

**PROPERTIES AND PERFORMANCE OF
NATURAL RUBBER LATEX (NRL) BAND: A
SCAVENGING MEDIUM TO CAPTURE
MICROPLASTIC WASTE IN WATER**

NUR SHAUQINA BINTI MOHD SABRI

**SCHOOL OF MATERIALS AND MINERAL
RESOURCES
UNIVERSITI SAINS MALAYSIA
2022**

PROPERTIES AND PERFORMANCE OF NATURAL RUBBER
LATEX (NRL) BAND: A SCAVENGING MEDIUM TO CAPTURE
MICROPLASTIC WASTE IN WATER ECOSYSTEM

by

NUR SHAUQINA BINTI MOHD SABRI

This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As partial fulfilment of requirement for the degree of

**BACHELOR OF ENGINEERING (HONS.)
(POLYMER ENGINEERING)**

School of Material and Mineral Resources Engineering
Universiti Sains Malaysia

October 2022

ACKNOWLEDGEMENT

Alhamdulillah, praise to Allah S.W.T, our creator. I am so blessed that I successfully managed to end my final year project with Allah's blessings. I would like to thank Him for giving me good health and the ability to go through my project peacefully and well. Thank you to my supervisor, Dr. Mohamad Danial Shafiq, who provides abundant information and helpful feedback to ease my journey during the final year project. Many thanks to the School of Materials and Mineral Resources, USM, for giving us, the students majoring in polymer engineering, such a huge opportunity to choose the project topic. I wish to extend my sincere gratitude to every technician who gave me advice on training equipment and helped me a lot during my research. Besides, I would like to thank my parents, who always supported my decision to do my project. Thank you so much to my colleagues and friends, who had been my backbones during my final year by helping me complete all the given work successfully.

ABSTRAK

Dalam beberapa tahun kebelakangan ini, kehadiran meluas mikroplastik dalam alam sekitar telah menjadi satu cabaran yang ketara, terutamanya kepada sistem marin. Kebimbangan kritikal adalah kesan ekotoksikologi ke atas ekosistem marin dan potensi ancaman kepada organ dan tisu manusia. Kajian ini dijalankan untuk membangunkan tangkapan sisa mikroplastik dalam air laut menggunakan jalur getah asli (NRL) melalui mekanisme tangkapan permukaan. Dalam kajian ini, kami mencadangkan agar cas permukaan permukaan getah teraruh menggunakan teknik kimia dan mekanikal. Bahan tambahan berasaskan tiolat logam akan ditambah kepada pendekatan kimia untuk mengaktifkan tapak ionik getah asli. Jalur lateks akan dikenakan tindakan mekanikal kitaran untuk menjana cas permukaan, seperti regangan dan kelonggaran berkala. Caj permukaan yang meningkat bagi jalur lateks boleh mencipta interaksi elektrostatik dengan sisa mikroplastik di dalam air, membolehkannya ditangkap dan ditapis keluar melalui tarikan. Caj permukaan yang dibangunkan pada jalur akan menarik mikroplastik bercas bertentangan dan memudahkan penangkapan. Jalur NRL akan dihasilkan melalui proses pengkompaunan dan pengawetan. Prosedur untuk menangkap sisa mikroplastik dalam air laut akan ditunjukkan dalam kerja ini. Berdasarkan keputusan yang diperolehi, pemuatan ZDEC yang lebih tinggi menghasilkan sifat tegangan dan ketumpatan pautan silang yang lebih baik daripada pemuatan ZDEC yang lebih rendah. Kekuatan koyakan jalur NRL menggunakan kurang ZDEC adalah lebih tinggi sedikit daripada jalur NRL menggunakan lebih ZDEC. Daripada keputusan FTIR dan SEM, ia boleh diperhatikan kehadiran polipropilena dan bahan cemar dalam jalur lateks yang tercemar. Ia boleh disimpulkan bahawa jumlah pemecut ZDEC mengubah ciri mekanikal jalur NRL, meningkatkan tangkapan mikroplastik.

ABSTRACT

In recent years, the widespread presence of microplastics in the environment has become a significant challenge, especially to the marine system. The critical concerns are the ecotoxicological impact on marine ecosystems and the potential threat to human organs and tissues. This study was conducted to develop the microplastic waste capture in seawater using natural rubber latex (NRL) band via a surface capturing mechanism. In this study, we proposed that the rubber surface's surface charge be induced using chemical and mechanical techniques. A metal thiolate-based additive will be added to the chemical approach to activate the natural rubber's ionic sites. The latex band will be subjected to cyclic mechanical action to generate the surface charge, such as periodic stretching and relaxation. The increased surface charge of the latex band can create an electrostatic interaction with microplastic wastes in the water, allowing them to be captured and filtered out via attraction. The surface charge developed on the band will attract the oppositely charged microplastic and facilitate the capture. The NRL band will be manufactured via compounding and curing processes. The procedure for capturing microplastic wastes in seawater will be demonstrated in this work. Based on the results obtained, higher ZDEC loading produced better tensile properties and crosslink density than lower ZDEC loading. The tear strength of the NRL band using less ZDEC was slightly higher than that of the NRL band using more ZDEC. From FTIR and SEM results, it can be observed the presence of polypropylene and contaminant in the contaminated latex band. It can be concluded that the amount of ZDEC accelerator altered the mechanical characteristics of the NRL bands, enhancing microplastic capture.

TABLE OF CONTENTS

| | |
|--|-------------|
| ACKNOWLEDGEMENT..... | II |
| ABSTRAK..... | III |
| ABSTRACT..... | IV |
| TABLE OF CONTENTS | V |
| LIST OF TABLES..... | VIII |
| LIST OF FIGURES..... | IX |
| LIST OF SYMBOLS | X |
| LIST OF ABBREVIATIONS | XI |
| CHAPTER 1 INTRODUCTION | 1 |
| 1.1 Research Background..... | 1 |
| 1.2 Problem Statement | 3 |
| 1.3 Research Objective..... | 5 |
| 1.4 Research Scope | 6 |
| 1.5 Thesis Outline | 7 |
| CHAPTER 2 LITERATURE REVIEW..... | 8 |
| 2.1 Microplastic..... | 8 |
| 2.1.1 Marine Ecosystem and Human Health Concern | 10 |
| 2.2 Film-based Technology..... | 11 |
| 2.2.1 Membrane Separation Process | 11 |
| 2.2.2 Membrane Separation Characteristics..... | 12 |
| 2.2.3 Limitation on Film-based Separation..... | 12 |
| 2.3 Review on Microplastic Removal by Film-based Technology..... | 19 |
| 2.4 Film Surface Hydrophilicity and Surface Charge..... | 22 |
| 2.4.1 Microplastic Hydrophobicity and Surface Charge..... | 25 |

| | | |
|------------------|--|-----------|
| CHAPTER 3 | METHODOLOGY | 28 |
| 3.1 | Introduction | 28 |
| 3.2 | Materials..... | 28 |
| 3.2.1 | Seawater. | 29 |
| 3.2.2 | Polypropylene (PP)..... | 29 |
| 3.2.3 | Natural Rubber Latex (NRL). | 29 |
| 3.2.4 | Compounding Ingredients. | 29 |
| 3.2.4(a) | Potassium Hydroxide (KOH) | 29 |
| 3.2.4(b) | Zinc Oxide (ZnO)..... | 30 |
| 3.2.4(c) | Zinc Diethyldithiocarbamate (ZDEC) | 30 |
| 3.2.4(d) | Tetramethyl thiuram disulfide (TMTD) | 30 |
| 3.2.4(e) | Sulphur | 30 |
| 3.3 | Preliminary Analysis | 31 |
| 3.3.1 | Total Solid Content (TSC). | 31 |
| 3.3.2 | pH | 32 |
| 3.4 | Preparation of NRL Band..... | 33 |
| 3.4.1 | Formulation. | 33 |
| 3.4.2 | Compounding. | 34 |
| 3.4.3 | Degassification. | 35 |
| 3.4.4 | Casting | 36 |
| 3.5 | Characterization | 36 |
| 3.5.1 | Tensile Properties. | 36 |
| 3.5.2 | Tear Strength. | 38 |
| 3.5.3 | Swelling Index and Crosslink density. | 39 |
| 3.5.4 | Scanning Electron Microscopy (SEM)..... | 40 |
| 3.5.5 | Microplastic waste capture via surface attachment..... | 41 |
| 3.5.6 | Analysis of microplastic..... | 42 |

| | | |
|--|---|-----------|
| 3.5.6(a) | Zeta Potential..... | 42 |
| 3.5.6(b) | Dynamic light scattering. | 43 |
| 3.5.6(c) | Fourier-Transform Infrared Analysis (FTIR)..... | 43 |
| 3.5.8 | Multimeter..... | 44 |
| CHAPTER 4 RESULTS AND DISCUSSION..... | | 45 |
| 4.1 | Effect of ZDEC loading on the properties of NRL band | 45 |
| 4.1.1 | Tensile Properties | 45 |
| 4.1.2 | Tear Strength | 52 |
| 4.1.3 | Swelling Index and Crosslink density | 52 |
| 4.1.4 | Scanning Electron Microscopy (SEM)..... | 56 |
| 4.2 | Microplastic in seawater analysis and NR band performance | 58 |
| 4.2.1 | Zeta Potential..... | 58 |
| 4.2.2 | Particle Size | 59 |
| 4.2.3 | Scanning Electron Microscopy (SEM)..... | 60 |
| 4.2.4 | FTIR Spectrum Analysis | 62 |
| 4.2.5 | Potential Measurement via Multimeter | 66 |
| CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATIONS | | 69 |
| 5.1 | Conclusion..... | 69 |
| 5.2 | Recommendations for Future Research | 70 |
| REFERENCES..... | | 71 |

LIST OF TABLES

| | Page |
|--|-------------|
| Table 2.1 Major influencing factors that can affect the performance of membrane processes for MP removal..... | 19 |
| Table 2.2 Microplastic removal by different wastewater treatment plants (WWTPs) | 20 |
| Table 3.1 NR Latex Band Formulation 1..... | 33 |
| Table 3.2 NR Latex Band Formulation 2..... | 33 |
| Table 3.3 NR Latex Band Formulation 3..... | 34 |
| Table 3.4 NR Latex Band Formulation 4..... | 34 |
| Table 4.1 Tensile properties for NR band by using different amount of ZDEC | 50 |
| Table 4.2 Crosslink density of NR at different ZDEC loading..... | 55 |
| Table 4.3 SEM image revealing details of the cross-sectional tensile fracture surfaces of NR membrane at different ZDEC loading for various magnification (x500, x1200)..... | 57 |
| Table 4.4 Zeta Potential for seawater with addition of PP..... | 58 |
| Table 4.5 Particle Size for seawater with addition of PP..... | 59 |
| Table 4.6 SEM image revealing details of surfaces of NR band at different ZDEC loading for various magnification (x500, x1000)..... | 61 |
| Table 4.7 FTIR peaks for contaminated NR band | 65 |

LIST OF FIGURES

| | Page |
|-------------|--|
| Figure 1.1 | Effect of microplastics in water and aquatic systems in graphical abstract 1 |
| Figure 2.1 | Comparison of membrane filtration techniques..... 13 |
| Figure 3.1 | Flow chart for NR latex band process..... 28 |
| Figure 3.2 | Degassification process..... 35 |
| Figure 3.3 | Band Casting..... 36 |
| Figure 3.4 | Dimensions of the sample according to the ASTM D412 Type C 37 |
| Figure 3.5 | Dimensions of the sample according to the ASTM D624 38 |
| Figure 3.6 | Laboratory plant- Demonstration of the water tank, containing microplastic wastes 41 |
| Figure 3.7 | Zeta Cell..... 42 |
| Figure 3.8 | Multimeter setup diagram 44 |
| Figure 4.1 | Tensile strength of NR band by using different amount of ZDEC 46 |
| Figure 4.2 | Elongation at break of NR bands at different loading of ZDEC..... 48 |
| Figure 4.3 | Modulus of NR membrane by using different amount of ZDEC 49 |
| Figure 4.4 | Stress-Strain curve for tensile at different ZDEC loading 51 |
| Figure 4.5 | Tear Strength of NR bands at different ZDEC loading 52 |
| Figure 4.6 | Swelling index of NR band at different ZDEC loading..... 53 |
| Figure 4.7 | Crosslink density of NR band at different ZDEC loading..... 55 |
| Figure 4.8 | FTIR spectra for contaminated NR band 64 |
| Figure 4.9 | FTIR spectra for Pure PP 66 |
| Figure 4.10 | Potential measurement of each of NR band..... 67 |

LIST OF SYMBOLS

| | |
|--------------------------|---|
| m_1 | mass in grams of the test portion |
| m_o | mass in grams of the dried material |
| pH_{pzc} | pH of the point of zero charge |
| ρ_r | Density of the latex |
| ρ_s | Density of the solvent |
| V_r | Volume fraction of latex in the swollen network |
| V_s | Molecular volume of the solvent |
| W_A | Weights of latex samples after solvent immersion |
| W_B | Weights of latex samples before solvent immersion |
| χ | Flory-Huggins latex-solvent interaction parameter |
| $[X]$ | Crosslink density |
| ζ | Zeta Potential |

LIST OF ABBREVIATIONS

| | |
|-------|--|
| ASTM | American Society for Testing and Materials |
| AFM | Atomic Force Microscopy |
| DDT | Dichlorodiphenyltrichloroethane |
| EB | Electron beam |
| EPS | Extracellular polymeric substance |
| FTIR | Fourier-Transform Infrared Analysis |
| HF | Hyperfiltration |
| HOCs | Hydrophobic organic contaminants |
| IR | Infrared |
| KOH | Potassium hydroxide |
| MF | Microfiltration |
| MPA | Megapascal |
| MPs | Microplastic |
| NF | Nanofiltration |
| NR | Natural rubber |
| NRL | Natural rubber latex |
| PDI | Polydispersity index |
| PE | Polyethylene |
| POPs | Persistent organic pollutants |
| PP | Polypropylene |
| pphr | Part per hundred rubber |
| PTFE | Polytetrafluoroethylene |
| PVDF | Polyvinylidenedifluoride |
| RO | Reverse osmosis |
| SDI | Silt Density Index |
| SEM | Scanning Electron Microscopy |
| TMTD | Tetramethyl thiuram disulfide |
| TSC | Total solid content |
| UF | Ultrafiltration |
| UTM | Universal Testing Machine |
| WWTPs | Wastewater treatment plants |

| | |
|------|------------------------------|
| ZDEC | Zinc diethyl dithiocarbamate |
| ZnO | Zinc oxide |

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, there has been a growing awareness of the impact of novel contaminants on water quality. Microplastics (MPs), defined as "any synthetic solid particle or polymeric matrix of either primary or secondary manufacturing origin, with regular or irregular shape and a size ranging from 1 μm to 5000 μm , have been identified as emerging contaminants of concern in aquatic systems around the globe. One of the primary concerns is that they attract other hydrophobic persistent organic pollutants (POPs) to their surface, serve as biofilm substrates, and may contain human-hazardous additives (Bermúdez, J.R. and Swarzenski, P.W., 2021). Figure 1 illustrates the effect of microplastics in water and aquatic systems in the graphical abstract.

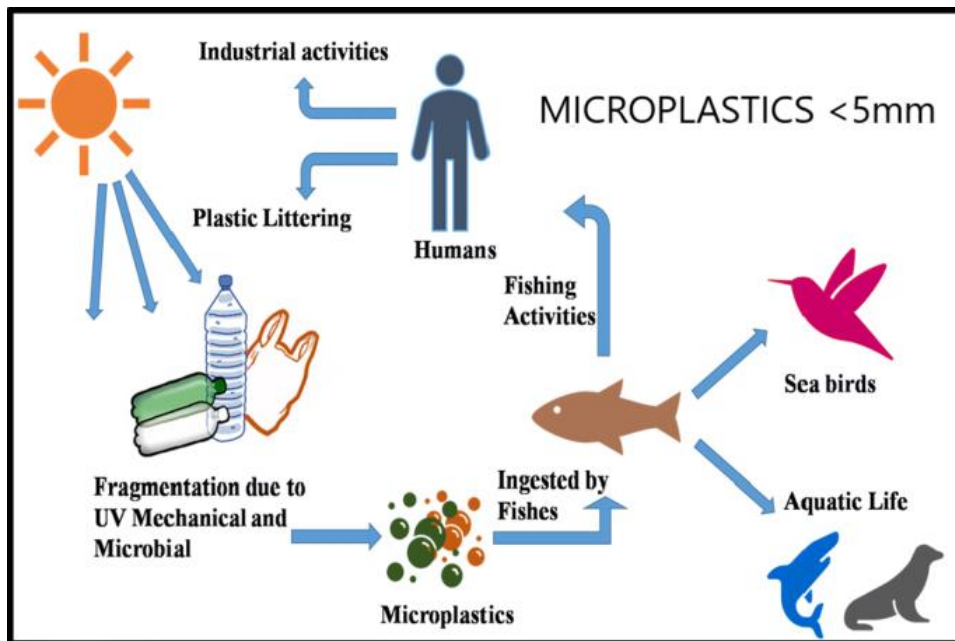


Figure 1: Effect of microplastics in water and aquatic systems graphical abstract

There are currently very few studies focusing on the technologies and their effectiveness for removing MPs from water, and they primarily rely on expensive operations that were initially developed for other purposes but are now being investigated for MPs removal. This research aims to find a way to capture microplastic waste in water ecosystems using natural rubber latex (NRL) to combat microplastic pollution in seawater.

Film-based technology, including membranes and bands, has long been recognised as a key technology for separating contaminants from polluted water and wastewater treatment sources. Membranes are selective barriers that separate two phases, allowing specific components to pass while others are retained. A pressure gradient and a chemical or electrical potential across the membrane can drive transport in membrane processes.

Membrane processes rely on physical separation, usually with no phase change and no chemicals added to the feed stream, and thus stand out as an alternative wastewater treatment technique to traditional processes (such as distillation, precipitation, coagulation/flocculation, adsorption by active carbon, ion exchange, biological treatment). The main advantages of these processes are their low energy consumption, reduced number of processing steps, improved separation efficiency, and higher final product quality. The membranes' limited chemical, mechanical, and thermal resistance, on the other hand, limits their application (Removal of dyes and pigments from industrial effluents, 2021).

The membranes have been tested extensively to improve their flux and selectivity. Furthermore, some researchers have highlighted membrane fouling as the most significant issue in using membranes in wastewater treatment. As a result, the

performance and commercial markets for membranes have exploded in recent years. As a result, we used natural rubber latex (NRL) as a medium to capture microplastic waste in the water ecosystem in this study. Overall, to address the issue of microplastic contamination, systematic management and innovative research on removing microplastic from seawater are required.

Currently, the number of work reported on using membranes to capture microplastic contaminants in the water is minimal. The purpose of this review is to highlight the growing interest of the scientific community in plastic pollution issues and to demonstrate the lack of knowledge in removing plastic, with a focus on membrane technologies. The membrane processes that are used to remove plastic have been described and critically examined. In this study, we focused on the band rather than the membrane; however, the band concept can be applied similarly to the membrane without the pores and filtering mechanism.

1.2 Problem Statement

Plastics are dumped into waterways at an alarming rate, resulting in fragmented debris that produces microplastics, which are microscopic plastic particles. The smaller microplastic size makes it easier for aquatic organisms to consume it, leading to the accumulation of toxic wastes and disrupting their physiological functions. Microplastics are abundant and have a high propensity to interact with the ecosystem, thereby disrupting biogenic flora and fauna. The oceans cover approximately 71% of the earth's surface and contains 97% of the world's water. The remaining 3% water can be found in ponds, streams, glaciers, ice caps, and atmospheric water vapour.

Microplastics can collect harmful pollutants from the environment and act as transport vectors while also leaching out chemicals (additives). Due to mechanical and photochemical processes accelerated by waves and sunlight, plastics in the marine environment splinter and shrivel to form micro/nanoparticles. Based on their origins, microplastics are classified as either primary or secondary based on their colour and density. 54.5% of microplastics floating in the ocean are composed of polyethylene, followed by polypropylene (16.5%), polyvinyl chloride, polystyrene, polyester, and polyamides. Due to their lower density than marine water, polyethylene and polypropylene float and impact oceanic surfaces, whereas materials with a greater density sink and impact the seafloor (Issac, M.N., Kandasubramanian, B. et al.,2021)

In the past decade, removing microplastics from the aquatic environment has emerged as a new urgent challenge due to their disastrous effects on aquatic species and humans. Due to ineffective waste management, the presence of microplastics in the environment has increased. Therefore, we utilised film-based technology to address this issue, as it is a proven method for removing microplastics from water.

The main advantages of these techniques are their low energy consumption, reduced number of processing steps, higher separation efficiency, and higher final product quality, but they also have limitations that can be overcome, such as fouling and chemical instability. Despite film-based technology's excellent performance in removing microplastics from water, there is still room for improvement in this technology's limitations. However, there is no doubt that film-based technology continues to be an excellent technology for removing microplastics from water. (Adewuyi, A., Campbell, A. J., & Adeyemi, O. G., 2021).

Whereas, natural rubber latex (NRL) is a current concern, exacerbated by the increased demand for rubber gloves during the COVID-19 pandemic. Greater quantities of latex products, such as industrial gloves, prophylactics, and other products, are being manufactured. Due to the need to meet stringent product quality standards and the volatile nature of latex, these industries generate a high proportion of non-recyclable liquid. NRL consists of high-quality rubber hydrocarbons with minimal crosslinking. If industries cannot effectively reuse NRL, they will face economic and environmental difficulties.

As a result, the proposed solution is to analyse the nature of interactions between MPs in seawater. The procedure for filtration and capture of MP wastes will then be controlled electrostatically using a latex band made of NRL. The conversion of NRL into a functional latex band will undoubtedly reduce the increasing amount of MP waste seawater and the environmental issues caused by the unnecessary use of advanced film-based technology.

1.3 Research Objectives

The objectives of this research are:

1. To formulate latex compounding for natural rubber (NR) band for microplastic waste capturing in water.
2. To examine the effect of ZDEC loadings on the mechanical properties of NR band.
3. To demonstrate the performance of microplastic waste capture using NR band via surface capturing

1.4 Research Scope

The first phase of this research highlights quality testing such as total solid content (TSC) to check the quality of the natural rubber latex and other ingredients. There are also preparations for ingredients so that they can use in the compounding process. Then, the second phase focus on formulating the latex formulation for latex band manufacturing for microplastic waste capturing in water and looking for the most suitable formulation with different amounts of Zinc diethyl dithiocarbamate (ZDEC) accelerator to be used in the compounding to produce latex membrane with excellent properties. After compounding, degasification and casting will be done to produce a latex membrane with desired thickness and size. Lastly, there are mechanical tests such as zeta potential, particle size, Fourier-Transform Infrared Analysis (FTIR), tensile test, tear test, crosslink density, and Scanning Electron Microscopy (SEM) have been done to compare the performance of each formulation formed. The third phase focused on microplastic studies and the measurement of rubber bands using a multimeter.

1.5 Thesis Outline

This thesis consists of five chapters:

Chapter 1: The introduction covers the research background, problem statement, objective and scope.

Chapter 2: Literature reviews of the research which includes microplastic, band mechanism, characteristics, limitations and fouling.

Chapter 3: Methodology and materials used in this research that covers the specification of ingredients and instruments used, process flow and experimental procedure and related testing.

Chapter 4: Results and discussion on the research conducted in more detail. It will depict all the charts and tables to represent the results.

Chapter 5: Conclusion of the research and a few suggestions for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Microplastics

Microplastics are currently regarded as a significant environmental threat due to their widespread use, ubiquity, persistence, and potential toxicity. Microplastics have been discovered in various ocean locations, including shorelines, deep and shallow water, sediment, beaches, and the benthic zone. Human activities such as fishing, tourism, marine transportation, and shipping contribute to releasing plastics and microplastics into the marine and coastal environments. According to field investigations, polystyrene, polyvinyl chloride, polyethylene, nylon, and polycarbonate plastic particles make up 60–80 percent of marine and ocean litter (Retama et al., 2016).

Microplastic is divided into two categories: primary microplastic, which consists of microparticles like microbeads, and secondary microplastic, which results from the breakdown of larger plastic materials (Duis and Coors 2016). Primary microplastics include microbeads in personal care products, plastic pellets used in industrial manufacturing, and plastic fibres used in synthetic textiles such as nylon. Secondary microplastics are produced when larger plastics degrade due to weathering, such as wave action, wind abrasion, and ultraviolet radiation from the sunlight (Kara Rogers 2020). Microplastic comprises fibres, fragments, films, pellets, beads, and styrofoam, depending on the morphotypes or types of morphologies. Low-density microplastic, such as polyethylene (PE) and polypropylene (PP), floats in water, while high-density microplastic sinks in sediment. (Sul and Costa 2014).

The majority of microplastics found in aquatic environments are secondary microplastics resulting from the breakdown of larger plastics (Waller et al. 2017).

Temperature and UV radiation intensity influence the fragmentation of larger plastics. (LI et al. 2016). Secondary microplastics are produced as a result of the progressive decay or disintegration of big plastics in the atmosphere as a result of ultraviolet light, wave abrasion, or microbial breakdown. In comparison to conventional plastic trash, microplastics in the environment degrade into nanoplastics 100 nm in size, which have virtually unknown dangers and hazardous qualities (Koelmans 2015). In aquatic systems, secondary microplastics outnumber primary microplastics due to intense weathering and other mechanical activities that produce plastic splintering.

During the production of microplastics, certain chemicals, such as additives, are combined and effectively sorb persistent bioaccumulatives and toxic contaminants (PBTs) from the environment. As microplastics have only been detected in the digestive tract of wild aquatic organisms, removing it from the majority of seafood species reduces the risk of microplastic consumption (FAO, 2017).

There are a few cases of microplastic exposure, such as when numerous bivalve and small fish species are swallowed without the removal of their gut contents. Even though there is a large information gap about the existence of smaller-sized microparticles (less than 150 microns) in aquatic environments and their effects on organisms, contamination will continue to increase in the near future, posing a threat to the safety of seafood. However, no relevant procedures or methods for observing and identifying microplastic in aquatic ecosystems and their living resources have been devised as of yet (FAO, 2017).

In recent studies, invertebrates such as barnacles, mussels, lugworms, crustaceans, and vertebrates such as fish, turtles, seals, and others have been shown to ingest and accumulate microplastic particle debris in marine environments (Wright et

al., 2013). Thus, causing marine wildlife and humans to face a complex challenge. Microplastic particles that are ingested can cause physical harm to organisms, such as internal scratching and obstruction. Due of their hydrophobic properties, microplastic particles increase toxicity in the marine environment by leaching toxic plastic additives and absorption and concentration of various types of organic pollutants (polyaromatic hydrocarbons, polybrominated diphenyl ethers, p,p'-Isopropylidenebisphenol, dichlorodiphenyltrichloroethane, polychlorinated biphenyls, etc.). (Andrady, 2011; Desforages et al., 2014; Dobaradaran et al., 2018; Zhao et al., 2014). The presence of most manmade substances in the environment is unavoidable, but when their overabundance manifests as pollution, it poses a threat and has negative consequences.

2.1.1 Marine Ecosystem and Human Health Concerns

The huge manufacturing and distribution of plastics within the marine ecosystem exacerbates the contamination of a previously polluted medium (Thushari and Senevirathna, 2020). Microplastics can easily accumulate and release dangerous organic pollutants such as Dichlorodiphenyltrichloroethane (DDT), polybrominated diphenyl ethers, and other additives that are present in water throughout the manufacturing process, thus increasing their concentration (Gonte and Balasubramanian 2012; Gore et al. 2017, 2018, 2019, 2020; Thakur and Kandasubramanian 2019; Rajhans et al. 2019; Campanale et al. 2020).

Although additive-free microplastics are not toxic to aquatic organisms on a chemical level, they do create physical issues such as intestine blockages (Udayakumar et al. 2021). Depending on commercial requirement, different additives are added to virgin microplastics, resulting in increased adsorption of water-borne contaminants and,

hence, impersonation as vectors. At every stage of the plastic lifecycle, from extraction of fossil fuels to consumer use to disposal, and additionally, research has proven the dangers that plastic poses to human health (Gore et al. 2016; Gore and Kandasubramanian 2018; Gharde and Kandasubramanian 2019; Issac and Kandasubramanian 2020). As microplastics can have detrimental effects on a variety of organisms, the possibility of microplastics impacting people cannot be ignored. Since humans are the final consumers of sea seafood contaminated with microplastics (Saha et al. 2021), there is a substantial danger of microplastic transfer to humans (Smith et al. 2018).

2.2 Film-based Technology

Film-based technologies have evolved as a viable and cost-effective alternative to wastewater, treated water, and air pollution treatment which include membranes and rubber band. The membrane process is preferred over traditional techniques because it is less time consuming, uses less energy, and is highly effective and selective. Furthermore, organic (natural rubber and polymer) and inorganic (ceramic, carbon, silica, zeolite, and other) membranes can be classified into two main groups based on their structure: porous and dense (non-porous) inorganic membranes. Hybrid organic-inorganic membranes are becoming increasingly popular.

In comparison to certain inorganic membranes, polymeric membranes have inferior separation performance. However, the versatility in processing and low cost of polymers make them particularly attractive for a wide variety of applications. Natural rubber (NR) has been utilised in numerous industrial and medical applications for decades. Recent attention has been drawn to NR compounds and membranes due to

their significant potential for biological and technological applications (Phatcharasit and Taweepreda, 2018).

2.2.1 Membrane Separation Process

In this work, we used film-based technology such as rubber band to capture microplastics, but membrane technology is discussed as a comparison of film-based technology used to filter wastes in water. Membrane filtration is known as a better pretreatment than traditional pretreatment because membrane pretreatment systems use less space and chemicals than traditional pretreatment systems. As membrane costs become more competitive, it may make sense to run a membrane plant from a business point of view.

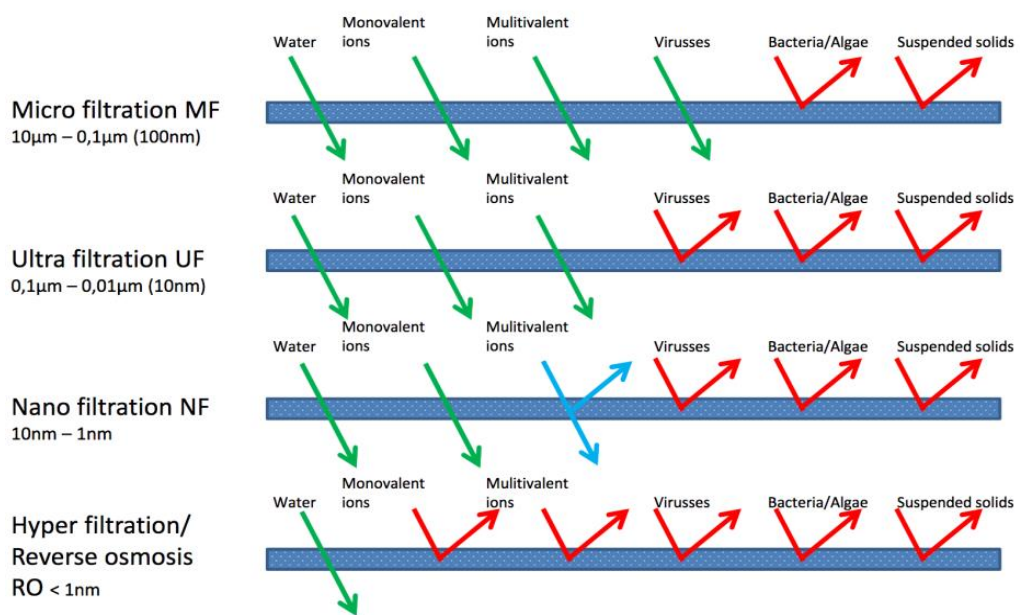
The way that membrane filtration technology stops microorganisms from getting through is through the effect of physiochemical interactions between the membrane and the microorganisms and the sieving effect. Microorganisms that are bigger than the pores of the membrane are kept inside. A negatively charged membrane, on the other hand, pushes microorganisms away (Jeong, Sanghyun et al., 2017).

Microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) are the four most common membrane separation processes. Low energy consumption, simplicity, and environmental friendliness are the main advantages of membrane technology over other separation processes (Igunnu and Chen, 2012; Wenten, 2002). Hyperfiltration (HF) or reverse osmosis (RO), which typically separates materials smaller than 0.001 m in size, such as monovalent salts from water, as used in the desalination of seawater and brackish water, nanofiltration (NF), which

separates larger molecules such as sugars and divalent salts while allowing monovalent salts to pass through.

Microfiltration (MF) is used for sterilisation by removing insoluble particulate materials (microbes) ranging in size from 0.1 to 10.0 μm . Ultrafiltration (UF) is used to separate materials in the 0.001 to 0.1 μm range, such as proteins or colloids, and finally ultrafiltration (UF) is used to separate materials in the 0.001 to 0.1 μm range, such as proteins or colloids (H Eccles, 1997). Figure 2.1 below depicts the comparison of membrane filtration techniques.

Comparison membrane techniques



© Logisticon Water Treatment b.v.

Figure 2.1: Comparison of membrane filtration techniques. (Logisticon,2022)

In addition, the kind of feed solution, operation parameters such as pressure and temperature, application type, and separation objectives regarding the type of material to be filtered out all influence membrane selection. (Morillo et al., 2014; Krishna, 1989). Organic and inorganic membranes are the two types of membranes accessible, and each

has its own merits and cons. It is essential to identify the membrane type that is optimal for the application (Synderfiltration, 2017).

There are numerous types of membrane materials, including polymeric, ceramic, and metallic. Although ceramic, metallic, and a variety of other materials are available, polymer constitutes the vast majority of commercial membranes. Because they are less expensive than membranes composed of other materials, polymeric membranes are chosen (Dickhout et al., 2016). Both manufactured and natural polymers are utilised to create polymeric membranes, and both forms are classified as organic membranes. Rubber, cellulose, and wool are examples of natural polymers, whereas polytetrafluoroethylene (PTFE), polysulfone, and polyvinylidenedifluoride (PVDF) are synthetic polymers.

Inorganic membranes include ceramic and metallic membranes. Metal (aluminium or titanium) and non-metal (oxides, nitride, or carbide) materials are utilised to construct ceramic membranes. Due to their inertness and resistance to fouling and chemical attack, ceramic membranes are extensively utilised in acidic and alkaline environments. Ceramic membranes are susceptible to breaking due to their high temperature sensitivity and relative expense. The surface poisoning effect is a drawback of metallic membranes.

Inorganic membranes provide a variety of benefits despite their disadvantages, including excellent thermal and chemical stability, resistance to microbiological degradation, and simplicity of cleaning after fouling. Despite this, the bulk of membranes are built of polymer because inorganic membranes have greater capital expenditures due to the need for a certain thickness to tolerate pressure drop changes (Synderfiltration, 2017).

2.2.2 Membrane Separation Characteristics

Membrane separation is characterised by the concurrent retention of species and flow of product through the semipermeable membrane. High selectivity and flux, as well as mechanical, chemical, and thermal stability, minimum fouling during operation, compatibility with the operating environment, and defect-free manufacture, determine membrane performance. Porous or non-porous polymers, ceramic or metal films with anisotropic or symmetric structures made of homogeneous, heterogeneous, or composite materials, ionic membranes, and liquid films containing selective carrier components are membranes that exhibit such selective behaviour under mild operating conditions (Obotey Ezugbe and Rathilal, 2020).

2.2.3 Limitation on film-based Separation

Film-based separation such as membrane processes can be plagued by serious membrane fouling problems when processing certain types of feed streams. Fouling can significantly reduce membrane permeation rates, making them unsuitable for such applications, especially if it is difficult to remove. Membrane fouling is one of the primary operational issues impeding the widespread use of ultrafiltration for a variety of contaminants. When investigating membrane fouling and its practical effects, it is critical to examine the source and mechanisms of foulant attachment to the membrane's surface. The dispersion interaction force and the polar interaction force are the two major forces that contribute to foulant attachment (Israelachvili 1992).

By balancing the Van der Waals attraction force and electrostatic double layer forces between particles and the membrane's surface, the Derjaguin, Landau, Verwey, and Overbeek theory quantified particle–surface interactions in aqueous environments.

These interactions shed light on the potential benefits of hydrophilizing the membrane's surface as a fouling remediation method (Abdelrasoul et al. 2014).

Membrane fouling takes place when particles, colloidal particles, or solute macromolecules are deposited or adsorbed onto membrane pores or a membrane surface due to physical and chemical interactions or mechanical activity in smaller or blocked membrane pores. Fouling of membranes can result in large flow declines and a decline in water quality. Severe fouling may require chemical cleaning or membrane replacement. This increases the operating costs of a treatment facility. In the past, pore blockage, pore constriction, and cake formation have all been considered as fouling mechanisms for membranes. Foulants include biological (bacteria, fungus), colloidal (clays, flocs), scaling (mineral precipitates), and organic substances (oils, polyelectrolytes, humics).

Membrane fouling is influenced by numerous variables, including particle or solute size, membrane microstructure, membrane, solute, and solvent interactions, as well as surface roughness, porosity, and other physical properties of the membrane. Consequently, we must prevent membrane fouling and prolong membrane life by selecting appropriate membrane materials, selecting a configuration, pretreatment of raw materials, optimising operating conditions, controlling inorganic salt solubility, regularly rinsing the membrane, using a disinfectant, increasing feed water temperature, and providing proper maintenance and care (Liu, Linling 2019).

Membrane fouling is usually categorised according to the foulants present in the feed stream, which can include particulate/colloidal fouling, biological/microbial fouling, scaling/precipitation fouling, and organic fouling, as described below. Each of these fouling kinds may be reversible, as when a simple cleaning can dislodge the

foulants and restore a membrane's full function, or irreversible, as when foulants chemically attach to the membrane material and damage its performance permanently. Four types of membrane foulants are distinguished: particle and colloidal fouling, biological and microbiological fouling, scaling or precipitation fouling, and organic fouling.

When dispersed particles and/or colloidal debris clog or stick to the surface of a membrane, particulate fouling occurs. As particles build on the membrane, they produce a "cake" layer that impedes water flow through the pores, resulting in symptoms such as increased pressure differential measurements and energy consumption. Particulate/colloid fouling is produced by the presence of non-biological and inorganic particles (e.g., silt or clay) in the feed water, which is particularly frequent when the stream originates from a body of surface water.

Water treatment professionals commonly analyse the Silt Density Index (SDI) of a feed stream to evaluate the danger of particulate/colloid fouling. RO systems feature the tiniest pores of any membrane filtering system and are therefore significantly more vulnerable to particulate fouling, making SDI measurements, particularly crucial during installation. Typically, particulate fouling is avoided by employing upstream coagulation and filtration.

Biofouling is the accumulation of microbes, plants, algae, and other biological pollutants in the pores and surfaces of filtration membranes. Biological and microbiological foulants flourish in warm, low-flow conditions, where they can attach and grow while emitting an extracellular polymeric material (EPS). Together, bacteria and EPS produce a coating of slimy gel known as biofilm. The chemical features of biofilm render it resistant to conventional cleaning methods such as backwashing and

the application of biocides such as chlorine. Although free chlorine is not a foulant, it is the most prevalent cause of membrane oxidation. It is permanent and permanent. Biofouling makes it harder to repair membranes, and they must be replaced in some situations. Over time, a biofouling membrane will restrict water flow from one side of the membrane to the other, increasing differential pressure from the feed to concentrate, decreasing membrane flux, increasing pressure-demand, and increasing energy expenditures.

Scaling, also known as inorganic fouling or precipitation fouling, is caused by crystalline salts, oxides, and hydroxides in the feed solution. Membrane scaling occurs when dissolved elements precipitate out of solution, collect on its surface, or lodge in its pores. When a solution against the feed side of a membrane becomes increasingly concentrated, it finally exceeds the solution saturation point, causing ionic constituents to crystallise or bind to the membrane surface.

Scaling is especially problematic for RO/NF systems with high conversion rates, mainly when the feed stream contains high calcium or magnesium concentrations. Inorganic fouling can be prevented through the use of treatment methods that restrict crystal formation, such as acid injection, softening, and the application of various chemical scale inhibitors. Although each method is effective, it is essential to avoid chemical treatments incompatible with the membrane material of choice.

Organic fouling is the buildup of carbon-based material on a filter membrane. Natural organic matter consists of carbon-based chemicals present in the soil, ground water, and surface water due to the decomposition of plants and animals. Organic matter is frequently highly reactive, and its risk as a foulant depends on several variables, including its affinity for the membrane material. By performing some form of raw water

treatment and/or selecting a membrane material that resists organic material adsorption, facilities can prevent organic fouling.

2.3 Review on Microplastic Removal by Film-based Technology

Plastic removal was discovered to be highly dependent on some parameters used as indicators to classify it, such as the shape, size, and mass of plastic particles. Table 2.1 lists the major influencing factors that can affect the performance of membrane processes for MP removal.

Table 2.1: Major influencing factors that can affect the performance of membrane processes for MP removal.

| | Influencing Factors |
|------------------|--|
| Membrane Process | Membrane material |
| | Membrane pore size |
| | Membrane thickness |
| | Membrane surface thickness |
| | Source of polluted water (Seawater, surface water, municipal water etc.) |
| Microplastic | Shape |
| | Size |
| | Mass |
| | Chemical composition |
| | Concentration |

Due to the variable content of the treated wastewater, the diverse MP characterization processes, and the size range of the MP studied, it is not straightforward to compare the published data about MP removal efficiency. Particularly, the absence of standardised characterization techniques has led to a vast amount of information that is not directly comparable due to the usage of different units (e.g., mass per volume, number per volume, etc.). Sun et al. 2019 reported on the removal efficiency of microparticles in some wastewater treatment plants (WWTPs), which is summarised in Table 2.2. Some cases reported very high MP removal, most likely due to the size range of the MP considered. Despite the high level of plastic removal, the vast majority of treated wastewaters are regarded as a source of plastic in effluents.

Table 2.2: Microplastic removal by different wastewater treatment plants (WWTPs)

(Data elaborated from Sun et al. 2019).

| Treatment Process | Microplastic Removal (%) | WWTP location |
|-----------------------------------|---------------------------------|----------------------|
| Primary, Secondary | 99.9 | Sweden |
| Primary, Secondary (Biofilter) | 88.1 | France |
| Primary, Secondary | 99.9 | United States |
| Primary, Secondary | 98.4 | Scotland |
| Primary, Secondary | 11-94 | Netherlands |
| Primary, Secondary | 95.6 | United States |
| Primary, Secondary | 98.3 | Finland |
| Primary / AnMBR | 99.4 | United States |
| Primary / MBR | 99.3 | Finland |
| Primary, Secondary, Tertiary (GF) | 97.2 | United States |

| | | | | |
|-------------------|------------|----------|------|---------|
| Primary, (BAF) | Secondary, | Tertiary | 97.8 | Finland |
|-------------------|------------|----------|------|---------|

The form of plastic particles affects removal effectiveness in WWTPs and can impact interactions with other pollutants or microorganisms. There are a variety of forms, including fibre, granular, fragment, film, and foam. Due to the discharge of residential washing machines containing synthetic polymers for clothing, the most prevalent form of plastic particles in wastewaters is fibre. According to some research, pretreatment is more successful at removing fibres than fragments, and secondary treatment is more effective at removing fragments than fibres (Poerio, Piacentini and Mazzei., 2019).

According to current research, nanometer-sized pieces of plastic can also be found in wastewater. This can be attributed to the fragmentation of synthetic fibres or the breakdown of polymers. In the process of decomposing polymer particles, the two basic processes that occur are fragmentation and degradation. Fragmentation occurs first. The process of separating longer polymer chains into a greater number of smaller pieces is referred to as fragmentation.

Degradation is a bond-breaking process followed by a chemical change that modifies the polymer's characteristics. This process can involve hydrolysis, photodegradation, mechanical/physical degradation, thermooxidative degradation, and biodegradation. Larger particles are more difficult for nanoparticles to get through biological barriers, penetrate tissue, alter organism behaviour and metabolism, concentrate in organs, and enter the base of the food chain (Poerio, Piacentini and Mazzei., 2019).

In addition, degradation activities increase the surface area of their degradation products, which has a significant biological influence. For instance, the surface area of 40 nm nanoparticles produced by the breakdown of a typical plastic bag is 2,600 m². A more detailed physical-chemical characterization of plastic, including size, mass, shape, and chemical composition, is required because it not only enables a better understanding of their true threat, but also enables the selection of appropriate methodologies that ensure more efficient plastic removal from effluents (Poerio, Piacentini and Mazzei., 2019).

2.4 Film Surface Hydrophilicity and Surface Charge

Membrane fouling is an issue that scientists have spent decades working to resolve. The bulk of polymers used in membrane production are extremely hydrophobic due to the continual demand for membranes with increased durability, solvent resistance, and long-term stability. Nonetheless, this hydrophobicity induces hydrophobic interactions with, for instance, proteins, resulting in a fouling layer on the membrane surface and a reduction in membrane performance (Breite, Went, Prager and Schulze., 2015).

Hydrophilization of the hydrophobic membrane material by means of grafting processes, electron beam (EB) irradiation, or plasma treatment is the most frequent solution. The creation of a water film on the membrane surface, which repels hydrophobic fouling chemicals, increases the fouling resistance of hydrophilized membrane surfaces. The membrane surface with the highest degree of hydrophilicity has and retains the highest fouling resistance. In any event, other conceivable interactions between membranes and fouling reagents, such as hydrogen bonds,

electrostatic or dipolar forces, which will also be affected by the aforementioned techniques, were rarely taken into account (Breite, Went, Prager and Schulze., 2015).

At the beginning of operation, hydrophilic organic matter will be the predominant pollutant; however, the interaction force between hydrophobic organic matter and the membrane is significantly greater than the interaction force between hydrophilic organic matter and the membrane, resulting in hydrophobic organic matter becoming the predominant pollutant later on. Hydrophilic carbohydrate organic matter and hydrophobic humic organic matter, both of which are common in the to-be-treated wastewater, are major components that lead to fouling of membranes (Tian, Ernst, Cui, Jekel., 2013).

The contact angle is commonly used to characterise the membrane's hydrophilicity/hydrophobicity. The greater the value of, the more hydrophobic the membrane surface. Angle has a relationship with the morphology of the membrane surface and the size of the membrane's pores. The hydrophilicity/hydrophobicity of the membrane material has a significant impact on the membrane's anti-fouling performance (Blandin, Gautier, Toran, Monclus, Rodriguez-Roda, and Comas., 2019).

In contrast to the hydrophobic membrane, the hydrophilic membrane is less susceptible to the effects of adsorption, possesses a higher membrane flow, and possesses anti-fouling qualities that are more effective. It is important to keep in mind that the hydrophilicity and hydrophobicity of the membrane often only have a major impact on membrane fouling during the first stage of the filtration process. (Xianjun, Yaoke, Veeriah and Izaz., 2020).

Strongly hydrophobic, mildly hydrophobic, polar hydrophilic, and neutral hydrophilic organic matter are isolated and filtered from organic matter found in

wastewater. Neutral hydrophilic organic matter has been identified as the most significant factor responsible for the reduction in membrane flux. It is believed that the presence of more hydrophilic organic materials in raw water causes more severe membrane fouling (Gao, Lin, Leung, Liao., 2010).

When the membrane surface charge and the charge of the contaminants in the wastewater are identical, membrane surface contamination is decreased and membrane flux is enhanced. Generally speaking, colloidal particles in aqueous solution are negatively charged. Due to the repelling effect of comparable charges, membrane fouling can be prevented by utilising a material with a negative potential as the membrane material (Xianjun, Yaoke, Veeriah and Izaz., 2020).

Due to its inherent mechanical and damping properties, the rubber-based membrane is widely used in building construction for water-, gas-, and sound-proofing requirements. Natural rubber latex is a stable aqueous colloidal suspension of cis-1,4-polyisoprene particles due to the presence of proteins and phospholipids adsorbed on the surface of the NR particles. Ammonia and other minor additives are commonly used to maintain the colloidal stability of NR latex. (Alenius and Palosuo., 2005).

These particles have a negative charge because they are surrounded by a protein membrane, which gives them their structure. Natural rubber has this membrane. As a consequence of this, the incorporation of a negatively charged electrolyte such as sodium hydroxide (NaOH) or an anionic surfactant could lessen the tendency of natural rubber particles to coagulate or become unstable (Santi, Asron, Nuruddin, and Muslich., 2019).

The negatively charged rubber particle surfaces are extremely sensitive to the latex emulsion's pH and acidity (Kumarn et al., 2018). However, cyclic mechanical