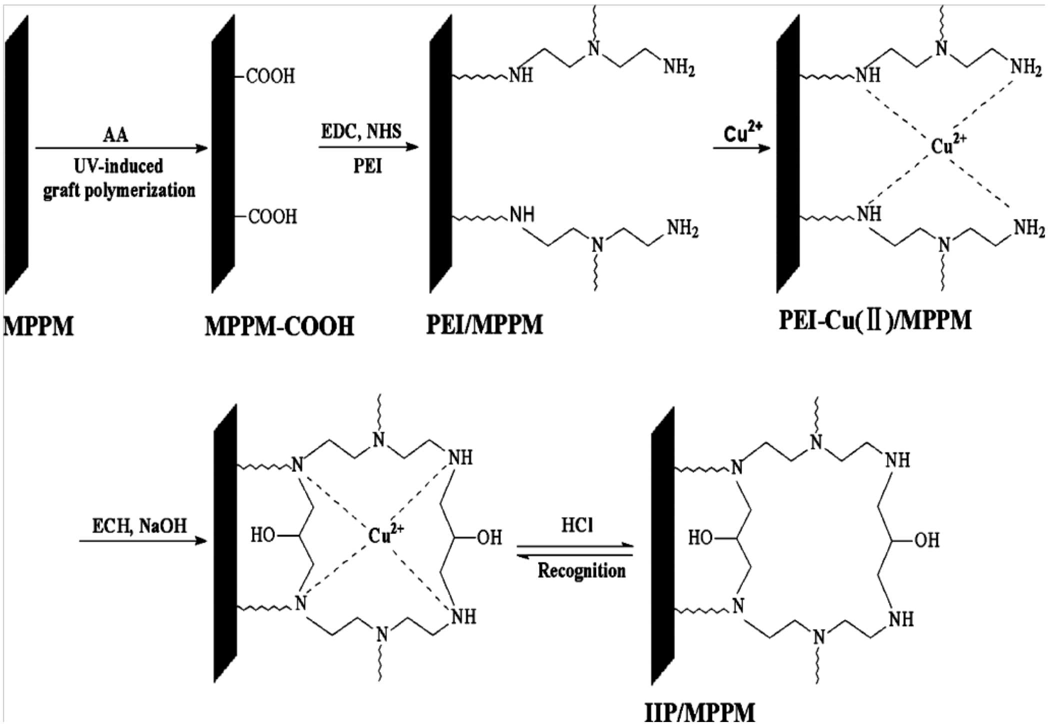

Figure 2.10 Preparation of ion-imprinted microporous polypropylene membrane by graft polymerization for the separation of copper (Zheng et al., 2012).

Zhai et al. (2008) prepared ion-imprinted membranes for zinc selective removal by complexing zinc with a 2,2'-bipyridyl chelating agent and then reacting the complex with 4-vinylpyridine monomer in the pores of a PVDF membrane substrate. the copolymerization reaction took place with cross-linker ethylene glycol, and the final step is to remove the target metal cation. In the permeation experiment in the presence of another cation, copper, the selectivity factor value reached 2.12 (Zhai et al., 2008).

Vahid et al. (2011) prepared an ion-imprinted selective membrane to separate nickel from cobalt. By using an ion-imprinting technique, the non selective chelating agent dithizone became nickel selective and was employed in the membrane by a copolymerization process. The ion-imprinted membrane shows a selectivity factor of 2 (Vatanpour et al., 2011).

Huning et al. (2014) prepared surface ion-imprinted cation exchange membranes for copper selective separation. A polyethylenimine PEI chelating agent was electrodeposited on a commercial cation exchange membrane and then imprinting was employed by immersion of this membrane in copper ion solution followed by soaking it in epichlohydrin as a cross-linker. The prepared membrane showed a selectivity factor for copper ion over zinc ion 2.11 (Saegusa et al., 1979).

2.2.4.2 Ion selective chelating membranes

The selectivity for certain metal ions can be achieved using specific chelating polymers. There are soluble polymers that are useful in the removal of heavy metals such as dendritic benzoylthiourea functionalized polyamide (DENBT), carboxymethyl cellulose (CMC), pectin (PEC) and polyethyleneamine (PEI). They are also effective for the adsorption of heavy metals from the aquatic solution in the pH range 4-7. Also, the PEI chelating polymer has high selectivity to Cu^{2+} over the other heavy metals (Schlichter et al., 2004). Polyamide-amine (PAMAM) dendrimer has a multi active NH_3^+ groups which act as a ligand. The polymer of (PAMAM) has an inner cavity that can act as an active carrier for selected ions as shown in Figure 2.11 (Jin et al., 2012).

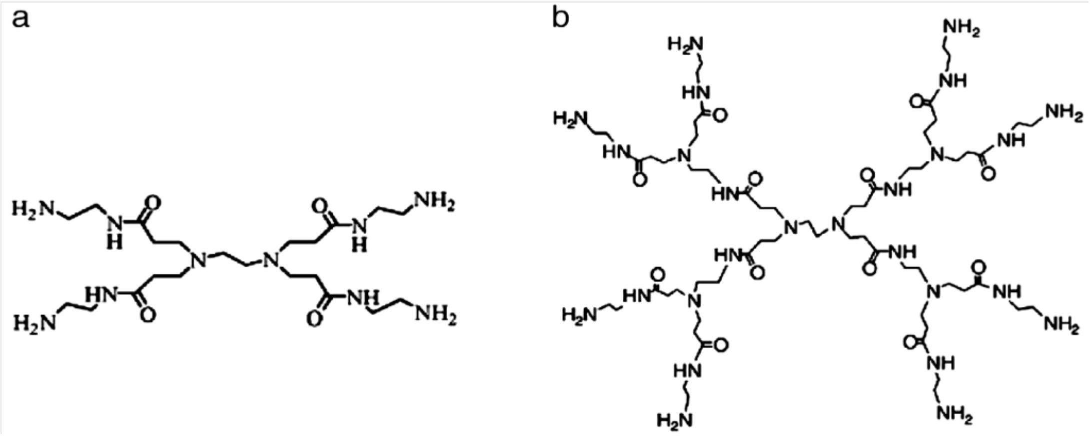

Figure 2.11 PAMAM chemical structure a) no generation, b) first generation (Jin et al., 2012).

A chelating hydrophilic ion exchange polymer (resin) for selective copper removal from other di-valent heavy metal ions (Ni^{2+},Co^{2+}, Zn^{2+} and Cd^{2+}) was prepared, as depicted in Figure 2.12, by anchoring the imidazole ligand bis(imidazo-2-yl)methylaminomethane (bimam) onto poly(glycidylmethacrylate-co-trimethylacrylate) (pGMT). The selectivity ratios of Cu^{2+} to Ni^{2+} and Zn^{2+} are 23:1 and 33:1 respectively at pH 5.8. Increasing the pH caused an increase in the uptake of di-valent heavy metal ions. The resin showed good durability after several times of loading/unloading of Cu^{2+}, which indicates a good chemical and mechanical stability (Sherringtonb, 1995).

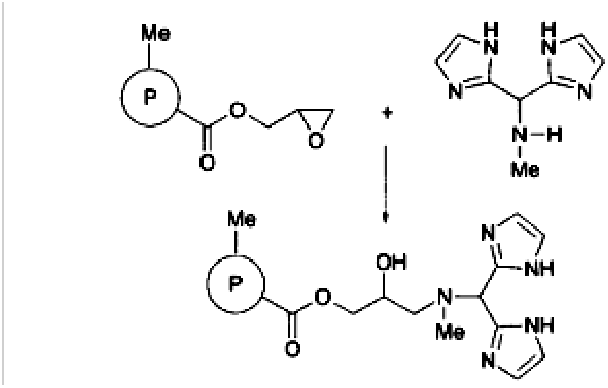

Figure 2.12 Introducing bimam ligand onto pGMT polymer (Sherringtonb, 1995).

Singh et al. (2000) prepared a selective chelating polymer resin for metal ions by fixing chelator complex geometry in the prepared polymer. For the preparation, a copper ion imprinted N-(4-vinylbenzyl) triethylenetetramine and N,N-di-(4-vinylbenzyl) triethylenetetramine were incorporated in (2-ethyl-2-(hydroxymethyl)propene-1,3-dioltrimethacrylate) the TRIM matrix then removal of copper ion by leaching to leave recognition sites selective for copper. The resin showed higher selectivity towards copper against nickel and zinc (Singh et al., 2000).

Different chelating membranes were prepared by introducing chelating polymers into a cross-linked network matrix. These polymers, which have a lone pair of donor electrons, can be selective for Cu^{2+} (Sherringtonb, 1995; Melby, 1974; Bessbousse et al., 2012; T. Kojima et al.,1994). T. Kojima (1994) prepared a cation exchange membrane with the chelating agent N-(8-quinolyl)-sulfonamide on the side chain of the polymer (polyacrylic acid) on a porous Teflon substrate as shown in Figure 2.13. The permeation experiment indicated that the membrane was more selective to Cu^{2+} than to Fe^{3+} because the chelating agent has a higher selectivity to copper.

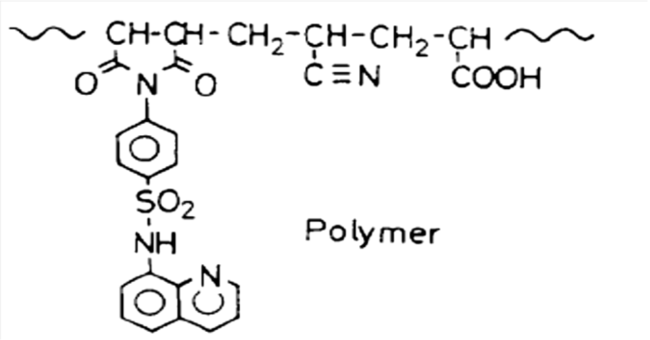

Figure 2.13 N-(8-quinolyl)-sulfonamide attached to an acrylic acid and acrylamide polymer (Kojima et al., 1994).

Chakrabarty et al. (2013) prepared a highly copper-selective zirconium triethylenetetramine complex membrane based on a cross-linked membrane as shown in Figure 2.14. This membrane was used for Cu^{2+} recovery through adsorption and ED. The copper ion transport mechanism through this membrane using ED is a three step process: (1) adsorption to the membrane, (2) ion migration through the chelating sites, and, finally (3) desorption on the other side of the membrane (Chakrabarty et al., 2013).

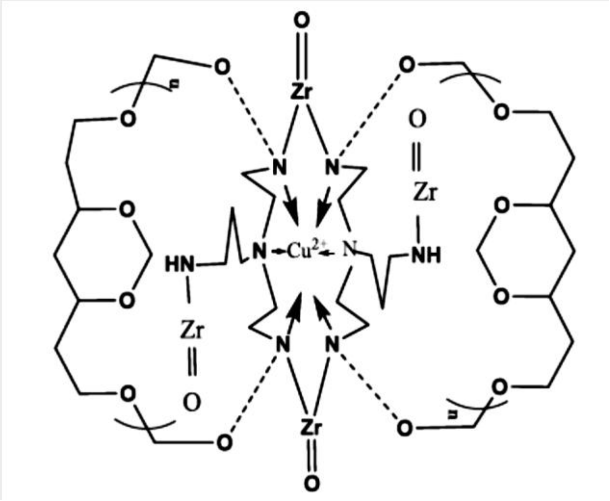

Figure 2.14 Chemical structure of zirconium triethylenetetramine chelating ligands complexed with copper (Chakrabarty et al., 2013)

Abd El-Rehim et al. (2000) synthesized a selective ion exchange membrane by introducing styrene/maleic anhydride (Sty/Man) functionalized comonomer into a low density polyethylene substrate (LDPE) by radiation graft copolymerization as described in Figure 2.15. The membrane was used for the removal of selected metal cations such as Cd(II), Cr(II), Cu(II), Fe(III), Ni(II) and Hg(II). Different functional groups were added to the prepared membrane such as hydroxylamine-HCl, semicarbazide, 2-aminopyridine, L-aspartic acid, thiourea and thiosemicarbazide in order to make the polymer selective to some heavy metals. The study showed that the selectivity towards Cu(II) by the chelating membrane originated from the thio semicarbazide (Abd El-Rehim et al., 2000).

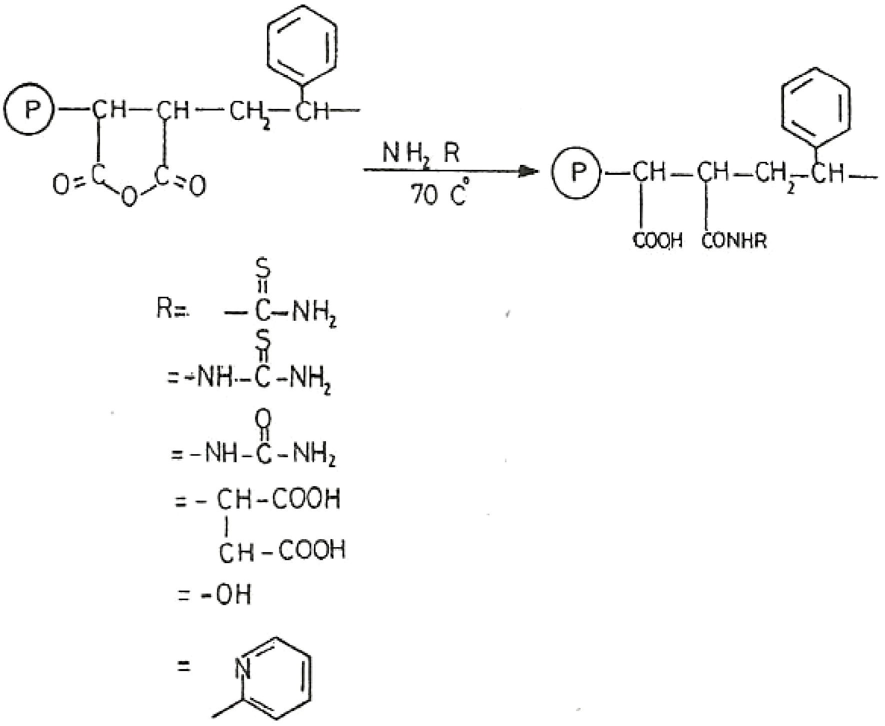

Figure 2.15 Anhydride (LDPE) –g- (Sty/Man) copolymer reaction with different amine groups to form different chelating compounds (Abd El-Rehim et al., 2000)

Sawicka et al. (1991) prepared a modified ion exchange membrane for the selective separation of metal ions using Donnan dialysis where a chelating agent Xylenol orange was applied to a commercial Teflon-based anion exchange membrane (Sawicka et al., 1991).

Saegusa et al. (1979) prepared a chelating ion exchange membrane from blending polyethyleneimine with polyepichlorohydrin. This membrane showed high selective permeation for Cu(II) over Ca(II) in diffusion dialysis permeation experiment with permeability ratio 3.8 (Saegusa et al., 1979).

Sheng et al. (2014) prepared cation selective permeable membrane by applying multiple layers of poly cations (poly[(N,N0-dicarboxymethyl) allylamine], PDCMAA), and poly(styrene sulfonate) and poly anion, poly(allylamine) (PAH), on an alumina substrate by adsorption. The membrane with alternating layers of PAH and PDCMAA and showed a selectivity factor of 50 Cu^{2+} over Mg^{2+} when used in diffusion dialysis selective separation process. For other copper metal ion mixtures Cu^{2+}/Ni^{2+} and Cu^{2+}/Ca^{2+}, the selectivity factor was around 10. The membrane with alternating layers of PAH and poly(styrenesulfonate) showed selectivity factor for Cu^{2+} over Mg^{2+} of 10 which is lower than the (PDCMAA)/(PAH) membrane because the sulfonate groups have no selectivity towards the permeating cations. In (PDCMAA)/(PAH), the iminodiacetate has an affinity towards Cu^{2+} over other cations in the solutions (Sheng et al., 2014).

It should be emphasized that ion-imprinting plays a key role in the design and implementation of the selective membranes. This is because the imprinting enhances selectivity by preserving the geometrical shape of the target cation during the membrane preparation, thus providing specific sites and channels for the selective permeation of the target cation.

In addition, it is observed that selective chelating polymers depend on the ligand part where multi dentate groups coordinate with a target cation with high K value (formation stability constant) compared to the other competitive cations. The coordination should be reasonably strong to give a mobility of the target cation from one chelating site to another adjacent one through the membrane during the permeation process. It seems that chelating agents, specially chelating polymers, have a great effect on metal ions selective separation using membranes.

2.3 Summary

Based on this literature review, the followings can be highlighted:

1- The fixed ionic groups in the membranes control the permeation of target ions. Type and charge of these groups affects the selectivity of the permeated ions through the membrane. Therefore, a cation selective membrane can be prepared by the good a choice of a chelating agent that has selectivity towards the target cation.

2- To guarantee the stable and reliable performance of the selective membrane, the chelating moieties have to be firmly bound in the membrane matrix. This can be achieved when a chelating agent is polymerized within the matrix of the host membrane. This requires a polymerizable chelating agent. As most of strong chelating agents are not monomers in the first place, monomerization is an essential pre-step. Hence, the selected chelating agent should be monomerizable. The selected chelating agent should not lose its selectivity property after the polymerization process is complete.

3- The polymerization of the chelating monomer should give a uniform distribution of the chelating groups across the host membrane during preparation.

4- The ion-imprinting technique is effective to enhance selectivity. The selected monomer should be able to preserve a geometrical shape of a target ion after polymerization with a suitable cross-linker when imprinting technique is employed. In addition, a linear structure of the polymerizable chelating agent is highly desirable.

5- As the concentration of the fixed ionic groups in the membranes is an important factor to improve permeation selectivity, it is preferable to select a chelating agent of a low molecular weight to insure a higher molar density which, in turn gives a greater number of chelating sites.

6- Durable membranes can be acquired by forming the selective polymeric matrix within or on a selected membrane as a supporting substrate.

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Chapter 3

Preparation and Characterization of Ion Selective Membrane and its Application for Cu^{2+} Removal

Abstract

Membranes are used in industrial wastewater treatment for the removal and recovery of heavy metals. A persistent challenge in heavy metals removal using membranes is the lack of selectivity for specific target ions, such as the removal and recovery of copper from other metal ions in industrial wastewater. This work reports the preparation of a new Cu(II)-selective ion-imprinted polymeric membrane. Membrane synthesis was conducted by applying an advanced immobilization method which comprises the preparation of polymerizable chelating monomer divinylbenzyl triethylenetetramine (diVB-TETA), the formation of the copper complex Cu-divinylbenzyl triethylenetetramine monomer (diVB-TETA-Cu), the polymerization/cross-linking of diVB-TETA-Cu within the Polyvinylidene fluoride (PVDF) pores to produce a copper-loaded membrane and finally the leaching of the copper (imprinting) from the membrane to produce ion-imprinted PVDF/diVB-TETA-Cu membrane. The chemical, elemental morphological properties of the synthesized ion-imprinted membrane were characterized by Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscope coupled with Energy dispersive X-ray spectroscopy (SEM-EDS). Proton nuclear magnetic resonance (^{1}H-NMR) and Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was used to confirm the chelating monomer chemical structure. To asses selective separation of Cu^{2+} from the mixture of Cu^{2+} and Ni^{2+}, adsorption at different pH settings and diffusion permeation experiments were carried out where Ion coupled plazma (ICP-OES) was used to measure the concentration of the metal ions. The results show that diVB-TETA-Cu was successfully synthesized and its immobilization through polymerization/cross-linking almost filled all PVDF pores. The PVDF/diVB-TETA-Cu selectively adsorbs Cu^{2+} at all studied pH, and its permeation flux ratio of Cu^{2+}: Ni^{2+} is 3.78. Based on this testing, the prepared membrane is suitable for Cu^{2+} ion selective separation processes.

Keywords: chelating membrane, PVDF, Cu^{2+} selectivity, heavy metal separation, triethylenetetramine (TETA).

3.1 Introduction

Membrane-based separation processes have a wide range of applications, industrial operations, environmental protection, and technology (Koseoglu et al., 2010; Khan, 2013). Separation by membranes is increasingly necessary because it is cost-effective, energy-efficient and environmentally friendly (Gohil et al., 2006 ; Ata et al., 2008; Hosseini et al., 2010; Fu and Wang, 2011). Selective separation of a specific cation by membrane is challenging (Lambert et al. 2006; Gopal et al., 1998). The specific cation separation can be used to isolate the targeted cation from other cations, even those belonging to the same type (e.g., d-block) and that have same valence (Chakrabarty et al., 2013). The needs for specific selective separation has several applications, including precious metal recovery, treatment of electronic waste, metal finishing, electroplating, and in industries such as the battery industry and metallurgical industries (Nabi et al., 2011; Lambert et al., 2006; Christensen and Delwiche, 1982;

Bessbousse et al., 2012; Abu and Moussab, 2004). The difficulty of such specific selective separation stems from the fact that similar cations may have similar permeation performance.

The most feasible approach to overcoming this difficulty is the synthesis of membranes by ion-imprinting technique. The ion-imprinting technique efficiently leads to tailored recognition sites within the three-dimensional mass of the membrane. These recognition sites are generated by configuring certain chelating ligand(s) around the template cation in a manner that memorizes solely that cation upon leaching. Such specific configuration by chelation sites is achieved through the matching of charge, size and coordination number of the targeted cation (Ulbricht, 2004; Singh et al., 2000).

The preparation of specific cation-selective polymer for this ion-imprinting technique can be achieved by the following four methods: (i) cross-linking linear chain polymers carrying metal-binding groups, (ii) trapping the non-functionalized (non-vinylated) chelating agent within the polymeric substrate matrix, (iii) imprinting the surface by simple or multiple emulsion polymerization, and (iv) using chemical immobilization of vinylated ligands by copolymerization/cross-linking within the polymeric substrate matrix. These methods are frequently used for the synthesis of polymeric particles and/or resins that usually applies for solid phase extraction, e.g. adsorption (Singh et al., 2000; Baghel et al., 2007; Branger et al., 2013; Piletsky et al., 1999).

For the membrane separation technique, a beneficial amendment can be derived from the fourth method with respect to synthesizing the specific cation selective membrane. The modification requires the selection of the used active chelating ligands to achieve the best permeation performance as possible. To achieve such permeation performance, the required active chelating ligands should meet the following criteria: (i) low molecular weight for ease of configuration with targeted template cation, (ii) multi-dentate to meet specified targeted cation, which can be defined according to its complex stability constant, (iii) appropriate hydrophilicity to provide the required media for ion transportation, and (iv) polymerizability to decrease the content of cross-linker within the membrane matrix to the expense of the content of chelating sites. Predomination of chelating sites should help in enhancing the membrane’s rebinding capacity and permeation flux due to the ease of hopping phenomenon (Zhai et al., 2008). The advantage of this method is that it provides the flexibility to chemically design a specific selective membrane through the proper selection of a chelating compound.

Previous discussions suggested that the synthesis of such new selective membranes may involve the following steps: (I) synthesis of polymerisable chelating monomer from a low molecular weight chelating compound by functionalizing it by two vinyl groups, where the selection of chelating compound depends on the targeted ion to separate, (II) complex formation of this targeted metal ion with the polymerizable chelating monomer, (III) polymerization/cross-linking of the complexed monomer within the substrate-membrane pores structure and, finally, (IV) stripping off and ion-imprinting the metal ion to leave vacant ion-recognition sites.

This work presents the synthesis of a specific selective membrane for di-valent cations utilizing the pervious suggested steps. Copper(II) was specified as the targeted cation due to the known various membrane separation applications that deal with it (Chakrabarty et al., 2013; Zheng et al., 2012; Deng et al., 2014; Deng et al., 2012). To investigate and assess the specificity of Cu^{2+} separation, the very similar cation, Ni^{2+} was selected as the competing cation to test accuracy; Cu^{2+} was separated from a Cu^{2+}/Ni^{2+} aqueous solution. Triethylenetetramine (TETA) was selected as the chelating compound because it matches the requirement of low molecular weight and hydrophilicity, and it is convertible to a polymerizable chelating monomer and has a higher complex stability constant with Cu^{2+} relative to that of Ni^{2+} ($\log K_{\text{Cu-TETA}}$ / $\log K_{\text{Ni-TETA}}$) = 20 / 14 (Irving and Williams, 1953).

In the present work, synthesis of the copper selective membrane follows the following steps: (I) preparation of the polymerizable chelating monomer by causing a reaction between TETA and bi-functional 4-vinylbenzyl chloride (4-VBC) to produce polymerizable TETA-4-VBC, (II) formation of the monomer complex of the target ion Cu(II)-TETA-4-VBC, (III) polymerization/cross-linking of monomer complex with divinylbenzene (DVB) within the pores of micro-porous PVDF substrate, and finally (IV) removal of copper template by acid treatment to produce Cu(II)-recognition sites within the membrane.

The produced samples were characterized using Proton nuclear magnetic resonance (^{1}H-NMR), Carbon-13 nuclear magnetic resonance (^{13}C-NMR), and Fourier transform infrared spectroscopy (FT-IR) to show the intended chemical structure of the membrane. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) were to reveal the morphological pattern of membranes' surfaces and to determine its elemental composition. To assess the selectivity of the membrane, a series of adsorption and diffusion permeation separation experiments of Cu^{2+} from Cu^{2+}/Ni^{2+} aqueous solution were carried out.

Results indicate that the synthesis of polymerizable chelating monomer and the polymerization/cross-linking of monomer complex within PVDF pores successfully produced the final selective membrane. Adsorption and diffusion permeation experiments indicate that the membrane has a high selectivity of Cu^{2+} over Ni^{2+}.

3.2 Experimental

3.2.1 Membrane synthesis

3.2.1.1 Materials

Hydrophilic micro-porous PVDF was supplied from Milipore Company and was used as the substrate (thickness: 125 µm, porosity: 70%, pore diameter: 0.65 µm, and water permeability: > 6 $ml/min.cm^2$). Vinylbenzyl chloride (VBC), divinyl benzene (DVB), benzoyl peroxide (BPO), triethylenetetramine (TETA), diethyl ether, acetone, chloroform and sodium amide were purchased from Sigma-Aldrich and were used for membrane preparation. Copper(II) and nickel(II) sulfates were also purchased from Sigma Aldrich. All chemicals needed no further purification, as they are of analytical grade reagent. Deionized water was used for all solution preparations.

3.2.1.2 Preparation of polymerizable chelating monomer diVB-TETA

diVB-TETA was prepared according to a previously reported method (Singh et al., 2000). TETA (6 g, chelating) was dissolved in the suspension of $NaNH_2$ (1.6 g, scavenger) in diethyl ether (50 mL). N_2 gas was bubbled in the suspension for 1 hour and then VBC (10.3 g) was added to the suspension. The mixture was allowed to react under reflux with stirring at 35^oC. After 5 hours, the products, monoVB-TETA and diVB-TETA, were produced and the reaction was terminated by the addition of water (2 mL). By rotary evaporation, ether was removed from the reaction mixture, leaving behind the orange-yellow mixture of monoVB-TETA and diVB-TETA. The mixture was dissolved in water (40 mL) and through the use of a separating funnel, extraction of the required di-substituted form (diVB) from the mixture was performed three times using chloroform (50 mL). The solution of diVB-TETA/Chloroform was treated by anhydrous $CaCl_2$ to remove any water residue to ensure the production of a pure diVB-TETA chelating monomer as an orange-yellow viscous liquid.

3.2.1.3 Formation of the diVB-TETA-Cu complex

Based on the previously reported method (Singh et al., 2000), diVB-TETA-Cu complex was prepared as follows: $CuSO_4.5H_2O$ (1.5 g) was dissolved in water/methanol mixture (3 mL/ 3 mL), diVB-TETA (1.85 g) was dissolved in a methanol/chloroform (10 mL/ 20 mL) mixture, and then both previous solutions were mixed together under effective stirring for about 15 minutes. The produced mixture was transferred to a separating funnel where a layer of dense navy blue organic product appeared on the bottom. This layer was collected and was treated with anhydrous $CaCl_2$ to remove any water residue. With ambient drying, solvent residue was evaporated to leave behind the pure diVB-TETA-Cu complex as a blue viscous liquid.

3.2.1.4 Polymerization and cross-linking of diVB-TETA-Cu within PVDF pores

diVB-TETA-Cu was polymerized with the presence of DVB as a cross-linking agent. Polymerization/cross-linking reactions were performed within the pores of PVDF substrate using a pore-filling technique according to a previously reported method (Jiang, 1999; Jiang et al., 2003; Mika et al., 1997). PVDF (sheets: each 8 × 8 cm^2) was treated by three consecutive soakings in acetone/water mixtures (1:3, 1:1, 1:0) each for 24 hours to remove original preserving organic filler within PVDF pores. After the filler removal, PVDF was vacuum dried and then weighed, a mixture of diVB-TETA-Cu/DVB/BPO (92:7:1) was prepared and then carefully poured into the bottom of the vessel reactor while PVDF sheets were affixed on the inner wall of a reactor vessel. The mixture was oxygen-degassed by three cycles of freeze pump thaw. The vessel was placed in a sonicator to aid in degassing and, finally, the reactor was filled with nitrogen gas. At this stage, PVDF sheets were evenly wetted by diVB-TETA-Cu/DVB/BPO mixture and polymerization/cross-linking reactions were commenced by submerging the vessel in a temperature controlled oil bath set at 85^{o}C. Polymerization/cross-linking reactions were allowed to continue for 10 hours. The produced PVDF/diVB-TETA-Cu membrane sheets were carefully removed from the reactor vessel and then purified by chloroform soxhlet extraction to remove non-anchored polymers and residual reactants. The extraction was repeated several times until no change in the dried sheets' masses was observed. The sheets were then dried under vacuum for 48 hours and were re-weighed.

3.2.1.5 Leaching of the copper (imprinting) from PVDF/diVB-TETA-Cu sheets

The prepared membrane sheets were immersed in HCl (1 M) to leach the copper and then were rinsed with plenty of water, and this process was repeated at least three times using freshly prepared HCl each time to guarantee complete leach of copper. The prepared membrane sheets were dried under vacuum for 48 hours and were weighed. Figure 3.1 demonstrates a schema for the synthesis of PVDF/diVB-TETA-Cu.

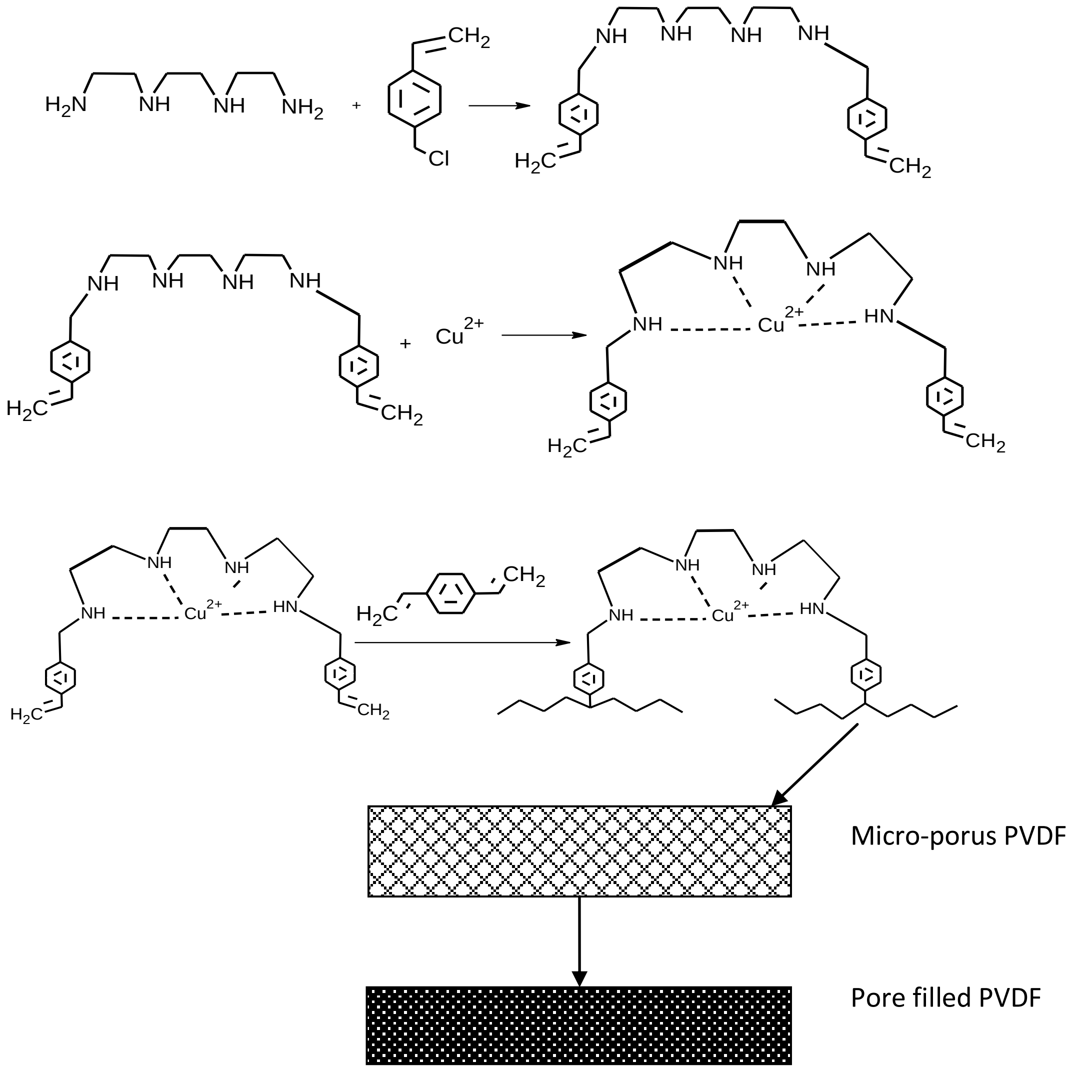

Figure 3.1 Reaction steps for TETA monomer, copper complexation and polymer synthesis onto micro-porous substrate PVDF.

The previous four steps were conducted to produce the ion-imprinted PVDF/diVB-TETA-Cu membrane. To prepare the non-imprinted PVDF/diVB-TETA membrane, the previous steps were re-applied excluding the second one. The control membrane preparation follows the same step preparation of the non-imprinted but without using the chelating monomer.

3.2.2 Membrane characterization

3.2.2.1 Structure study

^{1}H-NMR and ^{13}C-NMR spectra of chelating monomer (diVB-TETA) was recorded using Bruker NMR spectrometer to confirm the chemical structure of the prepared chelating monomer used in the polymerization reaction. For chemical structure, IR spectra of the substrate (PVDF), non-imprinted (PVDF/diVB-TETA) and ion-imprinted (PVDF/diVB-TETA-Cu) membranes were recorded using ThermoNicolet 6700 FT-IR spectroscopy (range: 4000 to 400 cm^{-1}, scans: 16 scans and resolution 0.5 cm^{-1}).

3.2.2.2 Morphology study

The surface morphology of the membrane was investigated by the field emission scanning electron microscopy SEM (FE-SEM, JEOL JSM 7000 F) coupled with energy dispersive X-ray spectroscopy (EDS) for elemental analysis. SEM was operated under a high vacuum at 5 kV. Prior analysis samples were dehydrated using a sequence of water/ethanol mixtures with increasing ethanol content (10-30-50-70-100%). The samples were dried for at least 48 hours under the vacuum. Samples were Pt sputter-coated with thickness of 5.6 nm so as to decrease the effect of charging on the examined membrane samples. EDS spectra were recorded by applying multiple points and selected area methods to the membrane.

3.2.2.3 Mass gain

The mass gain of PVDF/diVB-TETA and PVDF/diVB-TETA-Cu represents the amount of the anchored cross-linked/polymer in the substrate, PVDF, and it can be calculated from the following expression:

$$\text{Mass increase (\%)} = \frac{(m_\mathrm{f} - m_\mathrm{o})}{m_\mathrm{o}} \times 100 \qquad (3.1)$$

where m_f is the mass of the dried PVDF/diVB-TETA or PVDF/DVB-TETA-Cu, and m_o is the mass of the dried substrate, PVDF. The membrane samples were dried carefully in a desiccator under vacuum until a constant weight was achieved.

3.2.2.4 Water uptake

Water uptake represents the degree of swelling of the membrane and determines effects of the swelling on the membrane's on mechanical properties and conductivity (Kwak et al., 2012; Strathmann 2004; Khan, 2013). Water uptake can be calculated using the following expression:

$$\text{Water uptake (\%)} = \frac{(W_\mathrm{wet} - W_\mathrm{dry})}{W_\mathrm{dry}} \times 100 \qquad (3.2)$$

W_{wet} and W_{dry} are the masses of the membrane for the wet and dried forms respectively. The W_{wet} of a membrane was determined by immersing it into deionized water for 24 hours at room temperature. This step was followed by removing the membrane from deionized water and rejecting the non-texture water by pressing it between two filter papers, and then weighing. W_{dry} of a membrane was determined by drying it until no change in mass was recorded.

3.2.2.5 Ion exchange Capacity

The ion exchange capacity (IEC) gives information about the density of the active ionizable functional groups of the chelating polymer in the membrane. It was measured by the conventional titration method. The dried membrane immersed in a 1 M HCl solution and stirred for 24 hours to saturate the membrane with H^+. The membrane was then removed from this solution, rinsed several times with deionized water and dried under the vacuum for 24 hours. Then the H^+ saturated membrane was immersed in a known volume of 0.1 M NaOH solution to replace the H^+ with Na^+. The solution was then titrated with 0.1 M HCl solution using a phenolphthalein indicator to determine the H^+ released from the membrane. The IEC can be calculated form the following equation (Kwak et al., 2012):

$$\mathrm{IEC} = \frac{(\mathrm{V_{NaOH}} \times \mathrm{M_{NaOH}}) - (\mathrm{V_{HCl}} \times \mathrm{M_{HCl}})}{\mathrm{W}} \qquad (3.3)$$

W is the weight of the dried sample membrane, $\mathrm{M_{NaOH}}$ and $\mathrm{M_{HCl}}$are equivalent concentrations of NaOH and HCl solution, respectively, and $\mathrm{V_{NaOH}}$ and $\mathrm{V_{HCl}}$ are the

NaOH solution volume and HCl titrant volume consumed in acid-base titration, respectively.

3.2.3 Membrane selective separation

3.2.3.1 Adsorption experiment and pH effect

Adsorption experiments were conducted for PVDF, non-imprinted PVDF/diVB-TETA and ion-imprinted PVDF/diVB-TETA-Cu membranes. Prior to an adsorption experiment, a sheet sample (4 × 4 cm^2) of known weight of the membrane was conditioned by immersion in H_2SO_4 solution (1 M) using a shaking incubator at 110 rpm at ambient temperature and then was immersed in deionized water for 24 hours. After drying, the batch competitive adsorption of the metal ions was conducted by immersing the sheet in a solution (40 mL) of Cu^{2+} (100 mg/L) and Ni^{2+} (100 mg/L) with pre-adjusted selected pH value (2, 4 and 6). To guarantee equilibrium, adsorption was left to proceed for 48 hours under shaking. After this period, the sheet was removed from the solution and rinsed with plenty of deionized water to remove any traces of un-adsorbed ions and then left for ambient drying. To determine actual adsorbed amounts of ions, the sheet was immersed in a shaken H_2SO_4 solution (40 mL, 1 M) for 24 hours. After this period, the sheet was removed from the solution and the concentrations of leached Cu^{2+} and Ni^{2+} were measured using ICP-OES (VARIAN VISTA Pro.).

3.2.3.2 Permeation selectivity

The permeation selectivity of the prepared membranes towards examined cations, Cu^{2+} and Ni^{2+}, was determined by diffusion dialysis technique (Heinrich Strathmann, 2011). A diffusion dialysis cell was used where the concentration difference between the feed solution phase and the receiving solution phase is the driving force for ion transportation through the membrane. The cell is a lab-made and has two compartments (35 mL each) separated by a circular opening (effective area = 7.07 cm^2).

A sheet of the test-membrane was preconditioned in 1M of both HCl and NaOH solutions and was soaked in deionized water for 24 hours before the conduction permeation selectivity experiment, after which point it fitted firmly between the two compartments. The feed phase compartment was filled with solution of Cu^{2+} (100 mg/L= 1.6 mM) and Ni^{2+} (100 mg/L =1.7 mM) and the receiving phase compartment was filled with H_2SO_4 (1 M). The two compartments were stirred at an ambient temperature. An aliquot sample was withdrawn from receiving phase compartment every selected several hours up to 24 hours to analyze by ICP-EOS spectroscopy to determine the extent of permeation of for Cu^{2+} and Ni^{2+} competitive cations. Permeation rates of the cations through the control, non-imprinted and ion-imprinted membranes can be represented by their fluxes which were calculated from the amount of cations that permeated the unit area of the membrane in 24 hours. The separation factor is the ratio of the permeation flux of the selected cation to the permeation flux of the other existing cation, (α = flux [Cu]/ flux [Ni]), and relative selectivity ratio, ($\alpha' = \alpha_{membrane}/ \alpha_{control}$), were also calculated.

3.3 Results and discussion

3.3.1 Chemical structure (NMR and IR analysis)

To investigate the success of the production of diVB-TETA chelating monomer from diVB and TETA, NMR analysis was carried out. For ^{1}H-NMR spectrum as shown in Figure 3.2, the peaks at σ = 7.30 and 7.28 ppm are attributed to *H* in (C–*H*) in aromatic ring, the peak at σ = 7.15 ppm is attributed to *H* in (–CH=C*H*–), the peak at σ = 6.68 ppm is attributed to *H* in (CH_2=C*H*–), the peak at σ = 5.72 ppm is attributed to *H* in (C*H*H=CH–), the peak at σ = 5.21 ppm is attributed to *H* in (CH*H*=CH–), the peak at σ = 4.35 ppm is attributed to *H* in (CH_2N*H*–), the peaks from at σ = 3.7 – 3.9 ppm are attributed to *H* in (N–CH_2–CH_2–N–) and the peak at σ = 2.85 ppm is attributed to H in (N*H*–).

The ^{13}C-NMR spectrum shown in Figure 3.3 peaks at σ = 137.50, 136.50, 128.23 and 126.45 ppm and are attributed to *C* in aromatic carbon (Ar*C*), σ =136 ppm is attributed to *C* in (Ar*C*CH_2), σ = 114.50 ppm is attributed to *C* in (–CH=*C*H_2), σ= 45.89 ppm is attributed to *C* in (CH_2–*C*H_2–), the peak at σ =58.50 ppm is attributed to *C* in (Ar*C*H_2–NH–), which confirms bond formation of amine group with of TETA with vinyl benzyl chloride (the nucleophilic substitution) and the peak at σ = 52–48 ppm is attributed to *C* (NH–*C*H_2–CH_2–). The peaks at σ = 6.68, 5.72 and 5.21 ppm from ^{1}H-NMR spectrum and the peaks σ = 114.50 confirm the structure of the vinyl group that attached to the chelating monomer. The peak at σ = 58.50 ppm confirms the formation of the bond between TETA and vinylbenzyl chloride (Ar*C*H_2–NH–) from the nucleophilic substitution reaction. This confirms the functionalization of the chelating agent with the vinyl group and shows that it is ready for polymerization reactions.

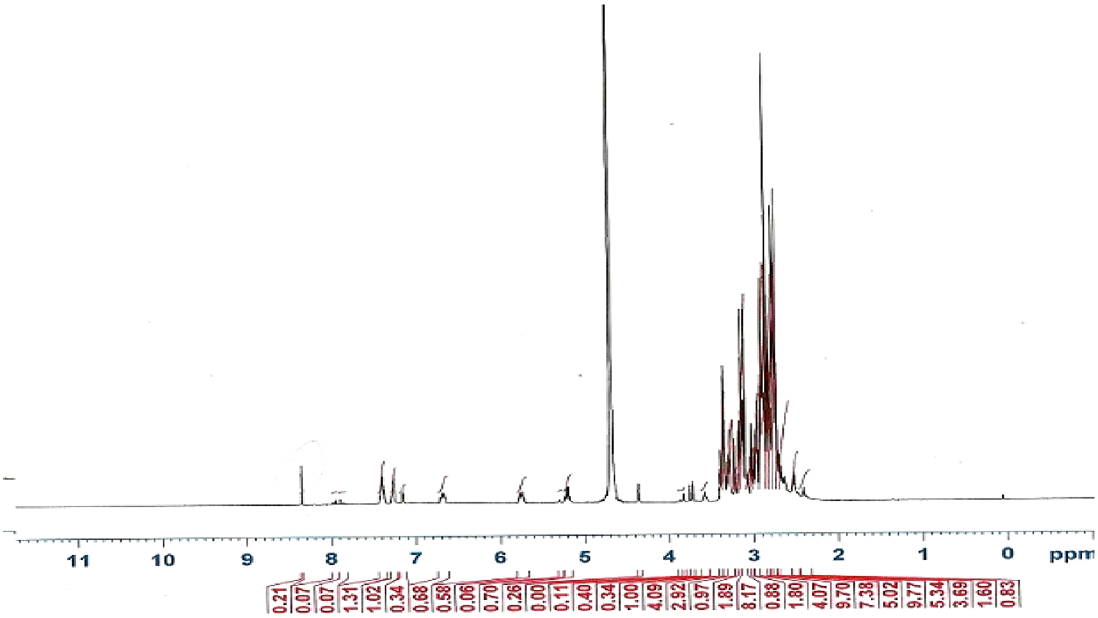

Figure 3.2 ^{1}H-NMR of diVB-TETA chelating monomer

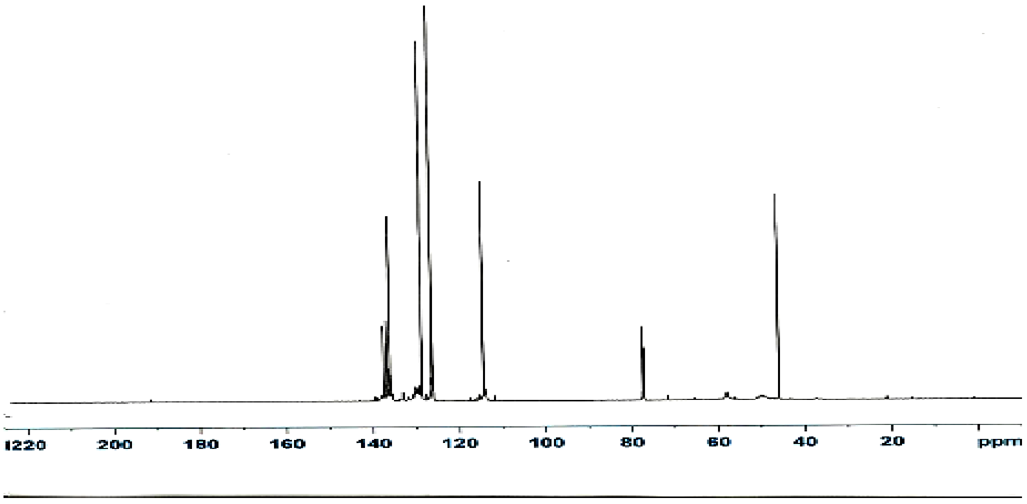

Figure 3.3 ^{13}C-NMR of diVB-TETA chelating monomer

Figure 3.4 shows the IR spectra of PVDF, non-imprinted PVDF/diVB-TETA and ion-imprinted PVDF/diVB-TETA-Cu membranes. For the spectrum of PVDF, peaks in the range of 3000-2840 and 1365-1120 cm^{-1} are respectively attributed to C-H alkane stretching and alkyl halide C–F bond stretch. These peaks confirm the known chemical structure of PVDF. For PVDF/diVB-TETA and PVDF/diVB-TETA-Cu, peaks in the range of 3050-2900 cm^{-1} confirms stretching of C–H bond in alkanes groups. Peaks in the range of 3500-3100 cm^{-1} are attributed to N-H secondary amines. Peaks of 3100-3000 cm^{-1} are attributed to the C-H in the aromatic ring. Medium peaks at 1500 cm^{-1} are attributed to C–C stretching in the aromatic ring. The peaks in the range of 1650-1580 cm^{-1} refer to N–H stretching bond of the aliphatic amine group and the 1140 cm^{-1} peak refers to the C–N stretch and confirms the presence of the amine group in the chelating copolymer in the PVDF/diVB-TETA and PVDF/diVB-TETA-Cu membranes.

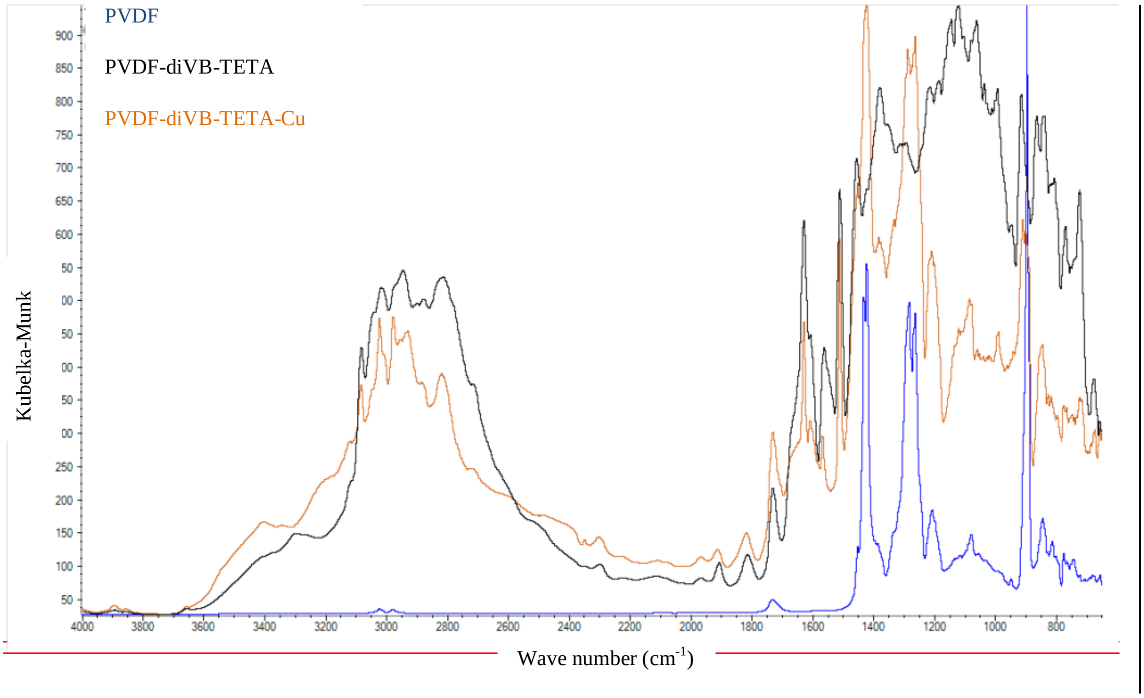

Figure 3.4 FT-IR spectrum for PVDF (blue), non-imprinted PVDF/diVB-TETA (black) and ion-imprinted PVDF/diVB-TETA-Cu membranes (orange).

The absence of peaks at 1264 cm^{-1}, which represent $–CH_2Cl$ groups, confirms that the amino group in TETA reacted with $–CH_2Cl$ group in VBC, and the produced chelating monomer used in the copolymerization reaction did not contain any residuals of VBC carrying with the $–CH_2Cl$ group.

3.3.2 Morphology and visual appearance of prepared membranes

Figure 3.5 shows SEM images of (a) PVDF, (b) PVDF/diVB-TETA, and (c) PVDF/diVB-TETA-Cu. In Figure 3.5(a), the PVDF substrate has a highly open micro-pore structure and a spongy texture with irregularly sized roughly circular openings cells with 1–2 μm diameter on average. In Figure 3.5(b) we can see that the incorporation of the PVDF membrane with diVB-TETA to form PVDF/diVB-TETA results in the pore-filling of PVDF with the diVB-TETA chelating polymer. This change suggests the success of pore-filling of PVDF with diVB-TETA and that permeation by PVDF/diVB-TETA should be through diVB-TETA. In Figure 3.5(c), the PVDF/diVB-TETA-Cu membrane shows no micro-pores, which means that the membrane substrate is completely pore-filled with the diVB-TETA chelating polymer. The PVDF/diVB-TETA-Cu surface is smooth, and this may be due to the final preparation step at which the membrane immersed in a 1 M HCl solution to remove copper form the chelating polymer.

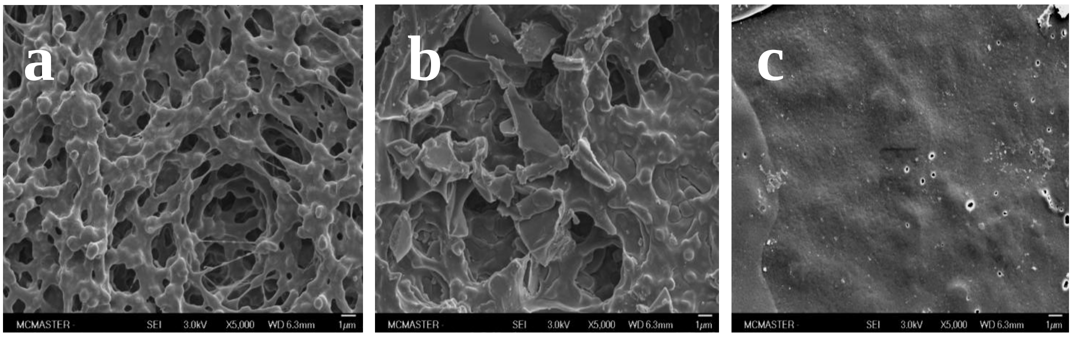

Figure 3.5 SEM surface images at 5000X of (a) PVDF substrate, (b) PVDF/diVB-TETA, and (c) PVDF/diVB-TETA-Cu pore filled membranes.

Figure 3.6(a) shows the white opaque micro-porous PVDF substrate membrane. Upon polymerization/cross-linking of the orange-yellow diVB-TETA within PVDF pores, an orange yellow PVDF/diVB-TETA membrane is produced as shown in Figure 3.6(b). Figure 3.6(c) shows the dark blue PVDF/diVB-TETA-Cu membrane before the imprinted copper was removed. Figure 3.6(d) shows PVDF/diVB-TETA-Cu ion-imprinted membrane after copper ions were removed by replacing them with H^+ in a strong 1M HCL solution.

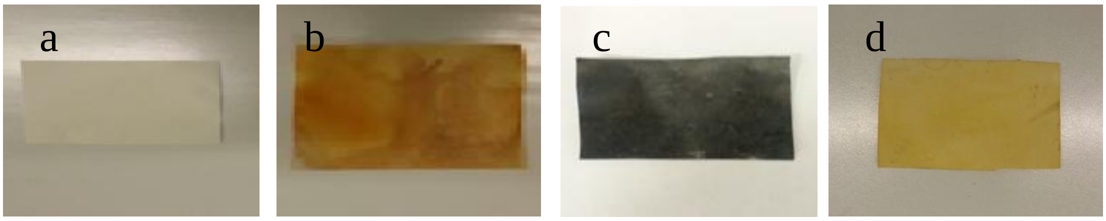

Figure 3.6 (a) PVDF, (b) PVDF/diVB-TETA, (c) Cu-loaded PVDF/DVB-TETA-Cu, and (d) ion-imprinted PVDF/diVB-TETA-Cu membranes.

3.3.3 Mass increase and water uptake

Table 3.1 shows the water uptake and mass increase result for PVDF, PVDF/diVB-TETA, PVDF/diVB-TETA-Cu membranes. The mass of the PVDF/diVB-TETA membrane increased by 113.48% from that of the PVDF substrate while the mass of the PVDF/diVB-TETA-Cu membrane increased only by 81.62%. This difference can be explained by the fact that copper was leached from the PVDF/diVB-TETA-Cu membrane. In general, both values are high enough to suggest that permeation should be controlled by the diVB-TETA anchored within these membranes' textures. Although mass increase in the non-imprinted PVDF/diVB-TETA is higher than that in the ion-imprinted PVDF/diVB-TETA-Cu, the amount of Cu^{2+} adsorption by the ion-imprinted membrane is greater than that in the non-imprinted membrane, as shown in the following adsorption section. This difference is due to the imprinting effect.

PVDF/diVB-TETA-Cu gains water almost three times higher than that of PVDF/diVB-TETA, and this could be due to vacancies left after the copper was removed. This nano-scale pore is thought to help separation of copper ions. The reasonable water uptake values of 10.77 ± 3.37% and 29.77 ± 5.3% for the membranes PVDF/diVB-TETA and PVDF/diVB-TETA-Cu, respectively, give an indication that the structures of the membranes are intact.

The IEC for the PVDF/diVB-TETA membrane was higher than that of the PVDF/diVB-TETA-Cu, and this difference is due to the greater amount of diVB-TETA in PVDF/diVB-TETA compared to its amount in PVDF/diVB-TETA-Cu.

Table 3.1. Mass increase and water uptake for PVDF/diVB-TETA and PVDF/diVB-TETA-Cu membranes

Sample	**PVDF/diVB-TETA**	**PVDF/diVB-TETA-Cu**
Mass increase (%)	113.48 ± 5.2	81.62 ± 11.7
Water uptake (%)	10.77 ± 3.37	29.77 ± 5.3
IEC (meq/g)	2.33 ± 0.23	1.052 ± 0.04

IEC: ion exchange capacity
Standard deviation was conducted from 3 different membranes

3.3.4 Effect of pH on Copper Adsorption

The results of the ICP analysis indicate that adsorption of Ni^{2+} by the PVDF/diVB-TETA membrane was not detected. Figure 3.7 shows the adsorbed amounts of Cu^{2+} by non-imprinted PVDF/diVB-TETA at different pH. Adsorption of Cu^{2+} increases gradually as pH increases from 2 to 6. The greatest amount of adsorbed copper was 17 mg/g at pH 6. It can be concluded that the PVDF/diVB-TETA membrane is specifically selective towards Cu^{2+} in the presence of Ni^{2+} due to diVB-TETA in the prepared membranes as previously reported (Xiong et al., 2012; Liu et al., 2010; Sherringtonb, 1995).

Figure 3.7 also shows the adsorbed amounts of Cu^{2+} by the ion-imprinted PVDF/diVB-TETA-Cu membrane at different pH levels, though the Ni^{2+} adsorption by PVDF/diVB-TETA-Cu was not detected. The adsorption of Cu^{2+} increases steeply as the pH increases from 2 to 6. The specific selectivity of PVDF/diVB-TETA-Cu towards Cu^{2+} in the presence of Ni^{2+} is due to the copper-leached diVB-TETA-Cu-anchored polymer.

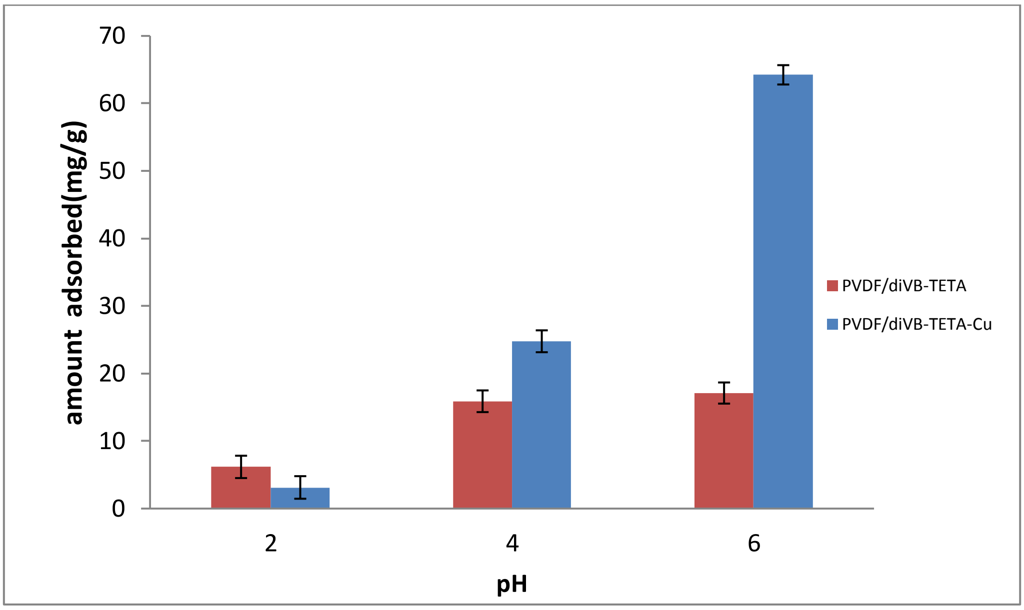

Figure 3.7 Adsorbed amount of copper by non-imprinted PVDF/diVB-TETA and imprinted PVDF/diVB-TETA-Cu membranes at pH values (2, 4 and 6).

In addition, the adsorbed amount of copper by ion-imprinted PVDF/diVB-TETA-Cu is 3.76 times greater than that by non-imprinted PVDF/diVB-TETA, although the number of copper-leached sites of diVB-TETA-Cu is less than diVB-TETA. The highest amount of adsorbed copper is 64 mg/g at pH 6. It can be suggested that stereo configuration of copper-leached sites of diVB-TETA-Cu is better at recognizing Cu^{2+} than diVB-TETA. (Singh et al., 2000).

Figure 3.8 shows EDS recorded spectra of PVDF, PVDF/diVB-TETA, and PVDF/diVB-TETA-Cu after Cu^{2+}/Ni^{2+} adsorption experiments at pH 5.6. Each spectrum is one of a triplicate with consistently similar measurements.

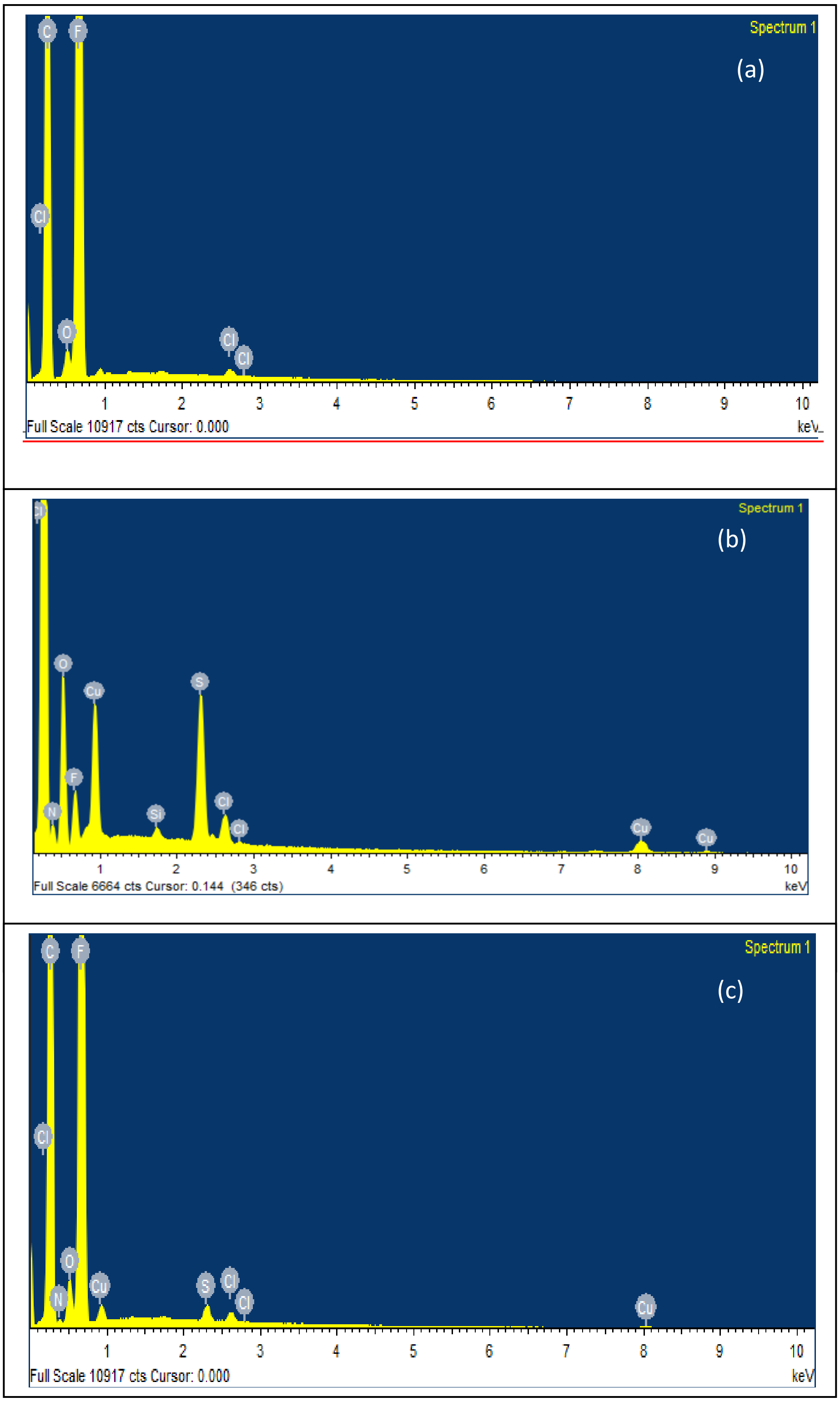

Figure 3.8 EDS of (a) PVDF, (b) PVDF/diVB-TETA and (c) PVDF/diVB-TETA-Cu membranes (adsorption solution of C_o = 100 mg/L for each Cu^{2+} and Ni^{2+} at pH = 5.6 and the leaching solution was 1 M H_2SO_4) .

The PVDF spectrum does not comprise copper or nickel peaks, which indicates that PVDF surfaces do not attract these ions. Spectra of PVDF/diVB-TETA and PVDF/diVB-TETA-Cu comprise peaks for copper, while nickel does not appear in the EDS results. This result implies the high selectivity of these two membranes for Cu^{2+} over Ni^{2+}.

3.3.5 Diffusion dialysis results

Figure 3.9(a) shows the diffusion permeation with respect to time through the control membrane for both Cu^{2+} and Ni^{2+}. From the figure, the increase of permeation of Cu^{2+} with time is similar to that of Ni^{2+}. Hence, it can be concluded that the PVDF membrane structure is neither selective for Cu^{2+} nor for Ni^{2+}. Both ions transport freely through the membrane without preference, as expected.

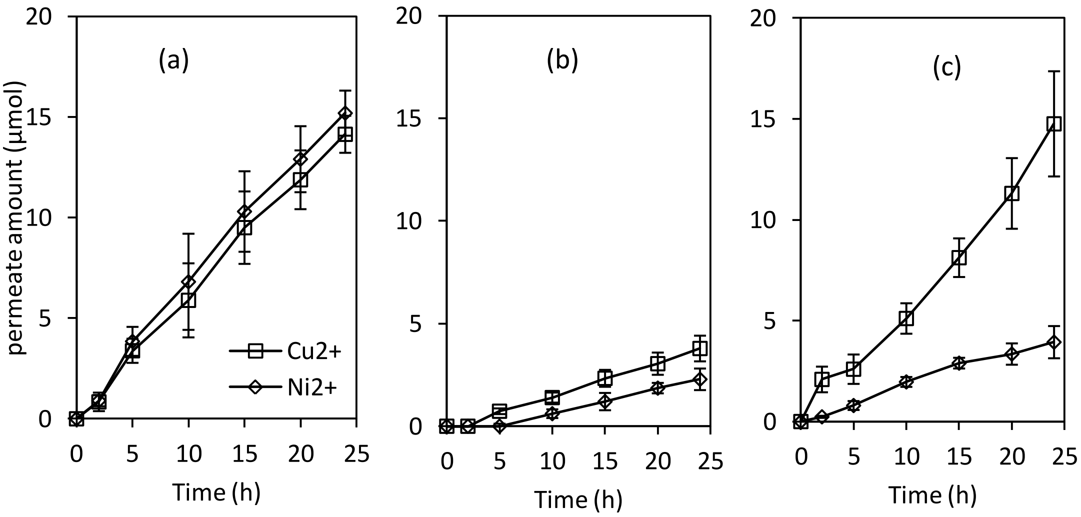

Figure 3.9 Cu^{2+} and Ni^{2+} permeation through (a) control.

(b) PVDF/diVB-TETA, and (c) PVDF/diVB-TETA-Cu membranes. (A = 7.07cm^2, $C_o(Cu^{2+},Ni^{2+})$ = 100 mg/L and solution receiving side is 1 M H_2SO_4)

The diffusion dialysis separation experiment using a non-imprinted PVDF/diVB-TETA membrane resulted in the slow permeation of both Cu^{2+} and Ni^{2+}, as shown in Figure 3.9(b). However, the permeated amount of Cu^{2+} was greater than the permeated amount of Ni^{2+}. At the end of the experiment (24 hours), the total permeated amount of Cu^{2+} is 1.65 times higher than that of Ni^{2+}. The permeated amount of Cu^{2+} through the ion-imprinted PVDF/diVB-TETA-Cu membrane increased more rapidly with time than the increase in the permeated amount of Ni^{2+}, as Figure 3.9(c) shows. At the end of the experiment (24 hours), the permeated amount of Cu^{2+} was 3.78 times higher than that of Ni^{2+}. In addition, the total permeated amount of Cu^{2+} through the PVDF/diVB-TETA-Cu membrane was greater than that of the PVDF/diVB-TETA membrane. Also, the total permeated amount of Ni^{2+} through the PVDF/diVB-TETA-Cu membrane was much smaller than that which came through the PVDF/diVB-TETA membrane. This result indicates that PVDF/diVB-TETA-Cu separates Cu^{2+} from its mixture with Ni^{2+} more efficiently. Thus, our membrane preparation method for PVDF/diVB-TETA-Cu membrane can be used to selectively separate Cu^{2+} from industrial wastewater containing Ni^{2+}.

In Table 3.2, the separation factor (α) of the control membrane is close to unity which indicates that the PVDF material is not selective to either cation. Both of non-imprinted and ion-imprinted membranes have $\alpha > 1$. This means that TETA present in the PVDF/diVB-TETA membrane shows a higher affinity to Cu^{2+} than it does to Ni^{2+}. Moreover, the $\alpha_{\text{ion-imprinted membrane}}$ is greater than $\alpha_{\text{non-imprinted membrane}}$, and this result indicates that the imprinting technique results in a greater affinity to Cu^{2+}. $\alpha'_{\text{ion-imprinted membrane}}$ is also greater than $\alpha'_{\text{non-imprinted membrane}}$, which confirms the effectiveness of the imprinting technique in improving the membrane selectivity to copper. It is thought that this improved selectivity can be explained by specific sites and channels produced during the imprinting process. Hence, the high selectivity for copper separation was initially created by the chelating monomer (TETA), and it was further enhanced by the imprinting technique.

It can be suggested that the mechanism of copper-selective permeation through an ion-imprinted membrane comprises the following successive (consecutive) steps: (I) selective adsorption of Cu^{2+} through chemical binding with recognizing chelating site (TETA), (II) several hoppings of Cu^{2+} from a recognizing chelating site to an adjacent one in the direction away from the feeding compartment under the influence of concentration gradient as a driving force, and finally (III) desorption into receiving compartment.

Table 3.2. Cu^{2+} and Ni^{2+} permeation flux through control, non-imprinted and membranes and copper selectivity and relative selectivity factors

Membrane	Flux (μmol cm^{-2} h^{-1})		α	α'
	Cu^{2+}	Ni^{2+}		
Control membrane	0.0831	0.0890	0.93	–
Non-imprinted membrane	0.0223	0.0135	1.65	1.77
Ion-imprinted membrane	0.0870	0.0230	3.78	4.06

α : is the selectivity factor
α' : is the relative selectivity factor

It is important to comment on the observation that the permeation experiment shows permeation of both Cu^{2+} and Ni^{2+} where permeation requires adsorption of these cations over the feeding side surface in the first place and then that these cations can hop to the other side, while the adsorption experiment shows that Ni^{2+} nearly does not adsorb and all adsorption is dedicated for Cu^{2+}. Similar results can be reviewed in some previous works (Zhai et al., 2008; Vatanpour et al., 2011; Nonaka and Takeda, 1996). These can be seen as a contradiction; however, it can be suggested that the reason behind this different performance stems from the fact that adsorption is a quasi-dynamic process and permeation is a true dynamic one. In adsorption, when Ni^{2+} adsorbs on the membrane surface, occupying a chelating site, it is always exposed to replacement by an ion with a stronger affinity, Cu^{2+}, whereas for permeation, when Ni^{2+} adsorbs on the membrane surface, occupying a chelating site, it has a chance to move away towards the receiving side.

3.4 Conclusion

The DVB-TETA was introduced well onto the PVDF substrate, which was confirmed by the FT-IR spectrum and the ^{1}H-NMR and C-NMR spectrum confirmed the starting monomer structure. Membrane selective separation can be enhanced by adjusting the chelating polymer content and the degree of cross-linking applied in heavy metal ion separation processes. The adsorption experiments show the selectivity for copper over nickel using an ion-imprinted membrane is higher than the selectivity using a non-imprinted membrane. Diffusion dialysis experiments also show the selective separation of copper, with a selectivity factor of 3.78, which is higher than that of the non-imprinted membrane, which is 1.65. The prepared membrane can be applied in copper selective separation in metal finishing and electroplating industries.

Enhancement of the membrane selectivity factor for copper and the permeation flux is the field for the next research.

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Chapter 4

Copper Selective Facilitated Transport through Chelating Composite Based Membrane

Abstract

Ion-selective chelating membranes are useful in the ion-selective separation processes. In this study, non-imprinted (polyvinylidene fluoride-divinylbenzyl-triethylenetetramine-N,N'-methylenebis(acrylamide) (PVDF/diVB-TETA-N)) and copper-imprinted (Cu-polyvinylidene fluoride-divinylbenzyl-triethylenetetramine-N,N'-methylenebis(acrylamide) (PVDF/diVB-TETA-N-Cu)) ion-selective chelating membranes were prepared through the *in situ* polymerization of the selective chelating monomers of diVB-TETA and diVB-TETA-Cu on a Polyvinylidene fluoride (PVDF) substrate, respectively. N,N'-methylenebis (acrylamide) (MBAC) was used as the cross-linker. Additionally, some membranes were functionalized by using different amounts of sodium 4-vinylbenzyl sulfonate as a cationic flux enhancer. Fourier transform infrared spectroscopy (FT-IR) analysis confirmed successful polymerization of the chelating monomers within the PVDF substrate. Scanning electron microscope (SEM) images showed successful polymerization of the on the PVDF substrate. The permeation study revealed that the ion-imprinted membranes were more favourable for the separation of Cu^{2+} from Ni^{2+} in an aqueous solution than non-imprinted membranes. Ion-imprinted membranes showed a decrease in flux when a greater amount of cross-linking agent was used. The addition of the sulfonate functional group using of sodium 4-vinylbenzyl sulfonate significantly enhanced the flux.

However, the separation factor of Cu^{2+} over Ni^{2+} cations decreased with the increasing content of sulfonate. This chapter shows that the membrane can be applied for the heavy metal selective separation processes.

Keywords: chelating membrane, selective separation, copper.

4.1 Introduction

Membrane-separation technology is currently employed in many applications such as in fuel cells, metal ion sensing and widely in wastewater treatment (Baghel et al., 2007; Yamaguchi et al., 2002). For industrial wastewaters, membranes are used for the removal of hazardous materials and for the recovery of precious metals. Electroplating, metal finishing and microchip productions are of primer attraction to treat their wastewater effluents.

Selective separation is an important aspect of membrane technology. Recent selective membranes are used in water softening process where mono-valent cations separated from multi valent cations based on the differences in their hydrated ion sizes and electrostatic exclusions (Lambert et al., 2006; Le et al., 2010; Yao et al., 2013). However, it is still a major concern to selectively separate cations of the same valence and similar hydrated ionic size such as di-valent heavy cations (Chakrabarty et al., 2013).

Selective separation between cations that have the same charge and similar hydrated ion size was studied using liquid membranes and liquid-supported membranes (

Ambashta and Sillanpaa, 2012; Akieh et al., 2010). The common mechanism of the ion transport through these membranes is by complexing with chelating ligand and transportation by diffusion through the membrane. However, these membranes suffer from low stability, which is the leakage of chelating liquid over time that results in the gradual loss of the selective carriers.

Another membrane that makes use of chelation is polymer inclusion membranes, which are designed to be fixed site carrier membranes (FCMs). FCMs are characterized by selective adsorption/permeation. This type of membrane does not suffer from the leakage or loss of the reactive chelating sites that the supported liquid membranes do (Kojima et al., 1995). These membranes use the mechanism of ion transport by ion hopping through fixed chelating sites across the membrane. Ion-selective separation is attributed to either (i) facilitated transport though these selective chelating sites to the target metal ions and the hindering of other ions or (ii) by the retardation of the target ion, allowing other ions to pass through the membrane (Thunhorst et al.,1997). Both of these mechanisms are dependent on a relative chelating affinity towards competing cations. A good application of FCMs is the case of the polymer inclusion membranes, as discussed by Saegusa et al. (1979) where a polyethyleneimine (PEI) polyepichlorohydrin interpolymer chelating ion exchange membrane was prepared by casting it for the separation of copper from calcium. Separation is dependent on the good chelating affinity of PEI towards heavy metal ions, such as copper ion. Using the prepared membrane in a dialysis process that approaches a selective separation ratio of 3.4 (Saegusa et al.,1979). This membrane has not been tested for its ability to separate similar di-valent heavy metal cations. In general, though, FCMs suffers from low permeability (low flux) due to its high thickness.

To avoid the leakage of chelating liquid and/or low flux, an attempt was made to develop a stable, reliable membrane for the selective separation of heavy metal cations. Chakrabarty et al. (2013) prepared a zirconium triethylenetetramine chelating membrane for the selective separation of copper from nickel, manganese and zinc using electrodialysis and reached a separating factor of about 3 to 4 (Chakrabarty et al., 2013). However, the homogenous dispersion of the chelating groups that is suspended on zirconium particles in PVA polymeric matrix cannot guarantee a continuum of chelating groups throughout the PVA matrix (Chakrabarty et al., 2013).

The aim of this work is to prepare a cation-selective permeable membrane for heavy metals that avoids both the leakage problem of selective chelating carriers in the liquid-supported membranes and the low ion permeability problem through the membrane. This was carried out by supporting the membrane by *in situ* polymerization of a chelating-selective monomer into PVDF micro-porous substrate to ensure that the chelating sites act as a continuum across the produced membrane.

The selection between the two di-valent heavy metal cations, as important required application, was considered to be improved in the membrane synthesis. To perform this, the first step is to select a chelating agent that has a high affinity to the target metal cation. Secondly, this chelating agent must be functionalized to be a chelating monomer, which was achieved by the simple addition of vinyl groups that work for the polymerization step. Finally, the enhancement of the cation flux can be achieved by doping the membrane with a suitable hydrophilic cation exchanger.

In this work, a chelating monomer that has a high selectivity to copper (target metal cation) was prepared, then *in situ* polymerized in PVDF membrane micro-porous substrate. Additionally, a compound holding a sulfonate group was introduced (sodium 4-vinylbenzyl sulfonate) to increase the rate of permeation through the membrane. The membrane surface morphology was studied using SEM (scanning electron microscopy), and the chemical structure of the prepared membranes were evaluated using FT-IR (Fourier transform infrared spectroscopy). Diffusion dialysis using a designed dialysis cell to study the selective permeation of the copper ion in the presence of another competitive cation (e.g nickel) was completed.

4.2 Experimental

4.2.1 Membrane synthesis

4.2.1.1 Materials

Vinylbenzyl chloride (VBC) and sodium amide were used for functionalizing triethylenetetramine (TETA), so that it could be converted into monomer form and sodium 4-vinylbenzl sulfonate was used as a hydrophilic enhancer. Diethyl ether, acetone, chloroform and dimethyl sulfoxide were used as solvents. N,N'-methylenebis (acrylamide) (MBAC) and 2,2-azobis(2-methyl propionitrile) (AIBN) were used as cross-linker and initiator respectively in the polymerization processes. All chemicals were obtained for Sigma Aldrich. The polyvinilidene fluoride (PVDF) membrane (Millipore Company) with a pore diameter 0.65 µm and a porosity of 70% was used as the host membrane substrate. Copper (II) and nickel (II) sulfates (Sigma Aldrich) were used for the preparation of Cu^{2+} and Ni^{2+} stock solutions. All chemicals did not require further purification, as they were already of analytical grade.

4.2.1.2 Preparation of the chelating monomer

The chelating monomer was prepared by adding vinyl groups to the chelating agent TETA. This was done by causing the VBC to have a nucleophilic substitution reaction with TETA (Singh et al., 2000). TETA (6 g) was added to a suspended solution of $NaNH_2$ (1.6 g) in diethyl ether (50 mL). The contents were purged with N_2 gas for 1 hour, and then VBC (10.3 g) was added. The whole mixture was left-stirred under reflux at room temperature overnight for functionalization. The reaction was terminated by the addition of deionized water (2 mL). The reaction mixture containing the products was then transferred to a rotary evaporator to remove the solvent. After removing the diethyl ether, deionized water (40 mL) was added to the residue materials. This mixture was transferred to separating funnel where chloroform was added to extract the di-substituted monomer (diVB-TETA) from the mono-substituted monomer (monoVB-TETA). The extraction process was repeated 3 times. The purified diVB-TETA was dried using $CaCl_2$ anhydrous to remove any residual water, yielding an orange-yellow viscous product.

4.2.1.3 Preparation of the chelating membrane

PVDF is the substrate membrane to host polymerized TETA. Prior polymerization, it was treated with acetone at a consecutive increasing ratio with water to remove the original preserving substances and, finally, was dried under vacuum. A mixture solution of diVB-TETA monomer (2.6 mmol), cross-linker MBAC (1 mmol) and initiator AIBN (16 mg) were prepared in 5 ml of chloroform. The solution was sonicated for 2 hours during which N_2 was bubbled into it to remove any dissolved oxygen. The PVDF substrate membrane (4 cm × 4 cm) was immersed in the solution for 24 hours. After that period, the membrane was removed from the solution and was clamped between two glass plates. To start the polymerization reaction, the clamped membrane was transferred to the reaction vessel where evacuation was carried out to remove air and was then filled with N_2 gas. To commence polymerization reaction, the reaction vessel was immersed in an oil bath at temperature $85^{o}C$ for 2 hours, during which the polymerization was completed. The membrane was then removed from the reaction vessel and was immersed in chloroform to remove the reactants' residues. Then, the membrane was dried under vacuum for 48 hours. After that, the membrane was conditioned in 1 M HCl and 1 M NaOH alternatively and repeatedly for 24 hours to remove any undesired attached materials. The final conditioning step was by 1 M HCl to attain an acidic form. Finally, the membrane was stored in deionised water for 24 hours before permeation experiment.

4.2.1.4 Membrane with (5-15% mol) sodium 4-vinylbenzyl sulfonate

Sodium 4-vinylbenzyl sulfonate content percentage in the contents for the membrane preparation was selected on bases of first trials for selected percentages. Using Sodium 4-vinylbenzyl sulfonate with 100% mol of the reaction contents without the chelating monomer was used for the membrane preparation and the preliminary results indicates high permeation flux for the tested cations (Cu^{2+} and Ni^{2+}) without any selective separation between them. Sodium 4-vinylbenzyl sulfonate content percentages (80, 50, 30, 20 and 15% mol) was tested and showed lower in the cations permeation flux but the same trend in selective permeation between Cu^{2+} and Ni^{2+}. Selectivity of Cu^{2+} over Ni^{2+} started when sodium 4-vinylbenzyl sulfonate in the reaction contents was below 15% mol. Based on these preliminary tests, the selected sodium 4-vinylbenzyl sulfonate percentages in the reaction content were (5, 10 and 15%). Sodium 4-vinylbenzyl sulfonate was dissolved in DMS (7 ml). The diVB-TETA monomer (2.6 mmol), the MBAC cross-linker (1 mmol) and the AIBN initiator (16 mg) were dissolved in methanol. The solutions were mixed together and sonicated for 2 hours during which N_2 was bubbled into the reaction mixture to remove any dissolved oxygen. 4 cm × 4 cm PVDF substrate membrane was immersed in the reaction solution for 24 hours then the membrane was removed and then clamped between two glass plates. The treated PVDF was transferred to the reaction vessel and then the vessel was evacuated to remove air and was then filled with N_2 gas. The reaction vessel was immersed in an oil bath at 85°C for 2 hours to polymerize the diVB-TETA. After polymerization, the membrane was immersed in methanol to remove any other reactants. The membrane was dried under vacuum for 48 hours. The membrane was then conditioned in 1 M HCl and 1 M NaOH for 24 hours alternatively and repeatedly to remove any undesired attached materials. The final step was the treatment by 1M HCl. The membrane was stored in deionised water for 24 hours before using. The pervious prepared membranes with/without sodium 4-vinylbenzyl sulfonate are non-imprinted membranes. For the preparation of the ion- imprinted membrane PVDF/diVB-TETA-N-Cu and PVDF/divb-TETA-N-Cu (5, 10, 15%) addition steps were considerd that copper reacted with the chelating monomer prior its *in situ* polymerization process. In addition the amount of the cross-linker MBAC used in the polymerization process is 5 mmol and the final step was leaching copper by immersion of the prepared membranes in 1 M HCl .

4.2.2 Membrane characterization

4.2.2.1 Structure study

The chemical structure of the prepared membranes was confirmed by using ThermoNicolet 6700 FT-IR spectroscopy (range: 4000 to 400 cm^{-1}, scans: 16 scans and resolution 0.5 cm^{-1}).

4.2.2.2 Morphology study

The field emission scanning electron microscopy SEM (FE-SEM, JEOL JSM 7000 F) was used to study the prepared membrane's surface morphology. SEM was operated under high vacuum at 5 kV. Samples were Pt sputter-coated with a thickness of 5.6 nm.

4.2.2.3 Mass gain

The mass gain of the prepared membranes after polymerization represent the anchored amount of the polymer to the PVDF substrate, the following equation is used to calculate the mass gain %:

$$\text{Mass increase (\%)} = \frac{(m_\mathrm{f} - m_\mathrm{o})}{m_\mathrm{o}} \times 100 \qquad (4.1)$$

Where m_f is the mass of the dried sample membrane, and m_o is the mass of the dried substrate, PVDF. The membrane samples were dried carefully in a desiccator under vacuum till constant weight.

4.2.2.4 Water uptake

The water uptake of the membranes can be calculated using the following equation:

$$\text{Water uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \tag{4.2}$$

Where W_{wet} and W_{dry} are the masses of the membrane for the wet and dried forms respectively. W_{wet} of a membrane was determined by immersing it into deionized water for 24 hours at room temperature. This followed was by removing the membrane from deionized water and removing the non-texture water by pressing the membrane between two filter papers, and then weighing. The W_{dry} of a membrane was determined by drying it until no change in mass was recorded (Kwak et al., 2012; Strathmann 2004; Khan, 2013).

4.2.2.5 Ion exchange capacity

The ion exchange capacity demonstrates the ability of the membrane's most active sites to take up the cation. The functional groups in the prepared membranes were protonated by soaking them in 1 M HCl for 24 h. The membranes were then rinsed carefully with deionized water to remove excess acid on the membrane. Membrane samples were then soaked in 50 ml of 1 M NaCl till equilibration for 24 h. The librated H^+ was titrated using 0.1M NaOH as a titrant. The ion exchange capacity can be calculated from the following equation:

$$IEC = \frac{M.V}{m} \tag{4.3}$$

Where V is the volume of the added titrant till equivalent point (mL), M is the titrant NaOH concentration (0.1M) and m is the dry membrane weight (g) (Hosseini et al., 2010; Klaysom et al., 2011).

4.2.3 Diffusion dialysis

Diffusion dialysis experiments were carried out using lab-made cells that consist of two Teflon compartments with a 35 ml volume each. One is the feed compartment and the other is the receiving compartment. The two compartments are separated by the membrane being tested, whose permeation effective area is 7.07 cm^2. During the permeation experiment, the solutions in both compartments were being stirred at 600 rpm using proper magnetic stirrer rods of the same size.

The feed compartment was filled with a sulfate solution of Cu^{2+} and Ni^{2+} (0.005 M each). The receiving compartment was filled with 1 M H_2SO_4. Aliquot of 1 ml volume was withdrawn from the receiving compartment solution each hour for a total period of 10 hours. The collected aliquots were diluted 10 fold using deionized water and then were analyzed by flame atomic absorption spectroscopy.

The flux of transported metal cations from feed compartment to receiving compartment through membrane (*J*) can be obtained from the following relation

$$J = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \qquad (4.4)$$

Where ΔC is the concentration of the permeated cation during the elapsed time Δt, *A* is the membrane effective area and *V* is the receiving compartment volume.

The separation factor (α) which is the ratio of the permeation flux of the selected cation to the permeation flux of the other existing cation can be calculated from the relation (α = flux[Cu]/ flux[Ni]).

4.3 Results and Discussions

4.3.1 Membrane characterization

4.3.1.1 Membrane morphological and chemical structure

Figure 4.1 (a) shows the morphology of the PVDF substrate. It has a micro-porous structure and of an irregular shape and size. Figure 4.1 (b) and Figure 4.1 (c) represent the non-imprinted membranes PVDF/diVB-TETA-N and PVDF/diVB-TETA-N 10% respectively, where the chelating polymer covers and fills all the PVDF substrate pores. The surface of the membranes is quite rough. Figure 4.1 (d) and Figure 4.1 (e) represent the ion-imprinted membranes PVDF/diVB-TETA-N-Cu and PVDF/divb-TETA-N-Cu 10%, respectively. The ion-imprinted membrane PVDF/diVB-TETA-N-Cu is smoother than non-imprinted membrane, PVDF/diVB-TETA-N. This difference can be attributed to the imprinting step.

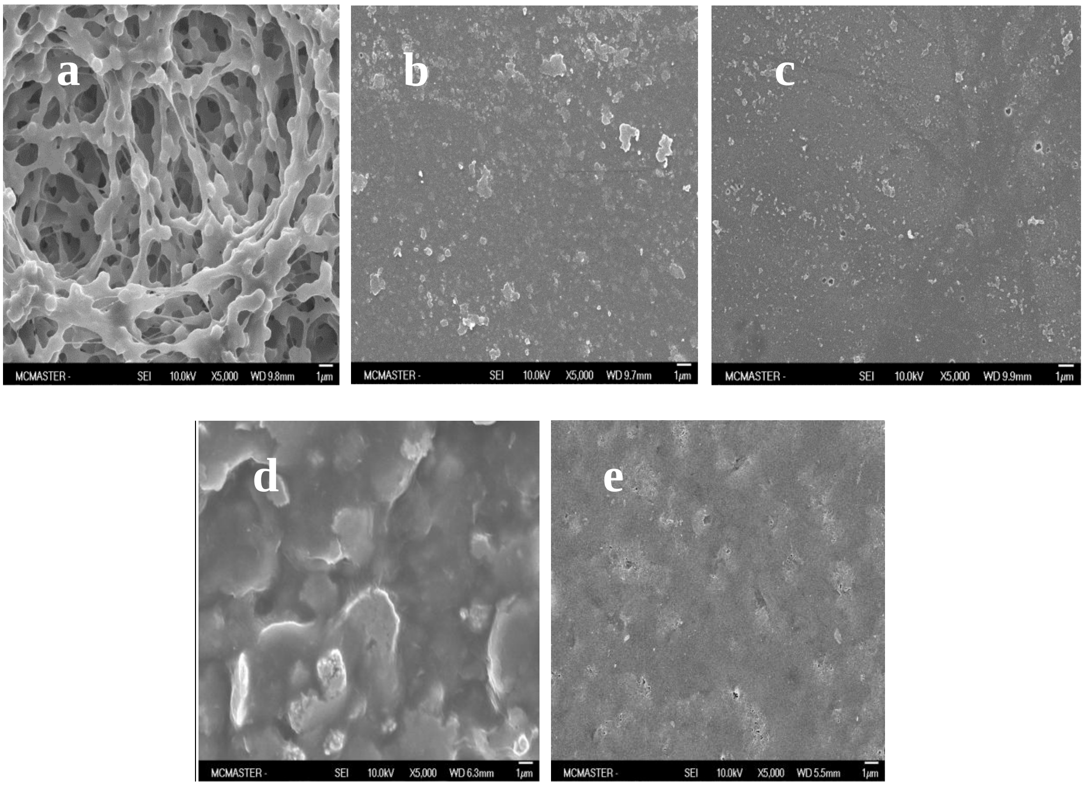
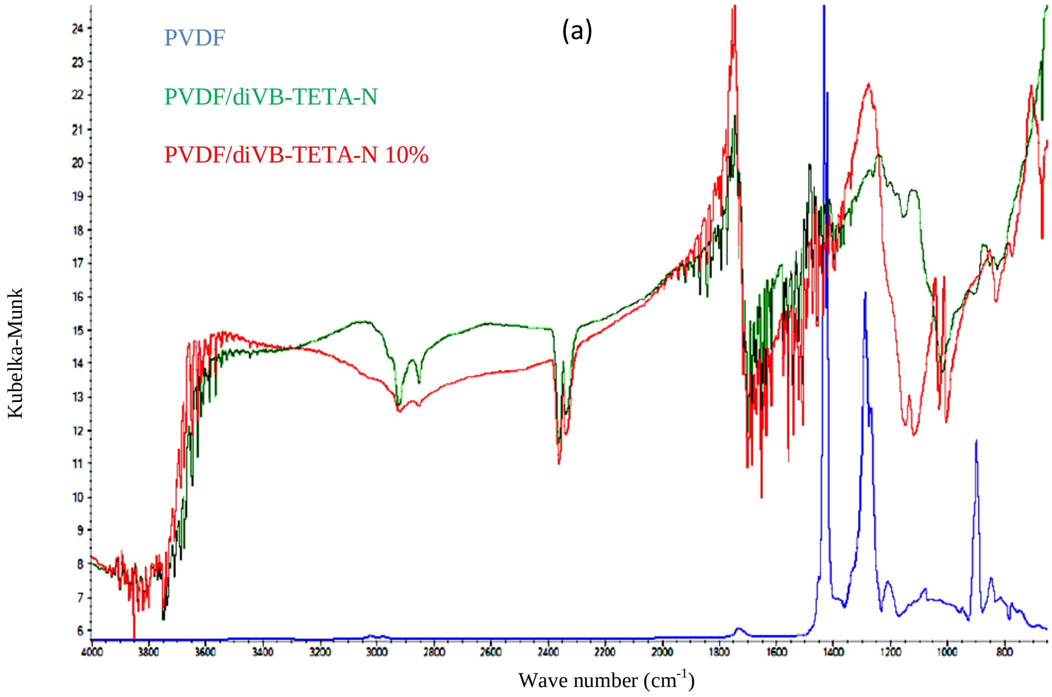


Figure 4.1 SEM images at 5000X of (a) PVDF substrate, (b) PVDF/diVB-TETA-N (c) PVDF/diVB-TETA-N 10%, (d) PVDF/diVB-TETA-N-Cu, and (e) PVDF/diVB-TETA-N-Cu 10% pore filled membranes.



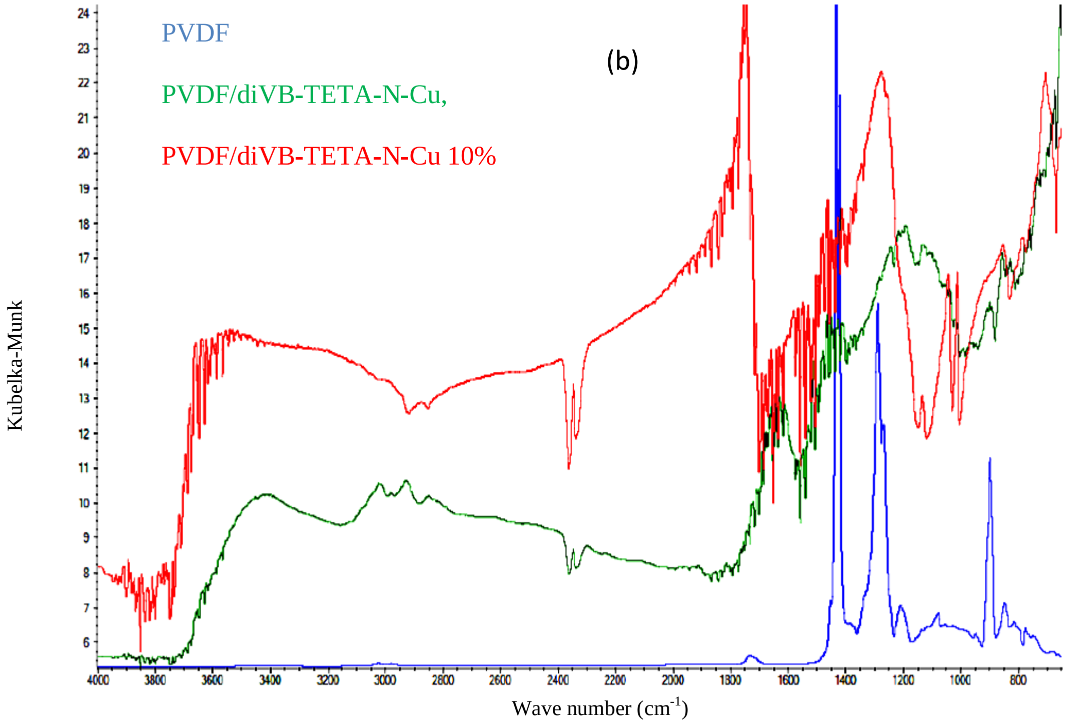


Figure 4.2 FT-IR spectra for (a) PVDF (blue), PVDF/diVB-TETA-N (green), PVDF/diVB-TETA-N 10% (red) and (b) PVDF (blue), PVDF/diVB-TETA-N-Cu (green), and PVDF/diVB-TETA-N-Cu 10% (red).

The chemical structure of the prepared membranes was investigated using FT-IR spectroscopy. Figures 4.2 (a) and (b) show the FT-IR of the membranes PVDF, PVDF/diVB-TETA-N, PVDF/diVB-TETA-N 10%, PVDF/diVB-TETA-N-Cu, and PVDF/diVB-TETA-N-Cu 10%. The peak in the range 1400-1450 cm^{-1} attributed to C-H bond in alkanes and peak 1300 cm^{-1} attributed to C-F which confirmed the PVDF structure. Peaks 3400–3250 cm^{-1} broad band peak attributed to secondary amines from the TETA in PVDF/diVB-TETA-N, PVDF/diVB-TETA-N 10%, PVDF/diVB-TETA-N-Cu, and PVDF/diVB-TETA-N-Cu 10% membranes. S=O and O=S=O were observed in the peaks 1300 cm^{-1} and 1050 cm^{-1} respectively for both PVDF/diVB-TETA-N-Cu PVDF/diVB-TETA-N-Cu 10%, and PVDF/diVB-TETA-N-Cu 10%. Also, this means that the chemical structure of the ion-imprinted membranes and the non-imprinted membranes are almost the same and the chemical treatment in the ion-imprinted membranes in the final stage of preparation does not affect the chemical composition of the prepared membranes.

4.3.1.2 Membrane mass gain, water uptake and IEC

Table 4.1 shows the mass gain, water uptake and IEC for the different prepared membranes. Considering the percent mass gain, each non-imprinted membrane has a higher value than the corresponding imprinted one. This is due to the imprinting step of preparation where the copper mass was deducted from the original mass of the membrane. For each group (non-imprinted and imprinted), mass gain decreased as sulfonate content increased. In preparation, the amounts of sodium 4-vinylbenzl sulfonate were added to the reaction mixture at the expenses of TETA on molar bases. As sodium 4-vinylbenzl sulfonate is two times less in mass than TETA, the final masses of the membranes decreased as the sodium 4-vinylbenzl sulfonate percentage increased. The water uptake increased as the sodium 4-vinylbenzl sulfonate content increased for each type of membrane, non-imprinted and imprinted. This is directly related to the sodium 4-vinylbenzl sulfonate increase because of its higher hydrophilic property compared to that of the deducted TETA.

Also from Table 4.1, IEC for the ion imprinted membranes is lower than that for the non-imprinted membranes. This can be attributed to the increase of the cross-linker amount used in the ion imprinted membrane preparation.

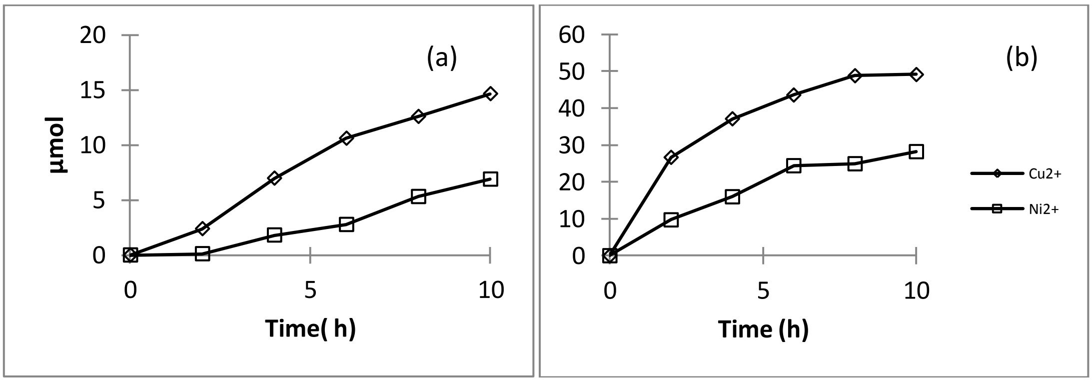
Table 4.1. Mass gain, water uptake and IEC for ion imprinted and the non-imprinted membranes with and without addition of (5-15% mol) sodium 4-vinylbenzyl sulfonate

Sample	**Mass gain (%)**	**Water uptake (%)**	**IEC (meq/g)**
Non-imprinted			
PVDF/diVB-TETA-N	112.90	27.28	2.01
PVDF/diVB-TETA-N 5%	97.79	36.47	1.95
PVDF/diVB-TETA-N 10%	95.12	41.20	2.70
PVDF/diVB-TETA-N 15%	87.72	54.53	2.35
Ion imprinted			
PVDF/diVB-TETA-N-Cu	92.20	20.45	1.60
PVDF/diVB-TETA-N-Cu 5%	81.62	23.36	1.65
PVDF/diVB-TETA-N-Cu 10%	79.87	26.23	1.74
PVDF/diVB-TETA-N-Cu 15%	62.74	32.47	1.71

IEC: ion exchange capacity of the prepared membranes

4.3.2 Permeation through membranes

Figure 4.3 shows the permeation rate of Cu^{2+} and Ni^{2+} through non-imprinted PVDF/diVB-TETA-N membranes (0, 5, 10, and 15% sodium 4-vinylbenzl sulfonate). All membranes permeate Cu^{2+} at a higher rate than permeation rate of Ni^{2+} over the experimental period, 10 hours. This performance successfully separates Cu^{2+} from Ni^{2+}. This is due to the ability of TETA to continuously chelate Cu^{2+}.



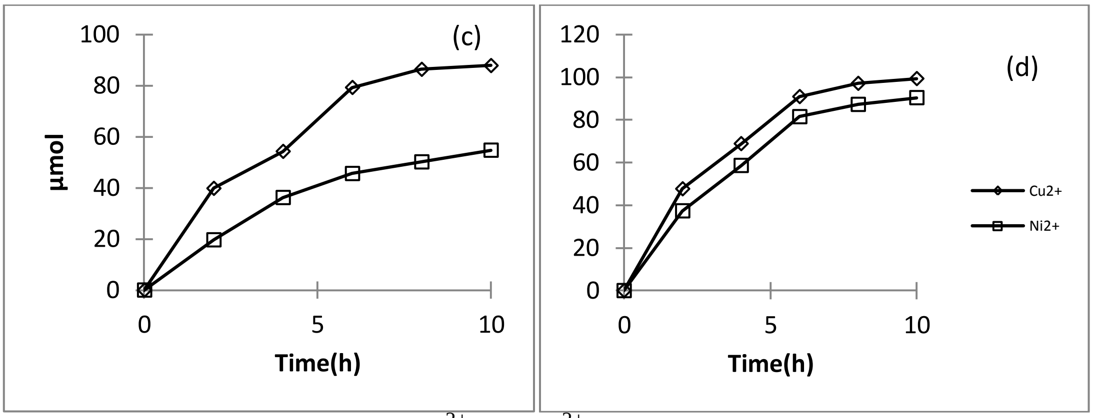


Figure 4.3 Permeation rates of Cu^{2+} and Ni^{2+} through non-imprinted membranes (a) PVDF/diVB-TETA-N, (b) PVDF/diVB-TETA-N 5%, (c) PVDF/diVB-TETA-N 10% and (d) PVDF/diVB-TETA-N 15% ($A = 7.07\ cm^2$, $C_o(Cu^{2+},Ni^{2+}) = 5$ mM and 1 M H_2SO_4 in the receiving compartment solution).

Table 4.2 gives the separation factors (α) for these membranes. As the sulfonate content increases, the separation factor decreases. This is due to the fact that sulfonate is a cation exchange functional group that does affect the selective permeation of Cu^{2+} and Ni^{2+}. Accordingly, as this functional group content increased, the number of cation exchange sites increased at the expense of chelating sites, which gives the Ni^{2+} cation more room to permeate. However, the intended aim of incorporating the sulfonate group into the membrane structure was achieved. The flux of both cations increased significantly with the sulfonate percentage: the Cu^{2+} increased 6.8 times and Ni^{2+} increased 13.1 times. The samples with the highest permeation and separation is 10%, which gives the optimum selectivity with flux.

Table 4.2. Flux and the separation selectivity factor of copper for the ion-imprinted and the non-imprinted membranes with and without addition of (5-15% mol) sodium 4-vinylbenzyl sulfonate

Membrane	Flux (μmol cm^{-2} h^{-1})		α
	Cu^{2+}	Ni^{2+}	
Non-imprinted membrane			
PVDF/diVB-TETA-N	0.2075	0.0976	2.154
PVDF/diVB-TETA-N 5%	0.6958	0.3997	1.741
PVDF/diVB-TETA-N 10%	1.2440	0.7752	1.605
PVDF/diVB-TETA-N 15%	1.4069	1.2804	1.099
Ion-imprinted membrane			
PVDF/diVB-TETA-N-Cu	0.3772	0.0891	4.234
PVDF/diVB-TETA-N-Cu 5%	0.4175	0.1203	3.469
PVDF/diVB-TETA-N-Cu 10%	0.4949	0.1498	3.304
PVDF/diVB-TETA-N-Cu 15%	0.7117	0.6570	1.083

α: selectivity factor

Figure 4.4 shows the permeation rate of Cu^{2+} and Ni^{2+} through imprinted PVDF/diVB-TETA-N membranes (0, 5, 10, and 15% sodium 4-vinylbenzl sulfonate). All membranes permeate Cu^{2+} at a rate higher than the permeation rate of Ni^{2+} over the experimental period, 10 hours. This performance successfully separates Cu^{2+} from Ni^{2+}. This is similar to the results for non-imprinted samples (considering separation and flux). The preference of TETA to continuously chelate Cu^{2+} is due to two factors, affinity and imprinting.

Table 4.2 gives the separation factors, α, for these membranes. From the table, as the sulfonate content increases, the separation factor decreases, which is the same performance as the non-imprinted membranes and due to the same reason. The flux of both cations increased significantly with sulfonate content: Cu^{2+} 1.9 times and Ni^{2+} 7.4 times. The sample with the highest permeation and separation is 10%.

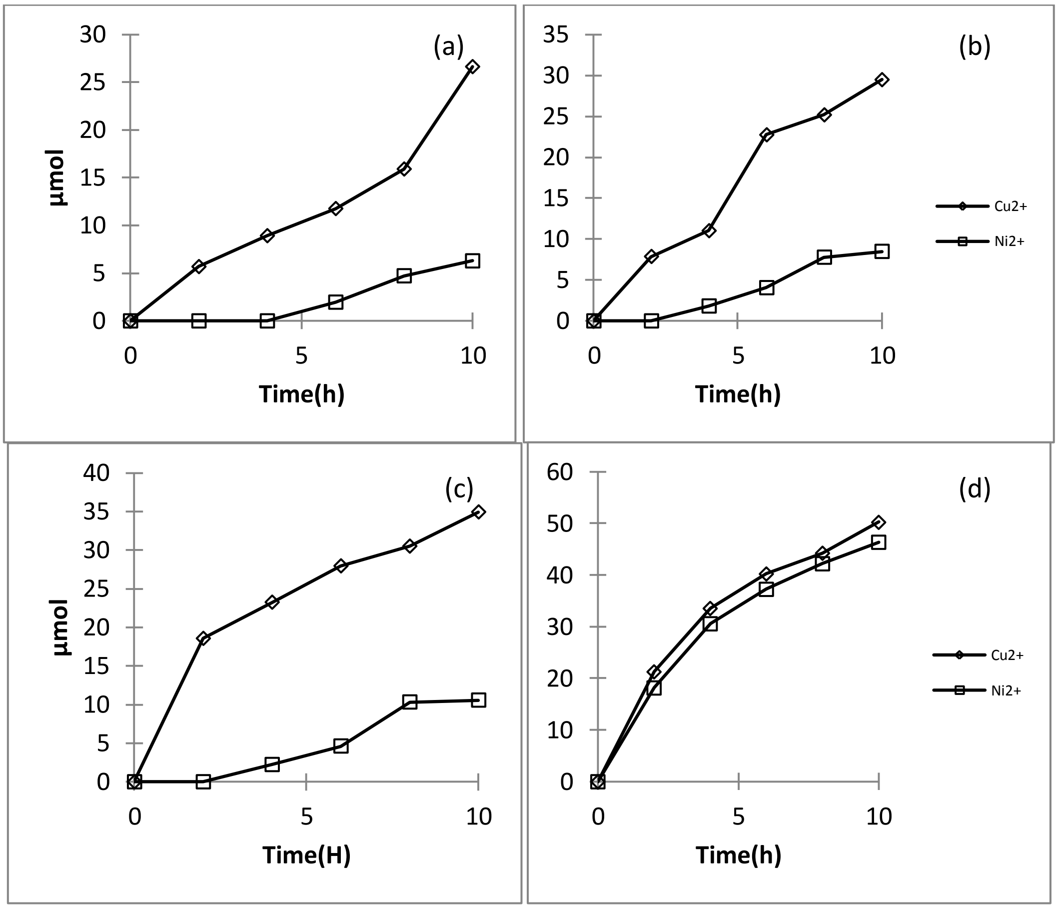


Figure 4.4 Permeation rates of Cu^{2+} and Ni^{2+} through ion-imprinted membranes (a) PVDF/diVB-TETA-N-Cu, (b) PVDF/diVB-TETA-N-Cu 5%, (c) PVDF/diVB-TETA-N-Cu 10% and (d) PVDF/diVB-TETA-N-Cu 15%. (A = 7.07 cm^2, $C_o(Cu^{2+},Ni^{2+})$ = 5 mM and 1 M H_2SO_4 in the receiving compartment solution).

In Table 4.2, the separation factors for imprinted membranes are higher than those of the corresponding non-imprinted ones. However, the flux is lower for imprinted membranes. The can be attributed to the amount of cross-linker used, as it was 5 mmol for imprinted membranes and 1 mmol for non-imprinted ones. In addition, the difference in flux is significant, which points to the careful deal with the cross-linker in the preparation process.

Additional discussion can be presented by comparing the results of the non-imprinted and imprinted membranes. When sulfonate was not added, Ni^{2+} spent a considerable amount of time before elapsing to permeation (2 and 4hours in Figure 4.3 (a) and Figure 4.4 (a), respectively). This fact supports the hypothesis that chelation is the major, and may be the first, step in the mechanism of permeation. At the beginning, both Cu^{2+} and Ni^{2+} are of the same concentrations (equal initial ones) and therefore TETA chelates only Cu^{2+} (due to high affinity to Cu^{2+}) and permeation of Cu^{2+} occurs to the receiving compartment. As time elapses, Cu^{2+} the concentration decreases in the feed compartment and this gives the Ni^{2+} cations some room to be chelated and hence permeated. In addition cations transport through the membrane can be explained as follow: (i) the main driving force in diffusion dialysis is the concenteration difference of species between the feed compartment and the reciving compartment, (ii) cations reach near the membrane surface by convection, (iii) and due to the high stirring the boundary layer near the membrane surface decreased that cations can reach the membrane surface by diffusion, (iv) then cations adsorption takes its place on the membrane surface,(v) transfer though the membrane by diffusion, and the cations transported though the membrane chealting sites by hopping mechanism, (vi) when cations reach the other side of the membrane surface it leaves the surface by desorption and transfer through the boundary layer by diffusion to the bulk solution of the receiving compartment.

4.4 Conclusion

FT-IR analysis indicated successful polymerization of both prepared chelating monomers (diVB-TETA-N and diVB-TETA-N-Cu) within the structural matrix of the

PVDF membrane. The resulting modified membranes showed high selectivity towards Cu^{2+} over Ni^{2+} due to the proper selection of TETA as the precursor for the chelating monomer. TETA has a higher chelating capacity with Cu^{2+} than that with nickel due to the substantial difference in the corresponding stability constants. Imprinting clearly enhances selectivity; however, the extra use of cross-linking agent during the preparation of imprinted samples resulted in a decrease in the metal flux. For non-imprinted membranes, the addition of sulfonate groups (10%) increased the flux about 6 times, whereas for ion-imprinted the increase was about 1.2 times. Although this approach significantly enhanced the flux, adding sulfonate higher than 10% to the extent of 15% strongly limits the capability of selective separation. This is due to the presence of sulfonate groups that convert the behavior of the membrane from selective cation chelating to non-selective cation exchange performance. In general, it can be suggested that PVDF/diVB-TETA-N-Cu 10% membrane is the most suitable for separation application of the tested cations, as it has a separation factor for Cu^{2+} of 3.304 with suitable cation permeation flux (0.4949 μmol cm^{-2} h^{-1}) compared to the selectivity factors and fluxes of the other membranes.

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Chapter 5

A Modified Cation Exchange Membrane by Surface Coating to Enhance Copper Ion Selective Separation from other Di-valent Heavy Metal Cation Solution Mixture

Abstract

In this chapter, the surface modification of the cation exchange membrane, Selemion (CMV-S type), was performed using chelating polymer divinylbenzyl triethylenetetramine (diVB-TETA) to operate for M^{2+} cation selective separation. The modification was carried out using a spin coating technique to control the thickness of polymer film, and its cross-linker content was considered as a factor as well. Two sets of membranes were prepared, non-imprinted and copper-imprinted. The prepared membranes were characterized by their ion exchange capacity, and Fourier transform infrared spectroscopy (FT-IR) was used to evaluate the membranes' structure, and scanning electron microscopy (SEM) was used to evaluate the membranes' surface morphology. Competitive adsorption and permeation experiments (considering Cu^{2+} and Ni^{2+}) revealed the membranes' capabilities for Cu^{2+} selectivity and flux. It was found that CMV-S/diVB-TETA-Cu adsorbs Cu^{2+} 6.5 times more effectively than CMV-S/diVB-TETA. CMV-S/diVB-TETA-Cu membranes have a higher selectivity for Cu^{2+} (α = 17) compared to CMV-S/diVB-TETA membranes (2.7), yet that latter has lower flux.

Keywords: surface modification, cation exchange membrane, selectivity, flux, chelating agent.

5.1 Introduction

Ion separation is required for many industrial and environmental applications. There are several techniques that can achieve such a goal, and separation by ion exchange membranes is a prime choice for many applications due to its versatility, cost-effectiveness, ease of scaling-up, possibility of combination with other processes and low operating costs(Kumar et al., 2013; Strathmann, 2004). Ion exchange membranes were first used to produce potable water from saline (Zuo et al., 2009; Hosseini et al.,2010; Tsuneda and Saito, 1995). Recently, ion exchange membranes are utilized in processes for many other applications dedicated to selectively extract cations for industrial wastewater treatment, acid effluents treatment, hydrometallurgy, water softening, and reverse electrodialysis etc (Tian et al., 2004; Hosseini et al., 2012; Srisuwan and Thongchai, 2002; Koseoglu et al., 2010). Because of the continual demand for safer products and a cleaner environment, industries and environmental applications that use ion separation applications strive for more advancement in ion separation technology through the use of membranes (Kumar et al., 2010).

Early ion exchange membranes were basically chemically designed for cation and anion separation (Strathmann, 2011; Strathmann, 2004). One advancement has been met the need for the separation of mono-valent and di-valent cations in some applications (Hosseini et al., 2010; Le et al., 2010). A further advancement has separated specific di-valent cations from a mixture of other di-valent cations (with or without the presence of mono-valent cations) for some applications (Sheng et al., 2014; Nonaka and Takeda, 1996; Chakrabarty et al., 2013). The separation of specific di-valent cations from a mixture, especially one comprised of heavy metals, is challenging due to the similarity of ionic radius and the equality of ionic charges (Chakrabarty et al., 2013).

To deal with this challenge, many researchers have tried to functionalize substrate cation exchange membranes by chelating compounds, as chelates have specific selectivities towards certain metal ions (Sherringtonb, 1995; Saegusa et al., 1979; Sawicka et al., 1991; Kobayashi and Sumitomo, 1978). Additionally, an ion-imprinting technique has been applied to enhance selectivity due to the ability to tailor target ion site recognition (Ulbricht, 2004; Deng et al., 2014; Deng et al., 2012; Piletsky et al., 1999; Zheng et al., 2012; Zhai et al., 2008; Vatanpour et al., 2011; Baghel et al., 2007). One efficient way for functionalization to take place is through the surface modification of the cation exchange membrane with a chelating compound that is selective towards target cation (Saegusa et al., 1979; Deng et al., 2014). An accustomed method of such functionalization is through dipping-adsorption (Le et al., 2010, Sheng et al., 2014), the electro-deposition of charged chelate-functionalized polymer (Tsuneda and Saito, 1995; Deng et al., 2014; Lambert et al., 2006) and surface polymerization (Kumar et al., 2013; Yao et al., 2013). There is a serious problem with this approach, the detachment of the modifying film from the base membrane occurs often due to the relatively weak binding between the functionalizing film and the cation exchange base membrane, where the electrostatic attraction is happening.

In the present work, which aims to separate di-valent cations, a roughened commercial cation-exchange membrane, CMV-S, was used as the substrate membrane surface, which was modified by the chelating polymeric diVB-TETA because TETA is a strong chelating compound of Cu^{2+}. The modification process was conducted by a spin coating method, where monomer and other needed reactants (cross-linker, initiator, etc) were uniformly distributed over the substrate surface. Hereafter, *in situ* polymerization and cross-linking were commenced to guarantee distribution of the produced modification film over the CMV-S surface. In addition, such polymerization should provide a well-attached film on the CMV-S roughened surface. Two types of modified membranes were prepared, non-imprinted and Cu-imprinted, and were examined for their selectivity and flux considering Cu^{2+} and the competitive cation, Ni^{2+}.

5.2 Experimental and analysis

5.2.1 Materials

The CMV Selemion cation exchange membrane (CMV-S, thickness: 100 μm, counter ion: Na^{+}) was purchased from AGC engineering Co. Ltd., and was used as the substrate membrane to be surface-modified. Vinylbenzyl chloride (VBC), divinyl benzene (DVB), benzoyl peroxide (BPO), triethylenetetramine (TETA), diethyl ether and sodium amide were purchased from Aldrich and have been used without any further purification for the preparation of the chelating monomer and the subsequent chelating polymer. For competitive adsorption and permeation experiments, copper (II) and nickel (II) sulfates, purchased form Aldrich, were used where the synthesized membrane was designed for the selective adsorption and permeation of copper ion.

5.2.2 Modification

5.2.2.1 Non-imprinted modification

The CMV-S membrane was first soaked successively in deionized water and sulfuric acid (3 M) each for 24 h, and then was washed with deionized water to remove excess acid. The membrane was then left to dry under a vacuum for 24 h. The dried membrane was cut into several pieces (each: 4 cm × 4 cm). A single side of each piece was roughened using abrasive paper (Buehler-Carbimet 2-7/8"). To prepare the modified membrane sample, the reactant mixture of the intended modifying chelating polymer film (89% diVB-TETA : 10% DVB : 1% BPO) was applied on the roughened surface of the membrane piece through a spin coating technique in order to produce a uniform film of reactants on the membrane surface. For spin coating, the selemion membrane fixed on a rotating disc and then the reaction content poured on its surface. The speed of rotation of the rotating disc was controlled using power supply. .After the coating process was complete, the surface-coated piece was transferred to a reaction vessel where air was evacuated by a vacuum pump and the vessel was filled with nitrogen gas. The polymerization reaction was commenced by placing the reaction vessel in an oil bath pre-adjusted at 85^oC. After 7 hours, the reaction was terminated, producing a diVB-TETA surface modified CMV-S membrane, CMV-S/diVB-TETA. The new membrane piece was removed from the reaction vessel and subsequently was immersed in $CHCl_3$ to remove any unreacted reactants or homo-polymerized residues. The piece was then rinsed with deionized water and was conditioned respectively in HCl (1 M) and NaOH (1 M) to get rid of impurities and was finally rinsed thoroughly with deionized water in preparation for the separation experiments. Non-imprinted membranes of different thicknesses were prepared to study the effect of the amount of modifying chelate-polymer on adsorption and permeation. Different thicknesses were developed by controlling spinning coating process. Non-imprinted membranes with different cross-linking DVB agent content (10%, 15% and 20% DVB) were prepared to study the cross-linking effect on the permeation process.

5.2.2.2 Imprinted modification

To prepare the Cu-imprinted modified membrane sample, CMV-S/diVB-TETA-Cu, all previous steps were performed except that the used cross-linker amounts were of higher values than those for CMV-S/diVB-TETA (18%, 20% and 22% DVB) because preliminary experiments showed that the adhesion of diVB-TETA-Cu to the CMV-S surface starts to be successful at 18% DVB. Furthermore, diVB-TETA-Cu was used instead of diVB-TETA. Also, a copper removing step was carried out after polymerization by immersing the membrane in 1 M H_2SO_4. As with non-imprinted modifications, samples of different thicknesses of the cross-linking DVB agent content were prepared.

5.2.3 Characterization

5.2.3.1 Chemical structure and surface morphology

IR spectra of substrate membrane before and after modification were recorded using ThermoNicolet 6700 FT-IR spectroscopy with smart diffusive reflectance (range: 4000 to 400 cm^{-1}, frequency: 16 scans and resolution: 0.5 cm^{-1}) to investigate the effect of the modification process on the chemical structure on the membrane's surface. Changes in the membrane's surface morphology were observed by FE-SEM (JEOL JSM 7000 F (under the vacuum condition, and the samples were sputter-coated with a Pt thickness of 5.6 nm).

5.2.3.2 Mass gain

The mass gain of the CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes at different thicknesses and cross-linking degrees can be measured using the following equation:

$$\text{Mass increase (\%)} = \frac{(m_{\text{f}} - m_{\text{o}})}{m_{\text{o}}} \times 100 \qquad (5.1)$$

where m_{f} is the mass of the dried CMV-S/diVB-TETA or CMV-S/diVB-TETA-Cu membranes, and m_{o} is the mass of dried CMV-S.

5.2.3.3 Water uptake

The water uptake of the CMV-S/diVB-TETA or CMV-S/diVB-TETA-Cu membranes at different thicknesses and cross-linked content can be measured using the following equation:

$$\text{Water uptake}(\%) = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \qquad (5.2)$$

where W_{wet} and W_{dry} are the masses of the membrane for the wet and dried forms, respectively. The prepared membranes were immersed in deionized water and left for 24 h at room temperature. The membranes were then removed from the deionized water and were pressed between filter papers and were weighed immediately to get the W_{wet} value. The membranes were dried in a desiccator under a vacuum until constant weight was reached to get W_{dry} (Kwak et al., 2012, Strathmann, 2004; Khan, 2013).

5.2.3.4 Ion exchange capacity

The prepared membrane samples were soaked in 1M HCl until equilibrium was achieved and were stirred for 24 h and then removed from the solution and rinsed with deionized water to remove excess acid. The membrane samples were soaked and equilibrated in 50 mL of 1 M NaCl for 24 h under stirring until H^+ ions were released in the solution as they exchanged with the Na^+ ions. The solution finally titrated against 0.1 M NaOH in the presence of a phenolphthalein indicator to demonstrate the equivalent point. The ion exchange capacity can be calculated from the following equation:

$$IEC = \frac{M.V}{m} \qquad (5.3)$$

Where V is the volume of the added titrant till equivalent point (mL), M is the titrant NaOH concentration (0.1 M) and m is the dry membrane weight (g) (Le et al., 2010; Hosseini et al., 2010; Koseoglu et al., 2010).

5.2.4 Separation experiments

5.2.4.1 Adsorption

To determine the adsorption binding behavior of the CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes with regard to Cu^{2+} and Ni^{2+}, a set of competitive adsorption experiments were carried out using, for each, a piece of well measured area (4 cm × 4 cm) of the tested membrane. The piece was immersed into a solution (50 ml) of Cu^{2+} and Ni^{2+} of specific initial concentrations (for both ions; 0.625, 1.25, 2.5 and 5 mM) at pH 5.6. All adsorption experiments were carried out with mixing at 110 rpm and at room temperature 25°C and lasted for 30 hours to guarantee equilibration. Aliquot samples 1 mL were withdrawn at timed intervals to analyze for Cu^{2+} and Ni^{2+} concentrations using ICP-OES. The amount of adsorbed Cu^{2+} and Ni^{2+} at any time t (q_t mg/g) was calculated from the difference between initial concentrations (C_o mg.L^{-1}) and concentrations at time t (C_t mg.L^{-1}) according to the following equation:

$$q_e = \frac{V(C_\mathrm{o} - C_\mathrm{t})}{m} \quad (5.4)$$

And for the adsorbed amount at equilibrium q_e (mg/g) can be calculated difference between initial concentrations (C_o mg.L^{-1}) and equilibrium concentrations (C_e mg.L^{-1}) according to the following equation

$$q_e = \frac{V(C_\mathrm{o} - C_\mathrm{e})}{m} \quad (5.5)$$

where m is the membrane mass (g) and V is the volume of solution (0.05 L).

5.2.4.2 Adsorption isotherm

The adsorption isotherm elucidates the physical/chemical nature of adsorption process. Two isotherm models were applied to investigate the binding nature of the membrane: the Langmuir model and the Fruendlich model. The Langmuir model assumes a mono-layer homogeneous-energy interaction over the membrane surface where chemical binding is the most probable (Bessbousse et al., 2012; Ghaee et al., 2012). The Freundlich model assumes a multi-layer non-homogeneous energy interaction where the physical binding is the most probable (Branger et al., 2013; Xiong et al., 2012; Xiong and Yao, 2009).

The applied linear formula of the Langmuir and Freundlich models are given respectively as follows:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{C_\mathrm{e}}{Q_\mathrm{o}} + \frac{1}{bQ_\mathrm{o}} \quad (5.6)$$

$$\ln(q_\mathrm{e}) = \ln(K_\mathrm{F}) + n\ln(C_\mathrm{e}) \quad (5.7)$$

where C_e is the solution concentration at equilibrium (mg L^{-1}), q_e is the amount adsorbed by the membrane at equilibrium (mg g^{-1}), Q_o is the maximum adsorption capacity of the membrane (mg g^{-1}), b is the Langmuir constant **,** K_F is the Freundlich constant and n is the heterogeneity factor of Freundlich isotherm.

5.2.4.3 Permeation experiment

To measure the membranes' permeation selectivity regarding the examined cations, Cu^{2+} and Ni^{2+}, a cell composed of two compartments (35 mL each) was used. A piece of the tested membrane of effective area (7.07 cm^2) was placed tightly between the compartments. The feed phase compartment contained a solution of Cu^{2+} and Ni^{2+} of 5 mM at pH 5.6, while the receiving phase compartment contained a 1 M H_2SO_4. The permeation experiment lasted for 48 hours with stirring of the two compartments under a constant temperature 21˚C. Aliquot samples were withdrawn from the stripping phase compartment at certain time intervals to determine the permeated concentration of Cu^{2+} and Ni^{2+} using ICP spectroscopy. The experiment was conducted for the CMV-S, CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes. The selective separation factor which is the ratio of the permeation flux of the selected cation to the permeation flux of the other existing cation of the membranes were (α= flux[Cu]/ flux[Ni]) where the flux, *J*, of the cation can be determined from the following equation:

$$J = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \qquad (5.8)$$

where ΔC (µmol/L) is the concentration of the permeated ion during the elapsed time Δt (h), A is the membrane effective area (7.07 cm^2) and V is the receiving compartment volume (35 mL).

5.3 Results and discussion

5.3.1 Surface chemistry and morphology

Figure 5.1 shows the IR spectra of CMV-S, CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes. There are some differences that point to the presence of the applied chelating polymer on the Selemion CMV membrane. The presence of the chelating polymer applied on the CMV membrane was confirmed from the FT-IR spectrum analysis. The peaks in the range 2960 - 2850 cm^{-1} attributed to C–H alkane stretching. The peak of 1600 cm^{-1} refers to C=C in the aromatic ring. The peak of 1040 cm^{-1} refers to S=O in the sulfonic group. The broad band peak at 3300 cm^{-1}confirms the CMV membrane's chemical structure. The peaks in the range 1650-1580 cm^{-1} is attributed to the N–H bond for the primary amines, and the 1360 cm^{-1} peak is attributed to C–N and the disappearance of 1923 cm^{-1}, which represent the C–Cl bond form the Selemion PVC polymer backbone of the network matrix. The 1040 cm^{-1} peak is attributed to the S=O sulfonic acid functional group, which disappeared in the coated CMV membrane due to the applied chelating polymer.

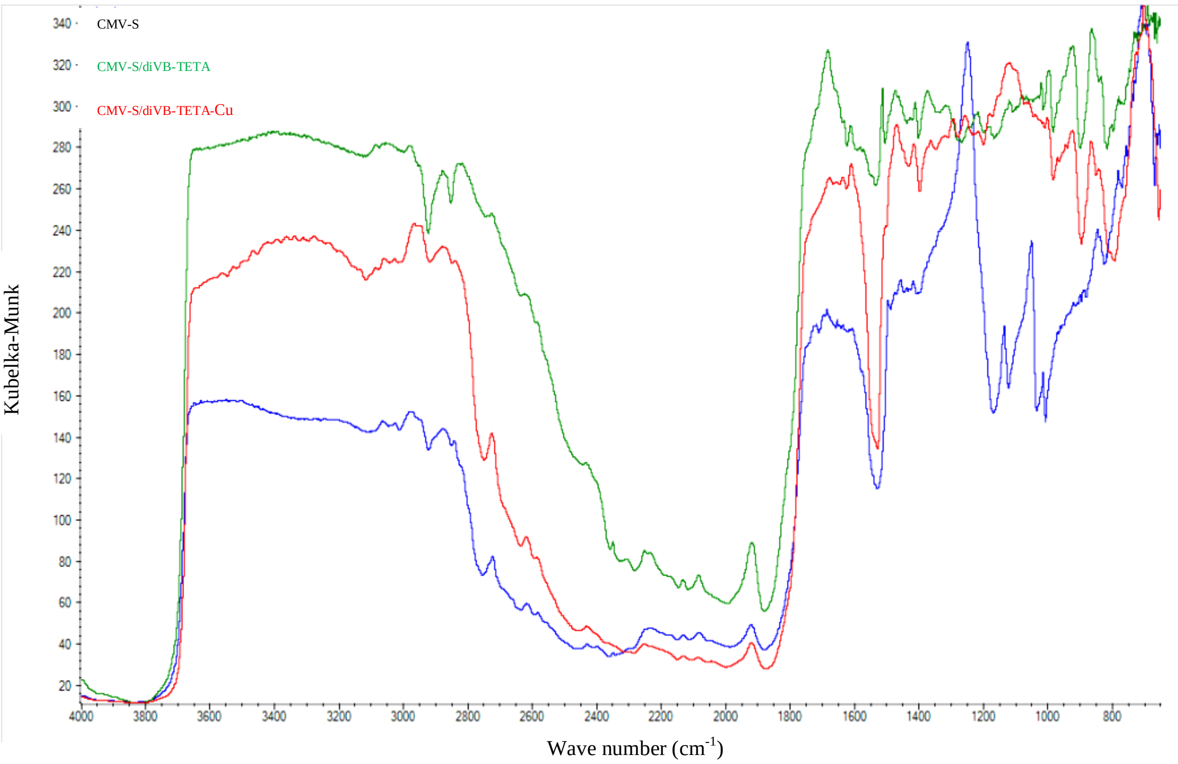

Figure 5.1 FT-IR spectra of (a) CMV-S(blue), (b) CMV-S/diVB-TETA(green), and (c) CMV-S/diVB-TETA-Cu (red) membranes.

SEM images of surfaces of the CMV-S, roughened CMV-S, CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu with the same magnification are shown in Figure 5.2. In Figure 5.2(a), the CMV-S surface is almost smooth with no openings or cracks. After roughening, surface became highly configured as shown in Figure 5.2(b). When roughened, the CMV-S was modified by chelate-polymer, which made the surface became smooth again and uniform as shown in Figure 5.2(c) and a good distribution of the selective chelating polymer can be implied. This result shows the successful polymerization and deposition of modifying chelate polymer on the roughened CMV-S membrane. Figure 5.2(d) shows the CMV-S/diVB-TETA-Cu membrane surface, which is smoother than the surface of the non-imprinted one and even smoother than the surface of the CMV-S membrane. This suggests the stability of the modification of the surface of the CMV-S membrane.

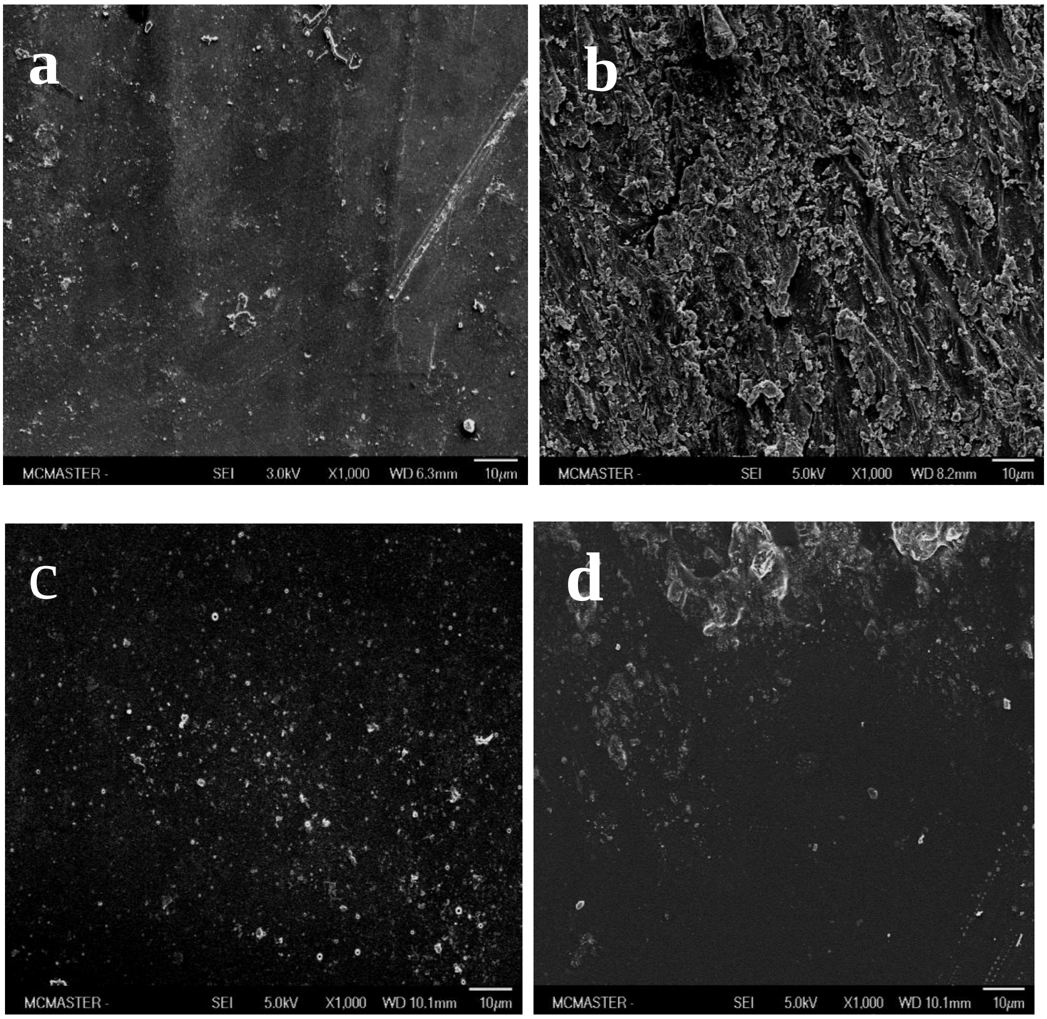

Figure 5.2 SEM images at 5000X of surfaces of the (a) CMV-S, (b) roughened CMV-S (c) CMV-S/diVB-TETA, and (d) CMV-S/diVB-TETA-Cu membranes.

5.3.2 Mass gain, water uptake, and IEC

The mass gain of these membranes after applying chelating polymers on the surfaces was determined for the same membrane surface area by the weight difference of the membrane before and after applying the chelating polymer. Table 5.1 shows that the coating density of CMV-S/diVB-TETA is higher than the coating density on CMV-S/diVB-TETA-Cu. This result can be attributed to the removal of the template ion (Cu^{2+}) from the applied chelating polymer in the final step. Also, the mass gain increased with the increasing cross-linking agent content.

The water uptake values give an indication of the hydrophilicity and swelling of the membrane. Results show that when the mass gain for both types of membranes is increased, the water uptake increases proportionate to the amount of the chelating polymer, which has a hydrophilic nature. However, when increasing the cross-linking degree (by increasing DVB%) to increase the applied chelating polymer, the water uptake decreases.

For the CMV-S/diVB-TETA membrane, the IEC at (0.115±0.005) mm is 1.636 (meq/g), which is slightly lower than the CMV-S 1.677 (meq/g), where the chelating polymer coating is on one side of the CMV-S and sulfonate groups on this side cannot exchange ions with the solution and the applied chelating polymer is very small such that its exchange capacity with ion in the solution is very small. Increasing the thickness of the membrane increases the amount of applied chelating polymer and the IEC reaches 1.687 (meq/g). IEC for CMV-S/diVB-TETA membranes decreased with the increase of the cross-linker content (DVB%), where the cross-linking may cause hindrance for ions to interact with the functionalized sites.

Table 5.1. Mass gain, water uptake and IEC for different prepared membranes

Sample	**Thickness (µm)**	**Cross-linking content (%)**	**Mass gain %**	**Water uptake %**	**IEC (meq/g)**
CMV-S	100			20.38	1.677
CMV-S/diVB-TETA	115±50	10	18.11	19.60	1.636
	135±22		32.20	22.43	1.670
	140±10		40.54	26.71	1.687
	112±20	15	12.47	16.23	0.970
	120±10		22.01	18.14	1.100
	132±31		45.48	20.20	1.230
	141±11		60.21	22.60	1.250
CMV-S/diVB-TETA-Cu	112±51	18	8.22	10.36	1.300
	132±10		15.24	12.14	1.340
	140±50		18.71	14.91	1.390
	110±10	20	10.10	6.07	0.974
	122±40		17.12	8.62	1.200
	131±14		20.30	12.86	1.230
	140±50		24.20	14.46	1.270

IEC: ion exchange capacity for the prepared membranes
Standard deviation conducted from 3 different membranes

The same effect of increasing the thickness of the chelating polymer and increasing the cross-linker content (DVB%) can also be seen in the CMV-S/diVB-TETA-Cu membranes. The IEC for the CMV-S/diVB-TETA-Cu membranes are generally lower than those in the CMV-S/diVB-TETA membranes because the CMV-S/diVB-TETA-Cu ion-imprinted membranes have a high cross-linker content starting from (18% DVB) due to its preparation, so the IEC is lower than that of the non-imprinted membrane and subsequently that affects the water uptake.

5.3.3 Adsorption

5.3.3.1 Adsorption process

As a cation exchange membrane, Selemion CMV has shown an adsorptive affinity towards both Cu^{2+} and Ni^{2+} (Le et al., 2010),(Deng et al., 2014). By modifying the CMV-S surface using chelating polymer, for all adsorption experiments that were carried out using non-imprinted and imprinted membranes, Ni^{2+} did not show any adsorption at all for all applied initial concentrations. This observation suggests that competitive adsorption by non-imprinted and imprinted membranes under static conditions exists in accordance with the fact that the stability constants of Cu-TETA and Ni-TETA are significantly different, $\log K_{\text{Cu-TETA}} / \log K_{\text{Ni-TETA}} = 20/14$.

Figure 5.3 shows the adsorption of Cu^{2+} by non-imprinted and imprinted membranes with time. For both membranes, the adsorbed amount of Cu^{2+} increases with time and the adsorption increases with the increase of the initial concentration of the feed solution till it reach the equilibrium point after 22h, which is a fundamental part of adsorption. This indicates the strong and specific affinity of chelating sites in the modifying film, TETA, with regard to Cu^{2+} and also indicates that there is no alteration in chelation-selectivity of TETA with regard to Cu^{2+} upon polymerization. In addition, the increased adsorption with the concentration indicates the importance of the initial concentration as a driving force to enhance the adsorption processes, which could have an effect on permeation. Moreover, adsorption by imprinted membranes is significantly higher than that by non-imprinted ones, which points to the effectiveness of imprinting for recognizing Cu^{2+}.

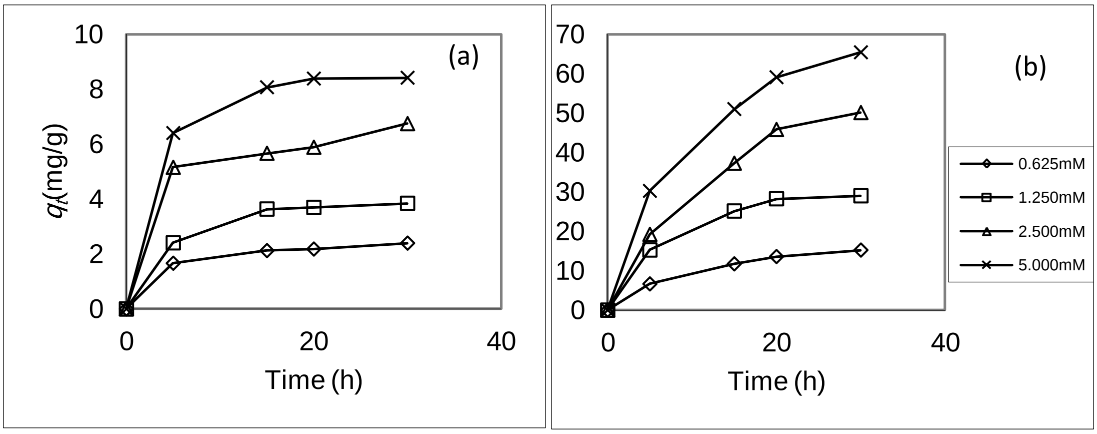

Figure 5.3 Adsorption amount of Cu^{2+} with time by (a) CMV-S/diVB-TETA (0.13 mm), and (b) CMV-S/diVB-TETA-Cu (0.11 mm) membranes.(A= 4 cm x 4 cm and $C_o(Cu^{2+}, Ni^{2+})$ = (0.625, 1.250, 2.500 and 5.000 mM)).

5.3.3.2 Adsorption isotherm

Effect of initial concentration on the adsorption capacity is shown in adsorption isotherm in Figure 5.4. From the figure, we can see that the adsorption by CMV-S/diVB-TETA-Cu is significantly more effective than that of the CMV-S/diVB-TETA membrane. This should be attributed to the chelate site recognition (shape conformation) for copper.

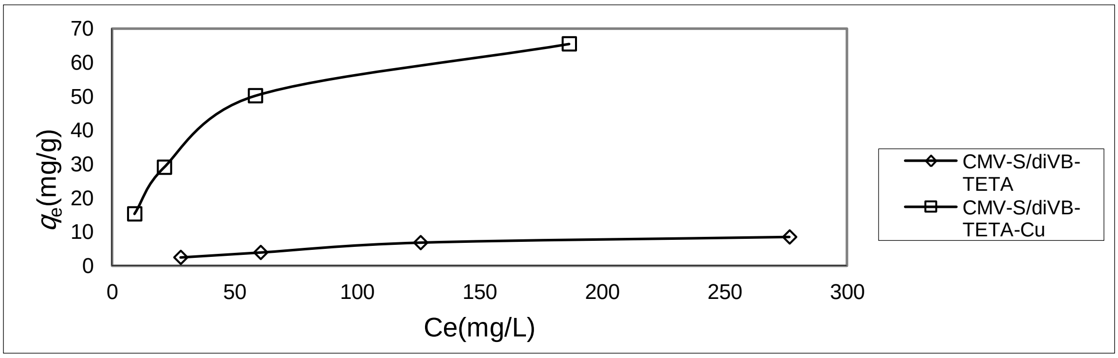

Figure 5.4 Cu^{2+} adsorption isotherm for CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes. (A= 4 cm x 4 cm and $C_o(Cu^{2+}, Ni^{2+})$ = (0.625, 1.250, 2.500 and 5.000 mM)).

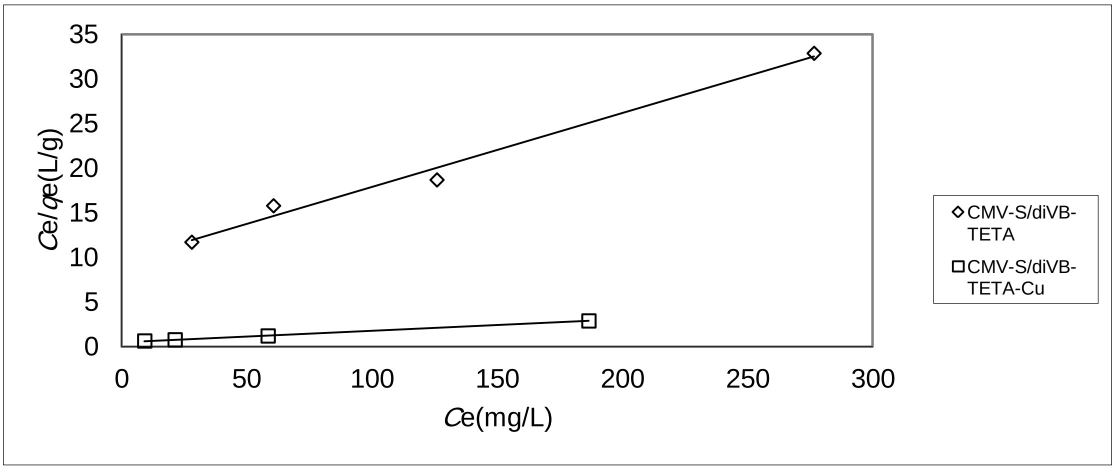

Figure 5.5 Langmuir modeling of Cu^{2+} adsorption isotherm for CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes. (A= 4 cm x 4 cm and $C_o(Cu^{2+}, Ni^{2+})$ = (0.625, 1.250, 2.500 and 5.000 mM)).

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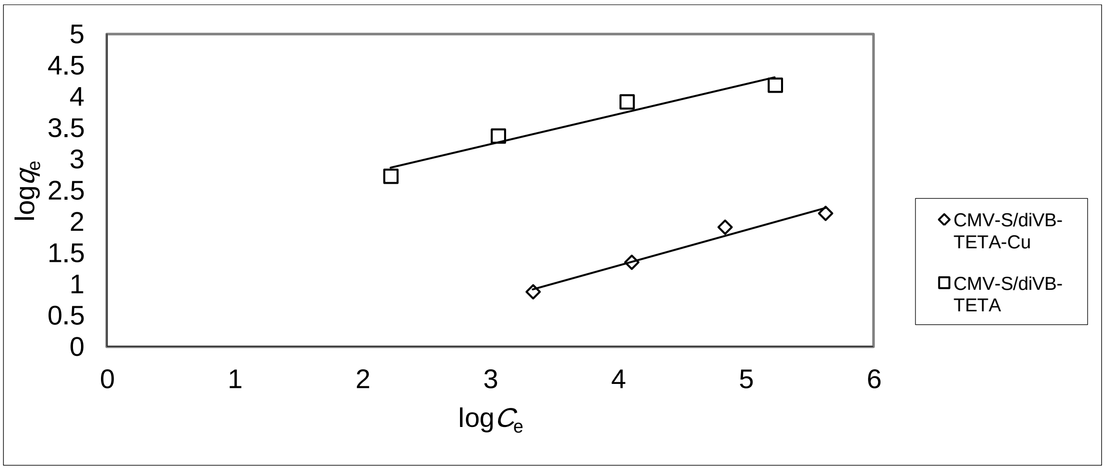


Figure 5.6 Freundlich modeling of Cu^{2+} adsorption isotherm for CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu membranes. (A= 4 cm x 4 cm and $C_o(Cu^{2+}, Ni^{2+})$ = (0.625, 1.250, 2.500 and 5.000 mM).

The isotherm plots, according to the Langmuir and Freundlich models, are shown in Figure 5.5 and 5.6. The models' parameters were determined based on linear fittings and are presented in Table 5.2. Based on the table, the values of R^2 suggest that

Langmuir better fits the isotherm data of adsorption by both CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu. This result suggests that the ion adsorption from an aqueous solution and the adsorption uniformly occurred on the membrane surface as a monolayer. Moreover, R^2 (0.9993) for IM is higher than R^2 (0.9869) for NIM, which means that the Langmuir isotherm is more favorable to work with IM, which means that all the active fixed sites are uniformly distributed on the membrane.

Table 5.2. Langmuir and Freundlich isotherm constants for Cu^{2+} adsorption onto imprinted and non-imprinted membranes.

Membrane	Langmuir			Freundlich		
	Q_o (mg/g)	b (L/mg)	R^2	n	K_F	R^2
Non-imprinted	12.077	0.0086	0.9869	0.4817	5.995	0.942
Ion-imprinted	78.125	0.0278	0.9993	0.5683	0.376	0.9702

Q_o: the maximum adsorption capacity of the membrane, b: the Langmuir constant, n : the heterogeneity factor of Freundlich isotherm, and K_F : the Freundlich constant.

From the Table 5.2 the Q_o is (78.125 mg/g), which is higher than previously published values that also use an ion-imprinted membrane for copper selective permeation (75.86 mg/g) (Zheng et al., 2012b). Cu^{2+} uptake capacity of CMV-S/diVB-TETA-Cu membrane compared to other ion imprinted polymers presented in Table 5.3. This Q_o value gives a good note that when using this membrane under the previous adsorption conditions, the maximum concentration can be absorbed by the membrane is (78.13 mg/g).

Table 5.3. Comparison of Cu^{2+} uptake capacity of CMV-S/diVB-TETA-Cu membrane to other ion-imprinted polymers

Ion imprinted polymer	Cu^{2+} uptake capacity (mg/g)	Ref.
Ion imprinted polymeric (IIP) nano-particles, (1,4-dihydroxy-9,10-anthraquinone)	22.00	(Shamsipur et al., 2011)
Ion imprinted 2-thiozylmethacrylamide (TMA)	4.85	(Yilmaz et al., 2014)
Cu(II)-imprinted poly(ethylene glycol dimethacrylate–methacryloylamidohistidine/Cu(II) micro-beads	48.00	(Say et al., 2003)
Cu(II) Ion-Imprinted Micro-porous Polypropylene	75.86	(Zheng et al., 2012)
CMV-S/diVB-TETA-Cu membrane	78.13	Current study

5.3.4 Permeation

5.3.4.1 Permeation through CMV-S

Figure 5.7 shows the diffusion of permeation of Cu^{2+} and Ni^{2+} through a CMV-S membrane over a 48 hour period. During the first 12 hours, a sharp increase of permeation was recorded for both of the cations with similar rates. No selectivity can be observed. The permeation of both of the cations gives the maximum amount in the receiving compartment (160-170 μmol) during this first 12 hours. CMV-S, like most of the commercial cation exchange membranes, separates cations from anions without distinguishing between the permeated cations. After the first 12 hours, the measured permeated amounts started to decrease slightly and steadily. This can attributed to the fact that water transported from the feed compartment to the receiving compartment because of the increase in the pressure head between the two compartments due to the taken amounts of samples in the receiving side decreased its solution volume and this cause water transfer from the feed compartment to the receiving compartment and caused an increase in the solution volume in the receiving compartment and this decreased the concentration of the metal ions.

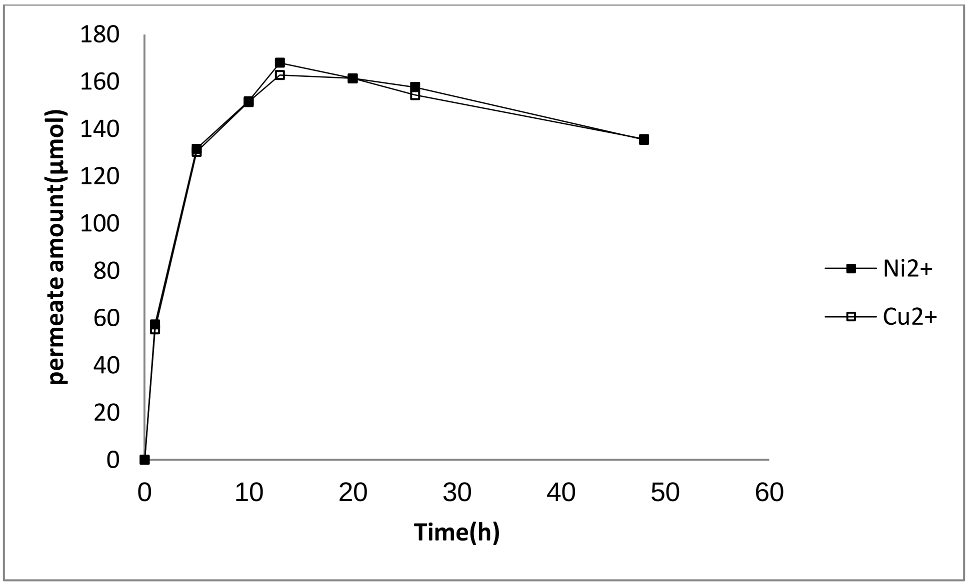


Figure 5.7 Permeation of Cu^{2+} and Ni^{2+} through CMV-S membrane ($C_o(Cu^{2+}, Ni^{2+})$ = 0.005 M, Thickness 0.1 mm and 1 M H_2SO_4 in the receiving compartment solution).

5.3.4.2 Effect of thickness on permeation through modified membranes

Figure 5.8 shows the permeation rate of Cu^{2+} and Ni^{2+} through CMV-S/diVB-TETA membranes (10% DVB) of different thicknesses: 0.100, 0.115 and 0.135 mm. From the figure, in general, applying successive thin layers of the chelating polymer decreases the flux of the ions, and this result is attributed to the adsorption, which takes place on the outer layer of the chelating polymer film. This step is followed by diffusion through the film layers at a resistance which slows the whole permeation rate. In addition, Ni^{2+} shows no permeation for the highest thickness (0.135 mm) and this may be due to the increase of TETA across the modified films, which increases the probabilities of transporting Cu^{2+} and the hindering of Ni^{2+}. Therefore, the membrane of the highest thickness gives the highest separation factor, but it has the lowest flux.

Figure 5.9 shows the permeation rate of Cu^{2+} and Ni^{2+} through CMV-S/diVB-TETA-Cu membranes (18% DVB) of different thicknesses: 0.100, 0.110 and 0.120 mm. According to this figure, the imprinted membrane shows a remarkably different permeation behavior compared to that of the non-imprinted membrane. First, the highest thickness (0.120 mm) hindered permeation of both cations. This could be due to the high amount of the cross-linker (of 18% content compared to only 10% content for non-imprinted). For thicknesses 0.100 and 0.110 mm, an interesting behavior can be observed: as thickness increases from 0.110 to 0.120 mm, Cu^{2+} permeation increases and Ni^{2+} permeation decreases. The increased thickness causes an increase of copper-selecting sites which has a positive effect in both the selectivity and flux of copper, but at the same time, the diffusion process increases which should reduce the copper permeation rate. The difference in thickness is only 0.01 mm, and it seems that the effect of transportation rate is higher than the effect of diffusion resistance for Cu^{2+} while for Ni^{2+} both copper selection sites and diffusion resistance are against Ni^{2+} permeation.

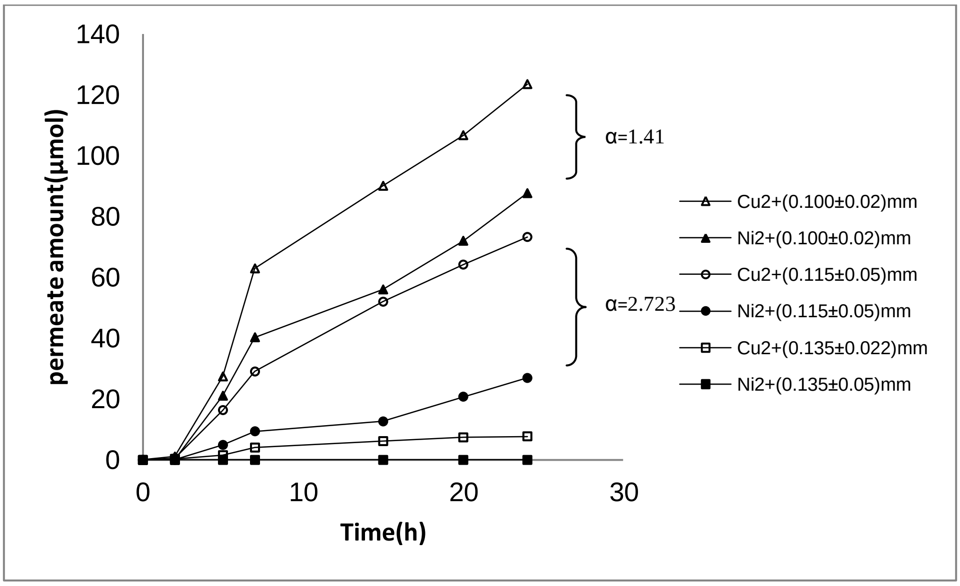


Figure 5.8 Permeation of Cu^{2+} and Ni^{2+} through CMV-S/diVB-TETA at different thicknesses (0.100, 0.115 and 0.135 mm) at (10% DVB). ($C_o(Cu^{2+}, Ni^{2+})$ = 0.005 M, and 1 M H_2SO_4 in the receiving compartment solution).

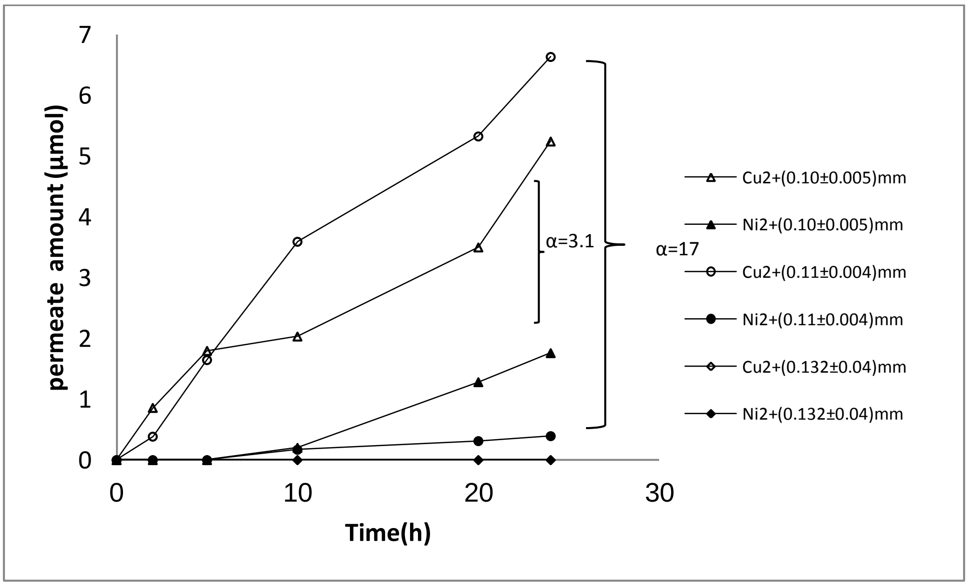


Figure 5.9 Permeation of Cu^{2+} and Ni^{2+} through CMV-S/diVB-TETA-Cu at different thicknesses (0.10, 0.11 and 0.132 mm) at (18% DVB). ($C_o(Cu^{2+}, Ni^{2+})$ = 0.005 M, and 1 M H_2SO_4 in the receiving compartment solution).

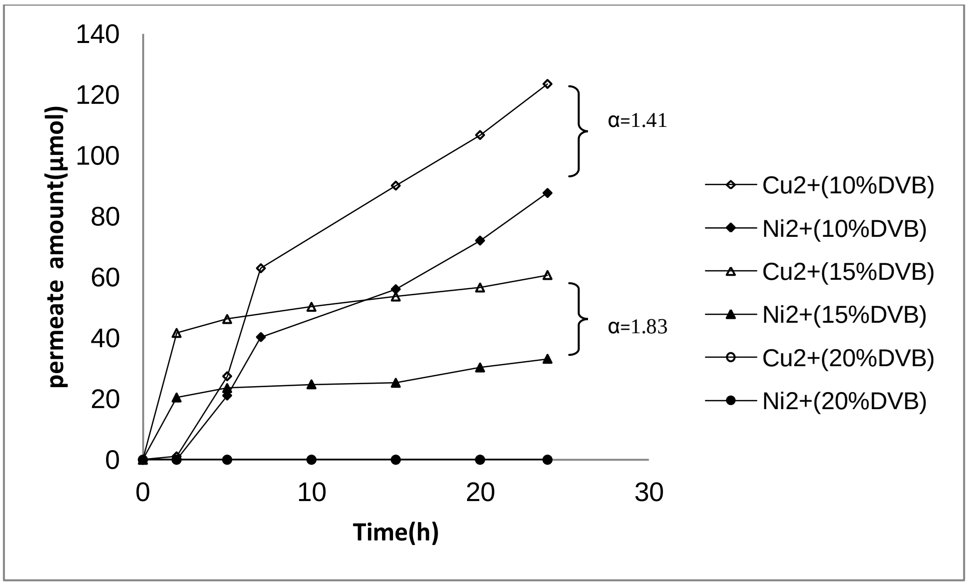
5.3.4.3 Effect of cross-linking content on permeation through modified membranes

Figure 5.10 shows the permeation rate through the CMV-S/diVB-TETA membrane considering the cross-linking amount (DVB%) for different thicknesses. For thickness 0.100 mm, as cross-linking increases, the permeation rate of both cations decreases until 20% DVB, where no permeation was observed for either. An increase of the DVB percentage should be at the expense of TETA, which will decrease the hydrophilicity of the membrane and tightens the matrix to the extent that it affects the pathways of the ions. The membrane of the 10% DVB shows a higher permeation rate of both cations compared to the membrane of 15% DVB. However, the permeation difference between Cu^{2+} and Ni^{2+} after 24 hours is almost non-existant (1.41 / 1.83 ≈0.79).

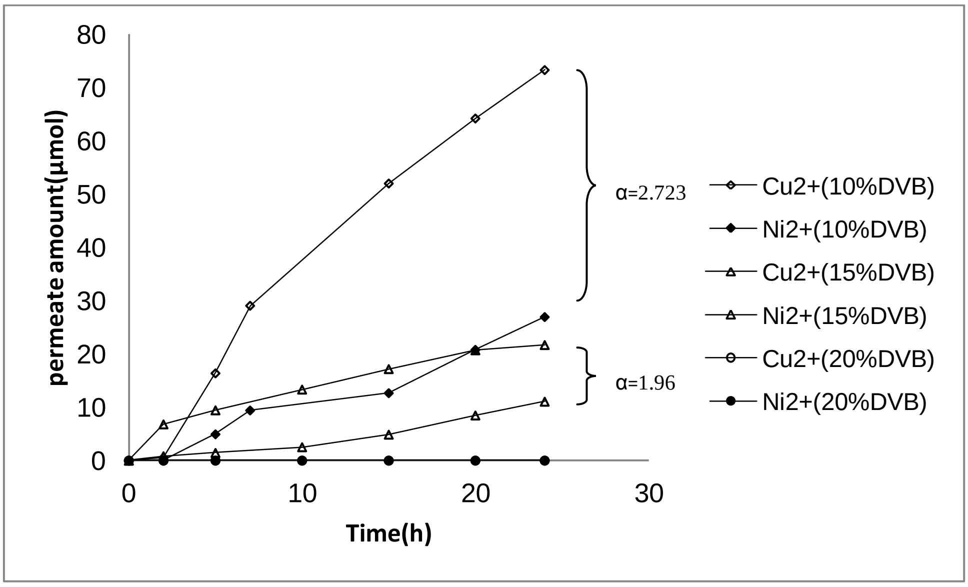
For the 0.110 mm thickness, the effect of cross linking is similar to that for thickness 0.100 mm. However, the permeation for cross-linking 10% and 15% DVB after 24 hours between Cu^{2+} and Ni^{2+} are significantly different (2.723 / 1.96 ≈ 1.39). The remarkable separation of copper from nickel in the case of 10% DVB is a result of the increase of chelating sites, compared to the same cross-linking content at a thickness of 0.100 mm.

For the membrane with the 0.135 mm thickness, the 15% DVB membrane shows no permeation for both cations and this is due to the increase of DVB content for this highest thickness. With the 10% DVB membrane, Ni^{2+} shows no permeation at all and this is due to the great amount of TETA content for this thickness. However,

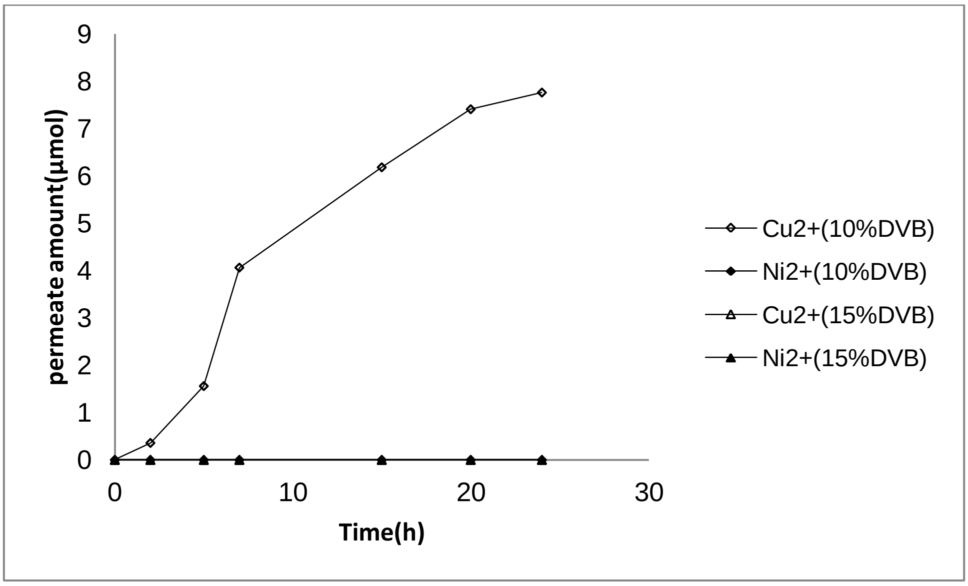
Cu^{2+}permeation is considerably lower here than in the previous thicknesses, due to the high content of DVB and diffusion resistance.



(a)



(b)



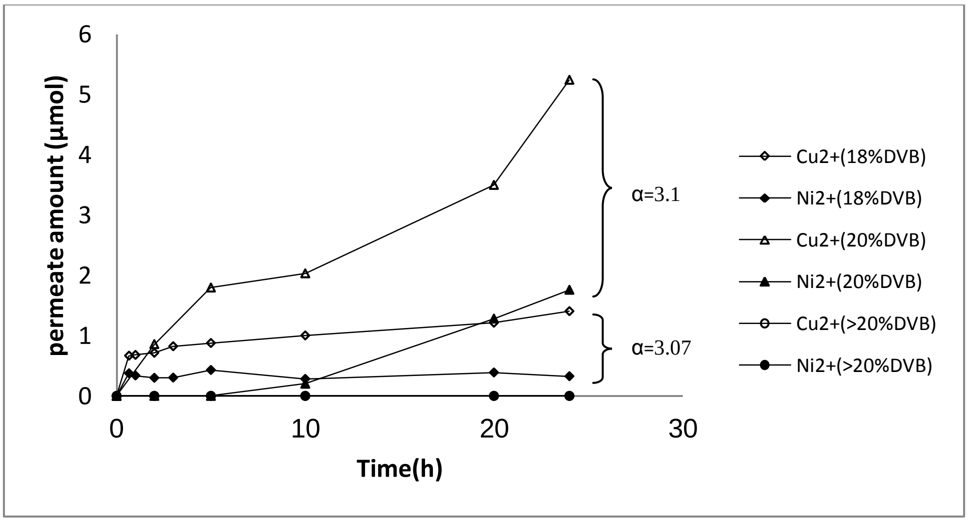
(c)

Figure 5.10 Permeation of Cu^{2+} and Ni^{2+} through CMV-S/diVB-TETA for thickness (a) 0.100 mm, (b) 0.110 mm and (c) 0.135 mm, at different DVB% (10, 15 and 20). ($C_o(Cu^{2+}, Ni^{2+})$ = 0.005 M, 0.1 mm and 1 M H_2SO_4 in the receiving compartment solution).

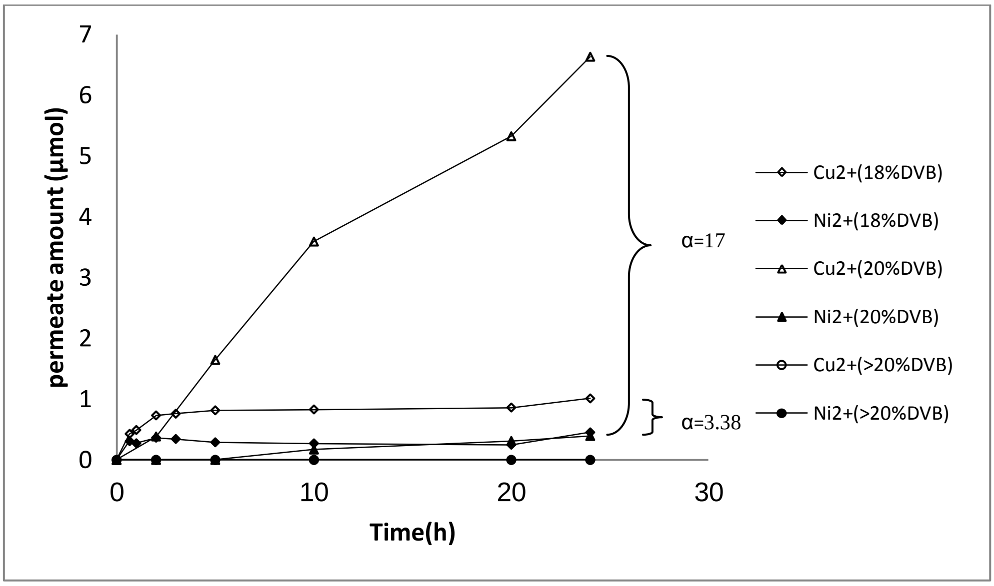
Figure 5.11 shows the permeation rate through the CMV-S/diVB-TETA-Cu membrane considering the cross-linking amount (DVB%) for different thicknesses. For a thickness of 0.100 mm, as cross-linking increases, the permeation rate of both cations decreases until 20% DVB is reached. When increasing the cross-linking content over this value, no permeation for both cations were observed because the increase of DVB percentage is at the expense of TETA, tightens the matrix, and decreases the hydrophilicity of the membrane. The membrane of 18% DVB shows a higher permeation rate of both cations compared to a membrane of 20% DVB. However, permeation differences for both after 24 hours between Cu^{2+} and Ni^{2+} are almost the same (3.1/ 3.07 ≈ 0.83).

For the 0.110 mm thickness, the effect of cross-linking is similar to that for thickness 0.100 mm. However, permeation for cross-linking 18 and 20%DVB after 24 hours between Cu^{2+} and Ni^{2+} are of significant difference (17/3.38≈4.47). The remarkable separation of copper from nickel in the case of 18% DVB originates from the increase of chelating sites compared to the same cross-linking content of the 0.100 mm thickness. (17/3.38 ≈ 4.47) value is due to the high cross-linking effect that outweighs the imprinting effect in that it drastically affects the separation factor, which is reduced 4.47 times.

The Cu^{2+} permeation after 24h through CMV-S/diVB-TETA membrane dropped from 75 µmol to 7.5 µmol for CMV-S/diVB-TETA-Cu for the same thickness 0.11 mm, which is 10 times lower. This is quite unexpected for the imprinted membrane. However, there is reasonable cause: applying the imprinted polymer on the CMV-S requires a minimum cross-linking content of 18% DVB to be attached firmly to the membrane surface.



(a)



(b)

Figure 5.11 Cu^{2+}/Ni^{2+} permeation through CMV-S/diVB-TETA-Cu

at thickness (a) 0.100 mm and (b) 0.110 mm at different DVB% (18, 20, ≥20).

($C_o(Cu^{2+}, Ni^{2+})$ = 0.005 M and 1 M H_2SO_4 in the receiving compartment solution).

In the non-imprinted membrane, CMV-S/diVB-TETA, increasing the cross-linking content over 15% DVB provides no permeation at all for either cation. This means that the cross-linking content plays an important role in considering flux to the extent that its amount is very critical in the range of 18-20%.

5.4 Conclusion

The commercial (Selemion) cation exchange membrane (CMV-S) was surface-modified by Divinylbenzyl triethylenetetramine (diVB-TETA) to produce the non-imprinted membranes and Cu-imprinted membranes, CMV-S/diVB-TETA and CMV-

S/diVB-TETA-Cu, with different film thicknesses and different cross-linking percentages. The produced membranes were dialysis-applied

to selectively permeate Cu^{2+} against the competitive Ni^{2+}. Adsorption experiments clearly confirmed the high selectivity of the produced membranes for Cu^{2+} where Ni^{2+} did not show any adsorption. Adsorption As predicted, the adsorption isotherm confirmed the higher capacity of CMV-S/diVB-TETA-Cu to adsorb Cu^{2+} than that of CMV-S/diVB-TETA (Q_o (CMV-S/diVB-TETA-Cu)/ Q_o (CMV-S/diVB-TETA)) = 6.5), which is due to site recognition. The isotherm suggests Langmuir as the model for adsorption to follow, which is in line with the chemical-chelation reaction. Permeation experiments show that selectivity for Cu^{2+} using CMV-S/diVB-TETA-Cu is better than that of CMV-S/diVB-TETA membranes, but this is remarkably at the expense of the flux. This is due the high content of the cross-linker. The CMV-S/diVB-TETA is better when considering flux, however, selective separation is still acceptable for some samples, such as $\alpha = 2.723$ at thickness 0.115±0.005 mm with 10% DVB.

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Chapter 6

Conclusions and Recommendations

6.1 Overall Conclusions

The preparation methods for several different Cu^{2+} selective membranes were developed in this study. The prepared membranes were examined for competitive permeation and the experimental results were presented in detail with an emphasis on the separation factor. In membrane preparation, the imprinting technique was employed and examined to enhance selective separation of the imprinted metal ion. All membranes were chemically and morphologically characterized.

Chapters 3, 4, and 5 present the works considering these three membranes. Chapters 3 and 4 used the same PVDF micro-porous substrate as a neutral substrate in the membrane preparation while in Chapter 5 the substrate was commercial cation exchange membrane Selemion (CMV-S) as an active substrate. Chapter 4 used different cross-linker, different from that in chapter 3, due to the preparation purpose when sodium 4-vinylbenzyl sulfonate was added to enhance the membrane metal ion permeation flux. From the results and according to discussions of these chapters, some important conclusions were derived and are presented as the following:

(1) The polymerization of chelating monomers within the matrix of the substrate membrane was successful to produce cation separating membrane for both PVDF membrane and commercial cation exchange membrane as a substrate.

(2) Type and amount of the used cross-linker are important to consider as both strongly affect the permeation flux. It is obvious for the preparation of membrane (CMV-S/diVB-TETA and CMV-S/diVB-TETA-Cu) that increasing the cross-linker content cause decrease in the metal ions flux. In addition, when a different type of cross-linker N,N'-methylenebis (acrylamide) was employed in the preparation of membranes (PVDF/diVB-TETA-N and PVDF/diVB-TETA-N-Cu) cause in a significant increase in the cations flux compared to the membranes in chapter1.

(3) Using CMV-S as an active substrate in preparation of cation selective membrane in chapter 5 showed higher cations permeation flux compared to the cation selective membrane prepared using PVDF membrane as neutral substrate.

(4) Relative concentrations of competing cations affect the selectivity in the separation process. This was clear for Ni^{2+} to start permeation after 2-4 hours when the concentration of Cu^{2+} became lower, (chapter 4).

(5) The fact that the prepared membranes are able to separate Cu^{2+} and Ni^{2+} strongly suggests the capability of these membranes to be applied for the separation of Cu^{2+} from other similar di-valent cations.

(6) Enhanced hydrophilicity by adding sodium 4-vinylbenzyl sulfonate should increase the permeation flux, however, careful employment should be considered because of probable negative impact on selective separation.

(7) Prepared membranes were examined in adsorption experiments. Experimental results were fitted to the isotherm models to understand how adsorption, which is

thought to be the first step of cation transport, affects the selective separation of the target ion.

(8) The prepared chelating monomer diVB-TETA of multi dentate groups has higher chelation selectivity to Cu^{2+} over Ni^{2+} and after the polymerization; it did not lose this selectivity which was confirmed by the adsorption study of the prepared membrane showing higher adsorptive selectivity to Cu^{2+} over Ni^{2+}.

(9) The ion-imprinting technique increased the selectivity to Cu^{2+} compared to that for the non-imprinted membranes.

(10) Chelating ligand TETA, due to its linear structure, was suitable for imprinting preparation step.

(11) The ion-imprinting technique requires attention to the type and amount of the cross-linking agent. The increased amount of the cross-linking agent enhanced the membrane stability but decreased the permeation flux.

(12) Spin coating is a proper method for controlling the thickness of the chelating polymer layers over the host membrane surface.

6.2 Recommendations for future work

A brief recommendations for the future work based on the previous results are mentioned below to implement the current membranes in the industrial field and for the production of selective membranes with more good selective and permeation properties.

(1) Preparation of such selective permeable membrane can be applied in plant scale like arranging in consecutive multiple cells to separate target metal cation from other same di-valent competitive cations.

(2) Using the prepared membranes in the ED separation processes as it is more practical demonstrated processes in industry.

(3) Studying the selective separation of another heavy metal cation in the presence of another one and/or in the presence of multiple other heavy metal cations

(4) Studying the mechanism of the cations transportation across the prepared membrane and building a mathematical model to investigate which is the most effective factor in the selectivity and the permeation rate of the studied selected cations.

(5) Studying the ability to withstand multiple cycles of use and severe conditions to evaluate its durability in the practical applications.