SYNTHESIS AND CHARACTERIZATION OF MEMBRANE WITH MOLECULARLY IMPRINTED POLYMERS FOR SELECTIVE ADSORPTION OF TRICLOSAN

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by

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DECLARATION

I, Siyabonga A. Mntambo declare that the dissertation submitted for the degree of Master of applied sciences: Chemistry at the Durban University of Technology is to my best knowledge and my original work. The work described in this thesis was performed by the author under the supervision of Dr P.S. Mdluli from 2016-2017 and no part of its content has been published or accepted at any other institution. Where the work of others is used, the author clearly referenced.

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This thesis or dissertation is dedicated to my ever-humble father Mr J.N. Mhlongo, thank you for being an awesome father, hope you are proud as I am proud of being your son. My mother Mrs Z. Mntambo-Mhlongo, thank you for being the best mommy, who have suffered and fought all odds to give us the bread of life (education) and for encouraging and supporting us as your six kids. My aunt, Nelisiwe Mntambo, she knows where we come from, her love for us is never forgotten. Lastly, this is dedicated to my late grandparents who both recently went to be with the lord, Sangiphile Mhlongo and Mantombazane MaDladla Mhlongo, thank you so much for the precious few years I shared with you.

‘So, this is what the Sovereign Lord says: See, I lay a stone in Zion, a tested stone, a precious cornerstone for a sure foundation; the one who relies on it will never be stricken with panic.’ [Isaiah 28:16, NIV]

ABSTRACT

Amongst many tenacious emerging traces of lethal organic pollutants in wastewater, triclosan (TCS) is typically the often-encountered compound. This pollutant has been reported in the water circle, including surface water, wastewater treatment plants, groundwater, aquatic sediments and aquatic organisms and, to a lesser extent, drinking water, at levels in the nanograms to low micrograms per litre range. Triclosan mainly find its way into the human system through its extensive use in pharmaceutical industries over the recent years. Excessive exposure to this water pollutant may result in adverse conditions like hematological disorders such as blood cancer. Despite the variety of its negative effects, triclosan is still used as a preservative in many pharmaceutical personal care products (PPCPs), e.g. toothpaste, disinfectants, hand wash, cosmetics, soaps and medication. In light of the aforementioned applications, it is imperative to remove triclosan to accepted levels and find more efficient, low-cost and less energy consuming methods of its removal in order to counter the challenges of water scarcity in the country and its wastewater channels.

In this study, a “fractionated approach” was used, as it accounts for the synthesis of selective polymeric membranes using a phase inversion by immersion precipitation technique. Hence, the quest to address these water challenges was through the application of polyvinylidene fluoride (PVDF) polymeric membranes for the removal of triclosan in effluent treatment plant (ETP) water. This was carried out by fabricating this polymer with selective micro composite particles called molecularly imprinted polymers (MIPs). This improved the mechanical behaviour and strength of the membrane. The MIPs were synthesised using a two-step bulk polymerisation process. The synthesized MIPs possess specific binding cavities within its structure.

The PVDF membrane were functionalised with MIPs and were characterised using Scanning Electron Microscopy (SEM), for their morphological properties. Thermogravimetric analysis (TGA) was used to study their thermal behaviour and the Fourier transform infrared coupled with universal attenuated total reflectance (FTIR-ATR) was utilized to determine the functional groups present in the membrane. The dynamic mechanical analysis (DMA) was used to study the mechanical behaviour and strength of the membranes.

The SEM images showed the equal distribution of micro particles on the membrane surface. The TGA analysis revealed that all the studied polymeric membranes were thermally stable up to an average temperature of 502°C. The FTIR-ATR analysis showed new absorption peaks that were brought by the functionalisation and revealed that the PVDF membrane does not interfere with the MIP chemical integrity despite being infused within the polymeric membrane. DMA revealed an improved stability and behaviour once the concentration of the additives was increased. Moreover, the water and porosity content percentage of the MIP infused PVDF membranes increased as the concentration of the adsorbent was increased.

Wastewater samples were collected from an effluent treatment plant (ETP)and pre-treated before analysis. Experimental parameters such as sample size, contact time, stirring speed were optimised. The synthesised PVDF/MIP membranes had an adsorption efficiency of 97% TCS in membranes compared to PVDF/NIP and PVDF bare membrane which had 92%, 88%, respectively. This might be due to the effect of the binding sites of the additives. The analytical method had limits of detection (LOD) and limits of quantification (LOQ) of 0.22, 0.71 μgL^{-1} in wastewater effluent, respectively. The percentage recovery for the effluent samples was 68 %. The results obtained therefore shows that MIPs have the potential modifier for the development and continuous progress in PVDF membranes.

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LIST OF ABBREVIATION AND NOMENCLATURE

Triclosan	TCS
°C	Degrees
mL	Millilitres
mg	Milligrams
mg/L	Milligrams per litre
wt	Weight percent
%	Percentage
HPLC	High Performance Liquid Chromatography
SEM	Scanning electron microscope
TGA	Thermal gravimetric analysis
DMA	Dynamic mechanical analysis
FTIR-ATR	Fourier transform Infrared-Attenuated total reflectance
MIP	Molecularly imprinted polymer
NIP	Non-imprinted polymer
PVDF	Polyvinylidene fluoride
UF	Ultrafiltration
MF	Microfiltration
WHO	World Health Organisation
DWAF	Department of water affairs and forestry
PSf	Polysulfone
PES	Polyether sulfone
TIPS	Thermally induced phase separation
NaOH	Sodium Hydroxide
DI water	Deionised water
MAC	maximum allowable concentration
pH	Pondus Hydrogenia
NMP	N-Methyl-2-pyrrolidinone
WWTP	Wastewater treatment plants
SERS	Surface-enhanced raman spectroscopy

CHAPTER 1: INTRODUCTION

1.1 Introduction

Over the past decades, continuous progress in environmental health has been made especially in the field of science, and this has led to major breakthroughs that have expanded and vastly improved human life in the area of exploration and development of pharmaceuticals [1, 2]. The simultaneous advancement in analytical technology now allows the detection and quantification of significant amount of unwanted and lethal pollutants in natural waters and WWTPs. Even at minimal concentrations, their presence in water have been of concern among stakeholders, such as drinking water regulators, Department of Water Affairs (DWA) water suppliers and the public, due to their potential risks to human health, aquatic or marine life. Exposure to traces of pharmaceutical chemicals via drinking water or flowing-river water may have adverse effects to life. Hence, product proliferation and ready access to pharmaceuticals coupled with burgeoning human population have significantly increased the deposition of these compounds into the environment [3-5]. Pharmaceutical industries are known to be the main contributors which causes the presence of certain drugs in water and may have a cumulative effect [6, 7]. If antibiotics accumulate in the environment and work their way back into the human population, for instance, it could contribute to antibiotic resistance. Another concern is that exposure to even trace amounts of drugs could have a negative impact on the health of more vulnerable members of the population, such as babies who drink formula mixed with tap water.

The presence of organic compounds in river water and water treatment plants has caught attention over the years due to the fact that they are very costly and energy consuming to mitigate because of variety of steps involved in these over thirty processes primarily used [8, 9]. As long as humans are using chemicals for the treatment of ailments, personal care products, medication and other cosmetics, trace levels of these substances are likely to be found in water. Figure 1.1 displays a schematic path on how these unwanted pollutants are discharged, and further find their way to the aquatic environment. What has changed abruptly and dramatically is the increased use and diversity of pharmaceuticals, analytical method sensitivity, and increased discharges of treated wastewater to water bodies [10]. Presently, more than 3000 prescription pharmaceuticals are registered for use in the U.S. and only an extremely small sub-set of these have been monitored in water. Median concentrations of detected pharmaceuticals in drinking water were again less than 10 ng/L. In both of these studies, the occurrence of pharmaceuticals in drinking water was governed by the degree of wastewater influence on source water and removal during treatment [11].

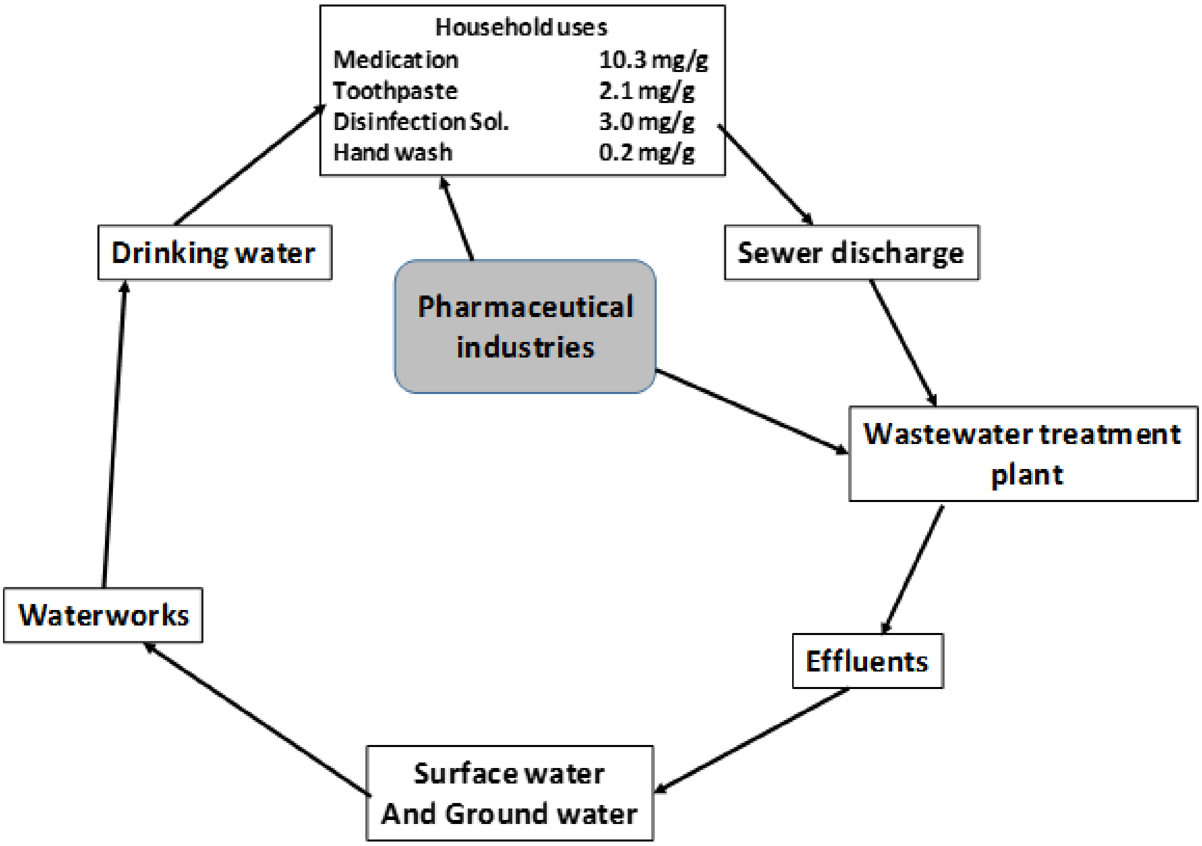


Figure 1.1: Life cycle of organic pollutants in the aquatic environment from pharmaceuticals

1.1.1 Triclosan - Target pollutant

Given its wide use in personal care products and consumer products, triclosan (TCS), which is fully retained in WWTP, enters the environment either through treated wastewater (effluent) and/or pharmaceutical personal care products (PPCP) [12-14].

TCS mostly referred to as [5-chloro-2-(2,4-dichlorophenoxy) phenol is a broad-spectrum antibacterial agent used in personal care, veterinary, industrial and household products. TCS is commonly detected in aquatic ecosystems, as it is not completely removed during the wastewater treatment processes [10, 15]. These traces of pollutant (TCS) are caused by the tabulated products shown by Table 1.1, which are daily used by human beings in their households.

Table 1.1: Specification values of TCS in various consumer products accessed from Singh Dhillon, Kaur [3] table.

Type of TCS-Based Product	TCS Concentration (%)	Reference
	Oral care products	
Tooth paste	0.3	[16]
Mouth wash	0.03	[17]
	Dermally applied products (rinse off)	
Dishwashing detergents	0.1	[11]
Skin cleansers	0.3	[18]
Liquid hand soap	0.1-0.45	[11]
	Dermally applied products (leave on)	
Facial moisturizer	0.3	[18]
Body lotions	0.3	[18]
Deodorants	0.3	[18]

TCS (see chemical structure Figure 1.2) or 2,4,4′- trichloro-2′-hydroxy-diphenyl ether is an antibacterial ingredient also known under the trade name Irgasan DP300. It has been found in consumer products since 1968 as an antiseptic, disinfectant, and a preservative in clinical settings. TCS has also been found in various consumer products including cosmetics, household cleaning products and toys and has also been incorporated on the surface of medical devices, plastic materials, textiles and kitchen utensils. However, TCS was removed in 2010 from the European Union (EU) list of additives used in plastic food-contact materials [18]. TCS have been detected more than once in the local rivers and this may be due to industrial processes and effluent discharge that have found their way into these streams [19]. TCS has lipophilicity nature since it has the ability to dissolve in fats, oils, lipids and non-polar solvents, i.e. hexane, toluene.

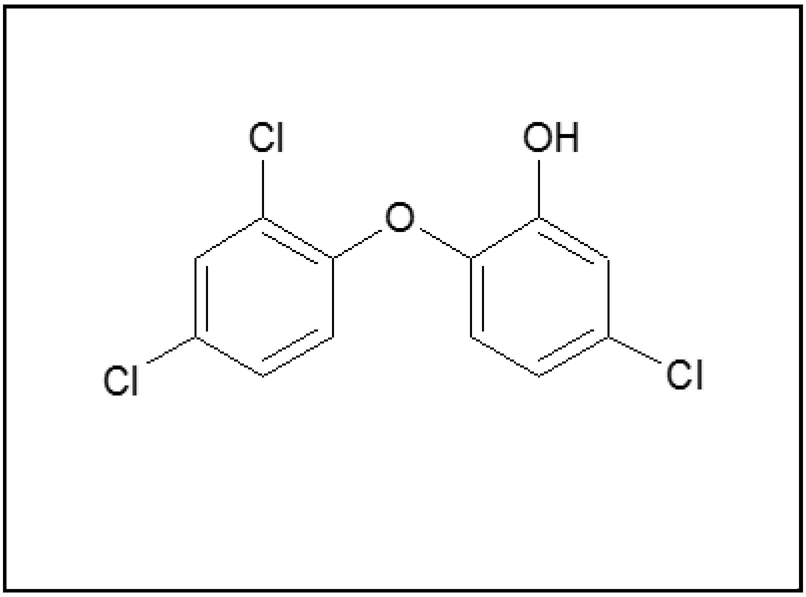


Figure 1.2: The chemical structure of TCS

1.1.2 Molecularly imprinted polymers (MIPs) and membrane technology

Molecularly imprinting technology has gained a significant recognition due to its selective capabilities with regards to being specific to a certain trace organic contaminant. These specific contaminants are referred to as templates or target molecule when imprinted in the presence of a suitable functional, cross-linking monomer. This interaction greatly influence the specific and selective adsorption of the MIP – to yield maximum specificity and selectivity [20, 21]. In these smart material powders, the selectivity is also determined by the covalent and non-covalent interactions between the target molecule and monomer [22]. The MIPs are synthesised using precipitation polymerisation mostly known as bulk polymerisation: The schematic diagram of the imprinting of these polymers is shown in Figure 1.3. Before bulk polymerisation could take place, a self-assembly process happens between the functional monomer and the imprinted template.

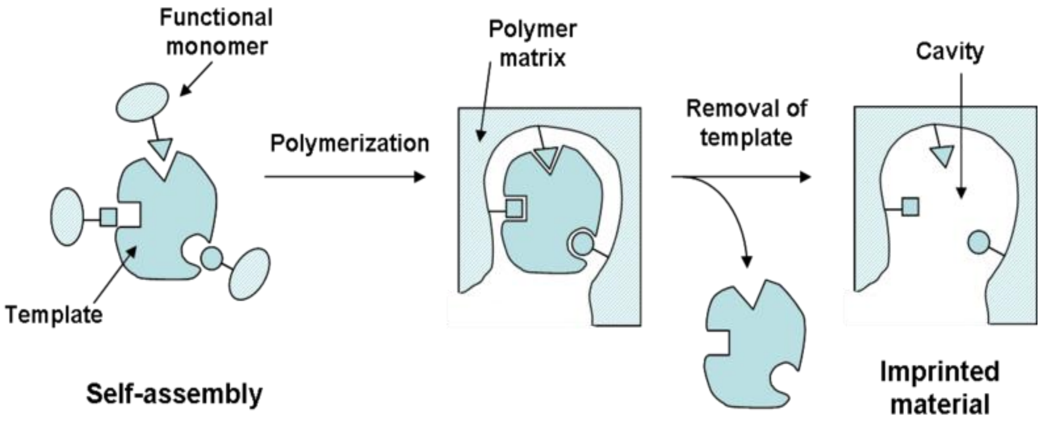


Figure 1.3: The schematic diagram of imprinting process [23]

Membrane technology is another drastically emerging technology with advantages of using reasonable energy, requires less chemical modification, good film forming ability, flexibility, toughness, separation properties, and their ease in integration with other processes. However, due to their hydrophobic nature membranes possess limited mechanical, chemical, and thermal resistance as well as poor antifouling abilities. Membrane technology has been effectively used lately in most industries because of its beneficial properties due to its fastness and easy use, high selectivity and its flexibility [24]. Using MIPs as powder limits their application in real water treatment bodies, as it may require constant filtration of the MIPs after use. Hence, this is tedious and impractical in real water treatment applications. Therefore, incorporating them into polyvinyl (dene) fluoride ultrafiltration membrane becomes a viable and practical alternative. However, incorporating these MIPs into PVDF ultrafiltration membrane has its own implication on the morphology, functional groups, and performance (flux, and rejection) of the resultant membranes. Therefore, the effects of incorporating these polymers onto the membrane structure need to be investigated and understood clearly. This research will focus on the synthesis and characterisation of these PVDF ultrafiltration membranes modified with MIPs for the removal of TCS in wastewater.

1.2 Problem statement

Polymeric membranes are the key techniques with regards to membrane separation technology, and it directly affects process efficiency and practical application value. At present, almost all membranes for industrial processes are made from inorganic materials and/or organic polymers, and the latter dominates the existing membrane market. A suitable porous membrane should have high permeability and excellent chemical resistance to feed streams. Although PVDF membrane is hydrophobic in nature and favours the selective absorption and transport of the organic component of an organic or water feed solution, it is liable to contamination by proteins and some other impurities in water and wastewater treatment, which leads to a sharp drop of pure water flux of the membrane. The synthesis of membranes infused with selective MIPs is therefore the focus of this work. However, the challenges that frequently arise are from the low purity and poor selectivity in the application of these membranes. Therefore, the main objective is to fabricate MIP active membranes to be applied as active sorbent for TCS as well as to evaluate the stability and the interaction between the membrane (polymer) and a modifier (MIPs sorbent).

1.2.1 Marine life and environmental exposure to triclosan (TCS)

The incomplete removal of TCS during the wastewater treatment processes have led to the continual exposure of aquatic organisms or marine life as a whole. The accumulation of the antimicrobial and its degradation products in tissues of aquatic organisms (Table 1.2). Algae, a primary food source for many aquatic species, constitute an important pathway for the accumulation of lipophilic water-borne contaminants, such as TCS [25]. Another study was done in the late 2000s, where a famous researcher sampled the filamentous algae in a receiving stream for the city of Denton (Texas) for TCS exposure, and a shocking measurement of 100–150 μg L^{-1} was detected [26]. What was drawn from this discovery, is the bioaccumulation factors of 1600 and this was estimated for the parent compound and its methylated by-product.

Table 1.2: Detected concentrations of triclosan (TCS) in aquatic organisms

Organisms	Type of sample	Site description	TCS (µg/L)	References
Algae and invertebrates Filamentous algae	Whole organism	Receiving stream for the city of Denton (TX, USA) WWTP	100–150	[26]
Freshwater snails	Muscle		50-300	[27]
Vertebrates Rainbow trout	Bile	Upstream from WWTP, Sweden (caged); downstream 2 km from WWTP (caged)	710-17 000	[28]
Breams, male	Bile Muscle	River-sites (Netherlands) River sites (Germany)	14000–80 000 0.25–3.4	[29] [30]
Pelagic fish	Plasma	Detroit River (USA)	0.75–10	[31]
Atlantic-bottlenose dolphins	Plasma	Estuary, South Carolina	0.12–0.27	[32]
Killer whale	Plasma	Vancouver Aquarium Marine Science Centre	9.0	[33]

1.3 Justification

The Republic of South Africa remains the water scarce country and thus it is essential for the public to formulate systems that will sustain and preserve water. Access to clean water and sanitation highly benefits the citizens of the country and the improved health of the living beings (including plants, aquatic plants) highly depend on these water systems. According to statistics obtained from the World Health Organisation (WHO) an estimated number of 1.1 billion people do not have access to clean water [34]. This arises because the earth is still overwhelmed by rural and under developed societies. For example, 60% of the land in South Africa is rural, and in most of these places, human beings share drinking water with animals. There have been several attempts that have been formulated by the department of water and sanitation to mitigate this crisis, but it has not been productive and significant as expected. The main purpose of purifying water and removing all these present contaminants in the water is to have drinkable, healthy and consumable water for generations to come.

During the removal of pollutants, which are lethal to human life, aquatic animals and many other living organisms, there are quite many processes that used by water treatment industries. These include physical processes; chemical processes; mechanical processes, biological processes and thermal processes. The two main processes that are mainly used to treat the industrial plants waste in the country are: (i) chemical process and (ii) mechanical process.

(i) Chemical processes for water treatment.

One example of chemical process is open plasma for water purification. This is a fairly new approach for purifying water and it involves the use of plasma under atmospheric pressure. Plasma is an ionized gas containing not only ions and electrons but also chemical radicals and electronically excited particles as well as short wave radiation. This plasma is ignited by means of an electromagnetic field (by applying high voltage). The plasma glow is characteristic and can be seen in the fluorescent lamps of neon signs used for advertising purposes. In a technical sense, plasma processes have already been used specifically for modifying and cleaning surfaces for a long time now.

(ii) Mechanical processes for water treatment.

The pollutants or the contaminants in the water body usually appear in a microscopic scale, that is, the particles are relatively very small and exist in an estimated diameter of few microns. During mechanical processes, the effluent is pre-treated with suitable solvents and absorbent to reduce the pollutant concentration before being disposed. This is done to produce environmentally safer treated wastewater.

The main preference and driving force of considering the employment of membranes over the already established separation methods (distillation or filtration), is the less use of chemicals and that most membrane polymers are serves to improve the existing wastewater treatment technique in terms of simplicity while treating aqueous solutions containing natural organic matters. The membrane technique will enhance the selectivity of the organic and inorganic pollutants; which simple means it is more reliable than most of the existing methods.

1.4 Aims and objectives of the study

1.4.1 Aim

The aim of this research was the synthesis of molecularly imprinted polymers (MIPs) as well as to investigate their potential to improve the selectivity of PVDF membranes for adsorption of TCS. In addition, the adsorption capabilities and removal efficiency of the produced membranes infused with MIPs and evaluation for screening of organic pollutants in wastewater samples from Umbogintwini Industrial Complex (UIC), south coast of Durban ETP wastewater, was investigated.

1.4.2 Objective

The objectives of this research are:

- To synthesize and characterise molecularly imprinted polymers (MIPs)
- To synthesize and characterise MIP-active PVDF membranes.
- To test the adsorption properties of the synthesised MIPs and infused membranes with cavities of TCS.

- To investigate the application of membranes and decorated MIPs.

1.5 Dissertation outline

This sub-section comprises of the outline of the dissertation and description of chapters in their order and what the chapters are expected to emphasise.

Chapter 1: In this chapter a source and the inspiration of the research is presented with regards to water issues, water quality, the initiative of membrane technology and mainly the main objective of the study is covered. This chapter is based more on the aims and expectations of doing this research and possible achievements.

Chapter 2: This chapter provides information on the literature review and the answers to the problem stated above in the first chapter using the formulation and validation of methods to execute the mentioned crisis on water purification. It enlightens more on the membrane technology and its modification for the investigation, quantification and qualitative analysis using the proper methods and instrumentation discussed in the next chapter (3). The material of the polymer (PVDF) is studied and learned more in this chapter, its chemical resistance, crystalline tendencies and mechanical properties.

Chapter 3: provides the analytical methods considered in the whole research during the synthesis of the membranes, synthesis of polymers (MIP) and more details on the critical stage of casting the membranes. Procedures of modification, the very steps of testing the material itself and the application of the material are outlined in this chapter. A detailed description of each of the characterisation technique in this research is also addressed here.

Chapter 4: This showcase the results and discussions obtained during the modification of using the MIPs and NIPs as a capable adsorbent to entrap the TCS during water purification and it will give us a clear understanding on the literature on organic pollutants found in water whilst providing the characterisation results on the MIP and NIP infused membrane. A paper will be considered on this work and it is currently under review.

Chapter 5: General conclusion and recommendations drawn from this study is represented on this chapter. This also comprise of insightful ideas on developing more studies and the study at hand.

Chapter 6: This chapter consists of an extra work performed on the study as whole. And further show the underground work in progress.

1.6 Key research questions

Before the research was executed, some key aspects were looked into in order to fulfil the objectives of the study, and these are the questions that rose:

- What will be the effect of the modification on the membrane?
- What would be the interaction between the membrane and the MIP?
- Will the membrane be considered as the perfect candidate to replace existing methods?
- How long is the MIP capable of holding the template?
- Are the synthesised membranes sustainable?
- How efficient and productive will the membranes be when placed in a large industrial scale?

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to imprinted micro-structured membrane technology

Membrane technology has generated interest in many researchers in South Africa and all over the world in the recent years [35]. In that way, micro-structured membranes, also referred to as micro-filtration membranes have pore diameters of between 100-10µm. The presence of organic pollutants, especially pharmaceutical organics in wastewater is a prevalent problem experienced by wastewater treatment plant hence finding better and more efficient methods for their removal is of paramount importance. Molecular imprinted polymers (MIPs) have gained several scientific applications because of their specificity of the analyte hence that creates a much improved selectivity, that include their use as chromatographic stationary phases, solid-phase extraction sorbents and their use as purification modulus [36]. The use of MIPs for screening or quantitative determination of pharmaceuticals in aqueous samples has been reported in foreign countries [37]. However, these smart materials have not been tested for TCS in South African conditions. Therefore, the MIPs will be evaluated for screening of TCS, as this organic compound is known to exist in local rivers and wastewater treatment plant [19, 38]. Table 2.1 represents different concentrations of TCS detected in different geographic environments.

Table 2.1: The occurrence of TCS in aquatic environments

Environmental matrices	Country or region	Detected concentration range	References
WWTP Effluents (ng/L)	Australia	23-434	[[39]
	Canada	63-80	[40]
	China	22.5-121	[41]
		35-1023	[42]
	USA	500-2700	[43]
		190	[44]
	South Africa	431	[45]
Drinking water (ng/L)	China	0.6-14.5	[46]
	USA	<LOQ-6.4	[47]

Apart from the synthesis of MIP-infused membranes, molecular modelling was employed as well to simulate the binding strength of each targeted molecule (pharmaceutical drugs) into the cavity of the MIPs. MIPs are smart materials that are known to be highly selective to a specific compound [48]. It is essential that the binding sites of the MIP are complementary to the template in size, shape and position of the functional groups to allow for selective uptake of the targeted compound. FTIR analysis of MIPs has been shown to be a better spectroscopic method to provide bonding information essential to the understanding of the interactions between the template molecule and the MIP [36, 49].

During the synthesis of an MIP, the target molecule (TCS) is used for direct organization of the functional groups pendent to the functional monomers [50, 51]. The functional monomer should be carefully selected to provide complementary interactions with the target molecule. A crosslinking agent fulfils three major functions: (i) it controls the morphology of the polymer matrix, (ii) it serves to stabilize the imprinted binding site and (iii) it imparts mechanical stability to the polymer matrix. The initiators are used as the radical source in free radical polymerization [52]. The formation of a complex between TCS molecule and functional monomers by self-assembly process will be the first step in the preparation of MIP. Binding energy is used to quantitatively evaluate the interaction between the template molecule and the functional monomer and for investigation of the nature of MIP recognition [53, 54].

With the application of MIP decorated membranes as surface-enhanced raman spectroscopy (SERS) probes, recently, molecularly imprinted polymers (MIPs) have emerged as substitutes for biological recognition materials (e.g., enzymes, antibodies) to enable selective detection of analytical targets. This is due to that MIPs have outstanding stability, durability and are cost effective [20]. MIPs are cross-linked polymers synthesized in such a way that they retain binding cavities for the template molecules used during polymerization [21, 22]. MIPs can be interfaced with a sensitive transducer, making these polymers an efficient tool for sensitive and easy quantification of propranolol [55].

The use of spectroscopic techniques with intensities augmented by nanostructured or micro-structured metal surfaces has attracted great interest in recent years. The SERS effect discovered in the seventies is largely attributed to the interaction of light with matter. Specifically, SERS is related to the inelastic scattering (or Raman scattering) of certain molecules in the presence of specially prepared roughened or discontinuous metallic nanostructures [56, 57].

2.2 PVDF considerations as a membrane material

Application of PVDF membranes in scientific researches and industrial processes have been extensively used due to its extra ordinary properties such as good chemical resistance, high thermal stability and most importantly, its membrane forming attributes. To further prove the reliability of this polymeric membrane, there have been a quite number of papers published on the preparation, characterization and application of PVDF membranes for water treatment [58-60].

When monitoring general properties of different materials of polymers used for membranes such as polysulfone (PSf), polyether sulfone (PES) and polyimide (PI), PVDF is relatively hydrophobic which makes it to have more surface tension since hydrophobicity indicates and associates with surface tension. PVDF membranes are said to be porous because they dissolve easily in most of the commonly used organic solvents, hence can be produced via phase inversion method [61]. In that way these polymeric materials have gained interest in a wide range of industrial processes and still continue to be the most preferable and considered.

2.2.1 Chemical resistance of the PVDF

Fu Liu [61] suggests that the PVDF membranes are extensively used due to the chemical stability against a wide range of harmful and toxic chemicals, for example, oxidants, inorganic acids, halogens, aliphatic, aromatic and chlorinated solvents. Many extensively used membranes, i.e. polyacrylonitrile (PAN), polyamide and polyimide membranes are prone to chemical attacks when exposed to oxidising agents such as monochloramine and hypochlorite used for the management of biofoulants. In other cases, membrane exposure to these oxidising agents is likely to occur during the accidental increase of chlorine in the membrane feed water or during the cleaning and purification of drinking water in the industrial methods but still PVDF remain resistance to these conditions [62]. The only shortcoming of the PVDF chemical stability that have been observed over the years of membrane technology existence is with the strong alkaline or bases, or to esters and ketones [61].

2.2.2 Crystalline properties of PVDF

Despite PVDF being a semi-crystalline polymer (known to contain 59 wt% fluorine and 3 wt% hydrogen [63], the polymeric unit of $–CH_2$-CF_2- bring about the extraordinary characteristics and attributes of PVDF directly from its crystalline structure. This important factor has a power to influence other properties of the polymer overall, which is mechanical strength properties and resistance of the membrane.

Lin D.J. [64] discovered the formation of larger spherulites in membrane morphology after the temperature has been increased. However, the crystallinity of all the membranes remained unaffected by the change in temperature and most interestingly, all membranes exhibited α-type crystal structure. This was once observed and examined after dissolving PVDF in *N,N*-dimethylformamide (DMF) at different temperature and then immersed the membranes in 1-octanol coagulation bath. PVDF is crystallise in more than one phases, i.e., α (form II), β (form I), γ (form III) and δ (form IV) [65, 66]. Figure 2.1 is the crystalline structure of PVDF membrane:

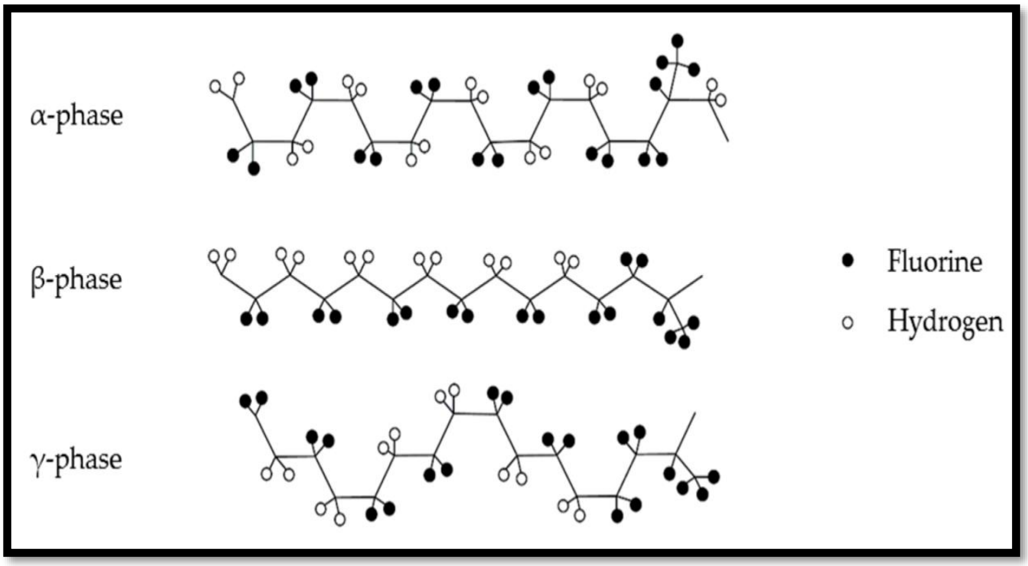


Figure 2.1: The crystalline structure of PVDF [60]

2.2.3 Thermal stability of PVDF polymer

One of the important parameters considered in selecting polymers for the engineering application or in industrial water treatment methods is *Thermal stability*. Recently, a number of studies on the effect of temperature on the chemical structure and physical properties of the PVDF polymer membrane have been conducted. It was found that at high temperatures the components of the long chain backbone of the polymer begins to break (chain scission) and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties[59, 67].

2.2.4 Application of PVDF membranes

PVDF membranes have been extensively employed as insulation on automobile, household appliances and electrical wires because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance. Most of the narrow 30-gauge wire used in wire wraps circuit assembly and printed circuit board rework is PVDF-insulated. Table 2.2 represents the common uses of PVDF membranes apart from water purification processes.

Table 2. 2 The application of PVDF membranes in different industrial scales

INDUSTRY	APPLICATION	REASON	References
Metal processing	• Production of composite electrodes for lithium-ion-batteries • Emulsion recycle (during metal forming)	It does not react with the electrolyte or lithium. Chemically inert over wide range of metals.	[68]
Biomedical sciences	• Immunoblotting as an artificial membrane in which proteins are transferred using electricity.	Heat resistance, resistance to chemical corrosion, and low protein binding properties.	[69, 70]
Pharmaceuticals and Food processing	• Microfiltration • Ultrafiltration • Reverse Osmosis • Ion Exchange	Because of its fouling resistance properties.	[71, 72]
Biochemistry and microbiology	• Nano filtration membranes and Nano-aqueous enzymology	Resistant to most organic solvents and inorganic solvents.	[73]
Pulp and paper	• Waste paper mill treatment	Simplicity and easy use.	[74]

In short, PVDF has been chosen as the main focal point of this study as it is the relevant and mostly used UF material among membrane manufactures. More so, it plays an important role in various industries (Table 2.2), such as pulp and paper, nuclear-waste processing and chemical processing [75], owing to its remarkable chemical and physical properties. Also, PVDF is known of its strong chemical resistance against corrosive chemicals including acids, oxidants and halogens which further makes it an excellent polymeric membrane material and popular among various research interests [66]. As far as membranes are concerned, it is the most widely used in water treatment for the same reasons and has the ability to be controllably porous for MF and UF application.

2.3 Synthesis of PVDF membranes

Various methods have been employed for the production and synthesis of micro-filtration membranes with enhanced flux and reduced fouling [76]. Different methods and techniques are used for the fabrication of the PVDF membranes. Immersion precipitation was preferred over phase inversion [77] and interfacial polymerisation [78] due to its simplicity and minimal use of chemicals or equipment during the synthesis process. Immersion precipitation and phase inversion techniques are discussed in the following sections.

2.3.1 Immersion precipitation

After 8 hours stirring and 2 hours settling of the polymer solution, the solution is casted or pasted on top of a suitable glass with a casting knife which is then immediately immersed in a coagulation bath with deionised water. Between the solvent and the coagulation bath, a phase separation happens [79]. This is better presented in Figure 2.2 and all this process takes place in the coagulation ice bath.

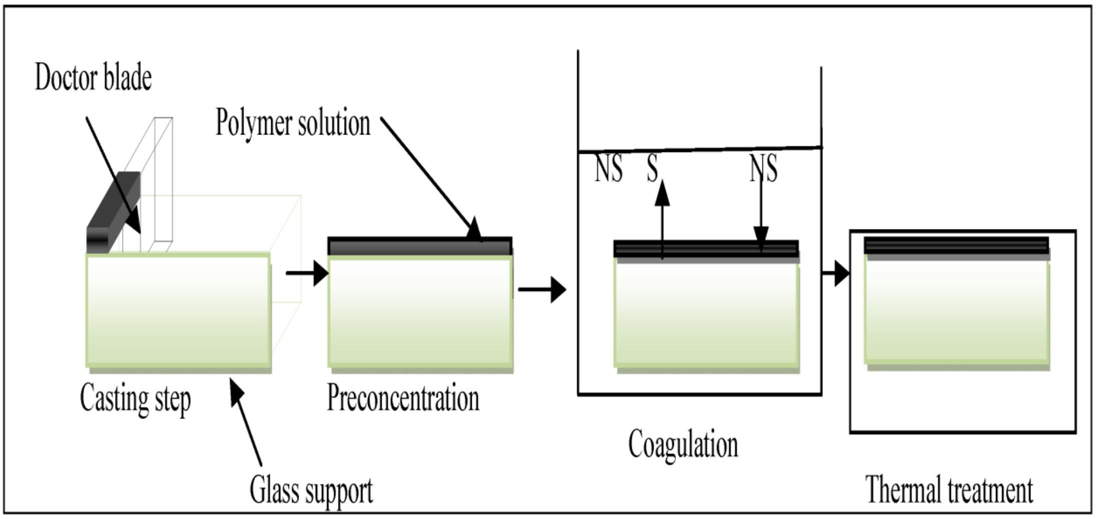


Figure 2. 2 The schematic diagram of immersion precipitation [80]

2.3.2 Phase inversion

The phase inversion process is achieved using many different processes, (i) thermally induced phase separation (TIPS), (ii) precipitation from water phase, (iii) controlled evaporation of a solvent, and (iv) immersion precipitation (IP) [81]. Amongst the four, TIPS and IP have been highly recognised more than any other due to their unique attributes. The only drawback is the preference of solvent to be used between the two; as it requires an optimisation step in order to distinguish which solvent meet the standard parameters. Phase inversion is one extensively utilised method to prepare microporous membranes because of turning a polymeric solution unstable, which can be achieved by the modification of the solution temperature or by the infusion of another component to the solution, e.g., a non-solvent (NS) to the base polymer as Figure 2.2 and Figure 2.3 presents. This happens in order to minimize the free energy of mixture, phase separation can occur and a new equilibrium state is reached [82, 83].

Figure 2.3 further describes that during the phase separation process, there are new possible phases observed: one rich and the other lean in polymer. Mass transfer between the two different phases makes the new disperse phase to exist, until viscous effects, which stops the process. Another physicochemical nature of the system such as crystallization, gelation or the crossing of glass transition of the system may begin to exist. The competition of such phenomena during liquid–liquid phase separation leads to the formation of membranes with different morphologies, which may vary from microfiltration to gas separation processes thus the membrane formation process must be controlled [84].

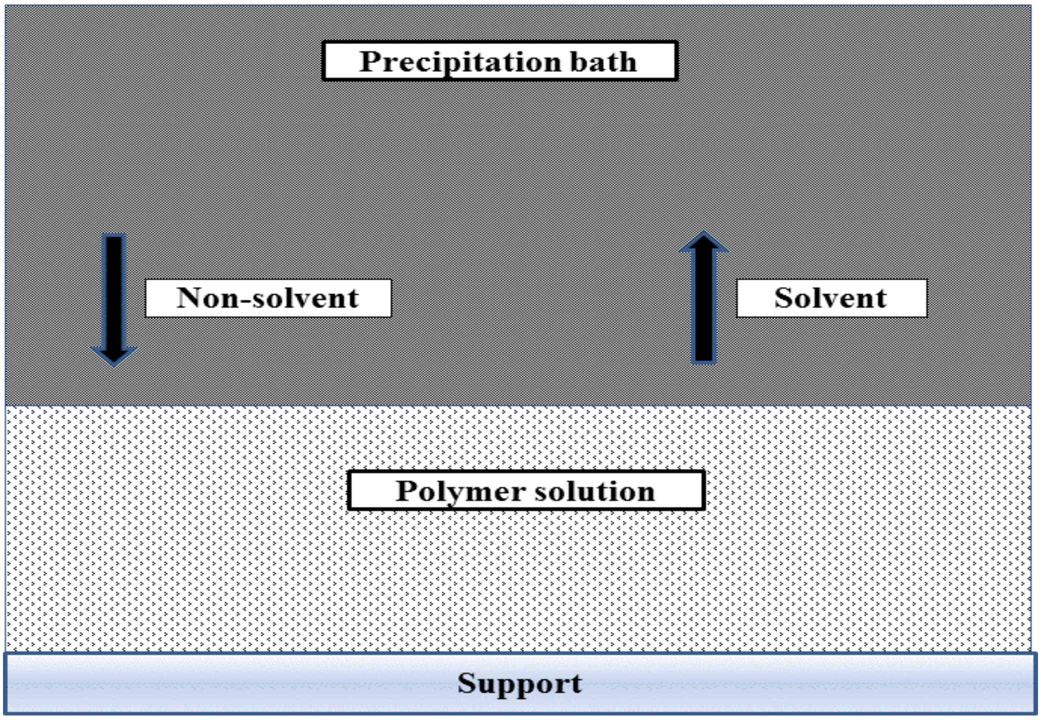


Figure 2.3 The schematic diagram of phase inversion by immersion precipitation

2.4 Hydrophilic and hydrophobic modification of PVDF membranes

Though hydrophobic nature is favourable for promoting the selective absorption and transport of the organic component of an organic/water feed solution, the neat PVDF membrane is susceptible to contamination by proteins and some other impurities in water and wastewater treatment, which leads to a sharp drop of pure water flux of the membrane [85]. Fouling is one of the main difficulties of most micro-filtration and ultra-filtration membranes in water treatment applications [61]. The hydrophobic nature of the PVDF membrane lands it susceptible to fouling while treating aqueous solutions containing natural organic matters, e.g. proteins, which are prone to be easily absorbed onto the membrane surface or block the surface pores.

Another profoundly discovered phenomenon matter about these membranes is that, an increase in hydrophilicity offers better membrane fouling resistance. A water layer is easily formed on highly hydrophilic surface, which can prevent the adsorption and deposition of hydrophobic pollutants onto the membrane surface, thus reducing fouling [58]. This means that PVDF membranes have become the main focussing area regarding the enhancement of hydrophilicity using different techniques and methods.

This will give rise to the membrane preparation methods and bring about the improvement in membrane technology, including the modification strategy within the produced membranes.

2.5 Membrane shortcomings and drawbacks

Many works have been studied previously to reduce or mitigate the shortcomings on ultra-filtration membranes and these drawbacks hinder the advancement of membrane technology in industrial application for drinking water and wastewater purification. It is unfortunate that the success of membrane technology is measured according to membrane fouling, membrane flexibility, membrane mechanical strength and membrane wetting. However, these can be countered using different methods such as (i) immersion method, (ii) flow through method and (iii) flow through combined with surface flow method [86].

Before modifying the membrane, few steps need to be considered in order to achieve a productive modification; A) the membrane has to be wetted by filtering DI water for 5 min. B chitosan is then dissolved in 2 wt.% aqueous acetic solution. The amount of chitosan has to be varied to obtain the chitosan solution with concentrations between 0.1 and 2.5 wt.%, before the membrane is modified.

(i) Immersion method:

In this method, the membrane is simply immersed in the chitosan solution with specific concentration over specific time.

(ii) A flow through method

This method requires the chitosan solution to be fed at an applied pressure of 2 bar, through the membrane module or lining.

(iii) A flow through combined with surface flow method

Here a combined flow through and surface flow method is slightly different and requires more attention. This is a two-step modification process in which the chitosan is fed through the membrane at an applied pressure of two (2) bar (ii). The operation is then switched to a surface flow mode in which the chitosan solution is made to flow (without applying any pressure) tangentially over the membrane surface.

C) The modified membranes from methods 1, 2 and 3 are then dried by annealing in a vacuum oven at 60 °C for 45 min. Thereafter, the dried membranes are neutralized by filtering sodium hydroxide (NaOH) solution (1.0 M in 50%v water–ethanol mixture) for 30 min. This is to ensure that all chitosan acetate is converted to chitosan (this is a very important step).

D) Then the membranes are cleansed by filtering 50%v ethanol solution for 10 min to remove the remaining NaOH and to prevent the osmotic crack. The membranes are then washed with DI water for 30 min.

E) Finally, the membranes are then left at 25 °C (room temperature) to dry.

2.5.1 Fouling

Fouling is one major shortcoming that has rendered the use of conventional polymeric membranes in water treatment technologies less successive and productive [87]. For example, polysulfone (PS) membranes easily get fouled because they possess low permeate flux due to the hydrophobic nature of PS material, hence its limitations for use in water treatment [88]. In order to prevent membrane fouling, the membrane fabrication technique employed is important. This can be achieved is by transforming the used membrane from hydrophobic nature to hydrophilic nature to make the membrane more resistant to fouling [89]. The smaller nanoparticles infused within the polymer could possibly improve the anti-fouling properties of the PVDF membrane more remarkably.

There are two (2) types of fouling based on the attachment strength of particles on the surface of the membrane. These are reversible fouling (this type of fouling can be easily removed by just washing (backwashing or shear force washing)) and irreversible fouling (fouling of an intense matrix after a continuous filtering or use of the membrane, that causes reversible fouling being unintentionally enhanced into irreversible fouling). Irreversible fouling is said to be the strong embedment of particles on the layers of membrane and no backwashing or physical cleaning can remove these particles [90].

2.5.2 Flexibility and mechanical strength

To date, there have been extensive studies concerning the flexibility and mechanical properties of PVDF membranes [91]. Due to efficient mitigation of these shortcomings PVDF have gained a considerable attention as most used polymeric membrane material. Flexibility is of paramount importance because it defines and highlights the quality of bending easily without breaking. Mechanical testing (or mechanical strength) is thus very essential to understand the properties of various recent polymeric materials.

2.5.3 Wetting

Wang, Fang [92] have previously investigated the mechanism of membrane wetting in the membrane absorption process at elevated temperature. Commercial polypropylene (PP) hollow fiber membrane was used to study the absorption by immersing the membrane into different absorbents at 60 °C up to 40 days. The membrane wetting eventually takes place in almost every polymeric membrane material after modification. This is because most polymers that are used to produce microporous membranes are naturally hydrophobic and have a wetting angle greater than (>) 90^o as shown in Figure 2.5 at the right. However, Figure 2.5, left, also displays the case after modification, where the wetting angle is reduced to less than (<) 90^o, which renders it hydrophilic (it can now be absorbing water).

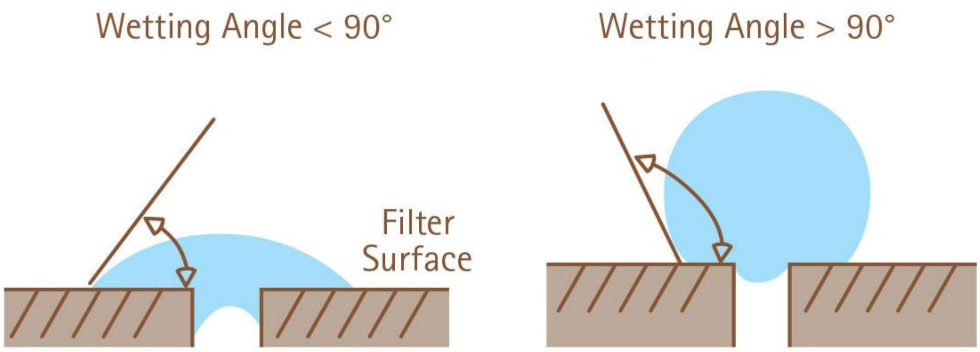


Figure 2.4 A diagram showing hydrophilic (left) and hydrophobic (right) [59]

Consequently, the liquid penetrates the pores of the membrane and will eventually wet it. A *penetration drop method* can be done to measure the maximum allowable concentration (MAC) for a (micro) porous membrane. On the basis of these measurements, the maximum allowable concentration under process conditions can then be determined [93].

2.6. Modification mechanism of the polymer (PVDF)

PVDF is one specific polymer whose membrane applications have gained recognition in the scientific research and been utilised in a number of industries due to their favouring properties. Modification of these polymers have not only improved properties like anti-fouling resistant, chemical resistant, thermal stability and other recognised properties, but it has also played a huge role in the basis of the major problems in PVDF applications [94]. Many studies done on improving the performance of polymeric membranes include physical blending [59], chemical grafting [95] and surface modification [61]. Intense knowledge exists on how to 'copy' the membrane's porous structure including its cross sectional of morphology by the choice of the polymer, solvents and non-solvents, additives, precipitation time, bath temperatures and other important parameters during immersion precipitation [96, 97]. Hence this varation of parameters results in different porous size of the produced membrane as Figure 2.6 shows, and these different sizes could be used in different processes for different purposes.

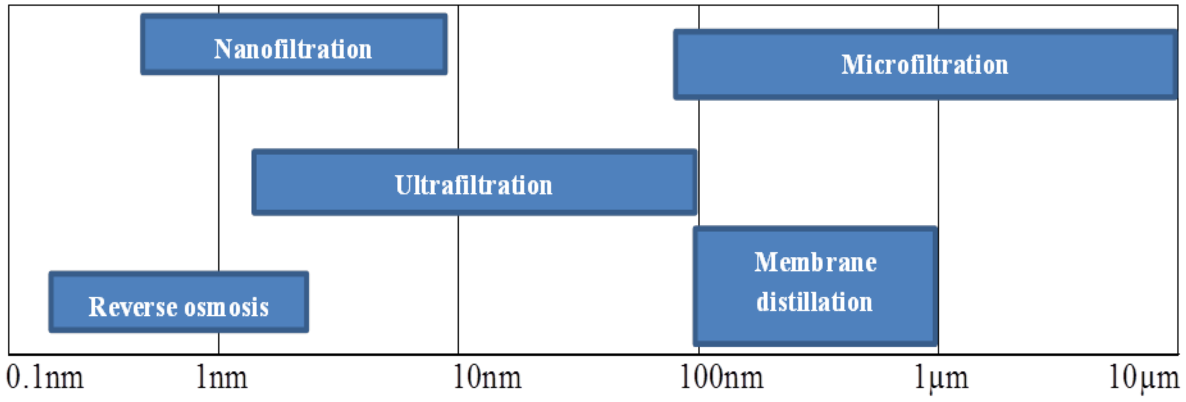
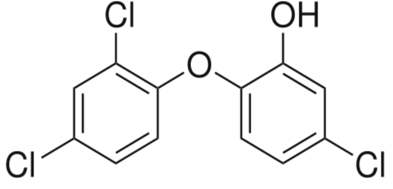
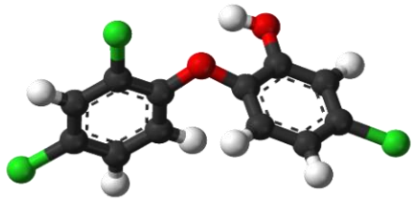


Figure 2. 5 Average pore sizes of the membranes used in different membrane processes

2.6.1 Effects of micro composite modification

In this work, the polymer of PVDF is functionalised with the micro-sized particles in order to be able to entrap polar organic pollutants or compounds in the water body through the minimal pores in the polymer. Most commonly treated non-polar pollutants, which are known to be irritant in the water technology as a whole are PAHs, bacteria and pesticides. These were thought to reside in water, wastewater and sludge over years until found their traces in soil [98]. PVDF polymer membranes have shown high performance and durability in water treatment, being able to transform poor quality waters to higher quality that can be used for drinking, adequate use in agriculture and recycling. However, to make these polymers even more effective in the environmental industry it would require the fabrication and modification of nanoparticles (or containing abrasive particles, micro and ultrafiltration membranes with enhanced physical durability) [99]. In this case, MIPs imprinted with TCS was employed to fulfil the purpose. They are quite many nanofillers including nanoparticles, carbon nanotubes (CNT) and nanoclays, which are employed for the effect on flux, fouling resistance, mechanical strength and abrasion resistance on PVDF membranes.

Table 2. 3 Physicochemical properties of TCS:

Formula	**$C_{12}H_7Cl_7O_2$**	**Chemical Structure**
Molecular weight (g/mol)	289.54	
Molecular width* (nm)	0.699	
Molecular height* (nm)	0.753	
Molecular length* (nm)	1.451	
Solubility in water (mg/L)	12	
pKa	7.80-8.14	
Log Kw	5.17	

**Calculated directly from molecular modelling software, version 9.0.

2.6.2 Effects of modification using MIP and NIP

The selection of a technique for membrane fabrication and modification highly relies on the structure and porosity of the desired resulting polymeric membrane. Hence, in this study immersion precipitation technique was chosen. Since molecularly imprinted polymers are smart materials that have selective binding sites, they were observed to be a suitable modifier in this study. MIPs have been effectively used in environmental scientific researches as an adsorbing sorbent alone in the removal of diclofenac in contaminated water and for the treatment of arsenic contaminated water, respectively [100, 101]. Recent studies show that MIPs have been incorporated into polymeric membrane backbone and have been found to improve the performance of the PVDF polymer regarding anti-fouling resistant, chemical resistant and most importantly, its mechanical performances [102].

2.7 Synthesis of MIP and NIP by Bulk polymerisation

The fabrication and modification of PVDF polymeric membrane is very essential in improving the properties polymeric membrane, for example, thermal stability, crystallinity, hydrophilicity, anti-fouling resistance and mechanical strength [60, 86]. The MIPs were synthesised using *bulk polymerisation* process. In this method (Figure 2.7), (adapted from Chao-meng Dai [100]), the reaction mixture of template, functional monomer, cross-linker, initiator, and orogenic mixture are added to a reaction flask (A). The mixture is then purged with nitrogen to remove oxygen, and the reaction flask sealed under nitrogen (B) at 70 ºC with constant stirring for 24 hours (C and D). The MIP obtained is then grinded and sieved (E). A control polymer, non-imprinted polymer (NIP), is prepared in the same way but in the absence of templates and is used as a control. The template is then removed from the MIP with constant washing and centrifuging using a proper organic solvent (90:10, Methanol: Acetic acid).

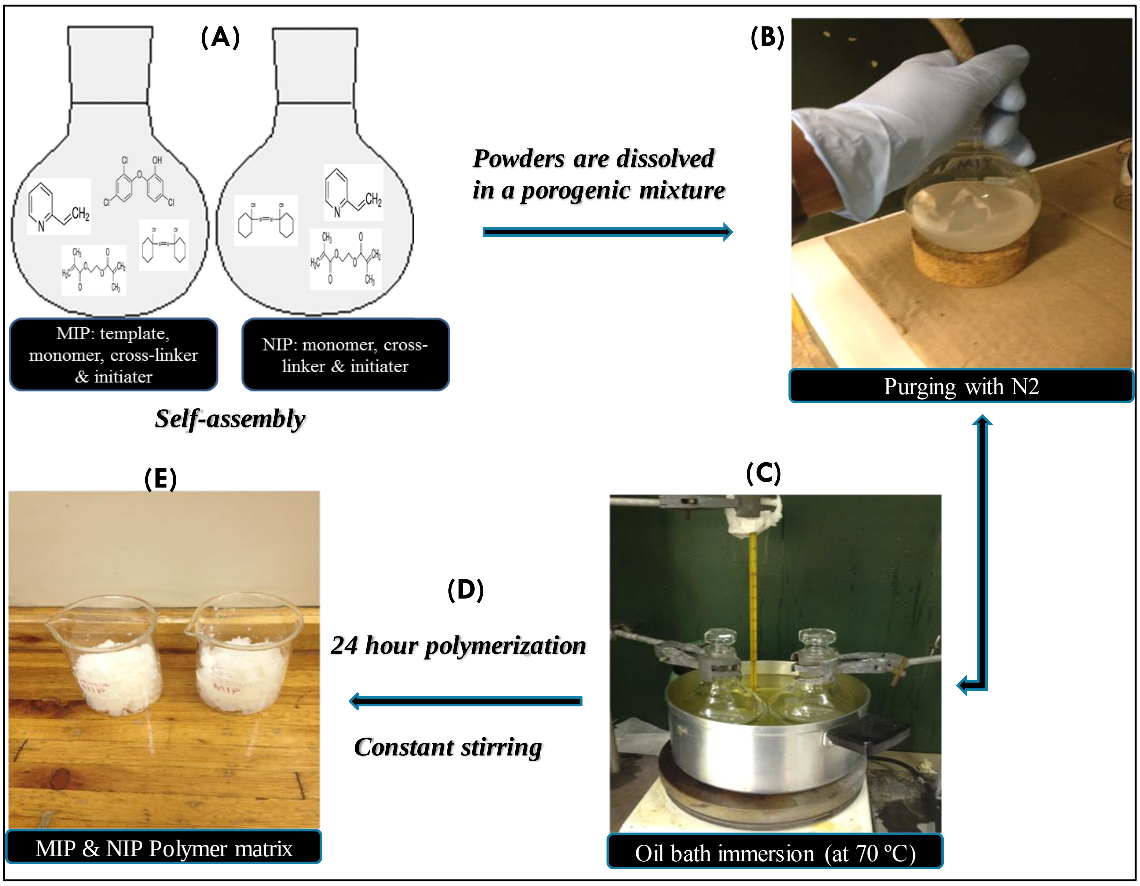


Figure 2.6: The graphical representation of MIP and NIP synthesis using bulk polymerisation

2.7.1 Imprinting of template (TCS)

There is considerable interest in the molecularly imprinting of TCS in this sorbent (MIP) because of a wide range of demand this organic pollutant has placed in the water and wastewater treatment. The toxicity of TCS has emerged especially in the water treatment and has caused effects on aquatic organism such being harmful to their internal organs, and causing breathing problems, etc. [103, 104]. The removal of the template (TCS) from the polymer is essential for opening the binding cavities for the TCS in the water body to be entrapped, hence the MIP is said to be a *'lock and key'* smart material or polymer.

2.7.2 Removal of the template

Removal of the template is of paramount importance as it allows the stable synthetic polymer (MIP) to open the selective binding sites of the removed template. This process of removing might take several runs depending on the amount of templated is imprinted on the polymer matrix. This becomes the vital part of molecularly imprinted polymer technology since the chemical integrity of the polymer matrix formed relies on this process [48, 55].

2.8. Binding characteristics of MIP

The maximum binding capacity (Q_{max}) and dissociation constant (K_d) were determined using the Scatchard equation

$\frac{Q}{C\mathrm{free}} = \frac{(Qmax-Q)}{Kd}$ ……….. (Equation 2.1), where Q and Q_{max} are the amounts and the maximum capacities of TCS adsorbed onto unit mass of dry MIP, respectively (mg/g); C_{free} is the concentration of TCS in equilibrium solutions (ppb); and K_d is the equilibrium dissociation constant of binding sites). To investigate the binding kinetics of microspherical MIP, binding efficiency of TCS at an initial concentration of 500 ppb (10 mL) to the MIP was measured as a function of time. The binding of TCS to NIP was also measured in a similar manner. All the experiments were performed in triplicate.

2.9. Regeneration or re-use of MIP

One most important advantageous attributes of the MIP as an adsorbent is the reuse to improve the wastewater financial feasibility. Hence the stability and regeneration was investigated and found to be capable of adsorbing atleast twelve (12) cycles before the obvious decrease in the removal efficiency for the template [100].

2.10. Selectivity of the MIP

MIPs are selective because they recognize their template molecules due to the existence of ‘memory cavities’ (after the template removal) with fixed sized, shape, binding sites and specific binding interactions between the target molecule and the opened cavities (binding sites). Most scientists have used competing compounds to evaluate the selectivity of the MIP because a competing molecule cannot bind strongly as the target molecule despite the case of coexisting, which may be due to common chemical structure. The size or the functional group position of the coexisting compound does not corresponds to the functional groups in the cavities hence cannot have the same binding efficiencies as the target molecule [105, 106].

2.11. Effect of pH

The pH of the solution is one important key factor in the adsorption process because it does not only affect the adsorbent capabilities on adsorption but also plays an important role in the adsorbate speciation in the analysed solution and template [107]. The effect of pH in adsorption of TCS as a template highly depends on the hydrophobic nature and the pKa of the template, the template adsorption in terms of its hydrophobicity and hydrogen-bonding interactions ends up becoming the cause of adsorption and the driving force behind the binding affinity. At low pH (below the pKa value of the compound), TCS exists predominantly as a neutral species and the effective hydrophobicity (log D_{ow}) is quite high. Consequently, the reduction in feed concentration of TCS due to adsorption was almost indiscernible in the ranges of pH (6-8). Now at pH 9-10, TCS exists mostly as deprotonated (negatively charged) species. It has been reported that the specific ability of the MIP to adsorb the template was lost just immediately when the solution pH went above the pKa of the polymer [108]. Consequently, partitioning of the anionic species of TCS to the aqueous phase becomes more favourable. The pH range that gave optimum adsorption was found to be at pH 3.0. This corresponds to the study conducted by [109] suggesting that decreased pH is an increase in the adsorption of the basic compounds to the polymer since the functional monomer possesses a negatively charged ion. The results also confirmed that the imprinted polymer have higher adsorption capabilities than the non-imprinted polymer over the pH range, hence this shows a decent imprinting effects and a good adsorption performance as expected.

2.12. Summary

The micro-structured membrane is an emerging technology that is still under intense exploration concerning the removal of organic pollutants in the water and wastewater treatment. The membrane technology however suffers from fouling and wetting of the polymeric membranes thus more studies have been conducted in mitigating these drawbacks. PVDF polymeric membrane was chosen due to its mechanical and chemical properties. PVDF polymeric membranes are also easy to fabricate and/or modify hence the techniques utilised in creating an anti-fouling polymer were reviewed.

CHAPTER 3: EXPERIMENTAL METHODOLGY

3.1. Introduction to methodology

The methodical aspects of this study and all the procedures, techniques and steps utilised to fabricate the poly (vinyldene) fluoride membranes are explained. It is noteworthy that some synthetic methods that have been investigated before having been improved to achieve the required results. This chapter also explains the instrumentation employed to analyse and characterise the synthesised materials.

3.2. Materials and Methods

3.2.1 Material and chemicals used

1-Methyl-2-pyrrolidinone (NMP) (99%) and polyvinylidene fluoride (PVDF) pellets were purchased from Capital Lab Suppliers CC, the casting knife was purchased from Trilab. Irgasan (TCS) (97%), ketoprofen (>98%), fenoprofen (>97%), 2-vinylpyridine (2-VP), ethylene glycol dimethacrylate (EGDMA), and 1, 10-azobis-(cyclohexanecarbonitrile) (98%) (AIBN) were all purchased from Sigma–Aldrich (Steinheim, Germany). HPLC grade acetonitrile (ACN) (99.9%), methanol, toluene, formic acid as well as glacial acetic acid (100%) were purchased from Merck (Darmstadt, Germany). Sodium hydroxide pellets were purchased from Associated Chemical Enterprise (Johannesburg, South Africa). Ultra-pure water was produced in the lab using Reverse osmosis. AIBN was recrystallized before putting to use and other chemicals were used without any further purification.

Table 3.1 outlines the composition (in mass) of the PVDF polymeric membrane used in this study.

Table 3. 1 The composition of the PVDF casting solution

Membrane	**PVDF (wt %)**	**MIP/NIP (wt %)**	**NMP (wt %)**
0.1 %	16.98	0.017	83
0.2 %	16.97	0.034	83
0.3 %	16.95	0.051	83

3.2.2 Synthesis of modified PVDF/MIP and PVDF/NIP membranes

The already prepared MIP and NIP micro particles (**in section 2.7**) were dispersed separately in 83 wt % 1-methyl-2-pyrrolidone (NMP) according to the ratios shown in Table 3.1 after which PVDF pellets (16,95 g) were slowly added with continuous stirring. The masses of MIP or NIP are presented in Table 3.1 The polymer solution was allowed to mix for a period of 8 hours and was then allowed to settle for 2 hours at a constant temperature of 40ºC. The solution was then pasted onto a clean glass plate using a casting knife with a blade height set at 50 µm. This was quickly followed by immersing the glass plate in a coagulation bath containing deionised water (DI) with ice for a period of 10 min, and the resultant ultrafiltration membranes were rinsed with DI water three times. The membranes were then placed in a refrigerator at 4°C before use. Overall, we had two separate polymeric membranes, one MIP-membrane and the other NIP membrane.

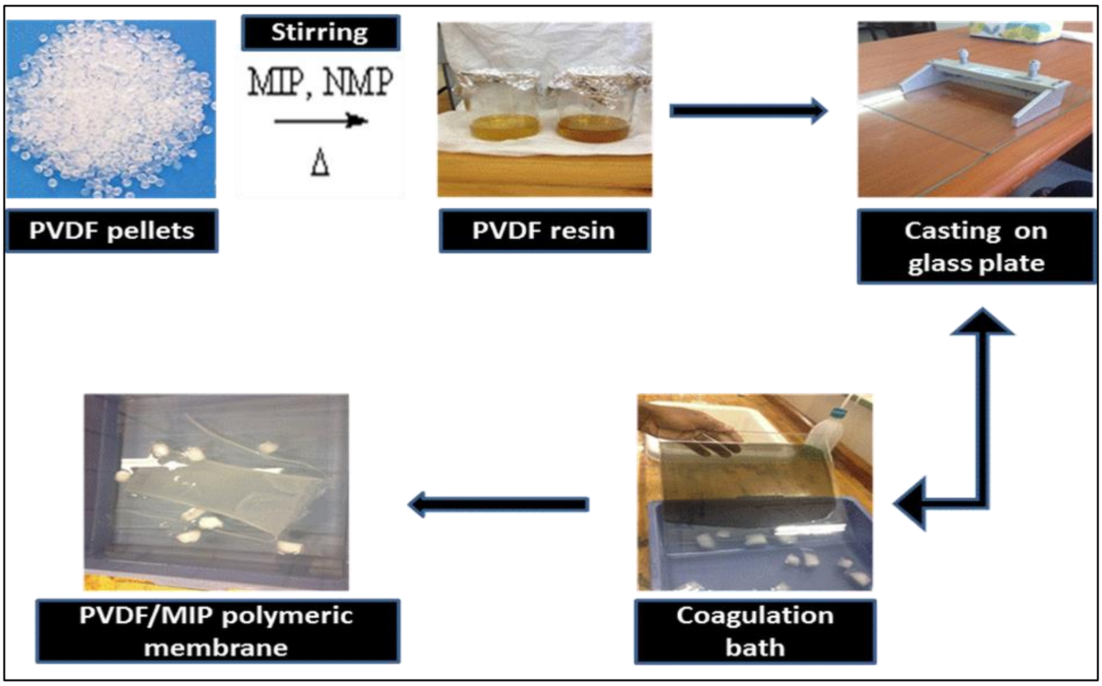


Figure 3. 1: The graphical representation of the preparation process of PVDF/MIP polymeric membrane by phase inversion

3.2.2.1 Removing of template in a MIP

Template was eluted repeatedly from the polymer using a mixture of 10% (v/v) acetic acid in methanol until the target compound was not detected by the HPLC instrumentation after triclosan optimised conditions. Then, 100% methanol was used to wash off the acetic acid residue within the sites of the polymer. And these was done by shaking a centrifuge vial at 150 rpm for 30 minutes and then a centrifugation for 10 minutes at 1000 rpm was done to separate the solvent from the polymer for HPLC detection. And this was repeated until the template (TCS) was completely not detected in the extraction solvent.

3.2.2.2 Binding character of the MIP

To evaluate the binding capacity of the MIP synthesised, adsorption tests were carried out through magnetic stirring. An amount of 50 mg of polymer microspheres were added to a 20-mL vial containing 10.0 mL TCS standard solution of 500 ppb. After being shaken for 15 minutes at room temperature, the samples were centrifuged and filtered. The free TCS standard concentration in the filtrate was detected by HPLC.

3.2.2.3 Re-use of the synthesised MIP

This was achieved after treatment with methanol/acetic (9:1, v/v). An amount of 50 mg of MIP was added to a vial containing 20 mL of 500 ppb TCS standard. After being having been agitated for 30 minutes at room temperature, the content was then centrifuged at 3000 rom to remove the MIP. Then the regenerated MIP was rinsed with methanol/acetic (9:1, v/v) to get rid of the template traces on the cavities of the MIP, followed by 100% methanol, and dried in an oven at 70^{o}C and was reused in the next cycle of adsorption experiments. The results showed that the MIP could be utilised repeatedly, therefore showing a great potential for positive cost reduction for water treatment in future.

3.2.2.4 Selectivity measures of the MIP

In this study, Ketoprofen, Fenoprofen and Gemfibrozil binding efficiencies were compared to that of TCS for both MIP and NIP binding efficiency to draw a conclusive hypothesis that the MIP is selective to the target template or not. This means there were no binding cavities and recognition sites formed by the NIP. The removal efficiency of the NIP was found to be lower than that of a MIP, and this proved the imprinting of the polymer was effective. And most importantly, suggest that the MIP possesses imprinting cavities based on size, shape and functional group.

3.2.3 Water content and porosity percentage

Water content measurements are usually neglected in most researches based on membrane technology; however, it is quite an important and essential parameter to be evaluated. This was conducted by a weight method s it has been done before in the previous studies [110, 111]. To conduct this, all samples were dried in an oven at 50 °C for 24 h and then transferred into beakers with DI water. After 12 h, the samples were then taken out and dried in an oven for another 24 h at 60 °C. The membrane weights of wet piece of membrane (Ww) and after drying (Wd) were recorded for calculating the water content percentage [112]:

$$Water\ content\ (\%) = \frac{Ww - Wd}{Ww}\ X\ 100\ \% \quad \ldots\ldots\ldots\ldots \text{Equation (3.1)}$$

where, W_w and W_d represents the membrane weights of wet and dried pieces, respectively. Measurements were taken three times, and average values were reported to minimize errors. Moreover, the results obtained from the above formulation can be used for overall porosity determination (using gravimetric method), as declared in equation 3.2.

$$Porosity\ (\%) = \frac{Ww - Wd}{\rho f Vm}\ X\ 100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation (3.2)}$$

where ρ_f represents the density of water (g/cm^3) and V_m represents the membrane small size volume (cm^3) [113]. All experiments were performed three times, and the mean values of the results were used to minimize experimental errors.

3.3. Characterisation studies

The techniques (TGA, FTIR-ATR, SEM and DMA) that were employed to study and evaluate the properties of the synthesised PVDF membranes and molecularly imprinted polymers (MIPs) are discussed in the following subsections.

3.3.1 Thermo-gravimetric analysis (TGA)

Thermal properties of the PVDF membranes were measured using a TGA 2050 thermo-gravimetric analyzer (TGA Instrument). For analysis, the samples were completely heated to 600°C at a rate of 10°C/min under dry nitrogen atmosphere. As the temperature increases, various compounds of the sample are decomposed and the weight percentage of each resulting mass change was measured [114, 115]. The thermal stability of the MIPs and NIPs were also studied under the same conditions.

Figure 3. 2: The pictorial representative of TGA instrument

3.3.2 Attenuated Total Reflectance- Fourier transform infrared (ATR-FTIR)

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) (Varian 7000e) was used to determine functional groups present in the synthesised PVDF-MIP mixed matrix membranes. The IR spectra analysis was also used to examine the interaction between MIP and the template. The NIP (non- imprinted polymer) was characterised first followed by the MIP; this was done to see if the functional groups displayed by the NIP would be the same as MIP since the template on the MIP had been removed.

PVDF polymeric membranes were also examined before and after being infused. All spectra were collected between 350 and 4000 cm^{-1} [116]. This instrument does not require sample preparation; the sample is pressed against the steel plate shown by Figure 3.3. This plate in Figure 3.3 was cleaned thoroughly with acetone before the next sample.

Figure 3. 3: The pictorial representative of FTIR-ATR instrument used

3.3.3 Scanning electron microscopy (SEM)

The surface morphology of the blank PVDF and PVDF/MIP or PVDF/NIP mixed matrix membranes were studied by a Hitachi S-4300 scanning electron microscope (SEM). The samples were mounted on the sample studs and a thin layer of gold was sputtered on the sample surface for imaging purpose. The SEM measurements were performed at an accelerating voltage of 10 kV and at different wavelengths. Figure 3.4 (a) represents the Gold sputter, where a sample is placed first to make it conductive if it is not before being analysed in the SEM instrument (Figure 3.4 (b)).

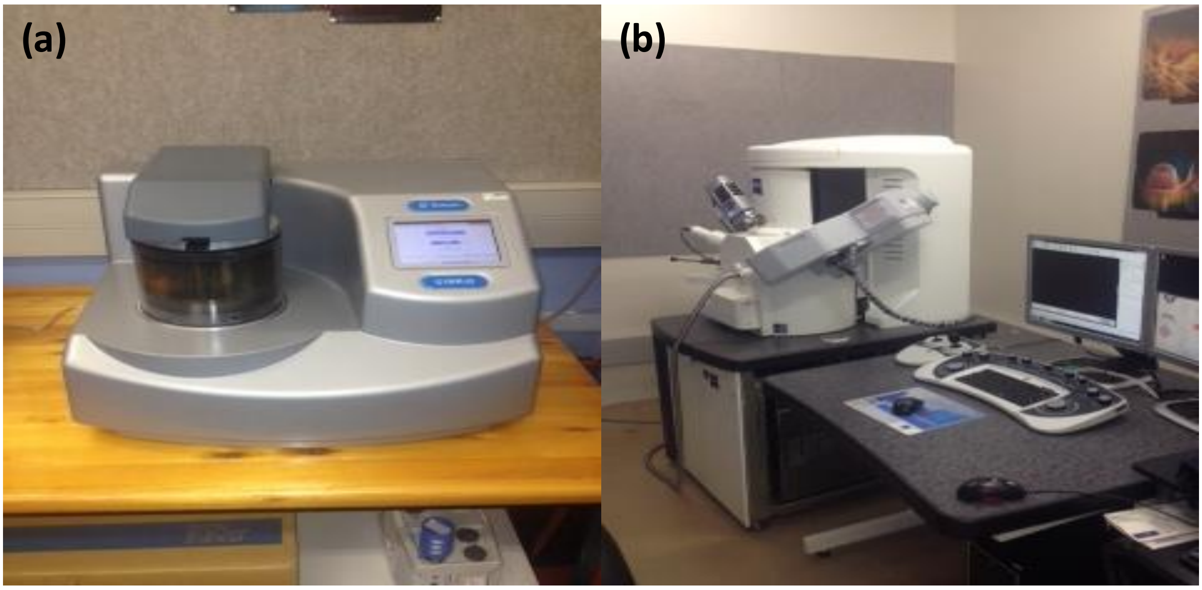


Figure 3. 4: The pictorial representative of (a) SEM gold sputter coating and (b) SEM instrument

The principle of SEM:

SEM operates at a high vacuum. A beam of electrons is generated by a tungsten filament. The electron beam is accelerated through a high voltage of 10kV and passed through a system of apertures and electromagnetic lenses to produce a thin beam of electrons, which will scan the surface of the specimen by means of scan coils. Electrons are then emitted from the specimen by the action of scanning beam and collected by a suitably positioned detector. This is where they get interpreted into images and displayed in a screen.

3.3.4 Dynamic mechanical analysis (DMA)

For studying the viscoelastic behaviour and mechanical properties of both the pure and modified membranes, a dynamic mechanical analysis (DMA) Q800 TA instrument was used. A sinusoidal stress was applied and the strain in the material was measured, allowing for determination of the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus. This approach was used to locate the glass transition temperature of the material, as well as to identify transitions corresponding to other molecular motions [117].

3.3.5 X-Ray diffraction

A Phillips PW 3710 was used to determine the crystallinity of both the modified membranes and the MIP or NIP powders. XRD is primarily used for determining the crystallinity, polymorphic form (“fingerprints”), to distinguish between amorphous and crystalline materials and also for quantification of the percent crystallinity of a sample.

The Phillips PW works with voltage and current settings of 40 kV and 40 mA respectively and uses Cu–Kα radiation (1.78901 Å). For qualitative analysis, XRD diffractograms were recorded in the interval $5° \leq 2\theta \leq 90°$ at a scan speed of 2°/min. The mean crystallite sizes “D” was determined according to the Scherrer equation ($D=0.9\lambda/\beta \cos \theta$, where λ is the X-ray wavelength (1.6208 Å), and θ is the diffraction angle).

3.3.5 Instrumentation: High Performance Liquid Chromatography (HPLC)

A high-performance liquid chromatography (HPLC) that consists of a Waters 600E pump, UV/Vis and florescence detectors was employed. Samples and standards were injected using a Rheodye7010 injector equipped with a 20 µl loop. Compounds were then separated using a Gemini C18 HPLC column (150 X 4.60 mm X 5 µm). Shimadzu LC Solutions software was used for recording of chromatograms.

3.4. The Adsorption Studies

The adsorption properties of the synthesised MIP/NIP (before incorporation) was evaluated first and then PVDF/MIP or PVDF/NIP membranes were also evaluated using the application of known concentration spiked deionised water and wastewater. The HPLC instrument used equipped with UV/Visible detector was employed for quantifying the recoveries of TCS. Three batches of different concentrations were prepared for TCS removal. The analysis concentration limits were 1.0 mg/L for TCS. A stock solution of 100ppm TCS was prepared in 1 litre of acetonitrile, where all other solutions used were drawn from. The pH values of solutions were adjusted by addition of formic acid and sodium hydroxide. The following adsorption experiments were carried out:

3.4.1 Removal of TCS using a MIP and NIP powder

Procedure 1: The effect of contact time: The effect of contact time was studied by shaking 50 mg of MIP or NIP for 30 minutes at 5 min interval with a 10-mL solution of 500 ppb of TCS.

Procedure 2: The effect of initial pH: The adsorption capabilities of the synthesised materials was studied at a pH range of 3 to 10. This experiment was operated at optimum contact time obtained from ***Procedure 1***. The effects of pH on adsorption were investigated at pH 3, 5, 7 and 10 using 10 mL solution of 500 ppb for TCS, with 50mg of powder MIP and NIP, respectively.

Procedure 3: The selectivity of the MIP was evaluated by the introduction of other compounds which naturally coexists with TCS in water bodies. This was done by preparing a mixed standard of TCS, ketoprofen, fenoprofen and gemfibrozil. The results were obtained using ***Procedure 2*** (optimized) conditions. This was done to study the binding cavities of the MIP towards the target molecule against the competing compounds.

Procedure 4: The suitable conditions to remove or adsorb TCS.

Equilibration time was determined at the optimum initial pH and initial concentrations obtained in procedure 2.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Introduction

The study was based on synthesis and application of PVDF micro-filtration and UF membranes. Following the successful synthesis of these membranes through phase inversion, the effect of adding MIPs and NIPs on the thermal stability and mechanical properties the polymer matrix was investigated. The physical stability of polymeric membranes can be improved by the addition of nanocomposite materials. These nanocomposite materials are most likely to improve the hydrophilicity and the strength of these membranes and this phenomenon has also been found to increase antifouling of the mixed-matrix membranes [118, 119]. The polymeric membranes were thus studied to understand the morphology, stability (thermal, mechanical properties), and flexibility of the bare membrane relative to the modified ones. The results obtained are discussed in the following subsections.

4.2. Characterisation studies of membranes.

4.2.1 Thermogravimetric analysis (TGA)

The thermal behaviour of the bare PVDF, PVDF/MIP and the PVDF/NIP-infused polymeric membranes is presented in Figure 4.1 (a), (b) and (c), respectively. The parent PVDF polymer was found to be a quite stable polymer with only about 25% weight loss at 510°C. The thermograms show weight loss associated with combustion of water and other volatile compounds before 100 °C since the membranes were oven dried at 70 °C before thermal analysis. Furthermore, the modification of PVDF with MIP (Figure 4.1 (b) and NIP (Figure 4.1 (c) was found to have even more benefits in terms of stability and physical reinforcement to the polymer network. The presence of the additives also played a huge role and influence in acting as morphology directors by stabilising a metastable or conventionally inaccessible polymer phase, or introducing new energy dissipation mechanisms [120]. Hence Figures 4.1 (b) and (c) revealed that the mixed-matrix membranes (PVDF/MIP and PVDF/NIP membranes) were less stable compared to the bare PVDF membrane (Figure 4.1 (a)). This could be attributed to the addition of particles which comprised of an added mass to be carried by the polymer, hence the polymer loses more weight. In Figure 4.1 (b) and Figure 4.1 (c), the only thermal degradation step observed takes place at about 495 °C and 498 °C, respectively and this is ascribed to the decomposition of the polymer chain. More so, the observed degradation event of pristine PVDF (Figure 4.1 (a)) membrane was agreeably reported by [86, 121]. It is essential to highlight that the bare PVDF membrane had a similar thermal behaviour, although it seemed as if it was slightly more stable compared to the modified polymeric membranes. This may be attributed due to the interaction of the polymer and the nanoparticles.

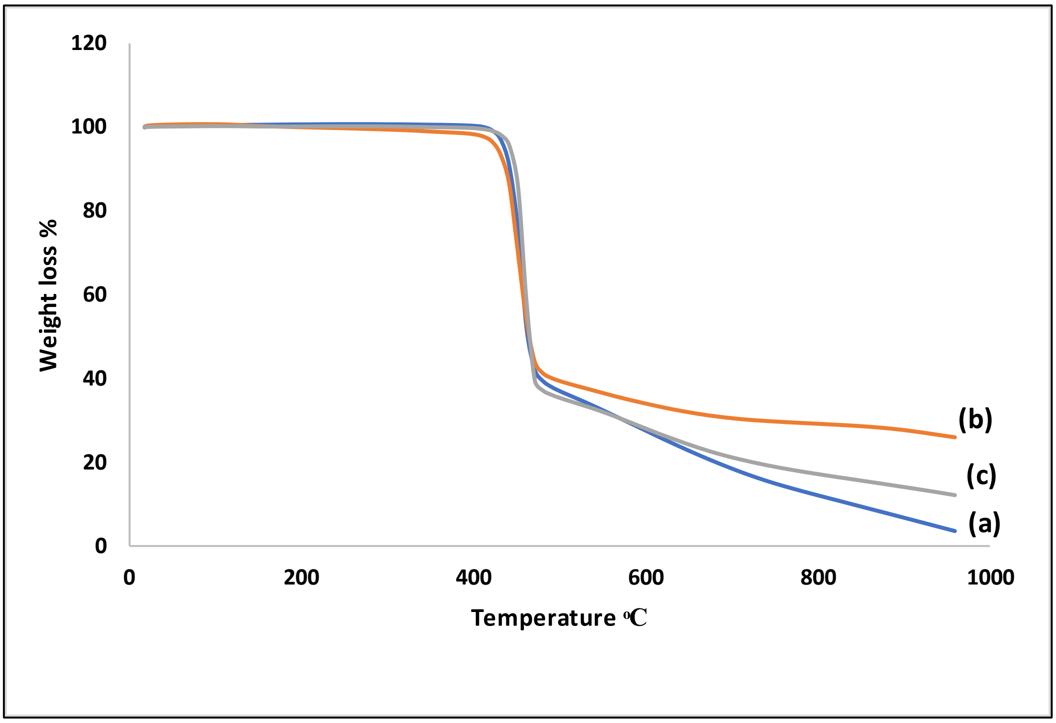


Figure 4. 1The weight loss % of (a) PVDF membrane (bare), (b) PVDF/MIP and (c) PVDF/NIP membrane

Figure 4.2 represents the sample exposed to the instrument with the heat flow, hence the curves for pristine PVDF (a), PVDF/MIP (b) and PVDF/NIP (c) membranes were obtained. In addition, the employed technique (direct scanning calorimetry (DSC)) has very sensitive properties (very sensitive to any change in the sample or crucible) and requires very good thermal contact with bottom of sample crucible [122]. As shown in

Figure 4.2, graph (c) had more sample exposed to the crucible (9.25 mg), followed by graph (b) (6.48 mg), and finally, (a), with only about 5.08 mg. It is important to make sure that the sample and reference crucibles are perfectly clean prior to tests and that heat capacity determination orientation of sample and reference crucibles are consistent between all replica tests. Making sure that the crucible material will not react or interfere with the sample material and vice versa. Brown [123] suggested that it is necessary to always build in an isothermal period prior to linear heating to allow the sample to reach equilibrium with the furnace conditions.

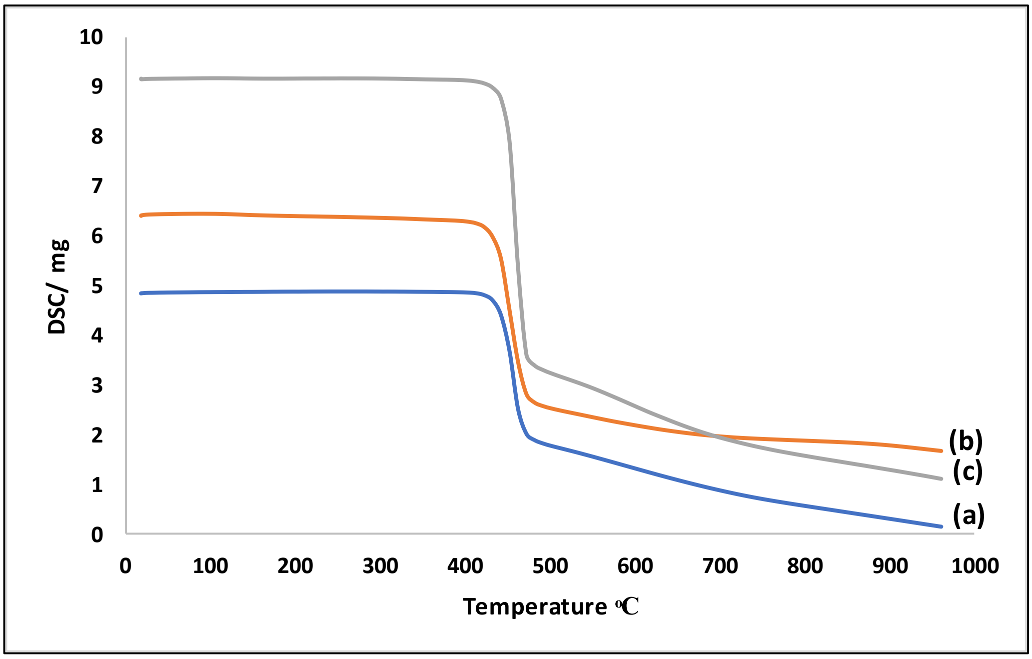


Figure 4. 2 The DSC curves showing the change in the sample with heat flow, (a) PVDF bare, (b) PVDF/MIP and (c) PVDF/NIP membrane

Table 4. 1 The tabulated decomposition temperatures of the polymeric membranes

Membrane type	Temperature/ ºC	Weight loss (%)
(a) PVDF membrane (bare)	510	25.49
(b) PVDF/MIP	495	58.49
(c) PVDF/NIP	498	62.57

**The values were obtained from the TGA analysis software

4.2.2 Attenuated total reflectance - Fourier transformed infrared (ATR-FTIR)

The qualitative characterization of functional groups on the surface of polymeric membrane samples was performed by the FTIR technique coupled with attenuated total reflectance (ATR). The results are illustrated in Figure 4.3 and they show that all the FTIR spectra possess common shapes with most of the bands located on the same wave number range but different intensities. The band at 3373 cm^{-1} can be assigned to C–H stretching and possibly traces of adsorbed water, if considering the intensity of the peak [124]. The bands at 2990 and 1393 cm^{-1} are said to be attributed to C–H stretch of the formed aliphatic carbon during the preparation of the casting solution, hence forming the asymmetric vibration of methyl groups or the bands maybe due to CH_2 of CH_3 deformation. The strong carbonyl (C=O) and around 1700 cm^{-1} in the imprinted membranes is assigned to the presence of MIPs in PVDF/MIP membranes (Fig 4.3 (c)). The band observed peak appearing at 1665 cm^{-1} corresponds to the formation of a weak C=C (alkene) and carboxyl or anhydride groups. This peak is not observed on Figure 4.3 (a) which represents PVDF pellets since the alkene is formed after dissolving the pellets in the NMP [125].

For the unmodified PVDF membrane (Figure 4.3 (d)), the absorption peaks of $-CF_2$ stretching and C=C stretching modes of PVDF were shown at 1170 and 1665cm^{-1}, respectively. The bands between 650 and 1100 cm^{-1} that appear to be significant in Figure 4.3 (b), (c) and (d) could be attributed due to the C—H out-of-plane deformation and this appear with dissimilar degrees of substitution [86]. As seen in Figures in 4.3 (b) and (c), there are no SiO_2 absorption peaks at 1100, 945, 790 and 470 cm^{-1} [126]; therefore the FTIR asserts that the infused additives (MIP and NIP) were well washed before being incorporated and were pure of any silicate interferences. Looking at Figure 4.3 and comparing between the unmodified PVDF membrane (Fig 4.3(d)) and two modified polymeric membranes (Fig 4.3 (b) & (c)), the six new absorption peaks (875, 1030, 1050, 1150, 1590 and 1650 cm^{-1}) were shown in the FTIR spectra of the modified PVDF membranes. The new peaks were the typical peaks of the polymer additives (MIP and NIP). These newly observed peaks may be from all the raw material used to synthesise these additives during bulk polymerisation process. Furthermore, these results confirm that, there was an MIP (Fig 4.3 (b)) and a NIP (Fig 4.3 (c)) coated on the PVDF membrane scaffold or surface.

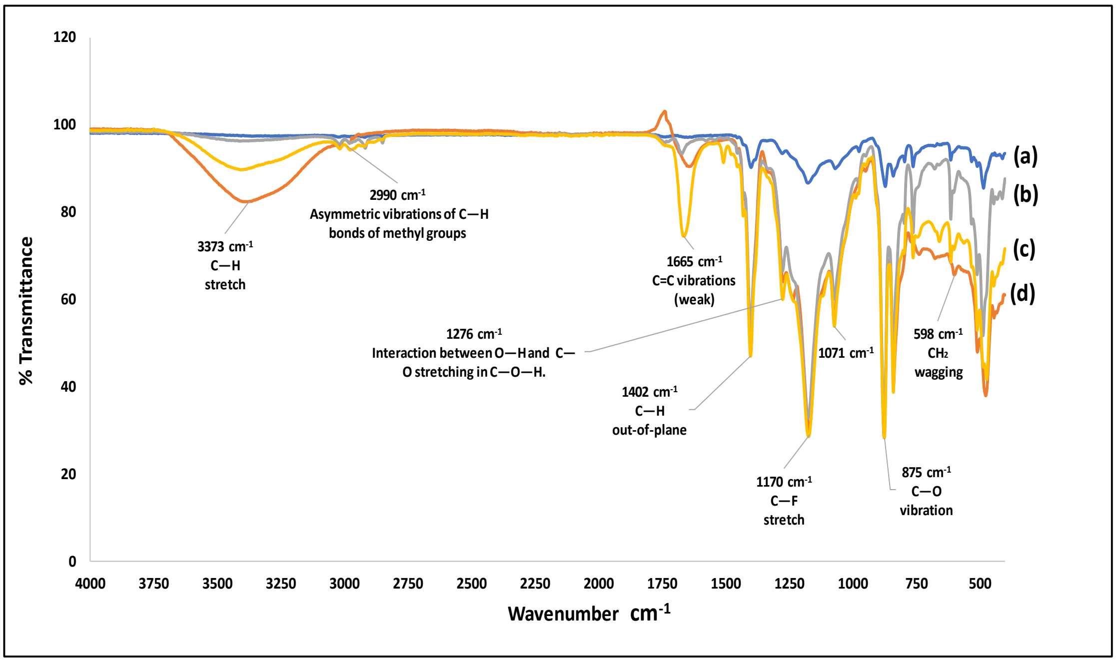


Figure 4. 3 The FTIR spectrum of (a) PVDF pellets, (b) PVDF/NIP, (c) PVDF/MIP and (d) PVDF membrane (bare)

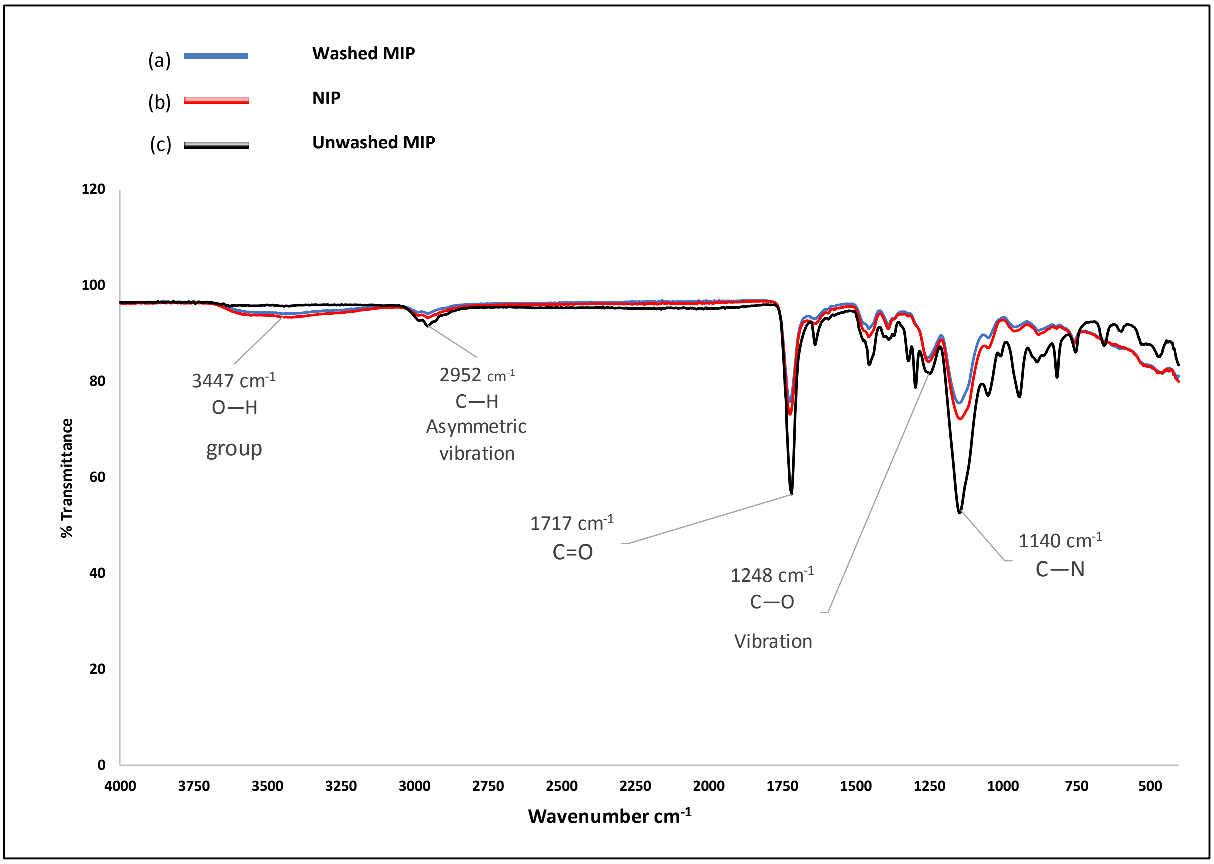


Figure 4. 4 The spectra of: (a) washed MIP and (b) washed NIP before incorporation and (c) unwashed MIP

Table 4. 2 The spectra of all functional groups and vibration modes

PVDF Pellets	**PVDF membrane**	**PVDF/MIP Membrane**	**PVDF/NIP membrane**	**Functional groups and vibrational mode**
602 cm^{-1}	620 cm^{-1}	598 cm^{-1}	598 cm^{-1}	CH$_2$ wagging
-	655 cm^{-1}	654 cm^{-1}	650 cm^{-1}	The C=O ring bending
-	682 cm^{-1}	-	680 cm^{-1}	Alkenes C–H out-of-plane vibrations between 650 and 1000 cm^{-1}
769 cm^{-1}	769 cm^{-1}	780 cm^{-1}	785 cm^{-1}	CH$_2$ out-of-plane
BENDING				
860 cm^{-1}	860 cm^{-1}	-	859 cm^{-1}	CH$_2$ rocking
-	860 cm^{-1}	875 cm^{-1}	870 cm^{-1}	C–O vibration (strong)
-	-	850 cm^{-1}	855 cm^{-1}	C–H out-of-plane deformation
932 cm^{-1}	932 cm^{-1}	1050 cm^{-1}	932 cm^{-1}	C–C backbone vibration (weak) stretching
1040 cm^{-1}	1040 cm^{-1}	-	1037 cm^{-1}	
-	-	1145 cm^{-1}	1145 cm^{-1}	C–N stretch
-	-	-	1037 cm^{-1},1225 cm^{-1}	C–O vibration stretching
1230 cm^{-1}	-	1234 cm^{-1}	1230 cm^{-1}	C–F out-of-plane deformation
1219 cm^{-1}	1170 cm^{-1}	1180 cm^{-1}	1180 cm^{-1}	C–F stretch
-	-	1280 cm^{-1}	1276 cm^{-1}	Interaction of O–H and C–O stretching in C–O–H
BENDING, STRETCHING				
-	-	1470 cm^{-1}	1443 cm^{-1}	C=C vibration, stretching,
-	-	1488 cm^{-1}	1500 cm^{-1}	CH$_2$ (C–H bond) vibration, bending
1470 cm^{-1}	1477 cm^{-1}	1402 cm^{-1}	1546 cm^{-1}	C–H out-of-plane deformation
-	-	1680 cm^{-1}	1665 cm^{-1}	C=C vibrations (weak) and unknown vibrations from fingerprinting
3240 cm^{-1}	3240 cm^{-1}	2990 cm^{-1}	2882 cm^{-1} 2948 cm^{-1}	Asymmetric vibrations of C–H bonds of methyl groups
-	3373 cm^{-1}	3370 cm^{-1}	3368 cm^{-1}	C–H stretching

Figure 4.4 (a & b), shows the FTIR-ATR spectra of the MIP and NIP, respectively. The spectra displays a similar range of peaks for the washed MIP and NIP since the template have been removed from MIP using methanol: acetic acid (9:1, v/v) [100], hence they possess the same backbone material structure. Figure 4.4 (c) further shows the interface between the functional monomer and the template (TCS). This information on the interactions between the organic pollutants (template) and the MIPs in the graph can also be observed by the presence of more absorption peaks from the infrared spectroscopy (c) compared to (a) and (b) of Figure 4.4. The FTIR spectra of the synthesized membranes, including PVDF/NIP membranes, are shown in Figure 4.4 (c). The peak at 1236 cm^{-1} is assigned to C—F stretching, and this is a typical absorption peak associated with PVDF [61]. A comparison of shifts between the MIP and NIPs showed that the C—F stretching peak at 1170 cm^{-1} slightly changed its position after loading MIP into the PVDF. Furthermore, the infrared bands associated with MIP also maintained their shifts in the imprinted membranes. This observation suggests that there were no chemical interactions between the MIP and the scaffolding polymer. It was demonstrated from the FTIR data as that the PVDF was a good support as it did not disrupt the chemical integrity of the MIPs [102].

FTIR analysis was used to study the interactions between the MIP and PVDF chemical nature. From Figure 4.4 (a) (washed MIP), a slight shift of the carbonyl group was observed after the MIP was incorporated in PVDF. This shift is also clearly visible in Figure 4.3 (d). This could be evidence of the involvement of the carbonyl group (which forms part of the MIP backbone) in MIP-PVDF interactions. It was interesting to note that the $–CF_2$ — IR band did not shift after permeation, which again could suggest there are no chemical interactions between PVDF and the additives studied, this has been shown by other researchers [59, 102]. The FTIR spectrum of (washed NIP), Figure 4.4 (b) suggested that the $–CF_2$ — does not partake in binding to the scaffold, as it did not change after perm selective studies. In addition, it is very essential to highlight the slight difference in intensities of Figure 4.4 (a) and (b), where a washed MIP displays low intensities relative to NIP, and this could be attributed to the number of times the MIP (Figure 4.4 (a)) was washed, hence losing some structural integrity.

4.2.3 Scanning electron microscopy (SEM)

Scanning electron microscopy analysis was used to study the surface morphology of membranes after the incorporation of MIPs and NIPs, and further evaluate the pore size of the imprinted and non-imprinted PVDF polymeric membranes. The SEM micrographs in Figure 4.5(d) and (e) revealed that the particles were successfully distributed on the surfaces of the polymer. Hence, there is no observable surface defect on Figure 4.5(d) and (e). Figure 4.5(c) displays a micrograph with visible pores on the surface. This is due to the polymeric MIP (Figure 4.5(d)) and NIP (Figure 4.5(e)) aggregates or particles, which are randomly dispersed across the PVDF scaffold. The dispersed particles of MIP and NIP are not observed from the micrographs, which also shows that the MIPs and NIPs are well embedded with the scaffold PVDF, which is an indication of good blending during casting. In contrast, these pore channels are less prevalent relative to the modified PVDF membranes, PVDF/MIP and PVDF/NIP, and this is caused by the distribution of these nanocomposite particles on the surface of the polymeric membranes. During the phase inversion process, the prepared membranes are typically characterised by the phenomena or the appearance of pore channels [96, 99]. More so, the pores also appear on the surfaces of the modified membranes with Figure 4.5(d), PVDF/MIP showing a dense and well-defined porous sublayer. Strathmann, Kock [96] previously discovered that functionalised polymeric membranes are asymmetrical in nature. It is clear that the phase inversion process can be controlled by controlling the rate at which the water penetrates the casting solution or by controlling the rate at which the casting solution solvent evaporates out [127].

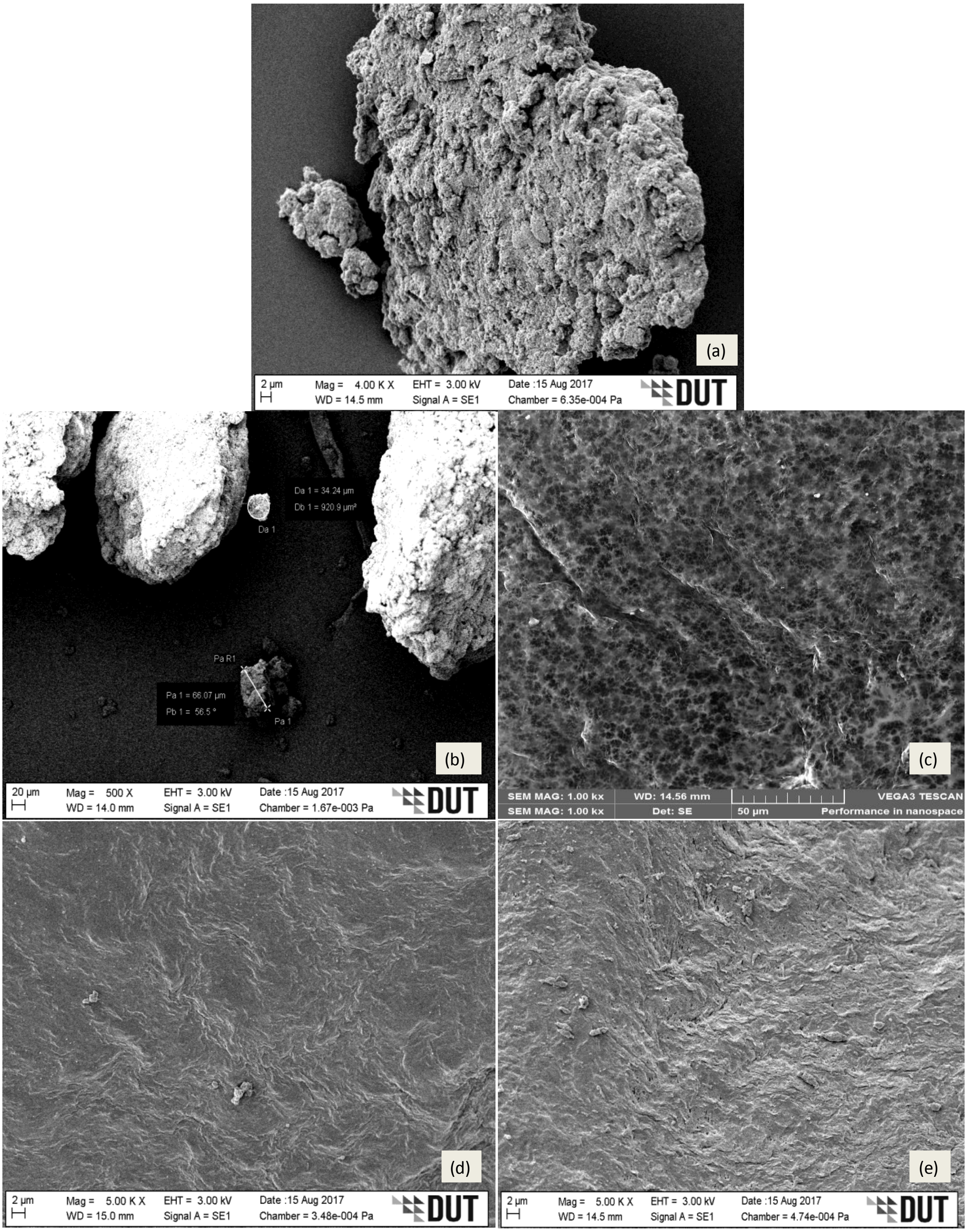


Figure 4. 5 SEM micrographs of (a) MIP polymer, (b) NIP polymer, (c) PVDF membrane (bare), (d) PVDF/MIP and (e) PVDF/NIP membrane

Furthermore, during the process of phase inversion, a phenomena of solvent exchange between the coagulation bath and the NMP in the casting solution occurs [128]. Moreover, the evaporation of solvent in the casting solution and the immersion precipitation of polymer results into the formation of voids, which are likely to appear as pores in the SEM analysis.

The chemical makeup of the MIP and NIP are relatively the same considering the similar process in synthesising, however, the structure of the MIP represented by Figure 4.5 (a) is rougher and irregular on the surface compared to that of the NIP (Figure 4.5 (b)) which have more regular and fine surfaces. This could be attributed to the binding capabilities that the polymer has. This is important as it is expected to create the porous channels for the permeation of TCS through the membrane once these MIPs are infused into the membranes’ backbone (Figure 4.5 (d)). Hence, that is why the MIPs were additionally characterized by SEM surface analysis and served as the basis to determine the degree of hybridization between the PVDF and MIPs. Lastly, the pore channels increased when the MIP polymer was infused (Figure 4.5 (d)), and this further highlights the role played by MIPs in the formation of pore channels. It is evident that the use of MIPs in membrane synthesis is likely to favour the formation of pore channels, which is desirable for enriching TCS in water. This was also observed with NIP infusion (Figure 4.5 (e)), but the only contrast with the infusion of MIP is that NIPs channels will not be a ‘lock and key’ since the NIP does not have selective binding sites on their makeup.

4.2.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) technique was employed for studying the viscoelastic behaviour of both bare and modified membranes. A sinusoidal stress is applied and the strain in the material is measured, allowing for determination of the complex loss modulus. The temperature of the polymer or the frequency of the stress are often varied, leading to variations in the complex modulus. This approach was used to locate the glass transition temperature of the material, as well as to identify transitions corresponding to other molecular motions.

The mechanical behaviour such as the stiffness and loss modulus of the bare PVDF membrane and the one decorated with MIP and (or) NIP were studied. Loss modulus measures the resistance of a material to elastic (recoverable) deformation under load. With regards to Yang, Zhang [129], the modification of PVDF membranes with inorganic or organic addictive tends to have an observable effect on the polymeric membrane.

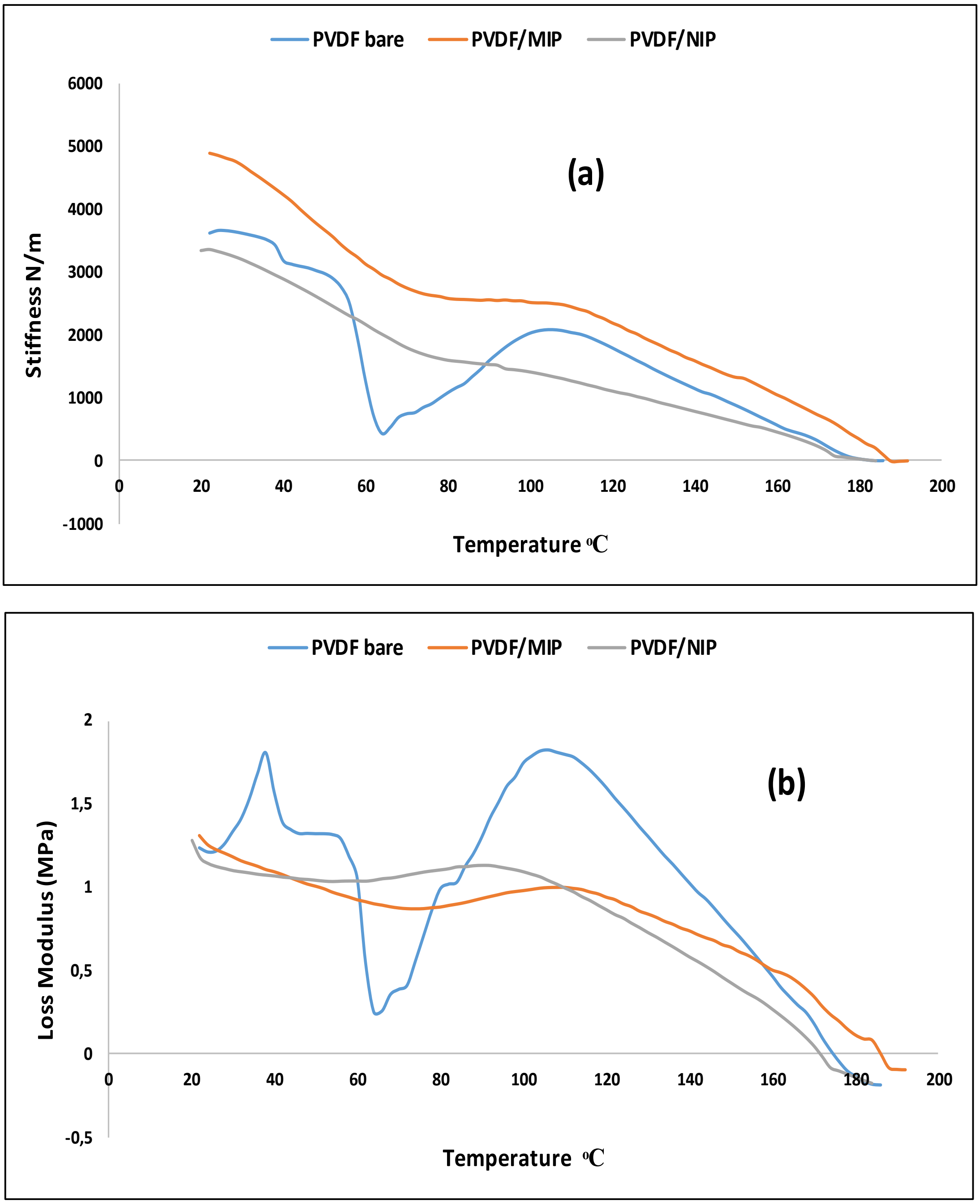


Figure 4. 6: The graphs comparing the (a) Stiffness of PVDF bare and modified membranes and (b) Loss modulus of PVDF bare and modified membranes

Figure 4.6 (a), displays a net dissimilarity and distinction in the stiffness properties between the PVDF membrane and PVDF/MIP polymer. For example, the addition of an MIP as a modifier to the PVDF membrane scaffold gave rise in the polymer stiffness properties from 3636 to 4889 N/m. This change in the stiffness properties of PVDF/MIP polymeric membrane could be attributed to the carbonyl bond energy, after the introduction of heat energy as the polymer is heated it tends to become more energetic and the polymer becomes more stable [130].

Equally important, loss modulus being the stretching and relaxing of the polymer in a presence of the load, the graphical presentation of the loss modulus (Figure 4.6(b)) accompanied with an observable change between the PVDF and PVDF/MIP or NIP polymeric membrane. As seen by the degradation curve, the bare PVDF membrane performs a common degradation for both the stiffness and loss modulus portrays, this is caused by the C—F bond when it burns at 64 °C [131]. In contrast, the addition of additives to the PVDF scaffold tends to improve the stability of the material, as no degradation was visible at 64 °C when the polymeric membrane was modified. Upon heating, the loss modulus decreased because less force is required for deformation [132]. In the region of the glass transition, it is estimated that molecular segmental motions described as molecular friction that dissipates much of the force are activated. Therefore, though the material is less stiff/hard, more force is dissipated as heat thus increasing the loss modulus.

4.2.5 X-Ray Diffraction

According to Bragg’s law of diffraction, no peak is observed unless the condition for constructive interference ($\delta = n\lambda$, with n, an integer) is precisely met, which further describes the condition on θ for the constructive interference to be at its strongest [133, 134]. The diffractograms shown by Figure 4.7 are in agreement with Bragg’s law. Hence, after XRD analyses of the membranes were performed. Figure 4.7 shows the XRD patterns of PVDF membranes with and without additives (MIP/NIP). Pristine PVDF membranes showed a familiar tendency to crystallize in four different polymorphs α, β, γ and δ, and each crystal structure displayed various polymorphs [135]. The diffraction peaks at $2\theta = 21.8°$ and 23.6° assigned to α (010) and α (110), respectively, were the characteristic of the α-phase crystal structure [135]. This was attributed to that the pristine PVDF membrane contained mainly α-crystal. After the addition of MIP or NIP, the diffractograms indicated one peak at 2θ = 28.2° that have disappeared, which was assigned to β (110). This phenomenon may be caused by the interactions between polymers. After incorporating 0.5 wt.% of the additive (MIP or NIP) into the scaffold PVDF matrix, no characteristic MIP or NIP peaks were observed in the patterns. This indicates that the hybrid membrane matrix has completely accommodated the additive micro particles without affecting much of their crystal form.

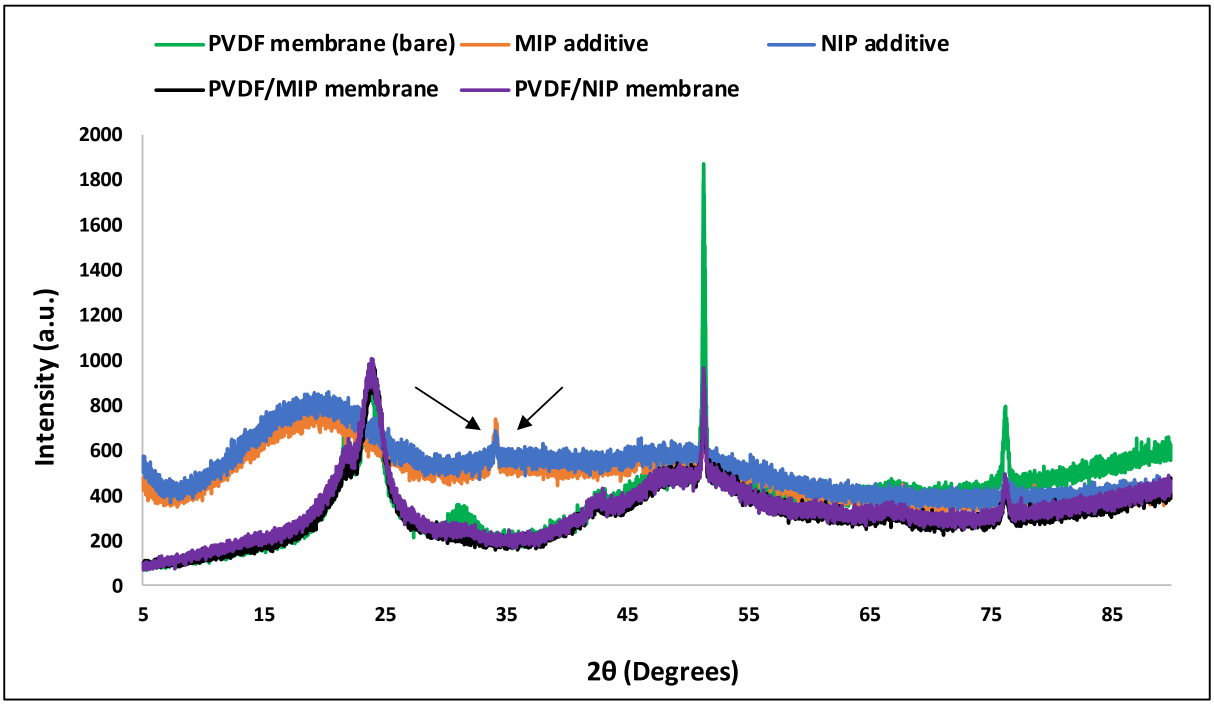


Figure 4. 7 XRD patterns of PVDF, PVDF–MIP/NIP membranes and the used additives

More so, the peak intensities of additives that appear (indicated with arrows) were reduced after the distribution of additives on the polymer matrix (PVDF/MIP or PVDF/NIP membrane). This reduction is due to decrease in PVDF transparency, which is caused by the micro-particle aggregation. In addition, the electronic field in the additive changed and led to a change in the relative intensity of the modified polymeric membranes. If PVDF and additives have low compatibility, each material would have their own crystal regions in the blend membranes, hence, this was also shown by the fact that the samples essentially maintain their crystal configuration throughout modification [136].

In particular, the strongest diffraction peaks at 2θ = 21.7°, 23.6° and 51.3°, occurred in all modified membranes, which indicated the maximum percent of *β* PVDF crystallinity. Thus, the bulk polymerized additives slightly changed the PVDF crystal formation during the phase inversion process, from the *α* -crystal structure to the *β* one.

4.3. Adsorption studies on MIP and NIP

4.3.1 Quantification of TCS with HPLC using MIP and NIPs

In the past decades, HPLC have been recognised to be the most competent technique to be utilised in the determination of pollutants in water [137]. High performance liquid chromatography was utilised to find the recoveries or percentage removal (extraction efficiency), limit of detection and limits of quantification. A high-performance liquid chromatography (HPLC) that consists of a Waters 600E pump, UV/Vis and florescence detectors was employed. The samples and standards were injected using a syringe 7010 injector equipped with a 20 μl loop and the compounds were separated using a Gemini C_{18} HPLC column (150 x 4.60 mm x 5 μm). A Shimadzu LC solutions software was used for recording of chromatograms and collection of data. UV/vis detector settings were 254 nm for TCS.

Table 4. 3 HPLC parameters used

HPLC Condition for TCS	
P_{max}	3000 psi
P_{min}	0
Column	Gemini 5µ C18 110A,length150x4.60 mm, ID 5µ
Mobile Phase	Acetonitrile/0.2% formic acid (80/20)
Detector Wavelength	UV-254nm
Flow rate	1.0 mL/min

4.3.1.1 Effect of pH on the adsorption of TCS

The pH value of the standards (500 ppb) is an important parameter and plays a vital role in the adsorption studies. Since pH can influence the dissociation status of target compounds as well as MIP, it was therefore necessary to study the effect of pH on adsorption. Figure 4.8 (a) and (b) shows the effect of pH on the adsorption of TCS by MIP in spiked deionized water. As shown in Figure 4.8, adsorption efficiency of TCS by MIP gave optimum efficiencies when the pH value of the solution was 2.50±0.02. This suggested that when the pH of the solution is approaching (or above) the pKa of the template (TCS) hydrophobic interaction and binding affinity between TCS and the selective binding sites play a predominant role in this pH range. Moreover, Figure 4.8 (b), representing NIP, show non-selective binding sites since there are no cavities that make up the polymer, hence, the adsorption is not stable. However, the maximum adsorption efficiency of TCS was observed at low pHs and it decreased significantly when the pH was between 7 and 10. This phenomenon could also be explained by the ionization of TCS. The pKa value of is 8.14 and thus its ionization would occur under strong acidic conditions [138].

As a result, the electrostatic repulsive interactions between TCS and MIP overcome the binding affinity and hydrophobic interactions became the main driving force during the adsorption at basic pH values hence the adsorption efficiency of TCS was reduced consistent with results obtained somewhere [19, 138]. Almost 60% TCS adsorbed onto the MIP at initial pH 10, which happens to be the lowest compared to the other evaluated pHs. This is an indication that the adsorption efficiency of TCS by MIP was mainly attributed to the electrostatic attraction and the contribution of hydrogen bonding mechanism.

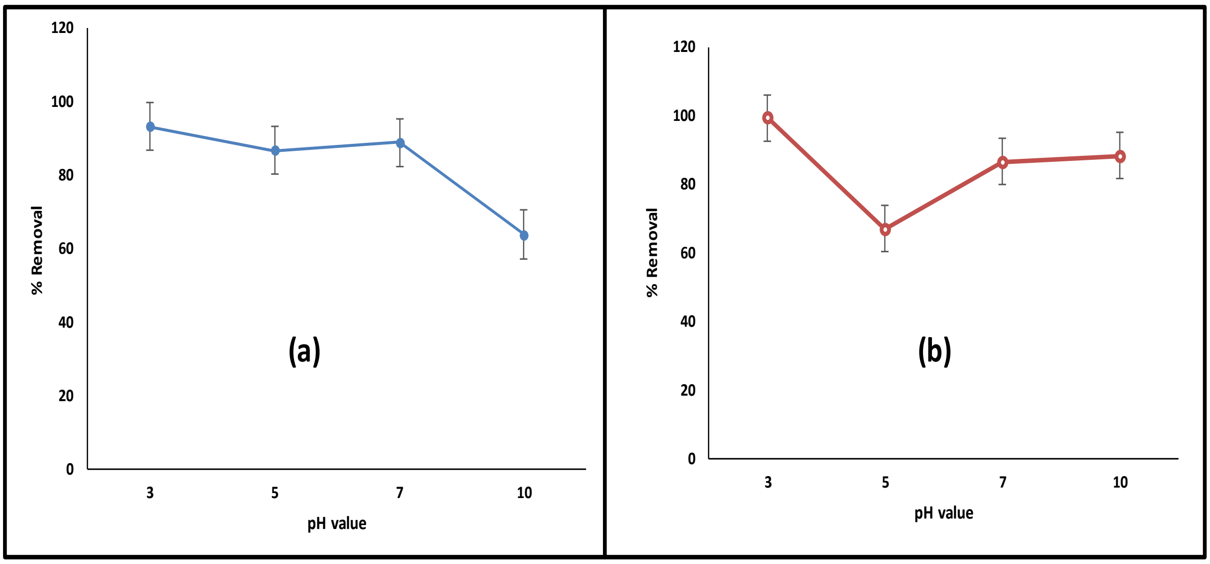


Figure 4.8: The percentage removal efficiency vs pH of: (a) MIP and (b) NIP

4.3.1.2 Effect of contact time on the adsorption of TCS

The results shown in Figure 4.9 (a) and (b), demonstrate that the MIP had higher molecular recognition selectivity to its template. The adsorption efficiency of NIP for TCS was lower than that of MIP, but their adsorption capacities for the structural analogs were close to each other. These results suggested that the imprinting method created a micro-environment based on the interaction of size, shape, and functionality to the template [139]. There was no proper cavities and recognition site formed in the NIP, so the NIP bind compounds only by non-specific adsorption [140]. As a result, the NIP adsorbed the template molecule much less compared to the MIP- If there are no binding cavities as in NIP, the compounds do not get ‘locked’ unto the sites of the polymer. Therefore, the high adsorption selectivity of MIP provides an effective method or technique to eliminate interferences of other competitive compounds with TCS and prevent other competing compounds from adsorbing.

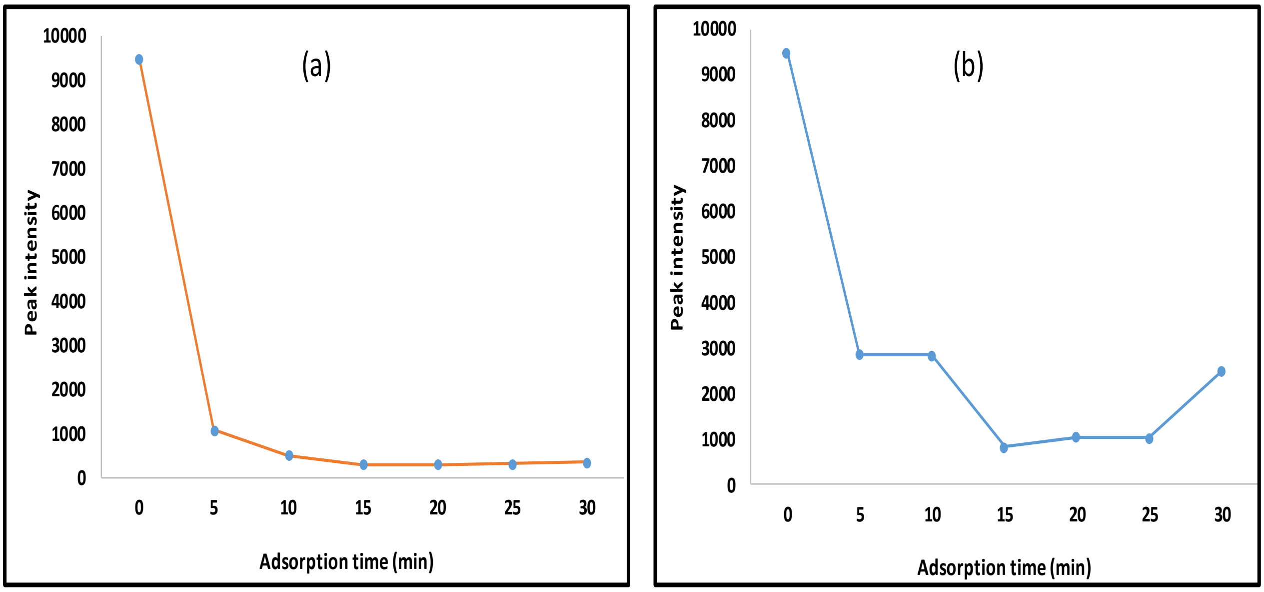


Figure 4. 9 The TCS peak intensity vs adsorption time: (a) MIP adsorption and (b) NIP adsorption

4.3.1.3 Regeneration or reuse of the MIP.

The MIP that had adsorbed TCS was washed with methanol/acetic acid (9:1, v:v), then 5 times with methanol, dried in vacuum, and reused in the next cycle of adsorption experiments. As shown in the Figure 4.10, the MIP can be regenerated after washing the selected template and retained its removal efficiency for utmost eleventh-time adsorption or sorption cycles. The demonstrated reusability of the MIP over several adsorption cycles is an advantage over conventional adsorbents and in the water treatment industry as a whole in terms of cost effectiveness.

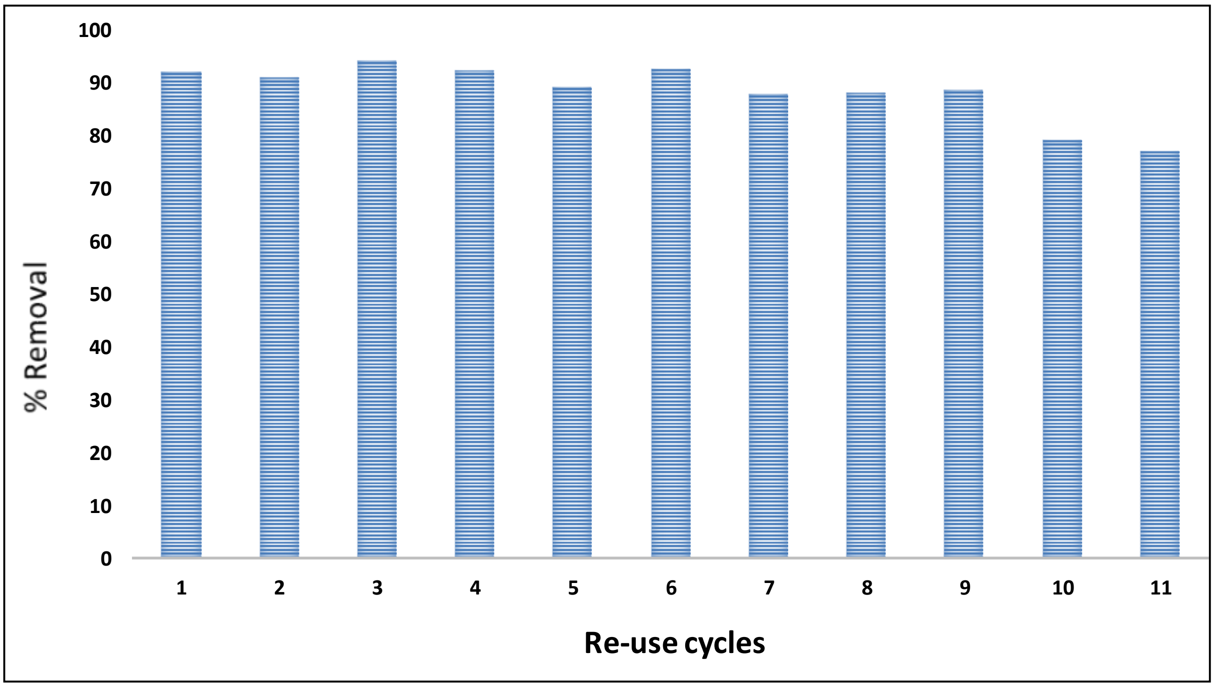


Figure 4. 10 MIP regeneration cycles in spiked deionised water

4.3.1.4 Selectivity of the MIP

The selectivity of MIP microspheres for TCS was estimated using three other pollutants (ketoprofen, fenoprofen and gemfibrozil) as interfering compounds. About 50 mg of MIP and NIP were each added to a 20-mL vial containing a 10-mL mixture of TCS, ketoprofen, fenoprofen and gemfibrozil at various concentrations (200-1000 ppb). After being shaken for 2 hours at room temperature, the samples were centrifuged and filtered. The TCS and interfering compound concentrations in the filtrate were quantified using HPLC. All the experiments were performed in triplicate. The target pollutant (TCS) and the other competing compounds are known usually to co-exist and between them, some are isomers.

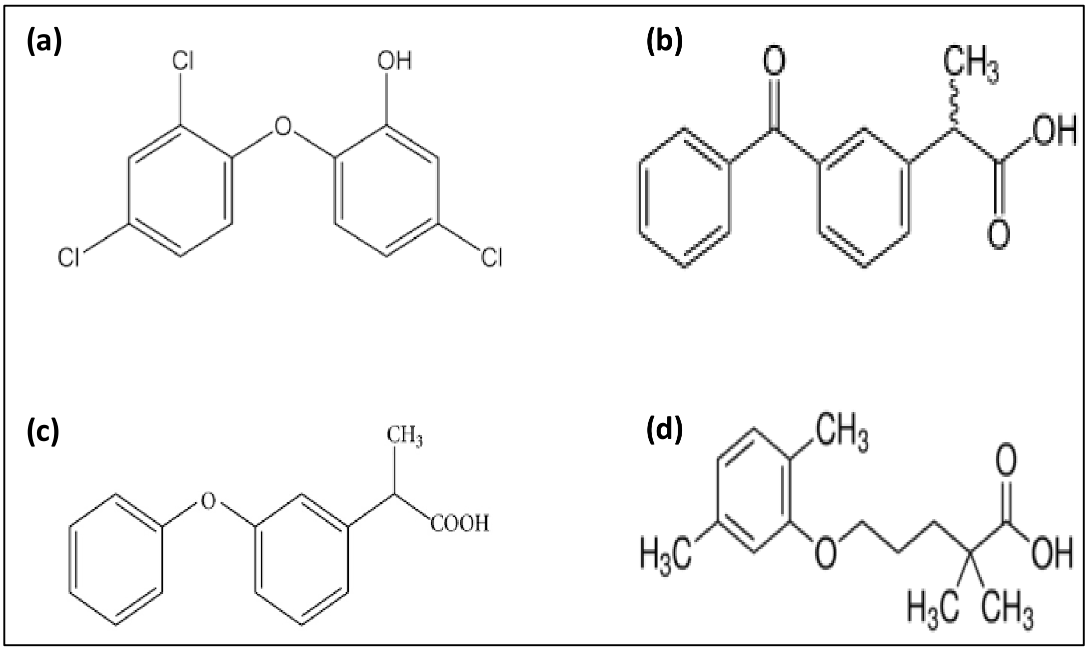


Figure 4.11: The structure of the target molecule (a) TCS and the competing compounds (b) ketoprofen, (c) fenoprofen and (d) gemfibrozil

Sorption selectivity: The binding selectivity of MIP for TCS was compared to that of ketoprofen, fenoprofen and gemfibrozil (Figure 4.12) because it widely coexists with most of these pollutants in water bodies. Our main objective was to apply the MIP to water remediation processes thus we evaluated the selectivity of MIP in different standard concentrations. As shown in Figure 4.13, the saturated binding capacity of NIP for TCS is lower than that of ketoprofen, fenoprofen and gemfibrozil. However, after being imprinted with TCS, the binding capacity of TCS on MIP is much higher than that of other pollutants (Ket, Fen, Gem) which suggests the presence of specific imprinting sites that favoured the adsorption of the target molecule and reduced the binding of the interfering compound. MIPs can recognize their template molecules due to the existence of memory cavities with fixed size, shape, binding sites and specific binding interactions between the target molecule and the sites. Ket, fen and gem cannot therefore bind as strongly as TCS because their sizes cannot match the cavities or its functional group position does not correspond to the functional groups in cavities and thus cannot bring about specific binding in the same way as TCS [105]. Moreover, the strength of the interaction between the target molecules and the binding sites also determines the selectivity of the MIP [49]. This finding is very beneficial for the treatment of large volumes of effluents.

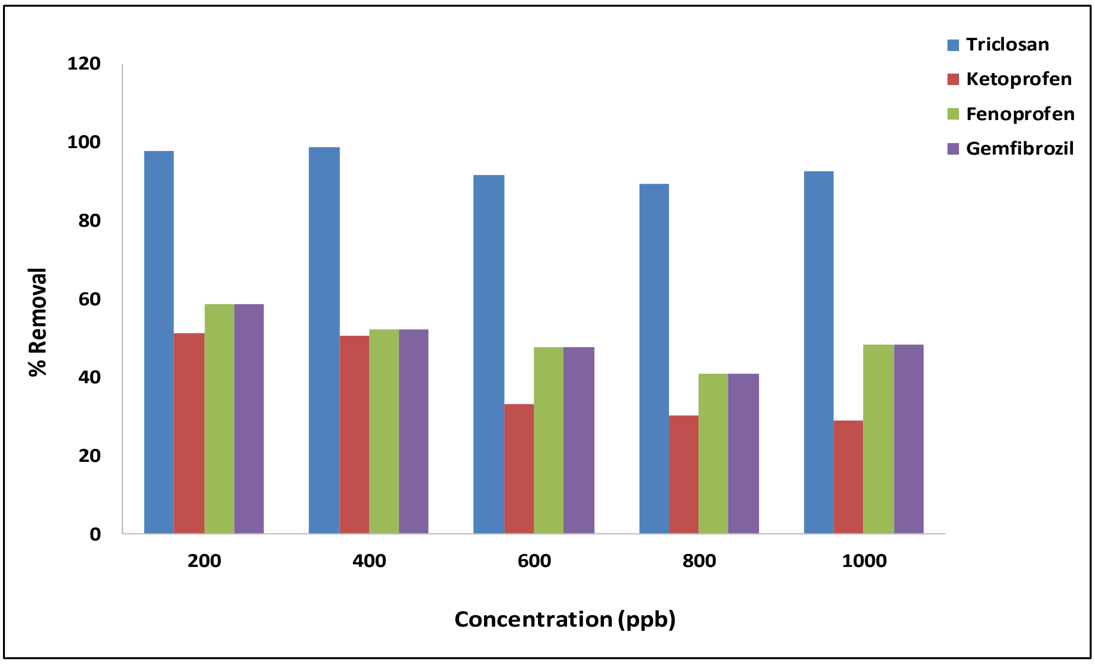


Figure 4.12: Removal efficiency of a MIP on different spiked deionised water

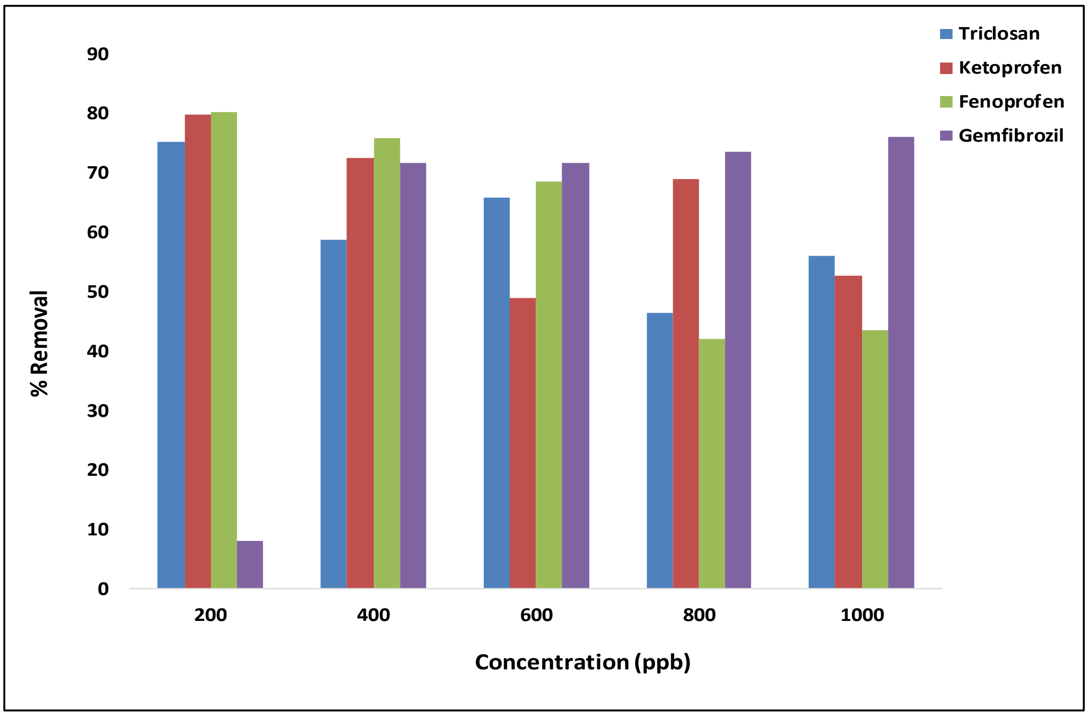


Figure 4. 13 Removal efficiency of NIP on different spiked deionised water

4.3.2 Enrichment studies of TCS on incorporated membranes

To evaluate the performance of the polymers (bulk polymerisation) and the synthesised polymeric membranes (phase inversion by immersion precipitation), binding experiments were carried out using water spiked samples enriched with TCS. The batch binding experiments were carried out by suspending 50 mg of MIP in 10 mL enriched water and PVDF/MIP membrane from 0.3 wt.%. The mixture was then allowed to reach adsorption equilibrium by shaking for 15-20 minutes at room temperature. The polymer and functionalised membranes were then removed through centrifugation, 3000 rpm for 15 min and filtering through a 0.22 µm syringe filter. This was directly pushed through an HPLC chromatographic separator and analysed. Figure 4.14 displays the different membrane types enriched with 500 ppb TCS spiked water, (1) PVDF/MIP, (2) PVDF/NIP and (3) pristine PVDF membrane.

The results obtained in Figure 4.14 confirmed the binding sites the MIP possesses for TCS, since it shows more percentage removal efficiency compared to the other membrane types. In addition, this was largely due to the interaction between the cavities of the MIP and the pH of the aqueous solution (pH 3.00). The MIP consists of a negatively charged functional monomer, with a substrate of N^- hence the pH of the spiked water will have to be adjusted with formic acid to lower the pH to cause attraction with the MIP cavities. Hence, the adsorption is maximised, and removal efficiency is enhanced.

The difference in percentage removal efficiencies are dependent on the pH and the additive used. The pristine PVDF membrane showed signs of adsorption though not as pronounced as the MIP and NIP infused membranes. This is as a result of the porous nature and pore channels present within the polymer membrane matrix [77].

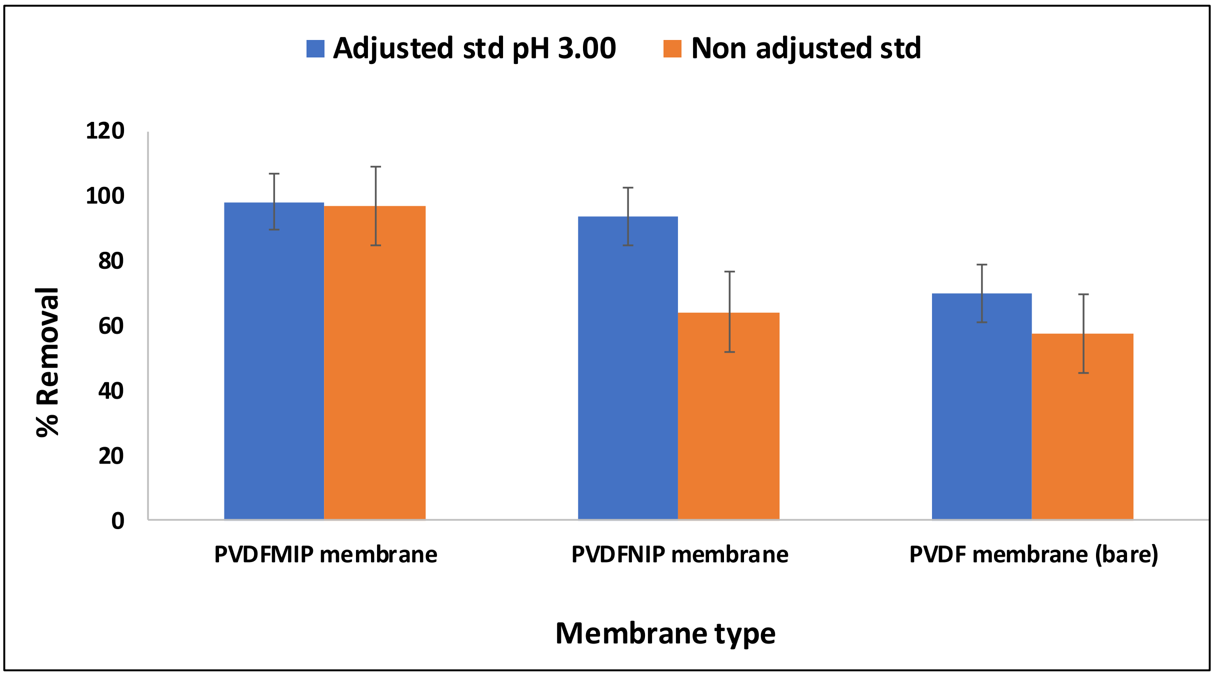


Figure 4. 14 The removal efficiency of TCS using different membrane types

4.3.3 Membrane and additives interaction

Polymer membranes incorporated with nanocomposite particles are often reported with increased hydrophilicity and improved antifouling behaviour [141]. The mechanically improved performances have been observed frequently in conventional composite materials and found to have great potential in increasing the robustness of MF and UF membranes. Given the wide varieties of micro particles that can be used in membrane technology and their abilities to enhance different properties, MIPs have found use in membrane science because of their unique properties of having a distinct integrity and selective binding sites within their material structure, hence they are referred as smart materials. Furthermore, as much as they are suitable micro-fillers and exploring how nanocomposites are developed for membranes, these MIPs could possibly improve the durability of low-pressure filtration membranes, increase water content and porosity percentage of the membrane. As the concentration or mass of the additives is increased in a polymer scaffold, both water content and porosity percentage are also increased resulting into a more hydrophilic polymer [142].

4.3.3.1 Water content and porosity percentage on functionalised membranes

Water content and porosity percentage are very vital to monitor when dealing with membranes since they determine the hydrophilic and hydrophobic nature of the synthesised polymeric membranes. These parameters were evaluated for the confirmation of increased hydrophilicity and porous properties of PVDF membrane. As expected, after the incorporation of the composite additives of MIP and NIP, these parameters increased and as the additives are added uniformly the water content also increased. From 0, 0.1, 0.2 and 0.3 % of MIP the water content of the PVDF/MIP increased from 69.06, 73.69, 73.98 and 74.09 %, respectively. The porosity also followed the trend. As seen in the bar graph in Figure 4.15, the membrane water content gradually increased due to the increasing MIP concentrations. This further expresses that a more hydrophilic membrane is produced as the MIP concentration is increased [110, 111]. This may be influenced by the hydrophilic characteristic of MIPs, as this modifier use the hydrogen bonding mechanism and said to have high chemical integrity because of variety of chemicals utilised during the bulk polymerisation. The existence of CF_2 on the PVDF polymeric membrane backbone with its electronegative nature highly influences the strong hydrophilic group on the MIP surface to cause more hydrophilic polymeric membrane after the functionalization or blending into the prepared casting solution [110]. Moreover, this phenomenon could result to an increase in cavities/voids size and numbers in the prepared polymeric membranes resulting to more space for water adsorption and accumulation, hence, water content and porosity increases on the membrane. These tests and similar trend was previously observed for sulfonated polyethersulfone (SPES) infused in PVDF membranes [143].

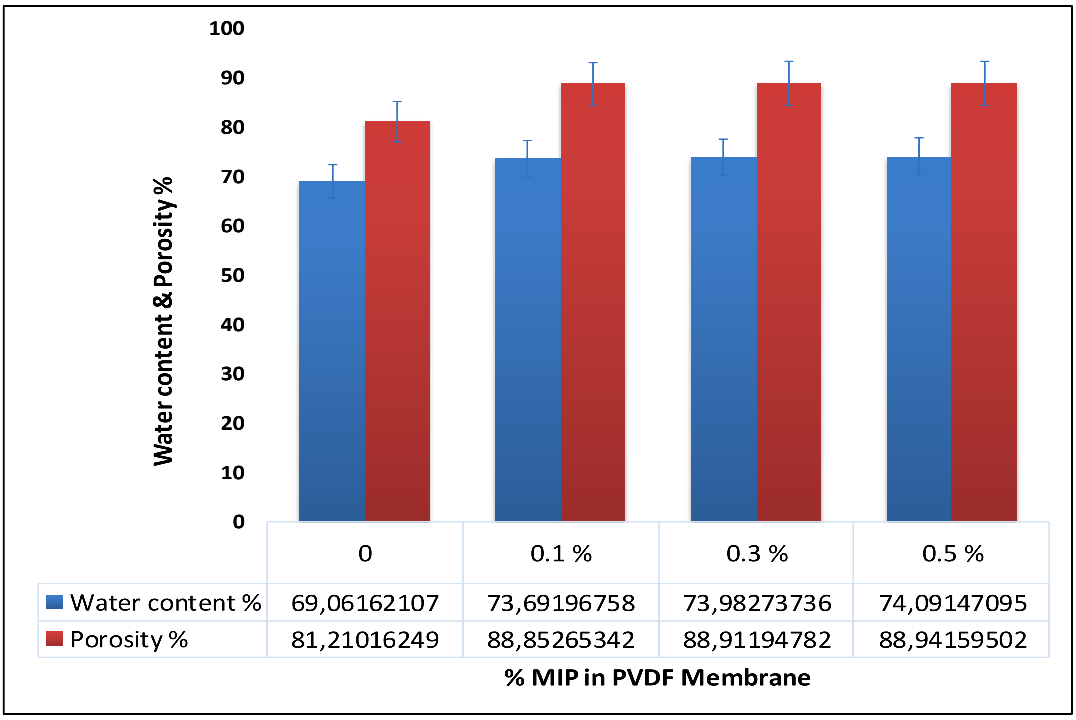


Figure 4. 15 The effects of polymer binder ratios in MIP concentration in PVDF membrane vs Water content and porosity %

Figure 4.16 shows the calculated porosity of prepared membranes against percentage NIP used to fabricate the membrane. The obtained results also revealed that infusing the NIP unto the PVDF membranes results in greater porosity in the membrane matrix compared to pristine PVDF membranes. The results are in agreement with the study previously conducted by Gardner [144].

The membranes infused with various percentages of MIP and NIP concentrations showed the formation of spherical macro-voids within their macrostructure. As can be seen, increasing the additives percentage in the casting solution gives rise to more porosity in membrane structure. Increase in porosity, macro-voids and spongy structure is as a result of increasing the hydrophilicity of the casting solution and its effect on the phase inversion occurrences [145].

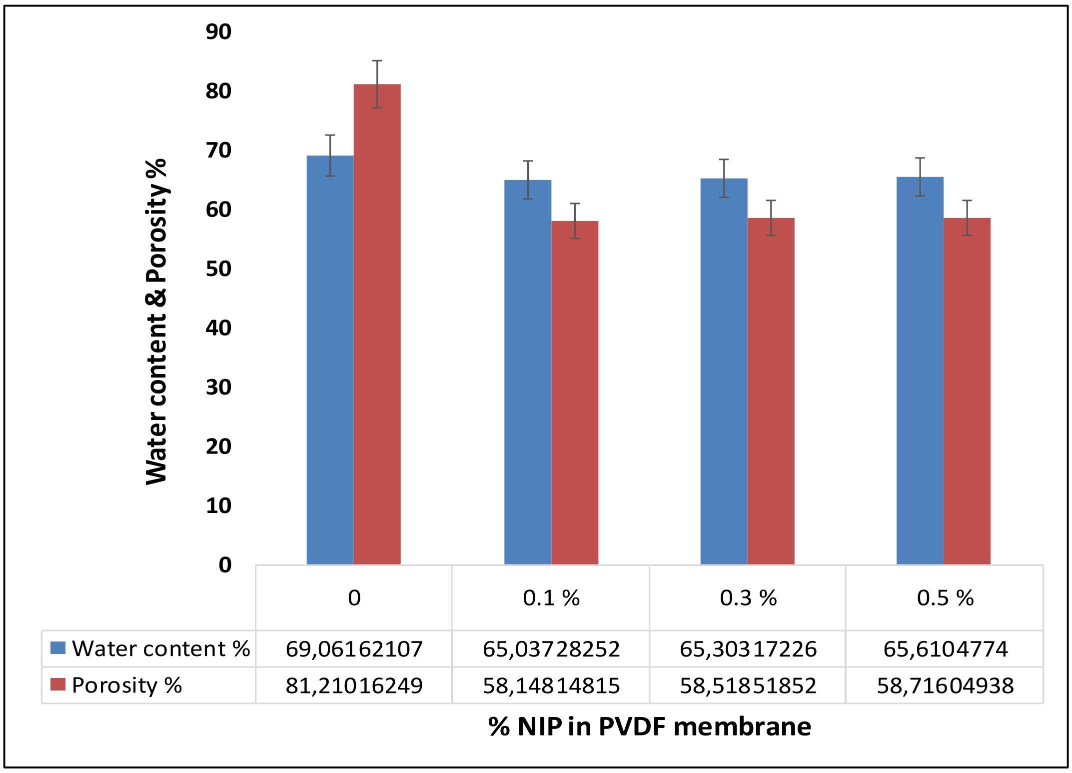


Figure 4. 16 The effects of polymer binder ratios in NIP concentration in PVDF membrane vs Water content and porosity %

4.4. Sampling and quantification

4.4.1 Short overview about the sampling site and geographical location

Acacia Operations Services (AOS): situated on the upper South Coast approximately 20km from Durban, the Umbogintwini Industrial Complex (UIC) is a secure, well-developed industrial park with a 100 years history. It consists of approximately 220 hectares of industrial land and 90 hectare of conservation area, comprising three nature reserves, Umbogavango, Vumbuka and Mamba Valley, which have been recognized as sites of conservation significance. This multi user site is home to many large recognised industries like Huntsman Tioxide, Evonik, Dulux, SA Bioproducts (Anchor Yeast), KK Animal Nutrition, and many subsidiaries of AECI.

Acacia Operations Services (where samples were collected) manages the site on behalf of its parent company, AECI, and provides several essential services, namely:

- Boiler station for superheated steam provision
- Water treatment works providing potable and industrial water.

- Electrical distribution via a 33-kVa electrical distribution network
- An organic and inorganic wastewater treatment plant, and a marine outfall for the disposal of the treated wastewater
- Sewage works
- Rail operations, weighbridge and a container gantry, storage and distribution facilities.
- A tank-farm
- Engineering workshops,
- Laboratory facilities
- Security

Land in the industrial envelope is still available for the development of factories that fit the strategic objectives of safety, health and environmental standards for the site. Figure 4.17 shows the sampling site (satellite view)

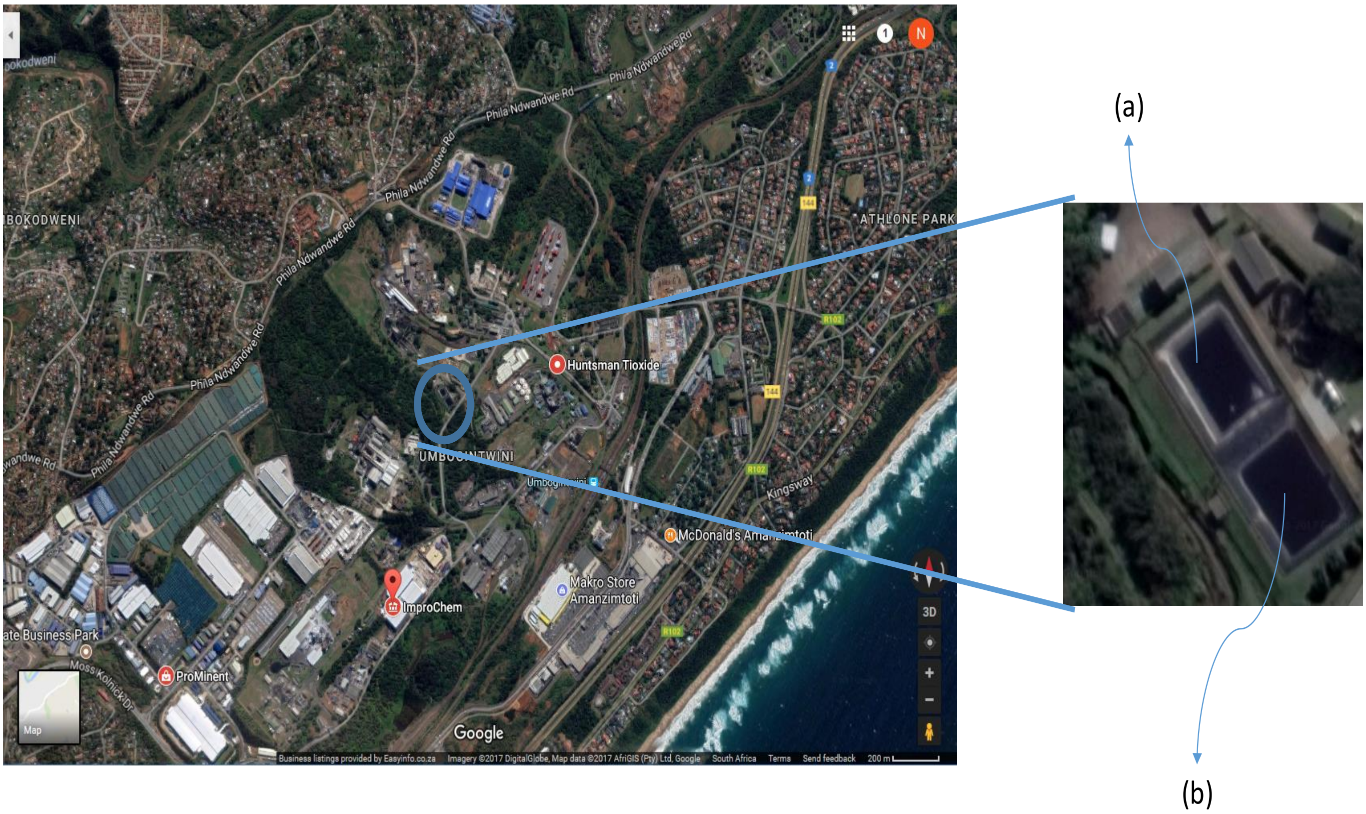


Figure 4. 17 The pictorial representative of the sampling site and ETP (satellite view): ETP plant (a) ETP process compartment and (b) ETP reservoir compartment

Acacia Operation Services are the proprietors of the complex and are subsequently the only industry licensed to dispose wastewater to the Kingsway Sea. Hence, all the other industries within UIC are required to push their wastewaters through the channel of effluent treatment plant (ETP). Figure 4.17 – (a) shows where the treatment takes place and (b), where the wastewater is ready to be released to the sea. Figure 4.18 represents the schematic channels for which the influents from companies use for their wastewater to be treated before carried over to the sea once they fall within the specifications placed by the Department of Water Affairs (DWA). Figure 4.19 displays the pictorial representative of the ETP dam where treated wastewater is stored, (Figure 4.17)-(a)). Acacia Operations Services have a structured wastewater testing laboratory in place to do the daily monitoring.

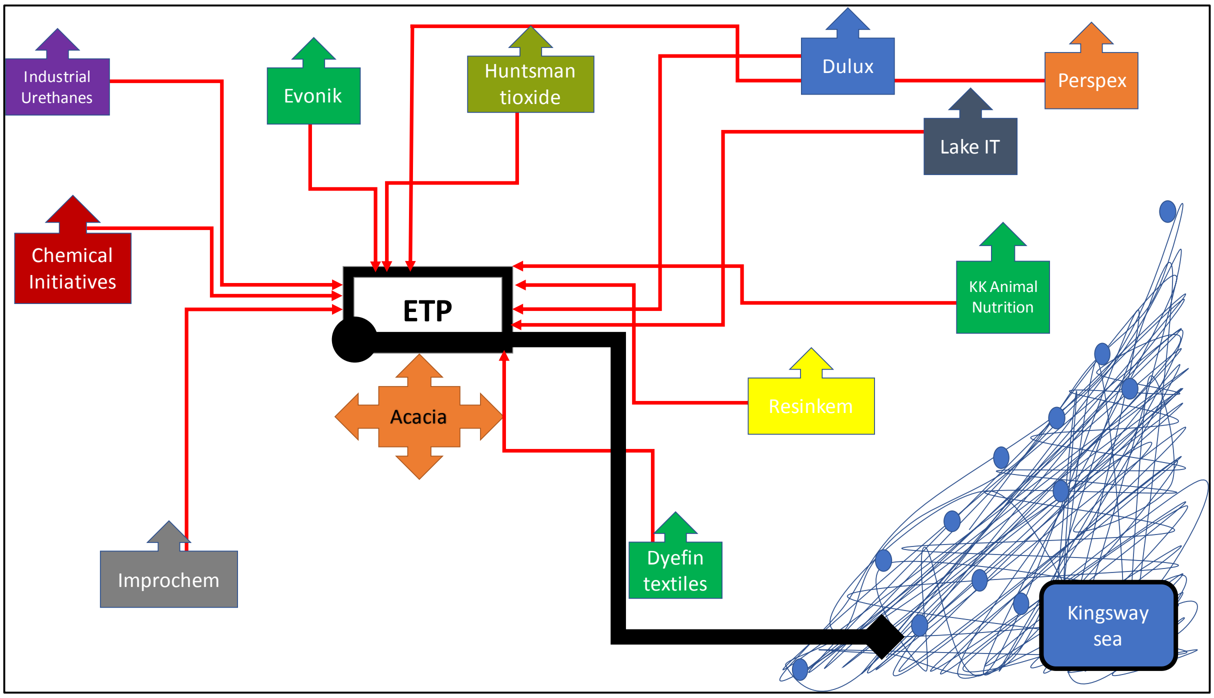


Figure 4. 18 The schematic diagram of the wastewater pipeline in the complex site

Figure 4. 19 The pictorial representative of wastewater ETP dam in UIC

4.4.2 Sampling and sample pre-treatment

In recent times, Acacia Operations Services laboratory have reported on unwanted variation of chemical oxygen demand (COD) during the daily monitoring of the ETP Dam, which signals a possible high organic material in the water body. This has raised concerns and continue to be a disturbing issue to be looked into. Hence, this study will play a vital role in investigating the possible traces of organic pollutants and further extract these organic pollutants (in this case, TCS) in the ETP dam. In this study, the change in organic pollutant was monitored in 10 successive days, from the 07th to the 17th of September 2017.

ETP samples were collected from Acacia Operations Services as composite samples, which denotes that each sample is a mixture of samples grabbed in three different intervals, that is, evening, midnight and morning. This is then mixed and called a composite ETP sample. Furthermore, ETP is a combination of all wastewater pipelines in the complex. The effluent lines are, namely: - Huntsman Tioxide, Evonik, Dulux, Chemical Initiatives, KK Animal Nutrition, Perspex, Industrial Urethanes, ImproChem, Lake International and many subsidiaries of AECI.

Effluent samples were collected from ETP for ten (10) operational working days and were labelled ETP Dam 1 – 10. These samples were collected in the month of September since this is primarily the busiest of the business in all industries based in the complex due to the coal and steam demand for the month of December break. Glass bottles were thoroughly cleaned with soap, deionized water, and rinsed few times with the real sample in sampling sites before taking the sample for analysis. Figure 4.20 shows the pictorial ETP dam samples before and after filtration:

Figure 4. 20 The pictorial representative of (a) ETP Dam samples from ETP sampling room, (b) ETP Dam samples transported to the lab, and (c) ETP Dam samples after filtration

4.4.2.1 Monitoring of physiochemical parameters

After collecting the samples, they were immediately taken to the testing lab for basic parameter tests, pH, conductivity, and suspended solids. The following day, the samples were filtered twice with 0.45 μm filter paper purchased from Millipore

(Darmstadt, Germany). The pH in each sample was adjusted to 3.0; thereafter, samples were stored in the refrigerator at 4 °C until further analysis was done. Physicochemical properties such as sample pH, conductivity, salinity, dissolved oxygen and total dissolved solids (on site) were measured using a calibrated Bante900P multi-parameter water quality meter that was purchased from Bante instruments (Shanghai, China). The calibration of the multi-parameter water quality meter was performed using the pH calibration buffers (pH 4, 7 and 10) and conductivity calibration solutions (84, 1413, and 12.88 mS/cm) that were provided by the Acacia laboratory.

Table 4.4: Physicochemical parameters of grabbed ETP Dam samples

ETP Dam sample	**Parameters**					
	pH	**Conductivity (mS/m)**	**Suspended solids (%, m/m)**	**TDS (mg/L)**	**Salinity (psu)**	**Dissolved Oxygen (%, m/m)**
Day 1	8.09	695	410	603	3.94	1.90
Day 2	8.06	744	340	605	3.77	0.38
Day 3	8.12	586	160	598	4.88	0.13
Day 4	7.67	418	112	515	4.13	0.45
Day 5	7.82	482	106	495	3.08	0.65
Day 6	7.54	733	290	674	2.88	0.38
Day 7	7.93	738	80	599	5.18	0.69
Day 8	7.96	1158	82	697	5.08	0.13
Day 9	7.66	1400	120	710	4.93	0.27
Day 10	8.09	835	204	605	3.88	0.22

******Suspended solids (%, m/m) results were obtained from the ETP testing laboratory

4.4.2.2 Physicochemical parameters of collected samples

Results for the physicochemical analysis are displayed in Table 4.4. Salinity was measured as practical salinity unit (psu) and it further gives an indication on the concentration of the dissolved salts in ETP wastewater. This expressed that most of the samples contained small amounts of soluble inorganic salts (however, this means there are negligible interferences on the proposed analytical method).The elevated concentration of salinity in water is known as water with large quantities of soluble inorganic salts and organic compounds [146]. The conductivity ranges of samples on the ten monitored days were along the same scale and still lied on the specifications placed by DWAF for wastewater effluents which is ≤ 3500, the highest conductivity being observed on Day 9, 1400 mS/m. Most of suspended solids were quite higher than the specification values of ≤ 150 and they were reported as fail. The only accepted values were 112, 106, 80, 82 and 120 % on monitored Day 4,5,7,8 and 9, respectively. From the testing laboratory, they informed us that this is under investigation since it has been failing from May 2017 and promised to give us an update as soon as the outcome is reported. On the other hand, a decent amount of TDS effluent was observed if you compare with the previously done studies. The results of this study were much lower than those reported in other studies, reporting the highest of 710 mg/L on Day 9, whereas Anderson, Joudan [147] reported a minimum of 981 mg/L for TDS in one wastewater treatment plant based in Canada.

4.4.3 Chromatographic separation and quantification

Separation and quantification of target compounds was performed on an HPLC system purchased from Shimadzu Corporation (Kyoto, Japan). HPLC was equipped with an online mobile phase degasser unit (Model: DGU-20A3), 20 µL sample loop, pump (Model: LC-20AB), and UV/Vis detector. Compounds were separated on a Gemini column (C18 110A, length 150 x 4.60 mm, ID 5µ) purchased from Phenominex (CA, USA) using a mobile phase mixture of acetonitrile: 0.2% formic acid in water (80:20, v/v) at a flow rate of 1.0 mL/min. TCS was monitored at 254 nm. The chromatographic system was equipped with Shimadzu LC solutions software for data collection and processing. These HLPC parameters used are shown in Table 4.3.

4.4.4 Occurrence of TCS in wastewater effluent treatment plant (ETP)

The occurrence and the observed concentrations of TCS showed high dependence on wastewater pre-treatment during the wastewater treatment process (aeration process and pH adjustment) in the ETP Dam as the physiochemical parameters displayed in Table 4.4. The aeration process is thought to the contributing factor in the amount of dissolved oxygen (DO) detected. Hence, this resulted in small traces of TCS to be detected in original collected ETP samples (Figure 4.21) where the concentration in varied monitoring days was found to be dissimilar. The traces of TCS were detected in the ETP dam samples in ppb concentrations, from Day 1 to Day 10, these concentrations were found to be, 35, 8, 6, 38, 22, 15, 44, 43, 55 and 18 ppb, respectively. As this graph displays, there are some days where the concentration of TCS in the ETP dam is influenced by the weather. This coincidence is specifically noticed on Day 2, 3 and 10 where we had rainfall measured to be 3, 5, 6mm, respectively. In contrast, on Day 7 (which was the 13th of September 2017), where the graph shows a pronounced bar, Dyefin textiles was doing a new trial work on weaving process, and this could be attributed to that. Hence the collected sample was very dense and navy in colour. Gracia-Lor, Sancho [148] suggested that such cases may be due to the matrix effects being higher in the influents than in the effluents of WWTPs which lead to higher matrix suppression and higher quantification limits in influents.

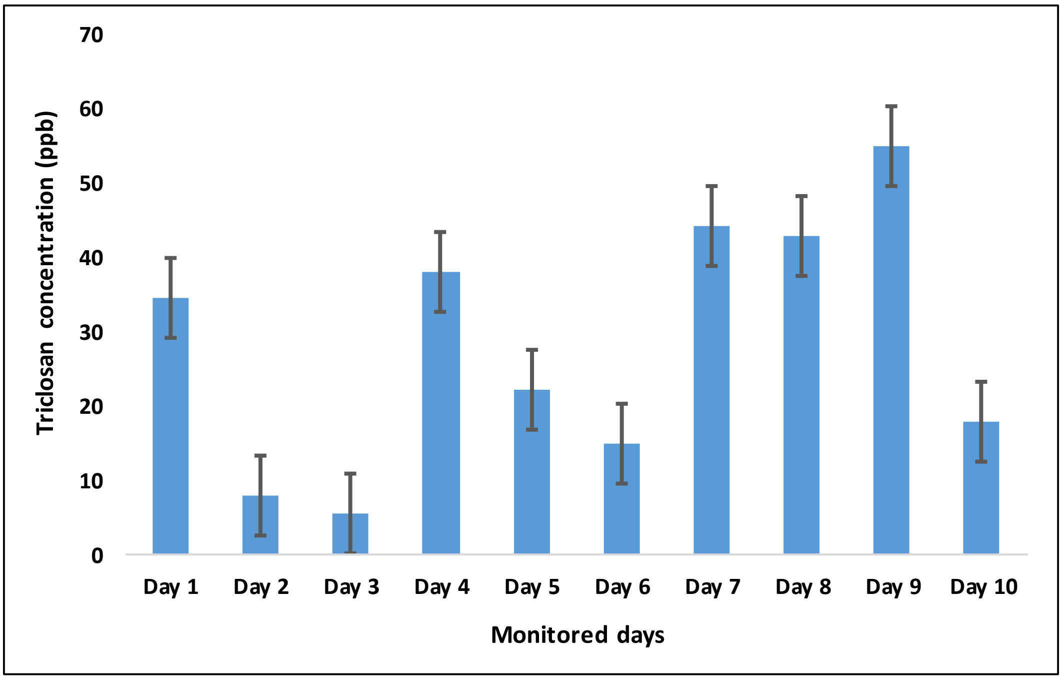


Figure 4. 21 The graph showing the concentration of TCS detected in the monitored days

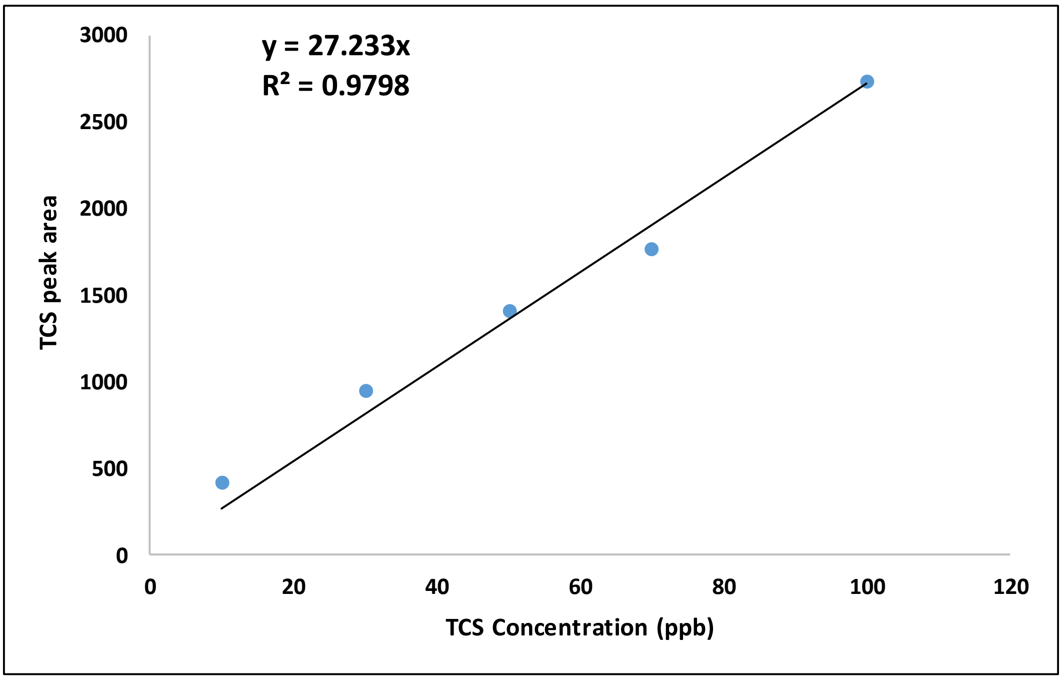


Figure 4. 22 The graph showing the calibration curve of TCS standards

4.4.4.1 PVDF membrane pre-treatment and sample pre-treatment

PVDF membranes are mostly used in Western blotting (amino acids analysis) and have various characteristics; however, the common question asked is *"Why do PVDF membranes require a methanol soak?" P*VDF membranes are very hydrophobic, meaning that aqueous buffers, such as the Western transfer buffers or deionized water, will not penetrate the membrane. This results in poor transfer and significantly reduced binding of proteins or organics.

A short rinse (10 minutes) in methanol (or other 100% alcohol (ethanol or isopropanol)) prior to enrichment with TCS rich samples was very essential and the membrane was "hydrated" and this allowed improved porous nature. Pre-incubating these polymers with methanol activates them and results in a successful adsorption potential. Methanol also displaces air trapped in the hydrophobic pockets of PVDF membrane allowing a subsequent replacement of methanol with the water contained in the used spiked sample or sample.

It was of paramount importance to consider the pre-treatment of the collected samples; as this allows and give rise to higher removal efficiencies. The pH for all the samples was more likely neutral; hence, it was reduced to pH 3.0 to allow for the protonation of the target compound (TCS). This is because the adsorption of the samples was expected to occur according to hydrogen bonding mechanism.

4.4.4.2 Removal of TCS in wastewater effluent treatment plant (ETP)

The total organic pollutant in the ETP Dam from the UIC is the combination or composite of all wastewaters within the complex. Removal efficiency was compared between the MIP/NIP infused membranes and the pristine PVDF membrane. The results of % removal efficiencies are listed on table 4.5:

Table 4. 5: Results obtained from removing triclosan

Membrane type	% Removal efficiency									
	Day 1	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**	**Day 7**	**Day 8**	**Day 9**	**Day 10**
PVDF bare	62	30	41	61	56	65	44	96	31	65
PVDF/MIP	78	61	67	92	79	95	62	98	75	89
PVDF/NIP	81	53	63	86	72	90	60	100	70	88

Figure 4.23 revealed graphically that the PVDF/MIP polymeric membrane had high adsorption efficiencies in almost all monitored days. and this is due to the strong binding sites located on the cavities of the MIP. All membranes evaluated showed a similar pattern in terms of increase in removal efficiencies. This additionally explains that the Instrumentation quantification parameters were reliable and efficient, specifically parameters like wavelength, 254nm and composition of mobile phase, 80%:20% (Acetonitrile: 0.2% formic acid). However, the enrichment of TCS on PVDF/NIP and bare PVDF membranes could be easily washed because the scaffolds or surfaces of both membranes are not ‘lock and key’ as PVDF/MIP membrane.

Table 4. 6: Recent data on the percentage removal efficiencies of TCS from WWTPs vs PVDF infused membranes on (This Study).

Country, City	% Removal efficiency	Reference
South Africa, Durban	62-100	This study
China, Xiamen	>20	[149]
USA, Atlanta	50-100	[150]
Sweden, Goteborg	>90	[151]
USA, Washington, DC	58-86	[152]
Tokyo, Juliung	45-65	[149]

Table 4.6 displays the efficiency of various WWTPs with in comparison with results obtained on this study. A drawn conclusion is that; the membrane performance does a better reduction of the target pollutant compared to the displayed plants.

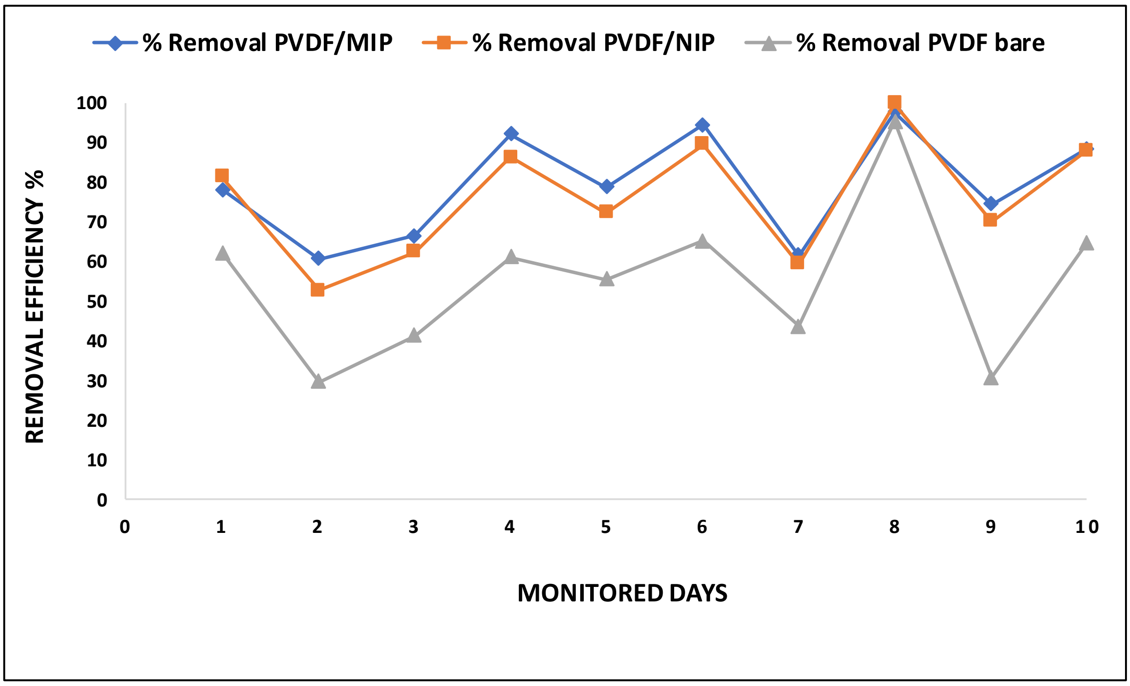


Figure 4. 23 The removal efficiencies of different modified polymeric membranes

In some cases, high concentrations of the compound were observed in the effluent on Day 7 than any other monitored days. This high unwanted quantity only allowed a removal efficiency of 62 % using a PVDF/MIP membrane. The low removal efficiency may be attributed to the amount of interferences (matrix effects) in the water body. This is likely to occur in the wastewater fields when studying or monitoring drugs in wastewater [153]. Moreover, as displayed in Figure 4.21, the removal efficiencies for the investigated organic pollutant in wastewater fluctuated in different days and in different sample concentration amounts. The estimated reasons could be the technique, or the uncertainty related to grab sampling and this could cause variations when not executed in the same manner or the same person every day. In addition, the variation could be a result of the fact that some industries do not operate daily, hence, their wastewater traces are not available in the water body sampled at ETP in some days.

Removal efficiencies in WWTPs depend on several factors such as compound physicochemical properties. These include among others the climate conditions, (e.g. temperature and sunlight intensity, rainfalls and cold days), the type of treatment process employed, the operational conditions of the treatment process (temperature of operation, redox conditions, solids retention time and hydraulic retention time) as well as the age of the activated sludge used in the plant [154, 155]. Therefore, removal efficiencies are likely to show meaningful dissimilarities from one plant to another, and within a plant at different times [156]. Hence, in this study, different days of industrial operations was monitored.

Table 4. 7: Detected concentrations of triclosan (TCS) in the aquatic environment

System type or medium	Sample description	Location or country	(TCS) conc. (µg/L)	Reference
WWTP	Effluent	South Africa	5.5-55.1	This study
WWTP	In-flowing wastewater	USA Japan	2.7-26.8 2.7-11.9	[43] [157]
WWTP	Treated water	USA	0.03-2.7	[43]
		UK	0.34-3.1	[158]
Sediment	Freshwater	Switzerland Spain	53.0 ND-35.7	[159] [160]
	Marine	Spain	0.27-130.7	[161]

4.5. Validation of the chromatographic method

The chromatographic analysis of triclosan was executed under reverse phase technique. This analytical method used selective PVDF/MIP polymeric membranes as a sorbent and was validated based on sensitivity, accuracy and precision. Limits of detection (LOD) and limits of quantification (LOQ) were conducted to prove the sensitivity of the method as shown in Table 4.8. LOD (3) and LOQ (10) are concentration of signal-to-noise ratio.

Table 4. 8: LOD, LOQ, recover (%) and RSD (%) values (n=3) for the spiked deionised water in the concentration range of 5 to 1000 µg/L

			Recovery (%) ± RSD (%)		
Spiked sample	LOD (µg/L)	LOQ (µg/L)	1000 µg/L	50 µg/L	5 µg/L
Effluent	0.22	0.71			68 ± 10
Deionised water	0.10	0.28	65 ± 5	78 ± 12	112 ± 12

The relative standard deviation (RSD) given as ± values represent the precision of the method. A linearity of R^2 equal to 0.99 was achieved for a calibration curve of six-points in the range of standards (10 to 100 µg/L). The results in Table 4.8 displays that the analytical method used in this study was accurate, hence the recoveries ranges between 65-112 %.

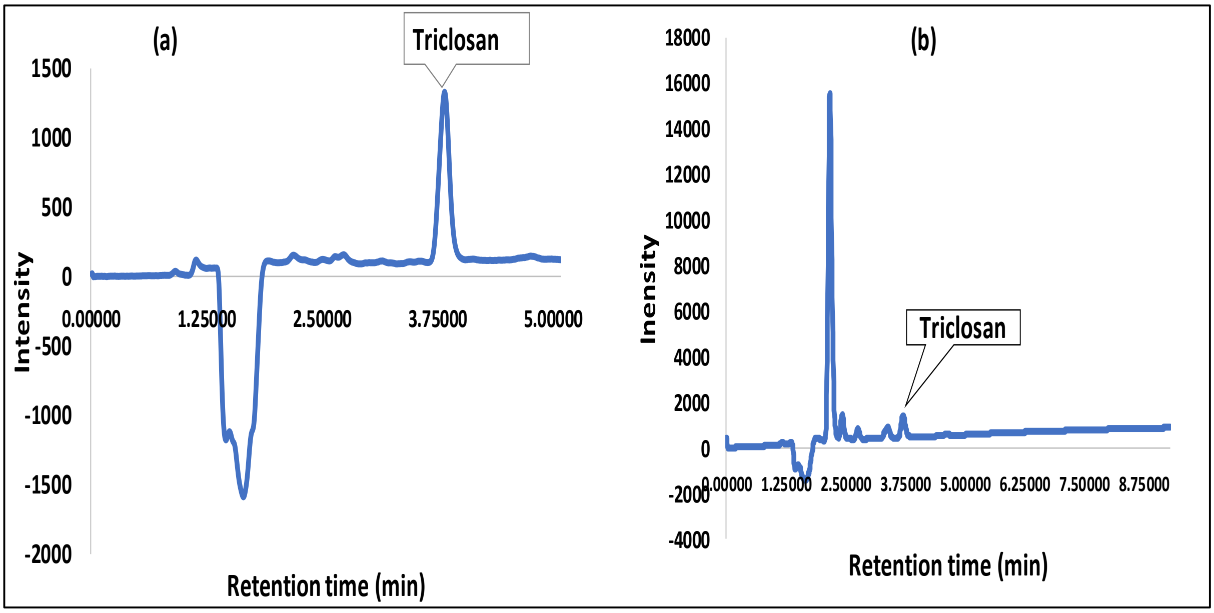


Figure 4. 24: Chromatographic analysis of (a) 500 µL-1 TCS standard (b) detected TCS in ETP daily samples

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The main objective of this study was to synthesise the PVDF nanostructured membranes decorated with MIP and NIP and to study their effect on the adsorption performance and its physicochemical properties. The functionalised membranes were then characterised using SEM, DMA, TGA and FTIR-ATR. The resulting membranes were eventually tested to ascertain their capability to remove TCS from wastewater effluent samples. This study was successfully conducted, and the following conclusions and recommendations are drawn:

Addition of additives or the micro composite particles in the scaffold of the PVDF increased the hydrophilicity of the membrane and this further led to an increased water content and porosity percentage of the polymer.

In this study, relationships between the synthesis of polymer membranes, their structure, surface properties and performance were discussed. It was found that there was a strong correlation between the structure, performance and properties of the membranes. It was also shown that remarkable progress has been made in the fabrication of membranes for wastewater treatment. However, there is still a challenge to produce reliable membranes with anti-fouling properties, high mechanical strength, and minimal thickness of the membrane barrier layer to provide a high flux.

Identification of many parameters, like water content and porosity percentage, which can be effectively utilised in determining the relationship between membrane fabrication, structure, surface properties and performance could be very suggestive for the continuous improvement and development of membrane-based technologies for water treatment. This investigation further showed a decent eye-catching subject on loss modulus and stiffness: where the obtained graphs on DMA displayed a conclusive thing that stiffness is a structural property, influenced by the geometry of the additives as well as the material(s) of which it is comprised. Moreover, loss modulus is a material property that is intrinsic to the material and less influenced by additives geometry. Both are useful parameters to be considered in the membrane technology. Material properties are extremely useful in design, and to see if the properties of a scaffold or surface change with time and heat. However, a structural property like stiffness was useful to tell how the additives (structure) will function, which is often important for polymer mechanics or evaluation steps to be conducted

To ensure progress in the membrane technology, more exertions are needed for further improvement of common membrane fabrication methods as well as the development of a modern or a more recent fabrication technique. An inclusive understanding between porous structure-surface properties and the performance of membranes in water treatment processes is crucial for further development of polymeric membranes and optimization of fabrication processes. Membrane performance (flux, rejection and fouling) was strongly influenced by membrane chemical composition and specific features of porous structure and the membrane surface, including hydrophobic/hydrophilic properties, membrane charge, pore size and pore size distribution. Many studies have been conducted, concerning the physiochemical properties of membranes to monitor and enhance the role of membrane structure and surface properties in membrane performance; however, more work still needs to be done to comprehend the subject fully.

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CHAPTER 6: APPENDIX

6.1. MIP and NIP Graphs

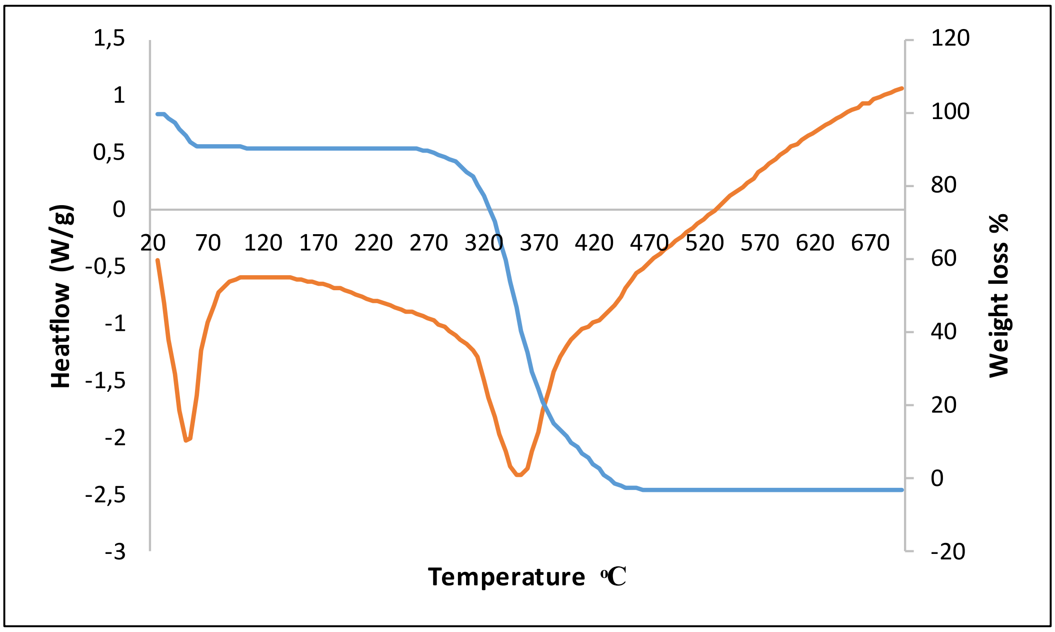


Figure 6. 1 The DSC of the MIP additive

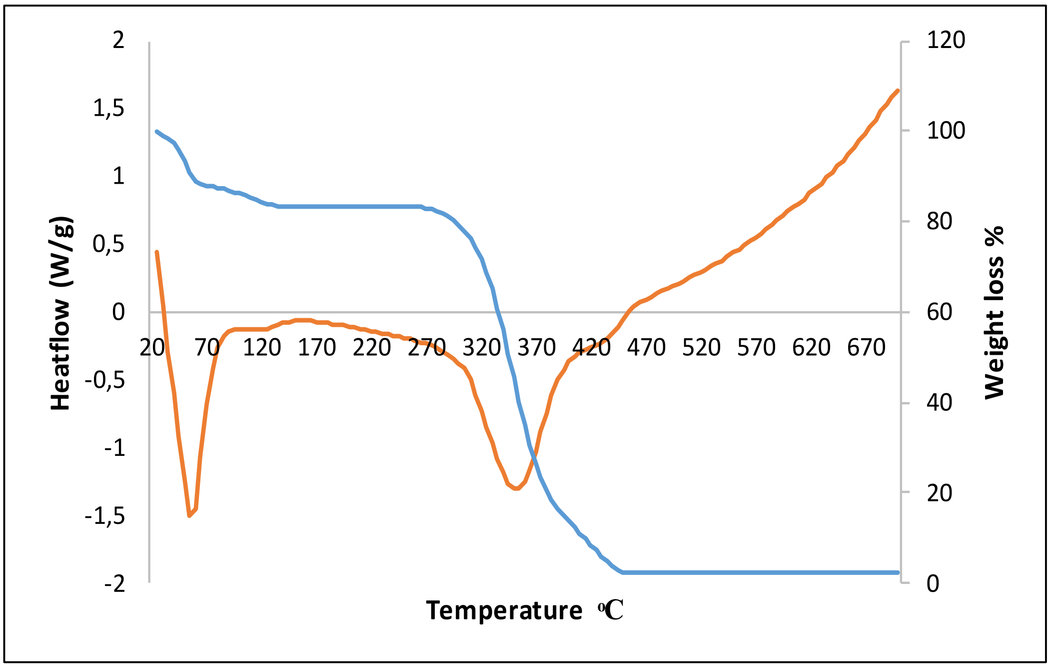


Figure 6. 2 The DSC of the NIP additive

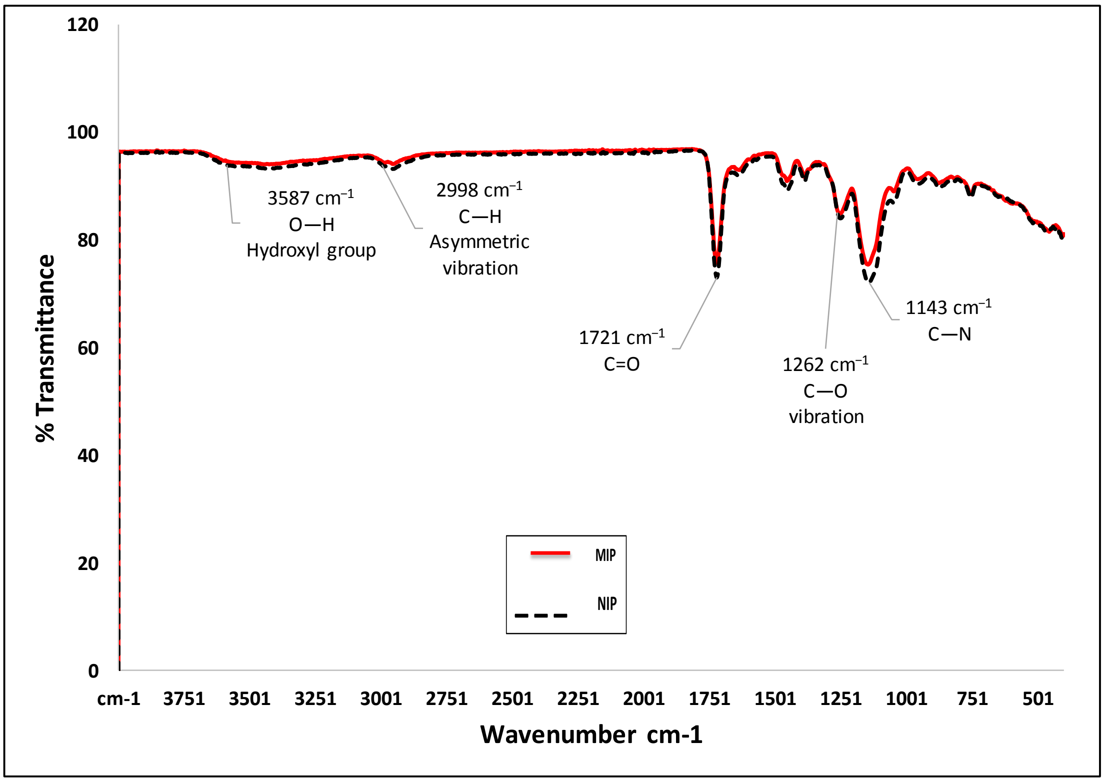
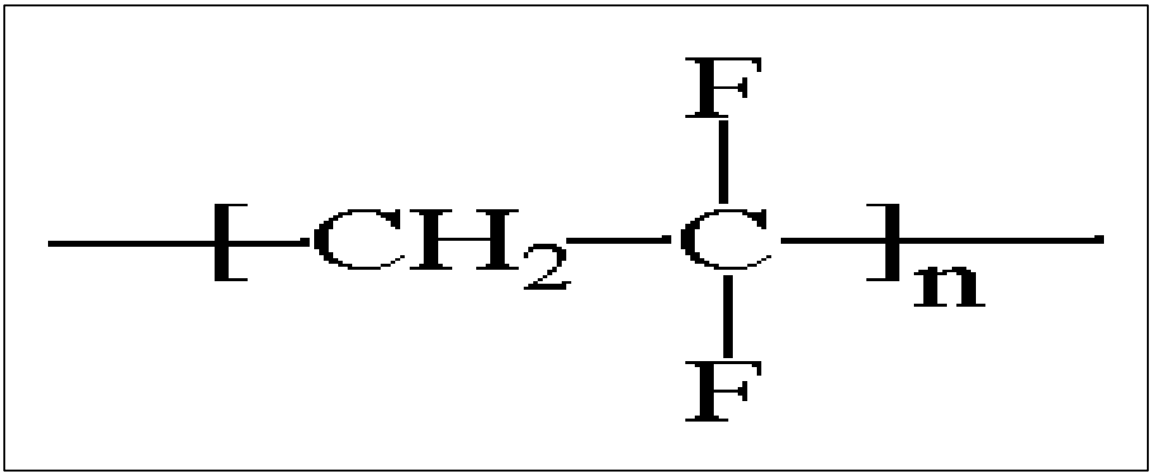


Figure 6. 3 The FTIR spectrum of washed MIP and NIP



$$-\!\left[CH_2-CF_2\right]_n\!-$$

Figure 6. 4 The chemical structure of the polymeric PVDF

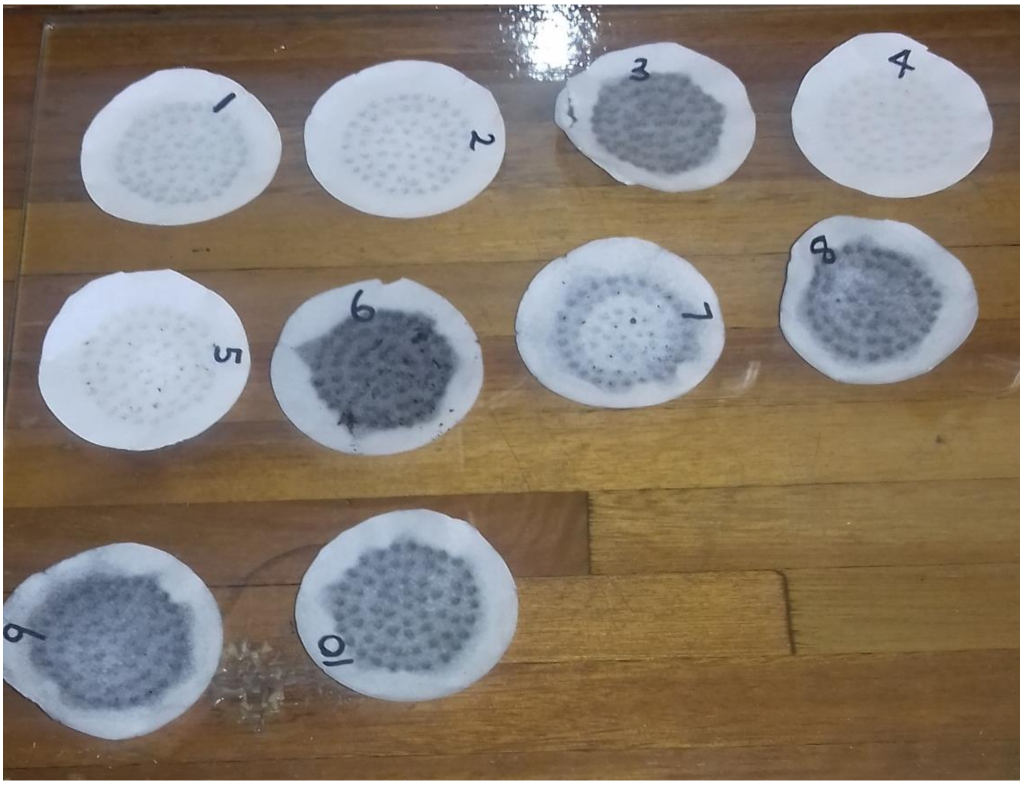


Figure 6. 5 The analysis of suspended solids on ETP Dam samples

Table 6. 1 The results of suspended solids performed in the lab

ETP Dam sample	**Parameters**		
	pH	**Conductivity (mS/m)**	**Suspended solids (%, m/m)**
Day 1	8.09	695	380
Day 2	8.06	744	404
Day 3	8.12	586	56
Day 4	7.67	418	80
Day 5	7.82	482	168
Day 6	7.54	733	156
Day 7	7.93	738	56
Day 8	7.96	1158	52
Day 9	7.66	1400	64

Day 10	8.09	835	208

6.2. Manuscripts in progress

a) Synthesis and characterisation of membranes functionalised with C18 as a modifier for adsorption capabilities on poly aromatic hydrocarbons (PAHs).

S.A. Mntambo, P.S. Mdluli, M.M. Mahlambi, S.C. Onwubu, N.L. Nxumalo

b) Preparation and characterisation of activated charcoal functionalised membranes for adsorption capabilities of heavy metals.

S.A. Mntambo, P.S. Mdluli, M.M. Mahlambi