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2024

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Ngwamba, Pamela Nadia . (2024). The removal of diclofenac, cypermethrin, ibuprofen and naproxen from wastewater using advanced membrane technology [Masters dissertation, University of the Witwatersrand, Johannesburg]. WIReDSpace.

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THE REMOVAL OF DICLOFENAC, CYPERMETHRIN, IBUPROFEN AND NAPROXEN FROM WASTEWATER USING ADVANCED MEMBRANE TECHNOLOGY

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

October 2024

DECLARATION

I hereby declare that:

- This research report is my original work;
- The contributions of my supervisor, to the research report were consistent with standard supervisory practice;
- There is no content in this research report that has been published or written by a third party unless properly cited through complete and accurate referencing;
- I am aware that plagiarism is the improper use of another person's work without their knowledge or consent. All direct quotations and paraphrased text have been properly acknowledged;
- I have acknowledged the contributions of external parties to the research report.

The Research Report was done under the guidance of Dr Precious Thabisile Biyela at the University of the Witwatersrand, Johannesburg.



15/10/2024

_____ _____

Signature (Pamela Ngwamba) Date

ABSTRACT

In recent years, emerging contaminants (ECs) such as pharmaceuticals, personal care products, endocrine-disrupting compounds, industrial additives, pesticides, nanomaterials, surfactant retardants, surfactants, and their metabolites and transformation products have been widely detected in both wastewater and water bodies. These compounds originate from a diverse range of point and non-point sources, consistently introducing them into wastewater and directly and/or indirectly introducing them to water bodies and the broader environment. The ECs have garnered attention due to their potential environmental impact and potential to induce adverse health effects. Conventional wastewater treatment processes are often not adequate to efficiently remove these compounds, thus leading to residual concentrations entering aquatic ecosystems and eventually, reaching drinking water systems. Although extensive research has been done over the past decade, there is limited literature covering the effects of long-term exposure to ECs, especially their metabolites and by-products, their fate, and toxicity levels. Consequently, additional research is imperative to establish limits and facilitate the regulation of these ECs.

Advanced treatment methods, including ozonation, activated carbon filters, and membranes, have proven effective in eliminating ECs from wastewater. It must be noted that the efficiency of these advanced processes varies significantly. Despite extensive testing of various technologies, limitations still exist. Although most of the advanced treatments are highly effective, none of them have the ability to remove a mixture of ECs effectively. This variation is attributed to the nature of the compounds (e.g., hydrophobicity/hydrophilicity and solubility) and operational parameters like temperature, hydraulic retention time, and solids retention time. Nanocomposite membranes have been identified as a viable technology for the removal of ECs from wastewater due to their unique properties and enhanced performance when compared to conventional membranes. They are highly selective and efficient, additionally, they can be designed to specifically remove ECs such as pharmaceuticals, pesticides, and endocrine disruptors. Furthermore, they show greater antifouling properties, reducing the accumulation of contaminants on the membrane surface and extending the lifespan of the membrane, thereby lowering maintenance costs and improving operational efficiency.

The aims and objectives of the research report were to compile a comprehensive literature review that highlights the importance of removing ECs from the environment; prepare and characterise four different flat-sheet membranes using polyvinylidene fluoride (PVDF) and imidazolium-based polymeric ionic liquids (PILs) and testing the membranes to determine the retention time and effectiveness of the prepared membranes in removing four different

pharmaceutical products which are diclofenac, cypermethrin, ibuprofen, and naproxen. The hypothesis assumed that the imidazolium-based PILS/PVDF flat sheet membranes would yield a removal efficiency greater than 90%. This expectation was achieved, and all the membranes achieved a removal efficiency greater than 90%. Various studies have shown that nanocomposite membranes yield high removal rates. The synthesised membranes had better features than PVDF alone. The PVDF alone was found to have the largest pore size and the least retention time, although the removal efficiency was high. The blended membranes lead to higher porosity and retention times. They had smaller pore sizes as compared to plain PVDF; hence, the retention time was increasing. The higher the concentration of the imidazolium, the lower the contact angle measured; this is an indication of a more hydrophilic membrane surface. Hydrophilic membranes are less prone to fouling. The method investigated in this report is simple and can be easily reproduced. Based on the findings of this research report, the methods employed are precise, accurate, highly sensitive, and rapid.

DEDICATION

To my dear mother and three angels, thank you for being my guiding lights, pillars of strength, and sources of inspiration. This research report is a testament to your love, support, and belief in me. I am forever grateful for your presence in my life.

With all my love and gratitude.

ACKNOWLEDGEMENT

I want to begin by expressing my profound gratitude to God for providing me with the strength and wisdom to persevere through the challenges encountered during the completion of this research report. Without His grace, I could not have made it to this point.

To my dear mother, Julia Zulu, and my aunt, Xolile Mamphaga, along with my family and friends, I am eternally grateful for your constant support and encouragement throughout this arduous journey. Your belief in me, even during moments of doubt, has been a beacon of light guiding me forward. Your words of encouragement were a constant reminder to never give up on my dreams.

I extend my heartfelt appreciation to my supervisor, Dr. Precious Biyela, for her invaluable contribution, patience, and guidance throughout the process. Her unwavering belief in my abilities, even during times when I felt overwhelmed, played a pivotal role in my success. I am truly grateful for her dedication and support.

I would also like to acknowledge the significant role played by the Lab Manager, Ms Namhla Maqubela, whose assistance and guidance were instrumental in the successful completion of this investigation.

Lastly, I would like to offer a gentle reminder to myself: I am worthy and capable of achieving anything I set my mind to. This journey has reinforced my belief in my capabilities and resilience, reminding me that with determination and perseverance, I can overcome any obstacle.

To everyone mentioned above and those who have supported me along the journey, thank you from the bottom of my heart.

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LIST OF ABBREVIATIONS

Automatic Film Applicator	AFA
Antibiotic-resistant Genes	ARGs
Activated Sludge Process:	ASP
Biochemical Oxygen Demand	BOD
Biodegradable Organic Matter	BOM
Biological Unit Processes	BUPs
Contact Angle	CA
Chemical Oxygen Demand	COD
Chemical Unit Processes	CUPs
Disinfection By-products	DBPs
Deionised	DI
Dissolved Organic Carbon	DOC
Department of Health	DOF
Department of Water and Sanitation	DWS
Drinking Water Distribution Systems	DWDSs
Drinking Water Quality Framework	DWQF
Emerging Contaminants	ECs
Electrodialysis	ED
Endocrine Disrupting Compounds	EDCs
Emerging Pollutants	EPs
Endocrine Systems	ECs
Food and Drug Administration:	FDA
Forward Osmosis	FO
Flat Sheet	FS
Hollow Fibre	HF
High-performance Liquid Chromatographic	HPLC
Hydraulic Retention Time	HRT
Membrane Bioreactors	MBRs
Microfiltration	MF
Mixed Liquor Suspended Solids	MLSS
Nanofiltration	NF
Non-solvent Induced Phase Separation	NIPS
Non-steroidal Anti-inflammatory Drugs	NSAIDs
National Water Act	NWA
National Water Service Act	NWSA

Polyethylene	PE
Polyethersulfone	PES
Persistent Bio-accumulative and Toxic Substances	PBTs
Polypropyle	PP
Priority Pollutants	PPs
Pharmaceuticals and Personal Care Products	PPCPs
Physical Unit Processes	PUPs
Polyvinylidene Fluoride	PVDF
Polymeric Ionic Liquids	PILs
Reverse Osmosis	RO
Scanning Electron Microscopy	SEM
Solid Phase Extraction	SPE
Solid Retention Time	SRT
Suspended Solids	SS
Ultrafiltration	UF
Ultraviolet	UV
Urban Water Cycle	UWC
Transmembrane Pressure	TMP
Thermally Induced Phase Separation	TIPS
Vapour-induced Phase Separation	VIPS
Water Treatment Plant	WTP
Wastewater Treatment Plant	WWTP
World Health Organisation:	WHO

CHAPTER 1: INTRODUCTION

1.1. Introduction

The proliferation of urbanisation, industrialisation (Vasilachi et al., 2021), rapid population growth (Selwe et al., 2022) and agricultural activities (Mhuka et al., 2020; Shetty et al., 2023) contribute to ever-increasing quantities of primary and secondary microcontaminants being deposited into natural water bodies. In areas where there is formal sanitation infrastructure, these contaminants are conveyed through wastewater collection systems. When these contaminants bypass the treatment barrier, which often happens as conventional wastewater treatment plants are not designed to remove microcontaminants, they can end up in water bodies (Pal et al., 2010; Selwe et al., 2022; Gaviria et al., 2023). Microcontaminants of concern, include, but are not limited to, pharmaceuticals (Muneer et al., 2017) and personal care products (PPCPs) (Daughton & Ternes, 1999; Kasprzyk-Hordern et al., 2009; Tran et al., 2018; Sengupta et al., 2022), disinfection by-products (DBPs), endocrine disrupting compounds (EDCs) (Godfray et al., 2019; Dubey et al., 2023), heavy metals, polar pesticides (Daughton & Ternes, 1999; Kasprzyk-Hordern et al., 2009; Tran et al., 2018; Bui et al., 2019), surfactant residues, plasticisers, and a cocktail of industrial additives (Petrovic et al., 2003). Collectively, these microcontaminants are called emerging contaminants (ECs). The ECs are newly created and continuously introduced into the environment from anthropogenic activities, prompting global academic attention to their prevalence, fate, and environmental impacts (Barber, 2014; Lamastra et al., 2016).

The ECs are also defined as a group or array of synthetic or naturally occurring microcontaminants in the environment at trace quantities, usually lower than 1 µg/L (Kümmerer, 2011; Noguera-Oviedo & Aga, 2016; Yahaya et al., 2020). They are called ‘emerging contaminants’ because they are not commonly monitored (Vasilachi et al., 2021; Kumar et al., 2022), historically not recognised as ‘contaminants’ and are not part of any environmental or water legislation and/or regulations (Barber, 2014). Additionally, the ECs have the potential to cause adverse health and environmental impacts to varying degrees, even at low concentrations (Daughton & Ternes, 1999; Kasprzyk-Hordern et al., 2009; Pal et al., 2010; Kümmerer, 2011; McEneff et al., 2015; Schoeman et al., 2017; Antunes et al., 2021; Dubey et al., 2023; Yang et al., 2024).

The ECs are not to be confused with priority pollutants (PPs). The ECs are 'newly' or 'more recently' detected in the environment but are not regulated (Puri et al., 2023). However, their persistence and potential adverse effects make them good candidates for future legislation (Lamastra et al., 2016; Archer, 2018; Kumar et al., 2022). The PPs are toxic substances that are produced in measurable quantities and frequently occur in the environment (Muñoz et al., 2008; Peng et al., 2023). The PPs are regulated at national and international levels as they pose a high risk to water bodies and human health (Teodosiu et al., 2018). Further to this, a contaminant is a substance present in the environment due to some human interference, but it is not necessarily a pollutant if it does not cause any environmental harm. In essence, a pollutant is a subset of a contaminant. Therefore, one can have a contaminated environment without it being polluted, but you cannot have a polluted environment without it being contaminated (Stengel et al., 2006; Chapman, 2007; Guidotti, 2015). Some literature uses the term ECs (Petrie et al., 2015; Sorensen et al., 2015; Stefanakis & Becker, 2015; Archer, 2018; Sengupta et al., 2022) and others use emerging pollutants (EPs) (Geissen et al., 2015; Arman et al., 2021; Krishnakumar et al., 2022). Whereas, Noguera-Oviedo & Aga (2016), Teodosiu et al. (2018), Chandel et al. (2023) and Gaviria et al. (2023) state that the terms have been used interchangeably. This report uses the term ECs because the threshold at which these compounds are deemed pollutants is still unspecified.

Most research on ECs is primarily conducted in the global north, while investigations on this topic in Africa have only emerged recently. Gwenzi & Chaukura (2018) reviewed the literature on organic contaminants in sub-Saharan African aquatic systems. The review aimed to comprehend the characteristics, sources, prevalence, and factors contributing to the risk related to organic contaminants in sub-Saharan Africa. Furthermore, it highlighted the knowledge gaps and research limitations. The review collated various papers from different sources between 1990 and 2017. The studies reported on by Gwenzi & Chaukura (2018) found that wide ranges of potentially toxic ECs, such as pesticides, plasticisers, pharmaceuticals, endocrine-disrupting compounds, and antimicrobial resistance genes, have been detected in aquatic systems. The ECs enter the environment through multiple diverse pathways, including effluents from wastewater treatment plants (WWTPs) (Daughton & Ternes, 1999; McEneff et al., 2015; Al-Farsi et al., 2017; Ebele et al., 2017; Schoeman et al., 2017; Norfazilah and Umairah, 2021), untreated wastewater (Geissen et al., 2015; Teodosiu et al., 2018), sludge from wastewater treatment (Petrie et al., 2015), agricultural runoff (Lamastra et al., 2016; Archer et al., 2017), animal farming, leaching from soils after herbicide treatment, erosion (Teodosiu et al., 2018), industrial facilities, food processing plants, mining activities (Stefanakis & Becker, 2015) and landfill sites (Gwenzi & Chaukura, 2018).

The prevalence of ECs in the environment can be predominantly ascribed to the effluent discharge from municipal WWTP effluents (Dubey et al., 2023; Yang et al., 2024); hence, ECs are more pervasive in surface water bodies than in other natural environments such as groundwater (Pal et al., 2010; Noguera-Oviedo & Aga, 2016). Conventional secondary treatment processes, for example, activated sludge and biological filters, are widely employed and extensively investigated in academia (Petrie et al., 2015). These conventional processes are not specifically designed for the removal of microcontaminants such as ECs, leading to their discharge into receiving surface waters such as rivers, lakes, and, ultimately, coastal waters (Stefanakis & Becker, 2015; Schoeman et al., 2017; Dubey et al., 2023). The ECs are generally hydrophilic, making them more challenging to remove from wastewater; thus, they usually persist through treatment and in the natural environment (Teodosiu et al., 2018). They are multifunctional and diverse, for example, the adsorption behaviour of pharmaceuticals varies significantly depending on the soil type, as they can occur in ionised and un-ionised states. This affects their interaction with the different substances in the soil (Geissen et al., 2015; Al-Farsi et al., 2017). Therefore, alternative treatment systems to enhance the removal efficiency of ECs in wastewater must be explored (Noguera-Oviedo & Aga, 2016) to address their unique chemical properties. Removal of ECs from wastewater effluents is imperative due to their ability to bioaccumulate, exert selective pressure that leads to antibiotic resistance, potential endocrine disruption, and other negative effects (Gani et al., 2021; Zahmatkesh et al., 2022). Exploring alternative treatment systems is an essential step toward sustainable water management and environmental conservation.

Several studies have investigated alternative advanced treatment methods, such as activated carbon, ultravoilet (UV), advanced oxidation and membrane filtration, to efficiently remove ECs from wastewater (Rott et al., 2018; Ahmed et al., 2021; Ismail & Mokhtar, 2021; Kumar et al., 2022; Morin-Crini et al., 2022). However, extensive research is still required to prioritise removing ECs and advancing conventional WWTPs. Furthermore, recent studies have explored three advanced treatment processes for the extraction of various ECs; (1) advanced biological treatment (Rathi et al., 2021; Morin-Crini et al., 2022), (2) membrane filtration (Clodt et al., 2017; Zahid et al., 2018; Vasilachi et al., 2021; Morin-Crini et al., 2022), and (3) advanced oxidation processes like ozonation (Zahid et al., 2018; Morin-Crini et al., 2022). These processes, as listed above, are highly effective and efficient in reducing ECs found in effluents from secondary wastewater treatment.

Of the processes stated above, membrane processes are the most effective for removing various ECs. Membranes are made up of semi-permeable materials that allow water to permeate and retain the micro-matter at the surface of the membrane et al., 2018). Membrane

technologies are easy to operate, cost-effective, and have a high contaminant removal efficiency (Zahid et al., 2018). There are two broad classes of membranes, polymeric membranes and inorganic membranes. Inorganic membranes include ceramics and other metals with high structural, mechanical, and thermal strength (Zahid et al., 2018). Ceramic membranes present good filtration performance; they are inert, display chemical resistance characteristics, and have a high hydrophilic ability. However, they are expensive and fragment easily. As technology upgrades, membrane development has moved towards polymers like polyvinylidene (PVDF), polyethersulphone (PES), polyethylene (PE) and polypropylene (PP) (Mutamim et al., 2013). Polymeric membranes are flexible, display high mechanical and chemical strength, have good film-forming properties, and are inexpensive materials (Zahid et al., 2018). However, they are porous yet hydrophobic, and thus more susceptible to fouling. The hydrophobicity of the membrane can be improved by coating its surface with a hydrophilic polymer layer (Mutamim et al., 2013).

Recently, polymeric nanocomposite membranes have received much attention due to their potential advancement of membrane technology. Furthermore, their ability to enhance permselectivity, membrane flux, and desired morphology formation to improve membrane fouling resistance (Zahid et al., 2018), as well as to improve efficacy and lifespan (Mahmoud et al., 2024), attracts many researchers. Technically, they offer improved flexibility, increased permeability, robustness, and economic viability, and they have exceptional separation properties (Rehan et al., 2019; Mahmoud et al., 2024). Additionally, they can improve freshwater supply, relieve environmental degradation, and improve green energy technologies. However, they also have shortcomings. For example, dense polymeric membranes have low mass transport, limited mechanical, chemical, and thermal resistance and poor anti-fouling capabilities due to their surface properties (Mondal, 2015). This research report investigates the removal efficiency of diclofenac, cypermethrin, ibuprofen, and naproxen using imidazolium-based polymeric ionic liquid (PILs)/polyvinylidene fluoride (PVDF) flat sheet membranes packed in solid phase extraction (SPE) cartridges.

1.2. Problem Statement

The ECs occur at extremely low concentrations (Monteiro & Boxall, 2009; Alcala, 2015); therefore, it is often difficult to determine their fate and mobility in aquatic ecosystems (Noguera-Oviedo & Aga, 2016). Numerous studies have documented the occurrence and risks of ECs in WWTP effluent; however, the majority focus on a limited number of ECs within small-scale areas, resulting in gaps in nationwide or larger-scale data (Yang et al., 2024). Although Lei et al. (2015) reported that several studies had made relevant connections for

various ECs with cancer and reproductive risks, a clear and finite conclusion cannot be made since limited literature exists.

The practical and efficient operation of WWTPs is critical in eliminating pathogens and pollutants from water bodies, thereby safeguarding wildlife and human ecosystems (Archer, 2018). Water treatment plants (WTPs) often draw water from these 'EC polluted' water bodies, which places WTPs under a lot of strain to remove these chemical contaminants. The potential ability of ECs to induce physiological effects on humans (Daughton & Ternes, 1999; Kasprzyk-Hordern et al., 2009; McEneff et al., 2015; Schoeman et al., 2017) and on wildlife (Archer, 2018) even at low concentrations calls for their effective removal during treatment (Teodosiu et al., 2018).

The occurrence, transport and fate of ECs in the aquatic environment are determined by their physicochemical characteristics, such as solubility, polarity, volatility, and other intrinsic properties (Stefanakis & Becker, 2015; Kumar et al., 2022). In addition to these characteristics, operational parameters like solids retention time, hydraulic retention time, and temperature play a key role in selecting appropriate treatment method to achieve optimum removal efficiency (Zahmatkesh, et al., 2022). Given the complexity of both ECs and environmental matrices, it is crucial to explore advanced and alternative treatment technologies to enhance the effective removal of pharmaceutical compounds and other ECs from wastewater, ensuring that discharged effluent meets environmental safety standards (Norfazilah and Umairah, 2021).

1.3. Research Question

This research attempts to address the question:
"What is the extent to which diclofenac, cypermethrin, ibuprofen, and naproxen can be removed using imidazolium-based PILs/polyvinylidene fluoride (PVDF) flat sheet membranes packed in SPE cartridges?"

1.4. Hypothesis

The PILS/PVDF flat sheet membrane is expected to yield a removal efficiency greater than 90%.

1.5. Rationale and Motivation

Globally, freshwater has become a scarce commodity due to high population growth and increased economic development, which has led to increased water demand, subsequently placing excess pressure on natural water resources (Liu et al., 2017). Additionally, the phenomenon of global warming amplifies the intensity and frequency of extreme weather events, thereby inducing unpredictability in water availability (Wang et al., 2024) and exacerbating instances of water scarcity (He & Rosa, 2023). This problem is further aggravated by inadequate sanitation services (Haseena et al., 2017) and ineffective pollution control, resulting in compromised water quality and degraded natural water bodies. The World Health Organisation (WHO) reported that 80% of diseases are waterborne because many countries do not meet the required water quality standards (Haseena et al., 2017). To safeguard public health, it is essential to replace the conventional approach to water pollution with strategies that prioritise pollution prevention and control. This requires sufficient infrastructure, best management practices, and improved water resource management policies.

Osunmakinde et al. (2013) and Archer (2018) noted that the primary contributors to compromised water quality and pollution are excess organic and inorganic substances derived from untreated and treated wastewater. Despite the goal of treating wastewater to meet national standards, ECs are not effectively removed during treatment because the treatment process does not specifically target them; moreover, they have been shown to accumulate in the environment and inevitably contribute to water pollution. Furthermore, little has been done to add ECs to water quality legislation in South Africa due to insufficient studies on the presence, risks, and short- and long-term of consistent exposure to ECs. The occurrence and fate of these microcontaminants are frequently neglected (Gani et al., 2021).

According to Schoeman et al. (2017), most conventional WWTPs in developing countries are primarily centred around the activated sludge process (ASP) because this process achieves the regulated effluent standards at reasonable operating costs. Conventional WWTPs are designed to reduce and/or eliminate various solids, dissolved organics, and nutrients through primary and secondary treatment processes depending on the level of contamination and the desired effluent quality (Alcala, 2015). However, conventional WWTPs are not designed to effectively reduce or completely remove ECs, leading to the discharge of ECs into water bodies (Stefanakis & Becker, 2015; Schoeman et al., 2017). Again, ECs have the potential to negatively affect the environment and living organisms (Geissen et al., 2015; Sorensen et al., 2015; Lamastra et al., 2016; Noguera-Oviedo & Aga, 2016). For example, PPCPs are

endocrine-disruptive substances that may impede the emergence and development of antimicrobial resistance in both humans and animals. Hormonal drugs interfere with the normal functioning of the endocrine system (ES). This disruption can lead to issues in the reproductive system, metabolic dysfunction, and developmental abnormalities. The ECDs can also significantly impact aquatic and terrestrial animals by inhibiting and modifying hormonal growth and cell functions (Yahaya et al., 2020).

The escalating demand for water has heightened concerns about the presence of ECs in wastewater, especially in direct wastewater reuse. Achieving effective removal of these ECs necessitates an assessment of the removal efficiency of ECs at different unit processes within the wastewater treatment process. To date, several studies have investigated alternative advanced treatment methods, such as activated carbon treatment, UV, advanced oxidation, and membrane filtration to effectively and efficiently remove ECs from wastewater (Rott et al., 2018; Ahmed et al., 2021; Ismail & Mokhtar, 2021; Kumar et al., 2022; Morin-Crini et al., 2022). Membrane filtration is an advanced treatment process that is expected to yield a high removal efficiency (Clodt et al., 2017; Zahid et al., 2018; Vasilachi et al., 2021; Morin-Crini et al., 2022).

1.6. Aim and Objectives

The study aims to prepare, characterise and investigate the efficiency of imidazolium-based PILs/polyvinylidene fluoride (PVDF) flat sheet membranes packed in Solid Phase Extraction (SPE) cartridges to remove diclofenac, cypermethrin, ibuprofen, and naproxen.

The objectives of the research report are to:

- Compile a comprehensive review of the literature exploring the characteristics, fate, and transportation of ECs in the environment and the current knowledge regarding the potential adverse effects of the presence of ECs on the natural environment and human health. Thus, highlighting the importance of removing these contaminants from the environment.
- Prepare the PVDF/imidazolium-based PILs flat-sheet membrane through thermally induced phase separation (TIPS).
- Characterise the prepared membranes using various identified methods to determine the membrane surface properties, pore size, porosity, and hydrophobicity or hydrophilicity.
- Determine the retention time and removal efficacy of prepared membranes.

1.7. Research Report Structure

The structure of the report is as follows:

Chapter 1: Introduces the research subject, highlights its relevance, and clarifies the aims and objectives of the research.

Chapter 2: A review of literature on the occurrence of emerging contaminants in the environment, their fate, behaviour and transformation in the complex matrix environment and highlighting the importance of removing these contaminants from the environment, followed by a discussion of removing ECs using membrane technology.

Chapter 3: Details the analysis procedures used for collection and analysis, as well as data processing.

Chapter 4: Results and Discussion.

Chapter 5: Summary of the results and their implications, conclusion of the research and recommendations and suggestions for future research.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

During water use, whether for domestic, agricultural, industrial, or other applications, various microcontaminants, including ECs, may be introduced, potentially causing adverse effects on both human health and the environment if not adequately treated (von Sperling, 2007; Aoyi et al., 2015; Sharma & Bhattacharya, 2017; Droste & Gehr, 2019). Recently, the presence of ECs like PPCPs and EDCs in water bodies have recently gained significant academic attention due to their persistence and potential toxicity (Pal et al., 2010; Meng et al., 2021;). In 2012, the European Commission listed several pharmaceuticals, including diclofenac, as priority hazardous substances (Petrie et al., 2015). Over 700 ECs have been identified in European water bodies (Geissen et al., 2015) prompting the development of the Water Framework Directive to protect water resources by establishing a priority list of ECs for regular monitoring. On the contrary, South Africa lacks comprehensive data on ECs. A study by Gani et al. (2021) found that, between 01 January 2000 and 30 April 2020, only 41 studies focused on ECs. Most of these studies addressed their occurrence and removal, with minimal attention given to risk assessment. Therefore, more studies must be conducted to determine the toxic effects and removal strategies of ECs. This will assist in the identification, listing and regulation of the priority ECs (Madikizela, 2024).

The WWTPs that process domestic sewage, hospital effluents, chemical manufacturing plant wastewater, livestock, and agriculture wastewaters are the primary sources of ECs that end up in water bodies such as rivers, aquifers, estuaries, and oceans (Petrie et al., 2015; Madikizela, 2024). From a global perspective, approximately 380 billion m^3 of wastewater are produced annually (Pratap et al., 2023). Of this volume, 268 billion m^3 is wastewater generated by households. Only 155 billion m^3 (58 %) of the generated wastewater is safely treated, while 113 billion m^3 (42 %) is not safely treated before being discharged into rivers or repurposed. Furthermore, only 60 % of water bodies have good ambient water quality (Du Plessis, 2022). According to WHO (2020), South Africa generates approximately 1700 million m^3 of domestic wastewater annually and only 41% of wastewater flow is safely treated, which means 59% of wastewater is not safely treated. The discharge of untreated wastewater presents significant risks to both aquatic ecosystems and human health. As a result, 71% of the country's water bodies are reported to have good ambient water quality (UN Water, 2022). The accumulation of water pollution in water bodies intensifies the pressures experienced by water management

authorities to deliver safe drinking water. Therefore, the improvement of water conservation is vital.

2.2. The Urban Water Cycle

The hydrological cycle is a conceptual model that depicts the continuous movement of water, both storage and circulation, between the Earth and the atmosphere (Marsalek et al., 2007; Allan 2012; Liu et al., 2017). As water moves between stages of the hydrological cycle, its quality and characteristics are changed. Also, the combined impact of urbanisation, industrialisation and population growth alters the hydrological cycle significantly. The hydrological cycle becomes more intricate in urban areas, given the multitude of anthropogenic influences and interventions, e.g., water supply systems, stormwater drainage networks, and wastewater collection and treatment systems. This more intricate cycle is termed the urban water cycle (UWC), and it incorporates water treatment, storage and circulation in the built environment and its interactions with the natural water system as illustrated in Figure 2.1.

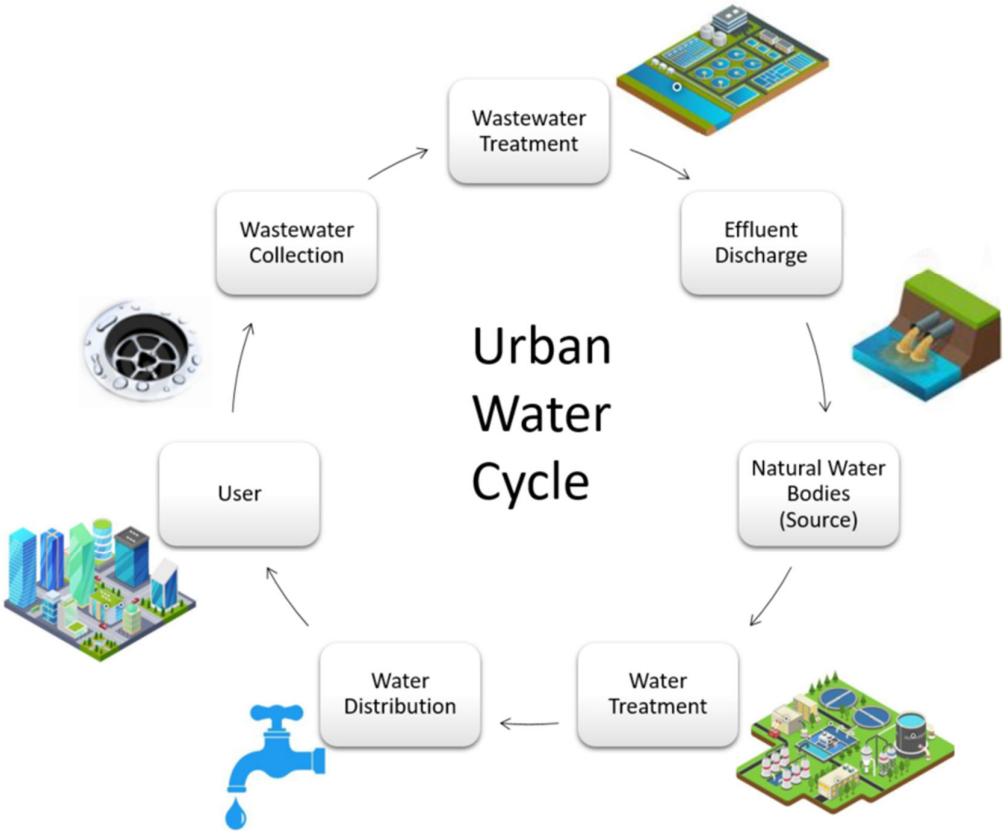


Figure 2.1: The Urban Water Cycle – Main Components and Flow of Water

Section 2.2 aims to highlight the influence of wastewater management on the sustainability of natural water bodies and the provision of safe drinking water. This research report has already established that wastewater is the most significant contributor to ECs found in natural water bodies. Two segments of the UWC are discussed, wastewater treatment and natural water bodies, to highlight the challenges South African water boards face in supplying quality drinking water. South Africa uses an open-loop system, meaning water and wastewater 'meet' in the environment. Therefore, activities in one segment cannot be isolated during analysis as they affect the next segment of the UWC. This means that the planning, design, construction, and water and wastewater infrastructure management are essential for water sustainability.

Hence, the Department of Water and Sanitation (DWS), as the custodians of nation's water resources, are entrusted with a legal obligation to preserve the integrity of these resources and to ensure the provision of adequate sanitation and wastewater systems. Therefore, a series of strategies, policies and legislation guide the provision and operation of sanitation and wastewater infrastructure and services. The National Water Service Act (NWSA), 1997, regulates the provision of sanitation and wastewater management in South Africa. The National Water Act (NWA), 1998, supports the NWSA as it regulates the effluent quality that may be discharged into receiving waters by WWTPs. The above-mentioned legislature and other policies and standards ensure that wastewater management is efficient in South Africa. The subsequent paragraphs discuss the status quo and management of wastewater infrastructure.

The official census (2022) conducted by Stats SA showed that the population was 60.6 million. When the size of the population is proliferating, there is a higher demand for freshwater and subsequently higher wastewater generation (Teklehaimanot et al., 2015). About 7.8 million South Africans were found to be living with HIV in 2022 (Human Sciences Research Council, 2022; Bisnauth, 2023). Although a national survey on the occurrence of pharmaceutical drugs has not been conducted, several studies have indicated the presence of this type of ECs in environmental and drinking water (Archer, 2018). Pharmaceutical drug concentrations found in the environment and ultimately, in drinking water are also increased by disposing of expired or unused medication in households (Kummerer, 2009; Stefanakis & Becker, 2015), amongst other pathways. The use of pharmaceutical products in the public and private sector are distinct (Osunmakinde et al., 2013). Table 2.1 indicates the 20 most prescribed drugs in both the public and private sectors. Overall, commonly prescribed drugs in the public health sector are hypertensive, analgesic, antiretroviral, and antibiotic drugs, in that order. Whereas the most prescribed drugs in the private sector are analgesic, expectorate, antihistamines, and anti-inflammatory, in that order (Osunmakinde et al., 2013). The data variance between the

public and private sectors shows the significance of the living standards and social environment among communities in each sector. Despite the complexity of the data and the challenges in measuring and interpreting prescription information, Table 2.1 serves as a valuable indicator of drug use. This is particularly noteworthy considering the numerous unknown factors and the absence of on-site measurements.

Table 2.1: Top 20 Most Prescribed Drugs in the Public and Private Sector

ITEM	PRODUCT	DRUG	CLASS
1	Ridaq	Hydrochlorothiazide	Hypertension
2	Austell Paracemol	Paracetamol 500 mg	Analgesic
3	Pharmapress	Enalapril maleate & Hydrochlorothiazide	Hypertension
4	Vitamin B Complex	Vitamins	Vitamins
5	Co-trimoxazole	Trimethoprim and sulfamethoxazole	antiretroviral (ARV)
6	Pacimol	Paracetamol 500 mg	Analgesic
7	Methyl Salicyl	Methyl salicylate	Non-steroidal anti-inflammatory drugs (NSAIDs)
8	Metformin	Metformin Hydrochloride	Antidiabetic
9	Amoxycillin	Amoxicillin	Antibiotics
10	Paracetamol	Paracetamol 500 mg	Analgesic
11	Adco-Dol	Paracetamol, 450 mg; Codeine, Caffeine	Analgesic
12	Alcophyllex	diphenhydramine, theophylline & etofylline	Cough mixture
13	Allergex	Chlorpheniramine maleate	Antihistaminic
14	DPH	Diphenhydramine	Antihistaminic
15	Panamor	Diclofenac sodium	Analgesic
16	Panado	Paracetamol 500 mg, codeine (8 mg	Analgesic
17	Broncleer with Cold	Diphenhydramine 125 mg, Codeine	Cough syrup
18	Corenza C	Aspirin, Chlorprophenpyridamine	Colds & flu
19	Sinucon	Phenylpropanolamine	Anti-itchiness
20	Sinuend	Chlorpheniramine and phenyltoloxamine	Antihistamines

Adapted from (Osunmakinde et al., 2013)

Figures 2.2, 2.3 and 2.4 indicate an improved standard of living in South Africa over a decade, reflecting an overall enhancement in quality of life and increased urbanisation. Urbanisation is closely associated with the proliferation of ECs in wastewater and water bodies (Vasilachi et al., 2021). Figure 2.2 highlights an improvement in housing conditions, with formal settlements rising from 65.1% in 1996 to 79.2% in 2016. Figure 2.3 illustrates the progress in sanitation services, showing increased access to formal sanitation. However, pit toilets remain widely

used, particularly in rural areas. According to the South African Institution of Civil Engineering (SAICE) (2017), many schools, clinics, and government facilities in rural regions continue to rely on poorly maintained pit toilets, some of which have been neglected to the point of becoming unusable. It must be noted that despite the progress discussed above, the overall condition of the country's infrastructure has been steadily deteriorating due to lack of maintenance. In 2022, South Africa received an Infrastructure Report Card (IRC) score of D, down from D+ in 2017, indicating that infrastructure is under strain, inadequately maintained, and at risk of failure (SAICE, 2022). Figure 2.4 shows improvements in water service delivery; however, many communities still lack access to piped water and must rely on alternative sources. A significant portion of the South African population lives in rural or underdeveloped areas, where water infrastructure is insufficient. These communities pose higher risk of contaminating water sources, as they often depend on surface waters, such as rivers, streams, and dams, as their primary water supply (Petersen, 2016). As a result, effective pollution control and sufficient wastewater treatment are essential to safeguard water quality for downstream users.

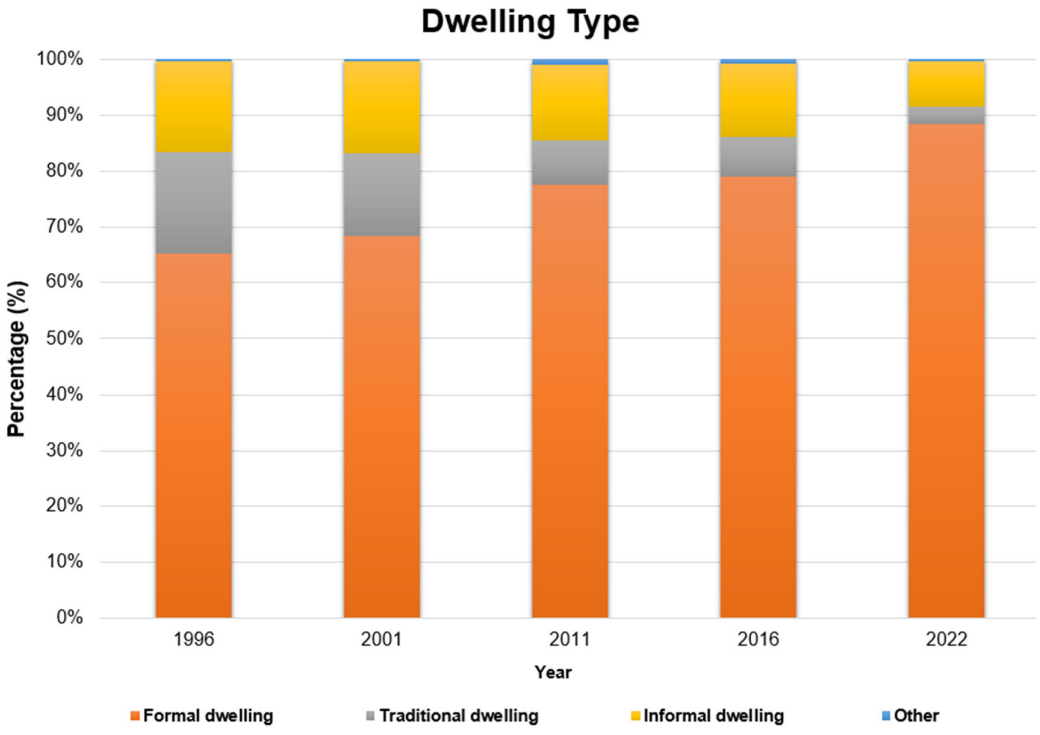


Figure 1.2: Dwelling Type in South Africa *(Stats SA, 2016; Stats SA, 2022)*

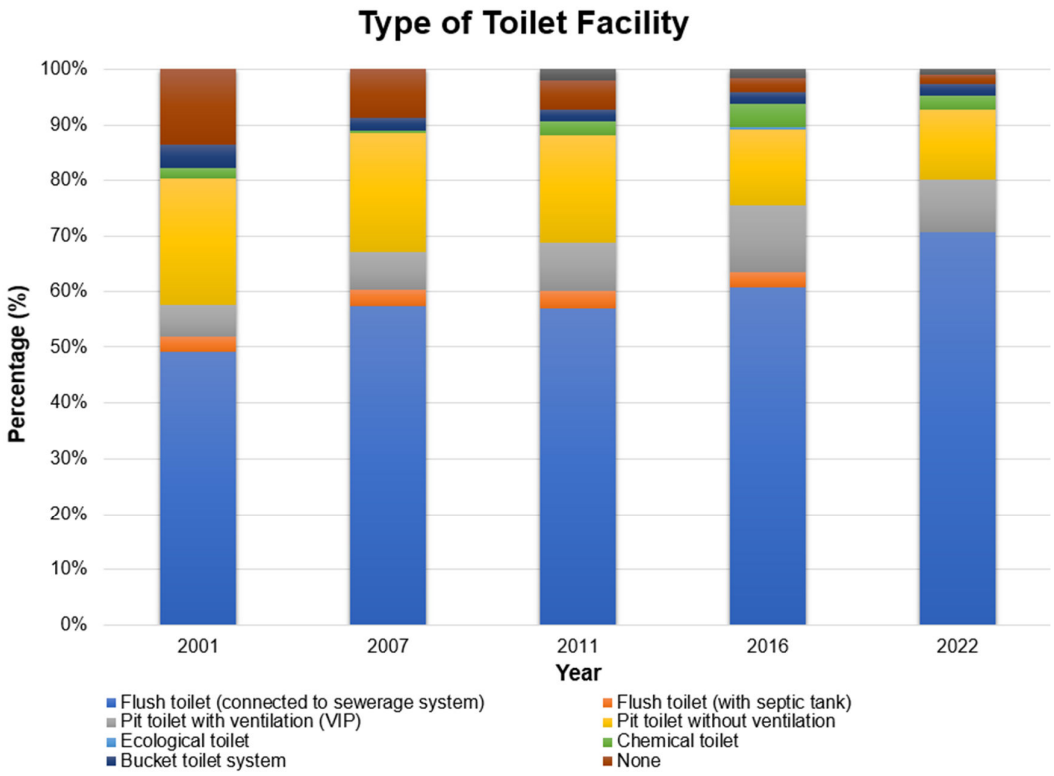


Figure 2.2: Type of Toilet Facility in South Africa *(Stats SA, 2016; Stats SA, 2022)*

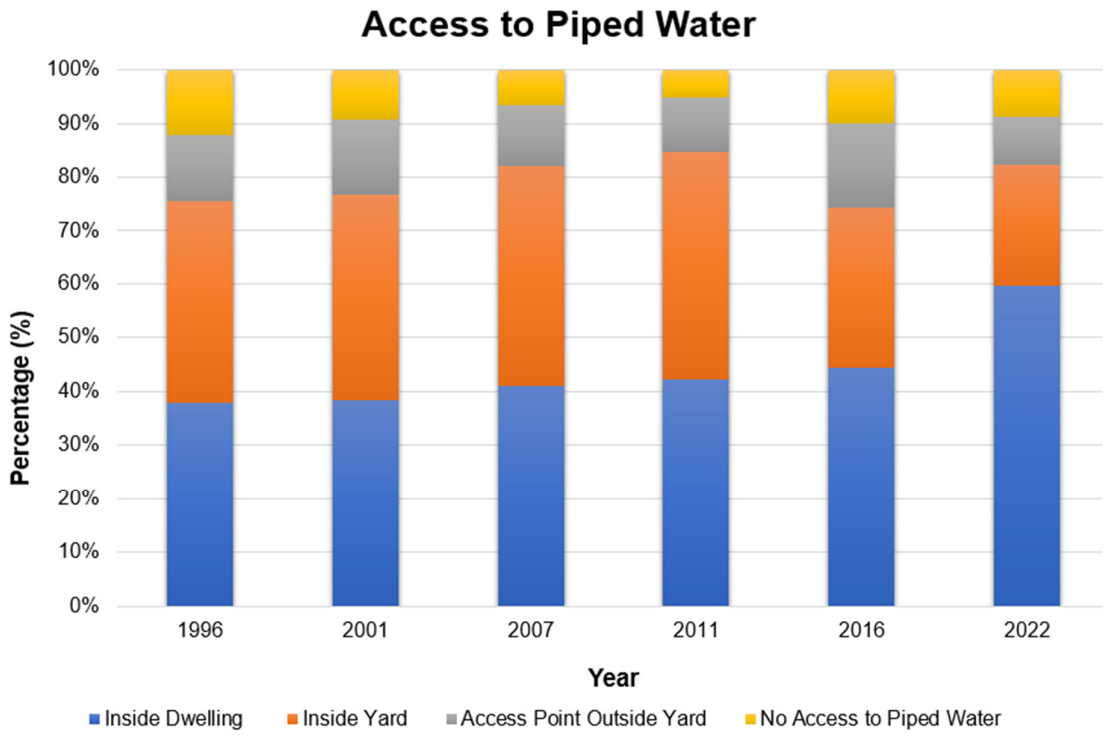


Figure 2.3: Access to Piped Water *(Stats SA, 2016; Stats SA, 2022)*

The major challenge experienced by households within their respective municipalities is the lack of a safe and reliable water supply. Only 82.4% of the surveyed communities had access to safe drinking water supply services (Stats SA, 2022). Hence, upgrading water conservation methods, efficient use of water, and improved water quality are of great importance to managing the integrity of natural water bodies. South Africa already has excessively strained water supply systems and water resources as water demand exceeds the available water supply (SAICE, 2017). More than 60% of South African water bodies are being overexploited; a third of the main rivers in the country are in good condition, while a quarter of the river ecosystems are critically endangered (Donnenfeld et al., 2018).

The prevailing conclusion from the above statistics and discussion is that wastewater management plays a crucial role in ensuring the sustainability of South Africa's natural water bodies and the provision of safe drinking water. The integration of water and wastewater systems within the environment highlights the need for comprehensive planning and effective infrastructure management. Despite progress in housing and sanitation services, significant challenges remain, including deteriorating infrastructure, inadequate access to water, and the growing presence of ECs. Addressing challenges requires improved pollution control, enhanced wastewater treatment, and stricter regulatory enforcement to protect public health and the environment.

Table 2.2 summarises the various groups of ECs found in the South African aquatic ecosystems. The potential toxicity and negative environmental impacts of ECs call for their removal from wastewater and natural water resources.

Table 2.1: Various groups of ECs found in the Water Bodies in South Africa

EMERGING CONTAMINANT	ORGANIC CONTAMINANTS	CONCENTRATIONS	REMARKS
NON-STEROIDAL ANTI-INFLAMMATORY	Ketoprofen	1.31µg/L	Pharmaceuticals in Umgeni River water system, KwaZulu-Natal
	Diclofenac	2.16 µg/L	
		1.1 - 15.6 µg/L	Surface water in KwaZulu-Natal
		0.3 - 2.2 µg/L	Surface water in Gauteng
		0.6 - 8.2 µg/L	Surface water in KwaZulu-Natal
	Aspirin	3.54 µg/L	
		2.2 – 10.0 µg/L	Surface water in KwaZulu-Natal
		13.7 – 25.4 µg/L	Surface water in KwaZulu-Natal
	Acetaminophen	16.06 µg/L	Surface water in KwaZulu-Natal

		5.8 - 58.7 µg/L	Surface water in KwaZulu-Natal
		0.02 - 0.2 µg/L	Surface water in Gauteng
	Ibuprofen	0.8 – 18.9 µg/L	Surface water in KwaZulu-Natal
		0.4 – 0.7 µg/L	Surface water in KwaZulu-Natal
		0.1 – 0.6 µg/L	Surface water in Gauteng
		0.81 µg/L	Umgeni River
		84.60 µg/L	Surface water in Msunduzi river
	Naproxen	0.2 – 1.9 µg/L	Surface water in Gauteng
ANTIRETROVIRALS	Zalcitabine	36.0 ng/L	Compounds used for HIV treatment in surface waters
		0.07 µg/L	Surface water in Free State
		0.03 µg/L	Surface water in Gauteng
		0.008 µg/L	Tap water in Gauteng
	Tenofovir	192.3 ng/L	
		0.25 µg/L	Surface water in Gauteng
		0.16 – 0.19 µg/L	Surface water in Free State
	Lamivudine	106.9 ng/L	
		0.09 – 0.24 µg/L	Surface water in Gauteng
	Didanosine	26.5 ng/L	
		0.05 µg/L	Surface water in Free State
	Stavudine	431.4 ng/L	
		0.41 – 0.78 µg/L	Surface water in Gauteng
	Nevirapine	0.24 – 1.48 µg/L	Surface water in Gauteng
	Lopinavir	0.28 – 0.31 µg/L	Surface water in Gauteng
PESTICIDES	Atrazine	0.15 µg/L	Drinking water in Johannesburg
	Terbuthylazine	0.15 µg/L	
	Carbamazepine	0.0015 µg/L	
ENDOCRINE DISRUPTING COMPOUNDS	Estrogen	0.16-16.0 ng/L	Surface, ground and river waters
FLAME RETARDANTS	BDE-28[c]	100 pg/L	PBDEs congeners in landfill leachate from a landfill site at Garankuwa
	BDE-47[d]	2670 pg/L	
	BDE-66[e]	290 pg/L	
	BDE-71[f]	2430 pg/L	
	BDE-75[g]	941 pg/L	

	BDE-85[h]	1240 pg/L	
HUMAN INDICATORS	Caffeine	0.1 – 3.3	Surface water in KwaZulu-Natal
		0.6 – 6.6	Surface water in Gauteng

Adapted from (Archer 2018; Gwenzi & Chaukura, 2018)
[a] 4'-dichloro-diphenyldichloroethylene
[b] 4,4'-dichloro-diphenyl-trichloroethane
[c] 2,4,4'-Tribromodiphenyl ethers
[d] 2,2',4,4'-Tetrabromodiphenyl ethers
[e] 2,3',4,4'-Tetrabromodiphenyl ethers
[f] 2,3',4',6-Tetrabromodiphenyl ethers
[g] 2,4,4',6-Tetrabromodiphenyl ethers
[h] 2,2',3,4,4'-Pentabromodiphenyl ethers.

The ECs that remain after going through wastewater treatment effluent are likely to end up in water bodies, the broader environment and ultimately, in drinking water. Therefore, it is imperative that more research is conducted to ascertain the amounts, fate, and potential environmental risks of these ECs.

2.3. Wastewater Treatment

2.3.1. Objectives of Wastewater Treatment

The primary aim of wastewater treatment is to eliminate harmful constituents from the wastewater before discharging it into receiving water bodies (EPA, 1998). WWTPs aim to (1) remove pathogens to protect human, animal, and plant health, (2) reduce nitrogen and phosphorus concentrations as excess nutrients cause eutrophication in natural water bodies, (3) reduce oxygen-demanding wastes, (4) operate efficiently and effectively in terms of power, energy and costing thereby creating a sustainable treatment plant (5) decrease the production of sludge and (6) extract recoverable resources, heat, and chemical energy in wastewater.

2.3.2. Sources of Wastewater

Wastewater is water whose physical, chemical and/or biological properties have been altered due to the introduction of constituents through various applications. It is now considered unsafe for most uses without treatment (Bani & Amoatey, 2011). It is essential to understand the nature of wastewater for the design, operation, and management of collection systems, treatment and reuse facilities, and protection of public and environmental integrity (Metcalf & Eddy, 2014). The source of the wastewater determines the wastewater's characteristics and how it must be treated (UN-Water, 2015; Bui et al., 2019). Generally, domestic wastewater contains faeces and urine, grease, scum, detergents, etc., while industrial wastewater contains a wide range of strong chemical contaminants, organic wastes, metals, and high-temperature wastes and agricultural waste streams may contain pesticides, salts, and fertilisers, and other compounds. Groundwater flowing through mineral deposits can introduce

arsenic, antimony, and fluoride into collection systems. Whereas air pollutants emitted from coal combustion (Masters & Ela, 2014) can mix thoroughly in the troposphere and be transported over distances, local to global ranges. Thereafter, it can be deposited into water bodies through wet and dry depositions. Some may be re-emitted into the atmosphere and continuously cycle between air and water phases (Kim & Zoh, 2021). Complexities arise when contaminants are introduced into the water from natural resources and human sources through non-aqueous routes (Masters & Ela, 2014). Figure 2.5 shows the various wastewater sources.

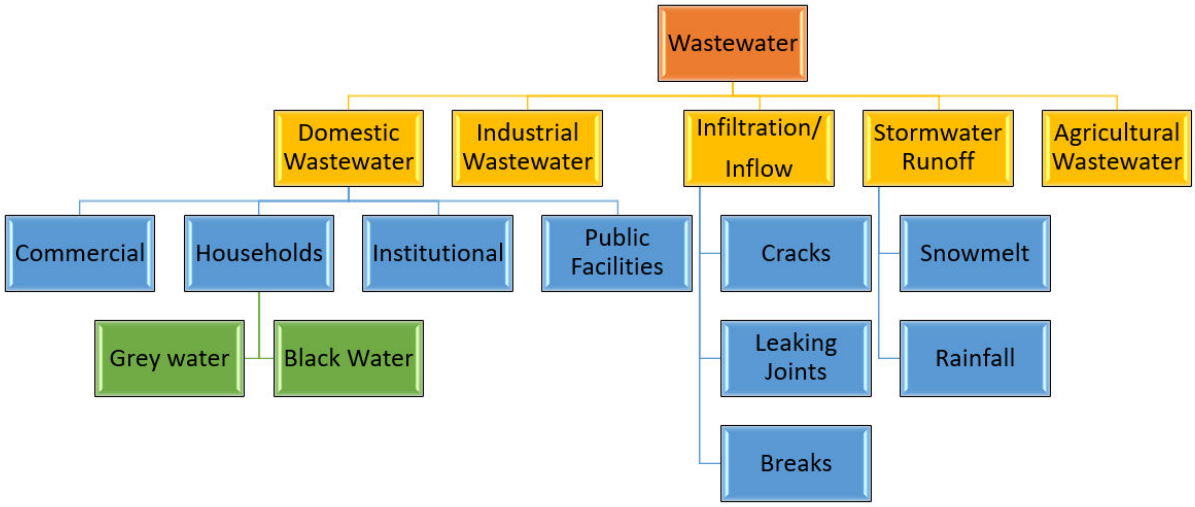


Figure 2.4: Common Wastewater Sources

2.3.3. State of Wastewater Management in South Africa

South African wastewater treatment plants (WWTPs) are being overloaded by a variety of chemical pollutants in increased volumes (Archer, 2018). Among others, these contaminants are pharmaceutical drugs, including antibiotics, anti-epileptics, diabetes medications, antihistamines, illicit drugs, and non-steroidal anti-inflammatory drugs (NSAIDs) (Daughton & Ternes, 1999; Kasprzyk-Hordern et al., 2009; McEneff et al., 2015; Schoeman et al., 2017; Archer, 2018). A prominent challenge in this century is the rising pollution of freshwater bodies due to increased chemical contamination (Lamastra et al., 2016).

As such, the Green Drop Certification Programme for Wastewater Quality Management Regulation has been put in place to ensure that legislature requirements are followed. It is an incentive-based regulation that ensures that service providers meet requirements and that public health is protected from potentially unsafe and unsustainable practices. To acquire the Green Drop Status, a wastewater treatment plant must achieve a score of 90% or higher when

scored. The process measures and compares results against pre-set stringent limits and standards for the disposal of wastewater effluent (Burges, 2016). Disposal standards listed in the National Water Act: Government Notice No. 991 of 1984 ensure that water authorities properly manage and regulate wastewater treatment plants so that they do not contaminate freshwater sources.

SAICE (2017) reported that sanitation infrastructure in South Africa is in a concerning condition partly due to the lack of maintenance and refurbishment of collection systems and treatment facilities. Other common challenges include poor enforcement of policies and laws, poor governance, inadequate and unsustainable financial planning, corruption, lack of skills to operate and manage modern technologies, and vandalism in the form of informal and illegal connections. In 2017, DWS reported that 66% of WWTPs required intervention, 35% had insufficient capacity, and 56% lacked adequate staff with skills and knowledge to operate and manage the plant (SAICE, 2017). Essentially, 40% of South Africa's wastewater remained untreated (Donnenfeld et al., 2018). SAICE (2022) reported that although some wastewater systems presented excellent results, others were still in critical condition. However, overall, the standards, state, and performance of the WWTPs have dropped over the past five years. The 2023 Green Drop Watch Report shows that 39% of the 850 WWTPs in South Africa are in a critical state, which means they received a Green Drop Score of less than 31%. Only 8% of WWTPs are in the low-risk category, and 34% are in the medium-risk category (Department of Water and Sanitation, 2023). DWS (2023) also noted that the key issues were (1) funding constraints, (2) theft and vandalism, (3) sewer spillages, (4) lack of technical capacity at municipalities, (5) operations and maintenance issues at the municipal level and (6) the ongoing deterioration of infrastructure.

Furthermore, the performance of WWTPs may also be negatively affected to the extent that they may fail to produce effluent that meets the national regulatory standards, especially in densely populated areas (Musingafi, 2014; Teklehaimanot et al., 2015). When a WWTP is inundated by sewage, surpassing its capacity, including temporary storage facilities, partially treated or untreated wastewater may be discharged into receiving waters (Department of Human Settlements, 2019). Disposal of non-compliant effluents into freshwater resources leads to deteriorated water quality, which poses health risks to downstream users and the ecosystem. Poor sanitation and contaminated water are associated with the transmission of diseases such as cholera, hepatitis A, typhoid, dysentery, and polio (WHO, 2019). The reasons stated above motivate the need for wastewater treatment for reuse or disposal into the environment to safeguard the public.

Considering the state of WWTPs in South Africa, additional interventions are required to improve wastewater treatment in the country. A wastewater effluent that is compliant with national laws will improve the conservation of water bodies. This will ultimately lead to an increase in the quantity of water supply and improve water quality (Donnenfeld et al., 2018). Table 2.3 shows ECs commonly found in drinking water. Drinking water treatment can be costly if the natural water body from which the water is being abstracted is highly polluted. Furthermore, this makes water resource management unsustainable. Hence, ensuring WWTPs comply with the national regulatory standards is important.

Table 2.2: Various groups of ECs found in Wastewater Influent

EMERGING CONTAMINANT	ORGANIC CONTAMINANTS	CONCENTRATIONS µG/L	REMARKS
NON-STEROIDAL ANTI-INFLAMMATORY	Ketoprofen	1.7 – 6.4	WWTPs in KwaZulu-Natal
		1.2 -4.3	WWTPs in KwaZulu-Natal
		0.02	WWTPs in Gauteng
		0.0001	WWTPs in Gauteng
		3.2	WWTPs in KwaZulu-Natal
		0.4	WWTPs in KwaZulu-Natal
		0.4 – 5.6	WWTPs in Gauteng
		0.2 – 0.7	WWTPs in Gauteng
	Diclofenac	222.7	WWTPs in KwaZulu-Natal
		123.7	WWTPs in KwaZulu-Natal
		2.7 – 5.6	WWTPs in Gauteng
		2.2 – 2.5	WWTPs in Gauteng
	Acetaminophen	5.8	WWTPs in KwaZulu-Natal
		136.9 – 343.6	WWTPs in Gauteng
		0.04 – 0.2	WWTPs in Gauteng
	Ibuprofen	39.8	WWTPs in Gauteng
		12.6	WWTPs in Gauteng
		111.9	WWTPs in Gauteng
		24.6	WWTPs in Gauteng
		0.02	WWTPs in Gauteng
		1.2	WWTPs in KwaZulu-Natal
		1.1	WWTPs in KwaZulu-Natal
		62.8	WWTPs in KwaZulu-Natal
		58.7	WWTPs in KwaZulu-Natal
		9.1 – 15.8	WWTPs in Gauteng
		0.3 – 1.2	WWTPs in Gauteng

	Naproxen	55.0	WWTPs in Gauteng
		13.5	WWTPs in Gauteng
		52.3	WWTPs in Gauteng
		20.4	WWTPs in Gauteng
		2.9 – 5.5	WWTPs in Gauteng
		1.8 – 2.9	WWTPs in Gauteng
ANTIRETROVIRALS	Ribavirin	0.02	WWTPs in Gauteng
		0.00004	WWTPs in Gauteng
	Famciclovir (Famvir)	0.02	WWTPs in Gauteng
		0.00006	WWTPs in Gauteng
	Zidovudine	0.45 – 0.97	WWTPs in Gauteng
	Lopinavir	0.13	WWTPs in Gauteng
HUMAN INDICATORS	Caffeine	4.5	WWTPs in KwaZulu-Natal
		0.6	WWTPs in KwaZulu-Natal
		5.1 – 1214.4	WWTPs in Gauteng
		0.5 – 3.8	WWTPs in Gauteng

Adapted from (Archer, 2018)

2.3.4. Wastewater Treatment Processes and Levels of Treatment

Wastewater contaminants can be removed by physical, chemical or biological means. Depending on the level of treatment that a WWTP is capable of, it can be classified as a primary, secondary or advanced treatment plant. There are two main approaches: (1) conventional and (2) advanced wastewater treatment processes. Conventional methods comprise activated sludge, biological filtration, primary settling, coagulation, secondary sedimentation, and sand filtration. Advanced processes comprise reverse osmosis, ozonation, UV irradiation, photolysis (UV/hydrogen peroxide), biomembrane, ultrasound, and a combination of these methods. The removal efficiency of different treatment processes, as shown in Table 2.4, is influenced by the physical and chemical characteristic and the diversity of the contaminant (Osunmakinde et al., 2013; Masters & Ela, 2014; Metcalf & Eddy, 2014). It is important to emphasise that removal technologies should be practical and efficient, ensuring effectiveness while being financially viable and environmentally friendly.

Table 2.3 Wastewater Treatment Processes

TREATMENT LEVEL	TREATMENT PROCESS	REMOVAL
PRELIMINARY	• Screening • Degritting • Pre-aeration • Flow metering and sampling	Wastewater constituents that may cause operational problems include rags, sand, sticks, floatable items, grease, and grit.
PRIMARY	• Sedimentation and flotation	Settleable suspended solids (SS) and other organic matter use physical treatment mechanisms.
SECONDARY	• Biological treatment • Sedimentation	Biodegradable organic matter (BOM) (in solution or suspension) and other suspended solids not removed during primary treatment, including nutrients like nitrogen and phosphorus. Conventional secondary treatment typically includes disinfection.
TERTIARY	• Granular medium filters • Cloth filters • Micro-screens • Biological treatment	Residual suspended solids, Pathogens, non-biodegradable compounds, metals, inorganic dissolved solids, remaining suspended solids and nutrients. Disinfection is typically a part of tertiary treatment.
ADVANCED	• Membrane filtration • Reverse osmosis (RO)	Dissolved and suspended materials remaining after normal biological treatment.
BIOSOLID TREATMENT	• Digestion • Disposal	Reduces pathogen levels, stabilises the remaining matter and overall reduces solids.

Adapted from (Metcalf & Eddy, 2014; Pennsylvania DEP, 2016)

The presence of various pharmaceutical drugs in water bodies has also generated much interest from researchers, primarily due to the disposal of inadequately treated wastewater. However, there is still limited knowledge on ECs like pharmaceuticals and their degradation products in South Africa, partly due to the lack of information on the effects and concentration levels, making it difficult to regulate, monitor, and manage these ECs (Walters, 2017). The ECs are present at very low concentrations in WWTP influent, effluent waters, and freshwater sources. It has been reported that PPCPs are found in surface water at concentrations ranging

between *ng/L* and *µg/L* (Gros et al., 2009; Grujic et al., 2009; Ebele et al., 2017; Yahaya et al., 2020). Although they are not detected frequently, most of the chemicals were also found to be present in drinking water (Zuccato et al., 2000; Benotti et al., 2009), drinking water distribution systems (Benotti et al., 2009), and in groundwater (McEachran et al., 2016).

The Activated Sludge Process (ASP) is the most commonly applied treatment process that produces the required effluent standard at feasible operating costs. Pharmaceutical compounds are more likely to form conglomerates (Noguera-Oviedo & Aga, 2016; Schoeman et al., 2017). Thus, sludge sorption processes will not effectively remove them (Stefanakis & Becker, 2015). Other ECs can penetrate throughout treatment and natural filtration mechanisms due to their physical and chemical characteristics, such as their high solubility and poor biodegradability (Janssens et al., 1997; Petrovic et al., 2003; Schoeman et al., 2017). Two critical processes adsorption onto suspended solids (wastewater sludge) and biodegradation. The effectiveness of adsorption hinges on hydrophobic and electrostatic interactions between pharmaceuticals and particulates, as well as microorganisms. Notably, acidic pharmaceuticals, such as acetylsalicylic acid, ibuprofen, fenoprofen, ketoprofen, naproxen, diclofenac, and indomethacin (with pKa values ranging from 4.1 to 4.9), along with clofibric acid, bezafibrate (pKa 3.6), and gemfibrozil, exist as ions at neutral pH and exhibit minimal affinity for adsorption onto sludge. However, their adsorption propensity increases under lower pH conditions. When the pH is neutral, negatively charged pharmaceuticals primarily exist in a dissolved state. Therefore, biodegradation is suggested for the removal of pharmaceuticals. Typically, the sorption of acidic pharmaceuticals to sludge is considered to have minimal significance in the overall removal from both wastewater and water bodies. As a result, monitoring studies have consistently shown relatively low concentrations of pharmaceuticals in treated sludge and sediments. This indicates that eliminating these acidic pharmaceuticals through sorption to sludge is not very effective.

Pharmaceutical biodegradation can take place in aerobic and anaerobic zones within the ASP, or alternatively, under anaerobic conditions during wastewater sludge digestion (Tambosi et al., 2010).

Generally, the effectiveness of removing pharmaceuticals from wastewater tends to improve with longer retention times (Tambosi et al., 2010). For example, Tambosi et al. (2010) concluded that diclofenac was shown to degrade more effectively when the age of the sludge was a minimum of 8 days. However, pharmaceuticals like carbamazepine were poorly removed regardless of the hydraulic retention times. Table 2.5 shows the removal efficiencies of the processes discussed; overall, ASPs were found to be more efficient in removing PPCPs

than biological processes. However, the study conducted by Tambosi et al. (2010) showed that advanced treatment processes were more effective.

Table 2.4: Removal Efficiencies of PPCPs Using Various Wastewater Treatment Processes

TYPE	SOURCE OF WASTEWATER	REMOVAL EFFICIENCY RANGE (%)
CONVENTIONAL WASTEWATER TREATMENT PLANT		
ACTIVATED SLUDGE	Raw	11 - 99
	Primary settled	7 - 100
	Not indicated	8 - 98
BIOLOGICAL FILTRATION	Primary settled	6 – 71
PRIMARY SETTLING	Not indicated	3 – 45
COAGULATION, FILTRATION AND SETTLING	Not indicated	5 – 36
SAND FILTRATION	Activated sludge effluent	0 - 99
ADVANCED WASTEWATER TREATMENT PLANT		
OZONATION	Activated sludge effluent	1 - 99
	Secondary effluent	86 - 100
OZONATION/ULTRASOUND AND SONOCATALYSIS	Not indicated	23 - 45
OZONATION AND CATALYTIC OZONATION	Not indicated	> 9 -10
UV IRRADIATION	Not indicated	29
PHOTOLYSIS HYDROGEN PEROXIDE	Not indicated	52 – 100
DARK & LIGHT FENTON	Not indicated	80 – 100
UV/TIO_2	Not indicated	> 95
BIOMEMBRANE	Treated effluent	23 – 99
REVERSE OSMOSIS	Secondary treated effluent	62 – 100
ULTRASOUND	Not indicated	24 – 100
GRIT-BIOLOGICAL REACTOR-CLARIFIER-SAND FILTRATION-OZONATIONBIOLOGICAL ACTIVATIONCARBON-MICROFILTRATIONUV-CHLORINATION	Wastewater	> 90

GRIT-ACTIVATED SLUDGE/UVMICROFILTRATION-REVERSE OSMOSIS	Wastewater	> 90
GRIT-ACTIVATED SLUDGEUV-MICROFILTRATIONCHLORINATION-REVERSE OSMOSIS	Wastewater	> 90

Adapted from (Osunmakinde et al., 2013)

2.4. Emerging Contaminants in the Environment

2.4.1. Introduction

Understanding the occurrence and presence of emerging contaminants (ECs) is essential due to their potential to harm both aquatic ecosystems and human health. Given these risks, it is critical to detect, identify, monitor, and quantify ECs and their metabolites in environmental matrices. This discussion will focus on the urgency of addressing EC contamination, highlighting the methods and technologies required for effective detection and management to protect environmental and public health

2.4.2. Classification of Emerging Contaminants

The ECs can be grouped into more than 20 different classes depending on their origin and characteristics. Figure 2.6 shows the types of ECs grouped according to their varying physical and chemical properties. The first distinction is classifying the contaminant as a substance or particulate contaminant. Particulate contaminants are nanomaterials and microplastics. Substance contaminants are categorised into organic and inorganic matter. Organic contaminants include persistent bio-accumulative and toxic substances (PBTs) and other organic matter. Organic contaminants are primarily from households, industries, hospitals (Geissen et al., 2015), and agriculture (Witte, 1998). Trace metals are classified as inorganic substance contaminants (Geissen et al., 2015).

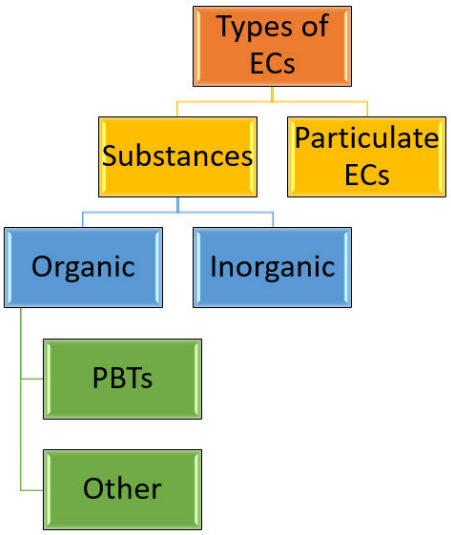


Figure 2.5: Types of Emerging Contaminants

Adapted from (Geissen et al., 2015)

Table 2.6 lists the major EC groups. The ECs are categorised considering their different properties listed below:

- CMR: carcinogenic, mutagenic, toxic to reproduction,
- EDCs: toxic contaminants,
- PBT: persistent, bioaccumulative, toxic,
- vPvB: very persistent, very bioaccumulative,
- POP: persistent organic pollutant (based on their environmental properties),
- PPCPs: pharmaceuticals and personal care products (based on their usage),
- Priority pollutants (regulated),
- Xenobiotics, exotics (foreign vs endogenic pollutants),
- Toxicants, toxins, toxics (based on the overall toxicity), and
- HPV: high production volume chemicals (Stefanakis & Becker, 2015).

Table 2.5: List of Major Emerging Contaminant Groups

EC GROUP	EXAMPLES
PHARMACEUTICALS	
HUMAN ANTIBIOTICS AND VETERINARY	Trimethoprim, erytromycine, amoxicillin, lincomycin, sulfamethaxozole, chloramphenicol
ANALGESICS, ANTI-INFLAMMATORY DRUGS	Ibuprofen, diclofenac, paracetamol, codein, acetaminophen, acetylsalicilyc acid, fenoprofen, acetaminophen, naproxen
ANTIRETROVIRAL DRUGS	Co-trimoxazole, acyclovir, abacavir, lamivudine, nevirapine oseltamivir, penciclovir, ribavirin, stavudine, zidovudine
PSYCHIATRIC DRUGS	Diazepam, carbamazepine, primidone, salbutamol, meprobamate, Carbamezapime
STEROIDS AND HORMONES	Estrone (E1), 17-β-estradiol (E2), and 17-α-ethynilestradiol (EE2)
ILLICIT DRUGS	Cocaine: (benzoylmethecgonine), methamphetamine, heroine, narcotic analgesic: (codine, hydrocodone, morphine, oxycodone, methadone, buprenorphine), benzodiazepines: (alprazolam, clonazepam, diazepam lorazepam) and club drugs: (ketamine, 1-(3-trifluromethylphenyl) piperazine (TFMPP)
B-BLOCKERS	Metoprolol, propranolol, timolol, atenolol, sotalol, salbutamol, atenolol, theophylline, and metoprolol.
LIPID REGULATORS	Bezafibrate, clofibric acid, fenofibric acid, etofibrate, gemfibrozil
X-RAY CONTRASTS	Lopromide, iopamidol, diatrizoate
PERSONAL CARE PRODUCTS (PCPS)	
FRAGRANCES	Nitro, polycyclic and macrocyclic musks, phthalates
PRESERVATIVES	Parabens (alkyl-p-hydroxybenzoate), Parabens (alkyl-p hydroxybenzoate), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT)
SUN-SCREEN AGENTS	Benzophenone, methylbenzylidene camphor, 2-hydroxy-4-methoxybenzophenone, 2-Ethylhexyl-4- methoxycinnamate
INSECT REPELLENTS	N, N-diethyltoluamide (DEET)
DISINFECTANTS AND ANTISEPTICS	Triclosan, Biphenylol, 4-chlorocresol, chlorophene, bromophene, 4-chloroxylenol and tetrabromo-o-cresol
ENDOCRINE DISRUPTING CHEMICALS (EDCS)	Octylphenols, nonylphenols, Di(2-ethylhexyl)phthalate (DEHP)
HORMONES AND STEROIDS	Estradiol, estrone, estriol, diethylstilbestrol (DES)

PERFLUORINATED COMPOUNDS	Perfluorotoctane sulfonates (PFOs), perfluoroctanoic acid (PFOA)
SURFACTANTS AND SURFACTANT METABOLITES	Alkylphenol ethoxylates, 4-nonylphenol, 4-octylphenol, alkylphenol carboxylates
FLAME RETARDANTS	Polybrominated diphenyl ethers (PBDEs): polybrominated biphenyls (PBBs) – polybrominated dibenzo-p-dioxins (PBDDs) – polybrominated dibenzofurans (PBDFs), Tetrabromo bisphenol A, C10-C13 chloroalkanes, Tris (2-chloroethyl)phosphate, Hexabromocyclododecanes (HBCDs)
INDUSTRIAL ADDITIVES AND AGENTS	Chelating agents (EDTA), aromatic sulfonates
GASOLINE ADDITIVES	Dialkyl ethers, Methyl-t-butyl ether (MTBE)
ANTISEPTICS	Triclosan, chlorophene

Adapted from (Osunmakinde et al., 2013; Geissen et al., 2015; Stefanakis & Becker, 2015; Yahaya et al., 2020)

2.4.3. Properties, Pathways and Transportation of Emerging Contaminants

There is a lack of knowledge of ECs pathways, properties and their effects (Lamastra et al., 2016). Petrovic et al. (2003) report that although more analytical methodologies are being developed for different EC groups, wastewater matrices are complex; thus, the currently available methods still need further 'polishing' to improve their selectivity and sensitivity. Various factors, e.g., the physiochemical properties of the ECs and water bodies parameters (e.g., pH, salinity and temperature), affect the occurrence, transportation, and fate of ECs in aquatic ecosystems. For instance, ECs may be soluble in water, making it easy for them to be introduced to aquatic ecosystems through runoff (Stefanakis & Becker, 2015) or ECs like ketoprofen, naproxen, and ibuprofen can be broken down by photosynthesis in the water bodies (Petrie et al., 2015). Furthermore, the transportation ECs from a diffuse source to water bodies depends on their properties. Whereas ECs transported via WWTPs (urban and industrial) effluent discharges are deposited directly into the water body, the primary concern is their fate (degradation, sorption, transport in aqueous phase) (Geissen et al., 2015). In essence, the properties of ECs define the lifetime of ECs in the environment (Stefanakis & Becker, 2015).

Moreover, the concentration of ECs varies as they are transported through different media (Teodosiu et al., 2018). For example, concentrations measured in surface waters are usually lower than those found in wastewater effluents, while concentrations are higher in surface

water compared to groundwater, as surface waters directly receive wastewater effluent streams and have shorter retention times compared to groundwater (Stefanakis & Becker, 2015). Due to their innate properties, the transportation mediums are mostly through aqueous forms and food chain dispersal (Ebele et al., 2017). Furthermore, Ebele et al. (2017) discussed that transportation through the different environmental mechanisms depends on the soil, sediment systems, and the behaviour and fate of the compounds within the WWTP.

Figure 2.7 illustrates the various origins and pathways of ECs in the environment. It comprises a schematic of the various points and diffuse sources. The fundamental principle is to account for the whole cycle of compounds, from production and consumption to disposal routes.

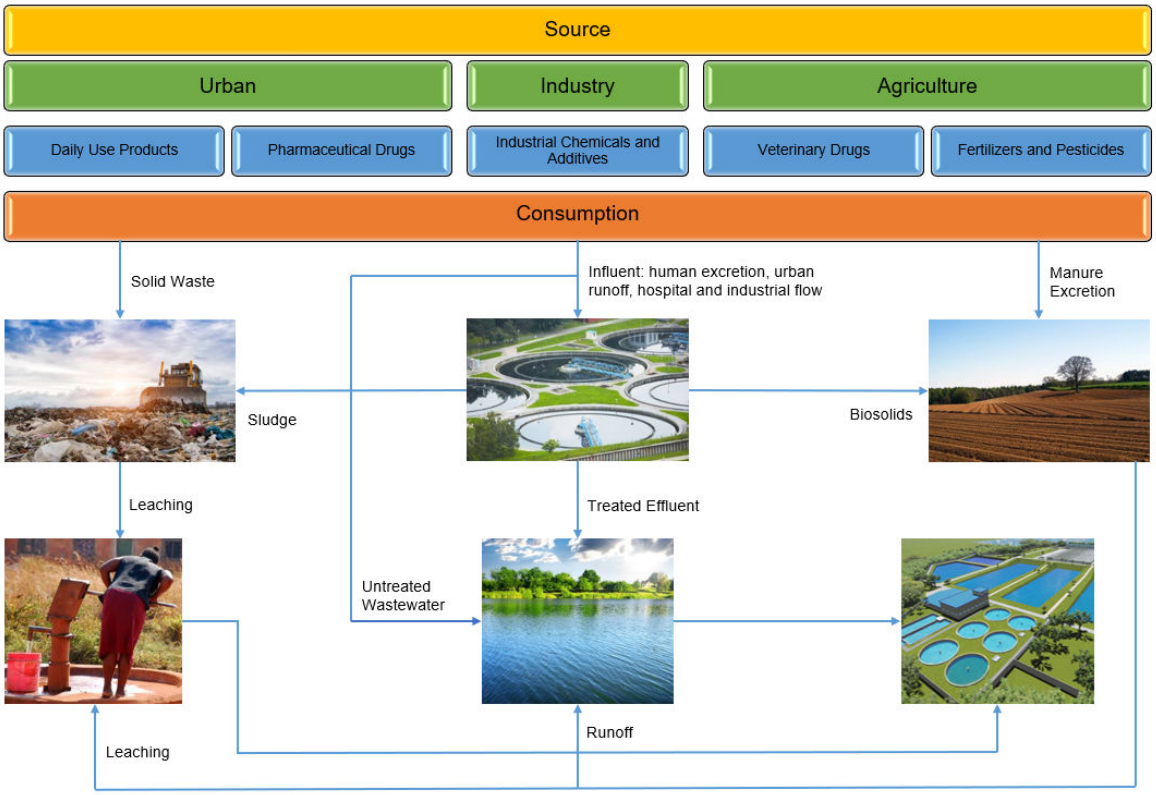


Figure 2.6: Numerous Paths and Interchanges of ECs Through Different Mediums *(Adapted from (Houtman, 2010; Lei et al., 2015; Stefanakis & Becker, 2015; Walters, 2017; Yahaya et al., 2020).*

One can see that urban and industrial wastes are generally point sources, while agricultural wastes are considered as diffuse sources. Diffuse sources are not easily attributed to a single source as they cover larger geographical areas. The exact source cannot be clearly defined; these include stormwater, terrestrial, urban, and agricultural runoff. Landfill sites are also considered as diffuse sources. Leachates containing several contaminants could potentially pollute groundwater. Point sources are emissions entering the body of water through visible,

confined, and distinct conveyance. These include WWTPs, industrial waste from medicine manufacturers, residual drugs in stormwater runoff and health facilities which contain waste discharge and other expired drugs. Contamination of this kind becomes an externality because it can affect a water body. Other pathways that introduce ECs into the environment include animal agriculture and aquaculture. In agriculture and aquaculture, antibiotics and other veterinary drugs are used for both prophylactic and other reasons. Furthermore, natural, and synthetic hormones are used to control reproduction and stimulate animal growth.

In addition, residential flows are also considered important point sources. As mentioned previously, high concentrations of ECs found in freshwater sources are due to inadequate wastewater treatment, overuse of drugs, disposal of expired or unused medication (Kummerer, 2009; Stefanakis & Becker, 2015), pesticides, industrial agricultural and animal farm streams (Teodosiu et al., 2018). Pharmaceutical drugs commonly found in drinking water are naproxen, ibuprofen, estrone, phenytoin, and atenolol. However, chronic exposure to these drugs remains unknown (Noguera-Oviedo & Aga, 2016). Human pharmaceuticals are generally excreted, either as non-metabolised parent compounds or as their metabolites, and thus end up in wastewater collection systems (Fent et al., 2006; Wille et al., 2010). Pharmaceuticals remain active even at low concentrations and ultimately degrade the quality of water bodies, consequently affecting the biosphere and humans (Mert et al., 2018). PPCPs are excreted from humans via urine, sweat, faeces and, at times, while bathing. For example, urine will have metabolised and unmetabolised conjugates that are vulnerable to hydrolysis. Meanwhile, human waste matter contains metabolites excreted through bile with unmetabolised conjugates that the gut cannot absorb. The degree of metabolism plays a crucial role in determining the excretion of unchanged or parent PPCPs. This metabolic process influences whether pharmaceuticals are excreted as metabolised or unmetabolised compounds through urine or faeces. Various literature has identified numerous metabolites, showcasing the complexity of the metabolic pathways involved (Osunmakinde et al., 2013). Table 2.7 shows various PPCPs and their metabolites.

Table 2.6: Pharmaceuticals, Personal Care Products and Their Metabolites

PHARMACEUTICAL	METABOLITES
IBUPROFEN	Hydroxy- Ibuprofen, 2- Hydroxy- Ibuprofen, Carboxy- Ibuprofen, Carboxy- Ihydratropic acid
NAPROXEN	O-Desmethyl-naproxen
ACETYLSALICYLIC ACID	Salicylic acid, Gentisic acid
KETOPROFEN	3-(Hydroxyl-carboxymethyl)-hydratopic acid 3-(Keto-carboxymethyl)-hydratopic acid

CARBAMAZEPINE	10, 11-Dihydro-10,11-epoxy carbamazepine, 10, 11-Dihydro-10,11-dihydroxy carbamazepine, 2 Hydroxy carbamazepine, 3 Hydroxy carbamazepine, 10 Hydroxy carbamazepine
SULFAMETHOXAZOLE	N_4-Acetysulfamethozazole
TRIMETHOPRIN	α-Hydroxy-trimethoprim Hydroxylated trimethoprim
ENALAPRIL	Enalaprilat
DICLOFENAC	3', 4,5-hydroxyl metabolites,3'-OH-4- methoxy, 4'5-dihydroxy diclofenac
ERYTHROMYCIN (HYDROLYSIS)	Dehydro-Erythromycin
ACETYL SALICYLIC ACID (ASA) (DEACETYLATION)	Salicylic acid, ortho-hydroxyhippuric acid, Gentistic acid (hydroxylated metabolite)

Adapted from (Osunmakinde et al., 2013)

Much focus has been placed on WWTP effluent being the primary source of pharmaceutical compounds. Whereas septic tank effluents are also contributors but are often overlooked. Functioning and malfunctioning septic tanks play a role in transporting these compounds in the environment. The fate of pharmaceuticals originating from septic tanks is poorly understood and still requires more research (Dougherty, 2011). According to Stats SA (2022), only 3.9% of households are connected to flush toilet systems and pour bucket-flush toilets connected to septic tanks. Therefore, the contribution to groundwater contamination through septic tanks is minimal in SA. Other pathways include treated wastewater that is used for irrigation and treated sludge that can be used as fertiliser in the agricultural sector (Lamastra et al., 2016). When biosolids and sludge are used for land application, ECs may be introduced into the environment. Pal et al. (2010) affirm this by stating that agricultural soils that are treated using pesticides, fertilisers and synthetic chemical substances have the potential to contaminate groundwater resources through seepage or direct discharge. It must be noted that most PPCPs are polar and hydrophilic and can easily leach from soils, sludge, and sediments (Ohoro et al., 2019). Predominantly, the higher the compound's hydrophilicity, the higher its concentration in the saturated phase. Conversely, the more hydrophobic the compound, the more it accumulates in the solid phase (Jones-Lepp & Stevens, 2007). More hydrophobic ECs are concentrated in biosolids and can desorb from biosolids and contaminate the soil and water. A complex matrix forms, making extracting and analysing these compounds displaced in biosolids extremely difficult. Hence, more studies are required on this topic. The addition of advanced treatment processes to conventional treatment plants like ozonation, UV oxidation, ultrasonication, thermal treatment, and bioaugmentation can be used to minimise ECs in biosolids (Noguera-Oviedo & Aga, 2016).

2.4.4. Environmental Risks Associated with Emerging Contaminants

Several of these chemicals that are used excessively daily, are persistent in the environment, and biologically active (Pal et al., 2010; Wille et al., 2010), display bioaccumulation and endocrine-disrupting properties (Caliman & Gavrilescu, 2009), biomagnification, toxicity, carcinogenic effects, hormone disruption, foetal malformation and in other cases show damages to the DNA structure (Teodosiu et al., 2018). The concerns about the occurrence of ECs in the aquatic ecosystems are their persistence, bioaccumulation (Ebele et al., 2017; Schoeman et al., 2017) and toxicity potential (Ebele et al., 2017). These are discussed in the subsequent sections.

2.4.4.1. Persistence

Geissen et al. (2015) reported that a high volume, more than 700 of ECs, their metabolites and transformation products are listed in the European aquatic ecosystem (www.norman-network.net). Presently, very little knowledge has been acquired about the levels of ECs that are present in the broader environment (Geissen et al., 2015; Ebele et al., 2017). As such, this area of study still requires further research. More specifically pharmaceuticals, since over 200 pharmaceuticals have been reported with concentrations up to 6.5 mg/L globally (Petrie et al., 2015). Pharmaceuticals and other ECs in the environment vary from region to region. It is also important to note that not all ECs are persistent. According to Ebele and colleagues (2017), many are considered 'pseudo-persistent' due to their continual extensive and increased use, and ultimate presence in water bodies. Compounds that normally degrade due to some environmental processes may behave as persistent compounds because of the constant release into the environment as the source replenishes (Wille et al., 2010). These contaminants have high removal rates and can easily form secondary pollutants, causing adverse environmental effects due to their continuous introduction into the water bodies. This critical issue needs further study (Petrovic et al., 2003).

2.4.4.2. Bioaccumulation

Certain environmental chemicals interfere with normal hormonal processes (hormone synthesis, action or metabolism), and this interferes with vital developmental processes in humans and animals. For example, active metabolites have been reported to have accumulated in the tissues of some aquatic organisms, potentially evoking immune responses or exerting toxic effects. Furthermore, laboratory studies reveal that there are adverse effects that have occurred in some animal species due to EDCs exposure. (WHO & UNEP, 2012; Godfray et al., 2019; Marlatt et al., 2022). These compounds are made to be stable to produce

a biological effect and cure human diseases. As such, they resist enzymes, flow freely in liquid phase and do not hydrolyse at acidic pH values or easily fragment once ingested (Mert et al., 2018). However, the potential impact of endocrine-disrupting compounds' accumulation and ecotoxicological effects, including pharmaceuticals, is not well-researched (Caliman & Gavrilescu, 2009; Stefanakis & Becker, 2015). Therefore, exposure quantification becomes very complex and challenging (Stefanakis & Becker, 2015). Given the above-mentioned limitations, the impact of prolonged contact levels and environmental impacts of ECs or even cocktail ECs are not well-defined. Thus, regulation of ECs often becomes difficult because there are no recommended limit values. Hence, field and laboratory studies are required to deepen our understanding and eliminate uncertainties regarding the fate and transformation pathways of ECs (Stefanakis & Becker, 2015; Yahaya et al., 2020).

Prolonged exposure to PPCPs presents a significant risk to both aquatic ecosystems and human health. Some PPCPs contain bioactive ingredients that could have a long-lasting impact on non-target organisms. For instance, goldfish exposed to high concentrations of PPCPs for 14 days showed a bio-concentration factor of 113, which could lead to gene mutations and a decline in fish population due to decreased fertility. Diclofenac may negatively affect fish organs as they are vulnerable to PPCP contaminants. The occurrence of specific PPCPs such as carbamazepine and diclofenac in aquatic settings can harm algal chloroplasts. Prolonged exposure to Sulfamethoxazole can lead to significant toxicity and hinder the process of photosynthesis. Furthermore, ciprofloxacin exhibits toxicity to green algae, and the indigenous bacteria in PPCP-contaminated environments can develop antibiotic resistance over time (Yahaya et al., 2020).

2.4.4.3. Toxicity

The levels of toxicity of ECs and their metabolites in the water vary depending on the aquatic organisms present, the duration of exposure, the concentration of the compound and the developmental state of the organism (Ebele et al., 2017; Schoeman et al., 2017). Some metabolites are present at higher concentrations in WWTP streams and could potentially exhibit greater toxicity compared to the original compounds, possibly 50% more toxic. Their fate will be influenced by the conditions of the environment, e.g., salinity, temperature, pH and microbial diversity (Mert et al., 2018; Yahaya et al., 2020). Detecting and quantifying these compounds requires improved analytical methods with low detection limits and greater sensitivity (Geissen et al., 2015; Lamastra et al., 2016; Noguera-Oviedo & Aga, 2016; Teodosiu et al., 2018). It should be noted that not all ECs will be known at the time of sampling

and analysis. As a result, they will first have to be identified (Geissen et al., 2015), which makes the process more difficult.

PPCPs normally have high polarity (Noguera-Oviedo & Aga, 2016) and low volatility and tend to dissolve in water (Ebele et al., 2017). This means that they are not easily degradable. PPCPs have the ability to interfere with the endocrine system (Caliman & Gavrilescu, 2009; Schoeman et al., 2017). Many PPCPs and their metabolites are biologically active. The complex mixture of these different chemicals has the potential to synergise and give rise to worse ecotoxicological effects (Ebele et al., 2017). Antibiotics have the potential to enhance and sustain antibiotic-resistant genes (ARGs) within bacteria and the soil ecosystem. (Noguera-Oviedo & Aga, 2016). This is a real threat to the effectiveness of preventing and treating several infectious diseases caused by "antibiotic-resistant pathogenic bacteria". William & Heymann (1998) discuss that developing new drugs in hopes of containing resistance is lengthy and costly. Furthermore, the bacteria will soon inevitably resist the new form of therapeutic drugs as they are introduced into the environment. Furthermore, it has been reported that some bacteria are resistant to antibiotics and this is undesirable as the bacteria will persist in the human and not respond to treatment (Williams & Heymann, 1998; Gilliver et al., 1999; Ebele et al., 2017). Ebele et al. (2017) highlighted that PPCPs pose environmental risks and have undesirable and detrimental effects on aquatic organisms exposed to the compounds. There has been limited understanding of their impact on human health. Hence, further research is essential, particularly in developing nations across Africa. Presently, the majority of data comes from central Europe and North America. Hence, forthcoming studies should prioritise broader geographical regions and consider seasonal variations concerning concentration levels.

The effects of pesticides on population dynamics and community structures are still not well-understood. More recently, some studies have attempted to quantify pesticide exposures' adverse effects on aquatic organisms and their recovery. A study in Australia revealed that the mortality of six mayfly species was linked to pesticide contamination caused by runoff streams from agricultural fields. Several studies have linked the mortality of invertebrate species to insecticides (Liess & von der Ohe, 2005). Overall, ecotoxicological data and the occurrence of most emerging contaminants are unknown or rather not well-studied (Petrovic et al., 2003; Fent et al., 2006). Therefore, a more thorough comprehension of the environmental impacts will enable improved comprehensive risk assessment in the future. Existing literature indicates the necessity for a greater understanding of the toxicological consequences of prolonged exposure or ingestion of a combination of pharmaceutical drugs. The focus should extend beyond the parent compound to include its metabolites and

transformation products. These secondary compounds have the potential to generate more toxic substances with enhanced resistance compared to the original compounds.

2.4.5. Fate and Behaviour of Emerging Contaminants in the Environment

The fate and behaviour of ECs during treatment are key to the use of water bodies (Petrovic et al., 2003). The gaps in the literature result in the increased complexity of the study of ECs (Archer, 2018). For instance, if we look at xenobiotic chemical compounds which have three possible behaviours: (1) mineralise entirely to water and CO_2, (2) be in a lipophilic form and not break apart easily, and (3) metabolise to a more hydrophobic form that becomes more resistant than the parent compound. The metabolites formed are polar, hydrophilic and biologically active compounds that are discharged from the human body to WWTPs (Mert et al., 2018).

The ECs can undergo significant biodegradation depending on the present microbial community in the water, sediments, and soils. Natural biodegradation varies from compound to compound. However, this process can lead to the creation of various degradation or transformation products. There is a lack of studies relating to the latter, specifically for ECs like pharmaceuticals, detergents, and hormones (Geissen et al., 2015; Petrie et al., 2015). Additionally, the fate and impact of ECs in drinking water treatment have not been well-researched (Petrie et al., 2015; Teodosiu et al., 2018). Due to their presence and persistence in freshwater bodies and their properties (i.e., degradability and ecotoxicological effects), they can potentially disrupt treatment performance and possibly affect treatment costs.

The human body often excretes parent chemicals along with various associated metabolites. For instance, ibuprofen is excreted as an unchanged drug (1%) along with several metabolites. Whereas, diclofenac, naproxen and are usually excreted as 10, 70 and 10% as un-metabolised drugs, respectively (Madikizela et al., 2017). It is essential to analyse these metabolites because they can be present in much higher concentrations than the original parent chemical and may exhibit pharmacological activity. For example, the primary metabolite of carbamazepine, known as carbamazepine epoxide, has been discovered in influent wastewater at concentrations between 880 ng/L and 4026 ng/L. In contrast, the parent compound was found at levels below 1.5 -113 ng/L. Therefore, removing the parent EC does not entail the removal of toxicity as there is a greater number of transformation products in the final wastewater effluent and receiving freshwater bodies (Petrie et al., 2015; Yahaya et al., 2020).

2.5. Removal of Emerging Contaminants from Wastewater Using Advanced Membrane Technology

Advanced treatment methods such as biological techniques like membrane bioreactors (MBRs) (Noguera-Oviedo & Aga, 2016) or physicochemical methods such as advanced oxidation processes (AOPs) (Schoeman et al., 2017), activated carbon adsorption (GAC) (Kummerer, 2009), or membrane treatment using nanofiltration (NF) or reverse osmosis (RO) (Ali et al., 2018) can either completely remove these ECs through mineralisation or transform them into substances that are less harmful to people and the environment (Tambosi et al., 2010). Research on the removal of specific ECs has been conducted at field-level or scale using the biological wastewater treatment processes as mentioned above. However, there are not many thorough investigations on the removal of a wide range of ECs across different full-scale conventional and advanced nutrient removal-based WWTPs. Although WWTPs receive a spectrum of contaminants, some of which are more degradable than others, the majority of previous research only examined a limited number of technologies on a limited list of contaminants. This highlights the need for a thorough assessment of various treatment technologies to determine their effectiveness in removing a wide range of ECs (Dubey et al., 2023). The biggest limitation regarding current technologies is that none of them can effectively remove a complex mixture of ECs because most of the treatment technologies are compound dependent. Additionally, treatment efficiency varies with the various methods and technologies. The chosen treatment will depend on the physicochemical properties of the contaminant, as well as the operational parameters required (Stefanakis & Becker, 2015). Many technologies have been tested; however, great limitations still surface (Kummerer, 2009; Madikizela, 2024).

One of the promising technologies in treating wastewater is the membrane bioreactor (MBR). It combines a biologically activated sludge process with membrane filtration for separating solids from liquids. MBRs have become more popular and affordable, making them key in treating wastewater in both industrial and municipal treatment plants. They might even become the primary method for recycling wastewater directly or indirectly. However, few studies discuss how well MBRs handle emerging contaminants during the treatment process, despite their widespread use in treating urban and industrial wastewater (Tambosi et al., 2010). Membranes are made up of semi-permeable materials that allow water to permeate and retain the micro-matter at the surface of the membrane (Teodosiu et al., 2018). Membrane technologies are easy to operate and have a high contaminant removal efficiency (Zahid et al., 2018).

Membranes can be classified as polymeric or inorganic membranes. Inorganic membranes include ceramics and other metals with high structural, mechanical and thermal strength (Zahid et al., 2018). Ceramic membranes present good filtration performance, are inert, display chemical resistance characteristics, and have high hydrophilic ability. However, they are expensive and fragment easily. As technology upgrades, membrane development has moved towards polymers like polyvinylidene (PVDF), polyethylsulphone (PES), polyethylene (PE) and polypropyle (PP) (Mutamim et al., 2013). Polymeric membranes are flexible, display high mechanical and chemical strength, have good film-forming properties and are inexpensive materials (Zahid et al., 2018). Additionally, they are porous but hydrophobic, thus more susceptible to fouling. The hydrophobicity of the membrane can be improved by coating its surface with a hydrophilic polymer layer (Mutamim et al., 2013).

The efficiency of the filtration process is affected by the membrane selected; therefore, the selection of the membrane is considered a very important decision (Sandoval, 2013). Different materials can be used depending on the desired characteristics, i.e., pore size, surface charge, hydrophobicity, influent constituent concentrations, and contaminant to be retained. These materials include ceramics, glass, metals and a variety of chemically and thermally stable polymers or polymer blends (Teodosiu et al., 2018). See Table 2.8 for several processes that may be used to remove ECs, which can be classified according to the force of separation used.

Table 2.7: Processes According to Force Separation

FORCE	PROCESS
PRESSURE DRIVEN	Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO)
ELECTRIC POTENTIAL GRADIENT	Electrodialysis (ED)
CONCENTRATION GRADIENT	Forward Osmosis (FO)

Adapted from (Teodosiu et al., 2018)

According to Teodosiu et al. (2018), the most suitable membranes to remove ECs are NF, UF, and RO. RO is the most effective for pesticides, PPCPs, toxic metals, and cyanide removal. RO was found to be the most effective method in removing the organic and inorganic matter from surface and ground waters.

The following criteria can be used to select processes/technology when attempting to remove ECs:

- EC type and physicochemical properties, e.g., hydrophobicity;
- Removal mechanism and treatment efficiency;
- Operational parameters- temperature, hydraulic and solid retention times, etc.;
- Environmental footprint;
- Operation and maintenance of the technology used;
- Cost-effectiveness of the process; and
- Social acceptance.

MBRs integrate the biological degradation and membrane filtration processes to achieve solid-liquid separation using physical straining and to deliver a more reliable and higher-quality effluent standard. MBRs are known to effectively remove organic and inorganic contaminants (Naghizadeh et al., 2011).

Two alternative membrane configurations exist: the first is submerged Membrane Bioreactors (MBRs), and the second is sidestream MBRs. See Figure 2.8 for the membrane configurations.

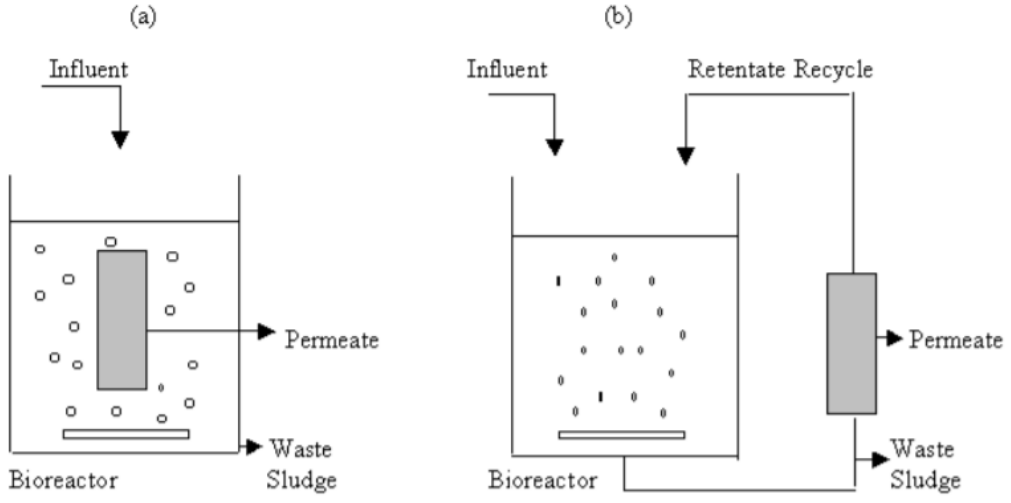


Figure 2.7: Configuration of Membrane Bioreactors: (a) submerged MBR and (b) Sidestream MBR configuration *(Adapted from (Kootenaei & Aminirad, 2014))*

There are different membrane configurations. Submerged MBRs are those that have the membranes fully immersed in the aeration tank, the membrane is placed directly in the liquid (Naghizadeh et al., 2011). This configuration type mainly uses flat sheets (FS) and hollow fibre (HF) membranes (Mert et al., 2018). Sidestream MBRs are pressure-driven, where the

membranes are separate from the bioreactor. This type of configuration requires an intermediate pumping step that will push the bioreactor effluent into the membrane unit and permeate through the membrane (Naghizadeh et al., 2011). The submerged MBR system improves mass transfer and has higher permeability than sidestream MBR systems (Judd, 2005). The membrane configuration plays an important role in determining energy use and the fouling potential of the process. Each configuration has its advantages and disadvantages (Mutamim et al., 2013).

The quality of the wastewater effluent produced will depend on the process's quality and the conditions created. To optimise the performance of an MBR system, the following operational facilities must be controlled: solid retention time (SRT), hydraulic retention time (HRT), mixed liquor suspended solids (MLSS), food to microorganism ratio (F/M), transmembrane pressure (TMP) and flux. Other limitations to the system include system environment conditions such as pH, and temperature (Mutamim et al., 2013).

MBR systems have the following advantages: (1) higher biodegradation efficiency; (2) smaller footprint, such as when there is limited space and where water treatment for internal recycling is desirable; (3) less sludge production; (4) produce an improved effluent wastewater quality (Wang et al., 2008; Erkan et al., 2018); (5) removes good amounts of organic and inorganic contaminants and is capable of resisting high organic loading (Mutamim et al., 2013); (6) efficiently and effectively removes organic and inorganic contaminants; (7) having modularity; (8) robust and reliable operation and (9) reduces downstream disinfection requirements (Naghizadeh et al., 2011).

Furthermore, membranes are susceptible to fouling, which is when contaminants accumulate at the surface of the membrane, causing a reduction in flux. This phenomenon leads to increased operational and maintenance costs (Wang et al., 2008; Zahid et al., 2018), reduced performance and lifespan (Lorhemen et al., 2016), making MBRs less desirable in cases where funds are limited or inaccessible. Sandoval (2013) and Lorhemen and team (2016) classified membrane fouling into three categories according to the composition of the foulants: organic fouling, inorganic fouling, and microbial fouling. Organic fouling occurs when biological polymers like proteins and carbohydrates accumulate on the surface of the membrane, clogging the membrane pores and reducing permeability. Inorganic fouling is also called mineral fouling and occurs when excess inorganic salts precipitate on the membrane. Lastly, microbial fouling occurs when microorganisms like bacteria grow on the surface of the membrane, forming a biofilm. A graphic representation of membrane fouling is shown in Figure 2.9.

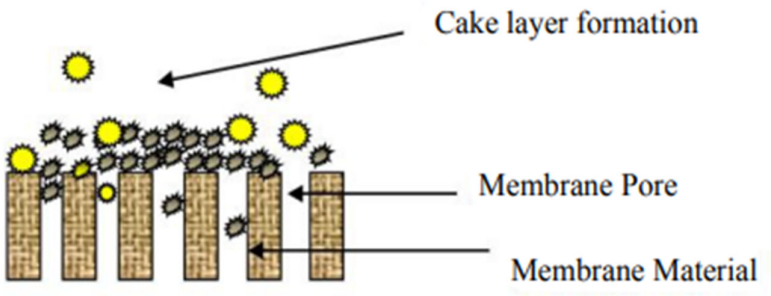


Figure 2.8: Blockage of Membrane Pores Due to Foulants *(Adapted from (Zahid et al., 2018))*

Polymeric membranes are hydrophobic by nature and more prone to fouling. Various traditional strategies can be used to mitigate fouling, for example, backwashing, relaxation, chemical cleaning using acids, caustic soda, and hypochlorite, changing flow mode and ultrasonic entrenchment. However, these chemical and physical pretreatment processes are not always effective and may cause damage to the membrane. Preferred methods are the additions of additives that will result in the improvement of the membrane hydrophilicity, water flux, selectivity, and permeability. The formulation of membranes using nano-materials is easy and cost-effective (Zahid et al., 2018). Minimising fouling is still an ongoing process that needs further research (Mutamim et al., 2013). Figure 2.10 shows the repelling of foulants after the membrane has been modified.

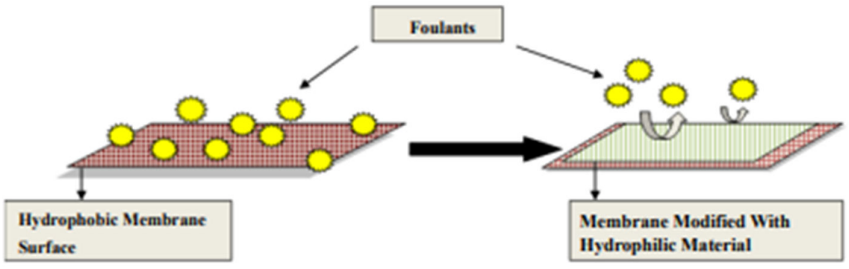


Figure 2.9: Repelling of Foulants after Modification with Hydrophilic Material Coating on Membrane Surface *(Adapted from (Zahid et al., 2018))*

Other limitations are that MBR systems require high capital and maintenance costs, although submerged MBRs have been reported to have lower operational costs when compared to other configurations (Mutamim et al., 2013); they require high energy inputs; therefore, operation costs tend to be high. Furthermore, the potential future cost of replacing the membranes may be high (Lorhemen et al., 2016).

Polymer nano-composite materials are formed when various materials of dissimilar properties and characteristics are mixed and bonded at specific proportions through chemical and/or physical means. The individual components still retain their physical and chemical identities;

however, in most cases, the properties of the composite material formed will govern. The properties of the composite material will depend on the dispersion and distribution of the reinforcing of the nano-filler in the continuous phase and the interaction of the surface of the nano-filler and the polymer matrix (Mondal, 2015). Figure 2.11 illustrates a good dispersion and distribution to achieve optimum results.

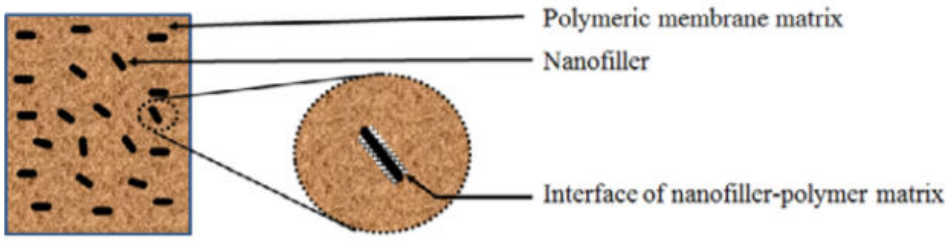


Figure 2.10: An example of good dispersion and distribution of nano-composite materials in a polymeric nano-composite membrane matrix and the interface of nanofiller-polymer matrix
(Adapted from *(Mondal, 2015)*)

Various techniques can be used to prepare nano-composite membranes, such as dip coating, sintering, track-etching, stretching, template leaching, and phase inversion. Phase inversion methods are the commonly used processes for preparing nanocomposite membranes due to their versatility, simplicity, and ability to produce membranes with controlled pore structures. Phase inversion is defined as a de-mixing process whereby a homogeneous polymer solution is carefully transformed from a liquid state to a solid state through the immersion of the cast polymer solution into a non-solvent bath (Ali et al., 2018; Zahid et al., 2018). The ease of controlling membrane morphology, including pore size, porosity, and mechanical strength, makes phase inversion highly adaptable to various applications. Additionally, it allows for the incorporation of nanoparticles, enhancing the membrane's functional properties, such as permeability, selectivity, and fouling resistance, which are critical for wastewater treatment and other environmental applications (Holda, 2015; Tan & Rodrigue, 2019).

Phase inversion methods can be classified into four categories depending on the selected solvent, the composition of the coagulation bath, non-solvent system, polymer solution composition and the conditions of film casting (Zahid et al., 2018). The categories are shown in Table 2.9.

Table 2.8: Characterising Phase Inversion Methods

PHASE INVERSION METHOD	DESCRIPTION
NON-SOLVENT-INDUCED PHASE INVERSION METHODS (NIPS)	A suitable solvent is used to prepare the homogeneous polymer solution, using a non-woven fabric support and cast on a flat surface. Thereafter, the polymer membrane is formed by immersing the worked solution in a coagulation bath containing non-solvent due to the exchange of solvent and non-solvent. The morphology of polymeric membranes is driven by the mutual exchange of two solvents. This type of method requires complex control of the solvent exchange rate in other to obtain the desired morphology and ascertain good performance. This can be done by varying the solvent composition, coagulation medium, quenching bath temperature or evaporation time.
THERMAL INDUCED PHASE INVERSION (TIPS)	TIPS is principally based on heat transfer. To prepare a homogeneous polymer solution, the solution is dissolved in a diluent at a high temperature followed by cooling to induce de-mixing and phase separation. The diluent must have low volatility, a high boiling point, high miscibility with the polymer and have good thermal stability. The diluent is the extracted using a volatile reagent to produce a porous membrane. Membranes prepared via TIPS are less likely to form defects and have diversity in the pore structures that are formed. Additionally, they have high mechanical strength, high porosity and uniform porous structures. NIPS and TIPS are the commonly used phase inversion methods due to their ability to deliver the desired morphology during membrane fabrication.
VAPOUR INDUCED PHASE INVERSION (VIPS)	The casted film is exposed to the atmosphere of non-solvent vapours in a vapour chamber to form a highly porous membrane like microfiltration membranes. The inflow of the non-solvent vapours into the polymeric casted film and outflow of solvent from the film is referred to as phase inversion.
EVAPORATION INDUCED PHASE INVERSION (EIPS)	The polymer solution is prepared in a solvent or a mixture of solvents. The solvent will evaporate due to its volatility to allow phase inversion to take place resulting in de-mixing to form a porous structure.

Adapted from (Zahid et al., 2018)

Figures 2.12, 2.13 and 2.14 show the various phase inversion methods discussed in Table 2.9.

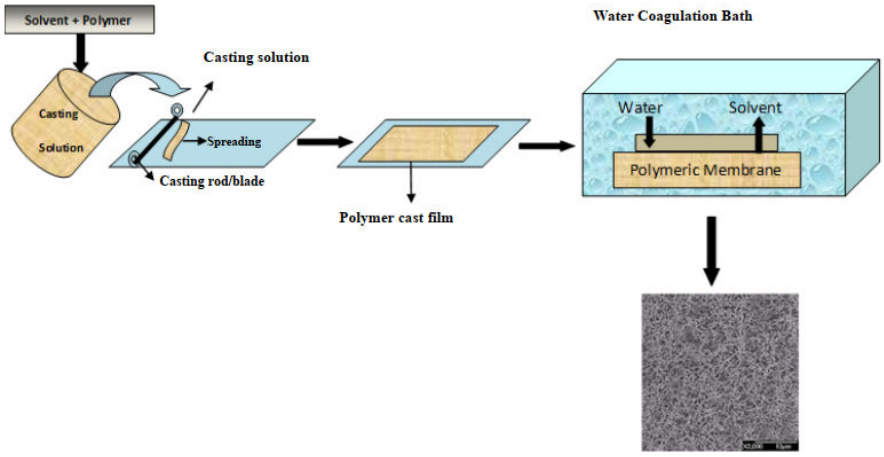


Figure 2.11: Schematic of the NIPS Method *(Adapted from (Zahid et al., 2018))*

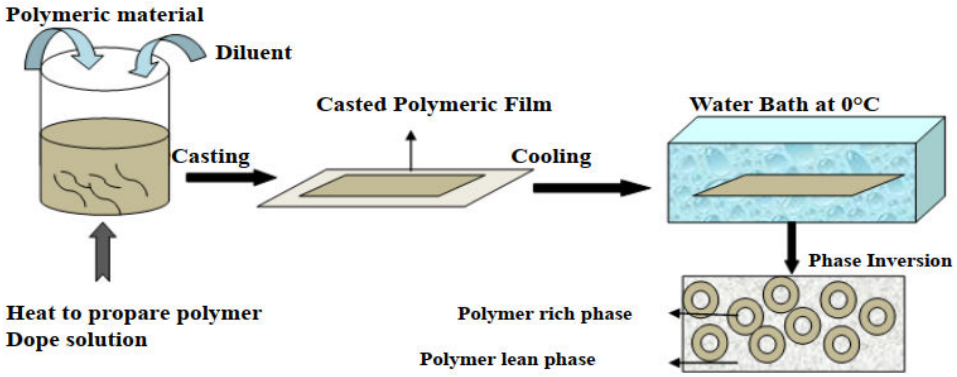


Figure 2.12: Schematic of the TIPs method *(Adapted from (Zahid et al., 2018))*

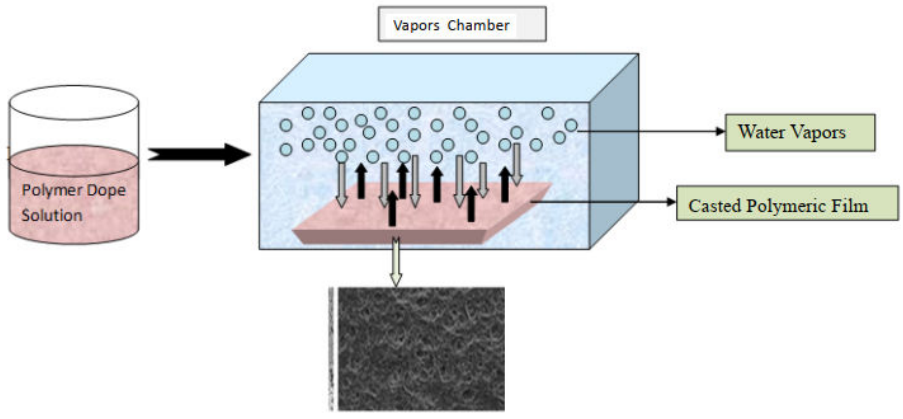


Figure 2.13: Schematic of the VIPS method *(Adapted from (Zahid et al., 2018))*

Polymeric nano-composite membranes have been used successfully in various industrial applications and have been studied by many researchers across the globe. Their ability to enhance permselectivity, membrane fluxes, and desired morphology formation to improve fouling resistance attracts many researchers. In this study, a polymeric composite membrane is fabricated to determine its efficiency and effectiveness in removing ECs from wastewater.

2.6. Analytical Methods

2.6.1. Sample Preparation

More sensitive analytical methods are needed to examine pharmaceutical residues in environmental samples such as WWTP effluents, river water, sediments, and soil (Tambosi et al., 2010), as these contaminants often occur in trace amounts within complex matrices. These methods allow for the accurate identification and quantification of pharmaceuticals and their metabolites, ensuring a comprehensive analysis. This is essential for assessing potential environmental and health risks and for meeting regulatory standards that require monitoring at ultra-trace concentrations, often as low as ng/L (Fatta et al., 2007; Tambosi et al., 2010). Effective analytical methods must be fast, sensitive and selective, have low detection limits, and be easily followed and reproduced. Ideally, the approach taken is to separate the analyte under investigation from the matrix through various extraction techniques for easy analysis. However, PPCPs, their metabolites and transformation by-products have a number of different forms (Osunmakinde et al., 2013). Depending on their hydrophilicity, these compounds may either dissolve into aquatic environments or adhere to solid particles (Fatta et al., 2007). Therefore, no single extraction method can be used universally. There are several extraction methods, i.e., solid phase extraction (SPE), solid phase microextraction (SPME), liquid phase microextraction (LPME), microwave-assisted solvent extraction (MASE), pressurised liquid extraction (PLE), Soxhlet, ultrasonication, fluid management system (FMS) and supercritical fluid extraction (SFE) (Osunmakinde et al., 2013). Among these, SPE is the most common abstraction method (Schoeman et al., 2017).

2.6.2. Separation Techniques

The diverse structural nature of these target analytes poses a challenge in devising a universal analytical method for analysing PPCPs. Ideally, a multi-residue analytical method capable of simultaneously detecting a broad range of PPCPs in a single analysis would be desirable. Such a method would efficiently separate polar, non-polar, and neutral compounds in a unified process, commonly referred to as a "one-pot" approach. However, this method is currently impractical. Mass spectrometry is the ideal detection technique as it is sensitive, selective and accurate in analytical measurements. Given the nature of the PPCPs and their intricate

composition of environmental sample matrices, there is a demand for highly selective separation techniques coupled with sensitive detectors. These methods are: Gas Chromatography - Mass Spectrometry (GC-MS), High-Performance Liquid Chromatography – Mass Spectrometry (HPLC-MS), Capillary Electrophoresis and Thin Layer Chromatography. Only a small percentage of PPCPs are volatile enough for GC applications without prior derivatisation. Therefore, GS is limited. The LC-MS is the preferred technique for analysing PPCPs (Osunmakinde et al., 2013).

2.6.3. Detection

Numerous methods have been used for the detection and quantification of PPCPs and their metabolites in water systems, sediments, and soils. In general, many detectors employed in HPLC exhibit lower sensitivity and/or selectivity, except for mass spectrometry. The developments in LC-MS instrumentation, such as the use of atmospheric pressure ionisation (API), particularly electrospray ionisation coupled with single ion monitoring (SIM) or multiple reaction monitoring (MRM) techniques, have established mass spectrometry as the preeminent detector. Despite its advantages, liquid chromatography-mass spectrometry (LC-MS) has limitations, including sensitivity issues and matrix effects such as signal suppression, particularly when analysing samples from water bodies (Osunmakinde et al., 2013).

Mass spectrometry offers high sensitivity and selectivity for detecting PPCPs. It proves effective in determining pharmaceutical compounds even at extremely low concentrations within complex matrices (Ohoro et al., 2019; Meng et al., 2021). High-resolution mass spectrometry instruments, such as time-of-flight and magnetic sector instruments, can operate in full scan mode, overcoming the limitations associated with target-type analyses. Detection includes UV, fluorescence, and MS/MS, allowing for the quantification of these compounds, individually or simultaneously, in biological matrices. This approach surpasses the constraints of target-specific analyses and provides a comprehensive solution for accurately identifying and quantifying pharmaceutical compounds in challenging environments (Schoeman et al., 2017).

2.7. Membrane Characterisation

Membrane characterisation is done to determine the nature, chemistry, morphology, surface charge, wettability, tensile strength, and characteristics of the nanomaterial. Morphological characterisation and performance characterisation can be used to classify membranes. Morphological parameters for a membrane include porosity, pore size, pore size distribution, tortuosity, surface roughness, molecular weight cutoff, and thickness. Pore size, for instance,

plays a vital role in classifying membranes into categories such as microfiltration (50–500 nm), ultrafiltration (2–50 nm), nanofiltration (≤2 nm), reverse osmosis (0.3–0.6 nm), and forward osmosis (0.3–0.6 nm). It is noteworthy that the performance of the membrane is directly influenced by its morphology, specifically pore size and distribution. Therefore, controlling the morphology is a critical factor in the fabrication of membranes (Zahid et al., 2018; Tan & Rodrigue, 2019). The performance of membranes is assessed based on their productivity (rate) and separation ability (selectivity). Parameters such as flux (J), permeability (P), and permeance (P') are crucial in evaluating membrane productivity, while efficiency, reflecting separation performance is determined by selectivity (α) and separation (β) factors. It is important to note that when polarisation effects are present, measurements of both the observed retention coefficient (Robs) and the actual retention coefficient (R) are necessary (Tan & Rodrigue, 2019). The Contact Angle (CA) is a qualitative way to establish whether the surface has hydrophobic or hydrophilic characteristics. Hydrophobic materials resist/repel water, whilst hydrophilic materials will attract water. When a material has hydrophobic interactions, the CA will be greater than 90º, whereas a CA less than 90º indicates a hydrophilic surface. A superhydrophilic surface has a CA of less than 5º (Ahmad et al., 2018; Zahid et al., 2018). Additionally, the CA indicates the antifouling behaviour of a membrane.

Various techniques may be employed to gather significant optical property information about the material being analysed; for example, Polarized light microscopy (PLM), SEM (Scanning Electron Microscopy), FTIR (Fourier Transform Infrared spectroscopy), XPD (X-ray Powder Diffraction), and TEM (Transmission Electron Microscopy). PLM is the oldest technique that was used to identify unknown materials, ascertain the presence of specific contaminants, or offer sights that can aid in optimising manufacturing or chemical processes. PLM is commonly the first technique used to identify unknown materials (Frandsen, 2016).

2.8. Literature Summary

The ECs are prevalent in the environment due to increased wastewater generation and other anthropogenic activities. The ECs can be synthetic or naturally occurring and include pharmaceuticals, personal care products, endocrine-disrupting compounds, industrial additives, pesticides, nanomaterials, surfactant retardants, surfactants, and their metabolites and transformation products. The ECs are generally not monitored because they are not regulated as environmental pollutants. As a result, the effect of these emerging contaminants on human health and aquatic life remains unclear, as they exist at trace concentrations, making it difficult to detect, monitor, and control.

Most of these compounds are not effectively removed by conventional wastewater treatment processes; consequently, residual concentrations reach the aquatic ecosystem and, ultimately, drinking water treatment plants. The problem is that it is not one compound occurring at a time but a mixture of different compounds that have the potential to form highly persistent and toxic metabolites. Therefore, more research is required for removing a mixture of these contaminants. Polymeric nano-composite membranes have been identified as one of the technologies that have the potential to efficiently remove ECs from wastewater. PVDFs are polymeric membranes used in ultrafiltration, microfiltration, and membrane bioreactor systems because they have good thermal and chemical resistance and mechanical stability. In addition, these membranes can be coated with a hydrophilic nano-composite material to modify their surface, thereby limiting fouling. The subsequent chapter presents a detailed discussion of the research methodology employed to conduct this research.

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1. Experimental Methods and Analytical Techniques

3.1.1. Preparation of the Flat Sheet Membranes

The flat sheet membranes were prepared according to the phase inversion method (Galiano, 2016; Zahid et al., 2018; Purnawan et al., 2021). Four beakers were rinsed with de-ionised (DI) water, followed by acetone. The beakers were allowed to dry, and then 85 mL of N-Dimethylacetamide (DMAc) (Product number: 271012; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) was measured into each beaker. The beakers were then placed on the laboratory flocculator (Product code: 4AJ-6258113, Model: AL50, Type ET 750; Aqualitic, Pretoria, South Africa). Poly(vinylidene fluoride) (PVDF) (Product number: 182702; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) and 1-Ethyl-3-methylimidazolium bis(triflouromethylsulfonyl) mide (Product number: 711691; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) were carefully measured on the analytical balance (Product number: 293607831, Model: Libror AEX – 200B, Capacity: 200.000g, Shimadzu, Roodepoort, South Africa). The constituents were then slowly added at room temperature into the four beakers in the compositions shown in Table 3.1. The mixing speeds are critical in this process to ensure proper mixing and homogeneity of the mixture. The mixture was stirred at 200 rpm to allow the components to begin mixing without introducing too much turbulence, which could cause uneven mixing or air bubble formation. The speed was gradually increased to 300 rpm to enhance the mixing intensity, promoting a more thorough distribution of the components throughout the mixture. This gradual increase also helps in avoiding sudden shifts in mixing dynamics, which could affect the mixture's consistency. The stirring continued for 30-40 minutes to ensure the mixture was thoroughly mixed and homogeneous based on the procedure used in Purnawan et al. (2021). This controlled stirring process is essential for the reliability and reproducibility of the final product.

Table 3.1: Composition of Membrane Constituents

BEAKER	PVDF (g)	DMAC (mL)	IMIDAZOLIUM (g)
1	15	85	0
2	12.5	85	2.5
3	10	85	5
4	7.5	85	7.5

The compositions shown in Table 3.1 were selected to cover a wider range of PVDF/imidazolium-PILs, from a ratio of 1:0 to 1:1. This was done to establish how the characteristics of the casting solution and fabricated membrane will change and to what extent. The range aimed to determine the optimum composition to enhance the membrane's overall performance in separating contaminants and general operating performance. The polymer solutions were then moved to the OrbiCult Incubator Benchtop Shaker (Model: OrbiCult™ IBS, ESCO, Singapore) at 60° C at a speed of 500 rpm for 3 hours to ensure that the solutions were completely homogeneous (Purnawan et al., 2021). Following this, the casting solutions were allowed to sit overnight in the shaker at 60° C at a speed of 300 rpm. This was done to ensure that the sample did not settle and become solid.

After 24 hours, the homogeneous polymer solutions (now called casting solutions) were ready for casting. The casting solutions were cast on an automatic film applicator (AFA) (Product number: 200058, Model 1133N, Sheen, Tashkent, Asia), during which time the temperature was maintained at 60° C. The AFA was then set to a speed of 150 µm and a thickness of 250 µm. The AFA glass plate was immediately removed and immersed in DI water. Placing the casted solution in the water bath is critical; therefore, this was done as carefully and steadily as possible to ensure that the whole membrane was immersed simultaneously. This step is crucial in membrane casting because it affects the formation and uniformity of the membrane surface. Ensuring that the entire membrane is immersed evenly and simultaneously helps to prevent defects, such as uneven thickness or inconsistent pore structure, which can compromise the membrane's performance. Proper immersion also ensures that the solvent exchange and phase separation processes occur uniformly, leading to a consistent membrane morphology with optimal filtration properties. Once the flat sheet rose and floated above the water, it was removed from the water bath and immersed in Polar Clean (Product number: 270733, Lot # RNBK6540, Sigma-Aldrich, United Kingdom) for 24 hours (Purnawan et al., 2021). The water bath was emptied and cleaned using soapy water, followed by DI water between the various casting solutions, and the glass plate was rinsed with DI water before casting the next solution. The soapy water ensured that all residues, and organic contaminants that could interfere with membrane formation were removed. While the DI water rinse ensured

that any remaining soap and impurities were fully eliminated. This thorough cleaning process helped prevent unwanted reactions and ensured consistency and reproducibility in membrane quality. The formed flat sheet membranes were stored in separate bags in the laboratory refrigerator at 3° C, awaiting characterisation. Characterisation was done within 4 weeks of casting.

3.1.2. Membrane Characterisation

Characterisation of the membranes included (1) the evaluation of the physical and visual characteristics, (2) observations of the casting solutions, (3) Polarised light microscopy, (4) water contact angle measurement and (5) calculation of the membrane porosity and average pore size.

Physical and Visual Characteristics and Observations of the Casting Solutions

The colour and texture of both the cast and formed membranes were systematically observed and recorded under controlled conditions to ensure unbiased data collection. To maintain consistency, observations were conducted in the laboratory with uniform lighting, minimising the risk of colour distortions caused by observer perception. Furthermore, a fixed viewing station was used, ensuring a consistent distance and angle of observation, thereby reducing perspective-based variations. All membranes were observed simultaneously, ensuring uniform environmental conditions of the room, such as temperature, humidity, and light intensity throughout the process. These controlled measures were implemented to ensure that the observations were accurate and reproducible, free from external variability.

Polarised Light Microscopy

The Nikon OptiPhot – Pol Labophot-Pol microscope (Model: 55569, Nikon, Tokyo City, Japan) was used to analyse the surface of the membranes. The membranes were cut into sizeable pieces (3cm x 2cm) in order to fit onto the glass slides for analysis. Before use, the glass slides were washed with soapy water and rinsed with DI water, and dried with Kimwipes. One membrane was analysed at a time. The membranes were secured to the glass slide using a coverslip. The refractive index oil (mineral oil – refractive index 1.47 – 1.48) was carefully applied by placing the oil drop next to the coverslip and allowing it to spread across. The oil drops were applied until the sample was covered entirely. Applying the oil ensures that a clearer view of the membrane is obtained (Frandsen, 2016). A Kimwipe was used to remove excess oil. The glass slide was then placed on the light path and analysed.

Measuring the Water Contact Angle

The water surface contact angle (CA) was measured at ambient temperature (Purnawan et al., 2021). The Optical Tensiometer (Model: TL100, Attension, Gothenburg, Sweden) was used to measure the water contact angle. Water and soap were used to clean the glass plate, and thereafter, the glass was rinsed with DI water and allowed to dry to ensure that the surface was not contaminated. The synthesised membranes were cut into small segments (1 cm x 1 cm) for testing. The system was calibrated to the manufacturer's settings and properly aligned. The camera was focused on the sample stage and the dispensing needle was set to 1.5 µL. The needle (dispenser) was allowed to form a small droplet before it was lowered onto the surface. The CA was measured without moving the droplet; it was captured and analysed according to Figure 3.1. The process was repeated five times on different areas of the membrane. The average CA from the measurements was calculated and adopted as the CA of the sample.

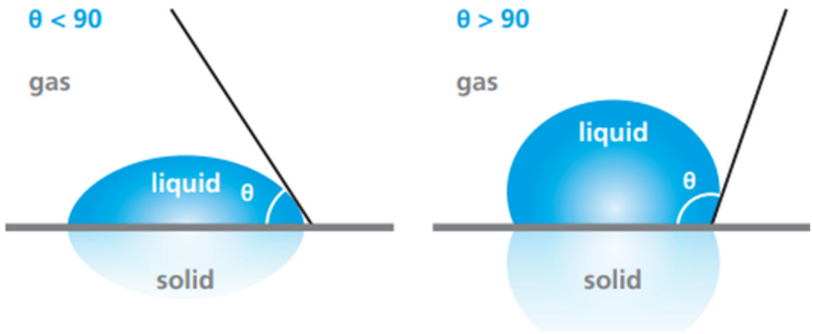


Figure 3.1: A Water Droplet on Hydrophilic and Hydrophobic Surfaces (Adapted from *(Lauren, 2021)*)

Calculation of the Membrane Porosity and Average Membrane Pore Size.

To determine the membrane porosity, equation 1 was used (Purnawan et al., 2021):

Equation 1: Membrane Porosity

$$\varepsilon\ (\%) = \frac{W_w - W_d}{\rho_w . A . l}$$

Where:
- ε = porosity (%)
- W_d = dry weight of membrane (g)
- W_w = wet weight of membrane (boiled in water for 2h and allowed to chill for 24h at room temperature) (g)
- ρ_w = density of water (kg/m^3)

A = effective area of membrane (m^2)

l = membrane thickness (m)

The Geurout-Elford-Ferry equation was used to estimate the membrane pore size:

Equation 2: Geurout-Elford-Ferry Equation

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)x\ 8\eta lQ}{\varepsilon \times A \times \Delta P}}$$

Where:

ε = porosity (%)

η = viscosity of pure water (8.9 x 10^{-4}. Pa. s)

l = membrane thickness (m)

Q = flowrate ($m^3.s^{-1}$)

A = effective area of membrane (m^2)

ΔP= transmembrane pressure ($kg.m^{-1}.s^{-2}$)

3.1.3. Preparation of SPE Cartridges and Analyte Samples

The SPE cartridges (Product number: 57026, Supelco – 6mL, PA 16823-0048, Bellefonte, USA) were packed with four layers of the formulated membranes using the SPE frit insertion tool for 6 mL tubes (Product number: 55219 -U, Supelco – 6mL, PA 16823-0048, Bellefonte, USA). The packed SPE cartridges were conditioned with 6 mL methanol (Product number: 1424109; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa), followed by equilibration using 6 mL deionised water (Osunmakinde et al., 2013; Mbhele et al., 2018). The conditioning process was necessary to prepare the cartridges for optimal adsorption of the target analytes. The conditioning with methanol and subsequent equilibration with DI water promotes consistent analyte retention, and reduces the risk of interference, ensuring a more accurate and reproducible result.

Four beakers were rinsed with DI water and acetone. A volume of 200 mL of DI water was measured in each beaker. The temperature and pH were measured using the multiparameter pH meter (Product number: HI2020, Hanna Instrument, USA). The solid analytes were dissolved in methanol (Product number: 1424109; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) and then spiked with the analyte concentrations as shown in Table 3.2. The analytes used were ibuprofen (Product number: I4883-1G; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa), cypermethrin (Product number: 1064947; Efekto), naproxen (Product number: N5160; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) and diclofenac sodium salt (Product number:

PHR1144; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa). Then, the temperature and pH of the spiked samples were measured. In this investigation, the samples (50 mL) were then run through the conditioned cartridges, and the retention times were measured. It must be noted that no pressure was applied, and the samples were allowed to filter through the membrane in response to gravity. The filtered samples were then placed in high-performance liquid chromatographic (HPLC) vials and stored in the laboratory refrigerator at 3° C, awaiting analysis. The HPLC analysis was done within 2 weeks after the preparation of the samples. Storing filtered samples at a refrigerator temperature of 3°C is crucial for maintaining sample integrity prior to HPLC analysis. This low temperature prevents the degradation of sensitive compounds, such as pharmaceuticals, by slowing down chemical and biological processes that could alter the sample composition. It also minimises microbial activity, which could metabolise or transform the analytes, leading to inaccurate analytical results. Additionally, refrigeration preserves the physical and chemical stability of the sample, ensuring consistency for reliable analysis.

Table 3.2: Analyte Spiking Details

COMPOUND	TYPE OF EC	PREVIOUSLY DETECTED CONCENTRATION (µg/L)	SOLUBILITY IN ETHANOL (mg/mL)	ANALYTE CONCENTRATION
DICLOFENAC	Antibiotic	2.16	35	20 mg/mL
CYPERMETHRIN	Pesticide	0.15	N/A	150 µg/l
IBUPROFEN	Antipyretic	0.81	60	8.75 mg/mL
NAPROXEN	Antipyretic	0.81	60	8.75 mg/mL

3.1.4. Preparation of the Buffer and Mobile Phase

The buffer was prepared using 1.75 g dipotassium hydrogen phosphate salt (Product number: SAAR55043600EM, univAR™, Merck Life Science (Pty) Ltd, Modderfontein, South Africa) and Polar Clean. The pH was adjusted to 6.8 using phosphoric acid (Product number: SAAR4818040LC, univAR™, Merck Life Science (Pty) Ltd, Modderfontein, South Africa) and sodium hydroxide (Product number: 1.93102.0500, Emparta®, Merck Life Science (Pty) Ltd, Modderfontein, South Africa) to produce a volume of 1000 mL. The buffer was then added to HPLC-grade acetonitrile (Product number: 34851 – 2.5L; Sigma-Aldrich; Merck Life Science (Pty) Ltd, Modderfontein, South Africa) at a ratio of 65:35 to form the mobile phase and then degassed using the Ultrasonic Cleaner (Model: 3800, Branson Ultrasonics). The mobile phase

volume was approximately 1000 mL (Jahan et al., 2014). Before HPLC analysis, the mobile phase was filtered and degassed.

3.1.5. HPLC Analysis

The HPLC analysis was done in the School of Chemical Engineering Biochemical Laboratory, Richard Ward Building, University of the Witwatersrand. The HPLC analysis aims to separate, detect, and measure the analytes in the given samples; see Figure 3.2 for the typical HPLC system. The analytes were dissolved in methanol at a 50:50 mixing ratio of methanol and water to ensure a concentration range of 1 - 5µg/L is achieved for the calibration of standards. Five standards were prepared for 5 µg/L, 3 µg/L, 1.5 µg/L, 1 µg/L and a blank (Osunmakinde et al., 2013; Jahan et al., 2014).

The mobile phase was used to condition the column before starting the analysis. The analytical column was selected based on the nature of the samples. Thereafter, the system was calibrated using the standards that were prepared. The HPLC system was set to the following chromatographic conditions: flow rate of 0.7mL/min for 7 minutes and wavelength UV detection of 222 nm (Jahan et al., 2014), the injection volume was 5 µL, and the column equilibrium column was 10 minutes at 40º C (Han et al., 2017). The results were then used to determine the removal efficiency of each formulated membrane.

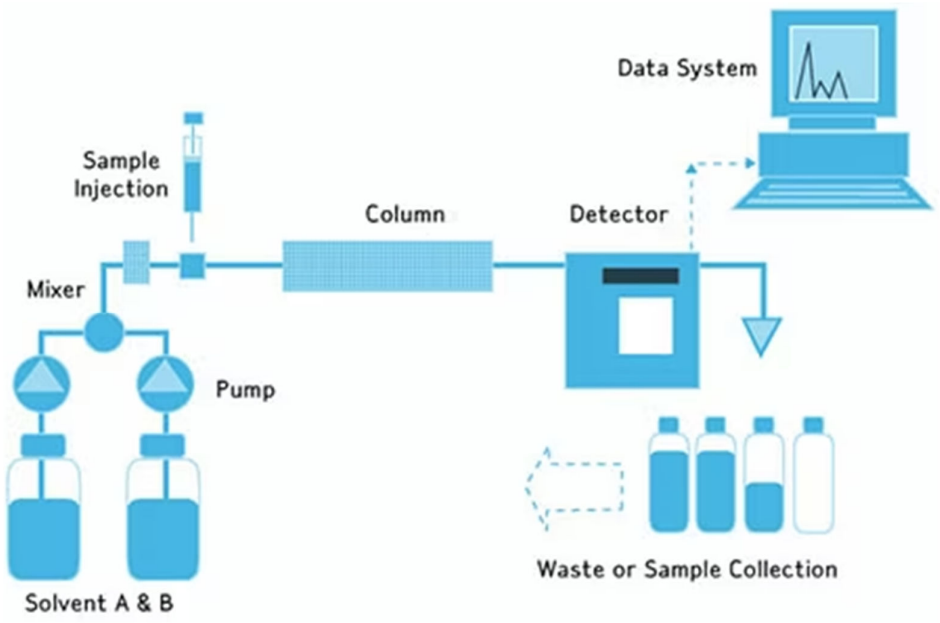


Figure 3.2: Typical HPLC System *(Adapt from (Merck, 2024))*

3.2. Data Analysis

The composite membranes were prepared as discussed in Section 3.1.1 of this report, the membranes were then prepared for characterisation. To determine the contact angle (CA), each membrane was cut into a small piece, and the sample surface was tested five times to account for any variability or inconsistencies in surface properties. Averaging these results provided a more reliable estimate of the true contact angle, minimising the impact of outliers. Since membrane surfaces can be heterogeneous, multiple measurements ensure that the average CA value is representative of the membrane's overall characteristics. The membranes were also analysed under a polarised optical microscope, visual and physical assessment as detailed in Section 3.1.2 of this report. For the HPLC analysis, four vials/samples were taken for each membrane. Section 3.1.5 of this report details the preparation and process for HPLC analysis. Similar to the CA measurements, using multiple samples and averaging the results improves the accuracy and reliability of the data. Analysing multiple vials accounts for potential variations between individual samples, enhancing the robustness of the findings. The data obtained was captured using Microsoft Excel (2016) and prepared for analysis. All outliers and errors were removed from the data to prevent the analysis from being skewed by irregular values or inconsistencies that may arise from experimental or external factors. Outliers can significantly affect the mean, especially in small datasets, leading to misleading conclusions. Excluding these outliers ensured that the final averages accurately reflected the typical behaviour of the samples. Careful data processing was essential for maintaining the integrity of the analysis, as it ensured that the results were precise and credible, providing a reliable basis for conclusions about the membrane characteristics.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Introduction

Amongst the objectives of this study were preparing and characterising four different flat-sheet membranes using PVDF and imidazolium-based PILs and testing the membranes to determine their retention time and effectiveness in removing four different pharmaceutical products which are diclofenac, cypermethrin, ibuprofen and naproxen. The details of the methodology used to achieve these objectives are in Chapter 3. Throughout Chapter 4, membrane 1 is PVDF only, membrane 2 is 12.5 g PVDF and 2.5 g imidazolium, membrane 3 is 10 g PVDF and 5 g imidazolium, lastly, membrane 4 is 7.5 g PVDF and 7.5 g imidazolium. These ratios are also outlined in Chapter 3 of this report. The raw data of results obtained in this study are attached in Annexure A.

4.2. Morphological Characterisation

Observations of the casting solutions and Physical and Visual Characteristics

Figure 4.1 shows the casting solutions in the order of the highest to lowest imidazolium concentration, i.e., left to right (beaker A to D). It can be observed that the plain PVDF sample (beaker D) is thick, foamy, and non-transparent. As the ratio of imidazolium was increased (beaker C to A), the solutions became clearer (more transparent) and more liquified, making them more difficult to work with, especially whilst casting. The plain PVDF casting solution had the highest viscosity as compared to the blended samples. The casting solution with the highest imidazolium concentration, which is the beaker on the left (A), had the lowest viscosity; the liquid formed was watery and more difficult to work with as compared to the other blended membranes. However, it was not viscous enough to run over the casting plate. It was also observed that all the casting solutions instantly solidified within seconds of contact with the DI water. Based on the above observations, it can be concluded that the addition of imidazolium-based PILs affects the viscosity of the casting solution, i.e., the higher the concentration of imidazolium, the lower the viscosity. The variance in the observed effect of imidazolium-based PILs on the viscosity of the casting solution may be attributed to differences in the chemical structure and interactions between the PILs and the PVDF polymer matrix. To the best knowledge of the author, there are no literature reviews that discuss the properties of

PVDF/Imidazolium-based PILS solutions; therefore, the visual observations cannot be compared to other studies. Although Giorno (2009) did note that increased concentration of the analytes/polymers can result in the increase of the viscosity of the casting solution. The discrepancy could be due to the unique molecular behaviour of imidazolium-based PILs when mixed with PVDF, as their interactions may reduce the affected solvent-polymer dynamics differently. Since no direct studies on PVDF/imidazolium-based PILs solutions are available for comparison, this observation remains speculative and highlights the need for further investigation.

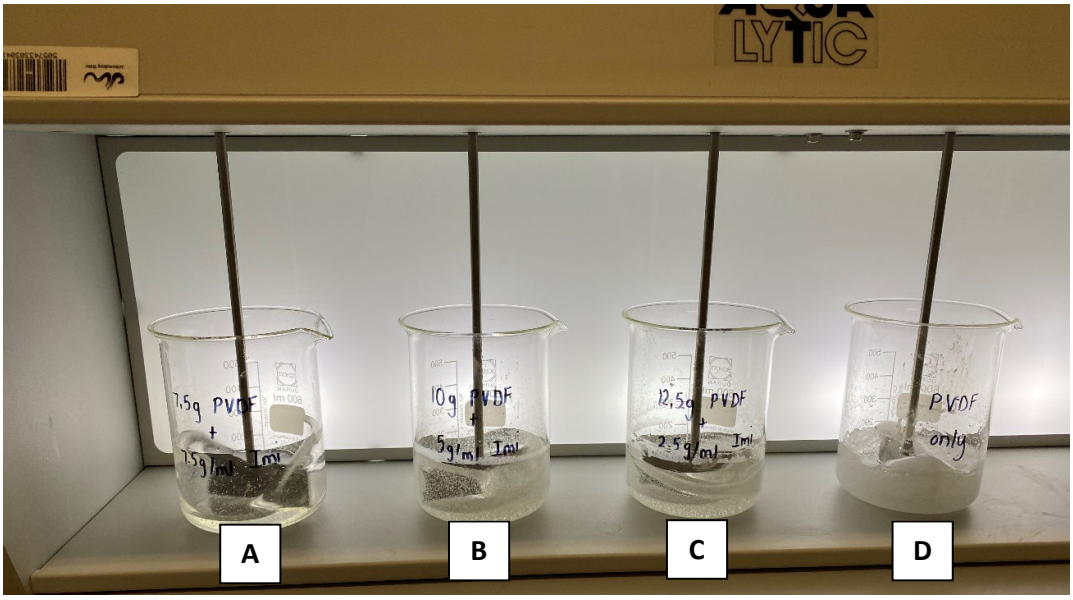
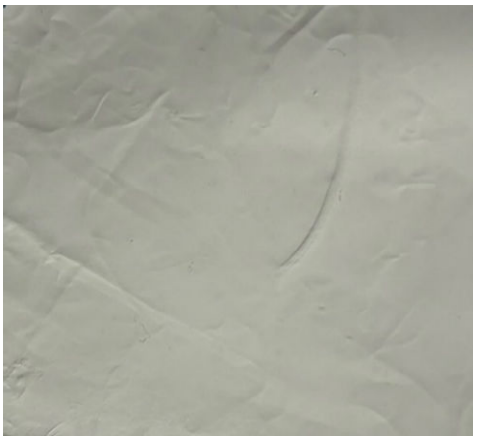


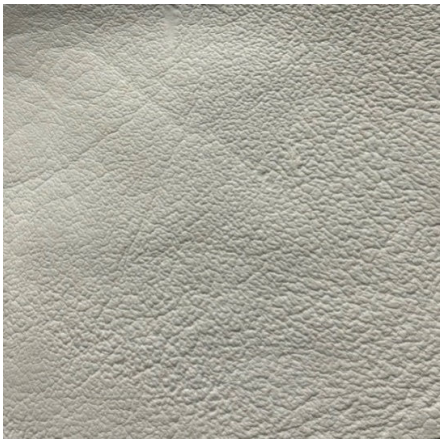
Figure 4.1: Polymer Solutions inside a Flocculator

Figure 4.2 shows the various textures of the synthesised membranes. Membrane 1 (top left corner) had a high-gloss (perfectly smooth and shiny) finish. The membrane was well-formed, not brittle, and displayed mechanical strength, flexibility, tensile strength (stretch), wear and water resistance. The membrane was gently bent and stretched to observe any response to deformation, the membrane maintained its structure without breaking or tearing; therefore, it was concluded that it is well-formed, tensile, and flexible. The membrane was subjected to friction and it displayed no changes to the surface. Furthermore, the membrane was immersed in water to see its response, the water flowed off the surface indicating its good water-resistant properties. The appearance and properties were as expected, as previously reported in the literature (Inderherbergh, 2017; Dallaev et al., 2022). When membranes 2, 3, and 4 were subjected to the same assessment as listed above, the results were not the same as Membrane 1. The addition of imidazolium changed the texture of the membranes. Membrane 2 (top right corner) was observed to be semi-glossy and rougher; Membrane 3 (bottom left corner) was rougher and less glossy (more matte than glossy), while Membrane 4 (bottom

right corner) had a matte to dull finish. Membrane 4 was soft to the touch, lightweight (compared to the other membranes), and absorbed water. It was the most brittle membrane and difficult to work with. Membrane 4 is comparable to tissue paper. The colour of the membranes was in the same spectrum of white colours: the variance was minimal. From the above, it was evident that the increased addition of imidazolium leads to a more sponge-like or inner orange-peel-like surface. Membrane 4, which had the least viscous solution, led to a brittle and soft-touch membrane. There is a clear relationship between the form of the casting solution and the final membrane morphology and properties. Galiano (2016) and Lanjewar et al. (2020) reported that lesser concentrations of the polymer produce a more porous membrane, whereas high concentrations of the polymer result in a membrane with a more dense structure. Membrane porosity is discussed in the subsequent sections. The findings presented in this research report align with those reported in previous studies, confirming the anticipated outcomes.



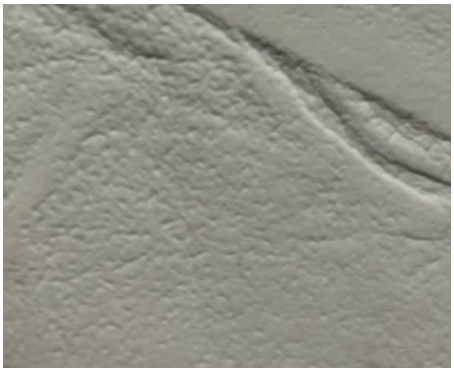
Membrane 1



Membrane 2



Membrane 3

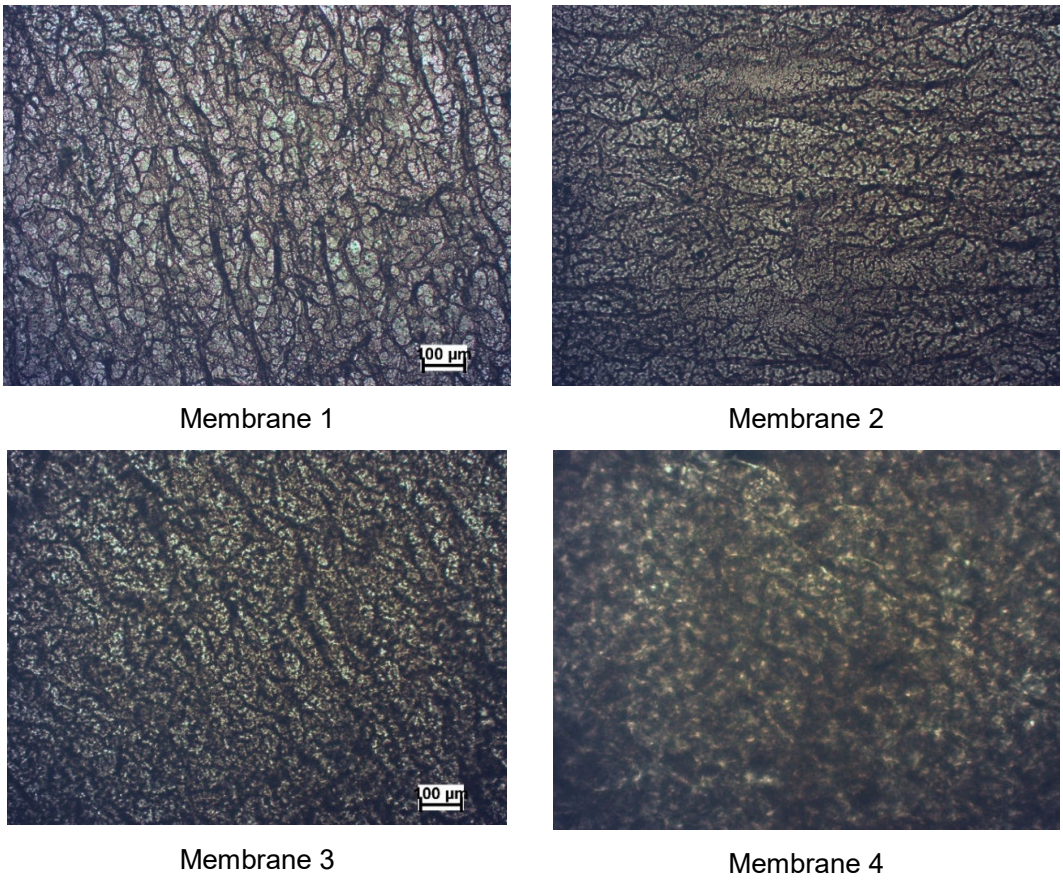


Membrane 4

Figure 4.2: Membrane Textures

Polarised Light Microscopy

As outlined in Chapter 3, Section 3.1.2, the formulated membranes were observed under the polarised light microscope for surface characterisation. The results from this are shown in Figure 4.3. There was a clear difference in surface morphology; Membrane 1 (top left corner) had wider openings than Membrane 4 (bottom right corner). The thickness of the synthesised membranes could not be confirmed using polarised light microscopy because this technique is not specifically designed for thickness measurements. Polarised light microscopy is primarily used to study the optical properties of materials rather than accurately measuring the thickness. Additionally, membrane thickness typically requires more direct and precise measurement techniques, such as SEM, which provides the necessary resolution to determine the membrane's exact dimensions. From the visual analysis, it was concluded that the most impenetrable membrane was Membrane 4. Overall, the membrane pore structure and surface roughness changed with the addition of imidazolim-based PILs. The surfaces had no defects and presented uniformity of the pore structure as the methods presented in Chapter 3 were duly observed to ensure that good quality membranes are formed. However, the findings need to be confirmed through the value of the water flux on each membrane. Similar results were previously reported, where the addition of a polymer to the PVDF membrane resulted in a decrease in the pore sizes for the composite materials (Mejri et al., 2016; Sabri et al., 2019; Purnawan et al., 2021). Following the uniformity of the synthesised membranes, it was concluded that there was no demixing between the solvent and non-solvent in the coagulation bath.



Membrane 1 Membrane 2

Membrane 3 Membrane 4

Figure 4.3: Polarised Light Microscopy- Results for Membrane 1, 2, 3 and 4 Surfaces

Membrane Porosity and Pore Size

The membrane porosity and pore size were calculated using equations 1 and 2 outlined in Chapter 3, Section 3.1.2, and the results are presented in Table 4.1, figures 4.4 and 4.5. Compared with plain PVDF, the blended membranes have higher porosity (ability to hold water) values and smaller pore sizes. This means that the addition of imidazolium-based PILs tends to close up and reduce the pore sizes and increase the membrane porosity. Membrane 1 had the lowest porosity (15.3%) and the highest pore size 17.09 ηm, while Membrane 4 had the highest porosity (91.35%) and least pore size (2.36 ηm), which suggested that the addition of imidazolium reduced the pore size and increased the porosity of the membrane. These results are supported by the findings presented in figures 4.2 and 4.3 in this report and by studies conducted previously. In summary, it can be concluded that the addition of a polymer increased the membrane porosity by altering the phase separation process during membrane fabrication. As reported in previous studies, in polymer blending, the introduction of a second polymer modifies the thermodynamic and kinetic properties of the casting solution, leading to a more controlled phase inversion. This then results in a more porous structure, with

interconnected pores that allow for greater water retention (Zahid et al., 2018). The smaller the pore sizes and the higher porosity in the blended membranes when compared to plain PVDF arise because the added polymer disrupts the uniformity of the PVDF matrix, promoting more pore formation during solidification. Consequently, this enhances the membrane's ability to hold water while maintaining finer pores for filtration (Ali et al., 2018).

Literature shows that the total porosity increases as the polymer concentration increases up to a certain threshold techniques (Galiano, 2016; Sabri et al., 2019; Purnawan et al., 2021). Research conducted previously found that the pore size initially increased due to the polymer's ability to speed up demixing while casting. This observation was attributed to the polymer's hydrophilic nature. It was also noted that the pore size will start to decrease at maximum loading (Sabri et al., 2019). Interestingly, other researchers reported that there is a limit to the addition of the polymer to modify the membrane. At a certain point, the porosity will decrease slightly. One can define this point as overloading, as the process begins to reverse. The researchers attribute this trend to the thermodynamics factors, such as the type of solvent and choice of polymer, that affect the demixing process and the selected inversion techniques (Galiano, 2016; Purnawan et al., 2021). To the best knowledge of the author, although there is extensive research on membrane technology, there is limited literature that is focused on the relationship between the composite membrane surface morphology and the parameters that affect membrane fabrication. The available literature focuses on the preparation methods and not their effects on the final membrane characteristics, particularly surface morphology. Critical factors such as polymer concentration, solvent choice, temperature, and the incorporation of nanomaterials significantly influence the membrane's porosity, roughness, hydrophilicity, and overall performance. Understanding this link is essential, as the surface properties of membranes directly affect their filtration efficiency, fouling resistance, mechanical strength, and suitability for various applications, such as wastewater treatment. Thus, further research is needed to systematically study how fabrication parameters alter membrane surface morphology and, consequently, the membrane's final functional properties. In this research, demixing was not encountered nor was the threshold at which the porosity starts to decrease established.

Table 4.1: Estimations of Membrane Porosity and Pore Sizes

MEMBRANE	PARAMETERS								POROSITY ε (%)	PORE SIZE r_m (ηm)
	W_d (g)	W_d (g)	ρ_w (kg/m3)	A (m^2)	l (µm)	η (Pa.s)	Q (m3/s)	ΔP ($kg.m^{-1}.s^{-2}$)		
1	0.0424	0.0394	998	7.85398×10^{-5}	25	0.00089	4.58716×10^{-7}	611.8988	15.31	17.0910
2	0.0376	0.0301	998	7.85398×10^{-5}	250	0.00089	3.5461×10^{-7}	611.8988	38.27	8.74829
3	0.0365	0.0239	998	7.85398×10^{-5}	250	0.00089	1.7301×10^{-7}	611.8988	64.30	4.20557
4	0.0361	0.0182	998	7.85398×10^{-5}	250	0.00089	1.05263×10^{-7}	611.8988	91.35	2.35683

The results tabulated in Table 4.1 are shown graphically in figures 4.4 and 4.5. An increasing trend can be observed for the porosity and a decreasing trend for the average pore size. The R^2 values are above 90% for both graphs.

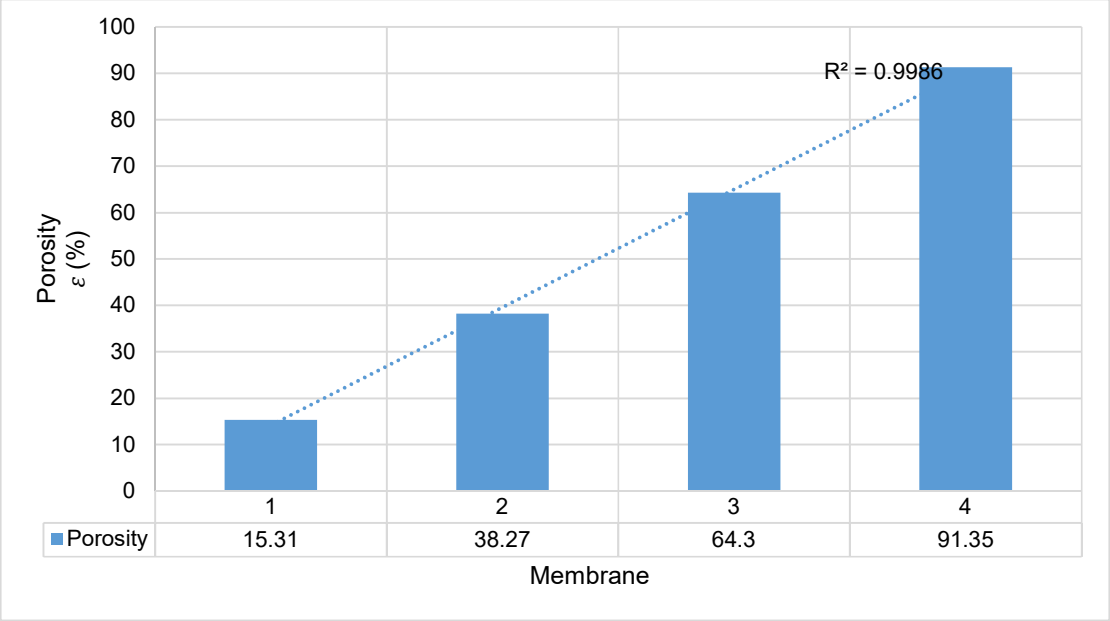


Figure 4.4: Total Porosity for the Synthesised Membranes

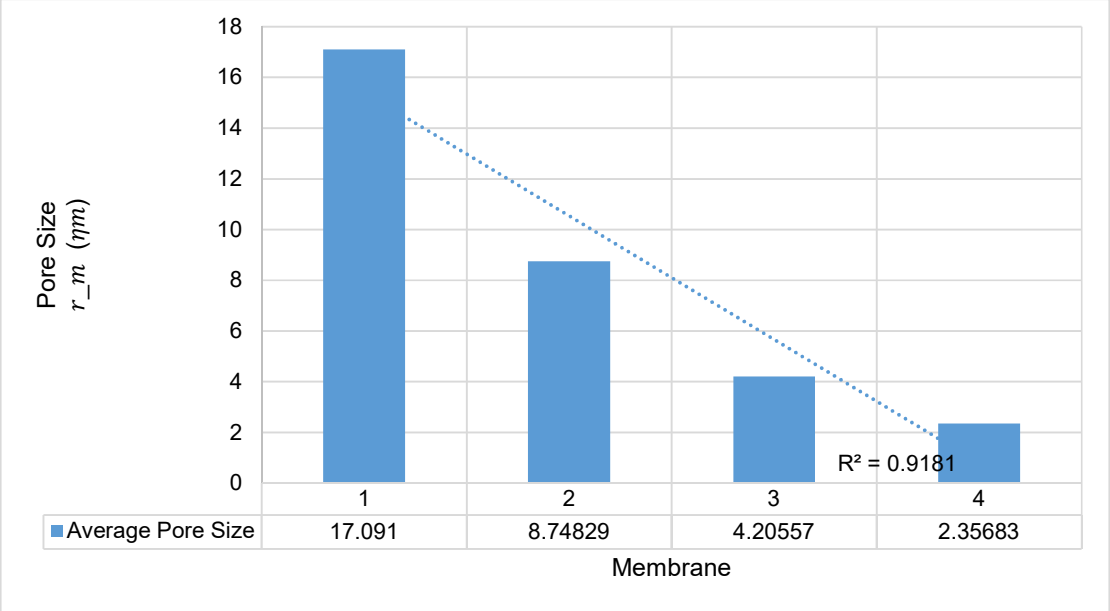
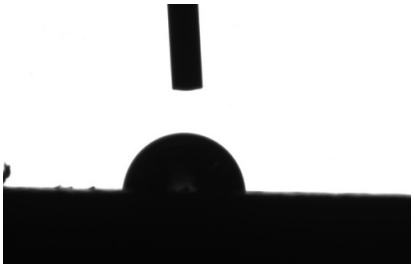


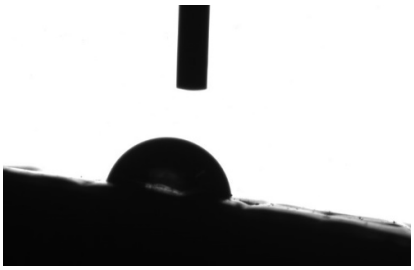
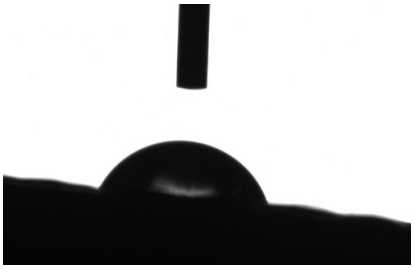
Figure 4.5: Average Pore Size for the Synthesised Membranes

Water Contact Angle

The CA was measured using the methodology described in Chapter 3, Section 3.1.2. The CA enables one to establish whether the surface has hydrophobic or hydrophilic characteristics. Table 4.2 reflects the CA values obtained for the different membranes. For each membrane, 5 measurements were conducted on the surface. Membrane 1 was confirmed to be hydrophobic as the CA was greater than 90º; the average CA was 106.57º. The composite membranes had CA values less than 90º; therefore, they are considered hydrophilic. From the results shown in Table 4.2, it can be concluded that the imidazolium-based PILs have the ability to increase the hydrophilicity of the PVDF membrane. Membrane 4 had the lowest average CA of 54.72º. Greater ratios (than that used in this study) of imidazolium could yield superhydrophilic properties, the threshold limit as discussed, is yet to be established. Following the above-discussed results, it is shown that as the concentration of imidazolium-based PILs increases, the contact angle (CA) value decreases. The trend can also be seen in Figure 4.6. Furthermore, this indicates that the addition of imidazolium-based PILs leads to a more hydrophilic membrane surface. The desired results were achieved as hydrophilic membranes are less susceptible to fouling. However, the optimum combination needs to be determined to ensure that the membrane solution is workable and the formed membrane is not brittle. The results obtained are as expected and consistent with previous studies. Several studies have previously reported that the addition of hydrophilic polymers tends to improve the hydrophilicity of the synthesised membrane (Ang et al., 2017; Zahid et al., 2018; Sabri et al., 2019; Purnawan et al., 2021).

Table 4.2: Contact Angle Values

MEMBRANE	CONTACT ANGLE (^{o})					IMAGE
1	102.67	115.33	107.40	106.88	103.56	
2	87.77	86.89	86.86	87.89	87.34	

3	72.43	75.10	64.75	68.12	74.12	
4	48.49	45.20	59.72	59.81	60.39	

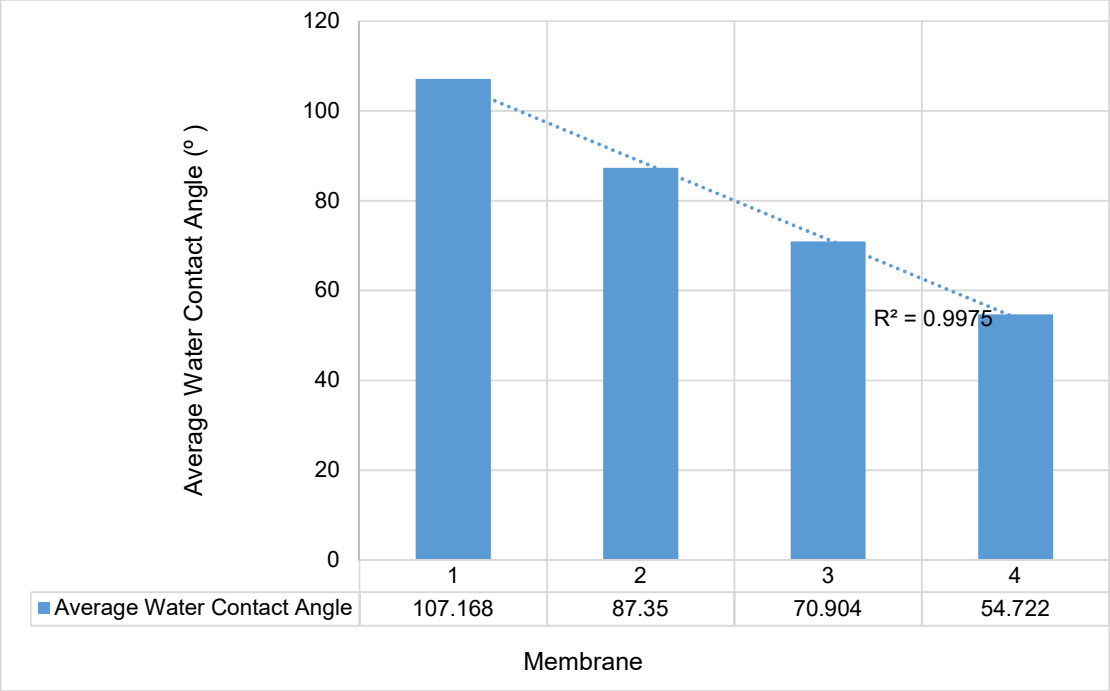


Figure 4.6: Average Water Contact Angle Measured

4.3. Performance Measurements

Table 4.3 depicts the pH and temperature of DI water and the spiked water samples, respectively. The results show that the analytes altered the pH of the water. It was observed that the DI water beakers were neutral (pH = 7), whereas the spiked water samples were acidic. Fin et al. (2012) reported that diclofenac is a weak acid; therefore, minimal changes are expected in the pH. When spiking the water with naproxen, ibuprofen, and cypermethrin, greater effects were observed. The lowest recorded pH was 2.94, which was attributed to the addition of cypermethrin to DI water. The recorded temperature for all samples averaged 19º C. The optimum pH in river water is approximately 7.4. Therefore, changes in pH of this nature is not desirable as it could be detrimental to aquatic life. Diclofenac, naproxen, and ibuprofen are acidic (Fini et al., 2012), have low solubility and are thus slow to break down in their salt form. The excretion of these drugs is usually 10, 70 and 10% as un-metabolised drugs, respectively (Madikizela et al., 2017). The above-mentioned further stresses the significance of removing these pharmaceuticals from wastewater. Furthermore, Fin et al. (2012) reported that wastewater containing these substances can have several detrimental (often resulting in death) effects on aquatic organisms and the environment, as they can be highly toxic even at very low temperatures. Cypermethrin is also undesired in natural waters, it is an insecticide that has a low aqueous solubility and vapour pressure. It is toxic to aquatic and human life. As mentioned above, the presence of these pharmaceuticals altered the pH (decreasing trend) of the water; this is illustrated in Figure 4.7.

Table 4.3: Temperature and pH Readings

		DI WATER BEAKERS		SPIKED BEAKERS	
ITEM	**Analyte**	**pH**	**Temp (ºC)**	**pH**	**Temp (ºC)**
1	Diclofenac	7.16	19.2	6.11	18.7
2	Naproxen	7.14	19.1	4.76	19.3
3	Ibuprofen	7.18	19.2	4.52	19.2
4	Cypermethrin	6.97	19.2	2.94	19.1

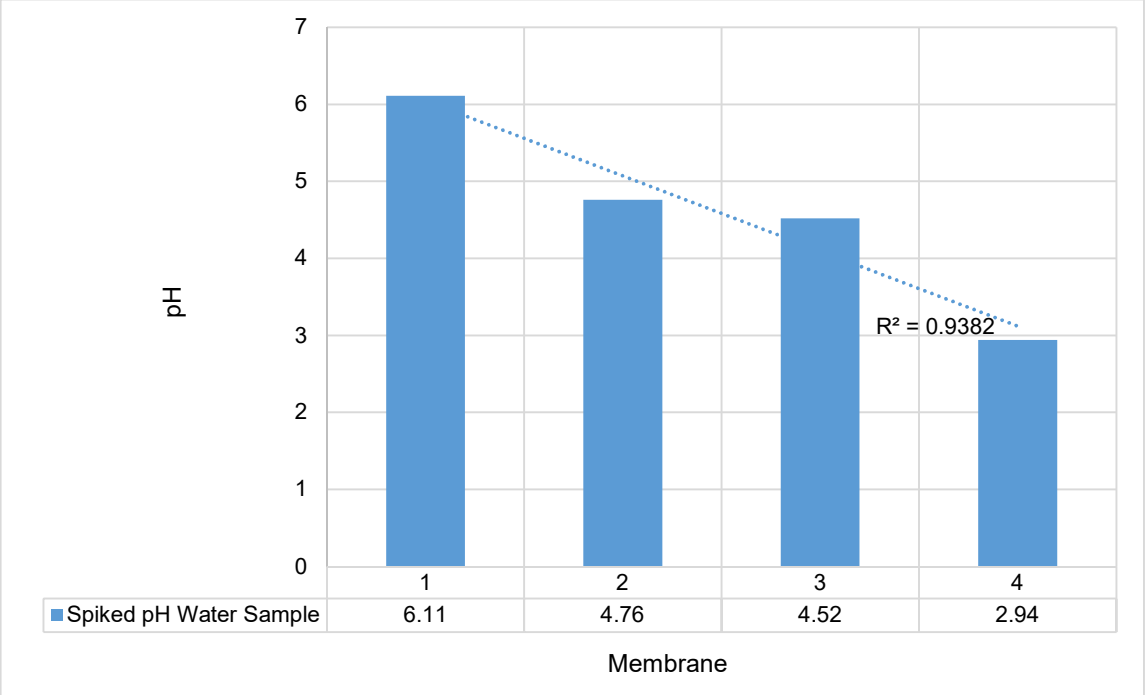


Figure 4.7: pH Values for Spiked Water Samples

The membranes have been evaluated for retention time (t) (the average time that a fluid or a solute remains in contact with the membrane system during filtration or treatment) and their separation ability (removal efficacy). Table 4.4 and Figure 4.8 show the retention results recorded for the various membranes. It must be noted that no pressure was applied; only the force of gravity was allowed. As discussed in this report, PVDF is made from vinylidene fluoride monomer through a free-radical polymerisation process. Although PVDF has exceptional mechanical and chemical characteristics and can be used in various applications, it has a hydrophobic inherent property. Therefore, it is prone to membrane fouling. Several studies, including this one, have shown that adding hydrophilic properties to plain PVDF is advantageous. Due to their efficiency and special properties, imidazolium-based PILs have been blended with PVDF at various ratios to improve their performance. Section 4.1 observed that the higher the imidazolium ratio, the lower the pore size and contact angle (measurement of hydrophilicity). Table 4.6 also indicates similar results obtained in previous studies. It was observed that the higher the ratio of imidazolium, the higher the retention time. These results could lead to higher efficiencies in wastewater treatment.

Table 4.4: Retention Times for 50mL (min:second:spilt-second)

MEMBRANE	BLANK	DICLOFENAC	NAPROXEN	IBUPROFEN	CYPERMETHRIN
1	1:48:78	1:46:98	1:27:90	1:28:22	1:33:70
2	2:21:17	2:46:95	2:39:33	2:45:33	2:12:53
3	4:48:68	4:29:49	5:01:33	4:49:26	4:48:28
4	7:55:52	7:56:42	8:05:92	8:20:94	7:59:70

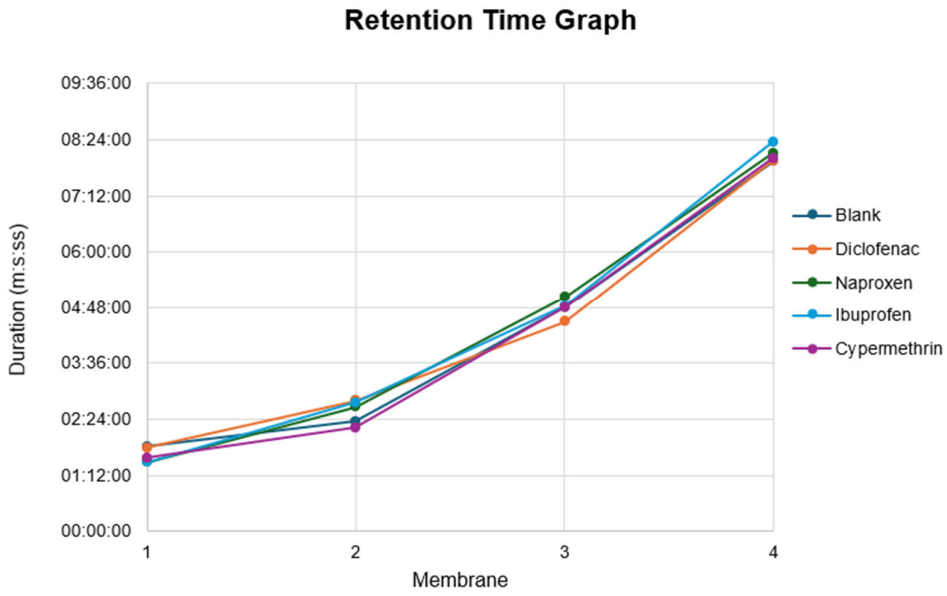


Figure 4.8: Retention Time Graphical Presentation

The HPLC analysis was done to determine the removal efficacy of each membrane. Table 4.5 shows the removal efficiencies recorded for the various membranes. The recorded removal efficiencies were greater than 90%. It was observed that plain PVDF performs as well as the PVDF/Imidazolium membranes. These results were expected as the removed efficacy of PVDF was not doubted. Several studies have investigated the removal of pharmaceutical products using nanocomposite materials; the removal efficiencies are tabulated in Table 4.6. Considering the results obtained in this study and those previously reported, it can be concluded that synthesised nanocomposite membranes yield high removal efficiencies. However, the drawback is membrane fouling which may require chemical cleaning. However, this study has also shown that imidazolium-based PILs have the ability to improve the hydrophilicity of the composite membrane. Therefore, fouling will be significantly reduced. Consequently, the high operational costs of running MBR treatment will be reduced if nanomaterials are employed.

Table 4.5: Removal Efficacy of the Membranes

MEMBRANE	DICLOFENAC			NAPROXEN			IBUPROFEN			CYPERMETHRIN		
	Concentration (mg/L)		Removal Efficacy (%)	Concentration (mg/L)		Removal Efficacy (%)	Concentration (mg/L)		Removal Efficacy (%)	Concentration (mg/L)		Removal Efficacy (%)
	Initial	Final		Initial	Final		Initial	Final		Initial	Final	
1	2.16	0.00132	99.94	0.81	0.03961	95.11	0.81	0.03567	95.60	0.15	0.00121	99.19
2	2.16	0.00040	99.98	0.81	0.03851	95.25	0.81	0.02994	96.30	0.15	0.001178	99.21
3	2.16	0.00069	99.97	0.81	0.04178	94.84	0.81	0.02622	96.76	0.15	0.00091	99.39
4	2.16	0.00086	99.96	0.81	0.04174	94.85	0.81	0.00689	99.15	0.15	0.000907	99.40

Table 4.6: Previously Reported Removal Efficiencies by Various Nanocomposite Membranes

TARGET PHARMACEUTICAL	REMOVAL EFFICIENCY RANGE (%)	REFERENCE
CIPROFLOXACIN	99.67	(Qalyoubi, et al., 2022)
DICLOFENAC	>93	(Loganathan, et al., 2023)
IBUPROFEN	>90	(Loganathan, et al., 2023)
NAPROXEN	>98	(Loganathan, et al., 2023)
FENOPROFEN	99.6	(Mbhele, et al., 2018)

4.4. Summary and Results Overview

The study investigated the preparation, characterisation, and performance of imidazolium-based PILs/PVDF membranes for the removal of ECs. Results revealed that the incorporation of imidazolium significantly impacted the properties of both the casting solution and the final membranes. Furthermore, the results highlight a strong interconnection between porosity, pore size, retention time, CA values, hydrophilicity, and the observed physical characteristics of the blended membranes.

As the concentration of imidazolium increased, the porosity of the membranes also increased while the pore size decreased. This is due to the way imidazolium affects the phase separation process during membrane formation, which leads to a more interconnected pore structure and a higher total pore volume. A highly porous structure allows for more water retention, which is advantageous for filtration applications as it enables the membrane to hold more contaminants within its structure; thereby, having a higher removal efficacy. As seen in this study, a higher porosity generally leads to increased retention time. Membranes with smaller pores and increased porosity tend to trap contaminants more effectively, which extends the time the fluid remains in contact with the membrane during filtration. However, Membrane 4, with the highest imidazolium concentration, was brittle, highlighting a limitation in achieving optimal membrane stability. This relationship is essential for applications requiring prolonged exposure to the membrane for improved contaminant removal. This trend aligns with previous study findings that indicate polymer blending modifies phase separation and promotes pore formation, resulting in a sponge-like structure and enhanced water retention.

The CA values decreased as imidazolium concentration increased, meaning the membranes became more hydrophilic. Hydrophilic membranes are less prone to fouling because they attract water, allowing contaminants to be washed away more easily and have better operational efficiency. As the imidazolium concentration increased, the casting solution's viscosity decreased, making the mixture more transparent but harder to handle during membrane formation. The final membranes exhibited diverse surface textures and mechanical properties compared to unblended PVDF. The physical characteristics, such as flexibility, gloss, and brittleness, also varied with imidazolium concentration. The blended membranes were less glossy and more brittle. Increased hydrophilicity often correlates with softer, less rigid structures, which was observed as the membranes with higher imidazolium content were more prone to brittleness and absorbed water more easily. The most porous membranes also tended to have more sponge-like textures, reflecting an increased capacity for water retention but also reduced mechanical stability. This effect was most observed in Membrane 4. While

removal efficiencies exceeded 90% for all tested contaminants, the addition of imidazolium did not significantly outperform plain PVDF in this aspect, suggesting that while the PILs improve hydrophilicity, they do not inherently enhance removal capabilities. Together, these findings illustrate that the addition of imidazolium concentration can improve membrane properties. While higher porosity and hydrophilicity improve contaminant removal and reduce fouling, they also affect mechanical strength and durability. Therefore, balancing these parameters is crucial for optimising the membranes for specific filtration applications.

The study faced limitations in establishing a precise threshold for imidazolium concentration where membrane stability begins to compromise, as well as in determining the full impact of polymer concentration on demixing behaviours and the membrane's physical properties. Despite these constraints, the study successfully demonstrated that PVDF/imidazolium-based PILs membranes show potential for wastewater treatment, especially in mitigating fouling and potentially reducing the operational costs associated with MBR systems. Future research should focus on optimising polymer ratios and exploring other ECs to better understand the broader applicability and performance limits of these composite membranes.

CHAPTER 5: CONCLUSION

This study aimed to develop and assess imidazolium-based PILs and PVDF membranes for the removal of diclofenac, cypermethrin, ibuprofen, and naproxen using SPE cartridges. The study began with a comprehensive literature review, exploring the characteristics, fate, and transport of ECs and their potential adverse effects on both the environment and human health, emphasising the need for effective removal. Following this, PVDF/imidazolium-based PILs membranes were prepared through TIPS, and then characterised to determine properties like surface structure, pore size, porosity, and hydrophilicity or hydrophobicity. The study also assessed the membranes' retention time and removal efficacy for the selected contaminants, offering insights into their potential application in environmental remediation and also paving the way for further research and development in this area.

Globally, the occurrence and prevalence of ECs such as, amongst others, pharmaceuticals, personal care products, endocrine disrupting compounds, heavy metals, polar pesticides, surfactant residues, plasticisers, and a mixture of industrial additives, in water bodies has emerged as a critical water pollution issue. Their rapid emergence can be attributed to high population growth, the proliferation of urbanisation and industrial activities, and climate change. Despite being present in trace amounts, ECs can induce harmful effects on both human and aquatic life due to their potential toxicity, ability to accumulate in organisms, and persistence in the environment. For example, antibiotic-resistant genes and antibiotics have the potential to create antibiotic-resistant bacteria that will potentially result in continuous exposure. Hence, it will be more difficult to eliminate these bacteria. Needless to say, this effect is undesired. Although significant research has been conducted on this topic, the ecotoxicological effects of some ECs are still unknown, as well as the effects of long-term exposure. Other studies have shown that some pharmaceuticals are highly toxic as they have been found to cause morphological endocrine changes in aquatic life that have ultimately led to their death. Therefore, it is crucial that these ECs be removed from wastewater before it is discharged into the natural environment. Moreover, further research remains necessary for the fate, behaviour, potential risk, and monitoring of ECs, especially in South Africa. A significant number of ECs are not regulated or monitored under national regulations. There are several natural and anthropogenic sources for the introduction of ECs to water bodies and the broader environment; however, effluent from wastewater treatment has been accentuated as the biggest contributor.

The main challenge of ECs, particularly pharmaceuticals, which are the subject of this report, is that they cannot be entirely removed by conventional WWTPs. Thus, they may end up in water bodies. As a result, many advanced treatment processes have been proposed to treat wastewater containing ECs. In recent years, nanocomposite membranes have received much attention from numerous researchers due to their high removal rate and enhanced performance. The PVDF are polymeric membranes used in ultrafiltration, microfiltration, and membrane bioreactor systems because they have good thermal and chemical resistance and mechanical stability. However, due to their hydrophobicity, these membranes have low water permeation and high fouling. These membranes can be coated with a hydrophilic nanocomposite material to modify their surface, thereby limiting fouling.

Composite membrane fabrication has become very popular with membrane researchers. The processes for composite membrane synthesis are simple and highly efficient. Additionally, the membrane results in elevated properties and performance. The objective of this study was to synthesise 4 composite membranes (Imidazolium-based Poly Ionic Liquids/PVDF) using the phase inversion method. The concentration of the additive ranged between 0 to 50% wt, it was used as a hydrophilic agent for membrane surface modification. The main focus was to achieve a membrane with high removal efficiency and decrease membrane fouling by enhancing PDVF hydrophilicity. Furthermore, the membranes were characterised using visual assessment, optical microscopy, calculation of porosity and average pore size, and measurement of the water contact angle. The performance of the membranes was evaluated using the separation efficiency of diclofenac, cypermethrin, naproxen, and ibuprofen and taking the retention time. The changes in temperature and pH were also investigated.

The results attained from the visual assessment and optical microscopy analysis indicated that the increased concentration of imidazolium-based PILs led to porous structure changes in the surface of the membrane with higher surface roughness being obtained. The plain PVDF was glossy and solid, like a plastic bag. Whereas the surface of the composite membranes was more sponge-like or had an inner orange peel appearance. The pores appeared bigger under the microscope when compared to the composite membranes. Plain PVDF had the lowest porosity (15.3%) and the highest pore size 17.09 ηm, while the membrane with the highest imidazolium concentration had the highest porosity (91.35%) and least pore size (2.36 ηm). The results from the water contact angle indicated that the introduction imidazolium-based PILs improved the hydrophilicity of the membrane surface. Plain PVDF was confirmed to be hydrophobic as the CA was greater than 90º; the average CA obtained was 106.57º. The composite membranes had CA values less than 90º; therefore, they were considered hydrophilic. The lowest average CA measured was that of the membrane with the highest

concentration of imidazolium, i.e., 54.72º. The membranes all showed high removal efficiencies greater than 90%. The results obtained and trends established in this research are supported by previous studies that obtained similar results and conclusions.

Furthermore, the findings of this research report indicate that the use of imidazolium-based PILs for membrane synthesis is a viable technology for extracting pharmaceutical products such as diclofenac, naproxen, ibuprofen, and cypermethrin from wastewater. Membrane fouling remains a universal problem. Therefore, treatment processes like nanocomposite membranes have the potential to solve this problem, as it has been shown that these membranes have high removal efficiencies and present substantial enhanced surface hydrophilicity and porosity. Additionally, the high capital and operational costs of membrane systems will be reduced due to the use of nanocomposite material. Most materials employed for this type of membrane synthesis are ready-to-use products that are widely available. Several studies have reported that nanocomposite materials are more economical. Nanocomposite membranes are also preferred because of the enhanced membrane hydrophilicity. It can be concluded that the membranes synthesised in this study are highly efficient, pose flexibility in designing for porosity, hydrophilicity and functionality, and are potentially economical.

RECOMMENDATIONS FOR FUTURE RESEARCH

Arising from the current study, it is recommended that researchers investigate:

- The limit threshold for the concentration of imidazolium-based PILs/PVDF. As discussed, there is a limit at which the porosity starts to decrease. This limit must be established. Establishing a precise limit threshold at which porosity begins to decrease would require extensive experimental work, involving multiple trials at various concentrations and in-depth analysis of the resultant membrane structures. This level of detail was beyond the current study's parameters, which focused on initial characterisation and evaluation rather than on optimisation.
- The effects of the choice of polymer and preparation method used for membrane synthesis. Investigating the effects of different polymers and preparation methods on membrane synthesis would involve a broader set of materials and techniques. Conducting such an investigation would require access to a wider range of polymers and a detailed exploration of alternative preparation methods beyond the TIPS technique used herein. This was not feasible within the confines of this study, which aimed to focus on one specific polymer and preparation method to provide a proof-of-concept.

- The removal efficiency of other groups of ECs using the synthesised membrane. While the study focused on a specific set of contaminants, investigating other classes would expand the study's scope significantly, requiring different analytical methods and possibly a more extensive timeline.

Based on the reasons stated above, it is recommendations that future research should build upon the foundational findings of this study.

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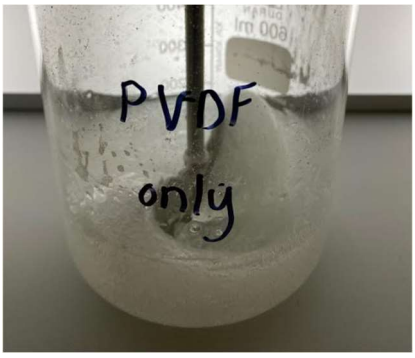
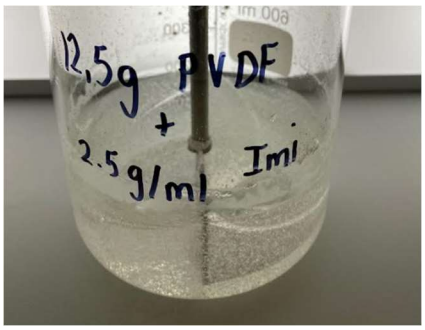
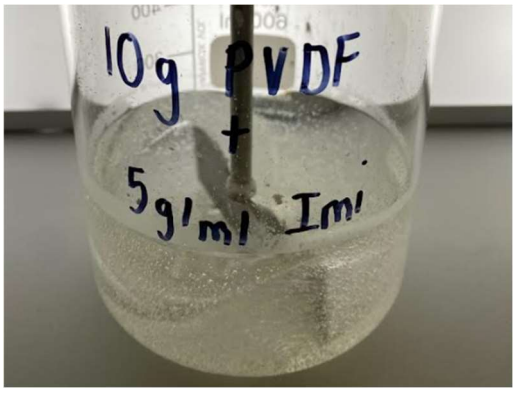
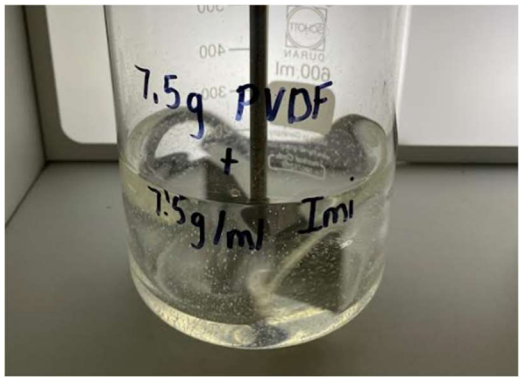
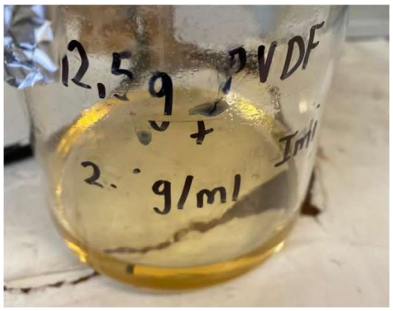
ANNEXURE A: RAW DATA

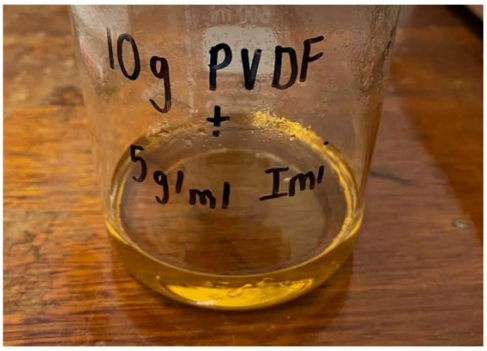
A1: PHOTOGRAPIC LOG

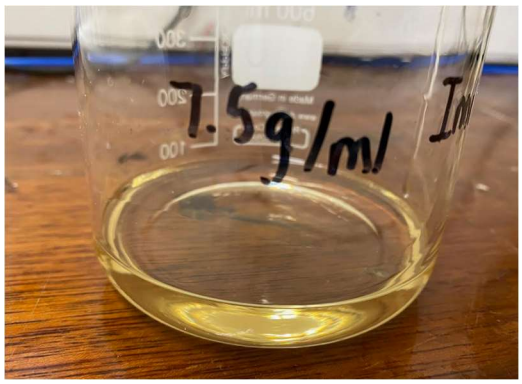
PHOTOGRAPHIC LOG

Casting Solutions	
	
	
	









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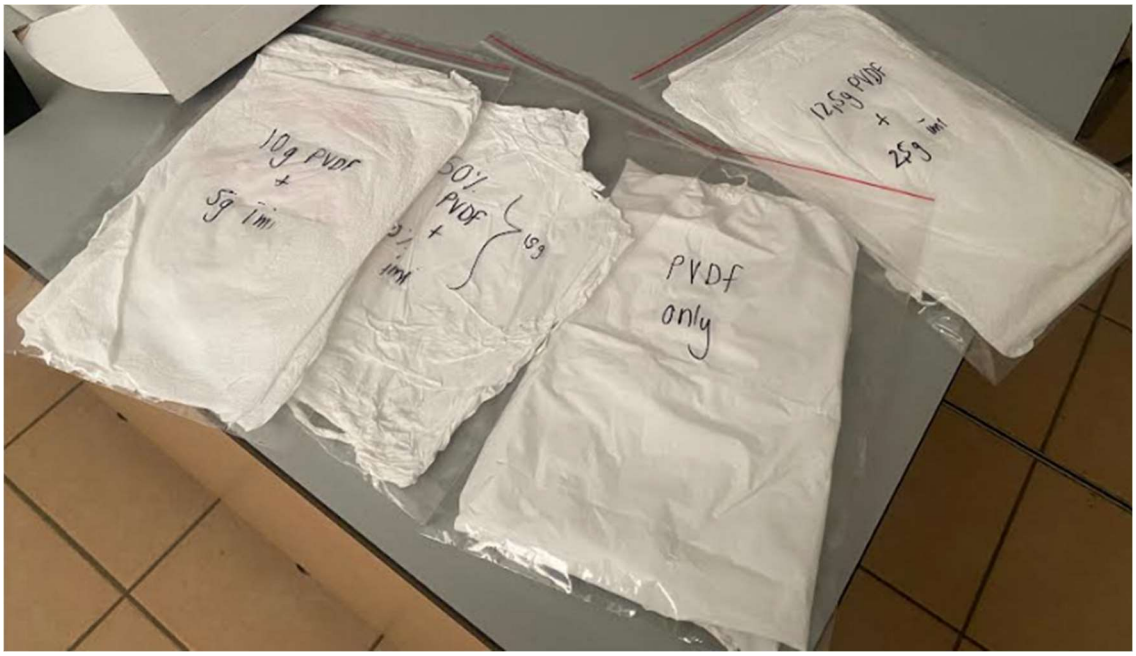

Optical Microscopy Results

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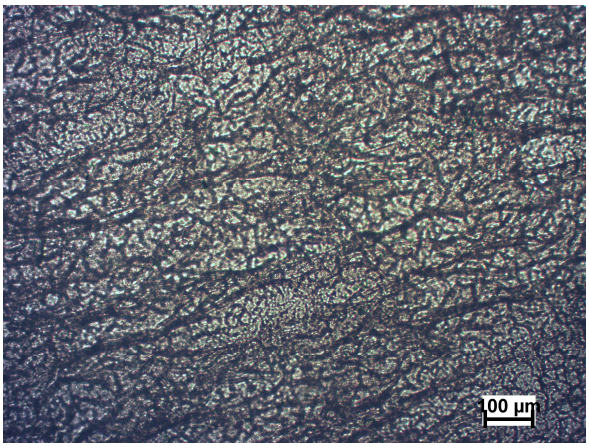

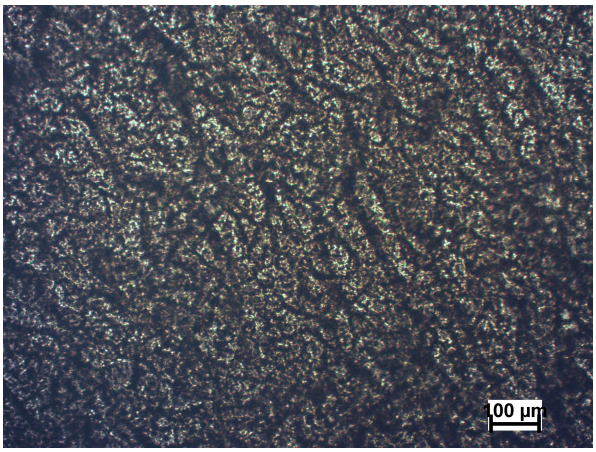

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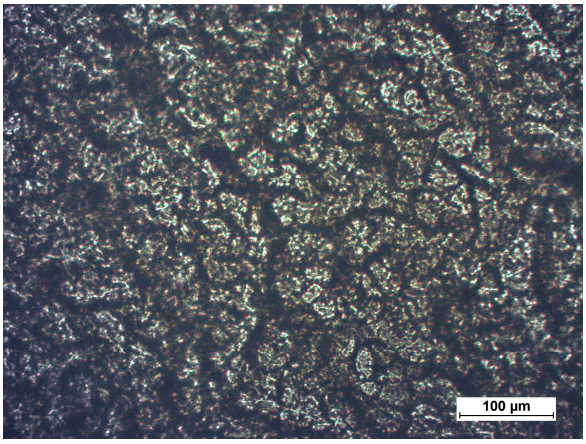

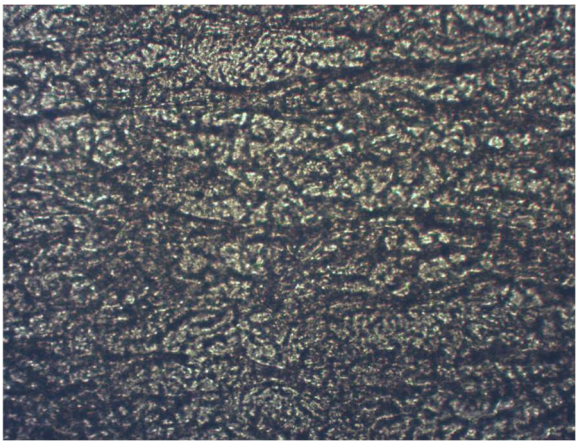

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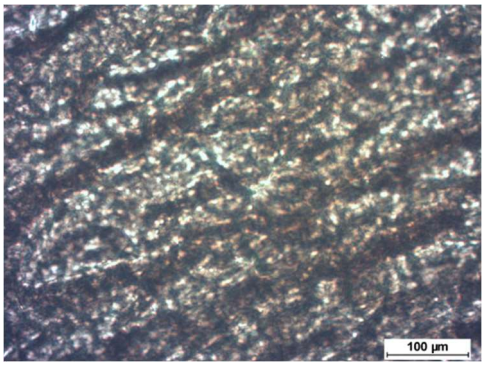

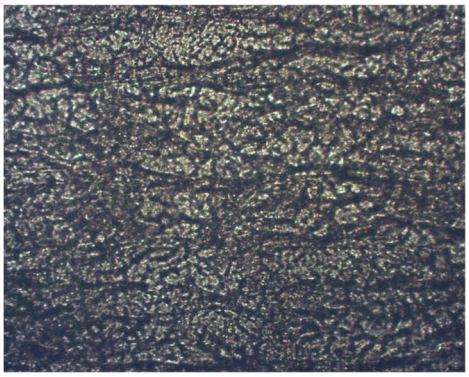

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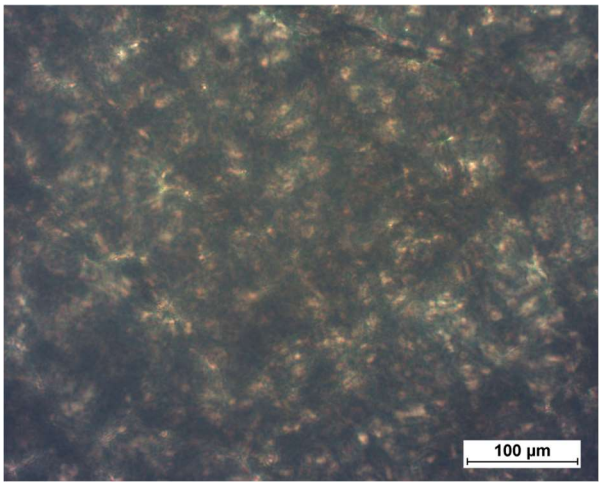
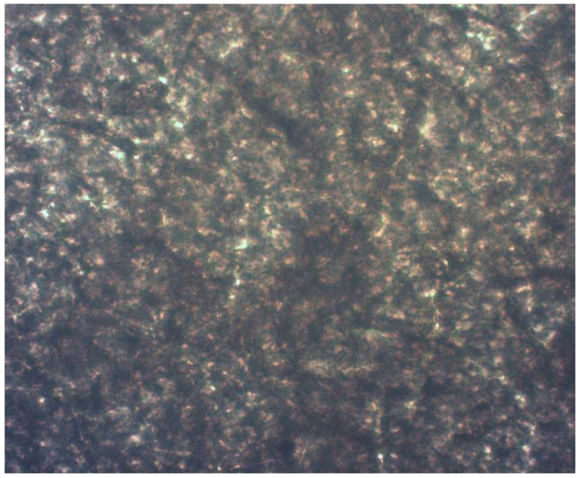
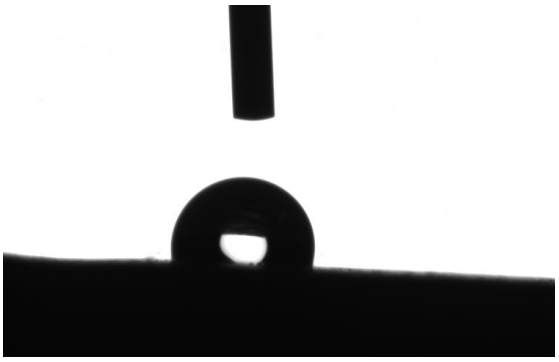




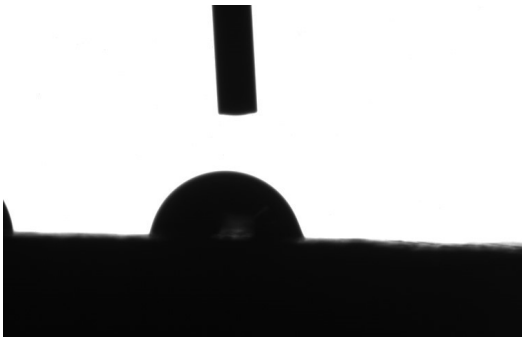
Water Contact Angle Results

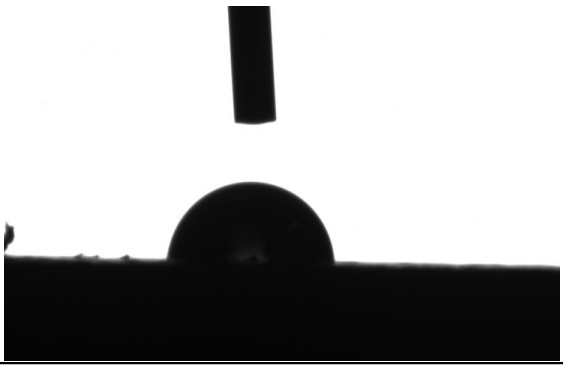
Membrane 1



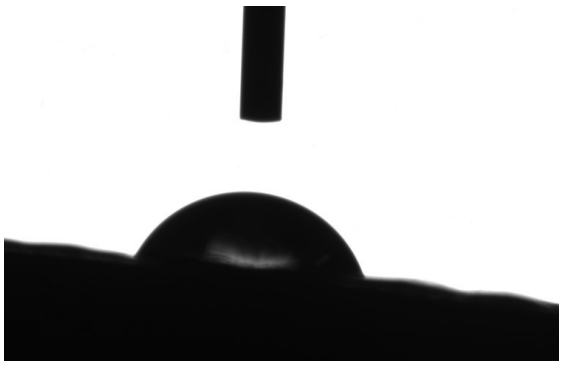
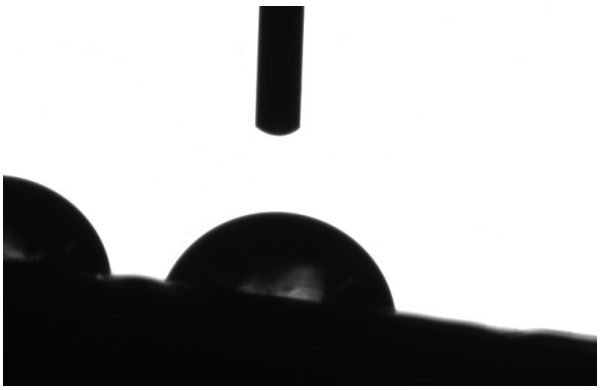
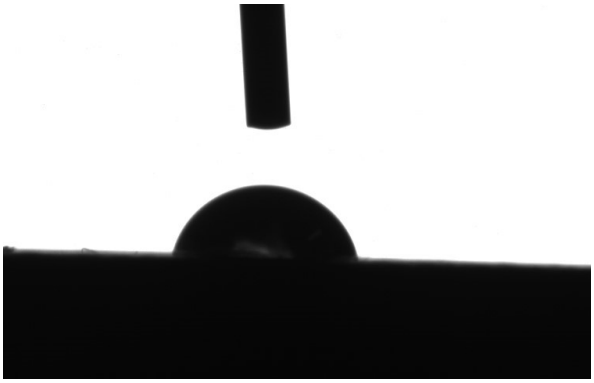
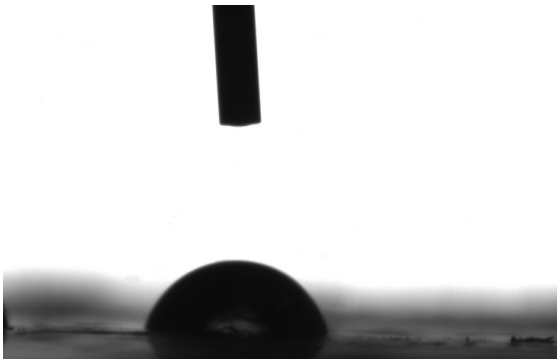


Membrane 2





Membrane 3

	
Membrane 4	
	

A2: WATER CONTACT ANGLE

MEMBRANE 1 : CA RESULTS

Device : Research
Customer : Research
Operator : Research
Remarks : Research

Run-No	CA(M)[°]		IFT[mN/m]		Err[µm]	Vol[µL]
1	102.67	0.00	21.20	110.86		
2	115.33	0.00	668.86	172.33		
3	107.40	0.00	20.79	116.94		
4	106.88	0.00	20.27	116.94		
5	103.56	0.00	23.37	103.20		

MEMBRANE 2 : CA RESULTS

Device : Research
Customer : Research
Operator : Research
Remarks : Research

Run-No	CA(M)[°]		IFT[mN/m]		Err[µm]	Vol[µL]
1	87.77	0.00	13.82	108.97		
2	86.89	0.00	9.67	114.71		
3	86.86	0.00	8.97	106.63		
4	87.34	0.00	8.33	120.89		
5	87.89	0.00	8.07	120.52		

MEMBRANE 3: CA RESULTS

Device : Research
Customer : Research
Operator : Research
Remarks : Research

Run-No	CA(M)[°]		IFT[mN/m]		Err[µm]	Vol[µL]
1	72.43	0.00	7.16	184.14		
2	75.10	0.00	2.45	177.66		
6	74.12	0.00	1.68	193.39		
4	68.12	0.00	2.54	195.50		
5	77.87	0.00	3.55	199.46		

MEMBRANE 4: CA RESULTS

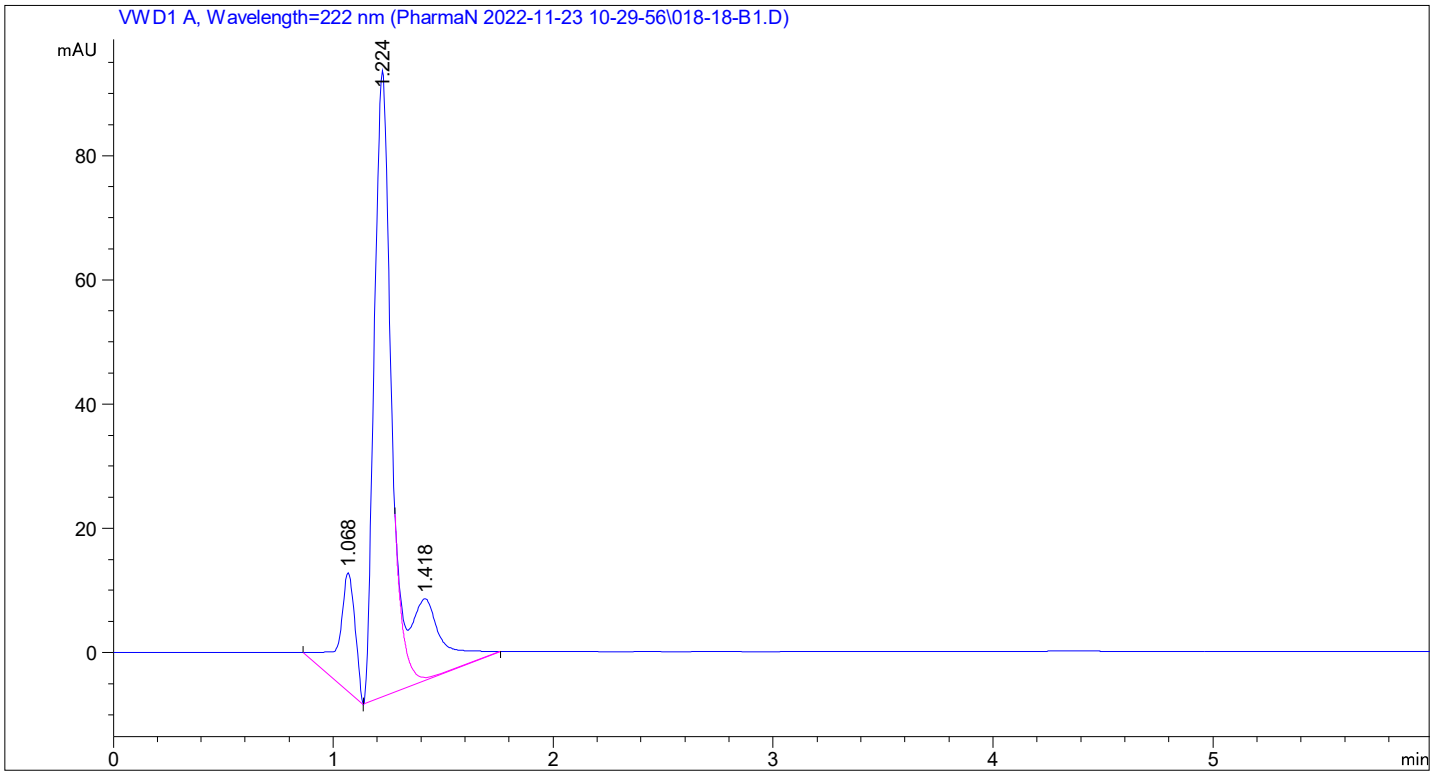
Device : Research
Customer : Research
Operator : Research
Remarks : Research

Run-No	CA(M)[°]		IFT[mN/m]	Err[µm]	Vol[µL]
1	48.49	0.00	80.78	11317176.00	
2	45.20	0.00	89.55	9045884.00	
3	60.39	0.00	1235.12	48317216.00	
4	59.72	0.00	870.66	42128632.00	
5	59.81	0.00	882.15	43441816.00	

A3: HPLC ANALYSIS

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\018-18-B1.D
Sample Name: B1

```
==========================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  18
Sample Operator : SYSTEM
Acq. Instrument : HPLC                          Location :   18
Injection Date  : 11/23/2022 2:12:26 PM              Inj :   1
                                               Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/23/2022 2:12:16 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.068 BB      102.06608 2.93295e-1   29.93545    I
  1.224 BV R    536.83588 7.17432e-2   38.51431    C
  1.418 VB E    126.28016    0.00000    0.00000    D

Totals :                               68.44976
```

1 Warnings or Errors :

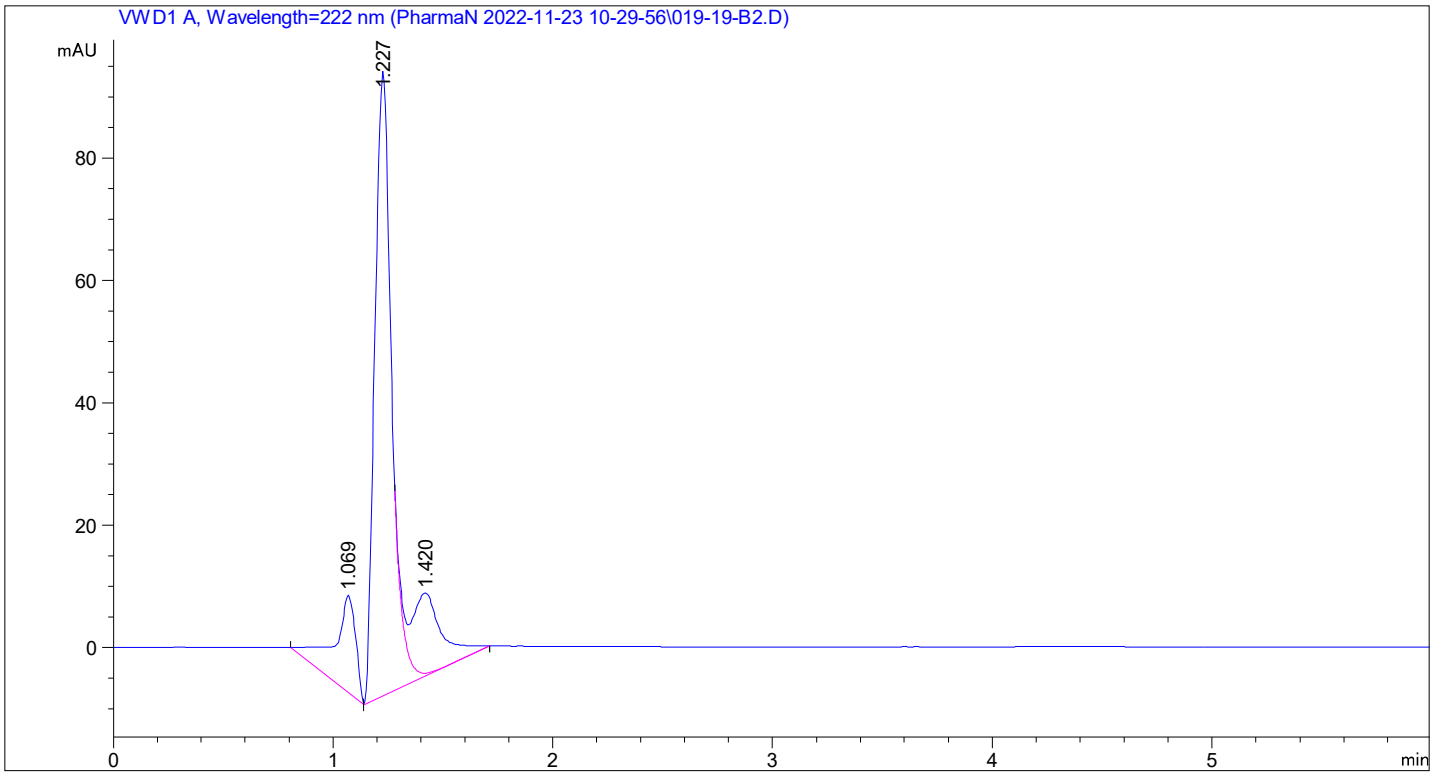
Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\019-19-B2.D
Sample Name: B2

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  19
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   19
Injection Date  : 11/23/2022 2:20:09 PM               Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/23/2022 2:12:16 PM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.069 BB      110.30096 3.23389e-1   35.67008    I
  1.227 BV R    546.92511 7.24189e-2   39.60770    C
  1.420 VB E    124.87886    0.00000    0.00000    D

Totals :                                75.27777
```

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\019-19-B2.D
Sample Name: B2

1 Warnings or Errors :

Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  25
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   25
Injection Date  : 11/23/2022 3:06:13 PM               Inj :   1
                                                Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/23/2022 2:12:16 PM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
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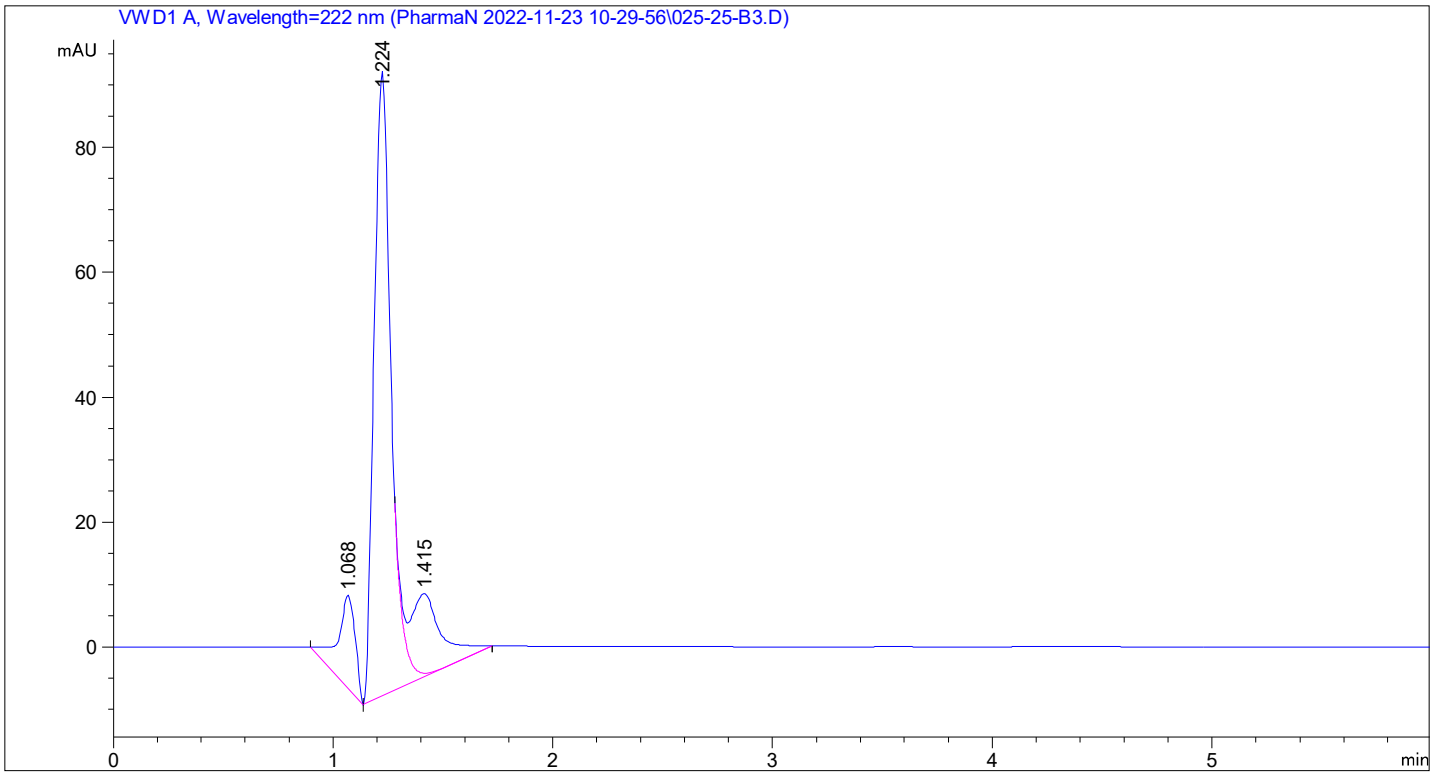


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==================================================================
                      External Standard Report
==================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.068 BB       82.39566 1.97065e-1   16.23731    I
  1.224 BV R    540.19708 7.19711e-2   38.87857    C
  1.415 VB E    123.84256    0.00000    0.00000    D

Totals :                                55.11588
```

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\025-25-B3.D
Sample Name: B3

1 Warnings or Errors :

Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\017-17-B4.D
Sample Name: B4

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  17
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   17
Injection Date  : 11/23/2022 1:59:25 PM               Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
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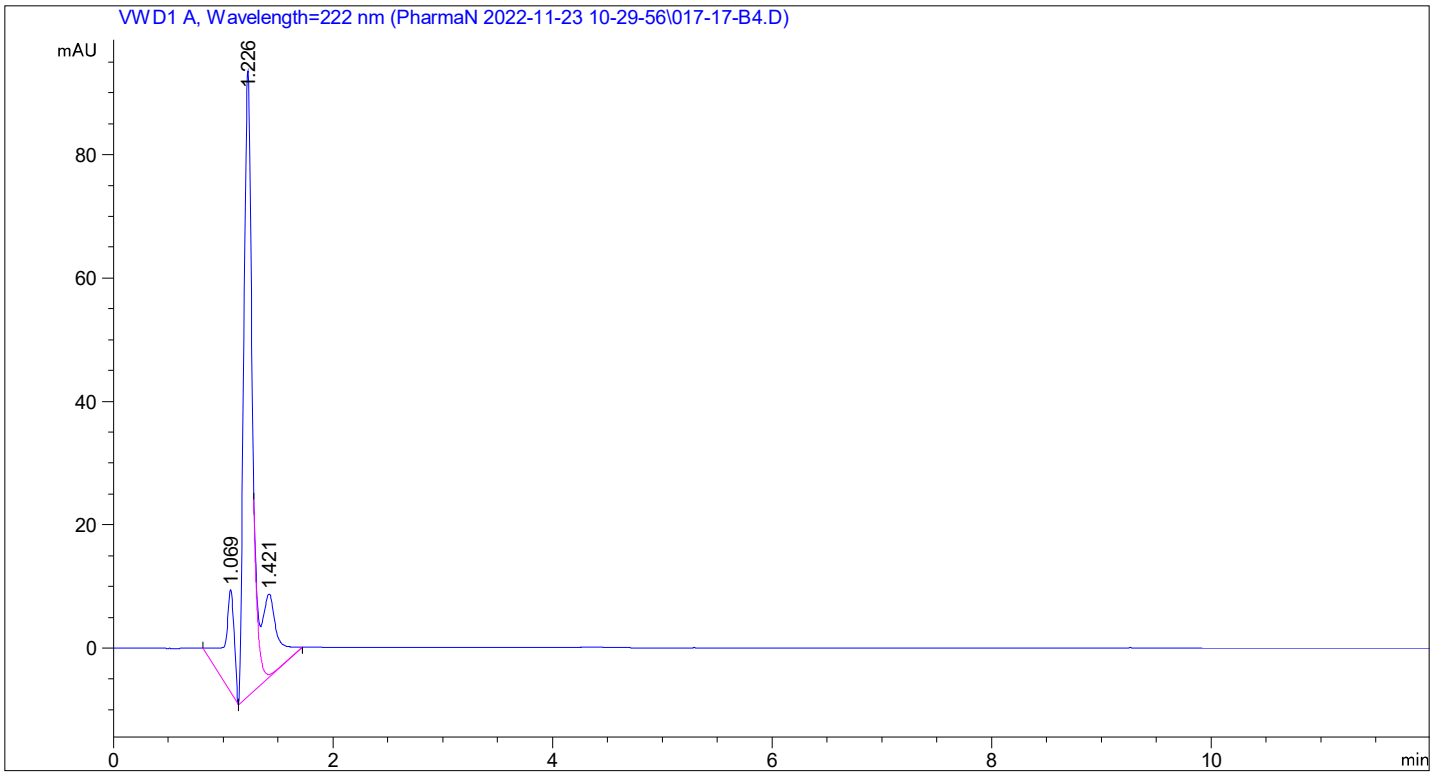


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==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.069 BB      108.30592 3.16518e-1   34.28077    I
  1.226 BV R    542.07751 7.20974e-2   39.08236    C
  1.421 VB E    125.22521    0.00000    0.00000    D

Totals :                                73.36313
```

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\017-17-B4.D
Sample Name: B4

1 Warnings or Errors :

Warning : Negative results set to zero (cal. curve intercept), (D)

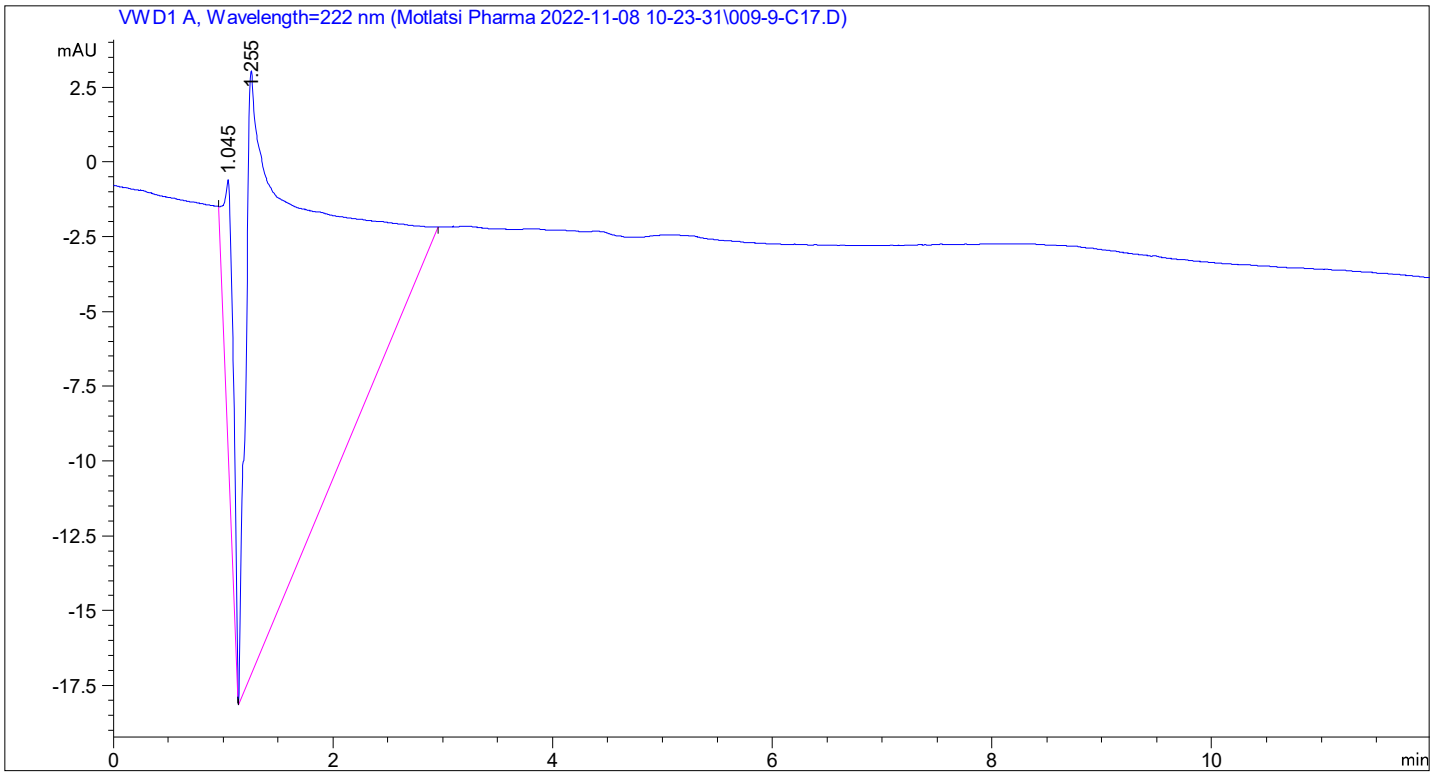
==========

*** End of Report ***

Data File C:\Users\P...\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\009-9-C17.D
Sample Name: C17

==========

Acq. Operator : SYSTEM Seq. Line : 9
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 9
Injection Date : 11/8/2022 12:08:22 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



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External Standard Report

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Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.045	BB	55.59757	0.00000	0.00000		Ibuprofen
1.255	BB	894.29657	5.42509e-2	48.51638		Cypermethrin
1.407		-	-	-		Diclofenac

Totals : 48.51638

2 Warnings or Errors :

Warning : Calibrated compound(s) not found
Warning : Invalid calibration curve, (Ibuprofen)

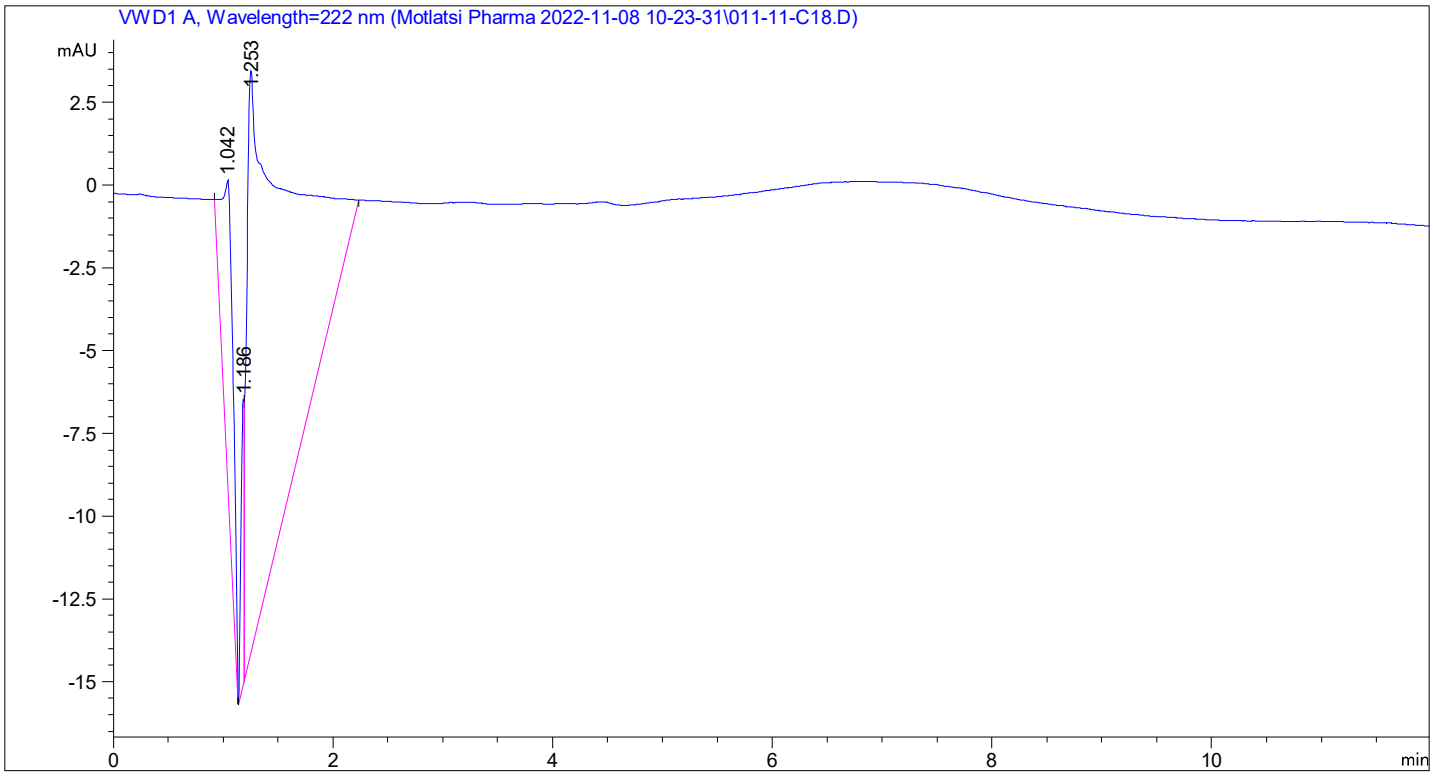
==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\011-11-C18.D
Sample Name: C18

==========

Acq. Operator : SYSTEM Seq. Line : 11
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 11
Injection Date : 11/8/2022 12:34:27 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



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External Standard Report

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Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.042	BB	65.94569	0.00000	0.00000		Ibuprofen
1.253	VB	473.54688	5.06637e-2	23.99162		Cypermethrin
1.407		-	-	-		Diclofenac

Totals : 23.99162

3 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
Warning : Invalid calibration curve, (Ibuprofen)

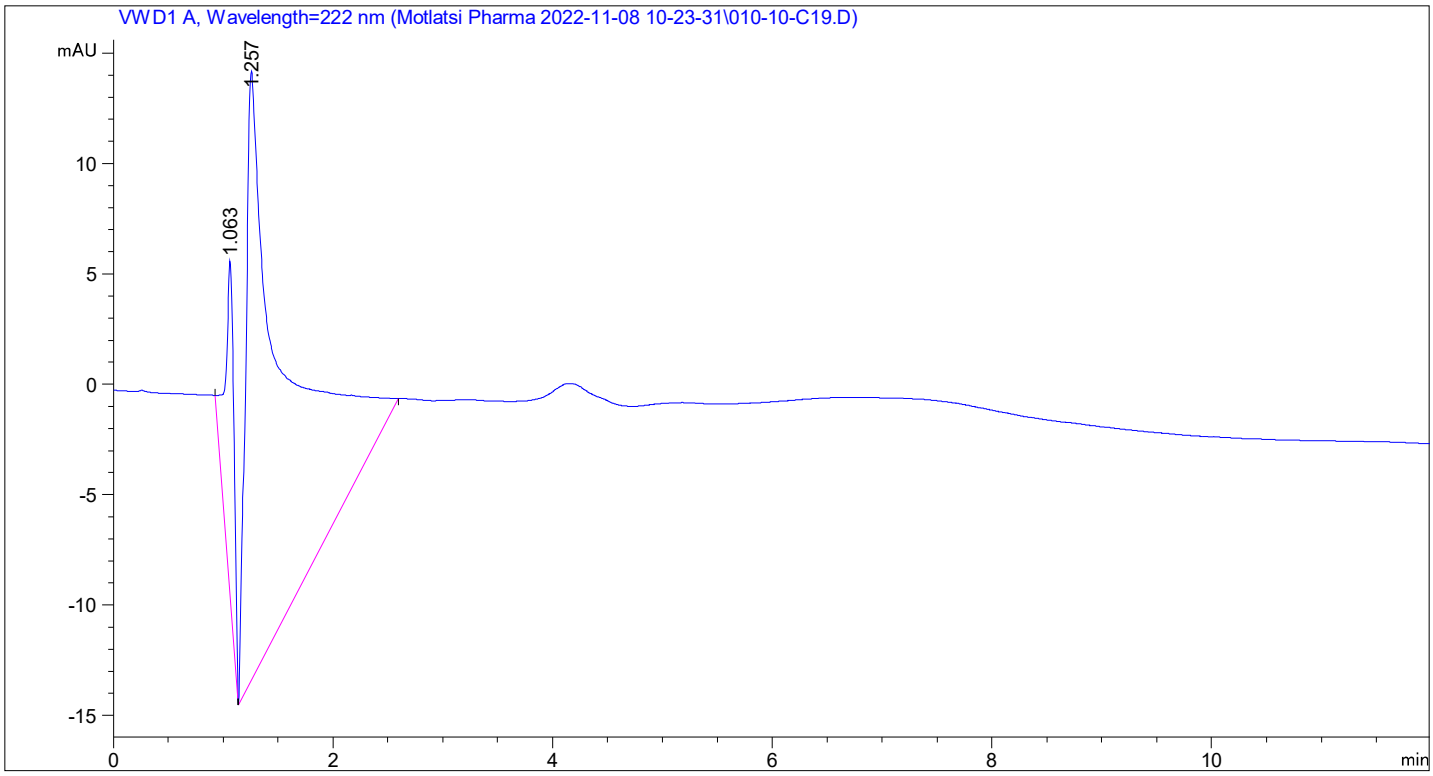
==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\010-10-C19.D
Sample Name: C19

==========

Acq. Operator : SYSTEM Seq. Line : 10
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 10
Injection Date : 11/8/2022 12:21:25 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



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External Standard Report

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Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.063	BB	84.24764	0.00000	0.00000		Ibuprofen
1.257	BB	718.37976	5.32622e-2	38.26250		Cypermethrin
1.407		-	-	-		Diclofenac

Totals : 38.26250

3 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
Warning : Invalid calibration curve, (Ibuprofen)

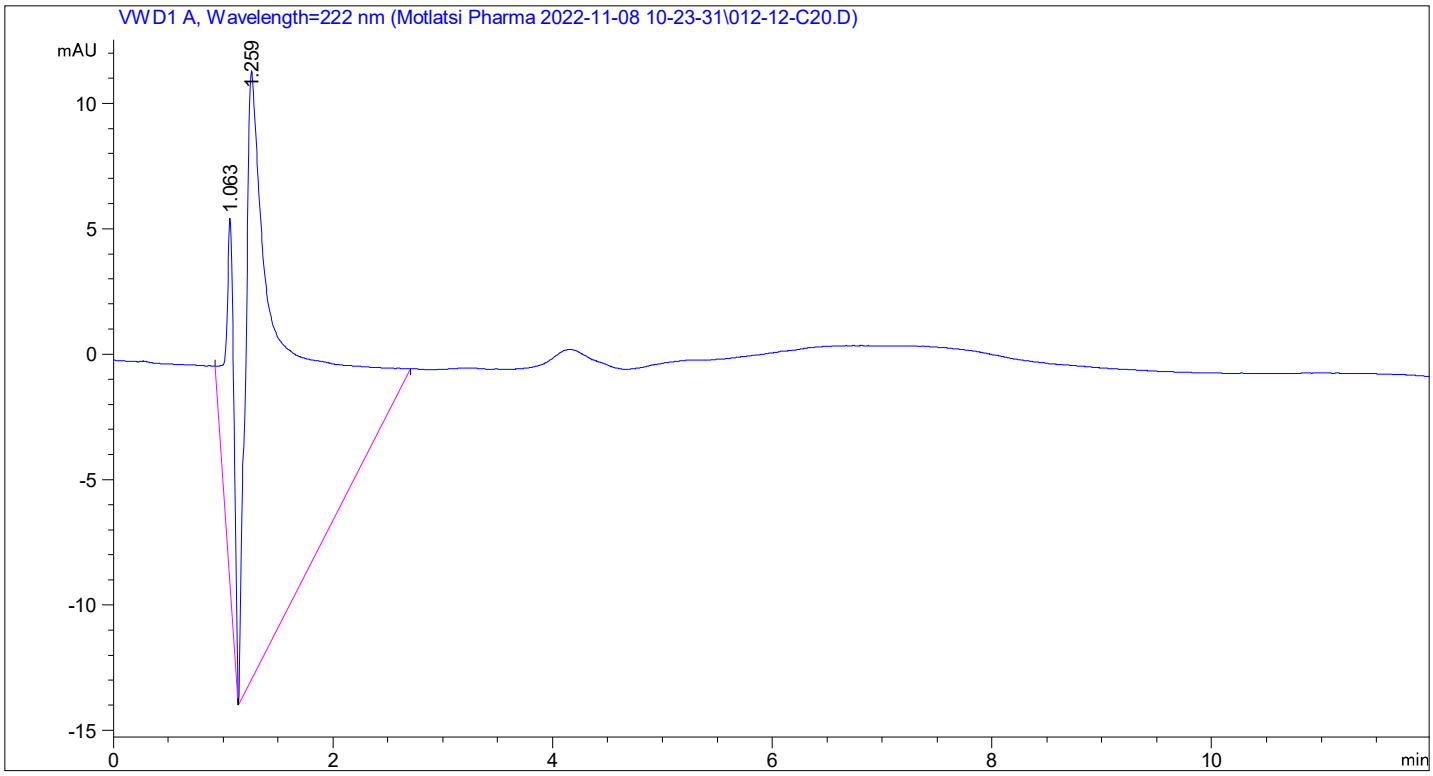
==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\012-12-C20.D
Sample Name: C20

==========

Acq. Operator : SYSTEM Seq. Line : 12
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 12
Injection Date : 11/8/2022 12:47:27 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



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External Standard Report

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Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.063	BB	80.47392	0.00000	0.00000		Ibuprofen
1.259	BB	717.23529	5.32542e-2	38.19579		Cypermethrin
1.407		-	-	-		Diclofenac

Totals : 38.19579

3 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found
Warning : Invalid calibration curve, (Ibuprofen)

==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\016-16-D13.D
Sample Name: D13

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  16
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   16
Injection Date  : 11/8/2022 1:39:29 PM                Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/10/2022 9:10:32 AM by SYSTEM
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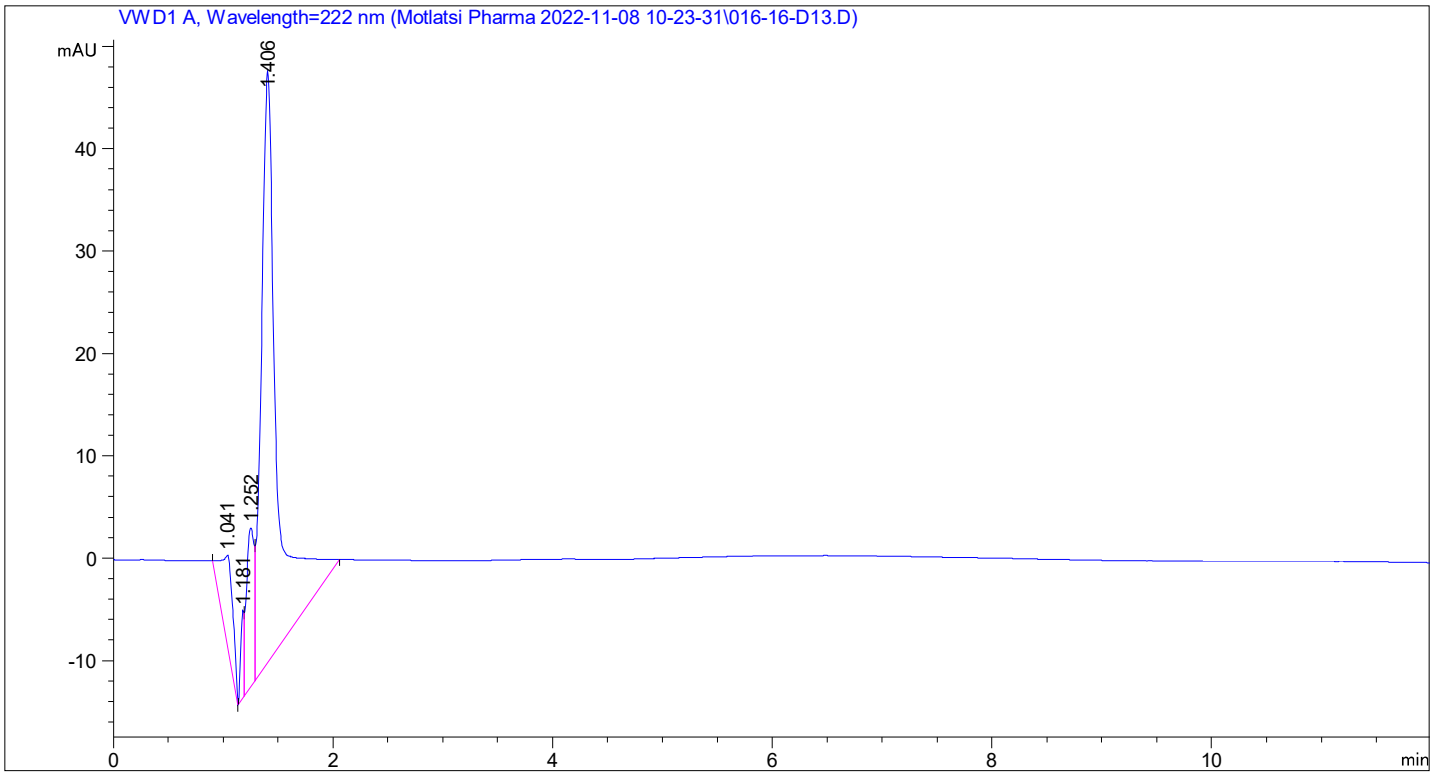



```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/10/2022 9:10:31 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.041 BB       68.29133    0.00000    0.00000    Ibuprofen
  1.252 VV       74.86925 1.00629e-2 7.53404e-1    Cypermethrin
  1.406 VB      590.37616 6.76669e-4 3.99489e-1    Diclofenac

Totals :                                 1.15289
```

2 Warnings or Errors :

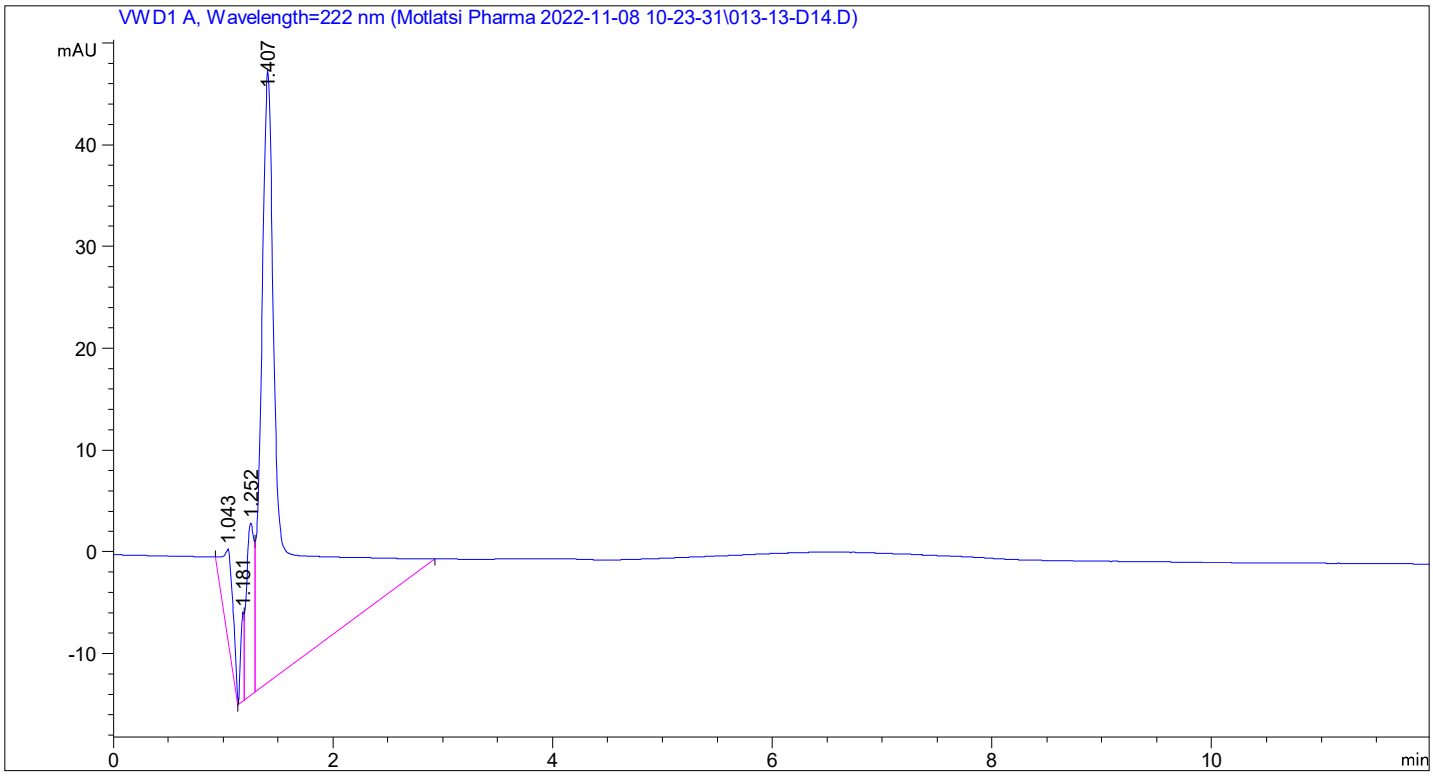
Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)

==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\013-13-D14.D
Sample Name: D14

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  13
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   13
Injection Date  : 11/8/2022 1:00:28 PM                Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/10/2022 9:10:32 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/10/2022 9:10:31 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.043 BB       59.29256    0.00000    0.00000    Ibuprofen
  1.252 VV       82.15864 1.43416e-2    1.17829    Cypermethrin
  1.407 VB      973.87476 1.35673e-3    1.32129    Diclofenac

Totals :                                2.49958
```

2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)

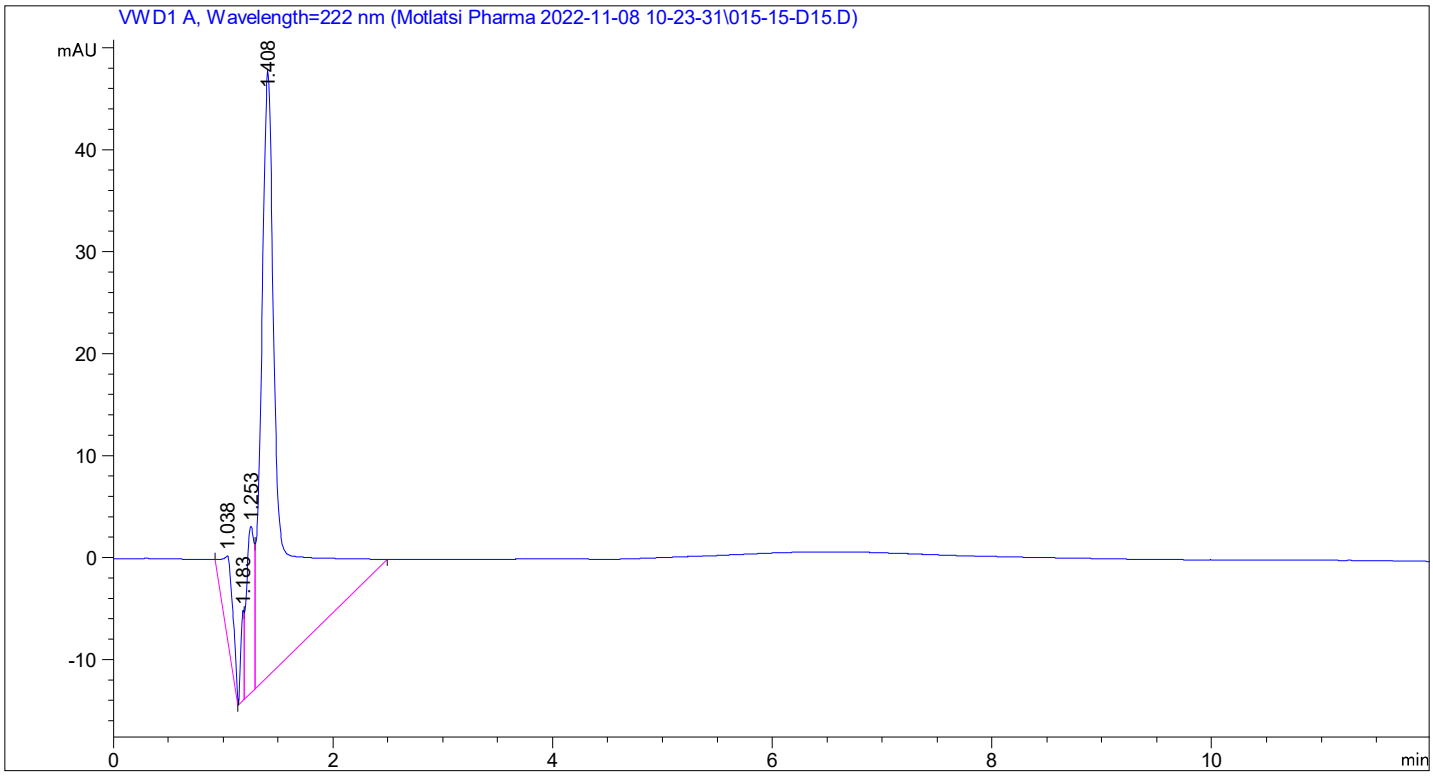
==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\015-15-D15.D
Sample Name: D15

==========

Acq. Operator : SYSTEM Seq. Line : 15
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 15
Injection Date : 11/8/2022 1:26:27 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



==========

External Standard Report

==========

Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.038	BB	57.78983	0.00000	0.00000		Ibuprofen
1.253	VV	79.29053	1.27520e-2	1.01111		Cypermethrin
1.408	VB	780.71405	1.09771e-3	8.56996e-1		Diclofenac

Totals : 1.86811

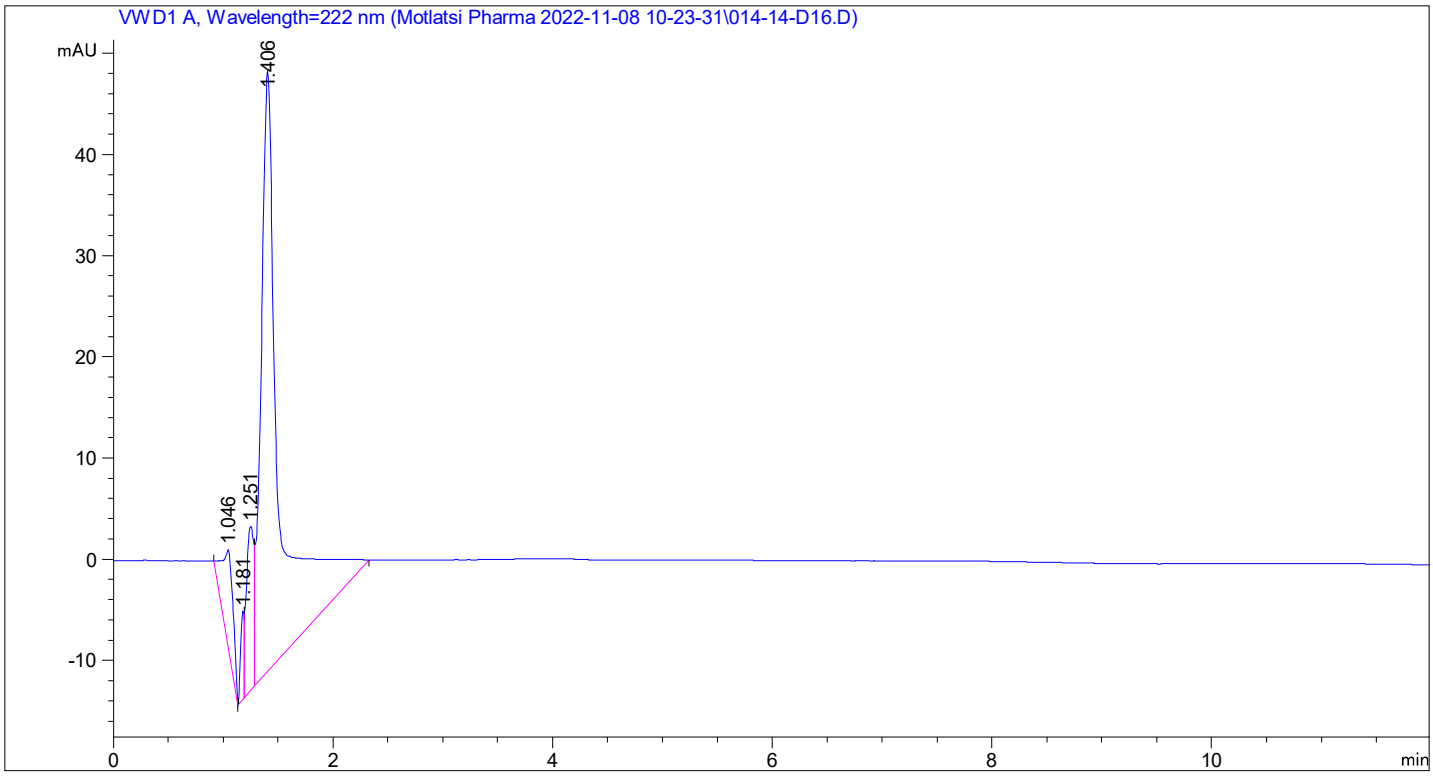
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)

==========

*** End of Report ***

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  14
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   14
Injection Date  : 11/8/2022 1:13:29 PM                Inj :   1
                                               Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/10/2022 9:10:32 AM by SYSTEM
```




```
==================================================================
                      External Standard Report
==================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/10/2022 9:10:31 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.046 BB       65.81516    0.00000    0.00000    Ibuprofen
  1.251 VV       79.09286 1.26382e-2 9.99591e-1    Cypermethrin
  1.406 VB      710.34698 9.68341e-4 6.87858e-1    Diclofenac

Totals :                                1.68745
```

2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)

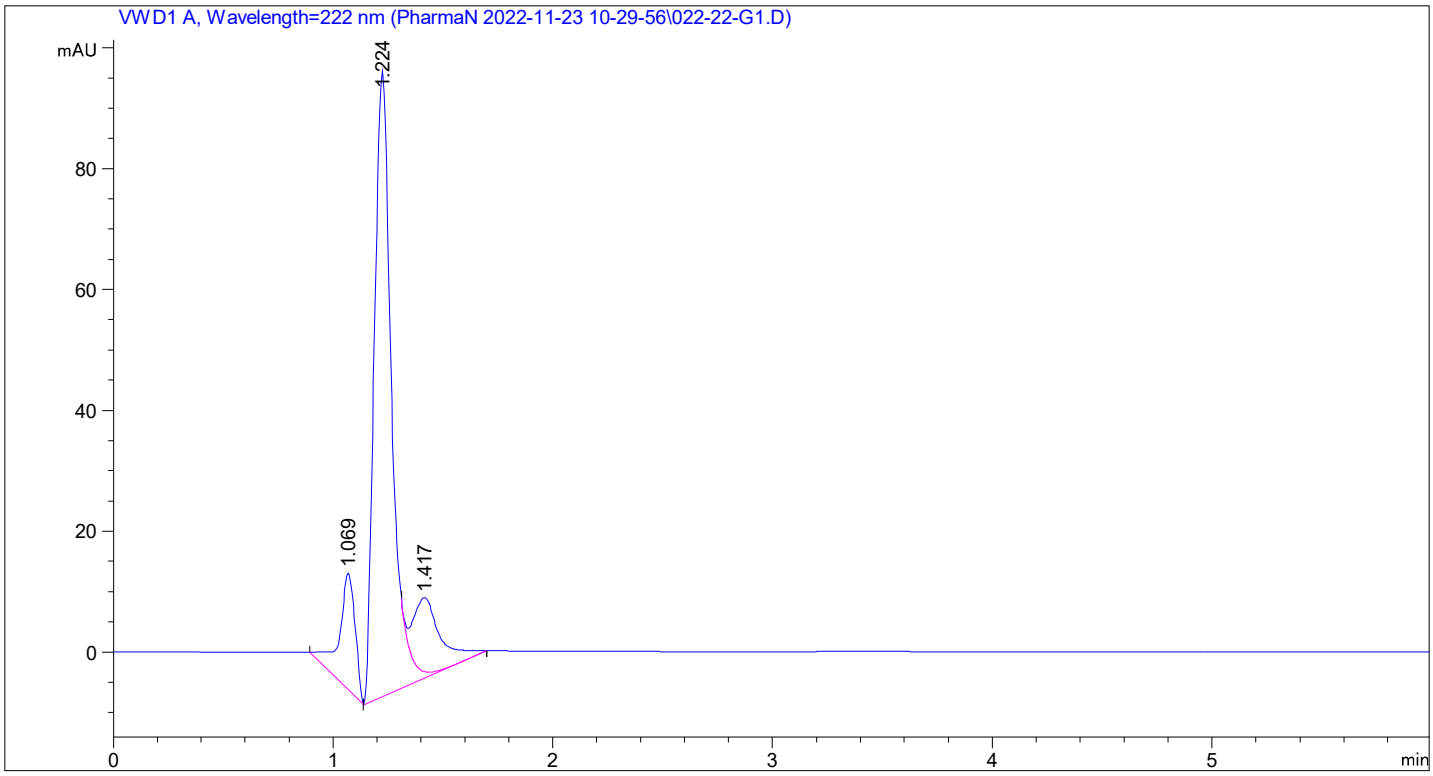
==========

*** End of Report ***

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\022-22-G1.D
Sample Name: G1

==========

Acq. Operator : SYSTEM Seq. Line : 22
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 22
Injection Date : 11/23/2022 2:45:07 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
\Motlatsi Pharma.M
Last changed : 11/23/2022 2:12:16 PM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/30/2022 11:07:50 AM by SYSTEM



==========

External Standard Report

==========

Sorted By : Signal
Calib. Data Modified : 11/30/2022 11:07:50 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.069	BB	96.73711	2.71090e-1	26.22445		I
1.224	BV R	567.01129	7.36925e-2	41.78447		C
1.417	VB E	105.07119	0.00000	0.00000		D

Totals : 68.00892

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\022-22-G1.D
Sample Name: G1

1 Warnings or Errors :

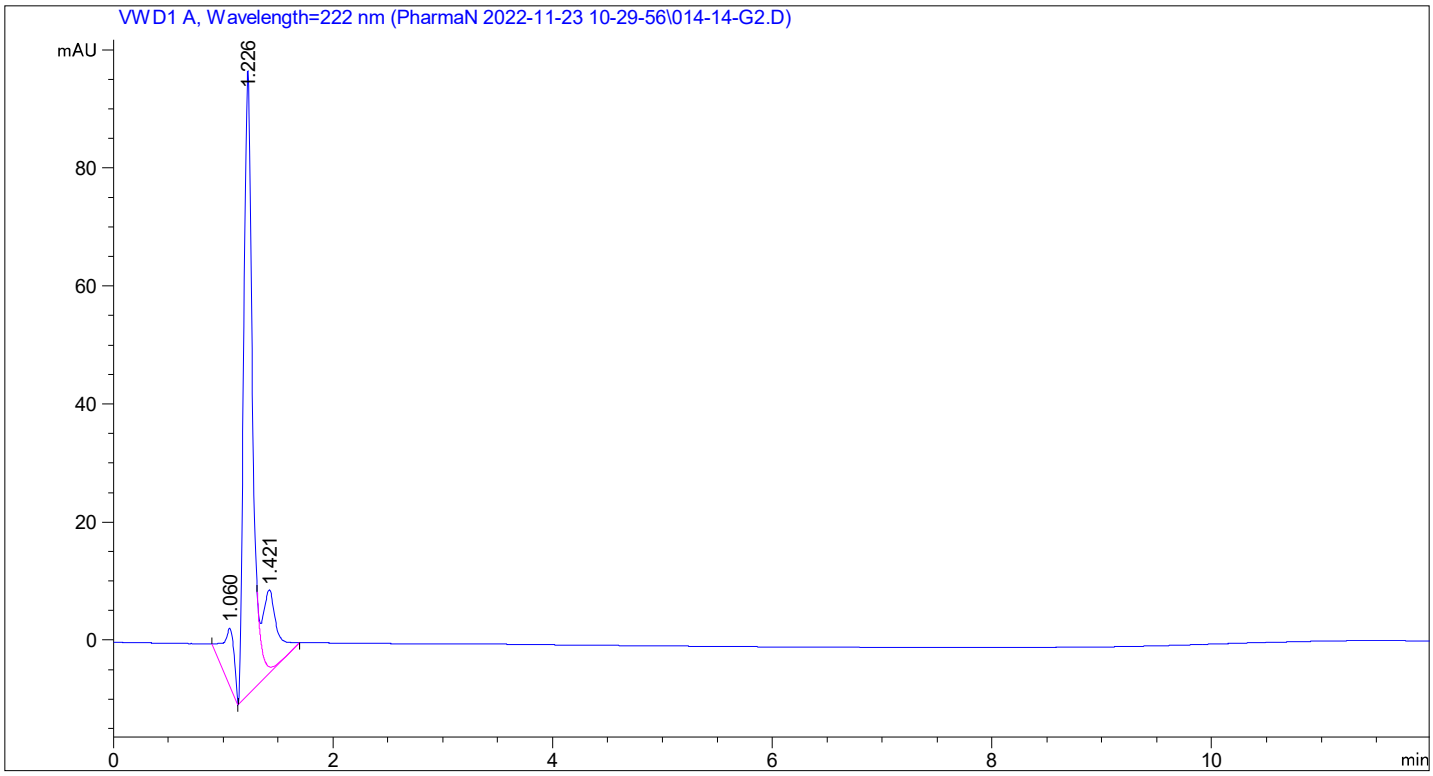
Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\014-14-G2.D
Sample Name: G2

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  14
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   14
Injection Date  : 11/23/2022 1:20:04 PM               Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.060 BB       67.85229 9.00419e-2    6.10955    I
  1.226 BV R    586.32849 7.48350e-2   43.87791    C
  1.421 VB E    113.14275    0.00000    0.00000    D

Totals :                                49.98746
```

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\014-14-G2.D
Sample Name: G2

1 Warnings or Errors :

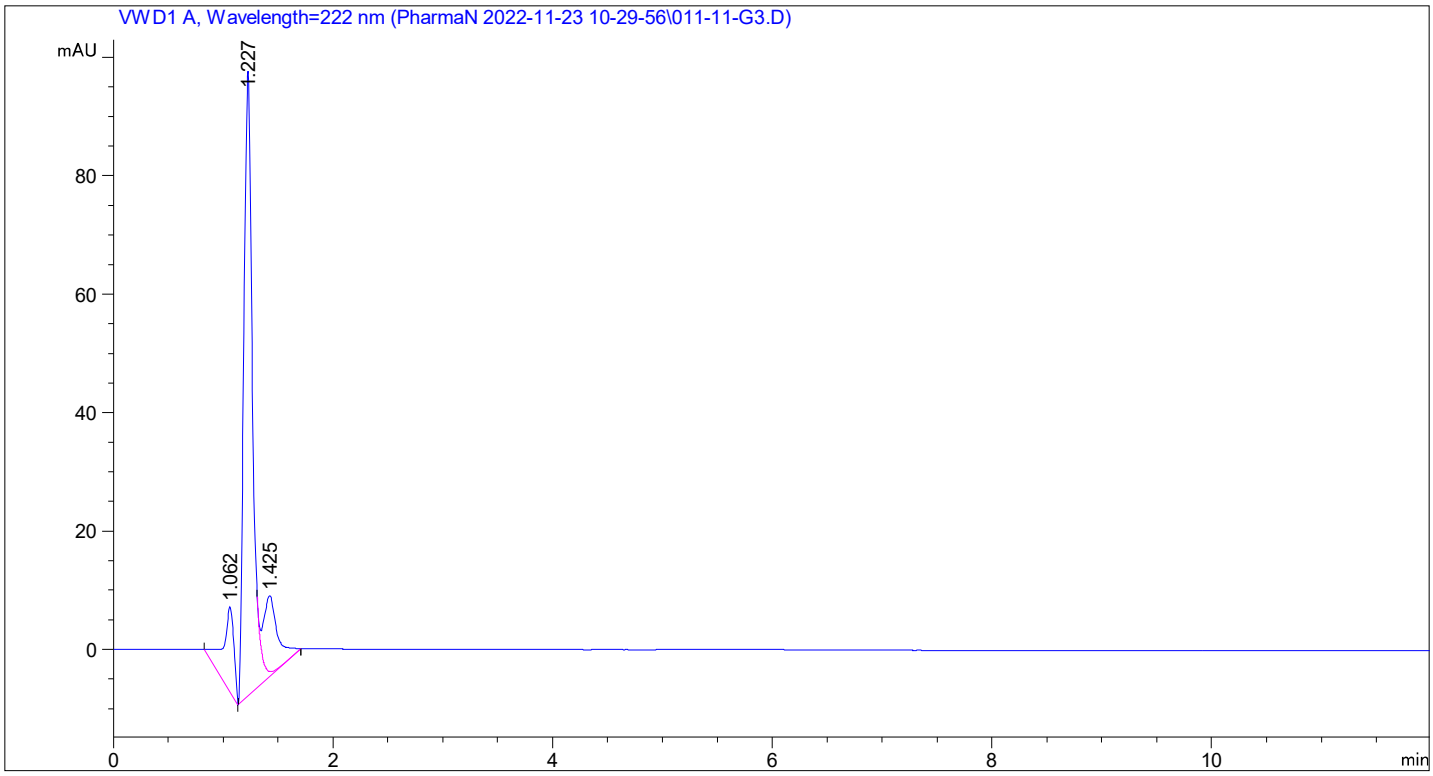
Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\011-11-G3.D
Sample Name: G3

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  11
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   11
Injection Date  : 11/23/2022 12:41:02 PM              Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.062 BB       99.07545 2.81127e-1   27.85283    I
  1.227 BV R    581.46570 7.45546e-2   43.35092    C
  1.425 VB E    111.67765    0.00000    0.00000    D

Totals :                               71.20375
```

Data File C:\Users\P...ocuments\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56\011-11-G3.D
Sample Name: G3

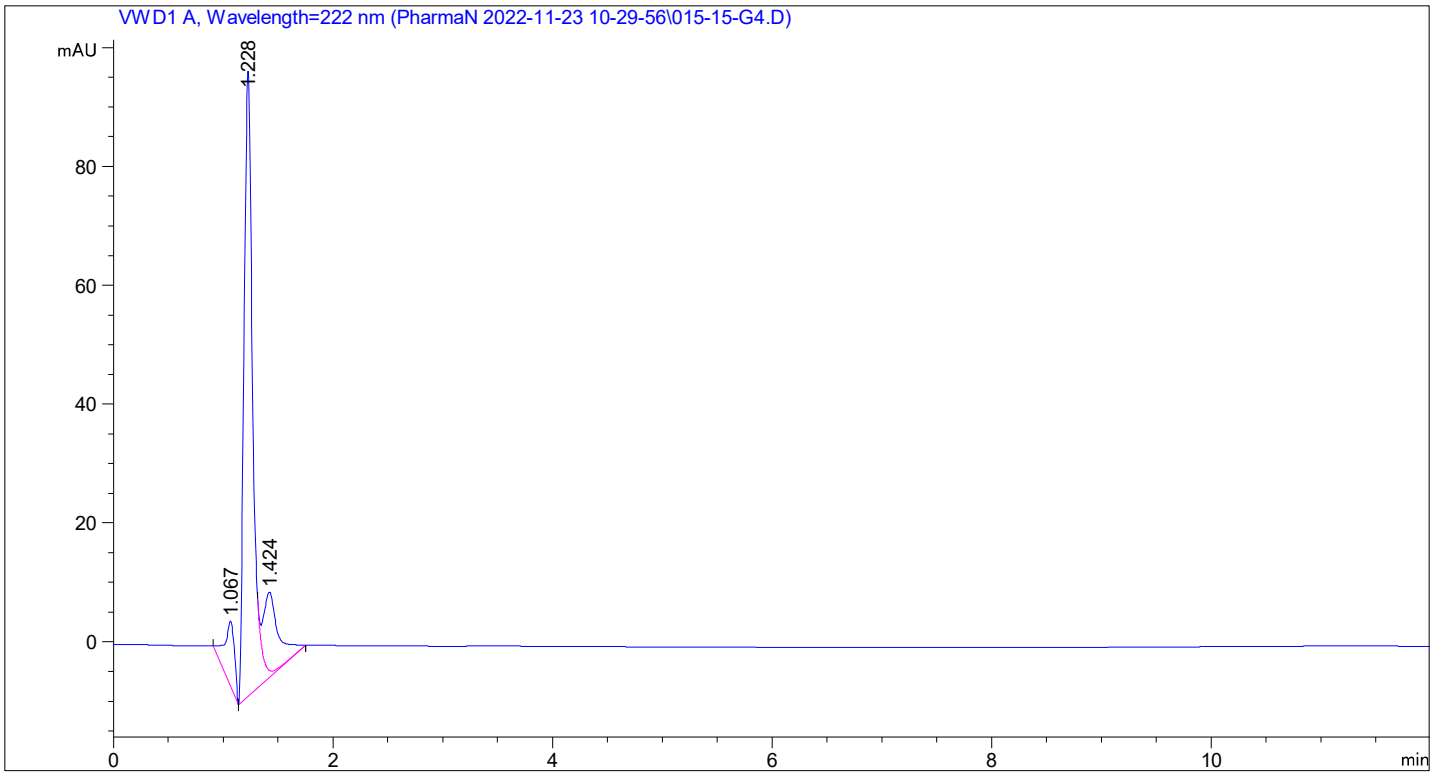
1 Warnings or Errors :

Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  15
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   15
Injection Date  : 11/23/2022 1:33:05 PM               Inj :   1
                                                Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\PharmaN 2022-11-23 10-29-56
                  \Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/30/2022 11:07:50 AM by SYSTEM
```




```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/30/2022 11:07:50 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.067 BB       68.78610 9.82734e-2    6.75984    I
  1.228 BV R    582.21564 7.45981e-2   43.43219    C
  1.424 VB E    123.53734    0.00000    0.00000    D

Totals :                                50.19203
```

1 Warnings or Errors :

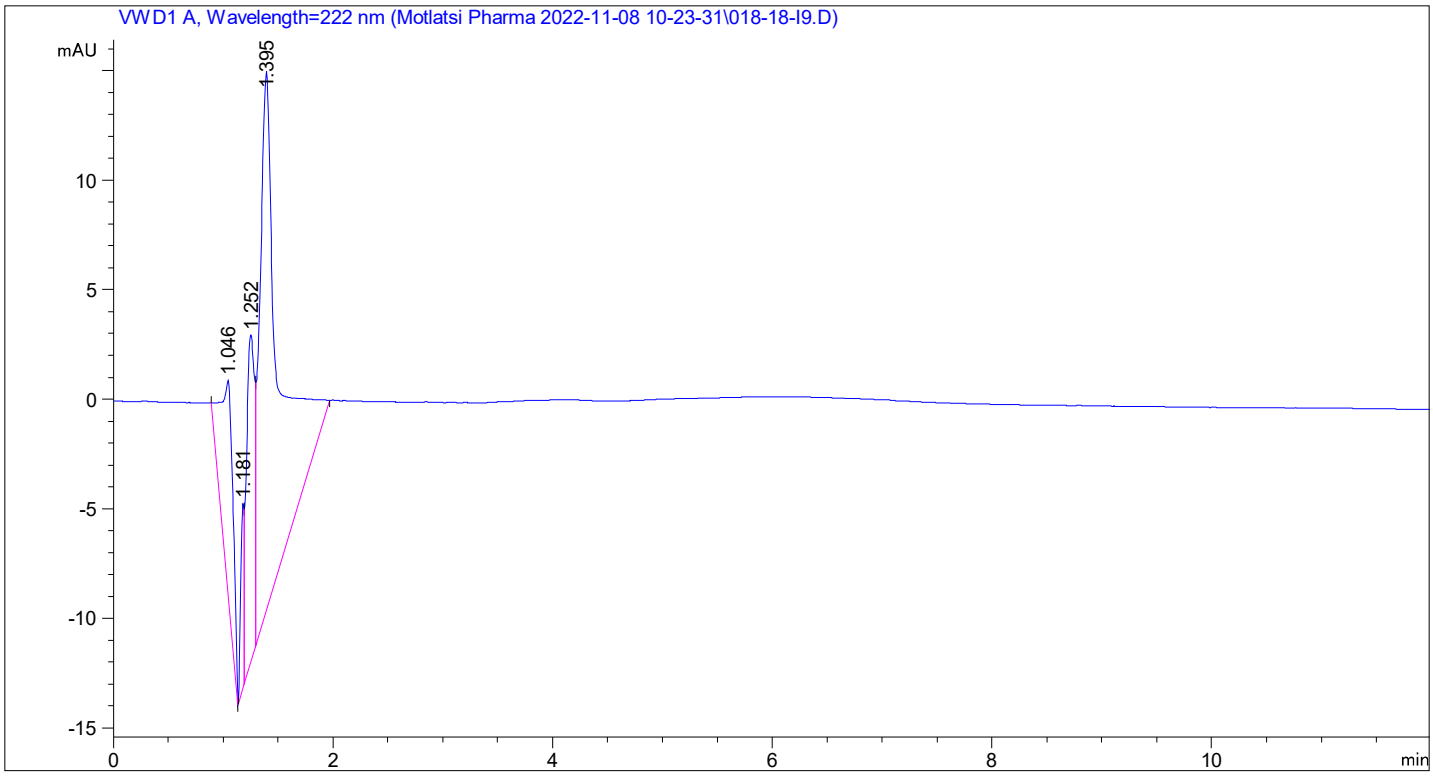
Warning : Negative results set to zero (cal. curve intercept), (D)

==========

*** End of Report ***

Data File C:\Users\P...\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\018-18-I9.D
Sample Name: I9

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  18
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   18
Injection Date  : 11/8/2022 2:05:30 PM                Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/10/2022 9:10:32 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/10/2022 9:10:31 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.046 BB       73.61845    0.00000    0.00000    Ibuprofen
  1.252 VV       77.55393 1.17323e-2 9.09889e-1    Cypermethrin
  1.395 VB      312.14771    0.00000    0.00000    Diclofenac

Totals :                               9.09889e-1
```

3 Warnings or Errors :

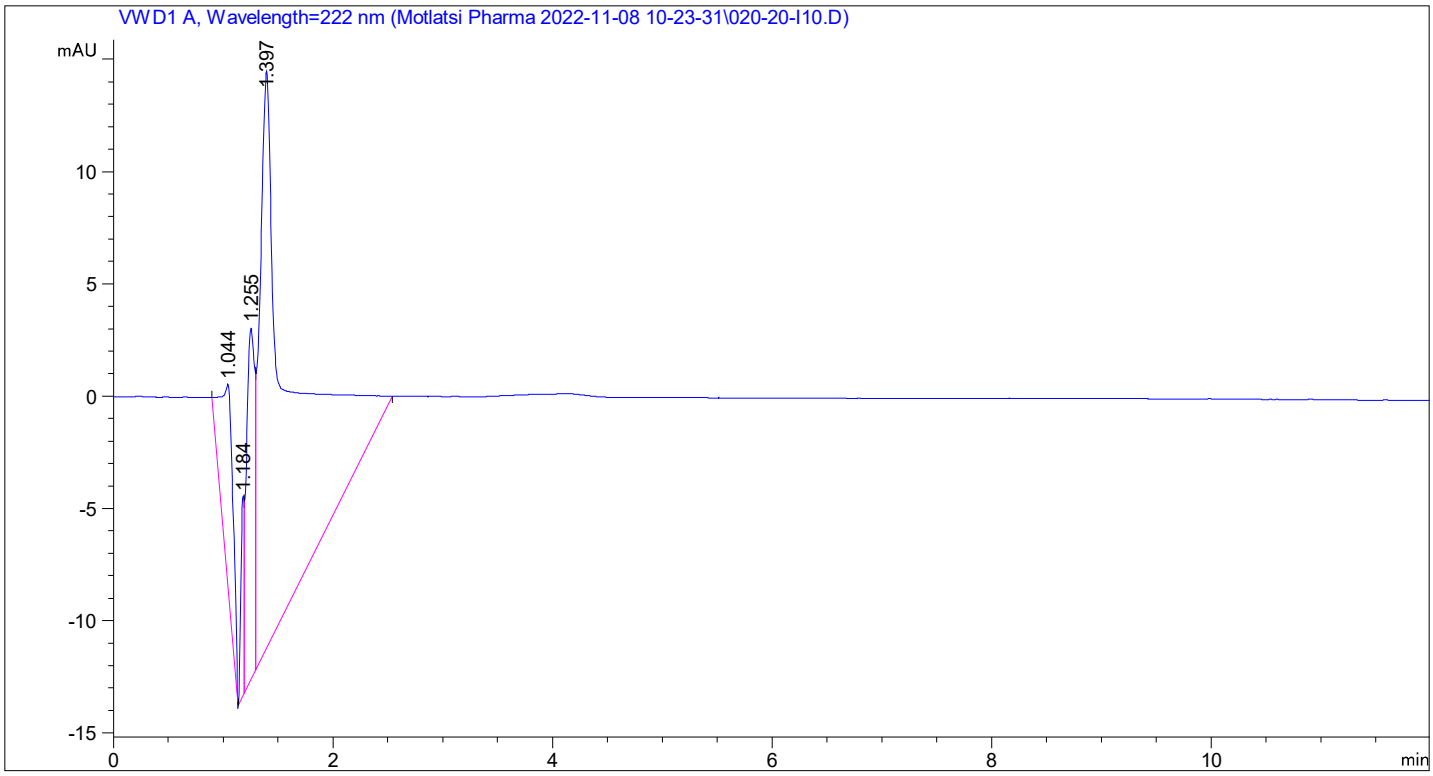
Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)
Warning : Negative results set to zero (cal. curve intercept), (Diclofenac)

==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\020-20-I10.D
Sample Name: I10

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  20
Sample Operator : SYSTEM
Acq. Instrument : HPLC                           Location :   20
Injection Date  : 11/8/2022 2:31:33 PM                Inj :   1
                                                 Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M
Last changed    : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-
                  23-31\Motlatsi Pharma.M (Sequence Method)
Last changed    : 11/10/2022 9:10:32 AM by SYSTEM
```




```
==========================================================================
                      External Standard Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      11/10/2022 9:10:31 AM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [mAU*s]                [ug/l]
-------|------|----------|----------|----------|--|------------------
  1.044 BB       69.40522    0.00000    0.00000    Ibuprofen
  1.255 VV       82.74510 1.46531e-2    1.21247    Cypermethrin
  1.397 VB      542.86346 5.25519e-4 2.85285e-1    Diclofenac

Totals :                                 1.49776
```

2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)

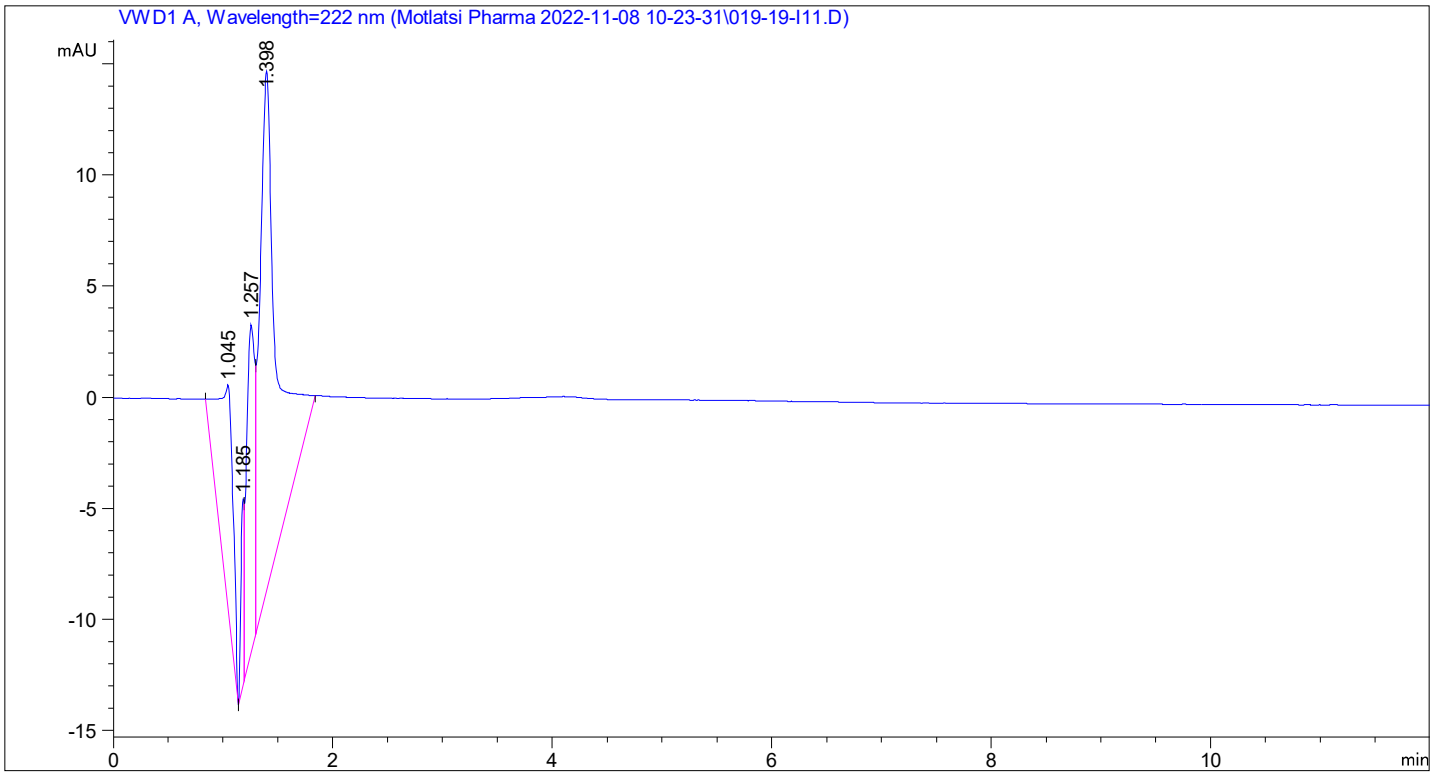
==========

*** End of Report ***

Data File C:\Users\P...ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\019-19-I11.D
Sample Name: I11

==========

Acq. Operator : SYSTEM Seq. Line : 19
Sample Operator : SYSTEM
Acq. Instrument : HPLC Location : 19
Injection Date : 11/8/2022 2:18:30 PM Inj : 1
Inj Volume : 20.000 µl
Acq. Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M
Last changed : 11/8/2022 10:23:28 AM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\Motlatsi Pharma 2022-11-08 10-23-31\Motlatsi Pharma.M (Sequence Method)
Last changed : 11/10/2022 9:10:32 AM by SYSTEM



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External Standard Report

==========

Sorted By : Signal
Calib. Data Modified : 11/10/2022 9:10:31 AM
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=222 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/l]	Grp	Name
1.045	BB	93.81686	0.00000	0.00000		Ibuprofen
1.257	VV	77.50037	1.17002e-2	9.06767e-1		Cypermethrin
1.398	VB	259.46954	0.00000	0.00000		Diclofenac

Totals : 9.06767e-1

3 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Invalid calibration curve, (Ibuprofen)
Warning : Negative results set to zero (cal. curve intercept), (Diclofenac)

==========

*** End of Report ***