Studies on Development of Waste Plastic Based Hydrophilic Membranes for Ultrafiltration Applications

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A thesis submitted in partial fulfillment of the requirements for the degree of

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By

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भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
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DEDICATION

Dedicated to my beloved parents, wife, children,

and the entire family of Alhaji Modu Aji Shugaba

CERTIFICATE

It is certified that the work contained in the thesis entitled *"**Studies on Development of Waste Plastic Based Hydrophilic Membranes for Ultrafiltration Applications**"*, by **Mohammed Modu Aji**, has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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STATEMENT

I hereby declare that this research work was performed by me. It has not been presented in any previous application for the award of the degree of Ph.D. in Chemical Engineering. Related work consulted on this project has duly been acknowledged and referenced.

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20/07/2020

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ABSTRACT

Plastic utilization overtook other materials for its outstanding properties and advantageous characteristics. This has no doubt increased the number of waste plastic generated in the world and has risen concern over its effects on the environment. This work shows the feasibility of the utilization of waste plastic as a membrane precursor and its application in the ultrafiltration process. The main aim of the work is to utilize waste polyvinyl chloride (PVC) as a precursor for membrane fabrication with surface modification by using sustainable polymers for effective utilization. Waste derived PVC was blended with various additives (polyethylene glycol, polyvinylpyrrolidone, cellulose acetate, gum arabic) to overcome the hydrophobic nature of PVC in membrane fabrication. All the additives used in this work tend to increase the hydrophilicity of the membranes, thereby hydrophilized the waste PVC membranes rendering it more efficient for ultrafiltration applications. The outcomes are discussed in independent chapters.

First of all, waste-derived PVC was blended with cellulose acetate to improve the membrane parameters. The membranes were prepared via phase inversion using N-dimethyl formamide (DMF) induced by non-solvent. The characterization of the membranes was done using various techniques including field emission scanning electron microscopy, Fourier transforms infrared spectroscopy in attenuated total reflectance mode, thermo-gravimetric analysis, and measurement of water contact angle. The membrane properties were assessed by pure water flux (PWF) and bovine serum albumin (BSA) rejection, respectively. The outcome showed that the membrane had improved hydrophilicity with PWF of 85 L/m^2 h.

In another development, the application of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and their combination on waste PVC based membranes and subsequent paraphernalia on the morphology, performance, thermal and mechanical properties were studied. A series of membranes were fabricated by immersion precipitation method using N-Methyl-2-pyrrolidone (NMP) and Dimethyl acetamide (DMAc) as a solvent. The effect of casting solvents was determined by Hansen solubility parameters (HSP). Field emission scanning electron microscopy (FESEM), equilibrium water content (EWC), contact angle, Fourier transform infrared in attenuated total reflectance mode (ATR-FTIR), porosity and, pore size was performed regarding the morphology. Pure water flux (PWF), and rejection of Humic acid in water were evaluated in regards to the performance. While tensile strength was tested using the electromechanical universal testing machine (UTM) and thermal degradation studies (TGA) were carried out with regards to the mechanical and thermal properties of the membranes. Hansen solubility parameters were computed and it indicated that the NMP solvent has better interaction with the base polymer (waste PVC). The outcome indicated that PEG has better rejection with compromised flux while PVP has high flux and the mixed additives give combined benefits.

In the same vein, utilization of waste PVC as membrane substrate was considered and its hydrophilicity enhancement by incorporation of a sustainable biopolymer gum arabic (GA) for natural organic matter removal in water was carried out. The phase transformation method was used in the membrane preparation by varying percentages of GA. The interaction between the waste polyvinyl chloride and gum arabic with different loadings were analyzed using various analytical techniques for morphology and evaluation studies. Furthermore, natural organic matter (NOM) removal from the water was carried out. It was confirmed that blending with gum arabic enhanced the hydrophilicity, improved the water permeation with a flux recovery ratio of around 80 %, and a rejection of 96 % was observed. The onset degradation temperature was

improved and the mechanical strength was enhanced by ~ 1.2 MPa. The outcome compared favorably with membrane prepared with a pristine precursor reported in the literature. Generally, the work proposed that waste plastic (PVC) could provide an alternative means for membrane precursor in water filtration and its properties can be tailored with appropriate additives and solvent for targeted applications. Optimistically, this outcome would help in adding value to waste plastic via membrane fabrication and its subsequent application in the filtration process.

LIST OF PUBLICATIONS FROM THE THESIS

Publication/Conferences

i. **Mohammed M. Aji**, S. Narendren, Mihir. K. Purkait, Vimal Katiyar, Utilization of waste polyvinyl chloride (PVC) for ultrafiltration membrane fabrication and its characterization, J. Environ. Chem. Eng. 8 (2020) 103650.

ii. **Mohammed M. Aji**, Mihir K. Purkait, Vimal Katiyar, Influence of additives and solvents on waste polyvinyl chloride (PVC) membrane: morphologies, performance, thermal and mechanical studies (Manuscript submitted, under review).

iii. **Mohammed M. Aji**, S. Narendren, Mihir K. Purkait, Vimal Katiyar, Biopolymer (gum arabic) incorporated waste polyvinylchloride membrane for hydrophilicity enhancement, fouling mitigation and natural organic matter removal in water (Manuscript communicated, revision submitted).

iv. **Mohammed M. Aji**, S. Narendren, Mihir K. Purkait, Vimal Katiyar, Waste PVC as a precursor for membrane fabrication blended with cellulose acetate. Presented in Research Conclave March 14-17, 2019 at IIT Guwahati.

v. **Mohammed M. Aji**, Mihir K. Purkait, Vimal Katiyar, Utilization of waste plastic for ultrafiltration membrane fabrication and its performance studies. Presented in research conference February, 27 - 28, 2020 at NIT Meghalaya.

vi. **Mohammed M. Aji**, Mihir K. Purkait, Vimal Katiyar, Valorization of Balanite Aegyptiaca (Desert Date) seed shell for isolation of crystalline cellulose and its characterization for membrane preparation, presented in the international symposium on sustainable polymers & National Symposium on Chemistry Education for Sustainable Engineering August 23-25, 2019.

vii. **Mohammed M. Aji**, Mihir K. Purkait, Vimal Katiyar, Effects of additives and solvents on waste polyvinyl chloride membrane: morphologies, performance, thermal and mechanical studies. Accepted in Research conclave March 2020 at IIT Guwahati.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1

Introduction and Literature Review

Chapter 1

Introduction and Literature Review

This opening chapter brings forward the contextual of the study, highlights on plastic, effects of waste plastic, and the waste plastic management. Fundamentals of polymeric membranes, history of membranes, types, class, and preparation method are discussed. The chapter also presents the background of present work, methods of membranes modifications, documentation of relevant pieces of literature, objectives, and the thesis organization.

1.1 Introduction

Plastic is a synthetic or organic material consisting of a wide range of organic compounds that are malleable and can be molded into various objects. The production of plastic products started to thrive during the 1940s and 1950s on an industrial scale; it kept on flourishing ever since [1]. Plastics are not just one material, it is a folk of hundreds of diverse materials with a broad range of properties. They are premeditated to congregate the needs of every single user in the most proficient way. Plastic materials are organic materials that can either be fossil fuel-based or bio-based [1][2]. Therefore, plastic that is used and discarded or any container that its contents have been used or consumed, that plastic has become "waste". As we continue to utilize plastic goods so is the waste generated keeps on increasing. A high percentage of the requirement of the plastic in the market is for packaging products and goods, the packaging applications have a greater share (39.6 %) as shown in Figure 1.1 among others. Therefore, waste plastics are generated daily based on the utilization of the products [2][3].

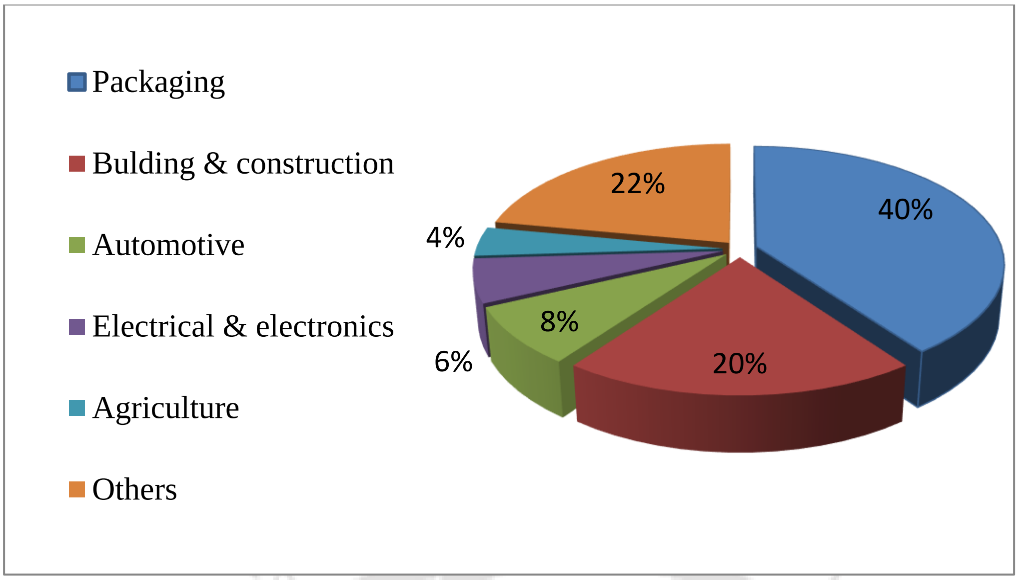

Figure 1.1: Plastic market segments [2]

1.1.1 **Types of plastic**

Plastic is manufactured using petroleum products as their primary feedstock and is one of the most commonly used materials for quite a lot of applications such as industrial, agricultural, and domestic activities, mainly due to their good mechanical properties, flexibility, low cost and ease of processing [4]. There are various kinds and understanding the different types can help in its utilization. The main two broad categories of plastic are:

1.1.1.1 Thermoset

Thermoset or thermosetting plastic: these are plastics that are hardened once cooled after processing. They retain their shapes and cannot be reshaped via heating [5]. They are hard and durable, usually used in heat resistant and mechanically stressed applications. For instance, these types of plastic include polyurethanes, polyesters, epoxy resins, and phenolic resins.

1.1.1.2 Thermoplastics

Thermoplastic: these are plastic that can be thermally processed, less rigid than thermosets. Thermoplastic tend to soften and flow upon heating which makes it easy to be molded and extruded into various films, shapes, packages, and fibers. It can still be reprocessed to maintain its original form or shape to another form when it undergoes a cycle of heating and cooling [5]. Examples of thermoplastic can be enumerated as polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC). Table 1.1 shows the types of thermoplastic and their recycling codes.

Table 1.1: Types of plastic and their recycling capability

Code	Polymer name	Abbreviation	Uses	Recyclable
1	Polyethylene Terephthalate	PET	Soda bottles, Water bottles, Salad dressing bottles, Medicine jars, Peanut butter jars, Jelly jars, Combs, Bean bags, Rope, Tote bags, Carpet, Fiberfill material in winter, clothing.	yes
2	High-Density Polyethylene	HDPE	Milk jugs, Juice containers, Grocery bags, Trash bags, Motor oil containers, Shampoo and conditioner bottles, Soap bottles, Detergent containers, Bleach containers, Toys.	yes
3	Polyvinyl Chloride	PVC	Some shopping bags, Plumbing pipes, Grocery bags, Tiles, Cling films, Shoes, Gutters, Window frames, Ducts, Sewage pipes, etc.	yes
4	Low-Density Polyethylene	LDPE	Cling wrap, Sandwich bags, Squeezable bottles for condiments such as honey and mustard, Grocery	yes

			bags, Frozen food bags, Flexible container lids.	
5	Polypropylene	PP	Plastic diapers, Tupperware, Kitchenware, Margarine tubs, Yogurt containers, Prescription bottles, Stadium cups, Bottle caps, Take-out containers, Disposable cups, and plates.	yes
6	Polystyrene or Styrofoam	PS	Disposable coffee cups, Plastic food boxes, Plastic cutlery, packing foam, packing peanuts.	yes
7	Miscellaneous Plastics (polycarbonate, acrylic, acrylonitrile, etc.)	Not available	Plastic CDs and DVDs, Baby bottles, Large water bottles with multiple-gallon capacity, Medical storage containers, Eyeglasses, Exterior lighting fixtures.	yes

1.1.2 Effects of waste plastic

Plastics are considered to be leading environmental pollutants. It is the most abundant constituent of the municipal solid waste, due to its non-biodegradability. It is becoming a continuing environmental predicament for today's age group and those to come in future generations if nothing serious is done to curtail it because its degradation takes up to a thousand years [6]. Most people depend on it for their various needs and applications. The greatest number of plastics is non-biodegradable types, i.e. they are not degradable by microorganisms. Plastic like polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polypropylene (PP) being the most abundant ones, are practically non-degradable. The totality of plastics production is more than 230 million tons per year which were predicted to cross over 500 million tons in 2020 [7].

Recently, there is an emerging apprehension over the environmental effects of use and applications of plastic which consequently leads to the generation of waste plastic, which is typically non-biodegradable and sometimes releases toxic by-products. Its disposal has a lot of associated challenges ranging from the large dumpsite, contaminated landfills, clogging of waterways, littering of the roads, environmental degradations, food chain depletion, flooding, the effect on water transport, river, and ocean’s contamination among others [8].

1.1.3 Waste plastic management

Waste plastic handling and management is an important matter. Over the years, more than 300 million tons of plastic are manufactured in the world yearly and almost 50 % of these products are disposed of within a year of their purchase [2]. Plastic nuisance is very difficult to contain, but environmentalists are still trying to manage the effects of indiscriminate waste plastic disposal. Various waste management and treatment processes have been established and applied for waste plastic disposal. The pyramid of waste plastic management routes is given in Figure 1.2. Recycling and reuse are a top priority within the hierarchy because it is environmentally and economically friendly [9]. There are different ways of waste plastic management as depicted in Figure 1.2 from the most preferred to the least desired methods, as you go down the pyramid. In the midst of it, is combustion through incineration which has a detrimental effect of releasing harmful gases to the atmosphere, burying the waste is considered as a way of management but this is also unfriendly as it affects the environmental process because it can lead to the formation of toxic fumes, a hindrance to the growth of agricultural products by interfering with their transpiration process as well as surface and groundwater pollution. Another way of managing waste plastic is via the route of reuse/recycling, compared to the other two ways mentioned earlier plastic recycling or reuse is therefore often the best environmental approach and could be taken as an area of specific interest, particularly for reducing the need to manufacture more plastics as well as other fossil-based products [7][8]. Among the different plastics that can be recycled include polyethylene terephthalate (PET), polyvinyl chloride (PVC), polypropylene (PP), and Low or high-density polyethylene (HDPE). These plastics are having different identification codes and they have been used in a wide range of applications, such as packaging, appliances, automotive components, piping, windows frame, toys, and electrical and electronic equipment. Energy generation [10], mechanical recycling [11], and membrane manufacturing [12] are among the recycling paths. Membrane manufacturing has gathered momentum due to its unique advantages.

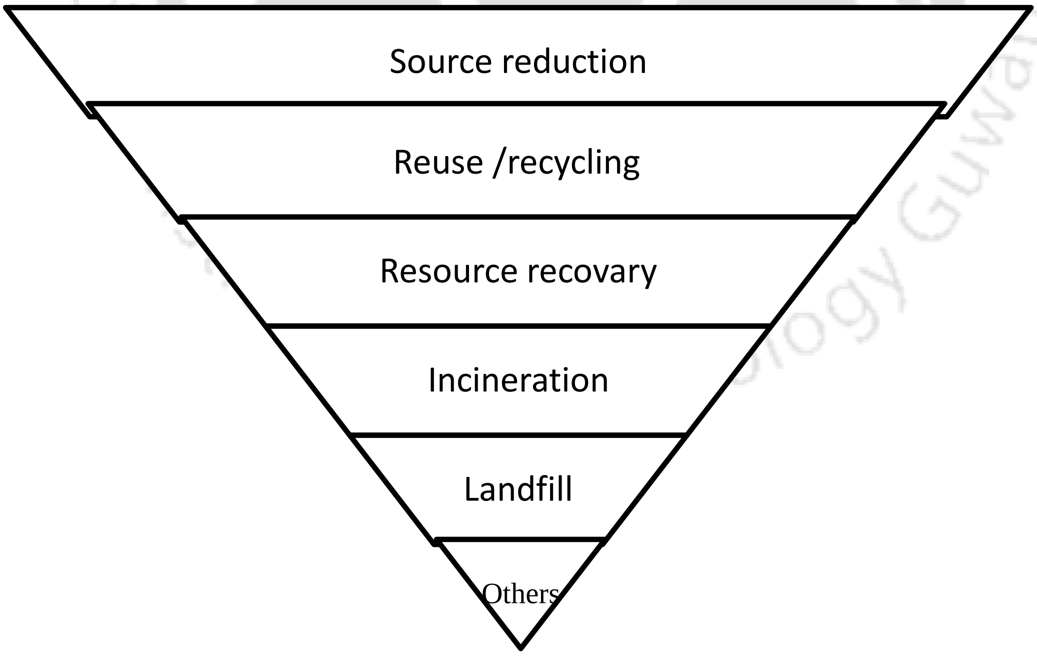

Figure 1.2: Waste plastic management route

1.2 Membrane

The history of the development of membrane can be traced back to the middle of the 18th century, primarily at that time membrane phenomena are observed and studied based on barrier properties rather than to develop membrane for technical and industrial applications. Table 1.2 given below shows some membrane processes developed for a specific application.

Table 1.2: History of the development of the membrane process [13].

Membrane process	Country	Year	Application
Microfiltration	Germany	1920	Laboratory use (Bacteria filter)
Ultrafiltration	Germany	1930	Laboratory use
Hemodialysis	Netherlands	1950	Artificial Kidney
Electrodialysis	USA	1955	Desalination
Reverse Osmosis	USA	1960	Seawater desalination
Ultrafiltration	USA	1960	Concentration of Macromolecules
Gas separation	USA	1979	Hydrogen recovery
Membrane Distillation	Germany	1981	The concentration of aqueous solutions
Pervaporation	Germany/Netherlands	1982	Dehydration of organic solvents

A membrane is the heart of every membrane separation process. It's normally placed between two phases where it allows the preferential transport of only the required components of the system while excluding or retaining the unwanted components [13]. Although, in some rare cases the retentate is the required component. Membranes have gained an important place in chemical technology and are used in a broad range of applications. Schematic representation of the membrane, its feed and permeate phases are depicted in Figure 1.3.

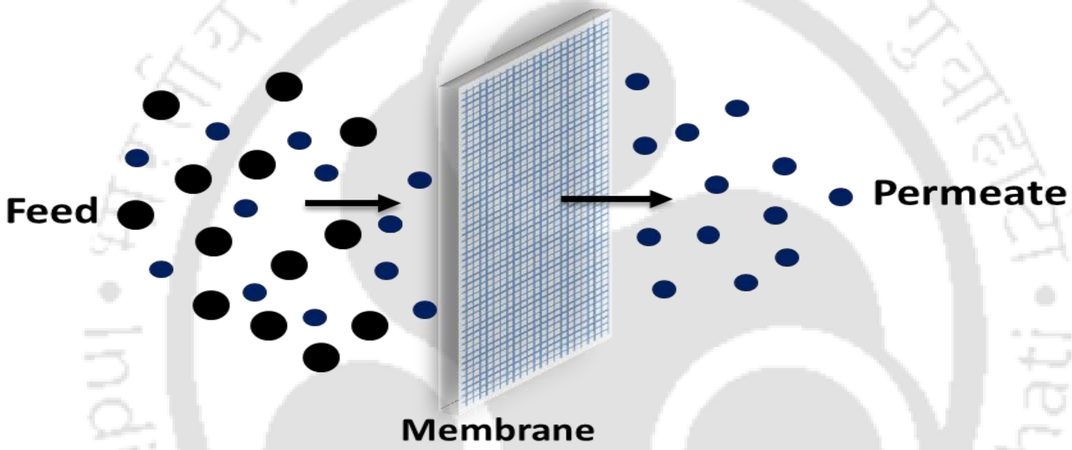

Figure 1.3: Schematic illustration of the membrane.

The membrane is used on various applications ranging from industrial effluent treatment, fractionation of macromolecular solutions in water and wastewater, food and drugs industry by ultra-filtration, controlled drug delivery, and removal of toxins and urea in human kidneys through dialysis [14]. Nevertheless, despite these various applications, they have a common feature which is the membrane. Although the process may vary based on the differences in their mode of operations, the material used, morphological structures, and driving force. In Table 1.3 membrane separation process, mechanism of separation, pore size, and transport regimes is presented based on pressure-driven membranes.

Table 1.3: Membrane separation process and membrane characteristics [13].

Membrane Process	Separation Mechanism	Pore size (nm)	Transport regime
Microfiltration	Size exclusion	50-500	Micropores
Ultrafiltration	Size exclusion	1-100	Mesopores
Nanofiltration	Size exclusion	0.5-2	Micropores
Reverse Osmosis	Size exclusion/ solution diffusion	<0.5	Molecular

1.3 Types of membrane

The membrane can be grouped based on the material that was used in the fabrication of the membrane as shown in Figure 1.4. Polymeric and liquid membranes are generally referred to as organic membranes. While ceramic and metallic membranes are referred to as inorganic membranes. It is also possible to employ a composite membrane which tends to have a ceramic membrane as a support with a skinned top layer of the polymeric membrane [15]. However, in some instances composite membrane is made up of different polymeric materials, one serving as the top layer as usual and others as a mechanical support and each layer can be optimized independently [16]. The nature of the membranes that is, their structural and material characteristic determines the kind of application that is suitable for it [13]. The most important types of membrane material are organic that is, polymeric materials. The choice of specific polymer for membrane material is not random but guided by the knowledge of polymer chemistry which can give you some basic properties.

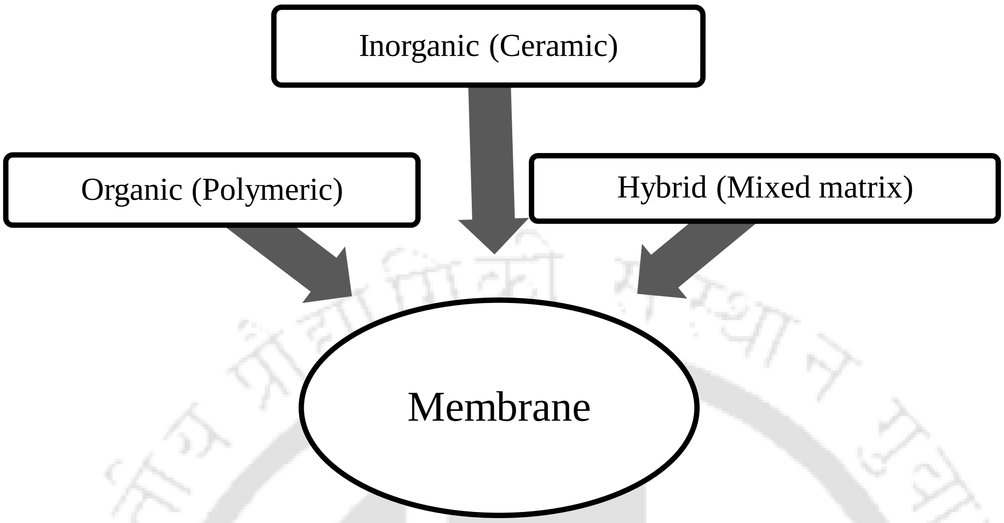

Figure 1.4: Types of membrane

1.4 Membrane preparation techniques

The choice of techniques for the preparation of membranes depends on the selection of the materials and the required structure and morphology of the membrane. Many processing techniques exist for the fabrication of membranes which include: Sintering, Stretching, Tract itching, Template leaching, Phase inversion, and Electrospinning among others. As summarized in Table 1.4 membrane fabrication techniques have different properties that result due to the inherent material characteristics and the particular techniques adopted in preparing the membrane. Some of the techniques are exceptionally used by polymeric materials; like the phase inversion due to the ability of polymeric material to dissolve in different solvents. Therefore, the fabrication technique applied depends on the material in hand, final properties desired for the membrane, and the intended application of the membrane.

Table 1.4: Membrane fabrication techniques [13,17]

Fabrication technique	Pore diameter (µm)	Porosity (%)	Properties
Sintering	0.1-10	10-20	Outstanding chemical, thermal and mechanical stability, both inorganic and organic material can be used
Stretching	0.1-20	90	High permeability for gases and vapors, it can be produced as flat sheets, tubes or capillaries.
Track etching	0.02-10	Max. 10	Low tendency to plug, good long-term flux stability
Template leaching	Min. 0.05	porous	High surface area
Phase inversion	0.21-20	Porous and nonporous	Properties vary according to the polymer used
Electrospinning	porous	Highly porous >80	Relatively high flux and less tendency to fouling, high surface area

Phase inversion or immersion precipitations are achieved by casting a polymer solution on a suitable support and then transferred or immersed the casted membrane into a coagulation bath [20]. The bath containing a non-solvent where an exchange of solvent and non-solvent takes place subsequently forming the membrane structure [18]. This type of membrane can be made from almost all polymers which are soluble in an appropriate solvent and can precipitate in a non-solvent [19]. Changing the type of polymer, precipitation medium, polymer concentration, and the precipitation temperature, the microporous membrane can be made with a very large variety of porous structures with varied thermal, chemical, and mechanical properties. This makes it the most favorable means of polymeric membranes fabrication. The schematic process of phase inverted membranes is depicted in Figure 1.5.

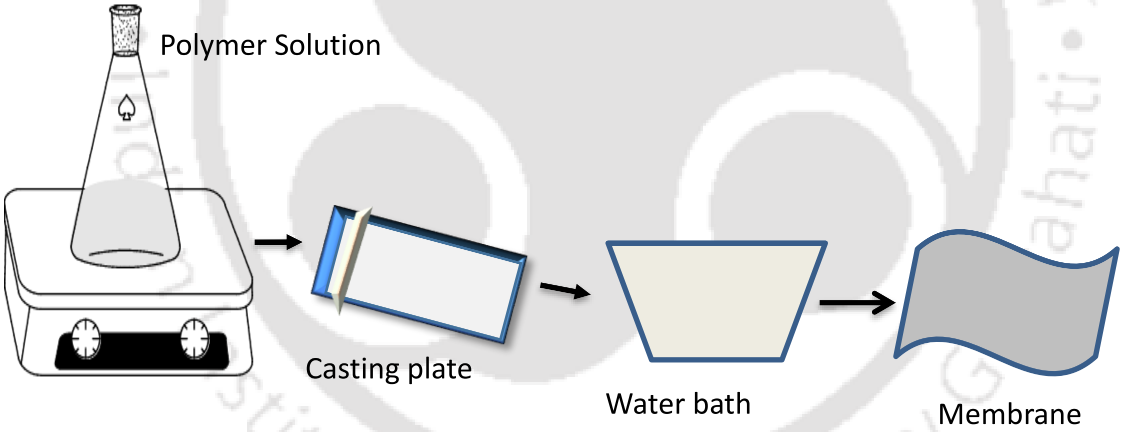

Figure 1.5: Representation of phase inversion.

1.5 Modifications of membrane

Surface modification is an effective approach to enhance the properties of polymeric membranes. Membrane modification or functionalization can be done or achieved through various means; either covalent or non-covalent, attachment is normally done to improve the membrane physicochemical and morphological properties. Blending, coating, grafting, and chemical modification are some of the techniques followed to enhance membrane properties and parameters.

1.5.1 **Physical coating**

The polymer coating can be achieved by either covalent bonding of the modifying polymer to the membrane substrate or by non-covalent attachment. The physical coating exists via physical interactions but mostly without covalent bonding, in other words, the interactions do not cause a change in chemical composition. However, a chemical reaction may occur during modification [21]. This kind of modification is normally done by carefully immersing the membrane into the chemically active solution which can subsequently tend to be coated onto the surface of the given membrane [22][23].

1.5.2 **Graft copolymerization**

The grafting approach to produce antifouling surfaces has been widely studied. An advantage of this technique compared to the polymer deposition lies in its capability to control the density of chains growing from the surface. Different techniques can be used for the surface modification of thin-film polymeric membranes such as UV-induced graft polymerization, plasma-induced polymerization, and plasma treatment [24]. UV-photo-induced graft polymerization is a convenient technique. Furthermore, the covalent attachment of the graft chains onto a polymer surface is stable, which is in contrast to physically coated polymeric layers [25].

1.5.3 **Chemical modification**

In a chemical modification, the polymeric surface is treated chemically via covalent bonding interaction. Mostly, base polymer chains are firstly activated by chemical reaction or high energy radiation followed by grafting of a high polymer modifier [26]. The membrane surface properties are enhanced without interacting with the bulk polymer properties significantly. The chemical covalent interaction of the modifier with the polymeric surface is greater than that of the physical method and it offers a long time chemical stability [27].

1.5.4 Blending

Blending the membrane polymer material with hydrophilic compounds to improve membrane hydrophilicity and fouling resistance is considered as an attractive method for the modification of microporous polymer membranes [28]. Blending with organic material is a simple way of improving membranes' characteristics. In this method, the additives are simply mixed or dissolved into the polymeric solution. Biopolymer, charged polymer, surfactants, organic acids, and other unique polymers [29] have been used as modifiers.

1.6 Background literature

This section consists of a brief overview of the research so far done and its outcomes to identify the areas that need to be explored further. The state of the literature is presented under subsections; membrane from waste plastic, PVC based membranes from a pristine source, modification of polymeric membrane, and blending with sustainable polymers. Some gaps are identified and subsequently, objectives are specified.

1.6.1 Membrane from waste plastic

Polymer resources play an important role in people's daily life and the fabrication level and handling have been rising for the last six decades. The exceptional performance of polymers is the product of the prospect of synthesizing novel materials for precise applications. Nevertheless, a good number of polymers are based on petrochemicals. As fossil fuels are being exhausted and fuel prices fluctuate widely, there is a need to build up a foundation for a new circular economy based on more sustainable ways or materials [30]. Thereby, utilizing the waste plastic generated in a benefitting way to improve sustainability. Hence, even in the field of membrane preparation researchers are now concerned about the environment and the future sustainability of the materials which results in researching the application of waste plastic in membrane fabrication.

Garcia-ivars et al. [4] reported the application of post-consumer recycled high-impact polystyrene in the preparation of phase-inversion membranes for low-pressure membrane processes. Commercially high impact polystyrene and recycled polystyrene were used in manufacturing low-pressure membrane via phase inversion method using N, N-Dimethylacetamide (DMA) as the solvent. The membranes were characterized and they found out that the recycled polystyrene membrane shows similar thermal and morphological properties as the one fabricated from the commercial high impact polystyrene. Its application in humic acid rejection was conducted and 95 to 96% rejection was recorded.

Fahrina et al. [32] studied the possibility of using recycled polymer (waste polyethylene terephthalate [PET] bottles) as a membrane material. Porous polymeric membranes were prepared via thermally induced phase separation by dissolving recycled PET in phenol. The unmodified PET membrane was prepared by dissolving 20 wt. % of the waste plastic in phenol and the solution was subsequently casted on a glass plate. For the modified PET membrane, 5 wt. % of polyvinylpyrrolidone (PVP) was added into a polymer solution. The solution was casted onto a glass plate at room temperature followed by evaporation before the solidification process as in the initial case. The membranes formed were characterized in terms of morphology, chemical group, and filtration performance.

A humic acid solution was used to identify the permeability and the solute rejection of the membranes. The maximum flux obtained from the pure water filtration test was 97 L/m^{2}hr and the highest humic acid rejection was reported to be 75.92 %.

Zander et al. [33] the team studied the application of recycled PET nanofibers for water filtration. The PET bottles were cut into strips and then fed into a cross-cutting paper shredder. Solutions were prepared by dissolving the PET shreds in Hexafluoro isopropanol (HFIP) and stirring at room temperature overnight. Tributyl ammonium chloride (TBAC) relative to the polymer weight was added to at 5 wt. % solution to reduce fiber bead formation. The PET nanofiber membranes were formed via solution electrospinning with fiber diameters as low as 100 nm. The fibers were modified with a biguanide and a quaternary ammonium compound to reduce biofouling. The biguanide functionalized mats achieved 6 log reduction for both gram-negative and gram-positive bacteria. Filtration efficiency was tested with latex beads with sizes ranging from 30 to 2000 nm. Greater than 99 % of the beads as small as 500 nm were removed using gravity filtration. Although fiber diameters as low as 100 nm was achieved, the mats were not suitable for ultrafiltration applications since particles under 500 nm were not effectively removed. However, the mats could be used in microfiltration applications such as a pre-filter in a wastewater treatment system.

Lin et al. [34] reported the synthesis of the composite membrane using waste plastic (polyethylene terephthalate) with water bamboo husk particles to form the porous composite membrane via water-vapor-induced phase inversion. The composite membrane was characterized in morphology, pore structure, surface area, and ion-exchange capacity. The pure PET membrane showed negligible dye adsorption. Moreover, it is found that the cationic dyes were adsorbed on to the composite membrane through a combination of electrostatic interaction, hydrophobic interaction, and hydrogen bonding.

Rajesh and Murthy, [35] studied the synthesis and characterization of asymmetric ultrafiltration membranes from recycled polyethylene terephthalate (PET) and polyvinyl pyrrolidone (PVP) using m-cresol as a solvent. They assessed the prospects of waste PET in the fabrication of UF membranes and the special effects of viscosity of the casting solution were studied based on the molecular weight of polyethylene glycol (PEG) added. The membranes were characterized in terms of pure water permeability (PWP), molecular weight cut-off (MWCO), and membrane morphology. The results show that the addition of PEG with high molecular weights leads to membranes with higher PWP. The presence of additives affects surface roughness and membrane morphology. Polyvinyl pyrrolidone (PVP) 90 kDa, and polyethylene glycol with molecular weights of 200, 400, and 600 Da respectively were used. The result reported indicates that water permeability is significantly affected by the molecular weight of the PEG added. The membrane with PEG 200 (10%) showed a PWP of 6.2 L/(m^2 h), whereas the one containing PEG 400 (10%) and PEG 600 (10%) showed 6.8 L/(m^2 h) and 7.7 L/(m^2 h), respectively.

Altalhi et al. [36] present a nanotechnological approach to convert commercially available and non-degradable grocery plastic bags into well-organized carbon nanotube membranes with tunable molecular transport properties. Carbon nanotubes were fabricated by a template and catalyst-free chemical vapor deposition (CVD) synthesis inside Nanoporous anodic alumina membranes (NAAMs). This process was carried out in a CVD system consisting of a two-stage furnace equipped with a cylindrical quartz tube (i.e. 43 and 1000 mm in diameter and length). CNTs were grown inside NAAMs featuring hexagonally arranged nanopores, which enable the control over the nanotubes' organization and geometry. The transport performance of the resulting CNTs–NAAMs is tested by several dye molecules with a positive, negative and neutral charge. These results demonstrated the ability of these membranes to selectively tune molecular transport as a function of the interaction between molecules and the inner surface of CNTs.

The above literature as summarized in Table 1.5 enumerated the utilization of various waste plastic as a precursor for membrane fabrication and the encouraging outcomes were conveyed. However, the utilization of waste PVC for membrane preparation has not yet been explored. On the other hand, the virgin (pristine) PVC has been used in membrane fabrication for different applications as discussed in the subsequent section.

Table 1.5: Waste plastic and solvent types used for membrane fabrication

Waste plastic	Solvent used	Application	Reference
Polyethylene Terephthalate (PET)	Phenol	Humic acid removal	[31]
Polystyrene (PS)	N, N Dimethylacetamide (DMA)	Humic acid rejection	[4]
Polystyrene (PS)	Toluene	CO_2/N_2 separation	[37]
Polyethylene Terephthalate PET	Hexafluoro isopropanol (HFIP)	Liquid filtration	[33]

Polystyrene (PS)	Dimethyl acetamide (DMAC)	Proton exchange	[38]
Polyethylene Terephthalate (PET)	Hexafluoro isopropanol (HFIP)/Tributyl ammonium chloride (TBAC)	Water filtration	[33]
Polyethylene Terephthalate (PET)	Dichloromethane (DCM)/ Trifluoroacetic acid (TFA) at the ratio of (30/70)	Smoke filtration	[39]
Polyethylene Terephthalate (PET)	M-cresol	Liquid filtration	[35]

1.6.2 PVC based membranes from pristine precursor

Polyvinyl chloride (PVC) is one of the versatile polymers that have a film-forming ability, ease of processability, good chemical resistance, suitable thermal stability, and other beneficial characteristics. These outstanding properties of PVC have made it a choice for membrane fabrication.

Arahman et al. [40] modified the morphology of pristine polyvinyl chloride (PVC) membranes for application in industrial separation. The modification of polyvinyl chloride (PVC) membrane was performed by combining the hydrophilic surfactant Pluronic F127 (PF127) in a polymer solution to improve the performance of the membrane. The preparation was carried out using the non-solvent induced phase transformation. Pluronic F127 was added as a modifying agent at different weight percentages to study the effects on the PVC based membranes. The results show that

PF127 is effectively proposed as a pore-forming agent. The mixing of the substance in various concentration shows an effect in the membrane performance. It was concluded that the blend tends to improve the characteristics and performance of the PVC membranes.

Alsalhy et al. [41] investigated the effect of embedding zinc oxide nanoparticles (ZnO-NP) in polyvinyl chloride (PVC) membranes. The membranes were prepared via phase transformation using DMAc as a solvent. The influence and antifouling properties of different ZnO-NPs loadings on the properties of the fabricated membranes were considered. The performance of the PVC films with ZnO-NPs in a membrane bioreactor (MBR) was efficiently explored. The attributes of PVC/ZnO films were investigated through various characterization methods. It was discovered that the ZnO nanoparticles affected the morphology of the films. The increase in the concentration of ZnO nanoparticles brought about a noteworthy increment in the mean pore size and pore size dispersion. The expansion of ZnO nanoparticles positively affected the hydrophilicity of the PVC/ZnO film by reducing the contact angle (CA) by 17.75°. Rejection of 73.5 %, antifouling behavior with improved pure water flux of 122.2 (L/m^2h), was noted respectively.

Behboudi et al. [42] investigated the blend of polyvinylchloride (PVC)/polycarbonate (PC) ultrafiltration membranes. The membrane preparation was executed via non-solvent induced phase separation using NMP as the solvent. The properties and parameters of the membranes were studied using different techniques and the performance was evaluated using BSA rejection. It was reported that PVC and PC are perfect matchings as it was affirmed by the investigations. The pore size distribution of films moved toward smaller pores as the concentration of PC in the dope was augmented. Likewise, hydrophilicity, elasticity, and fouling properties were improved. Although, increasing the PC content tends to mitigate the improvement. Pure water flux and BSA rejection were found to improve because of the influence of PC in the component of the membrane. It was discovered that the antifouling properties of films were enhanced with increased PC content. The outcome demonstrated that PVC/PC mix membranes were better in performance and fouling mitigation than the unblended PVC membranes.

Bhran et al. [43] experimented on the preparation of polyvinyl chloride (PVC) membranes blended with polyvinylpyrrolidone (PVP) as an additive. The membrane was fabricated via non-solvent induced phase separation using tetrahydrofuran (THF) and N-methyl pyrrolidone (NMP) as solvents. The fabricated films were examined by different characterization techniques. The morphology indicates that the membranes are smooth and have well-defined pores that are distributed to all parts of the membranes. This was ascribed to the role played by PVP in the membrane formation. The membranes' outcome indicated that salt rejection of 98 % with a high flux was achieved compared to the unblended one. This signifies that the prepared membranes can be utilized in the desalination process.

Fang et al. [44] considered the improvement of polyvinylchloride (PVC) membranes by blends with a zwitterionic polymer. The solubility of the additive in mutual organic solvents and the mixability amongst the blends. The copolymer that is, zwitterionic polymer and polyvinyl chloride are deliberated. The blends of PVC membrane with the copolymer was carried out by phase inversion technique using NMP as a solvent. The influence of the additives on the various parameters of the PVC based membranes was investigated. The result indicates that the antifouling effect of the membrane has been improved. It was revealed that this benefit is due to the strong hydration ability of the zwitterionic polymer which as a result improved the hydrophilicity and the antifouling characteristics of the PVC based membranes. Overall, the blend has shown an effect of the additive's utilization on the stability of PVC membranes.

Mishra et al. [45] studied the enhancement of hydrophilicity and antifouling properties of polyvinyl chloride (PVC) ultrafiltration membranes by blending with halloysites nanotubes (HNTs) for water treatment. The membranes were manufactured via phase inversion techniques using DMAc as solvent and polyvinylpyrrolidone (PVP) as pore former. The membranes were examined using different parameters by employing various techniques. Finely distributed HNTs were embedded in the membranes and the outcome revealed that hydrophilicity, pure water flux, and BSA rejection were all improved. The flux recovery ratio of 92% and a BSA rejection of 93% were observed at the optimum loading. The addition of HNTs as fillers has also enhanced the tensile strength of the films.

Rabiee et al. [46] evaluated polyvinyl chloride (PVC) blended with Titanium oxide (TiO_2) nanocomposite for the ultrafiltration application. The membranes were prepared via phase inversion techniques using N, N methyl pyrrolidone (NMP) as a solvent, and PEG as pore former. The effect of the additive was investigated at different loadings. BSA was used as a foulant and the antifouling behavior of the membranes was studied. The results showed that the addition of Titanium oxide has improved the hydrophilicity by reduction of the contact angle. Although, at high loading of TiO_2 agglomeration sets in due to the concentration of the nanocomposite thereby reducing the membrane flux. Generally, the outcome revealed that modification of the PVC membrane enhanced the rejection capacity and improved antifouling behavior than the unmodified one.

Roy et al. [47] utilized pristine polyvinyl chloride (PVC) in the membrane fabrication using polyethylene glycol (PEG) as an additive. The performance of PEG with different mole weights on the morphology of pristine PVC membrane prepared through non-solvent induced technique. N, N-dimethylacetamide (DMAc) was used as a solvent, while DI water was the nonsolvent. The outcome shows that PEG favors the demixing procedure. Various characterization was done and it was reported that the prepared membranes are asymmetric. The addition of PEG encourages the formation of microvoids on the PVC based membranes but at higher loading, the formation of finger-like structures with spongy morphology was obtained. The membrane showed thermal stability, and satisfactory mechanical strength applicable for ultrafiltration operation.

El-gendi et al. [20] the authors investigated polyvinyl chloride based membranes for desalination. The membranes were fabricated using the phase inversion technique for seawater reverse osmosis (SWRO) with the application of NMP as a solvent for the dope solution. The membrane performance was investigated using Red Seawater (El-Ein El-Sokhna-Egypt). The performance evaluation of the membrane was measured by investigating the effect of operating time on permeate volume, salt rejection, permeate flux, and permeability. They concluded that membrane performance results show that operating pressure increases permeate flux and rejection. Increasing operating pressure up to 40 bars leads to an increase in salt rejection percent to 99.99 % at low feed concentration 5120 ppm and 99.95 % for Red Seawater.

Yao et al. [48] fabricated an ultrafiltration membrane from polyvinyl chloride (PVC) with antifouling properties via phase inversion method using DMAc as a solvent. Polyvinyl chloride-co-acrylonitrile-co-sodium 4-styrene sulfonate (PVC-PAN-PSS), was used as a novel poly (vinyl chloride)- based co-polymer, through a non-dissolvable actuated stage partition (NIPS) technique, to improve the performance of the PVC membranes. The characterization of the membranes shows that the hydrophilicity and antifouling properties of the films were unmistakably appeared to increment with a growing level of poly (sodium 4-styrene-sulfonate) (PSS) in the copolymer; the membrane with 2 wt. % PSS showed the best antifouling properties, in particular, ~99% of transition recuperation proportion for humic substance was recorded. Moreover, the pore structures and antifouling properties of the PVC-PAN-PSS ultrafiltration membranes were kept up even after testing the chemical resistance of the membrane by 1000 ppm sodium hypochlorite solution for 168 h. The additive shows a beneficial outcome.

Zhao et al. [49] Studied the performance enhancement of polyvinyl chloride (PVC) modified by graphene oxide (GO) for ultrafiltration applications. Polyvinyl chloride (PVC) membrane was altered with graphene oxide (GO) through a stage reversal strategy to improve its hydrophilicity and mechanical properties. The films were prepared using phase inversion techniques employing DMAc as a solvent. The GO introduced a lot of hydrophilic moieties after the hydrophilization through the changed Hummers strategy. It was seen that with the expansion of the low division of GO powder, the GO/PVC half and half layers displayed a noteworthy upgrade in hydrophilicity, water permeation, and mechanical strength. The improved properties of the PVC/GO films are for the most part ascribed to the solid hydrophilicity of practical gatherings in a hurry surface, demonstrating that GO has a promising possibility for the alteration of PVC ultrafiltration layers in wastewater treatment.

Researchers have studied the virgin (pristine) version of PVC in membrane preparation and a beneficial conclusion was drawn. PVC has a film-forming ability and good chemical resistance and hence can be considered as a membrane material [50]. Other favorable characteristics of PVC as membrane material include its ability to dissolve in a various organic solvent like tetrahydrofuran (THF), N-methyl-pyrrolidone (NMP), N, N-dimethylacetamide (DMAc), and dimethylformamide (DMF) [43]. However, PVC has some drawbacks like hydrophobicity [51][52] which can be overcome by blending it with appropriate hydrophilic polymers as illustrated from the above reviews [29,54,55–62,63,67–70,]. Nevertheless, the utilization of abundant waste PVC for membrane fabrication has not been reported. The idea of using waste plastic as a precursor for the fabrication of membranes can result in curtailing the waste from our environment and serve as a sustainable means for low-cost utilization of fossil-based polymers as membrane fabrication material. Hence, it can benefit both the economy and the environment.

1.6.3 Membrane blended with sustainable polymers

Green initiatives for economic and environmental protection have been gathering momentum. This interest has led to regulations that tend to protect the environment for the future. Membrane fabrication is also tilted to that angle as researchers are now exploring the blending of sustainable polymers with the conventional polymers for membrane fabrication for improving its characteristics for better performance.

Manawi et al. [57] investigated the role of acacia exudate as a novel pore former and antifouling agent in polysulfone membranes. The membranes were prepared using the phase inversion method incorporating different weight percentages of acacia exudate into polysulfone. This in return improves the hydrophilicity, reduced fouling effect, and enhanced antibacterial properties. The antifouling properties were studied by BSA permeation. Whereas, the antibacterial parameters were checked using *E. coli* bacteria.

Over 90 % of rejection and increased flux were reported as an effect to the acacia exudate integration.

Elshaarawy et al. [58] the team reported the protocol for preparation of a poly-ionic liquid (PIL)-grafted chitosan Schiff base (PILCSB) and titanium oxide nanoparticles (TNPs) for application as an anti-biofouling nanocomposite in the fabrication of new polysulfone (PSU) ultrafiltration mixed matrix membranes (MMMs). The surface hydrophilicity of their MMMs was enhanced in comparison to the virgin PSU membrane (M0) as revealed from their wettability and contact angle outcomes. They found that the wettability result for the virgin and the modified are as follows 29.18 % and 93.48 % while the water contact angle results are given as 83.46° and 57.35 ° for M0 and MMM6, respectively. Hence, they conclude that incorporation of all additives into the mixed matrix membrane MMM6 has significantly improved membrane texture and permeation performance with and enhanced pure water flux by 2.5 times compared to the unincorporated PSU membrane (M0).

Morin-crini et al. [59] investigated the influence of chitosan and carboxymethyl cellulose on filtration performances of heavy metal removal, specifically nickel ion rejection or rather removal. Due to the vanishing of electrostatic interactions induced by a large amount of salt usually contained in effluents, ion rejection consequently drastically drops. However, it is hinted that a sufficient addition of polymer higher than 10^{-2} M of monomer unit can counterbalance this decrease and allow good metal removal, while permeation flux is reduced by increased viscosity. They inferred that performances are greatly affected by the pH of the filtered solution whose increase notably improves the metal rejection.

Kamrani, et al. [60] studied the chitosan-modified acrylic nanofiltration membrane for efficient removal of pharmaceutical compounds. Polyamide skin layer was synthesized by reacting 0.2 wt. % of ethylenediamine and 0.1 % w/v of trimesoyl chloride on acrylic membrane support via interfacial polymerization method. Afterward, amine groups in chitosan chains (0.1 wt. %) reacted with un-reacted acyl chloride to modify the membrane surface. Based on that they reported that surface roughness and contact angle decreased significantly. They concluded that the membrane had the best performance for diphenhydramine and mebeverine removal of 97 % and 98% respectively at pH=3 with the least fouling 22.6 L/ (m^2 h), FRR=94.21 % as reported in their work.

Padil et al. [61] reported the application of Gum karaya (GK), a natural polysaccharide. The biopolymer was added to polyvinyl alcohol (PVA) at diverse concentrations. Thereafter, the substrate was electrospun into PVA/GK nanofibers. Subsequently, Silver nanoparticles (Ag-NPs) were produced via chemical reduction of AgNO3 at various weight percentages. The membrane performance and other characteristics were studied via different standard characterizations' techniques. The antibacterial properties of the membranes were examined by Gram-negative Escherichia coli and Pseudomonas aeruginosa and Gram-positive Staphylococcus aureus. Their outcomes demonstrate that electrospun nanofiber membranes based on natural polymer (Gum Karaya), coupled with synthetic polymer have numerous possible applications, such as food packaging, medical uses, and water treatment.

Qian et al. [62] studied chitosan (CS) graphene oxide (GO) mixed matrix membranes (MMMs) to survey the improvement of water permeability for high-salinity water desalination and to understand the transport mechanism in the MMMs. The MMMs have rougher and more hydrophilic surface, dense structure, and better mechanical stability owing to the good chemical compatibility of GO with the CS matrix. The obvious activation energy results indicate the advantage of the MMMs in desalinating high-salinity water. They reported that the enhanced permeate flux of 30.0 kg/ m^2·h was obtained in desalinating 5 wt. % aqueous NaCl solution with one weight percent GO content and 99.99 % of salt rejection was achieved. The solubility and diffusivity of H_2O and NaCl in the MMMs demonstrate a trade-off effect on the water permeability and water/salt selectivity with increasing in GO content.

Lie et al. [64] investigated the preparation and evaluation of PET mesh cellulose acetate enhanced forward osmosis membranes. Polyethylene terephthalate mesh (PET) enhanced cellulose acetate membranes were fabricated via a phase inversion process. The water permeability and reverse salt flux were noted in forward osmosis (FO) mode. the determination of the most favorable membrane fabrication conditions. The best FO membrane shows a typical asymmetric pack in structure with a mean thickness of about 148.2 μm. The performance of the best FO membrane was tested using 0.2 mol/L NaCl as the feed solution and 1.5 mol/L glucose as the draw solution. The membrane shows a water flux of 3.47 L/ (m^2 h) and salt rejection of 95.48 % in FO mode. They inferred that the PET-enhanced CA membrane showed strong mechanical strength with a tensile strength of 38.67 N. The membrane showed both high water flux and salt rejection.

Kumar et al. [65] in this work, xanthan gum (XA) was utilized as a sustainable polymer additive. The properties of polyethersulfone (PES) membrane was modified to augment the rejection of humic acid (HA). The membranes were produced through the phase inversion method. Various loadings of XA were considered to establish the effect on the performance of the membranes. The membranes are assessed for their hydrophilicity, percent water content (EWC), porosity, and FTIR. The addition of Xanthan gum in the

PES membrane guarantees that increased hydrophilicity, improved water flux, and enhanced humic acid rejection.

Carneiro et al. [67] investigated the use of biopolymeric membranes prepared with chitosan (CS), alginate (AG), and combination of the two (CS/AG) for the adsorption of glyphosate present in water samples. The membranes were characterized based on membrane solubility, swelling, mechanical, chemical, and structural properties. The results of kinetics experiments showed that adsorption equilibrium was reached within 4 h and that the CS membrane gives the best adsorption of glyphosate 10.88 mg /g of the membrane, followed by the CS/AG membrane which has 8.70 mg of glyphosate gram of membrane. They concluded that the glyphosate herbicide can be absorbed by chitosan membranes and that biopolymer membranes can offer an adaptable means eliminating unwanted compounds from water.

Sabri et al. [68] conveyed the study of polysulfone (PS) membranes blended with a diverse concentration of arabic gum (AG) for antibacterial activity. The membrane was manufactured via the phase inversion technique. The parameters of the produced films were established using various analytical means. They inferred that adding AG to solutions shows a decrease in a bacterial attachment in the field emission scanning electron microscopy (FESEM). The inhibition of bacterial growth was also reported. Probable machinery for the deterrence of bacterial establishment was discussed. Suggestively, they conclude that the addition of arabic gum improved the hydrophilicity with robust biofouling inhibition striking for the water treatment process.

Hernández-Aguirre et al. [66] studied the modification of polypropylene (PP) membranes using three different biopolymers, chitosan, potato starch, and cellulose. The polypropylene membrane was cut into square-shaped pieces (5×5cm) and impregnated with a corresponding biopolymer solution. The UV energy induced graft copolymerization reaction among polypropylene membrane, acrylic acid, benzophenone (as a photoinitiator), and the biopolymer (chitosan, potato starch, and cellulose) was conducted. The change of surface wettability was measured by the contact angle. The grafting reaction depends on the natural polymer, reaction time, and concentration. To prove the potential application of the modified membranes, a preliminary study of the sorption of metal ion was carried out. They concluded that the modified membranes could be used for the metal ions removal, due to the affinity of the metal ions with the polar groups present in the modified membranes.

The above literature established that blending improves the properties of membranes. To hydrophilize the PVC based membrane, blending the base polymer with hydrophilic biopolymer is recommended to overcome the hydrophobic nature of the PVC and in the same vein hydrophilizing and improving other membrane parameters for beneficial applications.

1.7 Research gaps

Owing to the rising environmental concerns, poised by waste plastic coupled with the use of fossil-based polymers in membrane fabrication. Consequently, some authors have published reference works to shift the membrane production towards more environmentally friendly processes. Therefore, researchers are now exploring the sustainability of membrane fabrication. Especially, polymeric membrane through the use of sustainable polymers and in some instances recycling of waste plastic. From the literature review, it may be envisaged that researchers have developed an interest in the utilization of waste plastic as a precursor for membrane fabrication. It’s also clear that from Table 1.5 that most researchers utilized PET as a precursor but the use of waste plastic such as polyvinylchloride (PVC) has not been captured. On the other hand, researchers have studied the virgin (pristine) version of PVC in membrane preparation and a beneficial conclusion was drawn. Nevertheless, the utilization of abundant waste PVC for membrane fabrication has not been reported. Similarly, the role or effect of different solvents on the membranes fabricated from waste plastic was not considered. Likewise, several authors have utilized biopolymers and other polymeric additives as membrane modifiers. A growing number of sustainable polymers such as chitosan, quaternary ammonium compounds, cellulose acetate, and others have also been used in the preparation of conventional polymeric membrane but the incorporation of sustainable biopolymers in the preparation of membranes from waste plastic is scant. Therefore, in the present work, waste PVC is considered as a precursor for membrane preparation and also the effect of different solvents on the characteristics of waste PVC derived membranes was investigated. The role of additives, like sustainable polymers (gum arabic) on the morphology and characteristics of waste plastic derived membrane was considered. The idea of using waste plastic as a precursor for the fabrication of membranes can result in curtailing waste plastic from our environment and serve as a sustainable means for low-cost utilization of fossil-based polymers as membrane fabrication material. Hence, it can benefit both the economy and the environment.

1.8 Scope of the work

The scope of the work can be enumerated as follows: (i) membrane fabrication from waste plastic (PVC) and its characterizations, (ii) modifications of the fabricated membranes using sustainable polymers, and (iii) performance evaluation of the fabricated membranes in an ultrafiltration application.

It is worthy to note that, utilization of waste plastic for membrane fabrications and their viability has been reported in refereed journals but waste plastic such as PVC has not been captured. Therefore, it will be interesting to look into the feasibility of using such waste as membrane material considering the need for economic and environmental sustainability as no cost will be expended on the waste plastic.

Sustainability is a watchword in this 21st century, thus blending the waste plastics with sustainable polymers would be beneficial. In the past few decades, the potential for using biopolymers has been realized. Nevertheless, such studies are not reported in the fabrication of modified membranes from waste plastic with these organic materials. Hence, this area needs to be explored for overall membrane performance fabricated from waste plastic using sustainable polymers for more beneficial attributes.

1.9 Aim and Objectives

The main aim of this work is to utilize the available waste plastic (PVC) as a precursor for membrane fabrication with surface modification by using sustainable polymers for effective utilization. To achieve this goal, objectives have been structured and stated as follows:

- ❖ Fabrication and characterization of membrane from waste plastic: Efficacy of using waste polyvinyl chloride (PVC) as a precursor for membrane fabrication blended with cellulose acetate.
- ❖ An investigation on the effects of additives (PEG, PVP) and solvents on characterization, and performance of waste PVC-based membrane in water filtration.
- ❖ Modification of the waste plastic membrane using sustainable polymer: An insight into the effects of blending waste PVC with biopolymer (gum arabic) for the removal of natural organic matters from water.

1.10 Organization of thesis

The thesis is organized into chapters that can stand alone. It is a signpost that detailed how the thesis was structured. The thesis is arranged into the following six (6) chapters with brief outlines**. Chapter one** is the opening chapter that brings forward the contextual of the study, highlights on plastic, effects of waste plastic, and the waste plastic management. Fundamentals of polymeric membranes and preparation techniques were also captured. The chapter also presents the collection of background literature, methods of membrane modifications, documentation of relevant pieces of literature, and formulated objectives. **Chapter two**, materials and methods. The description of the major experimentation, materials, and preparation of the membrane was elaborated. It also gives information and procedures for the characterization involved. **Chapter three** presents the first objective. In it, the efficacy of the utilization of waste polyvinyl chloride (PVC) as a membrane precursor was carried out. Waste PVC was blended with cellulose acetate to overcome the hydrophobic nature of the base material in membrane preparation and the outcome was discussed. In **Chapter four,** the application of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and their combination in waste PVC based membranes and subsequent paraphernalia on the morphology, performance, thermal and mechanical properties were studied. **Chapter five,** gave an insight into the effects of blending and modification of the waste PVC membrane using sustainable polymer (gum arabic) for the removal of natural organic matter from water. **Chapter six** is the last chapter in which the findings of the work were summarized, conclusions drawn, and suggestions for further research were recommended.

Chapter 2

Materials and Methods

Chapter 2

Materials and Methods

This chapter presents the description of the major experimentation, materials, and method for the preparation of the membrane. It also gives information and procedures for the characterization involved. The chapter highlights the main material utilized and their sources. Similarly, it presents the details and procedure for the fabrication and characterization of membranes. Like Field emission scanning electron microscopy (FESEM), Fourier transforms infrared (FTIR), thermogravimetric analysis (TGA), equilibrium water content (EWC), contact angle (CA), porosity, pore size, pure water flux (PWF), compaction factor (C.F) and subsequently rejections.

2.1 Materials

Waste plastic was the base material used for the fabrication of the membranes. Specifically, waste polyvinylchloride (PVC). PVC is a linear polymer with high resistance to chemicals. The waste PVC was sourced from the campus of IIT Guwahati. Cellulose acetate (CA) and gum arabic (GA) were supplied by Sigma Aldrich Chemicals. N, N-dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), and Dimethyl acetamide (DMAc) which were used as the solvents were supplied by Sigma Aldrich Chemicals Co. with reagent grade purity. Details of the materials used for the preparation of the membrane are itemized in Table 2.1. A pore-forming agent like polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) was used. Deionized water from Milli-Q filtration source was used both as the non-solvent and in other activities where water was needed for the experiments. BSA with a molecular weight 68 kDa was considered as a medium for rejection studies and was purchased from Sigma Aldrich Chemicals. Humic acid (HA) was obtained from Otto Chemie Private Limited, India.

Table 2.1: List of the main constituents used in this work

S/ No.	Materials	Brand/supplier
1	Cellulose acetate	Sigma Aldrich Chemicals
2	N, N-dimethyl formamide	Sigma Aldrich Chemicals
3	Dichloromethane	Sigma Aldrich Chemicals
4	N-methyl pyrrolidone	Sigma Aldrich Chemicals
5	Dimethyl acetamide	SRL Chemicals, India
6	Polyethylene glycol (PEG)	Sisco Laboratories, India
7	Polyvinylpyrrolidone (PVP)	SRL Chemicals, India
8	Bovine serum albumin (BSA)	Sigma Aldrich Chemicals
9	Humic acid (HA)	Otto Chemie, India.
10	Gum Arabic	Sigma Aldrich Chemicals
11	Deionized water (DI water)	Millipore, France

2.2 Membrane fabrication

The preparation of the membranes was done based on the phase inversion technique. The different composition was used for the preparation of various membranes. Waste PVC was washed, dried, and mixed with a solvent. The mixing process was done with the aid of a magnetic bit stirrer at 500 rpm for 24 h at 60 ± 5 ºC to attain homogeneity in the dope solution. Fractions of additives were added based on the percentage weight of waste plastic alongside the solvent for complete miscibility. The solution was degassed and casted using a doctor's knife on a glass plate. It was then transferred to the water bath for solvent-non-solvent de-mixing and subsequent phase transformation. Lastly, investigations for its morphological and performance characterizations were carried out. The schematic representation of the phase inversion technique is presented in Figure 2.1 while the stepwise procedure in the block diagram is given in Figure 2.2 from a dope solution to the last point of membrane fabrication and characterization, respectively.

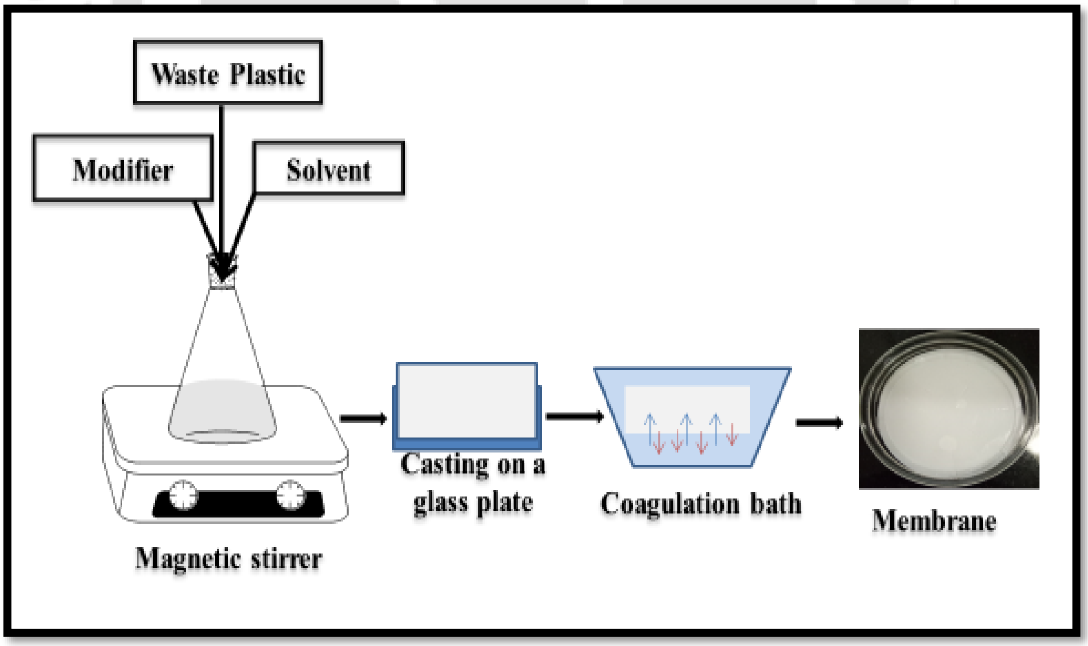

Figure 2.1: Schematic representation of the phase inversion method

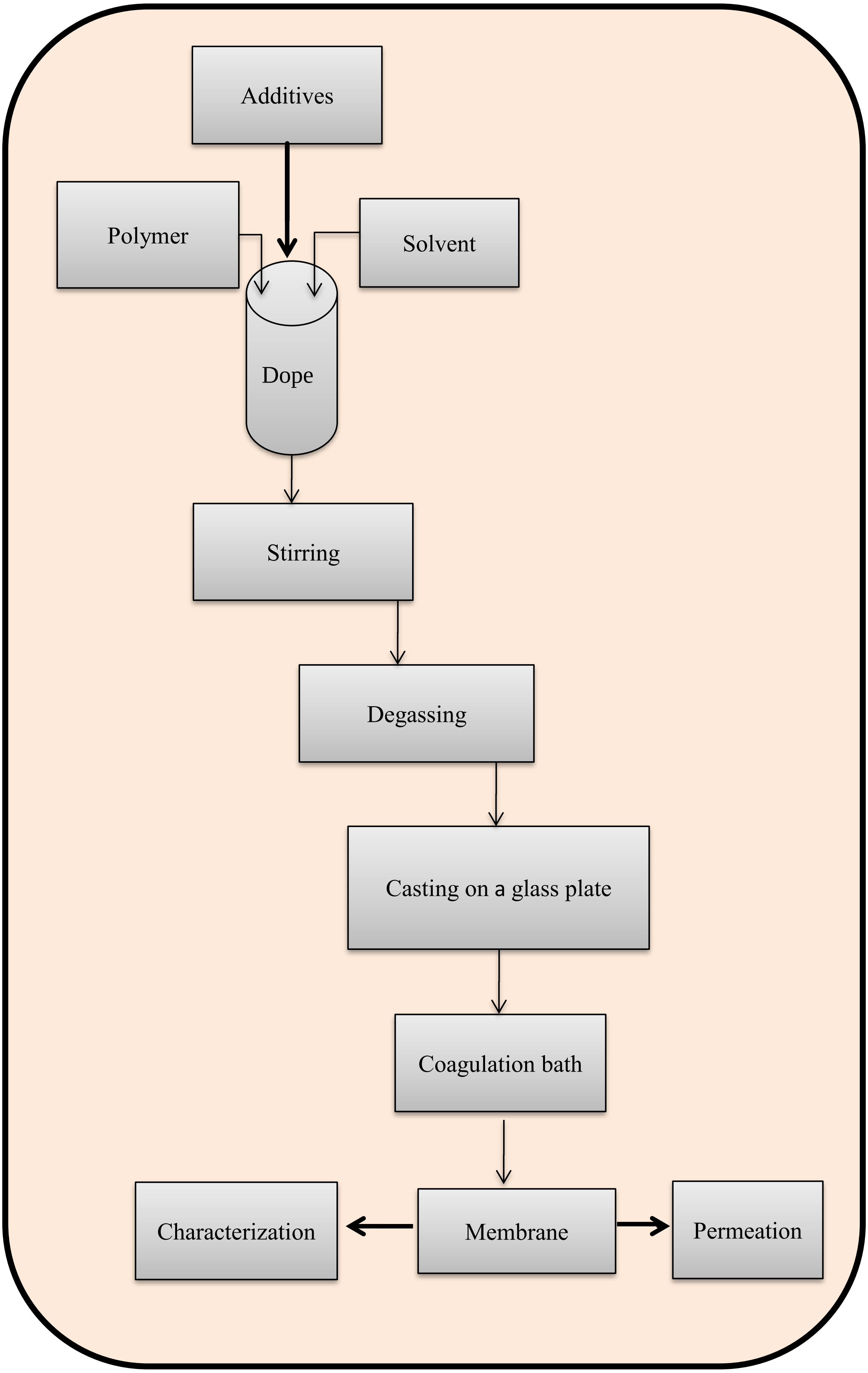

Figure 2.2: Block diagram of the process

2.3 Membrane characterization

The prepared membranes were characterized using different characterization techniques to investigate the features and the properties of the fabricated membranes ranging from surface morphology, performance evaluation, thermal analysis, to mechanical properties. The major instrument/equipment used in the course of the experiment were tabulated in Table 2.2 along with the parameters measured, model, and the specification of the instrument.

Table 2.2: List of major equipment used in this work

Equipment/Instrument	Parameters measured	Model /Specification
Amicon filtration cell	Filtration/ Flux	Amicon stirred cell, Millipore, Merck India
FESEM	Morphology	FESEM SIGMA 300, Zeiss USA
Goniometer	Contact angle	Kruss® DSA 25, Germany
TGA	Thermal analysis	Perkin Elmer TGA-4000, USA
FTIR-ATR	Functional group	Perkin Elmer, Frontier USA
UV spectrophotometer	Concentration	Perkin-Elmer, Lambda 25
UTM	Mechanical studies	Zwick Roell Z005TN

Magnetic stirrer	Mixing	Thermo Fisher scientific, India
Weighing balance	weight	Mettler Toledo, India
Ultrasonicator bath	Degassing	Digital heated ultrasonic, Indiamart
Hot air oven	Drying	Digital hot air oven, Indiamart

2.3.1 **Surface morphology**

To determine the image of the membrane structure, and topography field emission scanning electron microscopy (FESEM) analysis is required [69]. Therefore, the surface morphologies of all membranes fabricated were investigated using field emission scanning electron microscopy (FESEM) (Zeiss USA and model code FESEM SIGMA 300). Preceding the scanning, the membranes were dried in a hot air oven (40 °C) for 24 h and then were fixed to the stub with double-faced carbon tape and glazed with gold [26]. This technique can give us the information about the top layer view as well as the cross-sectional visual information. It is also useful in providing the information regarding pore size of the membranes with the aid of image J software [70].

2.3.2 **Hydrophilicity**

The contact angle is an effective indicator of membrane surface hydrophilicity and wettability. The contact angles were measured using a contact angle goniometer (Kruss® DSA 25) as reported elsewhere [71] by the sessile drop method. The membranes were kept in a hot air oven (40 °C) for an hour. Each sample was sliced, attached to a glass slide, and arranged on the instrument. Thereafter, 2.0 µl of Milli-Q water was dropped using the syringe on the surface of the membrane and the static water angle was recorded. To eliminate experimental error, contact angles were measured at different points of each sample and the average was reported.

2.3.3 Equilibrium water content (EWC)

Equilibrium water content is directly related to the porosity of the membrane, it also indicates the hydrophilicity or hydrophobicity of the membrane. The EWC is also sometimes been referred to as percentage water content and normally calculated using the wet and dry weight basis of the given membrane by following the Equation (2.1) given below.

$$Watercontent(\%) = \frac{Ww - Wd}{Ww} \times 100 \tag{2.1}$$

Where; W_w and W_d are wet and dry weight respectively.

2.3.4 Porosity and pore size of membranes

The sponginess of membrane is another factor that is thoroughly correlated to membrane flux and performance [69]. The porosity was estimated by using Equation (2.2) which is related to equilibrium water content (EWC) of the membranes. The pore size dissemination of the various membranes prepared was also determined. The FESEM images were calibrated based on the scale of the image. The software recognized each pore, measured the pore diameter, and then the average pore size was obtained from the pore size distribution. The average pore size of the membranes can be computed based on the porosity values and water filtration. Generally, the pore radius (r_m) is considered as an approximation of the true pore size of membranes [72]. The average pore radius can be estimated by using the Guerout–Elford–Ferry equation [73] as expressed in Equation (2.3).

$$\text{Porosity } \varepsilon\ (\%) = \frac{Ww - Wd}{\rho A \delta} \times 100 \tag{2.2}$$

Where W_w is the wet weight and W_d is the dry weight of membranes, A is the area of the membrane, ρ is the water density and δ is the thickness of the membrane.

$$r_m = \sqrt{\frac{(2.9 \ - 1.75\varepsilon)8\mu\delta Q}{\varepsilon A \Delta P}} \tag{2.3}$$

Where μ is the water viscosity (8.9 × 10−4) in Pa·s, Q is water flow and ΔP is the operating pressure.

2.3.5 Membrane permeation study

Membrane permeability shows how porous the membrane is, while pure water flux indicates the quantity of water that passes through the membrane of a given area at a certain pressure for a certain time. A filtration cell (Amicon Millipore Cell) was used to evaluate the pure water flux. Before each measurement, the membranes were compacted or compressed to get a stable filtration. The membrane compaction factor (CF) was determined based on the initial and final stable flux ratio [54] while, flux was estimated based on Equation (2.4). In this work, an Amicon Millipore cell (filtration cell) with a volume of 300 ml was considered to evaluate the flux (PWF) and compaction factor (CF). The membranes were cut using scissors which fitted into the filtration unit cell. The permeation area was estimated to be 38×10^{-4} m^2. The cell was filled with deionized water from a Milli-Q tank and nitrogen gas was used to provide the pressure needed. The permeation experiment set up is shown in Figure 2.3. The pure water flux of the membrane was calculated using equation (2.4).

$$J_w = \frac{Q}{(A \times T)} \tag{2.4}$$

Where, Jw is the flux (L/m^{2}h), Q is the quantity of permeation (L), A is the area of membrane (m^2), T is the duration taken for filtration in hour (h).

Figure 2.3: Membrane permeation set up

2.3.6 **Retention**

Retention or rejection is a parameter used to evaluate the quality and selectivity of the membrane among other parameters. It tends to indicate the amount of solute or unwanted component of the feed that was not allowed to pass through the membrane to the permeate side. This is a significant parameter that needs to be known in membrane characterization. Rejections of typical water-soluble substances were carried out to determine the retention of the various membranes casted using the observed retention equation by measuring the feed and the permeate concentrations. The concentrations were determined spectrophotometrically by using a UV VIS spectrophotometer and the percentage rejections were computed using Equation (2.5) accordingly.

$$R(\%) = \left(1 - \frac{Cp}{Cf}\right) \times 100 \qquad (2.5)$$

Where R is the retention, C_p and C_f are the bottom (permeate) and the top (feed) concentrations, respectively.

2.3.7 Studies on flux recovery ratios

The fouling behavior of the membranes was estimated using a model foulant. The same dead-end filtration set up that was used for the PWF was used in determining the fouling effects. In the first run, DI water flux (J_{w1}) was measured by permeating DI water in the membranes. Thereafter, the aqueous solution containing the foulant was run and the resulting flux (J_F) was noted. Finally, the fouled membranes were washed with DI water and another run was conducted to measure the DI water flux (J_{w2}) of the membranes after hydraulic cleaning. Hence, the fouling behavior of the membranes was analyzed using the following equations. These equations help determine the fouling ratios of membranes as stated elsewhere [69][42].

Total fouling ratio,

$$TFR = \frac{J_{w1} - J_F}{J_{w1}} \qquad (2.6)$$

Reversible fouling ratio, $$RFR = \frac{J_{w2} - J_F}{J_{w1}} \tag{2.7}$$

Irreversible fouling ratio, $$IFR = \frac{J_{w1} - J_{w2}}{J_{w1}} \tag{2.8}$$

Flux recovery ratio, $$FRR = \frac{J_{w2}}{J_{w1}} \tag{2.9}$$

Where; TFR is a total fouling ratio, RFR is a reversible fouling ratio, IFR is an irreversible fouling ratio, and FRR is a flux recovery ratio, respectively.

2.3.8 **ATR-FTIR spectroscopy**

FTIR spectroscopy is a technique used to determine the functional groups available within a given sample. Hence, the membranes fabricated were also investigated using Fourier transform infrared (FTIR) with the help of ATR (attenuated total reflectance) mode. Before the scanning, samples were oven-dried at 50 ºC for an hour to drive away residual moisture; thereafter, they were examined in the wavenumber series of 3500 – 700 cm^{-1} via transmittance mode. The samples of the membranes were clamped to the surface of the ATR within the FTIR for the functional group analysis.

2.3.9 **Thermo-gravimetric analysis (TGA)**

Thermo-gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature at a constant heating rate. The thermal stability of the membranes fabricated was evaluated using TGA, at a heating rate of 10^{o}C/min from 30 - 600 ^{o}C using nitrogen gas for creating the inert environment. A predetermined weight (10 mg) was used in the crucible for all the samples for the thermal analysis.

2.3.10 **Mechanical test**

The mechanical test can be used to predict the durability and pressure capability of membranes. An electromechanical universal testing machine (UTM) with a motorized screw mechanism model (Zwick Roell Z005TN) was used. The membranes were cut to a predetermined dimension (5 mm x 100 mm) with a gauge range (50 mm). The test was done by applying a 1KN at a rate of 2 mm per minute.

Chapter 3

Utilization of Waste Polyvinyl Chloride Blended with Cellulose Acetate for UF Membrane Fabrication and its Application

Chapter 3

Utilization of Waste Polyvinyl Chloride (PVC) Blended with Cellulose Acetate for UF Membrane Fabrication and its Application

In this chapter, the efficacy of waste polyvinyl chloride (PVC) as a membrane precursor was carried out. Waste PVC was blended with cellulose acetate to overcome the hydrophobic nature of the waste PVC in a membrane preparation. The membranes were fabricated via non-solvent induced phase transformation using N, N-Dimethyl formamide (DMF) as a solvent. The membranes were characterized using various characterization techniques as enumerated in the materials and methods sections. The membrane performance was evaluated by pure water flux (PWF) and Bovine serum albumin (BSA) rejection. The outcome shows that waste PVC can be utilized to fabricate an ultrafiltration membrane.

3.1 Background

The manufacturing of plastic products began to thrive during the 1940s and 1950s on an industrial scale, and since then it has kept on flourishing [74]. The production has been predicted to reach over 400 million tons by 2020 [7]. Plastic is the most utilized material these days and has substituted several conventional materials, with its applications ranging from packaging, constructions to industrial needs [4]. However, this has increased the amount of municipal waste. Plastic has a short useful life compared to centuries it takes to degrade [10]. Plastic like polyethylene terephthalate (PET), polyvinylchloride (PVC) and polypropylene (PP) are basically non-compostable [7][19] and their disposal has lots of associated challenges which have serious environmental effects. India alone generates greater than 26000 tons of waste plastic every 24 hours [1]. Several nations and international societies have called upon modifications in the conventional ways of managing plastic waste to establish environmental and economic sustainability [75].

There are different means of waste plastic management. One of them is incineration, which has a detrimental effect on releasing harmful gases to the atmosphere. Burying the waste is considered as another way of waste management, but this is also unfriendly, as it can lead to the formation of toxic gases, a hindrance to the growth of agricultural products by interfering with their transpiration process as well as causing surface and groundwater pollution. Another way of managing waste plastic is via the route of reuse/recycling, which is considered as the best tactic in controlling the need to manufacture more plastics along with other fossil-based materials [4,7,8]. Energy generation [10], mechanical recycling [11] and membrane manufacturing [15] are among the other recycling paths.

Fabrication of membranes as separation medium has gained recognition over the last three decades due to its many attractive features such as ease of fabrication, low energy requirement, easy scale-up, and flexibility [12]. Various inorganic and organic materials have been used for membrane preparation. Plastics have also been used for the fabrication of membranes because of ease in processability, low price, and film-forming ability [76][77]. Garcia-Ivars et al. [4] used post-consumer polystyrene for membranes preparations, Altalhi et al. [36] studied the use of plastic bags for preparing carbon nanotube membranes, and many other researchers have reported the application of recycled PET for membranes fabrication [32–34,64,78]. However, the utilization of waste PVC for membrane preparation has not yet been explored.

PVC has a film-forming ability and good chemical resistance and hence can be considered as a membrane material [50]. Other favorable characteristics of PVC as membrane material include its ability to dissolve in a various organic solvent like tetrahydrofuran (THF), N-methyl-pyrrolidone (NMP), N, N-dimethylacetamide (DMAc), and dimethylformamide (DMF) [43]. However, PVC has some drawbacks like hydrophobicity [51][52] which can be overcome by blending it with appropriate hydrophilic polymers in which hydrophilicity of various membrane materials was improved [53–56]. Several researchers have studied the use of neat PVC for membrane fabrication and beneficial conclusions have been drawn. Bhran et al., [43] investigated PVC based membranes for water treatment purposes. Haibo et al., [52] studied the preparations of blended PVC/PVC-g-PEGMA membranes for ultrafiltration. Ghazanfari et al., [51] reported the fabrications of PVC based membranes for wastewater applications. El-gendi et al., [20] considered the utilization of PVC membranes for desalination. Demirel and co-authors [79] investigated the performance of PVC mixed matrix composite membranes. Zhang et al., [80] evaluated the performance of PVC ultrafiltration membranes for wastewater treatment. However, the utilization of abundant waste PVC for membrane fabrication has not been reported. The idea of using waste plastic or recycled plastic as a precursor for the fabrication of membranes can result in curtailing waste plastic from our environment and serve as a sustainable means for low-cost utilization of fossil-based polymers as membrane fabrication material. Hence, it can benefit both the economy and the environment.

Therefore, in this study, the efficacy of waste polyvinyl chloride as a precursor for membrane fabrication was investigated. Waste PVC was blended with cellulose acetate (CA) to improve the hydrophilicity of the prepared membranes. The properties of the novel membrane were examined concerning the influence of various compositions of CA on the waste PVC membrane. Different characteristics of the membranes were studied and explained like surface morphology with the help of field emission scanning electron microscopy (FESEM), Fourier transforms infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR), contact angle, porosity, pore size distribution, equilibrium water content, thermal nature by thermo-gravimetric analysis (TGA) and performance by evaluation of pure water flux (PWF), bovine serum albumin (BSA) rejection, pore size, and compaction factor. The present work will help curtail waste plastic in the environment as well as the application of the membranes derived from waste PVC in the filtration process.

3.2 Experimental

Membranes were prepared using a blend of waste PVC with cellulose acetate (CA) via a non-solvent induced phase inversion method as depicted in the scheme (Figure 3.1). The detail of the phase inversion process and the characterizations were given in the previous chapter under section 2.

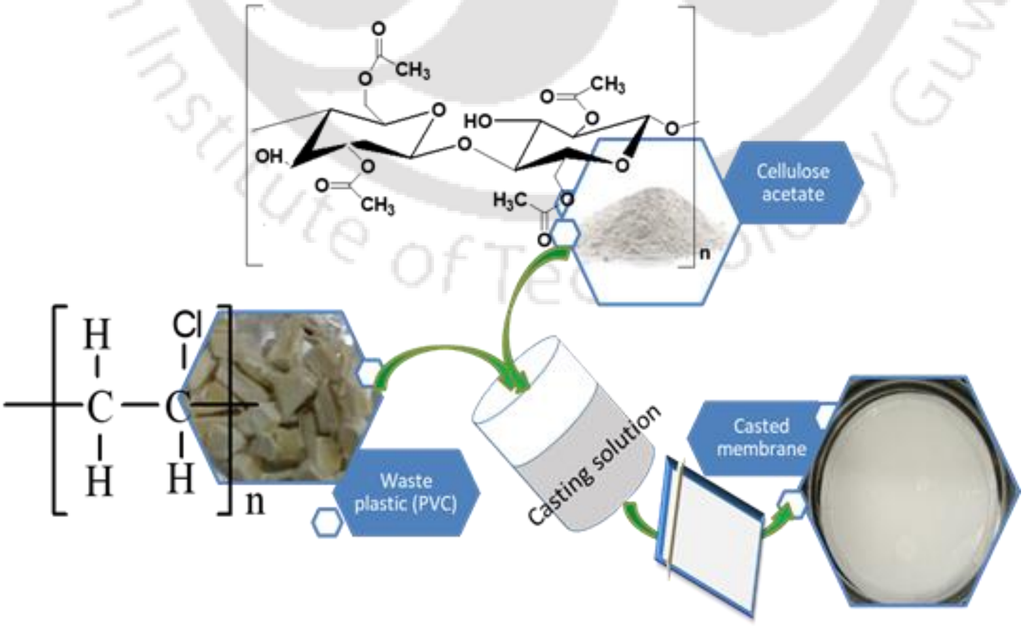

Figure 3.1: Schematic representation of the process

3.2.1 Materials

Waste plastic, specifically waste Polyvinylchloride (PVC) was used as the base polymer. Cellulose acetate was supplied by Sigma Aldrich chemicals. PVC is a linear polymer with high resistance to chemicals while cellulose acetate is sustainable and biodegradable with acetyl and hydroxyl groups (shown in Figure 3.2). N, N-Dimethyl formamide (DMF), which was used as a solvent was supplied by Sigma Aldrich chemicals. Deionized (DI) water from a Milli-Q filtration source was used both as non-solvent and other activities required water throughout the experiment. Bovine serum albumin (BSA) with a molecular weight of 68 kDa was used as a medium for rejection studies.

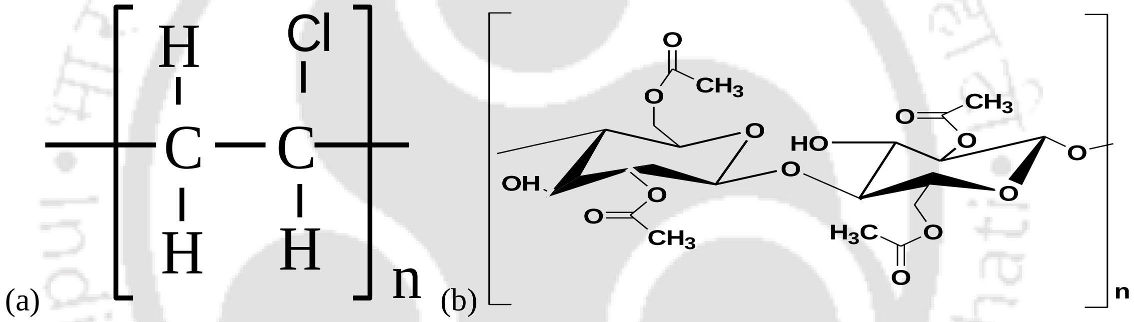

Figure 3.2: Structure of (a) Polyvinyl chloride and (b) Cellulose acetate

3.2.2 Membrane preparation

Four different membranes were prepared using a non-solvent induced phase inversion method. The different composition used for various membranes is shown in Table 3.1. The waste plastic (PVC) was chopped into smaller sizes with a cutter for easy dissolution. It was then washed, dried, and mixed with N, N-Dimethyl formamide (DMF). The mixing process was done with the aid of a magnetic bit stirrer to attain homogeneity in the dope solution. The detail of the phase inversion process was given in the previous chapter under section 2.3.

Table 3.1: Membranes composition

Membrane	Code	PVC (wt.%)	CA (wt.%)	Solvent (wt.%)
PVC	M0	20	0	80
PVC/CA 1%	M1	20	1	79
PVC/CA 3%	M3	20	3	77
PVC/CA 5%	M5	20	5	75

3.2.3 Membrane characterization and permeation studies

The membranes were characterized using field emission scanning electron microscopy (FESEM), attenuated total reflectance in conjunction with Fourier transform infrared spectroscopy (FTIR-ATR), thermo-gravimetric analysis (TGA), equilibrium water content (EWC), porosity and contact angle measurement. The membrane performance was evaluated by pure water flux (PWF), Bovine serum albumin (BSA) rejection and flux recovery ratios. Details of the membrane's characterization procedures were presented in the previous chapter (materials and methods) captured under section 2.4.

3.3 Results and discussion

3.3.1 Surface microscopic studies

The surface structures of the fabricated membranes for various cellulose acetate (CA) doses are displayed in Figure 3.3. The images show that the waste-derived PVC membrane (Figure 3.3 a) has a dense top layer, this membrane was casted from the waste PVC without the addition of any CA. Subsequently, Figures 3.3 (b-d) show porous surface structures based on waste PVC/CA membranes M1, M3, and M5 respectively.

The FESEM images concord with the average pore size estimated from the ImageJ software. The analysis of the images shows that the number of pores and the average pore size increase as the percentage of the CA increases. Hence, it could be stated that the pore density and the pore size increased by an increase of the CA content. Besides, from the pore size distribution curves (Figure 3.4), it can be seen that the pore size of the membranes is within the range of 1 – 100 nm which falls to the category of ultrafiltration. It can also be observed that the pore size distribution shifted towards the lager pore size this agrees with the outcome of an improved flux with reduced rejection as discussed in subsection 3.4.7. The asymmetric porous nature of the surface increased from 13 to 58 % as the CA weight percent varied from 0 wt. % to 5 wt. %. This may be attributed to the water-tolerant nature of CA whereby the non-solvent (water) penetrated the casted polymeric film displacing the solvents and creating more pores. This phenomenon can best be described by the thermodynamic mechanism of the system. Similar microscopic features have been reported elsewhere for a pure PVC [48].

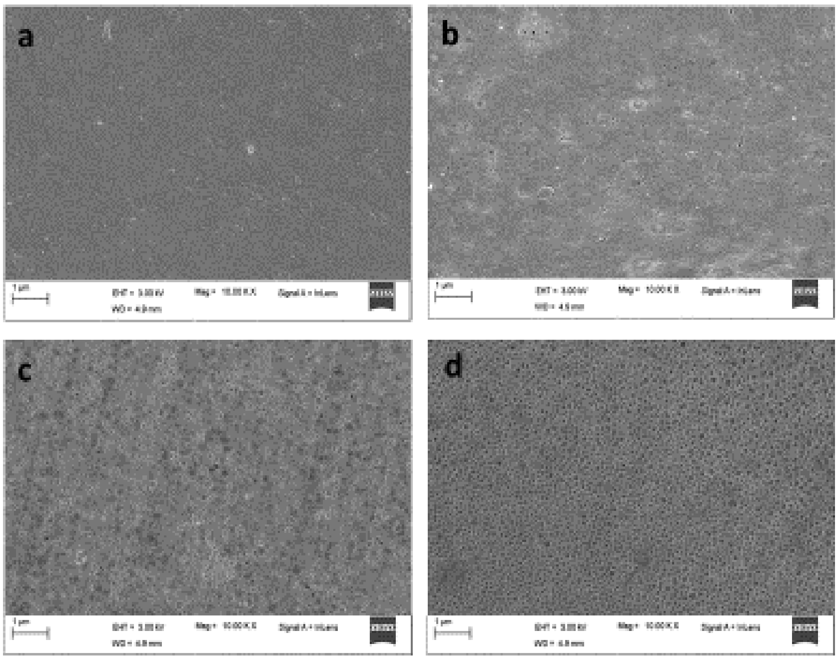

Figure 3.3: FESEM images of PVC/CA membranes. (a) M0 (b) M1 (c) M3, and (d)M5

3.3.2 Membrane porosity and pore size

The membrane porosity and pore size are some of the important parameters in estimating the membranes category. Hence, the membrane porosity as calculated using Equation (2.2) is reported in Table 3.2. The result shows that the porosity of the membranes; M0, M1, M3, and M5, are 13%, 23%, 55%, and 58%, respectively. The variations in the CA content improved the porosity from 13 to 58%. The porosity was low initially due to the hydrophobic nature of PVC. The blends had more pores which could be ascertained from the pore size distribution curves (Figure 3.4), and that happened because the interaction between the non-solvent (water) and the casted membrane was friendly. In the case of the M0 membrane, the pore size distribution was narrow in the range of 1-20 nm. While for the membranes M1, M3, and M5 the pore size distributions were in the range of an ultrafiltration membrane (1-100 nm), which was attributed to the water-loving nature of CA due to which solvent-non-solvent de-mixing took place creating pores.

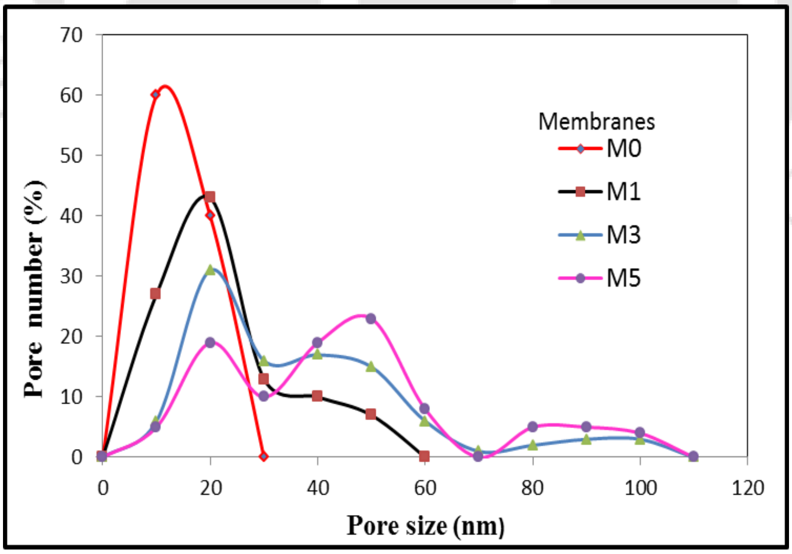

Figure 3.4: Pore size distribution curves of various membranes

3.3.3 **Equilibrium water content (EWC)**

Water content is a factor that measures the hydration of the membrane and it was calculated from Equation (2.1). The membrane hydration also determines the affinity of water which can help in reducing fouling [56]. The equilibrium water content was calculated based on the gravimetric method by using Equation (2.1) and the result is presented in Table 3.2. It may be seen from the table that the percent water content was enhanced from 62% to 76% as the fraction of CA was enriched in the dope (from 0 wt. % to 5 wt. %) which agrees with the outcome of the surface porosity. Water uptake capacity has a very close relation with porosity as the pores in the membranes can serve as an abode for the water molecules. Similar trends were reported elsewhere [81]. This outcome agreed to the results obtained in contact angle measurement confirming the blending of CA in the membrane, it becomes more hydrated than that of pure PVC. This is due to the hydrophilic characteristics of the CA.

Table 3.2: Various characteristic parameters of the prepared membranes

Membrane	Code	T_{onset} (^oC)	T_{max} (^oC)	Water content (%)	Porosity (%)	Average pore diameter (nm)
PVC	M0	230	345	62.0	13	17
PVC/CA 1%	M1	280	360	66.9	23	23
PVC/CA 3%	M3	282	375	70.6	55	41
PVC/CA 5%	M5	285	380	76.0	58	50

3.3.4 **Hydrophilicity**

One of the means of determining surface hydrophilicity is through contact angle measurements [69]. The wettability of the surface is connected to the hydrophilicity of the surface. The higher the surface wettability, the lesser the contact angle [82]. The contact angles of the various membranes are presented in Table 3.3. The unmodified waste PVC membrane (M0) had the highest value of contact angle 86 °±1.1 which was comparable to a reported value for a neat PVC [51]. It could be deduced that the addition of CA improved the hydrophilicity as the contact angle value reduced to about 64.7°±1.7 when 5 wt. % of CA was added to the dope solution. This in return improved the flux and the fouling behavior of the membranes as discussed in subsection 3.4.7 and 3.4.8 respectively. A similar outcome was reported for PVC based membrane with ZnO-NP as an additive elsewhere [41]. This improvement of the surface hydrophilicity could be credited to the hydrophilic characteristic of cellulose acetate which hydrophilizes the membrane surface.

Table 3.3: Permeation behavior of the various membranes

Membrane	Code	PWF (L/m^2h)	BSA rejection (%)	Compaction Factor (CF)	Water contact angle (θ)
PVC	M0	36	91.7	1.12	86.0±1.1
PVC/CA 1%	M1	48	74.0	1.21	75.3±1.8
PVC/CA 3%	M3	72	78.0	1.12	72.9±0.7
PVC/CA 5%	M5	85	78.4	1.25	64.7±1.7

3.3.5 **Thermogravimetric analysis (TGA)**

Thermal studies were done to investigate the onset degradation temperature of the membranes, sequel to the addition of CA. Thermo-gravimetric analyses of the samples are depicted in the thermogram as shown in Figure 3.5. The non-single step degradation curves confirmed the presence of more than one component in the fabricated membranes. Although, PVC generally has more than one successive degradation stage [83]. It was observed that the degradation temperature was altered as the weight percent of CA varied in the waste PVC. The T_{onset} for M0 membrane was found to be ~ 230 ^{o}C and the T_{max} of ~345 ^{o}C for the first stage degradation which could be attributed to dehydrochlorination, while the second stage degradation onset was ~420 ^{o}C and T_{max} of about 600 ^{o}C were observed. The introduction of CA shifted the degradation temperature to the onset of ~ 280 ^{o}C and a T_{max} of ~ 360 ^{o}C. All the other curves (M1, M3, and M5) showed similar characteristics as the fraction of CA changed from 1 wt. % to 5 wt. %. Nevertheless, it could be deduced that at a higher temperature of about 480 ^{o}C (Figure 3.5), all the curves of PVC/CA blends merged as the result of the flow temperature (T_f) of CA which is around 480 ^{o}C [84].

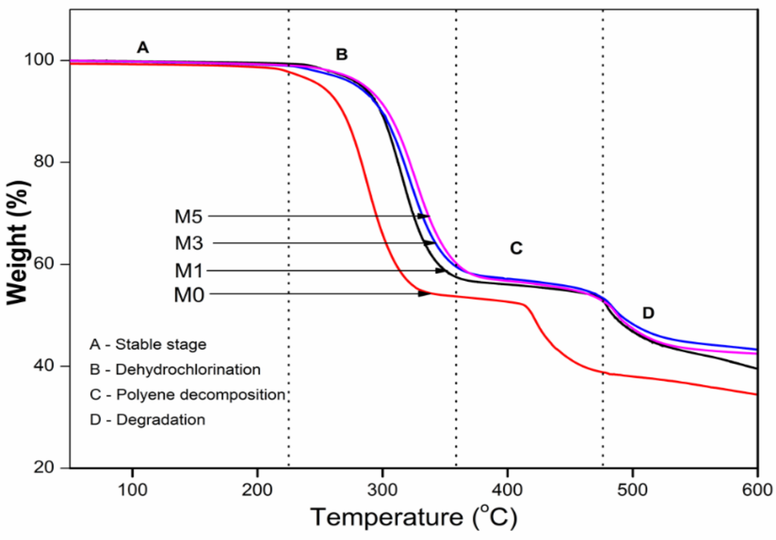

Figure 3.5: TGA (thermogram) of various membranes

3.3.6 **FTIR analysis**

FTIR-ATR was used to confirm the constituents of the blends. Spectra were generated via scans of the membrane samples from 3500 to 700 cm^{-1} range as shown in Figure 3.6. The absorbance spectra of the characteristic C-Cl stretching vibration band of PVC were recorded at the absorption peak of 867 cm^{-1} which falls in the range of alkyl halide group [43]. The other membranes showed a similar pattern of spectra confirming the fingerprint of PVC. Other peaks were recorded at 1259 cm^{-1} which signified the existence for –CH band and 1430 cm^{-1} which was the prominent peak of $-CH_2$ and another peak at around 3000 cm^{-1} in the functional group region which related to –OH group in CA. This signified the constituents of the blends.

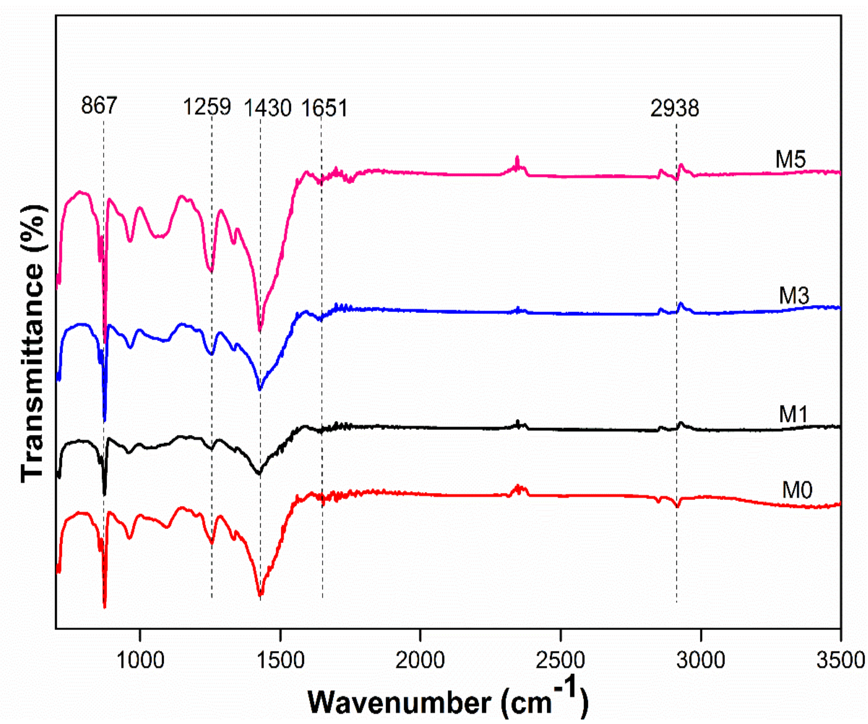

Figure 3.6: FTIR spectra of various membranes (M0, M1, M3, and M5)

3.3.7 **Permeation behavior and rejection**

The flux of pure water and the rejection of BSA for the casted membranes were investigated and the results are shown in Table 3.3. It could be observed that (Figure 3.7) the PWF improved as the composition changes from 0 to 5 wt. % of CA. The flux of pure water increased from 36 L/m^2 h to 85 L/m^2 h due to surface porosity and hydrophilicity. Initially, there was a decline in the flux, but later it became steady due to compaction. Compaction tends to reorganize the membrane pore structure resulting in a decline of flux. The compaction factors of the membranes are presented in Table 3.3. Other factors that can affect the flux are hydrophilicity, membrane thickness, and pore size distribution [85]. The improvement in the flux was also supported by the result of water content, the average pore size, and contact angle of the membranes. Thus, membranes were hydrophilized which means it became favorable to water, thereby facilitating the permeation. BSA rejection of 91% was recorded in the M0 membrane which could be attributed to its dense nature and narrow pore size distribution. Whereas for the M2, M3, and M5, the rejection was somewhat consistent. Although, there was a decrease in the rejection when the CA content was increased because of the creation of voids on the structure which in return improved the pure water flux.

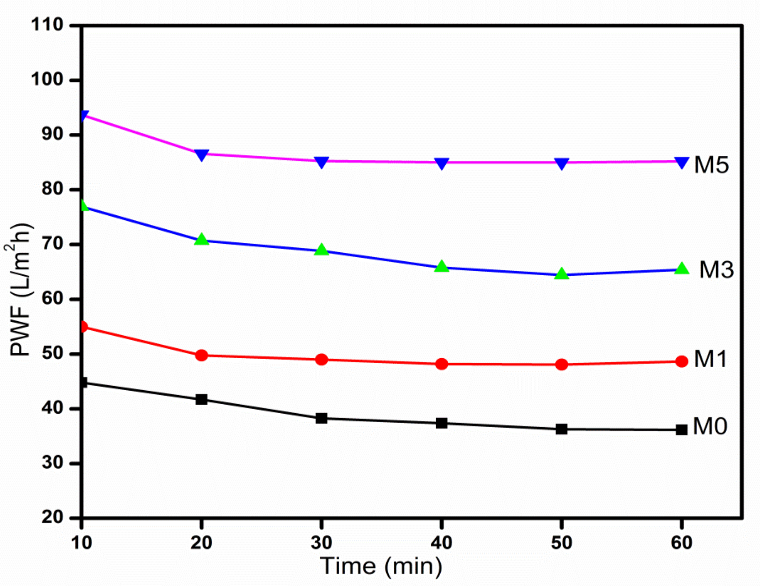

Figure 3.7: Pure water flux patterns of the casted membranes

3.3.8 Flux recovery and fouling behavior of the membranes

In determining the fouling behavior of the membranes, a model foulant (BSA, 1000 ppm) permeation was carried out and the various fouling parameters; reversible fouling ratio, irreversible fouling ratio, total fouling ratio, and the flux recovery ratio were calculated based on Equations (2.6 – 2.9) and the outcome is presented in Figure 3.8. The total fouling ratio (TFR) is the sum of the reversible (RFR) and the irreversible (IFR) fouling ratios. Whereas, the flux recovery ratio (FRR) was calculated based on the PWF before and after permeation with the foulant. It was observed that the flux recovery ratio of the membranes increased from 56% (M0) to 78% (M5) while the TFR decreases from 83% (M0) to 74% (M5) respectively as the percentage of the CA was increased from 0 - 5 wt. % within the waste PVC based membranes. This behavior is attributed to the improved hydrophilicity of the membranes, as hydrophilicity tends to recuperate antifouling properties [86]. The higher the FRR the better the membrane because it is an indication for fouling resistance. Therefore, M5 with the highest FRR has better fouling resistance than the M0 with the least FRR. Another indicator is the total fouling ratio, after the BSA permeation. The TFR of M0 membranes was found to be the highest (83%) which comprised of the RFR (39%) and the IFR (44%) this leads to the least flux of BSA due to adhesion of the molecules on the membrane. The extent of protein (BSA) adhesion on the membrane surface depends on its surface chemistry [54]. Hence, the blend membranes with waste PVC/CA tend to have improved surface hydrophilicity as explained earlier and thereby having least TFR. Although, M3 and M5 membranes are both having the same TFR (74%). However, M5 has higher RFR (52%) because of enhanced hydrophilicity as illustrated by the measured contact angle. This means that it can easily recover a higher percentage of its flux by hydraulic cleaning, whereas the irreversible fouling requires chemical or biological cleaning. Hence, it is desirable to have membranes with high FRR and low TFR. Therefore, the blend of the waste PVC with CA in this study has shown the beneficial outcome as the FRR increases while the TFR decreased and this indicates a better fouling behavior of the casted membranes.

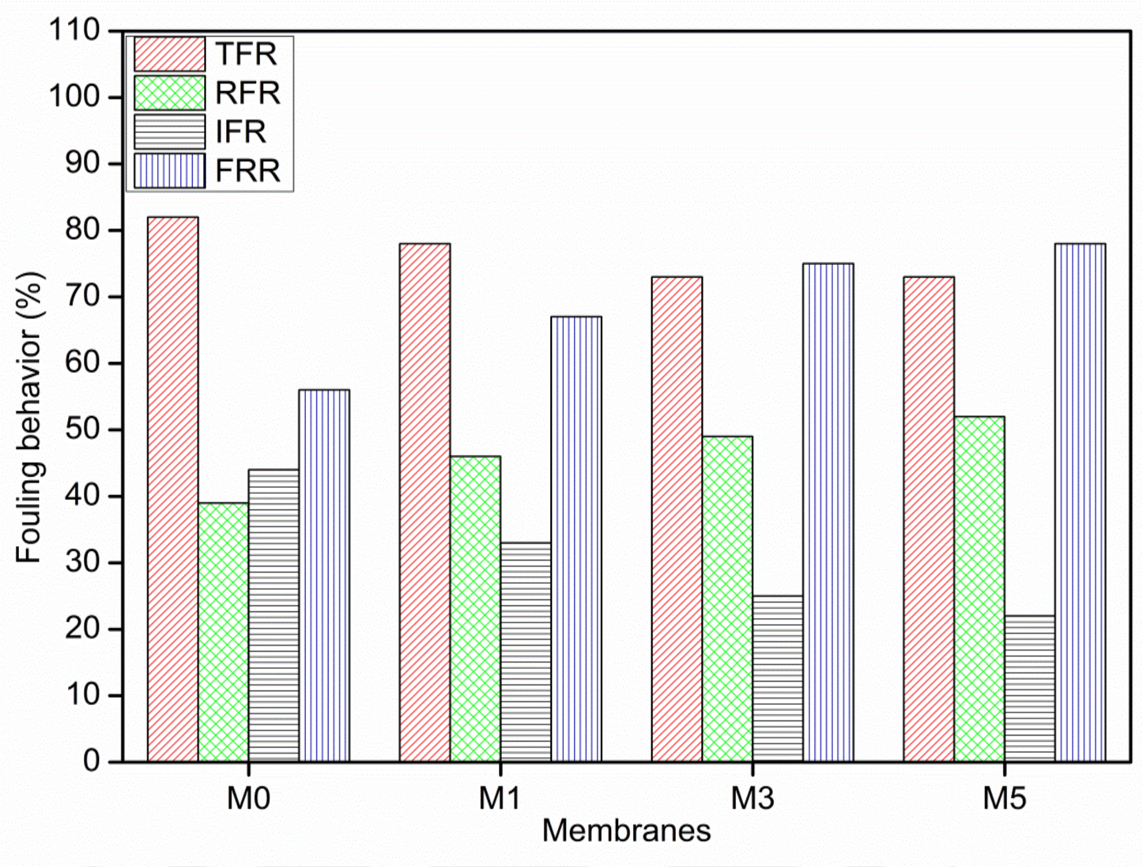

Figure 3.8: Flux recovery and fouling behavior of the membranes

3.3.9 **Comparison of the membrane performance**

The comparison was done with some existing literature as presented in Table 3.4. The findings were found to be favorable compared to existing works even though the material used was not pristine. It could be seen that membrane performance parameters and rejection are greater than those reported elsewhere [40] while in some cases the rejections are better. Although some literature [79][45] showed superior performance than this work, in such cases, the material used for the blends was inorganic nanoparticles which are quite expensive and may leach out to cause environmental concerns, especially now that sustainability is the watchword. Nevertheless, BSA was taken as a model for protein rejection and the membrane was found to be suitable for an ultrafiltration application considering its average pore size.

Table 3.4: Flux and rejection comparison with other reported works

Membrane	Material source	PVC (Wt.%)	Contact angle (θ)	Rejection (%)	Flux (L/m^{2}h)	Reference
PVC/Al_2O_3	Pristine	15	58.1	-	403	[51]
PVC/ PVP	pristine	15	38	98	6.2	[20]
PVC/ Fe_2O_3	Pristine	12.8	62	91.9	782	[79]
PVC/ZnO-NPs	Pristine	13	46.2	73.5	122.2	[41]
PVC/Tween 20/80	Pristine	16	58.4/55.7	87.0	328	[85]
PVC/PF127	Pristine	15	67	45.6	68.6	[40]
PVC/HNTs	Pristine	14	77.2	93.0	92.1	[45]
PVC/CA	Waste	20	64.7	78.0	85.0	This work

3.4 Summary

Waste plastic derived PVC membranes were fabricated. The hydrophobicity of PVC was overcome by blending it with different weight percentages of CA (1 wt.%, 3 wt.%, and 5 wt.%) and the contact angle was reduced from 86º to 64º which led to improved hydrophilicity. The porosity of the casted membranes was also enhanced from 13% to 58%. The pore size distribution (1–100 nm) was found to be within the range of an ultrafiltration membrane. CA addition shows to be effective both in terms of water permeation and thermal analysis. The flux was improved from 36 L/m^2 h to 85 L/m^2 h with 91% BSA rejection in the neat PVC membrane although there was a decrease of BSA rejection with an increase of CA content. PVC membranes degrade in a non-single stage and the onset thermal degradation temperature was enhanced from ~230 ºC to ~280 ºC. FTIR spectroscopy showed the presence of peaks corresponding to both C-Cl and OH functional groups which confirmed the constituents of the blends. The outcome is in line with existing literature in addition to the advantage of waste utilization. Therefore, it could be concluded that waste PVC can be used as a precursor for membrane fabrication and can be explored further to optimize its characteristics for appropriate applications.

Chapter 4

Influence of Additives (PEG, PVP) and Solvents on Waste PVC Membrane: Characterization and Performance Studies

Chapter 4

Influence of Additives (PEG, PVP) and Solvents on Waste PVC Membrane: Characterization and Performance Studies

The application of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and their combination on waste PVC based membranes and subsequent paraphernalia on the morphology, performance, thermal and mechanical properties were studied. A series of membranes were fabricated by immersion precipitation method using N-Methyl-2-pyrrolidone (NMP) and Dimethyl acetamide (DMAc) as a solvent. The effect of casting solvents was determined by Hansen solubility parameters (HSP). Pure water flux (PWF), permeability, and rejection were appraised regarding the performance.

4.1 Background

Plastic utilization overtook other materials for its outstanding properties and advantageous characteristics. Over a 9 % growth in the worldwide manufacturing of plastic has been witnessed in the last two decades [87]. This has no doubt increased the number of waste plastic generated in the world and has risen concern over its effects on the environment. Although plastics utilization made existence stress-free in different applications but has left the environs flustered [6] especially due to their non-biodegradability [88]. Conservationists have called on reforms in ways of handling waste plastic to create economic and environmental sustainability [89]. This has led researchers to explore the possibilities of utilization of waste plastic as a material for membrane fabrication [89][12][35]. Growing the quantity of waste plastic recycled is presently a primacy point on the world agenda of global sustainability [90]. Polyvinyl chloride

(PVC) is the second biggest thermoplastics manufactured, after polyethylene [87][89]. This could be linked to its low cost, collective physical, chemical, and enduring properties which made it a versatile polymer with various applications [87]. This flexibility in applications leads to the generation of a high quantity of waste PVC with disposal and management problems. The good thing is that PVC can dissolve in various organic solvents and it has a film-forming ability, these characteristics rendered it suitable to be used as membrane material through phase inversion process [89][47].

Phase transformation can be achieved through various techniques [15]. The non-solvent stimulated phase inversion is the common method for membrane fabrication [77][76][91]. Among the techniques to get diverse morphological configurations through phase inversion process is the use of various additives and solvents for effective preparations [92][93]. The incorporation of additives as ternary constituents in the dope solution has been beneficial for membrane preparation [56][94][3]. Membranes morphology, especially, the extent of pore disseminations may be influenced by choosing an appropriate polymer, additives, solvent, non-solvent, and preparation parameters [15][72]. The commonly used constituents as enhancers in the phase separation process are materials like polyethylene glycols (PEG) [95], polyvinyl pyrrolidone (PVP) [43], glycerol, polyethylene oxide, alcohols [96], and salts; TiO_2 [97], LiCl, and ZnO [41]. The membrane enhancers can be alone constituent or a combination [96].

Several scholars have investigated the influence of the concentration of additives, molecular weights of constituents, and solvents on the characteristics of the membrane [72][28][18][98]. For example, Roy et al. [47] studied the performance of PEG with different mole weights on the morphology of the pristine PVC membrane prepared through non-solvent induced technique. Sinha and Purkait [98] conveyed the use of different mole weights of PEG on improving the hydrophilicity of PS membranes. Mukesh and co-authors [99] studied different mole weights of PEG as a modifier in cellulose acetate membranes. Ahmed et al. [43] examined the enhancement of PVC membranes with PVP as an additive and reports improved flux and performance. Chakrabarty et al. [100] studied the outcome of PVP of different mole weights on the morphology and flux of polysulfone (PSF) membranes. However, both PEG and PVP play roles in pore formation, and as hydrophilicity enhancer but with unique characteristics.

The morphology and effectiveness of membranes fabricated in various solvents are tailored by the dynamic variables such as polymer-solvent interaction, solvent-nonsolvent miscibility rate and thermodynamic factors like Hansen solubility parameters (HSP) [72][18]. The properties of the dope solution are related to polymer characteristics, additives, and solvents. In general, polymer additives are indispensable to improve membrane characteristics [72][100][101]. The effectiveness of the polymeric membrane depends on the properties of the forming solution and phase separation rate during the transformation process [98]. To our understanding, there is no report regarding the appraisal of the influence of two different additives PEG, PVP, and their combination PEG+PVP on the structures and performance of membranes made-up from waste plastic (waste PVC) using two solvents (NMP and DMAc) in the literature. Hence, it is motivating to investigate the activity of the external pore-formers in the matrix of waste PVC and likewise to explore the effect of the combined additives and influence of the solvents on the features of the waste PVC based membrane.

Therefore, this work focused on the determination of the influence of additives and diluents on the waste plastic-based membrane morphology, performance, thermal and mechanical properties. Hence, two practically comparable membrane-additives and their combination (PEG, PVP, and PEG+PVP) were studied along with the solvent (NMP and DMAc). The schemes comprising of waste PVC/N, N-dimethylacetamide (DMAc)/water, and waste PVC/N, methyl-2-pyrrolidone (NMP)/water as the polymer, solvent, and non-solvent were considered. The interaction was investigated by different membrane characterization techniques and performance was analyzed based on humic acid rejection and water flux. Likewise, the HSP was computed to assess the thermodynamics of the system and to establish a better solvent for the waste PVC in membrane fabrication.

4.2 Experimental

The schematic representation of the process is given in Figure 4.1. While the detailed procedure for the preparations and characterizations of the prepared membranes are reported in the materials and method section (chapter 2).

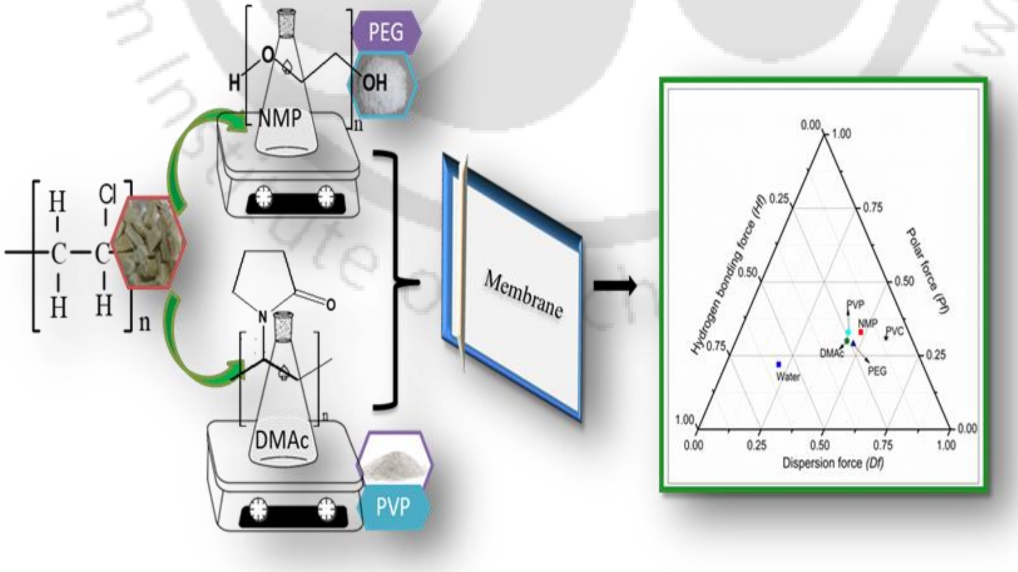

Figure 4.1: Schematic representation of the process

4.2.1 **Materials**

Waste plastic (PVC) was the base material used in the dope solution. N-methyl pyrrolidone (NMP) and Dimethyl Acetamide (DMAc) are the solvents used in the process, supplied by Sigma-Aldrich Co., with reagent grade purity. While, deionized (DI) water from the Millipore system (Millipore, France) was used as the non-solvent in the coagulation bath. Polyethylene glycol (PEG) and Polyvinylidene pyrrolidone (PVP) were used as an additive in the dope solution. Humic acid (HA) was obtained from Otto Chemie Private Limited, India for performance studies.

4.2.2 **Preparation of membrane**

The membranes were prepared through the phase inversion method as detailed in chapter 2. Various membranes with different compositions as depicted in Table 4.1 was fabricated by dissolving the materials in borosilicate glass, the solution was casted on a glass plate and then immersed in a water bath for the phase transformation. Detailed procedures for the preparation of the membranes were conveyed in the materials and method section.

Table 4.1: Composition of the fabricated membranes

Membranes	PVC (wt. %)	PVP (wt. %)	PEG (wt. %)	Solvent (80%)
M1	15	5	0	NMP
M2	15	5	0	DMAc
M3	15	0	5	NMP
M4	15	0	5	DMAc
M5	15	2.5	2.5	NMP
M6	15	2.5	2.5	DMAc

4.2.3 Membrane characterization

The membranes were characterized using field emission scanning electron microscopy (FESEM), equilibrium water content (EWC), contact angle measurement, porosity, pore size, attenuated total reflectance in conjunction with Fourier transform infrared spectroscopy (FTIR-ATR), thermo-gravimetric analysis (TGA) and electromechanical universal testing machine (UTM). The membrane performance was evaluated by pure water flux (PWF) and Humic acid (HA) rejection. Details of the membrane's characterization procedures were presented in chapter 2 (materials and methods).

4.2.4 Hansen solubility parameters (HSP)

In understanding the interactions between polymer, solvent, and non-solvent which influences the properties of the membranes, the Hansen solubility parameter plays a role. HSP comprised of three components; the dispersion bonds forces (δ_d), the dipolar intermolecular forces (δ_p), and the hydrogen bonding forces (δ_h). These forces are used in calculating the HSP (δT) and the HSP differences ($\Delta\delta$) [73][18]. The equations used for the calculations of the HSP for the different pairs of interactions between polymer-solvent ($\Delta\delta p, s$), and polymer-nonsolvent ($\Delta\delta p, n$) are displayed below.

$$\delta T = (\delta d^2 + \delta p^2 + \delta h^2) \tag{4.1}$$

$$\Delta\delta p, s = \sqrt{(\delta d, p - \delta d, s)^2 + (\delta p, p - \delta p, s)^2 + (\delta h, p - \delta h, s)^2} \tag{4.2}$$

$$\Delta\delta p, n = \sqrt{(\delta d, p - \delta d, n)^2 + (\delta p, p - \delta p, n)^2 + (\delta h, p - \delta h, n)^2} \tag{4.3}$$

Where, δT is HSP, p, s, and n denote polymer, solvent, and non-solvent respectively.

4.3 Results and discussion

4.3.1 Morphological studies of the membrane

The morphology; FESEM pictures of the various membranes fabricated were depicted in Figure 4.2. Observation of the images reveals that pores are uniformly distributed within all the membranes surfaces. The pores are more significant in M1 and M2 membranes than M3 and M4 because of the peculiarities of the additives used. PVP was used in the former which has a higher solubility rate of 1000 mg/ml in water (the non-solvent) than the latter PEG with a solubility rate of 630 mg/ml in the non-solvent. While in M5 and M6 the pore distribution is somewhat consistent because the additives were used in mixed and equal proportion. It can be observed that all the membranes are asymmetric because of a porous finger-like structure that runs across the sub-layers and a selective uniform pore distributed at the top surface. High porosity and interconnected pores are the roles of pore formers [54]. Dissolution of pore formers and instantaneous de-mixing can leads to fingerlike structures within the membranes [70]. Fairly broader and less tortuosity finger-like structures can be seen in M1 and M3 membranes, while M2 and M4 show a relatively tortuous finger-like structure. M5 and M6 strike a balance between the two. These may be due to the more hydrophilic nature of PVP and enhanced mass transfer of the different solvents (NMP/DMAc) used in the non-solvent (water) during phase transformation.

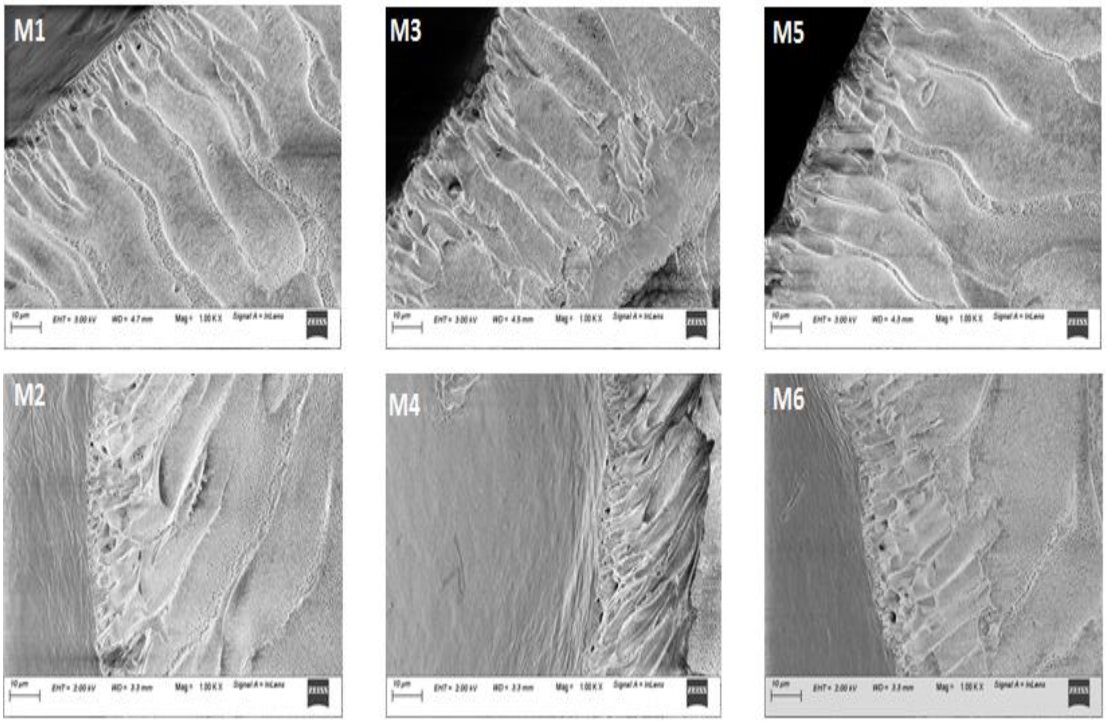

Figure 4.2: FESEM images (cross-sectional view) of the waste PVC based membranes

4.3.2 Equilibrium water content

One important parameter that is closely linked with pure water flux and porosity in membrane characterization is the equilibrium water content (EWC). The equilibrium water content of different membranes is presented in Figure 4.3. It can be observed that the equilibrium water content varies across the membranes. The membrane M1 having the highest (77. ±1.9%) value and M4 with the least (60±1.5%) while the rest of the membranes falls in between these two. This is due to the type of additives used as PVP was used in M1 which has a high solubility in the non-solvent (water) with a solvent NMP which has better interaction with the base polymer (waste PVC). Thereby creating more pores that can accommodate water molecules within the cavity of the membranes and PEG was used in M4 which has less solubility in the non-solvent with DMAc that has poor interaction with the base polymer as confirmed by the HSP. This result shows that there is a direct link between EWC, porosity, and water flux. Hence, the assertion that the value of EWC depends upon the number of pores and cavities present in the membranes can be held as the pores and cavities are considered to be the abode for molecules of water. While the rest of the membranes falls in between these two values of M1 and M4, respectively.

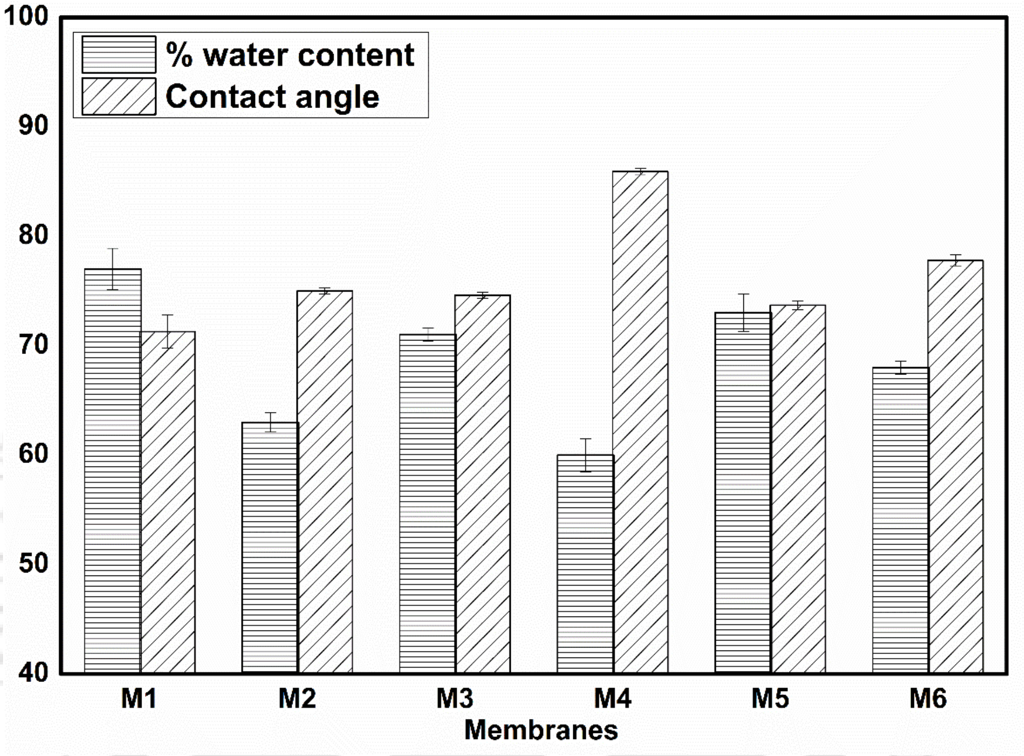

Figure 4.3: Graph showing the EWC (% water content) and contact angle (CA)

4.3.3 **Water contact angle (WCA)**

The static water contact angle is used to estimate the hydrophilicity or hydrophobicity of casted membranes. Generally, it is believed that when the contact angle is larger than ninety degrees, the membrane is considered to be hydrophobic, if it is less than ninety degrees it is hydrophilic [54][13]. This can be ascribed to the way that the hydrophilicity of the defined film relies upon the pore size and porosity which in turn linked to the type of additives used. The values of the contact angle are displayed in Figure 4.3 the results indicated that M1 has about 66.7 ± 0.5 ° and M4 has the highest value of 85.6 ± 0.3 ° these values are in line with what was reported for pristine PVC [43]. The rest of the membranes are within close range to each other. The WCA result indicates the trend of hydrophilicity which is in concord with the outcomes obtained for the PWF. The result shows that the more hydrophilic membranes have better pure water flux than the less hydrophilic ones. This finding agrees with other works that reported improved hydrophilicity leads to increased PWF [98][69]. The WCA results indicate the trend of hydrophilicity which agrees with the results obtained for the PWF.

4.3.4 **FTIR**

Fourier transform infrared spectroscopy (FTIR) is a technique used to determine the functional groups of samples. It used to obtain an infrared spectrum of emission or absorption of the test material via various modes. In this study, the attenuated total reflectance mode was used coupled to the Fourier transform infrared spectroscopy (FTIR-ATR) to produce the spectrum. The FTIR-ATR spectra of the samples were generated via scans of the films (M1, M2, M3, M4, M5, and M6) from a wavenumber range of 3500 to 700 cm^{-1} and the results are presented in Figure 4.4. The lower range of the wavenumber is ascribed to the fingerprint region of the materials. Hence, the peak at 896 may be attributed to the C-Cl of the waste PVC membrane which is present in all the membranes fabricated. The wavenumbers at 1253 cm^{-1} implied the presence for –CH band, although no additional peak was determined for PEG this is due to the coinciding –CH bands with the strongest bands of PEG. A similar result was reported elsewhere, where the bands of PEG overlapped with that of PES [102]. The peak at 1657 is attributed to the residual amide in PVP while the one at 2936 can be credited to the existence of C-H stretching vibrations. This outcome confirmed the constituents of the membranes.

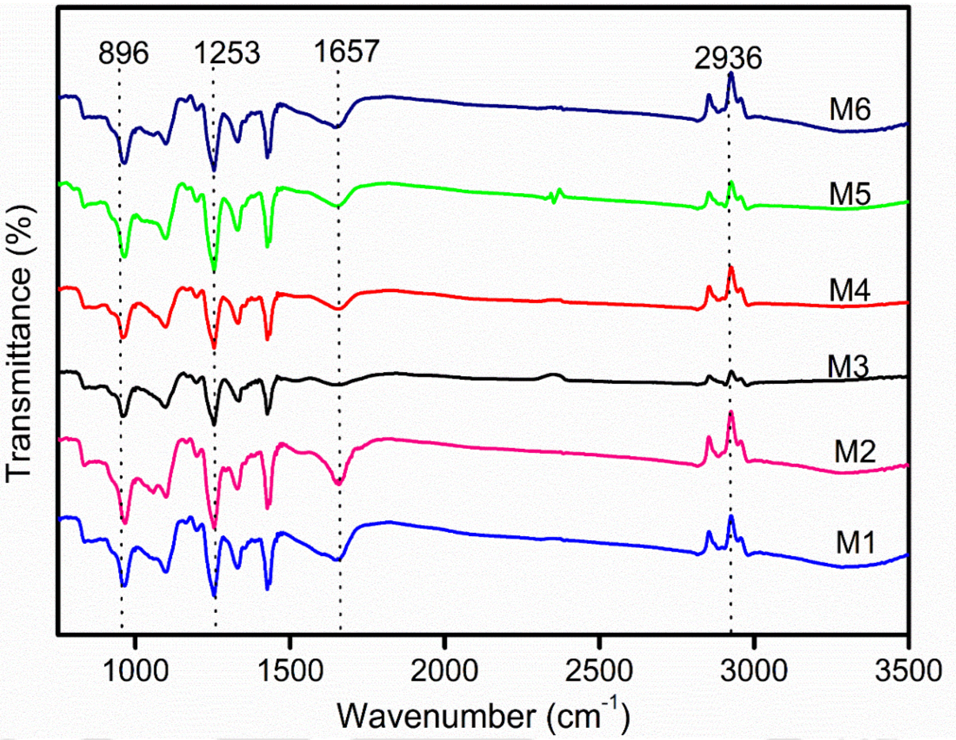

Figure 4.4: ATR-FTIR of the various membranes fabricated

4.3.5 **Thermogravimetric analysis (TGA)**

The thermogram of all the membranes (M1, M2, M3, M4, M5, and M6) casted was analyzed and shown in Figure 4.5. All membranes showed three degradation stages which confirm that the waste material used was PVC. Polyvinyl chloride generally has three stages of degradation [83][26]. The T onset for all the membranes initiated at ~ 230 ^{o}C and the T_{max} of ~ 345 ^{o}C for the first step degradation which can be ascribed to stripping of HCl (dehydrochlorination), the other two stages are chain elimination and finally thermal decomposition (char formation) respectively. This concord with what was reported elsewhere for thermal degradation of PVC [89][83]. It is observed that all the samples have similar onset degradation temperatures ~ 230 ^{o}C, although six membranes were evaluated in the TGA curves. This is attributed to the fact that the two additives (PVP and PEG) used as modifiers have lower degradation temperature than the PVC

[94]. While the solvents were expected to have leached out during liquid-liquid de-mixing at the phase inversion process. Therefore, the presence of residual additives or solvents has shown no significant impacts on the thermal degradation of the membranes. This implies that waste-derived PVC membranes has sufficient thermal stability even after modified with additives and can also be applied in hot streams up to ~ 230 ^{o}C apart from the water filtration.

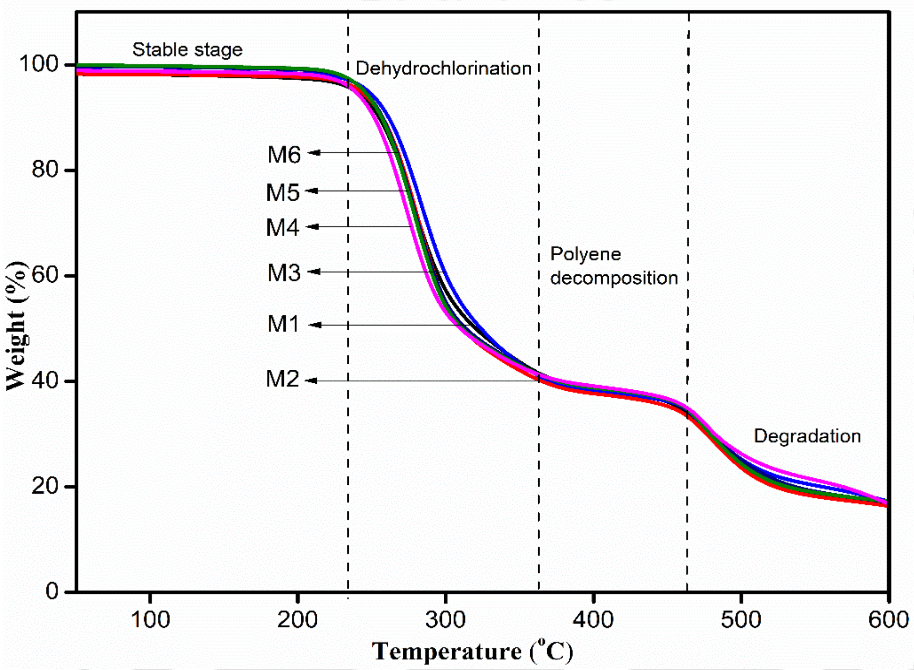

Figure 4.5: TGA thermogram of the membranes

4.3.6 **Mechanical properties**

Mechanical property is one of the parameters that were investigated through the test of tensile strength using a universal testing machine (UTM) at the critical breaking point of stretching. The outcomes of the tensile strength and percent elongation at break are displayed in Figure 4.6. It can be observed that M4 shows ~ 35% greater mechanical strength and percent elongation than other membranes. This can be credited to the polymer chain entanglement which tends to draw more before breakage due to the suppressed nature of its porosity as a result of the type of additive (PEG) and solvent used. However, M1 and M5 are having lower mechanical strength of < 2 MPa and percent elongation of ~ 10 %, respectively. This is due to their macro-voids' formations and porosity of ~ 38% and ~34% higher than M4. It was identified that films obtained from DMAc are more cross-linked and stronger than those obtained from the NMP solvent. A similar outcome was reported elsewhere [103]. This agrees with the Hansen solubility parameter result which shows that NMP has a superior affinity to the waste PVC than the DMAc as discussed in section 3.7. The other membranes (M1, M2, M3, M5, and M6) showed similar mechanical strength of < 2 MPa and percentage elongation of around 10 – 20 %, respectively.

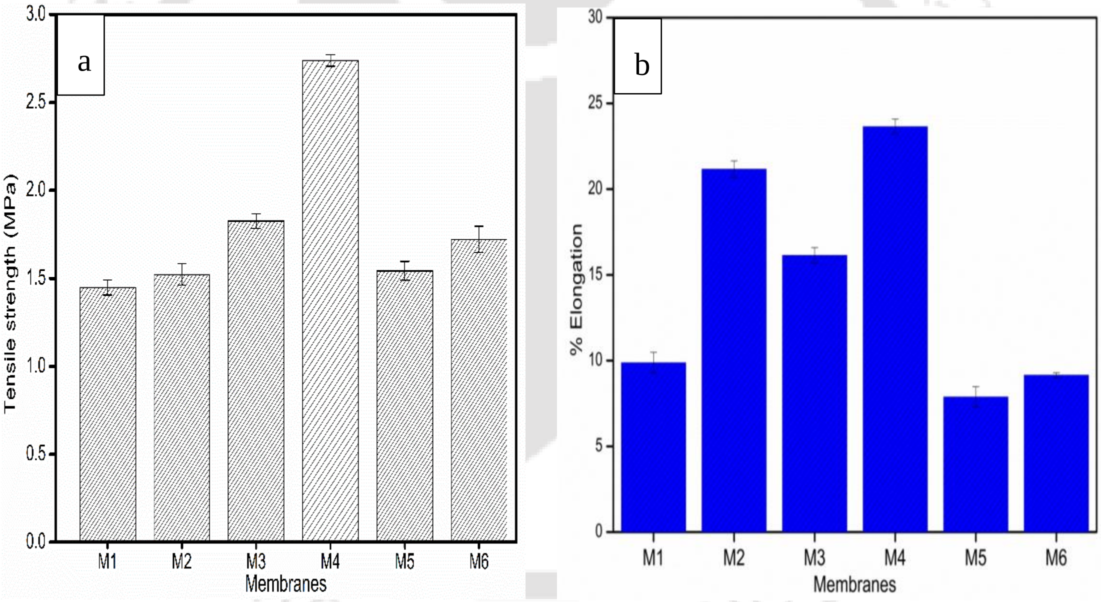

Figure 4.6: Mechanical Properties (a) Tensile strength (b) % Elongation

4.3.7 **Hansen solubility parameters (HSP)**

The influence of solvents on the prepared membranes was evaluated by Hansen solubility parameters (HSP). Based on polymer-solvent and polymer-non-solvent interactions. The HSP and the calculated HSP differences ($\Delta\delta$) using Equations (4.1- 4.3) are shown in

Table 4.2. It is ingrained that the solvency of a casting solvent towards a polymer depends on the HSP differences. The solubility is inversely related to the HSP difference [73]. Therefore, the lesser the difference of the parameter better the interaction. Centered on this analogy it can be observed that the sequence of HSP differences between waste PVC and the solvents can be arranged as waste PVC/NMP < waste PVC/DMAc. This shows that NMP with HSP difference of 4.8 $(MPa)^{1/2}$ was better solvent for the waste PVC than DMAc with 7.5 $(MPa)^{1/2}$ because it has lesser solubility parameter difference between them. This is in concord with what was conveyed by Alvi et al. [18]. While in the case of the additive polymers (PEG and PVP) with non-solvent (water) the values indicated that PVP has a better affinity than PEG which concords with their solubility rates of 1000 mg/ml and 630 mg/ml, respectively [15][72].

Table 4.2: HSP of the components [72][18] and the calculated HSP differences

Material	$\delta_d(MPa)^{1/2}$	$\delta_p(MPa)^{1/2}$	$\delta_h(MPa)^{1/2}$	$\delta_T(MPa)^{1/2}$	$\Delta\delta p\text{-}s(MPa)^{1/2}$	$\Delta\delta_{p\text{-}ns}\,(MPa)^{1/2}$
PVC	18.7	10.0	3.1	21.5	-	-
NMP	18	12.3	7.2	23.0	4.8	-
DMAc	16.8	11.5	10.2	22.8	7.5	-
PVP	16.1	12.1	8.8	23.9	-	33.8
PEG	16.8	10.2	8.6	21.5	-	34.3
H_2O	15.6	16.0	42.3	47.8	-	-

To visualize the solubility parameters in space relative to each other, the Teas graph (ternary diagram of fractional solubility parameters) based on the Cartesian coordinates of fractional solubility parameters was drawn in Figure 4.7. This allows the visualization of the positions of each component in a two-dimensional plot concerning each other. The polymers, solvents, and non-solvent were all displayed. The distance between the components determines their affinity [104]. When the points of the solute and the solvent are close in the Hansen space, the solvency of the solvent to solvates the solute increases. Hence, it can be visualized that the NMP is closer to the waste PVC than the DMAc, therefore, NMP has better interaction with the waste PVC than the DMAc.

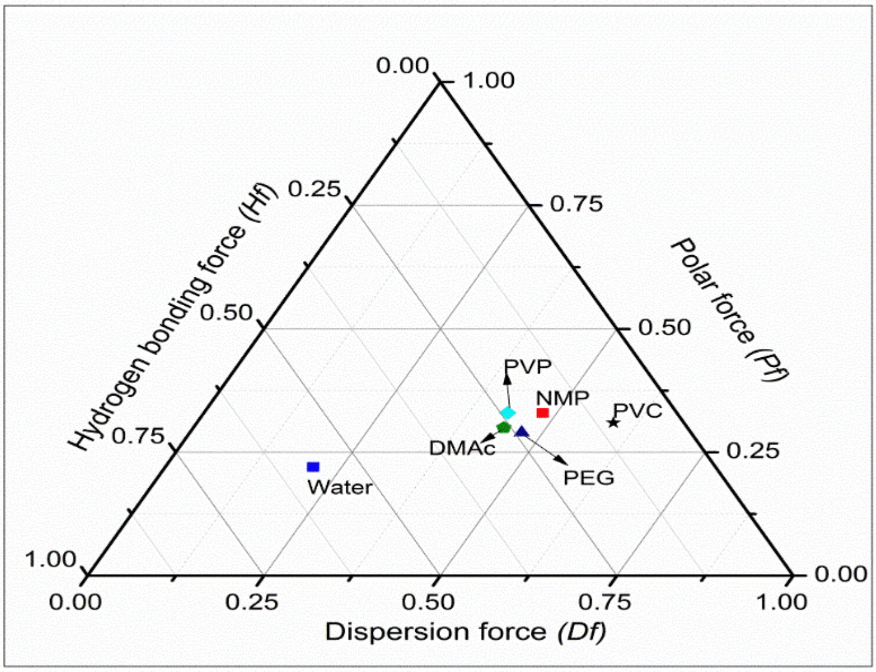

Figure 4.7: Teas graph of the various components

4.3.8 Porosity and mean pore size

The porosity of all the casted membranes was computed by using Equations (2.2). The results are presented in Table 4.3 accordingly. M1, M2, M3, M4, M5, and M6, are having porosity of 72%, 59%, 62%, 44%, 67% and 53%, respectively. Likewise, the mean pore size (r_m) of the samples was computed based on Equation (2.3) and shown in Table 4.3 accordingly. The variations in the porosity can be ascribed to the type of additive and solvent used. The values of the porosity and the mean pore sizes recorded have similar trends with the PWF. It correlates with EWC results as it can be observed that the M1 membrane had more pores because of better interaction between the non-solvent and the additive (PVP) used in the casting process. This agrees with the works of Roy et al., [94] which modified pristine PVC with additives.

Table 4.3: Permeation parameters of the various membranes

Membranes	CF	PWF(L/m^2h)	% HA rejection	Porosity %	Pore size (r_m)
M1	1.14	101	85	72	35.6
M2	1.18	88	89	59	24.8
M3	1.17	92	87	62	25.9
M4	1.18	81	93	44	21.3
M5	1.11	95	86	67	29.3
M6	1.16	86	90	53	22.8

4.3.9 Water flux (PWF), permeability and compaction factor (CF)

The membrane flux (pure water permeation), and compaction factor (CF) are vital parameters that estimate membrane performance. PWF of the different membranes is given in Table 4.3, along with the values of the compaction factor, respectively. The flux tends to decline slowly and remains almost constant after 60 minutes as shown in Figure 4.8. As a result of compaction, the walls of the pores becomes closer and denser because of the effect of the pressure resulting in pore size reduction and decline in water flux [19]. The membrane compaction was evaluated using the initial and final stable PWF. The impact of compaction on the membranes flux was depicted in all the membranes prepared from both the solvents and the additives. The membrane with higher flux (101 L/m^{2}h) was found to be M1 with porosity and of course relatively higher pore size. Thereby, it has less hydraulic resistance and in turn, gives rise to high pure water flux. While M4 is having less flux (86 L/m^{2}h**)** due to less surface porosity and narrow pore size. This concord with what was reported from the FESEM analysis section 5.4.1.

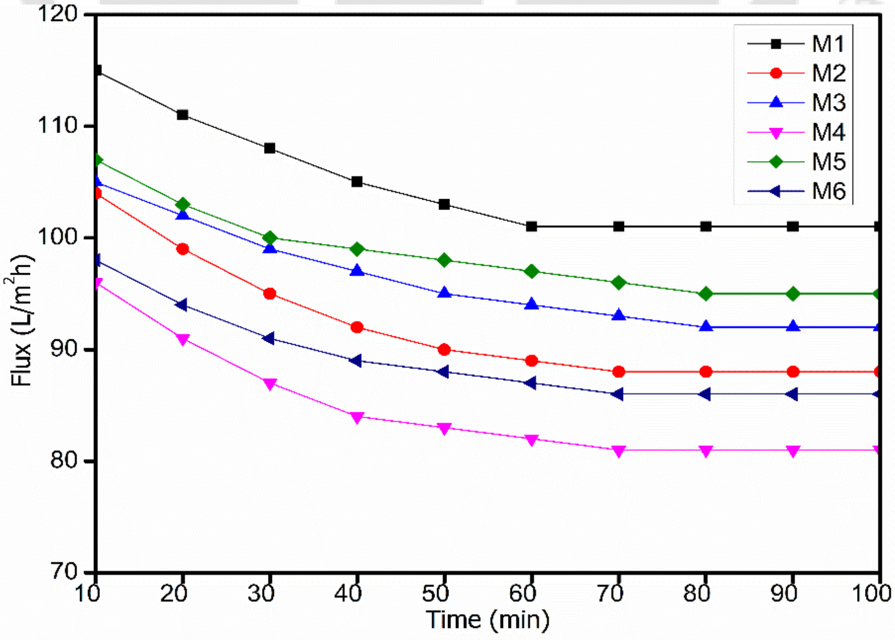

Figure 4.8: PWF pattern of various membranes

4.3.10 **Rejection studies**

The rejection of the membranes was examined by the removal of humic acid (HA) in water using the same set up used for the permeation studies. The concentrations of the humic acid in permeate were evaluated employing UV-Vis spectrophotometer and estimated by using Equation (2.5) and the values are presented in Table 4.3, respectively. The trends of the HA rejections are very similar to the PWF of the casted membranes in an inverse manner. The M4 membrane has the highest rejection (93%) in comparison to other membranes. This can be credited to its suppressed pore radius and the nature of its surface due to the additive and the solvent used. Whereas, M1 with the highest flux recorded the least rejection (85%). This shows that there is a tradeoff between flux and rejections. The outcome supports the result of the morphology studies where it was shown that the M4 membrane has a narrow finger-like pore in its sub-layer structures while the M1 has fairly broader and less tortuous finger-like structures as discussed in section 4.4.1.

4.3.11 **Studies on flux recovery ratios**

The flux recovery of the membranes was investigated through humic acid (HA) rejection in water. The performance was studied using different fouling ratios; IFR (irreversible fouling ratio), RFR (reversible fouling ratio), TFR (total fouling ratio), and FRR (flux recovery ratio). These parameters were computed based on the equations given in section 2.4.7 and the outcomes are presented in Figure 4.9. The outcomes showed the various FRR of 77%, 70%, 72%, 70%, 74%, and 75% for M1, M2, M3, M4, M5, and M6, individually. The range is in agreement with what was reported for pristine PVC elsewhere [86]. The irreversible fouling ratio is lower for all the membranes. While there are marginal variations in RFR and TFR for all membranes. The higher the flux recovery ratio the better the membrane since it is a sign for fouling opposition. Thus, M1 with the maximum flux recovery ratio (77%) has superior fouling resistance compared with M2 (70%) and M4 (70%) with the least FRR.

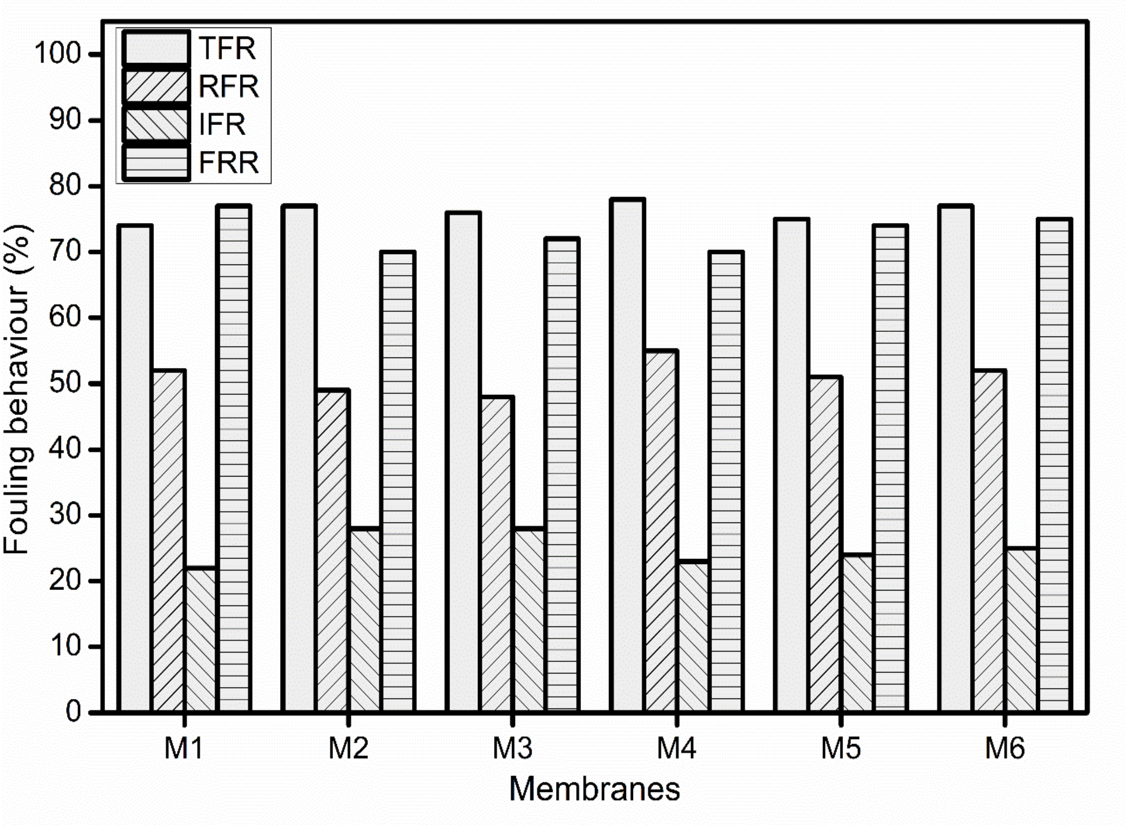

Figure 4.9: Fouling ratios of the membranes

4.3.12 Comparison of membrane parameters with existing literature

A comparison of the performance parameters of the fabricated membranes with some existing works is shown in Table 4.4. The outcome of the present work compared favorably with the existing literature. [86][40] Although the precursor used for the fabrication of this membrane is waste plastic (PVC). The polymer concentration used was 15 wt. %, in the range of 13-17 % as compared with the reported works. Similarly, in terms of rejection and flux, it competes satisfactorily. Although, in some instance, it's either the flux or the rejection that is better but remain almost in line with the pristine one. Nevertheless, this indicates that there is hope in establishing waste plastic as an alternate source for low-cost membrane material.

Table 4.4: Permeation and retention assessment with other works

Membrane	Precursor origin	Polymer (wt. %)	Contact angle (θ)	Rejection (%)	PWF (L/m^{2}h)	Reference
PVC+PVP	pristine	15	38	98	62	[43]
PVC+ZnO-NPs	Pristine	13	46.2	73.5	122.2	[41]
PVC+PEG	pristine	17	86.1	66.67	72	[86]
PVC+Tween 20	Pristine	16	58.4/55.7	87	328	[85]
PVC+HNTs	Pristine	14	77.2	93.0	92.1	[45]
PVC+PVP	Pristine	17	-	90	328	[105]
PVC+PF127	Pristine	15	67	45.6	68.6	[40]
PVC+PEG/PVP	waste	15	66.7	93.0	85.0	This study

4.4 Summary

Waste plastic-based flat sheet membranes were prepared from waste polyvinyl chloride (PVC) as the main polymer. The characteristics of the waste PVC membrane using different additives and solvent were evaluated to ascertain their performance for subsequent application. The introduction of the additives improves the hydrophilicity and porosity of the casted membranes. PVC membranes degrade in three-step which are inscribed from TGA. The incorporation of additives (PVP and PEG) has not affected the thermal stability as the onset thermal degradation temperature for all the membranes was detected at ~230 ºC. FTIR spectroscopy exhibited the peaks conforming to C-Cl, C-H, and -CH functional groups which confirm the components of the films. In the mechanical test, M4 shows ~ 35% greater tensile strength and percent elongation than other membranes. This can be credited to the polymer chain entanglement which tends to draw more before breakage. However, M1 and M5 are having lower mechanical strength and percent elongation due to their macro-voids' formations. The membranes fabricated by PVP additive exhibited greater voids and finger-like structures with a pure water flux of 101 L/m^2h and HA rejection of 85 % when compared to the ones formed with PEG which recorded the pure water flux of 81 L/m^2h and a rejection of 93 %. While the combination of the two for the first time gives a striking balance of 86 L/m^2h with 90 % rejection. Among the two solvents used, NMP with HSP difference of 4.8 $(MPa)^{0.5}$ showed better interaction with the waste PVC than DMAc with 7.5 $(MPa)^{0.5}$. This was ascertained from the result of the Hansen solubility parameter. In conclusion, the outcome suggested that waste plastic (waste PVC) could provide an alternative means for low-pressure membrane precursors and its properties can be tailored with appropriate additives and solvent for targeted application.

Chapter 5

Biopolymer (Gum arabic) Incorporated Waste PVC Membrane for Hydrophilicity Enhancement and Removal of Natural Organic Matter in Water

Chapter 5

Biopolymer (gum arabic) Incorporated Waste PVC Membrane for Hydrophilicity Enhancement and Removal of Natural Organic Matter in Water

The utilization of waste plastic as a membrane substrate was considered and its hydrophilicity enhancement by incorporation of a sustainable biopolymer gum arabic (GA) for natural organic matter removal in water was carried out. The phase transformation method was used in the membrane preparation by varying percentages of GA. The interaction between the waste polyvinyl chloride and gum arabic with different loadings were analyzed using various analytical techniques for morphology and evaluation studies. Field emission scanning electron microscopy, thermogravimetric analysis, Fourier transforms infrared spectroscopy, equilibrium water content, contact angle, porosity, water flux, and compaction factor were assessed. Furthermore, natural organic matter (NOM) removal from water was carried out. It was confirmed that blending with gum arabic enhanced the hydrophilicity, mitigate fouling, and improved the water permeation.

5.1 Background

Surface water is assiduously contaminated by natural organic matter (NOM) from various sources like the chemical, microbiological, anthropogenic, and phytochemical transformation of flora and fauna [65][106]. NOM are those complex heterogeneous organic substances resulting from terrestrial and marine origins that affect the quality, purity, appearance, and other physicochemical parameters of water [106][107]. These problems are generally compounded when the water source is purified by a conventional method. During chlorination in drinking water treatment, the complex substances can react and produce health-threatening compounds like trihalomethanes (THMs)[108][109]. Humic acid (HA) is a category of NOM which exists in surface and river water. The presence of HA in water can result in bad odor, color alteration, absorption of metals, and an increase in turbidity and microbial activities [1][97]. Therefore, HA has to be removed to produce safe water for public utility. Coagulation is one of the traditional methods of NOM removal but coagulants have to be purchased repeatedly to sustain the process [5]. Moreover, HA may combine with coagulants to hinder the overall process and generate sludge that requires additional removal [108][110]. Adsorption is another established technique that can take away NOM in water. However, the adsorbent needed to be regenerated and separated from the water system [108]. Similarly, ion exchange is another viable method for the removal of NOM. Nevertheless, this requires resin and resin revival and handling attracts additional operational and disposal costs [111]. Likewise, during chlorination, the phenolic hydroxyl moiety of the HA may react with the disinfectant (chlorine) and produce trihalomethanes [65][107]. The membrane filtration is proven to be an efficient process for NOM removal to make water usable [14]. However, the major challenge of this separation process is the high cost and membrane fouling [107][111][48]. This article is focused on the preparation of low-cost hydrophilic membrane addressing the said challenges. The application of the prepared membrane was confirmed using NOM removal from synthetic wastewater. Waste plastic was used to reduce membrane cost and to protect the environment as well.

The pressure poised by waste plastic on the environment is enormous. Suitable discarding of post-consumer plastic is a challenge [87]. To manage this challenge, many waste management and treatment approaches like burying, combustion, and incineration have been established, but which are unfavorable to ecological progressions due to the release of poisonous gases leading to contamination of air and water bodies [90][89]. Hence, waste plastic reprocessing and reuse are consequently considered the best environmental methods of getting rid of waste plastic [12]. Accordingly, scholars across the world are continuously exploring the potentials of reprocessing waste plastic as a substance for the fabrication of membrane [89][12]. Waste recycling is a primary aim of the world program of global sustainability because of its combined benefits of economic and environmental conservation [90]. Polyvinyl chloride (PVC) is the second-largest thermoplastic manufactured in the world in terms of quantity, after polyethylene [87][89]. This could be linked to its collective physical, chemical, and enduring properties which make it a versatile polymer having various applications [51][48]. The versatile applications lead to the generation of a high quantity of waste PVC with disposal and management problems. PVC can dissolve in various organic solvents and it has a film-forming ability, these characteristics rendered it suitable to be used as membrane precursor [89][50]. The virgin version of PVC has been established as membrane material by researchers with a drawback of hydrophobicity [51][42][112][43]. Hydrophobic surfaces are susceptible to fouling, which can be controlled by incorporating hydrophilic additives [22].

Membrane fouling resulted in higher operating pressures, hinders the membrane permeability, selectivity, reduced lifecycle, affects its productivity, induced frequent washing, and deteriorate the permeate quality [65][107][113][70]. This can be managed by the incorporation of suitable additive to improve membrane hydrophilicity [89][53]. Researchers have published that films with hydrophilic characteristics are more resistant to fouling by organic materials and microbes owing to the dealings among the organic materials and the film interface [42][113][114]. Thus, integrating hydrophilic additives in membrane fabrication to enhance its hydrophilicity and fouling mitigation by incorporating enhancers has been of great interest. Polymers like polyethylene glycol [69][99], polyethylene glycol methyl ether [98], and polyvinylpyrrolidone [112][100][43] have been used as traditional additives. Nevertheless, the problem of membrane fouling continues to hinder the operation of membranes in water treatment, and its inhibition remains a focus of study [70][115].

Recently, biopolymers have been gaining attention as membrane modifiers due to their hydrophilic moieties, environmental friendliness, sustainability, and other inherent properties. Padil et al. [61] used gum karayana and its consequential effects on the properties and characterization of electrospun polyvinyl alcohol membranes. Asim et al. [116] investigated the role of acacia exudate conjugated cellulose nanocrystals for their antibacterial and chlorine resistance effect on polyvinyl alcohol membranes. Kumar et al. [65] used Xanthan gum to improve the properties of polyethersulfone membranes for the effective separation of humic acid. Sabri et al. [68] studied the antibacterial effects of arabic gum in the polysulfone membranes. The amphiphilic polymers like Tween [85] and Pluronic [117][40] were used for the enhancement of hydrophilicity. Amphiphilic polymers have a propensity to isolate the film surface with hydrophilic parts, while the hydrophobic fragments firmly attached to the membrane matrix [117][36]. Gum arabic (GA) was used for membrane modification to improve antibacterial ability [116][68]. The GA contains -OH groups in its structure which have the potential to enhance hydrophilicity [21]. However, enhancement of hydrophilicity, fouling mitigation, and removal of NOM in water is scant for the GA modified membrane. Contrary to the use of expensive polymer, this work explores the use of waste PVC as a membrane precursor that addresses the environmental problem and the economy of the membrane process as well. The novelty of work also enhanced by increasing hydrophilicity of prepared waste plastic-based membranes by using gum arabic (GA) as a biopolymer.

Therefore, the objectives of the study are to utilize an environmental pollutant (waste plastic, i.e. waste PVC) to tackle another environmental issue (water treatment) by fabrication of membrane using waste PVC and improving its hydrophilicity through the incorporation of gum Arabic (GA) which is a sustainable biopolymer as a green alternative. Waste PVC was chosen as an alternate source of membrane precursor in this study because of its dual benefits of reduction in membrane cost as well as reduction of adverse effects on the environment. Thus, waste PVC incorporated GA based membranes were made-up through the non-solvent stimulated phase transformation process. The interactions between the waste PVC/GA (at different loadings) were analyzed using various analytical techniques and subsequently, it was used for natural organic matter (humic acid) removal from water. The outcome delivered environmental benefits, conforming to the circular sustainability policy.

5.2 Experimental

The interaction between the waste polyvinyl chloride and gum arabic with different loadings (1 - 5 wt. %) investigated. The experimental process diagram is presented in Figure 5.1. Whereas, the aspect of methodology regarding the preparations, characterization, and filtration techniques are stated in detail under Chapter 2: Materials and methods section.

Figure 5.1: Schematic representation of the process

5.2.1 **Materials**

The main polymer utilized in the dope solution was waste polyvinyl chloride (PVC), while gum arabic (GA) was incorporated as a green additive supplied by Sigma-Aldrich Co., India. N-methyl pyrrolidone (NMP) the solvent used was supplied by Sigma-Aldrich Co., with reagent grade purity. While deionized (DI) water obtained from the Millipore system was the non-solvent used in the coagulation bath. For the rejection studies, Humic acid (HA) was obtained from Otto Chemie Private Limited, India.

5.2.2 **Preparation of membranes**

The membranes were prepared through the phase inversion method, details presented in chapter 2 (materials and methods). Various membranes with different compositions as depicted in Table 5.1 were fabricated by dissolving the materials in an organic solvent (NMP) using borosilicate glass, heated with a heating mantle at 60 ± 5 ◦C for overnight at an agitation speed of 500 rpm. The solution was later degassed by keeping in a vacuum oven for 12 hours after five minutes of sonication. As detailed in chapter two: materials and methods under section 2.2.

Table 5.1: Composition of the fabricated membranes

Membranes	Codes	Waste PVC (wt. %)	GA (wt. %)	Solvent NMP
PVC/GA0%	MG0	15	0	85
PVC/GA1%	MG1	15	1	84
PVC/GA3%	MG3	15	3	82
PVC/GA5%	MG5	15	5	80

5.2.3 Membrane characterization

The membranes were characterized using field emission scanning electron microscopy (FESEM), equilibrium water content (EWC), contact angle measurement, porosity, pore size, attenuated total reflectance in conjunction with Fourier transform infrared spectroscopy (FTIR-ATR), thermo-gravimetric analysis (TGA) and electromechanical universal testing machine (UTM). The membrane performance was evaluated by pure water flux (PWF) and Humic acid (HA) removal. Details of the membrane's characterization procedures were presented in chapter 2; materials and methods under section 2.4, accordingly.

5.3 Results and discussion

5.3.1 Morphological studies of the membrane

The FESEM images of the membranes were scanned via Sigma 300 and are displayed in Figure 5.2. It was observed that the GA incorporated membranes are having better pore formation than the unincorporated one (MG0). This can be ascribed to the hydrophilic moieties of the polysaccharides that influence the phase inversion process. Although, the sponginess and pore dimensions tend to suppressed when the loading of GA was improved in the dope solution from three to five percent. It is visible in Figure 5.2 that the surface of MG0 is smooth with less porosity while the porosity was enhanced by the addition of GA from 1 wt. % and 3 wt. %. Nevertheless, the porosity repressed when the concentration of GA was amplified to 5 wt. %. The micro-void formation is noticeable at 3 wt. % loading of the GA. This is also discussed in the subsequent section. The task of the biopolymer (GA) in the development of the membrane porosity is clearly like other macromolecular additives, that are identified to influence the subtle stability of thermodynamics and kinetics in a dope solution [15][100]. Subsequently, a permeable film structure with a finely spongy skin layer is obtained. Similar morphology was reported when biopolymer was added as a new pore-former by other researchers [65][15].

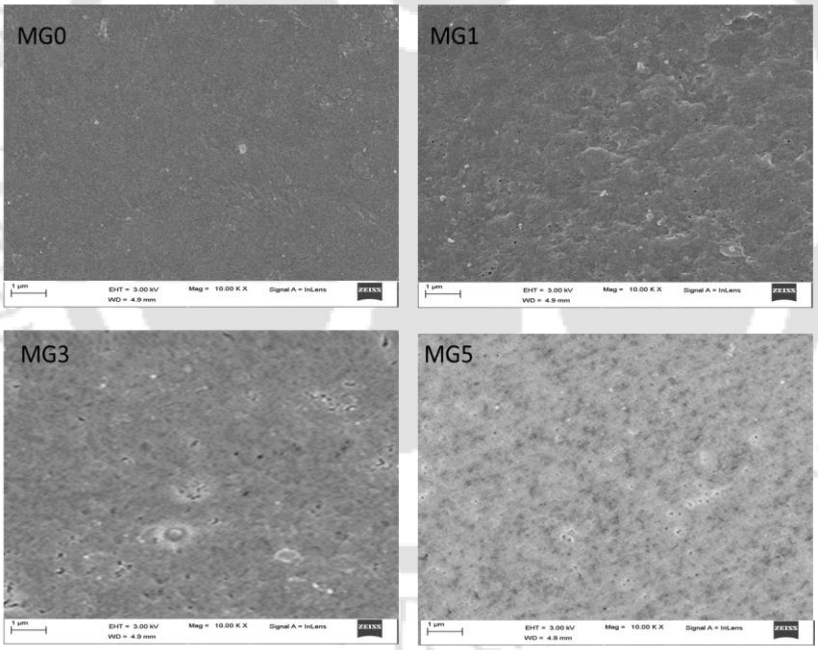

Figure 5.2: FESEM images of MG0, MG1, MG3, and MG5 membranes

5.3.2 **FTIR**

The FTIR-ATR spectra of the prepared films (MG0, MG1, MG3, and MG5) are depicted in Figure 5.3. The spectrum of the GA powder and the waste PVC/GA blended membranes are generated via an upper and lower wavenumber gap of 3500 to 700 cm^{-1}. The lower region of the wavenumber is credited to the unique fingerprint of the materials. Thus, the wavenumber at 864 cm^{-1} might be credited to the C-Cl of the waste PVC layer which is existing both in the incorporated and non-GA incorporated waste PVC base membranes. The wavenumbers at 1013 cm^{-1} which implied the presence for – CH band have also been observed representing the band from polysaccharides. The characteristic band of C-C stretch for both aliphatic and aromatic galactoproteins of the GA can be seen at around 1602 cm^{-1} [118] and its corresponding appearance was also noted after the blend. This may be due to the synergistic interaction between the waste PVC and the biopolymer (GA). The characteristics band in the wavenumber section of 3000 – 3500 cm^{-1} for the amino group has been concealed by the broad absorption peak at 3234 cm^{-1} for -OH group [61][119]. This could be one of the recipes for the hydrophilicity enhancement within the membrane. While the one at 2916 cm^{-1} indicates C-H stretching vibrations. Therefore, this justifies the components of the membranes.

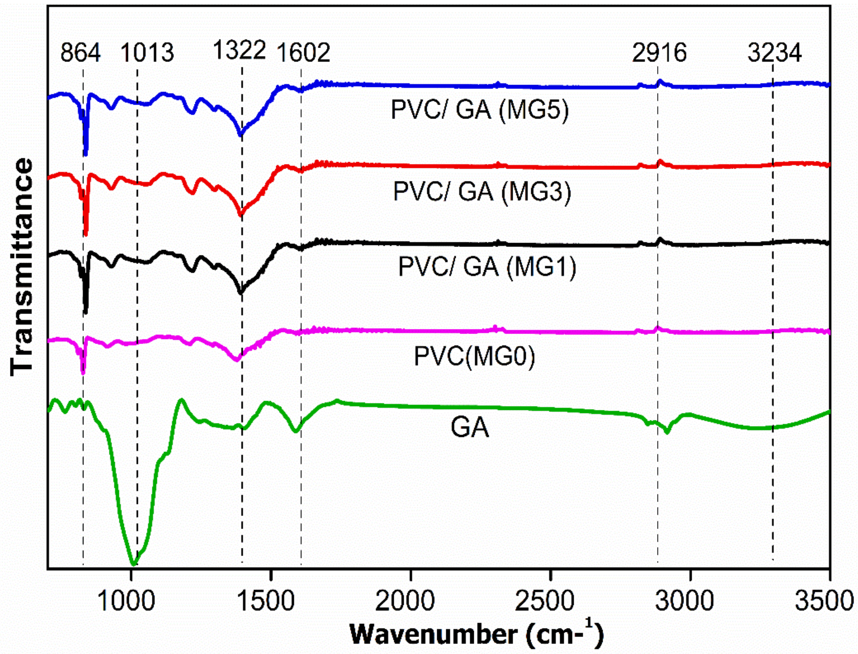

Figure 5.3: ATR-FTIR of the casted membranes

5.3.3 **Thermal analysis (TGA)**

Heat stability of the membranes (MG0, MG1, MG3, and MG5) was analyzed using TGA. The result was displayed in Figure 5.4. All the samples showed three degradation stages which affirm that the waste material utilized was PVC. Polyvinyl chloride normally has three levels of degradation [17] [18]. The first stage represents dehydrochlorination, and the other two are chain elimination and decomposition (char formation). These segments were appropriately demarcated in the thermogram (Figure 5.4). The onset degradation temperature for the unmodified waste PVC based membranes (MG0) was seen at ~ 230 °C. Whereas, for the films which are incorporated with different concentration of GA shows improved onset decomposition temperature around ~ 260 °C. This could be attributed to the addition of GA, it has been conveyed that the onset degradation temperature for polysaccharides gums is about 260 °C [119]. This signified that GA incorporated membranes have satisfactory heat stability much after modified with the biopolymer. Hence, it can also be applied in hot streams apart from the water filtration.

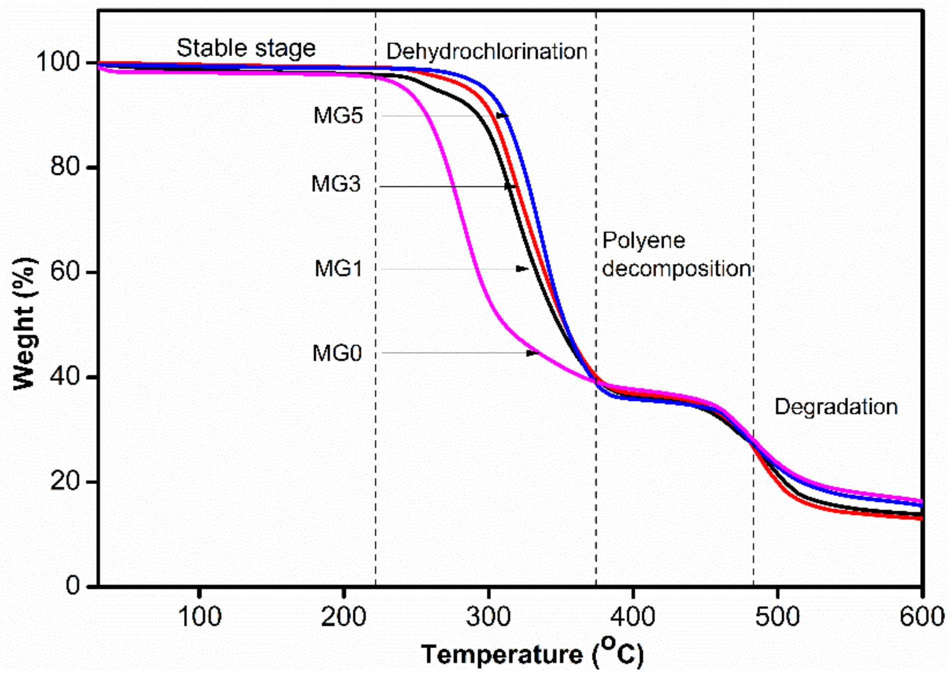

Figure 5.4: TGA of the different membranes casted

5.3.4 **Mechanical studies**

The mechanical test helps in predicting the durability and pressure capability of the membranes. An electromechanical universal testing machine (UTM) with a motorized screw mechanism was employed to determine the tensile strength and percentage elongation of the membranes. The outcomes are revealed in Fig. 5.5. The incorporation of GA into the membrane solution affected the mechanical properties of the samples. The membrane MG0 was prepared without the addition of GA, had about 3 MPa tensile strength. Incorporation of GA improved the tensile strength to 3.6 MPa at 1 wt.% and 3.4 MPa at 3 wt. % loading. The slight decrease of the mechanical strength and % elongation for the MG3 membrane could be ascribed to the enhanced porosity of the membrane. Similar behavior was reported elsewhere that membrane with loose porous structure has lower mechanical properties [120]. At 5 wt. % loading of GA into the solution, the membrane demonstrated the highest tensile strength of 4.2 MPa. This phenomenon could be attributed to the suppressed porosity nature at higher loading (as explained in Section 5.4.1). Suppressed micro-voids tend to increase tensile strength [79]. Likewise, the % elongation also enhanced as the GA concentration was amplified from 0 wt. % to 5 wt. % within the waste PVC casting solution. The % elongation of around 23.8 % was recorded for the MG5 membrane as against 14.2 % for the MG0 membrane. This improvement could be attributed to its plasticizing effect and the amphiphilic moieties of the gum arabic interacting with the hydrophobic backbone of waste PVC. A similar scenario was reported in another study [121]. Nevertheless, the MG3 membrane showed a low percent elongation of ~ 17 %, compared to the MG1 membrane. This was due to the formation of micro-voids and its corresponding relatively highest porosity of ~ 67 %, as elucidated in the subsequent section. However, MG5 has a higher voidage and better mechanical strength than MG1. This is because it has a higher percentage of gum arabic having a plasticizing effect which resulted in improved mechanical strength. Therefore, the incorporation of GA not only improved permeation parameters but also the mechanical characteristics which could be beneficial for the mechanical and pressure durability of the membranes in real-life applications.

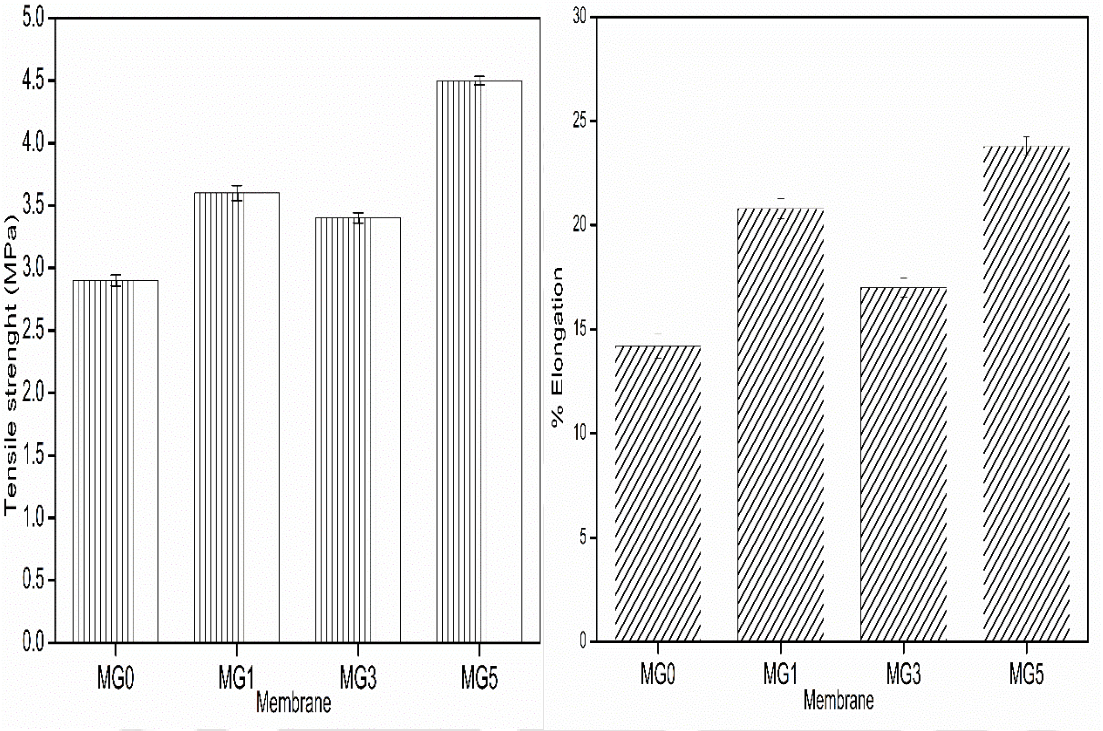

Figure 5.5: Tensile strength and % elongation of the membranes

5.3.5 Percentage of water content

Percent of water content is one of the important parameters that is closely linked with pure water flux and porosity in membrane characterization. It is also termed equilibrium water content (EWC) [89]. The results of the EWC is presented in Figure 5.6. The percentage of water content increased from 60% to 73% when the GA incorporation increased from 1 wt. % to 5 wt. %. Increasing the GA percentage in the casting solution enhanced the EWC significantly. This is credited to the hydrophilic/amphiphilic characteristics of GA [68]. However, EWC is closely linked with membrane porosity which by extension relates to pure water flux. Again, pure water flux is mutually related to surface hydrophilicity [54]. The improved hydrophilicity is also evident from the contact angle results and porosity as discussed in the subsequent section. As pores normally happened to be water molecules abode [14]. This outcome agreed with the result of pure water flux and porosity as described in the subsequent sections.

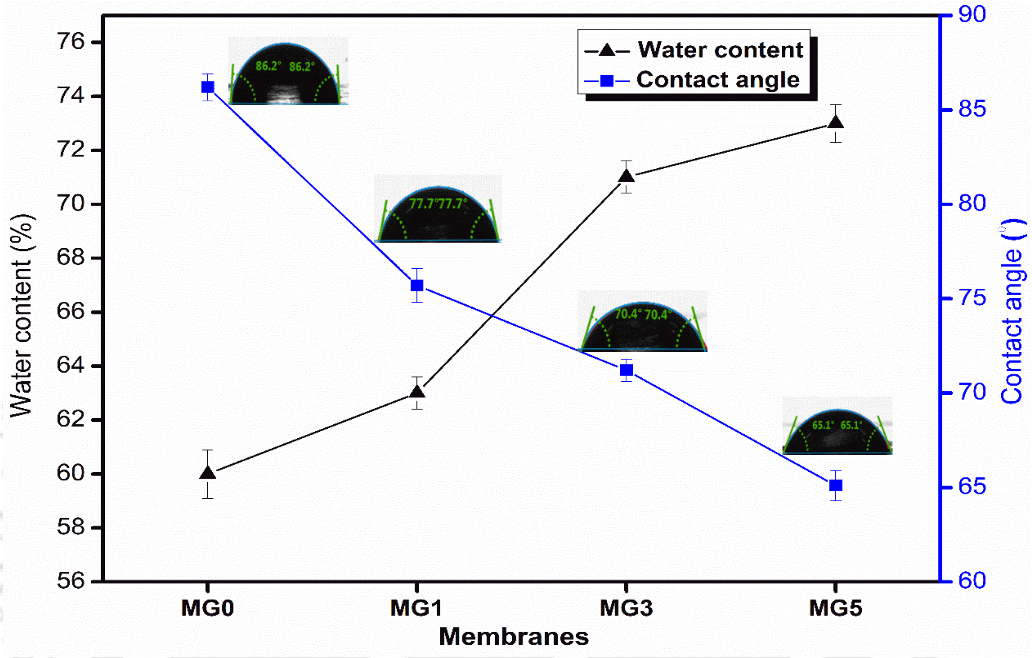

Figure 5.6: Percent of water content and contact angle

5.3.6 **Hydrophilicity**

Static water contact angle (SWCA) measurement is an analytical means of determining the hydrophilicity of membranes [22]. The result is shown in Figure 5.6 along with that of EWC. The outcome illustrates that hydrophilicity of the samples was boosted by the incorporation of GA into the membrane due to its affinity with water. The MG0 showed the highest SWCA of 86.2 ± 1.7 ° signifying the least hydrophilicity owing to the hydrophobic behavior of the base polymer. Incorporation of GA reduced the SWCA to 77.7 ± 1.9° (MG1), 70.4 ± 1.6° (MG3), and 65.1 ± 1.4 (MG5), respectively. This translates to a reduction in contact angle thereby indicates improved hydrophilicity

[98][98]. The reason behind the drop might be ascribed to the polysaccharides fragments of GA to hydrophilized the membrane surface [121]. Whereby, the hydrophobic polypeptide chain could link to the hydrophobic backbone of the waste PVC exposing the hydrophilic polysaccharide moieties to the surface thereby enhancing the hydrophilicity of the membranes (Figure 5.7). This outcome is supported by the data of EWC and pure water flux. Improvement of hydrophilicity would enhance the membrane characteristics especially in water flux and fouling mitigation.

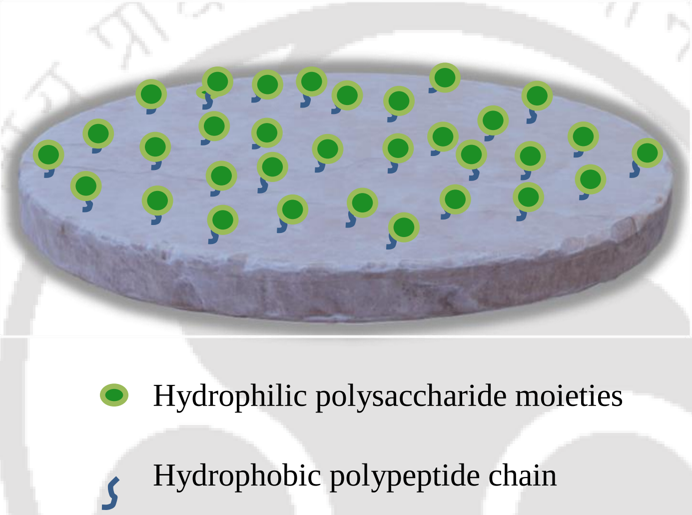

Figure 5.7: Plausible scheme depicting the role of AG for hydrophilicity enhancement

5.3.7 **Porosity and pore size**

Porosity and pore size are significant factors in determining membrane performance [69]. The membrane sponginess and pore radius are presented in Table 5.2. The porosity signifies an increasing trend from 43.1% (MG0) to 66.6% (MG3) as the fraction of GA augmented from 0 to 3 wt. %. This rise in sponginess might be credited to the hydrophilic moieties of GA. This outcome is also in agreement with the results of EWC as discussed in the previous section, as pores tend to accommodate water molecules. Nevertheless, when the concentration of GA incorporation was amplified to 5 wt. %. The porosity dropped by 7% (MG5). This could be clarified based on the fact that an intensification in viscosity of dope solutions reduces the de-mixing progression and as a consequence, a membrane with lesser penetrability could be made [100]. Similarly, the pore radius tends to improve as the GA supplemented the waste plastic dope solution. About 33% pore size variation was noted. Although the pore radius decreased by around 10% when 5 wt. % of the biopolymer (GA) was introduced. This is because rising the polymer concentration (wt. %) while keeping the solvent constant leads to an increase in solution viscosity. Hence, delayed de-mixing happened, and suppressed void formation was obtained due to thermodynamic instability. This phenomenon has been explained by researchers [99][93]. The membrane pore size varies between 22 – 33 nm which falls within the range of 2 – 100 nm and can be classified as an ultrafiltration membrane.

Table 5.2: Permeation parameters of the various membranes

Membranes	Codes	PWF (L/m^2h)	CF	Pore size (nm)	Porosity (%)
PVC/GA0%	MG0	51	1.17	22	43.1
PVC/GA1%	MG1	85	1.08	27	54.6
PVC/GA3%	MG3	98	1.08	33	66.3
PVC/GA5%	MG5	93	1.05	30	61.7

5.3.8 Pure water flux (PWF) and compaction factor

The permeation abilities of the films were determined by using Equation (2.4) and the outcome is presented in Table 5.2. The advantage of the integration of GA into the membrane matrix was evident from the outcomes of PWF. The flux increased from 51 L/m^2h to 93 L/m^2h as the percentage of GA was augmented up to 3 wt. %. This could be ascribed to the hydrophilicity and porosity enhancement by the biopolymer (GA) as explained in the previous sections. A similar outcome was reported by others on integrating Xanthan gum into polyethersulfone membranes [65]. However, the flux decrease was noted when GA loading was increased further. This was expected as 5 wt. % loading showed a slight reduction in sponginess and skewed pore size due to the increase in viscosity of the dope solution. Rising the polymer concentration (wt. %) leads to an increase in solution viscosity which reduces the de-mixing progression. MG3 has the highest pure water flux due to greater surface pore size and porosity. Apart from membrane surface hydrophilicity, porosity, and pore radius are the important factors influencing membrane permeation [15]. The membrane compaction was evaluated using the initial and the final stable PWF. The influence of compaction on the membrane's flux is represented in Figure 5.8. All the membranes showed some decline in flux at the initial onset and reached flux stability at around one hour of pure water permeation because of compaction (C.F). This was due to the suppression and reorientation of the pores because of the applied transmembrane pressure [54]. The membranes prepared from both the components displayed a similar compaction rate.

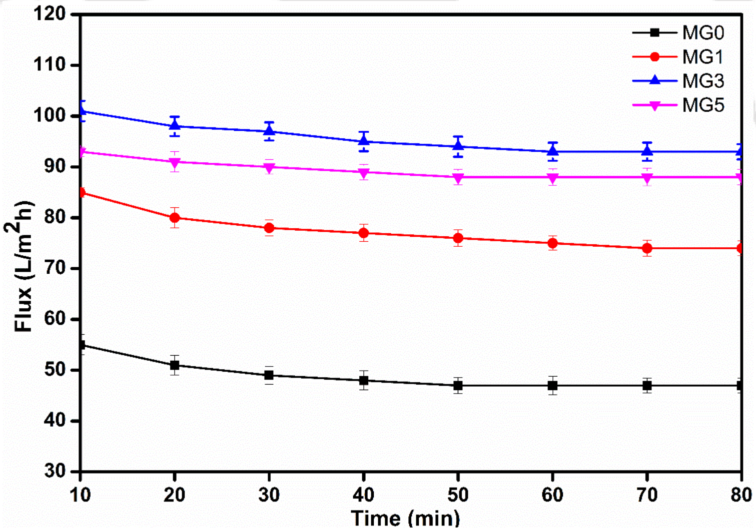

Figure 5.8: Flux pattern of the membranes

5.3.9 Removal of natural organic matter

The samples (MG0, MG1, MG3, and MG5) were applied for the rejection of Humic acid as a model for natural organic substances in water using the same set up for the water permeation studies. The concentrations of the Humic acid in the filtrate were evaluated using spectrometric at a wavelength (λ) of 254 nm and estimated by using Equation (2.5). The outcome is presented in Figure 5.9. The MG0 membrane has a rejection of around 81% whereas the incorporation of GA tends to increase the HA rejection by up to 96%. A similar improvement was also noted in the water flux. Although, during the permeation of humic acid decline of flux was noted due to fouling, and the effect was studied in the subsequent section. The molecular weight of the HA is up to 500 kDa. Hence, the membrane with the pore size range of 22 - 33 nm can be able to reject the molecules based on size exclusion mechanism. Even though, size exclusion is not the only mechanism in this process. The carboxyl group of GA has a negative charge [121], and HA contains acidic functional groups [116]. Deprotonation would cause the molecule to exhibit negative surface charges, generating charge repulsion [122]. Hence, under this condition repulsion of HA molecules electrostatically between the surface and the solute may increase the rate of rejection of the natural organic matter. Thus, MG5 has the highest rejection (96 %) owing to its pore dimensions, porosity, and surface chemistry because of the GA incorporation. While, MG0 with no GA, have the least rejection. This indicates that the biopolymer (GA) is an effective additive for HA mitigation and hydrophilicity enhancement in the waste PVC based membrane for the removal of NOM in water.

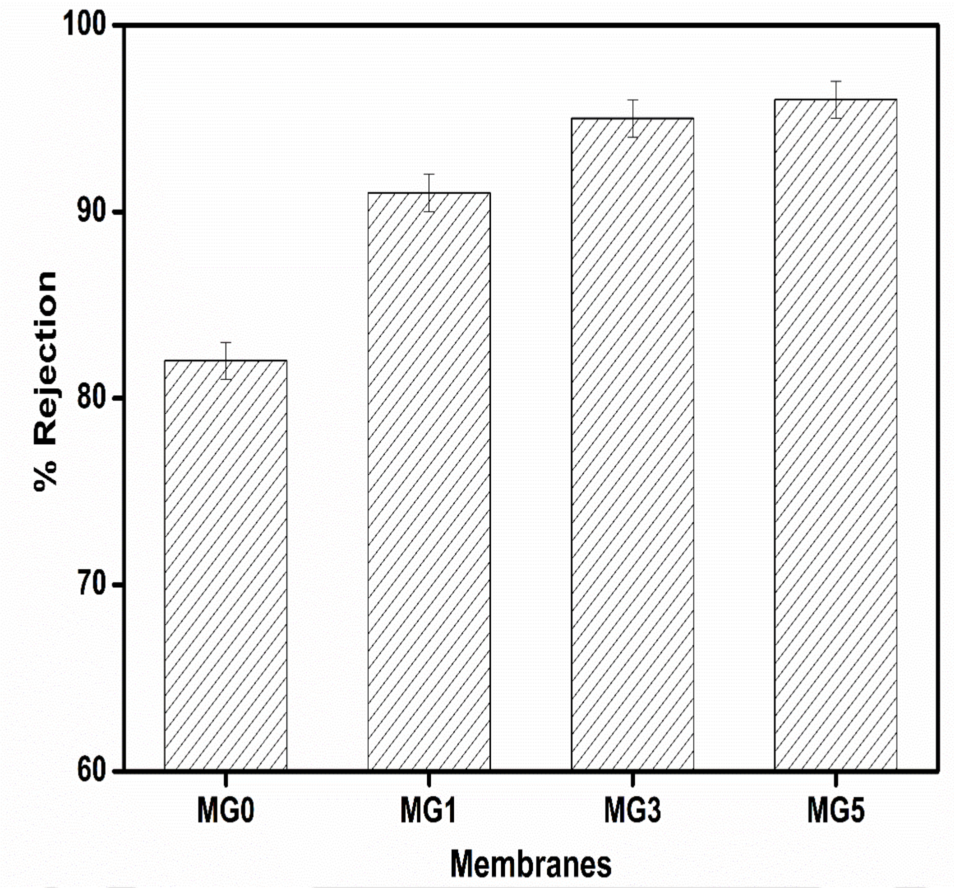

Figure 5.9: Percentage rejection of Humic acid

5.4 Studies on fouling ratios

The pure water flux (F_{W1}), flux during filtration of HA (F_{HA}) solution, and the second cycle of pure water flux (F_{W2}) after HA filtration are shown in Figure 5.10. The pure water flux of 51 L/m^{2}h (MG0), 85 L/m^{2}h (MG1), 98 L/m^{2}h (MG3) and 93 L/m^{2}h (MG5) were observed. While the flux during permeation of HA were 11 L/m^{2}h (MG0), 23 L/m^{2}h (MG1), 31 L/m^{2}h (MG3) and 32 L/m^{2}h (MG5) respectively. The decline in the flux was noted due to membrane fouling during the permeation of the HA solution. Thereafter, the membrane was cleaned using DI water as described in section 2.3.7 and the second cycle of pure water permeation was carried out with the following flux 31 L/m^{2}h (MG0), 62 L/m^{2}h (MG1), 76 L/m^{2}h (MG3) and 74 L/m^{2}h (MG5). These variations in flux were used to study the fouling and flux recovery ratios of the membranes. The fouling properties of the membranes were estimated by the different fouling ratios and the flux recovery ratio (FRR). The total fouling ratio (TFR) is the summation of the reversible fouling ratio (RFR) and the irreversible fouling ratio (IFR) [54]. These parameters were calculated based on the permeation of the HA (F_{HA}) and the corresponding pure water fluxes (F_{W1} and F_{W2}).

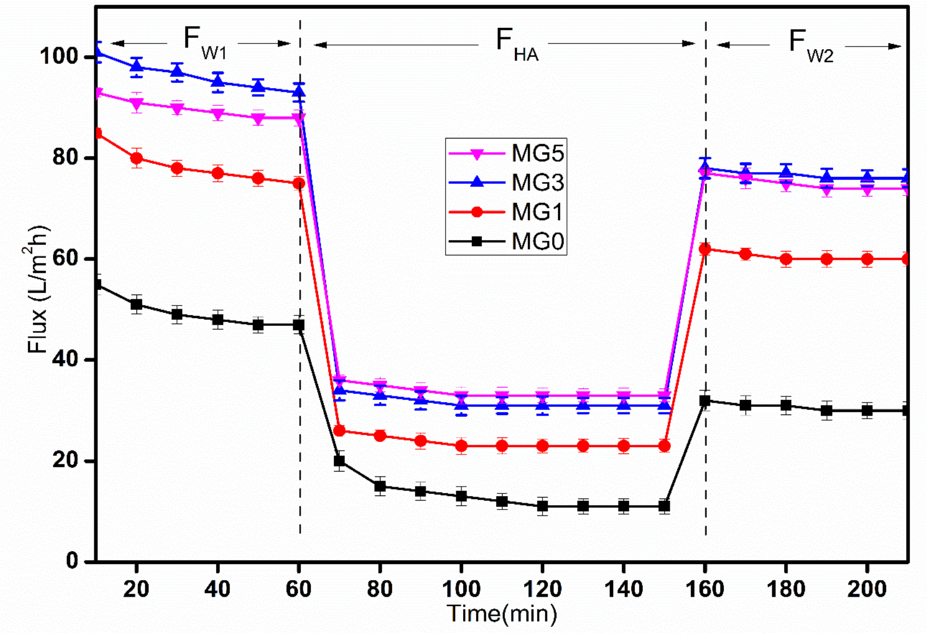

Figure 5.10: Fouling profile flux rate of the membranes

The outcomes of the ratios are shown in Figure 5.11. The TFR of MG0 was 79 %, indicating a substantial decrease in flux. The TFR decreased to 73 % with the incorporation of 1 wt. % GA into the waste PVC dope solution. Subsequently, 68 % and 66 % TFR were recorded for MG3 and MG5, respectively. The total fouling ratio is an index of membrane flux loss. The reduction of TFR from 73 % to 66 % showed an improvement in the antifouling effect of the membranes. Hence, the lesser the TFR, the better the membrane. Another beneficial aspect was the pattern observed for the RFR and the IFR. The RFR increased from 40 % to 46 % while the IFR decreased from 40 % to 20 % as the loading of GA increased from 0 wt. % to 5 wt. %, respectively. This meant that the blended membranes could easily be washed to reverse their flux. The flux recovery rate (FRR) is an indicator of membrane durability and the rate of recovery after hydraulic cleaning [14]. The FRR of the membranes improved significantly as the GA wt. % was increased. The FRR of 60 % (MG0), 73 % (MG1), 77 % (MG3) and 80 % (MG5) were observed. This showed an enhancement of about 32 % FRR at 5 wt. % GA loading. This is credited to the hydrophilic behavior of the additive which inhibited the hydrophobic moieties of the waste PVC. It also agreed with the outcomes of the contact angle, as explained in Section 5.4.6. Higher FRR signifies better antifouling property [56]. This indicated that the incorporation of the biopolymer (GA) into the backbone of the waste PVC improved the antifouling behavior of the prepared membrane.

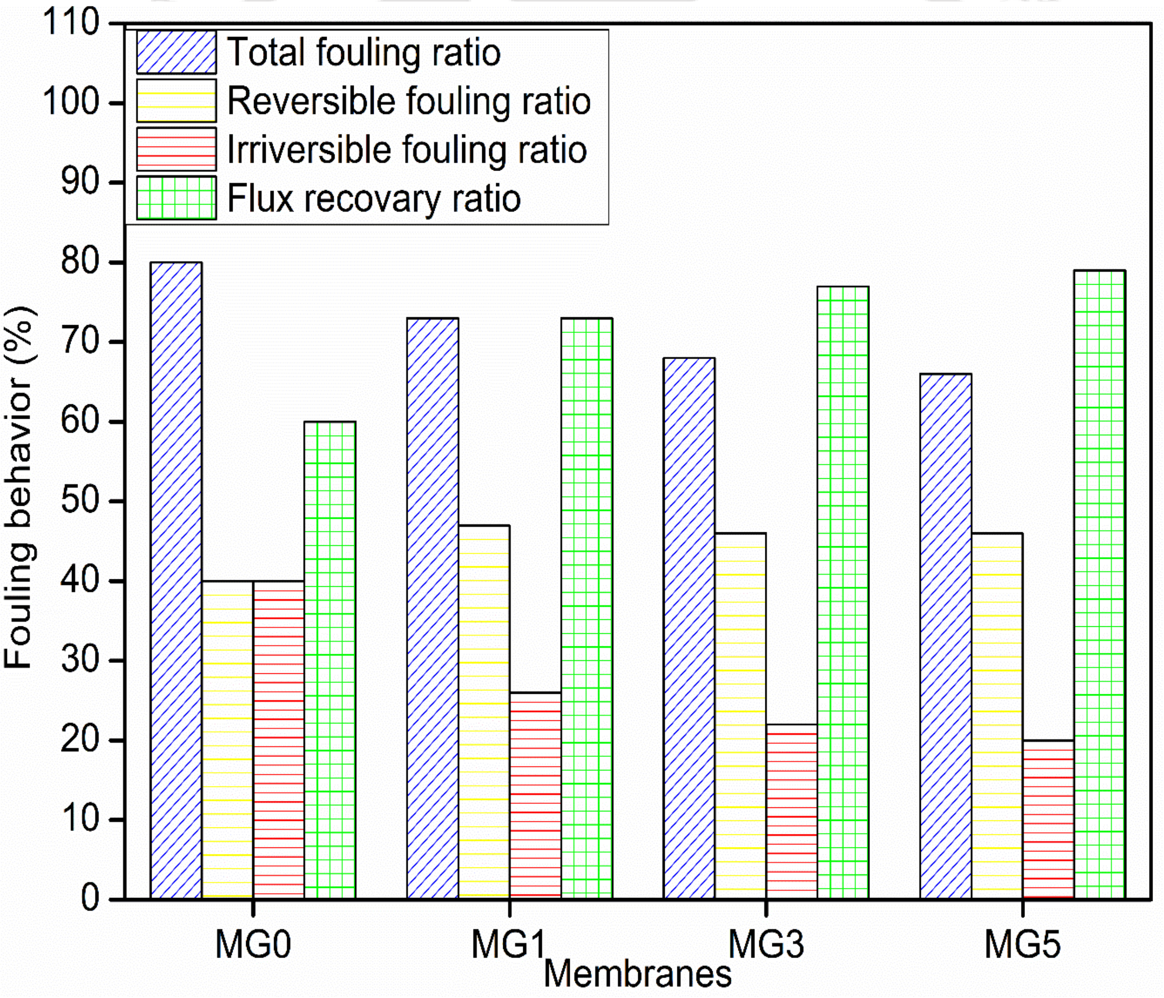

Figure 5.11: Fouling and flux recovery ratios

5.5 Performance comparison with existing work

The performance of the prepared membranes was compared with some articles that reported the removal of humic acid. The compared parameters are presented in Table 5.3. It can be envisaged that the result of the current work relates well with reported works [48][41]. Membrane permeability and selectivity are two outstanding membrane parameters that determine performance [113]. Hence, the flux (98 L/m^{2}h) and rejection (96 %) in this work compared positively with other cited reports [86][44]. Hence, this indicates that the incorporation of a biopolymer (GA) into the waste PVC has enhanced the parameters and performance judiciously.

Table 5.3: Humic acid removal compared with referred articles

Membrane	Material origin	Polymer (Wt. %)	Contact angle (θ)	HA (%) Rejection	PWF (L/m^{2}h)	Reference
PVC-PAN	New	15	-	94	114	[48]
PVC-ZnO-NPs	New	13	46.2	73.5	122.2	[41]
PVC-PEG	New	17	86.1	66.67	72	[86]
PVC-MPC-PPGMA	New	15	130	96	97	[44]
PVC-PF127	New	15	67	45.6	68.6	[40]
PVC-GA	**waste**	**15**	**66.7**	**96.0**	**98**	**This study**

Furthermore, most of the cited literature has a similar range in weight concentration (15 %) of base polymer for membrane fabrication. Although, the material used for the fabrication in this work is not pristine. This has shown the precursor is of low-cost compared to the existing literature as no cost was expended on the base polymer. Signifying economic and environmental benefits. Thereby, conforming to the circular sustainability policy of the world.

5.6 Summary

Waste plastic incorporated gum arabic base membranes were fabricated and their properties were assessed. The biopolymer incorporation improved hydrophilicity as it reduced contact angle from 86 ° to 65 °, and in turn, improved water flux from 51 L/m^2h to 93 L/m^2h. The outcome infers that gum arabic (GA) is a good hydrophilicity enhancer, fouling mitigator as it decreases fouling ratio by ~18%, and a green alternative for membrane improvement. The FTIR spectroscopy revealed wavenumbers conforming to C-Cl, OH, and CH_2 that indicates the components of the films. The outcome of TGA also confirmed that the waste material used is polyvinyl chloride (PVC) as three degradation stages were observed with an improved T onset of ~ 30 °C due to GA incorporation. Porosity was enhanced to around 35%, although suppressed porosity (~ 10%) and pore radius were observed at higher loading. A substantial amount of natural organic matter (HA) was removed in water and an improved flux recovery ratio (80 %) was noted. In short, this investigation shows that GA is a promising substance that can be utilized for improving waste plastic-based ultrafiltration membranes with enhanced parameters for the execution of water treatment processes.

Chapter 6
Conclusions and Recommendations

Chapter 6

Conclusions and Recommendations

This is the terminal chapter in which the findings of the work are summarized in a conclusive form to highlights the inferences. It also presents some suggestions recommended for future work based on the present work.

6.1 Conclusion

The work focused on the utilization of abundant waste plastic to reduce the menace of waste plastic on environmental degradation. The use of waste plastic as a precursor for polymeric membrane material has been tested and was found to be beneficial. Waste plastic derived PVC membranes were fabricated by blending with cellulose acetate. The result shows an improved pure water flux with a BSA rejection in water. In another development, the effects of additives and solvents on the waste plastic base membranes were ascertained. Efforts were also made to incorporate a biopolymer (gum arabic) as a green alternative additive to improve the characteristics and performance of the waste plastic base membranes for the removal of natural organic matter (humic acid) in water. This enhanced the hydrophilicity, mitigate fouling, and improved flux recovery ratio with sufficient natural organic matter (Humic acid) removal in water. The outcome compared favorably with membrane prepared with a pristine precursor. Generally, the work proposed that waste plastic (PVC) could provide an alternative means for membrane precursor in water filtration and its properties can be tailored with appropriate additives and solvent for targeted applications. Optimistically, this outcome would help in adding value to waste plastic via membrane fabrication and its subsequent application in the filtration process.

A recap of the conclusion drawn from the experimental work is highlighted below in points chapter wise.

Utilization of Waste Polyvinyl Chloride (PVC) Blended with Cellulose Acetate for UF Membrane Fabrication and its Application (Refer to chapter 3)

- Waste plastic derived PVC membranes were fabricated by blending with cellulose acetate.
- TGA results confirmed that the waste material used was PVC, as it shows the three degradation stages of PVC.
- Blending with cellulose acetate has improved the porosity and the hydrophilicity of the casted membranes.
- BSA rejection of 91 % and water flux of 85 L /m^2 h were recorded, respectively.
- Therefore, it can be concluded that waste PVC can be considered as a precursor for membrane fabrication.

Influence of Additives (PEG, PVP) and Solvents on Waste PVC Membrane: Characterization and Performance Studies (Refer to chapter 4)

- The properties of waste PVC based membrane using different additives and solvent were evaluated.
- The membranes prepared using PVP additive showed greater voids and finger-like structure when compared to the ones formed with PEG.
- HSP was computed and it indicated that the NMP with 4.8 $(MPa)^{1/2}$ has better interaction with the base polymer than DMAc with 7.5 $(MPa)^{1/2}$.
- The performance was evaluated by the removal of humic acid.
- The outcome indicated that PEG has better rejection with compromised flux while PVP has high flux and the mixed additives give combined benefits.

Biopolymer (gum arabic) Incorporated Waste PVC Membrane for Hydrophilicity Enhancement and Natural Organic Matter Removal in Water (Refer to chapter 5)

- Waste plastic incorporated gum arabic membranes were fabricated with enhanced hydrophilicity.
- The modified membrane exhibited an improved flux from 51 L /m^2h to 93 L /m^2h with 96 % Humic acid rejection in water.
- Biopolymer (gum arabic) incorporation improved antifouling properties with an enhanced flux recovery ratio of 80 %.
- The onset degradation temperature was improved and the mechanical strength was enhanced by ~ 1.2 MPa
- Generally, the outcome support incorporation of gum arabic as a green alternative additive for enhancing waste plastic-based membranes parameters in water filtration.

6.2 Recommendation for future work

In this section, a brief outline of the recommendation for carrying out future research in line with the present outcome is presented.

- Exploration of other waste plastic for membrane fabrication for a selective application can be investigated.
- Application of waste PVC membrane for other filtration processes like oil/water separation can be considered.
- Comparative studies on the development and performance of waste plastic membrane in relation to its pristine counterpart under the same preparation conditions can be carryout out.

- Modification of waste plastic membrane using other sustainable polymers as an absorptive membrane for the removal of heavy metals can be deliberated.
- Incorporation of crystalline cellulose for its, mechanical, performance, and antimicrobial properties of waste plastic-based membrane in water filtration can be studied.

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