

ENHANCED BIOFOULING PROPERTIES OF POLYETHERSULFONE MEMBRANES USING MULTI-
FUNCTIONAL THERMO-RESPONSIVE POLYMERS FOR ULTRA-FILTRATION APPLICATIONS

by

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ABSTRACT

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The accumulation and growth of microorganisms on a membrane surface, known as membrane biofouling, has been a significant issue in the effective use of membrane technology for water and wastewater treatment. To overcome these challenges, this study aimed to modify the surface of a polyethersulfone (PES) membrane through the use of a multi-functionalized thermo-responsive polymer. The primary objectives of chemical treatment on membrane surfaces are to enhance surface hydrophilicity and provide anti-bacterial/biocidal properties.

To evaluate the effectiveness of these modifications, the performance of the modified membranes was tested for their ability to resist biofouling through filtration of bovine serum albumin (BSA), and to inhibit adhesion and growth of *Escherichia coli* bacteria, respectively. The membrane's separation performance was evaluated based on its ability to separate oil-water emulsions and bovine serum albumin (BSA).

The experimental results clearly demonstrated that grafting poly(N-isopropyl acrylamide) and immobilizing copper oxide nanoparticles on the membrane surface enhanced its hydrophilicity, which was indicated by a significant decrease in bulk contact angle. This increase in contact angle plays a crucial role in preventing bio-foulants from attaching to the membrane surface. The mechanism by which increasing the hydrophilicity reduces the biofouling is related to the

interactions between the membrane surface and the foulants. A more hydrophilic membrane surface can form a thin layer of water on its surface, which can act as a barrier to prevent the adhesion of foulants[1], [2]. A more hydrophilic membrane surface can also reduce the interfacial tension between the membrane and the feed water, which can lower the resistance to water permeation and enhance the self-cleaning effect of the membrane. Additionally, a more hydrophilic membrane surface can reduce the electrostatic attraction between the membrane and the foulants, especially for negatively charged foulants such as bacteria or proteins [3]–[6]. Moreover, the receding contact angle of the thermo-responsive grafted membrane exhibited changes with variations in solution temperature, whereas this value remained constant for both the pristine PES membrane and unmodified membranes, indicating the phase volume transition behavior of PNIPAm in this study [7].

The surface charge of the membrane demonstrates (in sections 5.1.1.4 and 5.1.2.4) that grafting thermo-responsive polymers does not have a significant effect on the surface charge. However, the immobilization of copper oxide nanoparticles enhances the surface charge negativity, which occurs due to the deprotonation of the membrane's surface in the presence of metal oxide nanoparticles [8]. In addition, the synthesized membranes were subjected to surface characterization using scanning electron microscopy (SEM). The results showed that the membrane morphology and pore size were not significantly affected by the polymer grafting and copper oxide functionalization as discussed in “Chapter 5-Results and Discussion”.

A water filtration test was conducted using a cross-flow filtration system, and the results indicated an improvement (from 68.8 ± 0.16 L/m²h for bare PES to 80.0 ± 0.19 L/m²h for PES-g-15% PNIPAm) in water flux rate after the modification processes, likely due to the enhanced

hydrophilicity of the membrane surface. Since more hydrophilic membrane surface can reduce the interfacial tension between the membrane and the feed water, the resistance to water permeation can be lowered and enhance the water flux rate. Moreover, after cleaning the membrane with cold and warm water cycle, the thermo-responsive grafted membrane exhibited a higher flux recovery ratio and reversible fouling ratio, verifying that fluctuations in temperature did result in phase transition, and that the phase transitioning resulted in foulant detachment.

Furthermore, the results revealed that the incorporation of organic and inorganic materials had an adverse effect on the phase transition behavior of PNIPAm, resulting in a decrease in the membrane's cleaning efficiency. This was evidenced by lower flux recovery ratio and reversible fouling amount in the modified PES membrane.

The membrane's separation performance was evaluated in terms of its ability to separate oil-water emulsions. All membranes showed good performance in removing oil-water emulsions, but the membrane functionalized with copper oxide nanoparticles exhibited a superior rejection rate compared to the others, with a separation efficiency of >99% due to its increased surface hydrophilicity. Meanwhile, the PNIPAm-grafted PES membranes exhibited only slightly improved oil rejection performance compared to the unmodified PES membrane. Specifically, the bare PES membrane had a rejection rate of 96.9%, while the PES-g-25%PNIPAm membrane showed an even better rejection rate of 98.4%.

In general, the oil-in-water emulsion separation capability in membrane filtration is determined by two mechanisms, namely size exclusion and hydrophobic/hydrophilic interactions between the feed solution and the membrane surface. The hydrophilic nature of the membrane surface plays a crucial role in regulating the water/oil attraction. Therefore, a membrane surface with

increased hydrophilicity will easily form a hydration layer to impede oil passage, resulting in improved water permeability and higher oil rejection rate. Additionally, the membranes functionalized with copper oxide nanoparticles demonstrated high toxicity towards *E. coli* and *B. cereus* bacteria strains, effectively killing >99% of bacteria in the suspension after 90 minutes of contact time [9].

Furthermore, we assessed the concentration of copper ions released into the permeate water through ICP-MS analysis. The findings revealed an exceptionally low concentration of copper ions, measuring less than 14.5 ppb (the ratio of leached Cu ions to total CuO on the membrane=2.40%). The achieved value resulted from five recycling runs, with each run involving 60 minutes of water flow followed by 150 minutes of BSA solution flow. This value represents approximately 2.40% of the total copper that can leach into the solution. The maximum allowable level of copper in drinking water, as set by the United States Environmental Protection Agency (EPA), is 1.3 mg per liter (1.3 ppm).

This underscores the remarkable stability of copper nanoparticles on the membrane surface, achieved by employing organic ligands to firmly immobilize the copper oxide nanoparticles through chemical bonds. These findings demonstrate the potential of modified PES membranes for water treatment applications and highlight the effectiveness of polymer grafting as a membrane modification method.

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To my beloved husband, Saeed, and my dear parents, whose unwavering inspiration, care, and love have been a constant source of support and encouragement

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Chapter 1 – Background and Introduction

1.1. Polymer membranes applications in ultra-filtration

Nano, ultra, and microfiltration are all membrane filtration processes that differ primarily in the size of particles they can separate. Microfiltration (MF) involves membranes with pore sizes typically ranging from 0.1 to 10 micrometers (μm). Ultrafiltration (UF), with a pore size range of 0.001 to 0.1 micrometers (μm), is utilized for the separation of macromolecules, colloids, proteins, and larger particles from liquids. Ultrafiltration is a membrane separation process that can be used for various applications, such as water treatment, food and beverage processing, pharmaceutical production, and biotechnology. Ultrafiltration membranes have different capabilities, limitations, and successful applications depending on their material, shape, configuration, and flow type. Ultrafiltration membranes can be made from different materials, such as polymeric, ceramic, or metallic. Polymeric membranes are the most widely used because they are cheaper, easier to fabricate, and more versatile. However, they also have some drawbacks, such as lower chemical and thermal stability, higher fouling tendency, and lower mechanical strength.

There are various types of polymeric membranes that can be used for ultrafiltration application as listed in Table 1-1, such as Polyether sulfone(PES) Polyvinylidene fluoride (PVDF), Polyamide (PE) , and Cellulose Acetate (CA) membranes. PE are microporous membranes with pore sizes ranging from 5 to 250 microns. They have good chemical resistance and can be used for microfiltration of particles, bacteria, and suspended solids. There are also other polymeric membrane such as Polypropylene (PP) which is also microporous membranes with pore sizes ranging from 100 to 300 microns. They have high thermal stability and can be used for microfiltration of hot liquids and gases. PVDF are hydrophobic membranes with pore sizes

ranging from 20 to 30 microns. They have good mechanical strength and can be used for ultrafiltration of proteins, enzymes, and viruses. [10], [11].

Table 1-1: comparison in terms of capabilities, limitations, and successful applications

Membrane	Advantages	limitations	Applications
PES	• High thermal resistance • Wide pH tolerance • Wide range of pore size (based on fabrication method) • High chlorine resistance	• Low operating pressure limit • Hydrophobicity	• Separation of nickel ions from aqueous solutions[12] • BSA Separation [13]
PVDF	• High mechanical strength • High thermal stability	• Hydrophobicity	• BSA Separation [14], [15]
PA	• Wide pH tolerance • High thermal stability	• Poor chlorine resistance	• Salt rejection [16]
CA	• Low cost • Hydrophilicity	• Low thermal resistance • Low chemical resistance	• Brackish water desalination [17]

1.1.1. Membrane filtration challenges and technology gaps

Membrane filtration is one of the major water treatment techniques that are commonly used due to their cost-effectiveness, rapid purification speed, and compatibility with other processes [18], [19]. The primary obstacle to membrane separation is the undesirable accumulation of microorganisms, primarily bacteria, on the membrane surface, which leads to the formation of biofilms [20],[21]. Bacteria fouling has severe impact on permeate flux and rejection rate, reducing the membrane's lifetime [22]. Studies reveal that nearly half of the weight of dry fouling layers in nanofiltration and reverse osmosis membranes are biologically derived [23]. Modification of the membrane's morphology, surface chemistry, charge, and hydrophilicity is crucial to better manage membrane fouling [24]. Although primary cleaning methods such as

chemical pretreatment of feed water can remove approximately 99% of bacteria, the remaining bacteria can regenerate and proliferate on the membrane surface. Hence, modification processes using active biocidal agents are critical in controlling bacterial growth during filtration processes [25].

1.2. Polyethersulfone membrane (PES)

Polyethersulfone (PES) is a widely used polymeric membrane in the fields of separation and purification, biomedical engineering, and medical devices due to its excellent mechanical, thermal, and oxidative properties [26].

What is unique about PES membranes is their high glass transition temperature (225 °C), which gives them high thermal stability and mechanical strength. They also have good chemical resistance and low protein and protein based drug substance binding characteristics, which make them ideal for nanofiltration and ultrafiltration of biological fluids, pharmaceuticals, and water [26]. PES membranes have an asymmetric pore structure, which enables controlled rejection at the surface while promoting maximum throughput of the membranes [27]. PES membranes are stable in water and act solely as a barrier during the separation process. However, one of the major challenges with PES membranes is their high fouling rate, which is attributed to their relatively hydrophobic surface and high adsorption rate for nonpolar solutes [28], [29]. The water contact angle (WCA) of polymeric membranes can vary depending on the fabrication method, the additives used, and the post-treatment applied. For example, in a study involving a pristine PES membrane, the water contact angle (WCA) was initially measured at 75.2°. However, when 0.2 wt% TiO₂ was introduced to create PES–TiO₂ membranes, the hydrophilicity improved, resulting in a reduced WCA of 66.4° [30]. In a distinct study, it was demonstrated that a grafting

yield of 12.8% of Poly(ethylene glycol) Methacrylate resulted in a decrease in the contact angle of the PES membrane from 72° to 10° [31].

1.2.1. PES membrane fabrication and modification

PES membranes are primarily produced using the phase inversion method. Phase inversion refers to the transition or change in the physical state of a system from one phase to another. In the context of membrane fabrication or polymer processing, it typically involves a transition from a homogeneous solution phase to a solid or porous membrane phase. The phase inversion reaction is the process of transforming a homogeneous polymer solution into a solid membrane with a porous structure. The phase inversion reaction condition can affect the PES properties in terms of morphology, permeability, selectivity, and antifouling performance [32]–[35]. The phase inversion reaction conditions depend on several factors, such as the polymer concentration, the solvent type, the non-solvent type, the additive type, the evaporation time, and the coagulation bath temperature.

For example, increasing the polymer concentration can increase the viscosity and the critical gelation point of the dope solution, which can slow down the phase separation process and result in a denser and smoother membrane surface [36]. A higher polymer concentration can also increase the mechanical strength and the selectivity of the membrane, but decrease the permeability and the porosity [37]. Additionally, the choice of solvent can affect the solubility parameter and the thermodynamic stability of the dope solution, which can influence the rate and mechanism of phase separation. A good solvent can dissolve more polymer and create a more stable solution, while a poor solvent can induce more phase separation and create a more

porous membrane. Different solvents can also affect the swelling and shrinkage of the membrane during coagulation [38].

The addition of additives can also modify the properties and interactions of the polymer, solvent, and non-solvent in the dope solution. Some additives can increase the hydrophilicity and antifouling performance of the membrane, such as polyethylene glycol (PEG), polyvinyl alcohol (PVA), or zwitterionic polymers. Some additives can increase the porosity and permeability of the membrane, such as nanoparticles, surfactants, or salts [39].

The evaporation time is the time interval between casting and immersion of the dope solution into the coagulation bath. During this time, some solvent can evaporate from the surface of the dope solution, which can increase the polymer concentration and induce skin layer formation. A longer evaporation time can result in a thicker and denser skin layer, which can increase the selectivity but decrease the permeability of the membrane. Furthermore, the coagulation bath temperature can affect the diffusion rate and direction of solvent and non-solvent during phase separation. A higher coagulation bath temperature can accelerate both solvent outflow and non-solvent inflow, which can result in a more porous and sponge-like membrane structure. A lower coagulation bath temperature can slow down both solvent outflow and non-solvent inflow, which can result in a less porous and finger-like membrane structure [37], [39].

1.2.2. Hydrophilic PES membrane

The demand for functional hydrophilic membrane materials has led to significant attention being placed on the development of hydrophilic PES membranes. These membranes are useful in various applications, including desalination, water treatment, wastewater treatment, textile applications, and protein purifications, due to their interaction with water. There are two different

strategies which are commonly used to modify the properties of PES membranes: (1) bulk modification (e.g., blending) and (2) surface modification (e.g., grafting and coating). These strategies aim to balance hydrophobicity and hydrophilicity, and reshape and modify the pore structure to enhance flux and permeability while reducing fouling. Various membrane modification methods exist, including annealing or heat treatment, surface coating, chemical treatment (such as fluorination, crosslinking, and pyrolysis), grafting, and blending [40]–[43]. Many studies have demonstrated that enhancing the membrane's hydrophilicity can reduce fouling and improve performance. Table 1-2 provides a summary of modifications and applications of hydrophilic PES membranes. Based on Table 1-2, bulk modification, coating and grafting has advantages and disadvantages. For example, bulk modification can achieve a uniform and consistent modification throughout the material, while grafting modification can create a heterogeneous and selective modification on the surface of the material. Bulk modification can alter the intrinsic properties of the material, such as mechanical strength, thermal stability, and chemical resistance, while grafting modification can enhance the surface properties of the material, such as hydrophilicity, biocompatibility, and functionality [44].

Therefore, the choice of modification method should be based on the specific requirements and objectives of the application. We opted for the grafting method as our choice because our goal is to preserve the integrity and structure of PES while solely modifying its surface properties and enhancing its antifouling behavior.

Table 1-2- Summaries of the modification process and applications of treated PES membranes

Additive	Modification process	Applications	Decrease in WCA	Reference
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MWCNT ¹	Blending (Bulk Modification)	Wastewater treatment	75.1° to 62.9°	[45]
Fe ₃ O ₄ -SiO ₂ -amine	Blending (Bulk Modification)	Water treatment	78° to 69°	[46]
SBMA ²	Grafting/Coating (Surface Modification)	Wastewater treatment	101° to 48°	[47]
PA and Imidazole	Grafting	Water treatment	68° to 49° and 35°	[48]
PHMB-PAMPS ³	Blending (Bulk Modification)	Protein purification /Antibacterial	85.8° to 38.4°	[49]
EDOT ⁴	Coating (Surface Modification)	Flux control	Not mentioned	[50]
Fe-TCPP ⁵	Coating (Surface Modification)	Water treatment	~55° after modification	[51]

1.3. Biofouling in polymeric membrane

Microbial biofouling is characterized by the adhesion of microorganisms onto a surface, resulting in the growth of microbial communities in the form of a film layer. This process is facilitated by the production and accumulation of Extracellular Polymeric Substances (EPSs) [52]. EPSs provide a nutrient-rich and highly hydrated environment for bacterial communities to thrive and are composed of various compounds including proteins, polysaccharides, lipids, nucleic acids, and other low molecular weight substances containing functional groups such as acetyl, succinyl, pyruvyl, and sulfate. These compounds contribute to the formation of weak physico-chemical

¹ MWCNT: Multiwall carbon nanotubes

² SBMA: sulfobetaine methacrylate

³ PAMPS: poly-2-acrylamido-2-methylpropanesulfonic acid, PHMB: poly(hexamethylene biguanide)

⁴ EDOT: 3,4-ethylenedioxythiophene

⁵ Fe-TCPP: iron tetrakis(4-carboxyphenyl)porphyrin

interactions, providing bacterial communities with adhesion, mechanical stability, and resistance to external environmental effects [53] [54].

The composition of EPSs varies depending on the operating conditions and feed water constituents [55]. It is commonly believed that microbial attachment to the membrane surface and subsequent EPS production leads to biofilm formation. Komlenic et al. [56], suggested that Transparent Exopolymeric Substances (TEPs), highly electronegative and coarse particulate-like substances released by planktonic organisms, serve as the precursor for biofilm formation. TEPs initially attach to the membrane surface, followed by microbial attachment [57]. The stages of biofouling can be classified as follows: (1) Adsorption of TEPs on the membrane surface and conditioning of surfaces for subsequent colonization, which lasts for minutes to hours; (2) Induction phase involving the deposition of motile bacteria and light flocs on the membrane surface, forming the first microcolonies, which lasts for hours to days; (3) Logarithmic phase involving the growth of a biofilm to form a monolayer composed of EPS matrix with agglomeration and retention of microbes. This stage contributes more to biofouling than the previous step and continues to develop filamentous projections of bacterial communities with porous water channels, lasting for days to weeks; (4) Clogging of membrane pores due to deposits of cell debris, carbohydrates, microbial products, and growth plateauing based on the limitation of nutrient availability, lasting for weeks to months; (5) Aging of the biolayer with eventual detachment of some cells and debris due to fluid flow shear forces, leading to regrowth at different downstream sites [25], [58].

The nature and structure of biofilms vary depending on hydrodynamic conditions. The fouling mechanisms of low-pressure membranes, such as micro-filtration (MF) and ultra-filtration (UF),

differ somewhat from those of high-pressure membranes, such as nano-filtration (NF) and reverse osmosis (RO). For MF and UF, pore adsorption and clogging are more common, while for NF and RO, surface fouling is relatively more frequent due to the precipitation of small particles like minerals and salts on the membrane surface, leading to fouling [59].

Under low shear forces and low pressure (typically observed in ultra and microfiltration applications), the biofilm has filamentous growth with porous water channels, whereas the structure near the membrane surface is continuous. The filamentous extensions, or offshoots, detach under high shear forces and cause dispersal of the microcolonies into the downstream flow, which could lead to their attachment onto new surfaces. This poses a health hazard if they are distributed in the water system [60].

When microorganisms come close to a membrane surface under hydrodynamic forces, their adhesion to the surface is facilitated through various mechanisms, as depicted in Figure 1-1. Firstly, primary adhesion of bacteria to the membrane surface occurs due to a physicochemical interaction, followed by secondary adhesion due to the cohesion between the adhered and free bacteria in the water. Secondly, ligand-receptor interactions occur between the receptors of the cell membrane and the binding sites of the conditioning film layer, such as polarized bonds, charged groups, or OH groups. Lastly, adhesive interaction occurs due to the sticky nature of EPSs and the appendages of some microorganisms. The appendages of a microorganism surface can

remove the water film between the microorganism cell and the membrane surface, thereby allowing the cell to adhere to the surface directly [52].

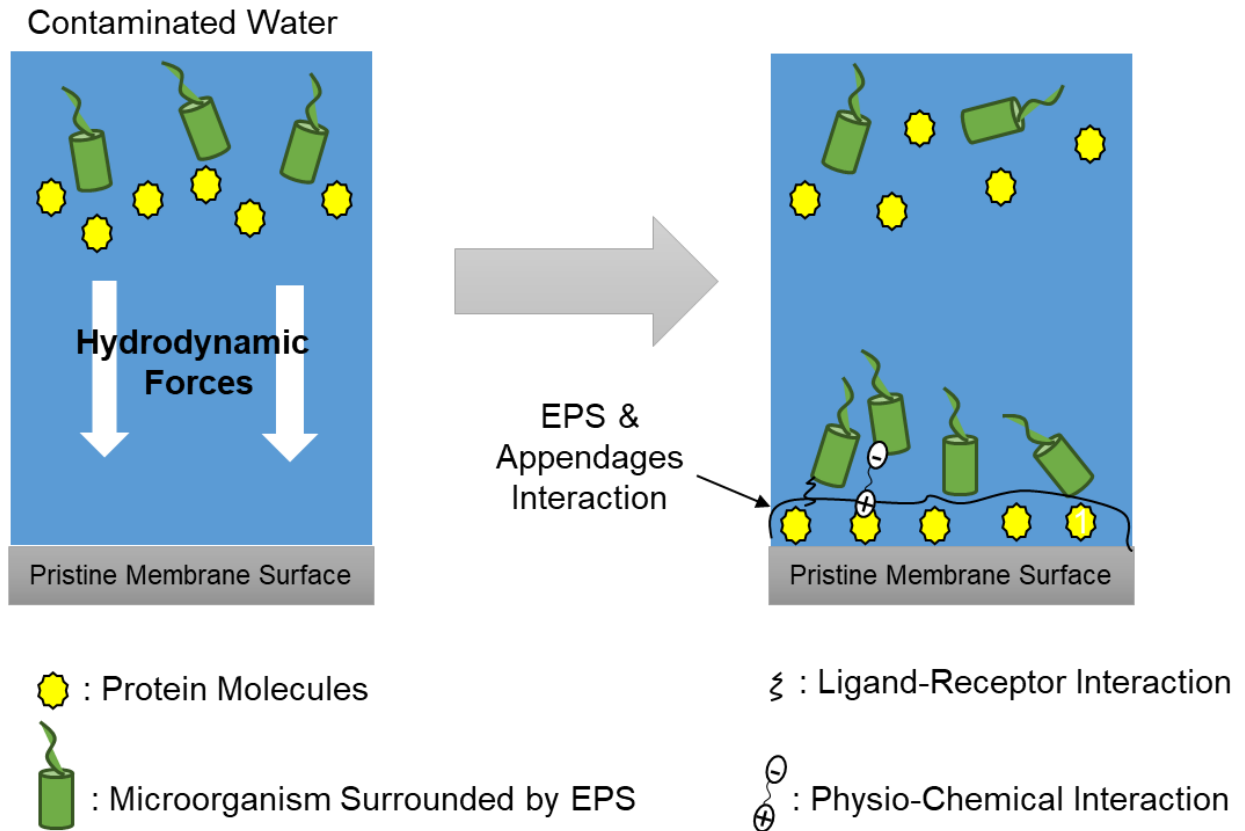


Figure 1-1. Driving forces of the microbial adhesion onto the membrane surface.

The adhesion of bacteria to biofilms is significantly impacted by the hydro-phobicity/-philicity of the surface. Hydrophilicity is caused by the presence of charged groups, while hydrophobicity is caused by the presence of aromatic and aliphatic groups. The hydro-phobicity/-philicity of EPSs is determined by its composition, which can be influenced by operational parameters such as dissolved oxygen, ionic strength, pH, etc. These parameters play a crucial role in membrane fouling since adhesion and flocculation rely on them [61]. In order to reduce the affinity of the membrane surface to EPSs and bacterial colonies in the feed water, the hydro-phobicity/-philicity

of the membrane surface can be modified. Figure 1-2 illustrates the adhesion mechanisms of EPSs to both hydrophobic and hydrophilic membrane surfaces [54].

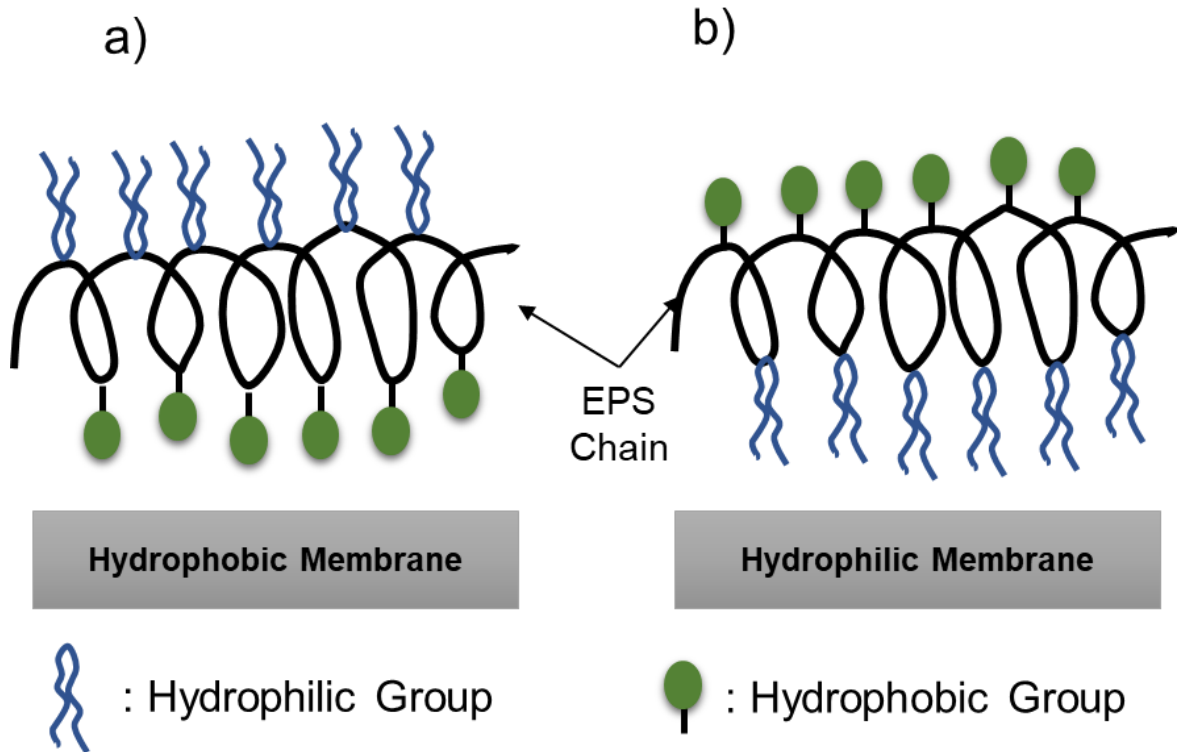


Figure 1-2: Adhesion of EPSs on the surface of (a) hydrophobic membrane and (b) hydrophilic membrane.

The adhesion process is also influenced by other factors related to feed water and membrane material. These include ionic strength, nutrient content, bacterial content, and hydrodynamic conditions of the feed water. The hydrodynamic parameters, such as cross-flow velocity, permeation drag, and back transport diffusion, can affect the residence time and shear forces, thereby influencing bacterial adhesion. Higher ionic strength was found to increase bacterial adhesion, while pH was found to have a lesser effect [58]. Moreover, membrane parameters, such as surface roughness, surface charge, and surface tension, can also affect bacterial adhesion. Rougher surfaces have a higher bacterial adhesion due to increased surface area and

more sites available in the form of peaks and troughs. Most bacteria have a negative charge, and hence negatively charged surfaces are expected to repel bacteria, as shown in zeta potential experiments [25].

1.4. Biofouling mitigation

To prevent membrane biofouling in water treatment, the first step is to pretreat the feed water to eliminate the sources of foulants. This typically involves coagulation/flocculation and UF/MF, followed by disinfection and granular media filtration. Even when UF/MF membranes are used for pretreatment, they can still be susceptible to biofouling, requiring membrane cleaning. Disinfection techniques such as biocide dosing, chlorination, ozonation, and UV irradiation are effective at eliminating planktonic bacteria, but may not work on bacterial communities that exist in flocs surrounded by an EPS matrix. In addition to pretreatment, different antifouling strategies (Figure 1-3) like physical and chemical cleaning, and surface modifications can be employed to improve the fouling resistance and cleaning efficiency of fouled membranes [62]. For example, Muszanska et al. [61] reported a decrease in bacterial adhesion on membranes grafted with polymeric brushes. They hypothesized that polymeric brushes do not provide a continuous surface for bacteria to attach to, thereby inhibiting bacteria from producing EPSs.

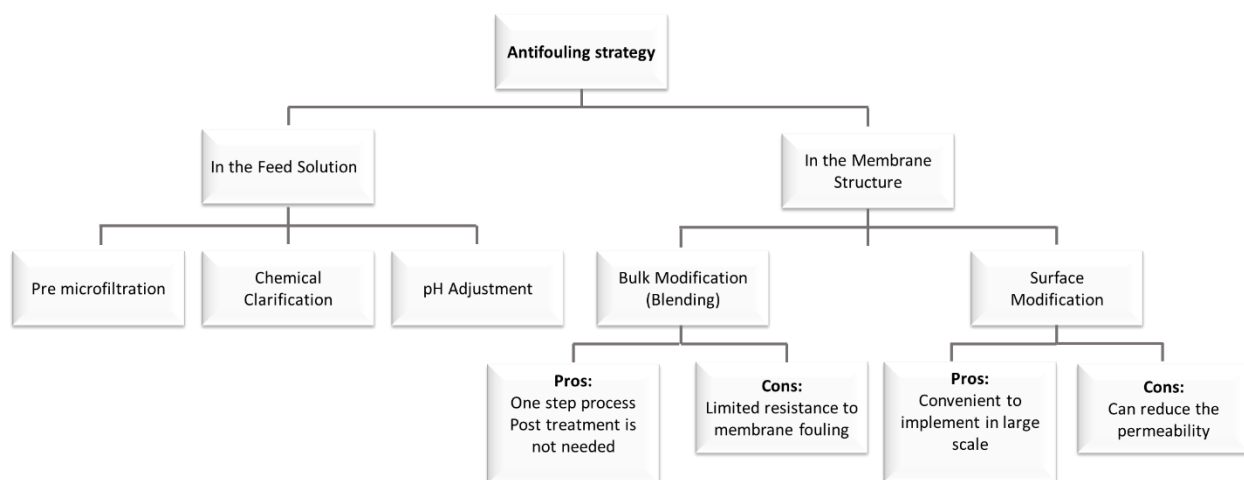


Figure 1-3: Different antifouling strategies.

As previously elucidated, one of the central and pervasive challenges in membrane-based filtration across various applications is the susceptibility to fouling. This issue is particularly pronounced in aqueous filtrations and processes involving proteins [63], [64]. Fouling transpires when undesirable substances adhere to the surface of the membrane, impairing its functionality and leading to an increase in hydraulic resistance [63].

To remove fouling, three major strategies can be employed [65]–[69]. A detailed list of these strategies, along with their respective advantages and disadvantages, can be found in Table 1-3.

Table 1-3: Summaries of strategies for reducing and cleaning of fouling

Strategies	Advantages	Disadvantages	References
Chemical cleaning	1- Used as a pre-treatment or prevention method 2- Reversible fouling can be partially or fully restored 3- Irreversible fouling can only be removed by chemical cleaning	1- Use of chemical agents like acid/ base damages the membrane 2- Chemical agents are expensive	[70]–[72]
Physical cleaning	1- Used as a preventive and control methods	1- It is time-consuming	[73], [74]

	2- Involves physically scrubbing the membrane surface	2- Most of the polymeric membranes are delicate and physical cleaning can damage the membrane surface	
Membrane modification	1- Membrane is less susceptible to fouling 2- Can increase the membrane's selectivity, permeability, and stability	1- Can be expensive and may require specialized equipment. 2- The process of modifying the membrane surface can also be complex and time-consuming	[75], [76]

1.4.1. Chemical cleaning

Chemical cleaning is a commonly used method for cleaning biofouled membranes. It involves chemical reactions, such as hydrolysis, saponification, solubilization, dispersion, chelation, and peptization, which break down the bonds and cohesion forces between the membrane surface and the foulants [9]. However, the use of extremely acidic or alkaline chemicals, such as hydrochloric acid and sodium hydroxide, can cause corrosion of water pipes. Moreover, chelating agents, such as EDTA, have poor biodegradability and can cause environmental concerns. EDTA also undergoes chelation with heavy metals, forming complexes that increase the mobility and bioavailability of heavy metals, which can be harmful to human health [77].

Similarly, chemical cleaning with a sodium hypochlorite solution can lead to the production of adsorbable organic halides (AOX) and trihalomethanes (THMs), which can cause harm to animals, plants, marine life, and the entire ecosystem. Additionally, frequent chemical cleaning can result in a substantial economic burden due to cleaning downtime, severe decline in the quality of permeate, and reduction in the membrane's useful life. Therefore, it is essential to consider the

potential environmental and economic impacts of chemical cleaning and explore alternative cleaning methods that are more sustainable and eco-friendly [78].

The process of chemical cleaning of membranes involves several steps. Firstly, there is a bulk reaction where cleaning reagents such as hydrolysis and ionization occur. Secondly, there is transportation of the cleaning reagent to the interface, followed by its penetration into the fouling layer/foulants. Subsequently, there are reactions for the solubilization and detachment of foulants. After this, there is back-transportation of waste cleaning agents along with the detached/solubilized foulants to the interface, and the transportation of waste matter to the bulk solution or cleaning reagent. It is crucial to note that high cleaning efficiency depends not only on the reaction between the reagent and foulants but also on other steps such as the reagent reaction rate, mass transfer rate, and back-transportation velocity [78].

Chemical reagents such as metal-chelating chemicals (citric acid, ethylene diamine tetra acetic acid (EDTA), sodium tripolyphosphate (STP), and diethylene trinitrilopenta acetic acid (DTPA)), surfactants (sodium dodecyl sulfate (SDS)), and other detergents are used for membrane cleaning. Metal chelating agents can form a stable complex with metal ions, which replaces biopolymers initially associated with metal ions via a ligand exchange reaction, releasing the biopolymers to their original loose conformation. This process results in the destruction of intermolecular bridges within biopolymers and between biopolymers and the membrane surface, leading to the loss of cross-linked, gel-layer structure of the fouling layer. The detached biopolymers can be easily transported away from the membrane surface in the presence of turbulence. It is important to use specific reagents to effectively clean the membrane fouled by particular substances. Although different chemical agents have different cleaning efficiencies

towards different foulants, combining chemical cleaning agents is not always useful in certain situations [79], [80].

1.4.2. Physical modification: Additive blending

Physical modification is a general term that refers to any technique that changes the surface properties of a membrane without involving chemical reactions. Blending is a specific type of physical modification that involves mixing two or more polymers or additives in the casting solution before forming the membrane by phase inversion. blending is recognized as the most significant and extensively studied subcategory of physical modification. The blending approach is a versatile and practical procedure that can be performed under mild conditions to improve the hydrophilicity and performance of PES membranes [30], [81], [82]. This technique offers the advantage of creating a novel, desirable property resulting from the selective combination of polymers, while simultaneously avoiding the undesirable property of molecular level miscibility that can arise with the blending of different polymers [83].

The miscibility of polymers refers to their ability to mix and form a homogeneous blend when they are in the molten or dissolved state. Polymers can be classified as either miscible, immiscible, and partially miscible based on their ability to mix. In general, the miscibility of polymers depends on several factors, such as their molecular weight, chemical structure, polarity, and intermolecular interactions. If two polymers have similar molecular weights and chemical structures, they are more likely to be miscible. Similarly, if two polymers have similar polarities, they are more likely to be miscible. When blending different phases, a miscible mixture produces consistent and stable thermal and mechanical properties in the resulting product. Therefore, electing the right polymer is a critical factor in achieving desirable physical and chemical

properties in a polymer blending system [83], [84]. The additives utilized in the blending process can be broadly categorized into two categories: organic and inorganic.

1.4.2.1. Organic additives

Poly(ethylene glycol) [85], [86] and its derivatives, Poly(vinylpyrrolidone) [87], Cellulose nanocrystals, Poly(vinyl alcohol) [88], Poly(acrylic acid) [89], Polydopamine [90], Zwitterion/amphiphilic zwitterion [91], [92], Amphiphilic copolymer [91], and Chitosan and Chitin [93], [94] are widely employed as organic additives to enhance membrane permeability and antifouling performance. These materials are preferred due to their high compatibility with PES and reasonable cost.

Shi et al. [92], produced a novel zwitterionic polymer named tertiary amine-modified PES (TA-PES), comprising cationic tertiary amine groups and anionic sulfonic groups. The TA-PES was utilized to produce ultrafiltration membranes via a wet phase inversion process. Results indicated that the hydrophobic PES contact angle was greatly reduced following the chemical modification. Additionally, ultrafiltration experiments revealed that the TA-PES membranes exhibited exceptional resistance to protein fouling as depicted in Figure 1-4.

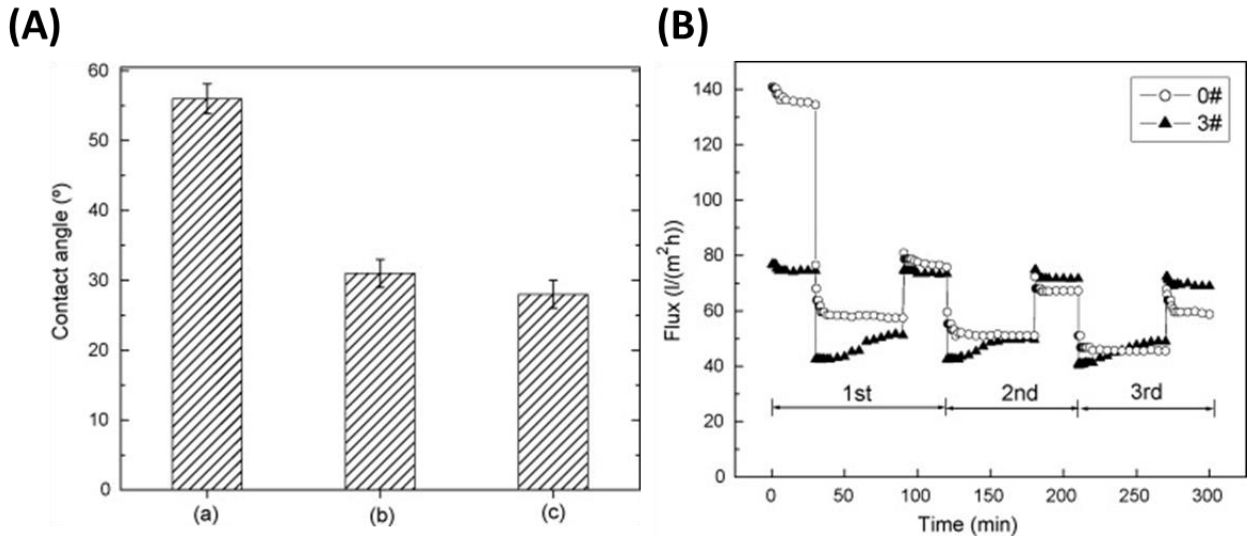


Figure 1-4: The experimental results, including (A) the contact angles for the PES control membrane (0#), S-PES membrane (b), and TA-PES membrane (1#) (c), and (B) the flux variations of the 0# PES control membrane and 3# TA-PES membrane after undergoing ultrafiltration of a BSA solution three times. Reprinted with permission from ref [92] Copyright 2008 Elsevier.

In a different investigation, Liao et al. [95], employed phosphomolybdic acid (PMo_{12}) as a functional additive in the production of PES composite ultrafiltration membranes using a non-solvent induced phase separation method. By incorporating PMo_{12} , the composite membranes gained improved hydrophilicity, which increased with higher concentrations of PMo_{12} . The results demonstrated in Figure 1-5 indicate a noteworthy enhancement in filtration performance, with the optimized composite membrane exhibiting a water flux of $572.67 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and a bovine serum albumin rejection of 99.31%, representing a water flux increase of higher than 300% over those of the control PES membrane, respectively.

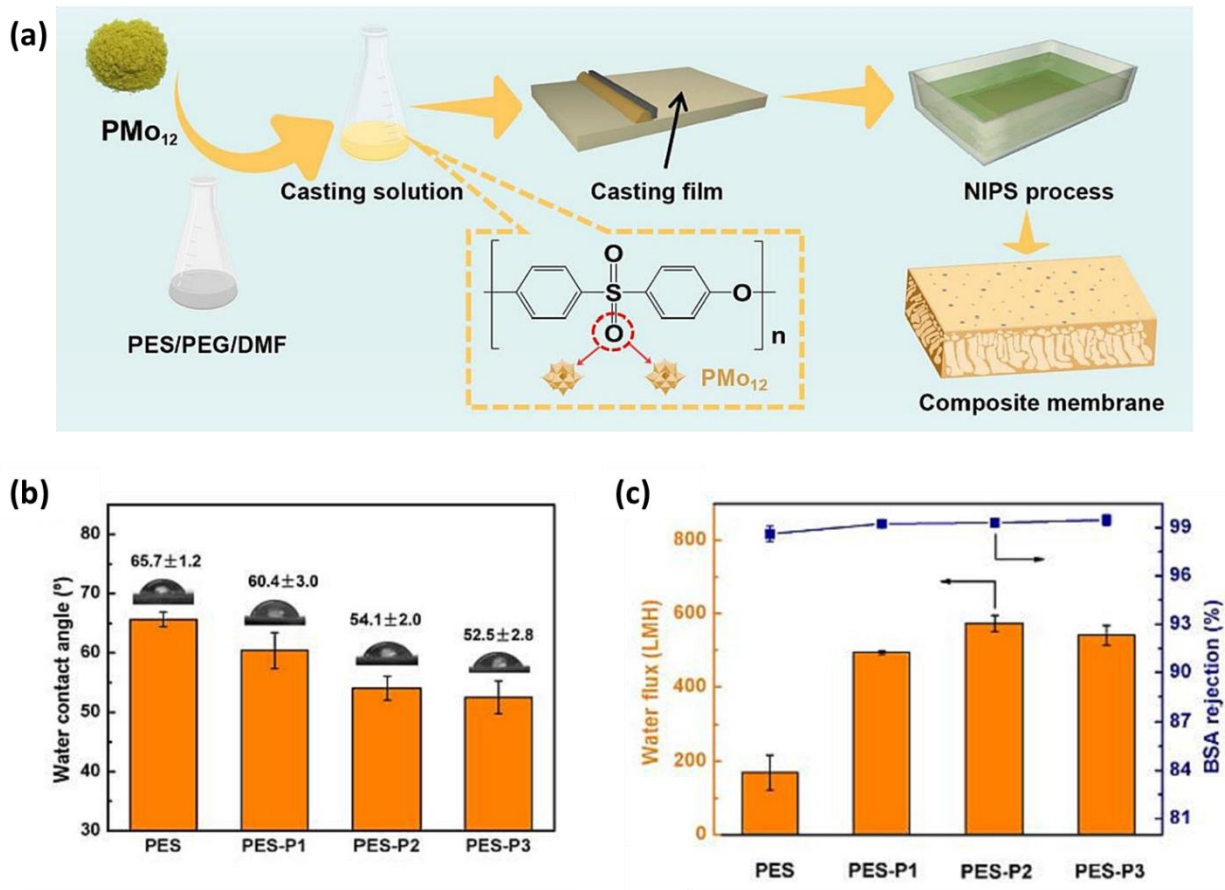


Figure 1-5: (a) a schematic illustration of the process for producing composite membranes, (b) the water contact angle measurements of the membranes, and (c) a comparison of the filtration performance of PES-P2 with previously reported findings and commercial membranes. PES, PES-P1, PES-P2, and PES-P3 correspond to membranes with 0, 0.45, 0.90, and 1.35 PMo_{12} concentration, respectively. Reprinted with permission from ref [95] Copyright 2023 Elsevier.

1.4.2.2. Inorganic additives

Instead of using organic polymers and copolymers, the use of inorganic nanoparticles is a promising alternative for modifying polymeric materials. Adding inorganic nanoparticles to the PES matrix has become a popular technique for creating polymeric membranes and has gained significant attention in recent years [30]. Various inorganic materials have been added as additives to the PES matrix, including titanium dioxide [96], silicon dioxide [97], carbon nanotubes [98], copper nanoparticles [99], and metal-organic frameworks [100]. When adding these

nanoparticles to the PES membrane during preparation, there are two methods: blending them in a coagulation bath or in the polymer solution. The dominant method has been to blend the nanoparticles in the polymer solution, compared to blending them in a coagulation bath.

Gan et al. [96], employed a novel vapor-ventilated in situ chemical deposition technique to construct a continuous inorganic $\text{TiO}_2\text{-SiO}_2$ modification layer on the PES membrane. They applied Ti and Si precursors on the organic PES substrate, followed by in situ hydrolysis to convert them into metal oxides. This modification resulted in efficient water purification by promoting the rapid movement of water molecules while effectively resisting and releasing typical pollutants, as evidenced in Figure 1-6. The $\text{TiO}_2\text{-SiO}_2$ /PES composite membrane exhibited a high water permeance of $187.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a relatively lower water contact angle (31° for $\text{TiO}_2\text{-SiO}_2$ /PES-2) compared to pristine PES (72°).

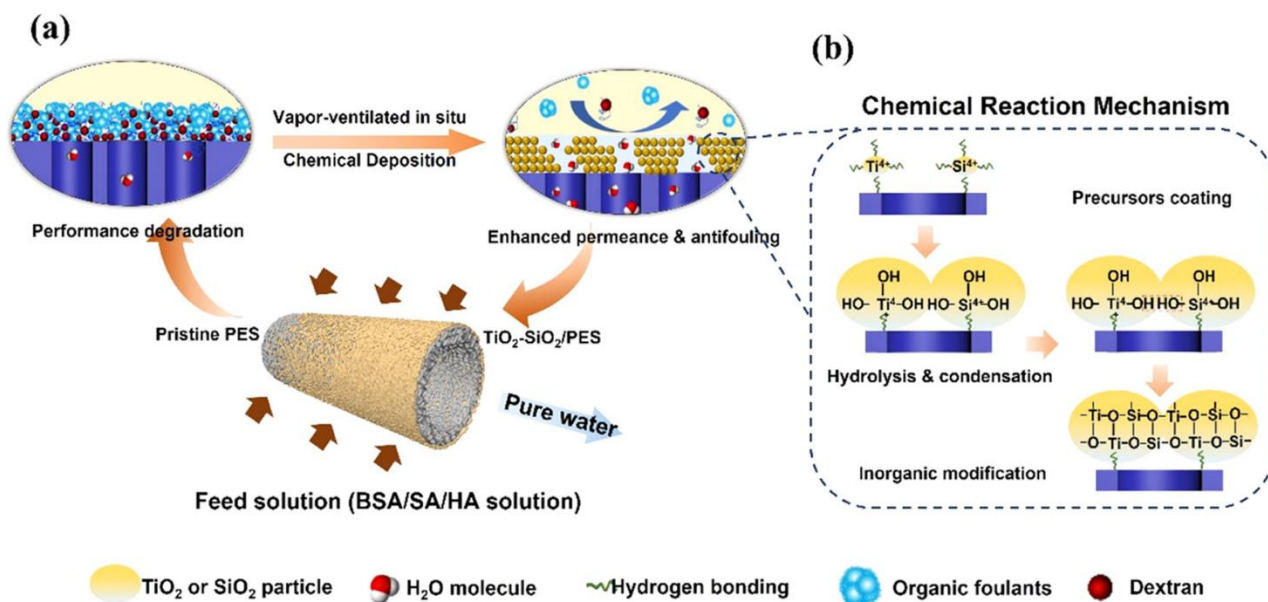


Figure 1-6: a schematic representation of the $\text{TiO}_2\text{-SiO}_2$ /PES composite PES hollow fiber membrane developed using the vapor-ventilated in situ chemical deposition method for water treatment. The diagram includes (a) the composite membrane structure and (b) the chemical deposition process. Reprinted with permission from ref [96] Copyright 2022 American Chemical Society .

Metal oxide nanoparticles have been extensively investigated and when dispersed in the PES matrix, they can enhance the membrane's hydrophilicity and antifouling ability. For instance, Sotto et al. [101], incorporated TiO_2 into PES membranes and observed that the hydrophilicity improved with a reduction in the water contact angle from 75.2° to 67.5° upon modification with 0.1 wt.%. Additionally, the water flux rate increased from $15 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for bare PES to about $58 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for PES with 0.1 wt.% TiO_2 . The improvement was attributed to the greater occurrence of macrovoids featuring a finger-like structure following the addition of TiO_2 to the polymeric solution, as shown in Figure 1-7.

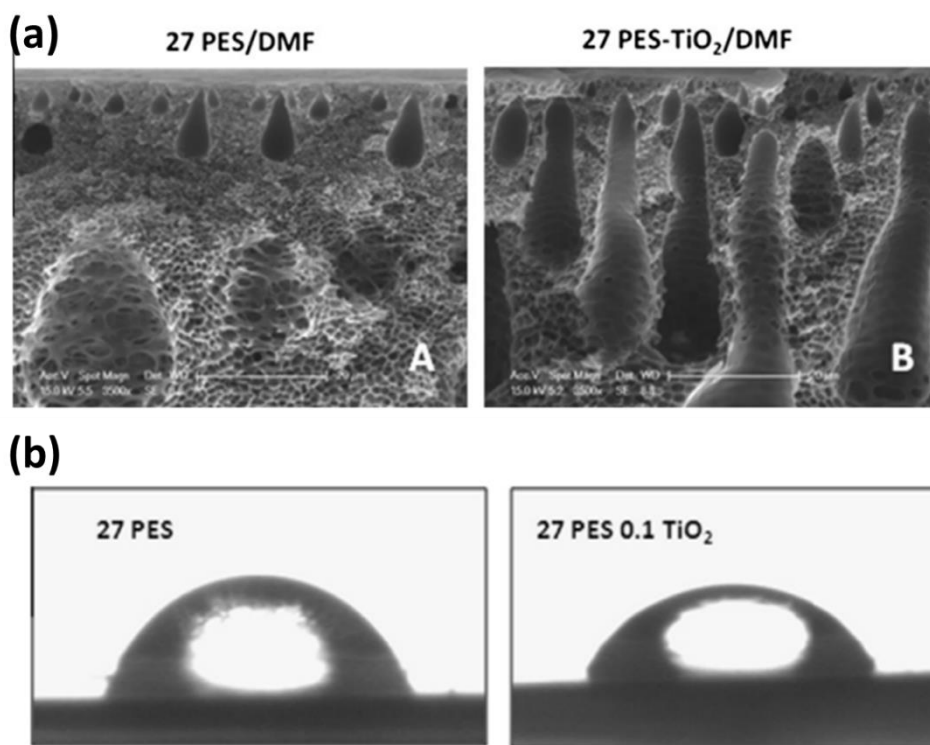


Figure 1-7: (a) scanning electron microscope images of the unmodified PES membrane and the PES-TiO₂ modified membrane, and (b) pictures of water droplets captured on the unmodified PES membrane and the PES-TiO₂ modified membrane. Reprinted with permission from ref [101] Copyright 2011 Elsevier.

1.4.3. Surface modification

Surface modification of membranes, such as altering surface roughness, surface charge, and hydrophilicity, has been shown to enhance biofouling resistance and cleaning efficiency. Membranes with smooth and hydrophilic surfaces are less prone to fouling compared to those with rough and hydrophobic surfaces. However, in certain cases, hydrophilic membranes may attract hydrophilic substances and exacerbate fouling. To reduce microbial adhesion, negatively charged membranes have been proposed as they can repel most species of bacteria. There are various ways to increase membrane surface smoothness and hydrophilicity, such as surface modification, novel materials, and synthesis processes [75], [102].

On the other hand, surface modification aimed at altering the membrane's charge and enhancing its hydrophilicity has emerged as a cost-effective strategy. This approach has garnered considerable attention and research focus in the ongoing endeavor to effectively combat fouling and improve membrane performance [103]–[105].

To enhance the hydrophilicity of the membrane surface, various methods, such as attaching polymer chains to the surface and blending with hydrophilic materials in the solution, have been extensively documented [106]–[109]. Surface modification is a widespread strategy used to reduce membrane fouling, which includes surface coating (SC) as a physical modification and surface grafting (SG) as a chemical modification [59].

1.4.3.1. Surface coating

To enhance both permeability and fouling resistance of polymeric membranes, especially hydrophobic membranes, a hydrophilic layer can be applied to the surface of the membrane through a process known as coating. This involves the formation of a thin layer on top of the base

material, which non-covalently adheres to the membrane substrate. In their study, Nady et al. [110], identified five main coating methods, including physical adsorption, physical adsorption followed by curing with heat, coating with a monolayer using the Langmuir–Blodgett method, casting or extrusion of a two polymer solution, and deposition from a glow discharge plasma. Despite the benefits of improved hydrophilicity and fouling resistance, most coating techniques can decrease membrane performance, particularly the pure water flux, due to the accumulation of the coated layer on the pore surface. However, there is still a lot of research focusing on the coating method for surface modification.

For example, Yao et al. [111], developed a novel method for creating a highly effective and chemically stable antifouling coating on the surface of ultrafiltration membranes. The traditional approach to antifouling coatings has been to develop mussel-inspired coatings that use polydopamine (PDA) as a base material. However, these coatings often suffer from poor chemical stability, particularly in strongly alkaline environments. The new method involves the co-deposition of PDA and a polyethylenimine-quaternized derivative (PEI-S) on the surface of a PES ultrafiltration membrane at room temperature. The combination of PDA and PEI-S creates a cross-linking and unexpected cation- π interaction that enhances the coating's chemical stability as depicted in Figure 1-8.

In addition to its improved stability, the PDA/PEI-S coating is highly effective at preventing fouling. Tests demonstrated that the coating could prevent the adsorption of bovine serum fibrinogen and lysozyme and could reduce the adhesion of both Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli*.

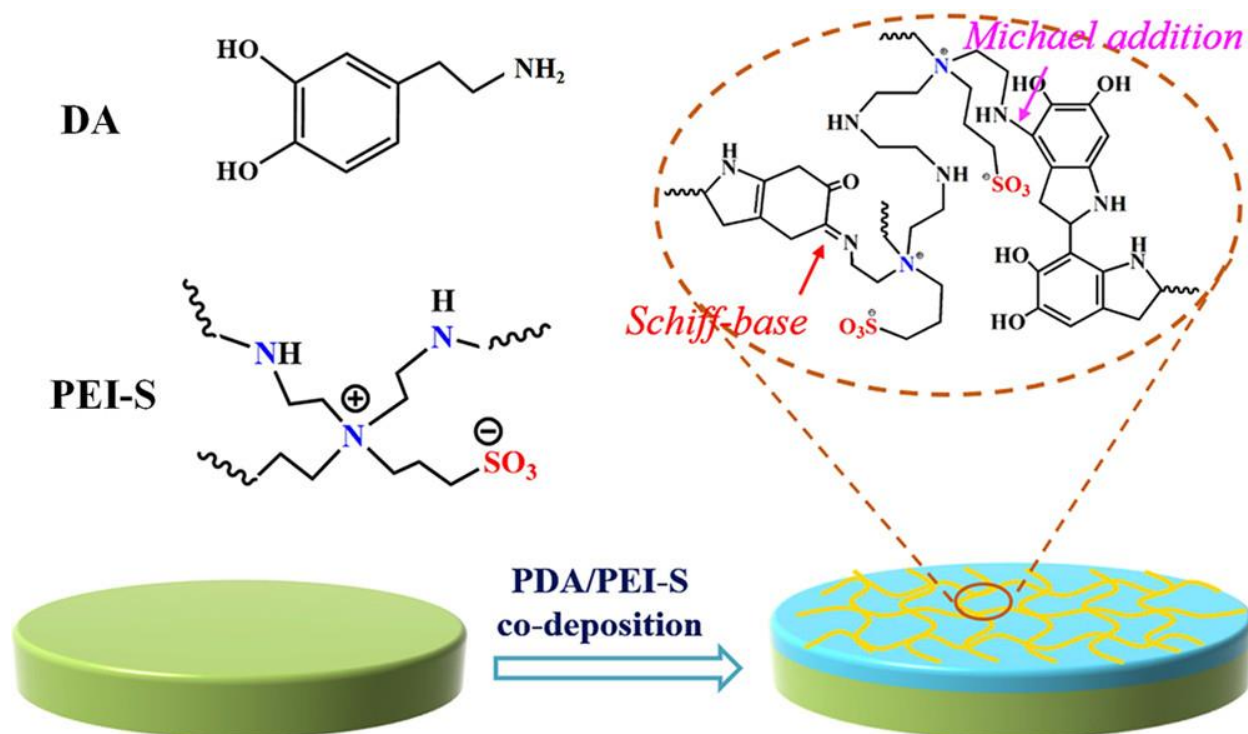


Figure 1-8: This diagram depicts the one-step process for modifying the PES membrane using a mussel-inspired antifouling approach. Reprinted with permission from ref [111] Copyright 2019 American Chemical Society.

In another study, Li et al. [112], developed a new method to create antifouling and high-flux nanofiltration membranes using bioinspired polydopamine (PDA). The researchers first prepared a PDA-coated membrane, called the PDA/PES composite membrane, by immersing PES in a PDA solution. They then modified the membrane further by grafting a fluorinated polyamine to produce fluorinated PDA/PES composite membranes as shown in Figure 1-9. The PDA coating significantly reduced pore sizes and enhanced separation performance, and a grafted fluorinated polyamine on the PDA layer prevented the accumulation of foulants and lowered the adhesion force, resulting in a fouling-release property. Tests showed excellent antifouling properties, with minimal flux decline and high flux recovery. The PDA layer also enhanced the structural stability

of the membrane due to covalent bonds and other intermolecular interactions with the support membrane.

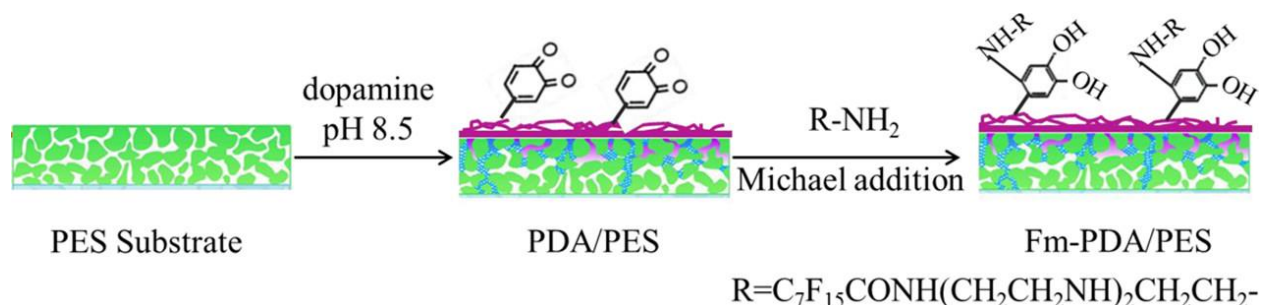


Figure 1-9: Illustration of the process of preparing the PDA/PES composite membrane, including the surface fluorination step. Reprinted with permission from ref [112] Copyright 2014 American Chemical Society.

1.4.3.2. Plasma treatment

Plasma treatment is a technique that utilizes partially ionized gas, known as plasma, to modify the surface properties of a material. This process can introduce functional groups, alter surface morphology, and enhance the surface energy of a material, resulting in improved hydrophilicity, biocompatibility, or reactivity. Plasma treatment has found extensive application in membrane modification. For instance, when polyacrylonitrile (PAN) based membranes are subjected to plasma treatment with carbon dioxide (CO₂) gas, it leads to a remarkable 22% increase in membrane surface hydrophilicity and a 2.2-fold increase in permeability for the treated membrane. Furthermore, these findings demonstrate that the introduction of carboxyl and hydroxyl groups on the membrane's surface enhances its fouling resistance [113].

In a separate study, a polytetrafluoroethylene (PTFE) membrane underwent plasma treatment using nitrogen (N₂), oxygen (O₂), argon (Ar), and hydrogen (H₂) gases. This treatment resulted in a reduction of the water contact angle (from 140° to 109°) and improved the wettability of the membrane by introducing polar groups like C-O, C=O, and C-N on its surface. In summary, the

results demonstrated that plasma treatment can effectively adjust surface properties while preserving bulk properties. However, the researchers noted that plasma treatment alone was insufficient to create a lasting hydrophilic surface, and the achieved hydrophilicity was not durable over an extended period. [114]. Among all treatment methods, plasma treatment is notably sensitive to environmental factors, including humidity, temperature, and air quality. Furthermore, it is an expensive and intricate process that necessitates specialized equipment and trained personnel. Additionally, plasma treatment may lead to undesired effects on material surfaces, such as oxidation, etching, cracking, and aging, which can vary based on plasma parameters and material properties. Moreover, it's essential to note that the effects of plasma treatment can be temporary, as surface modifications may deteriorate over time when exposed to air, water, or other substances. So it cannot be considered as an effective membrane modification method.

1.4.3.3. Surface grafting

Surface grafting techniques are widely utilized to attach monomers, functional groups, or polymers to the membrane surface via covalent bonding. Several parameters can influence the degree of grafting yield, including the composition and concentration of the backbone, monomer, solvent, initiator, and additives, as well as the temperature and duration of the grafting reaction. The grafting methods and their properties will be further discussed in the following section [115], [116].

Tables 1-4 offer a comprehensive summary of the advantages and drawbacks associated with different membrane modification methods. It is evident that the grafting process stands out as a

favorable choice with its primary limitation being the relatively low grafting density it can achieve. In contrast, other methods come with their own significant shortcomings.

For instance, plasma treatment and additive blending, while being effective to some extent, may be cost-prohibitive, making them less practical for certain applications. Additionally, their overall effectiveness may not match the results attained through grafting. On the other hand, surface coating, although a valuable technique, has the potential to form a resistive layer on the membrane's surface, which can negatively impact its permeability and efficiency. Comparison between different method of fouling resistance membrane development were demonstrated in Table 1-4.

Upon considering these comparisons, it can be concluded that the grafting method is an effective approach to enhance the surface characteristics of the membrane while preserving its integrity, structure, and intrinsic properties. Therefore, opting for the grafting process emerges as the suitable choice for our study on PES membrane. In the upcoming sections, we will provide a more detailed review of membrane grafting and its antifouling behavior.

Table 1-4: Comparison between different method of fouling resistance membrane development

Method	Advantages	Disadvantages	Ref
Surface Grafting	- Control over structure and properties of the membrane - Easy and simple - Nanoparticles can be added	Grafting efficiency can be low	[24], [117]
Plasma treatment	- Short reaction time - High reproducibility - Low environmental impact	- High cost - Vacuum is required - Monitoring and control of the treatment time is necessary	[118], [119]
Blending	- Low cost - Simple method	Low effectiveness	[120], [121]

Coating	• Easy and simple	• Addition of resistive layer which can affect permeability • Leaching is possible	[122], [123]
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1.5. Polymer grafting

There are three techniques that lead to the formation of a polymer by causing monomers to stick together: physisorption, grafting, and crosslinking. Physisorption is related to physical attractive forces bonding and results in weak bonding, making it a reversible reaction. End-functionalized polymers are used for physisorption onto a solid surface or self-assembly of polymeric surfactants [124].

Grafting is a covalent attachment process and is permanent and irreversible. It can be accomplished using two different approaches: grafting-to and grafting-from. Grafting-to involves functionalized monomers reacting with the backbone polymer to form the grafted polymer (see Figure 1-10). On the other hand, grafting-from proceeds by treating a substrate with a method to generate immobilized initiators that run the polymerization [125], [126]. The purification process for graft polymers produced via the "grafting-to" method can be intricate, and the determination of the number and location of grafted polymer chains is challenging due to the complexities involved in post-polymerization modifications. In contrast, the "grafting-from" approach streamlines the purification process, as any unreacted monomers can be readily removed. Moreover, this method provides greater control over the initiation sites, enabling the creation of higher molecular weight side chains.

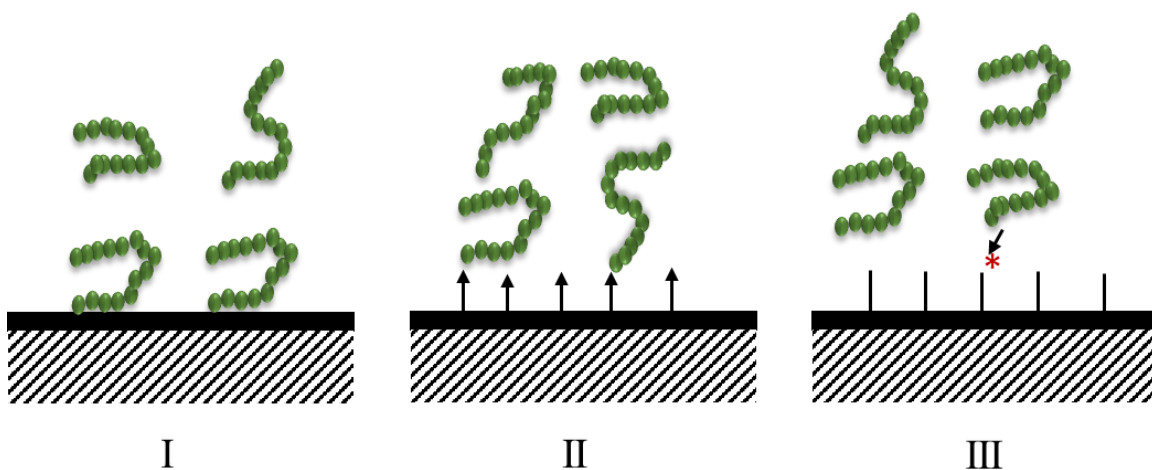


Figure 1-10: Schematic diagram of (I) physisorption, (II) grafting-to, (III) grafting-from.

1.5.1. Graft copolymers

Graft copolymers consist of macromolecules comprising two or more chemically different chains, where the backbone chain has multiple branches formed from macromolecular chains with a chemical composition distinct from that of the backbone. The covalent bonds along the backbone chain are randomly distributed and found at the end of the grafted branch. Graft copolymers can be easily synthesized using almost any co-monomer and macromolecular compound through the grafting process. In the case of coded monomer residues A and B, a segment of a graft copolymer would have a structure resembling that of Figure 1-11 [127].

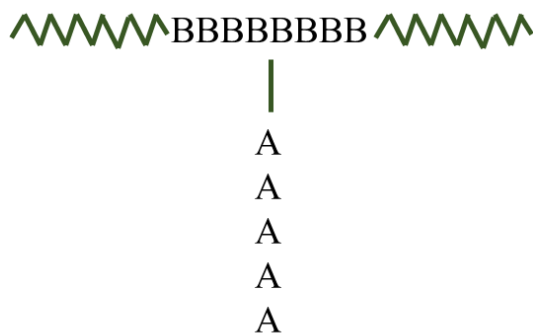


Figure 1-11: Schematic structure of graft copolymer.

1.5.2. Chemistry of Grafting

Various chemical techniques can be employed for grafting, and the key methods of chemical reactions are elaborated upon below.

1- Redox Reaction

The conventional method to generate free radicals is through a redox reaction. There are various redox reagents that can create and transfer radicals to the polymer to initiate grafting reactions. The chemical reactions have the following characteristics: (1) they are easy to perform and are not location-specific, (2) they can be carried out at room temperature or even in aqueous solutions, and (3) the degree of grafting can be controlled by adjusting reaction variables such as monomer/initiator composition, reaction time, and temperature [128]. The possible reaction pathways are:

- (I) With Fenton's reagent (Fe^{2+} / H_2O_2) the reaction of Fe^{2+} and H_2O_2 leads to the production of $\text{OH}^\bullet$ [129].
- (II) With Fe^{2+} /Persulphate, they act as source of $\text{SO}_4^{\bullet-}$ [130].
- (III) With using persulfate in combination with a reducing agent such as sodium/potassium bisulphite, thiosulphate, or Ag^+ is another method to generate $\text{SO}_4^{\bullet-}$, which can then produce $\text{OH}^\bullet$. This process allows for the direct or indirect initiation of polymer free radicals by $\text{SO}_4^{\bullet-}$ [131].

- (IV) With Fe^{2+} /Hydroperoxides, hydroperoxides and Fe^{2+} comprise another important redox system. Free radicals are generated by the interaction between the two through thermal decomposition. The activity of the system is due to the formation of a t-butoxy radical resulting from a one-electron transfer between tertiary butyl hydroperoxide (TBHP) and Fe^{2+} [132].
- (V) Direct oxidation is a different system for generating free radical sites on a polymeric backbone. It involves the direct oxidation of the polymeric backbone by certain transition metal ions such as Ce^{4+} , Cr^{6+} , V^{5+} , and Co^{3+} . Metal ions with low oxidation potential are preferred for this reaction. The proposed mechanism involves the intermediate formation of a metal ion polymer complex of chelate type (I). However, this complex formation is not possible for all polymers, especially cellulose types, where there is a possibility that glycol groups may participate in the reaction [133].
- (VI) Metal Chelates can be used to control the redox potential and prevent undesired reactions during the grafting process. Metal chelates such as $\text{Fe}(\text{acac})_3$, $\text{Zn}(\text{acac})_2$, $\text{Al}(\text{acac})_3$, and $\text{VO}(\text{acac})_2$ (where acac stands for acetyl acetate) are effective in the grafting reaction. The metal ions in these complexes react with the monomer to generate free radicals, which then undergo a chain transfer to the polymer [134].
- (VII) By Indirect Method, secondary free radicals are generated in the system, which may eventually induce the free-radical sites necessary for grafting [125].

However, redox polymerization has certain limitations, including (a) the need for continuous initiation in conventional free-radical graft polymerization, (b) the termination step resulting in

an unreactive polymer, (c) broad molecular distribution in the grafted product, and (d) a time-invariant degree of polymerization.

2- Living Radical Formation

This technique allows for the avoidance of the chain termination step in two ways: either by increasing the rate of initiation in comparison to the rate of propagation or by eliminating chain termination and transfer reactions. This results in polymer chains that grow at a constant rate, with similar chain lengths. As a result, it allows for the continuous growth of the polymer whenever additional monomers are provided. This method can be applied in various types of reactions, such as atom transfer, nitroxide mediated, and degenerative transfer. The key features of this method include: (1) the process continues until all monomers are consumed, (2) continued polymerization occurs with the addition of more monomers, (3) the rate of initiation (R_i) is much smaller than the rate of propagation (R_p), whereas in conventional free-radical grafting, $R_i > R_p$, (4) there is a dynamic equilibrium between propagating radicals and dormant species, (5) it allows for the production of mono and/or narrow dispersities of the products, (6) the molar mass of the grafted/crosslinked polymer molecules can be predetermined, and (7) it is possible to synthesize telechelic polymers by using proper terminating reagents. [135], [136].

- (I) Atom Transfer
- (II) Nitroxide Mediated
- (III) Degenerative Transfer

3- Enzymatic Technique

Enzymatic catalysis is a notable characteristic of this technique, which enables grafting and crosslinking reactions to be performed with the aid of biological protein catalysts. Oxide reductase enzymes, such as horseradish peroxidase and tyrosinase, are commonly used for grafting reactions. These enzymes can generate free radicals (e.g., phenol/amine derivatives) by either abstracting electrons or providing molecular oxygen to the molecules. The resulting active species can then either condense with each other or react with nucleophiles. Enzymatic reactions are more commonly used for natural polymers than synthetic polymers. One of the advantages of enzymatic reactions is their flexibility to combine with chemical reactions. For instance, well-defined polymethacrylate-g-polycaprolactone copolymers have been synthesized by combining atom transfer radical polymerization (ATRP) and enzymatic ring-opening polymerization in CO₂. However, this method can be costly and is not suitable for high-temperature reactions

4- Radical mechanisms

Free radical intermediates can be generated through various methods, including the thermal or chemical breakdown of an initiator, the redox reaction between two species, or the excitation of a photoinitiator. Additionally, exposing a material to sufficient energy, such as γ -irradiation, photoirradiation, thermal treatment, or an electron beam, can also introduce radical intermediates by homolytically cleaving chemical bonds. If initiation occurs through irradiation, the generated radical flux will be proportional to the radiation flux. Pre-irradiation of a material by ionizing radiation may be used to generate in-situ radical initiator species like peroxides. Initiation is the first reaction of a chain carrier with a monomer or polymer molecule, forming a

new covalent bond and regenerating the reactive center at a new location. Addition and abstraction are the two ways initiation can occur, with the thermodynamic driving force being the replacement of a high-energy π -bond with a σ -bond (addition) or a weaker R-H or R-X bond with a stronger R'-H or R'-X bond (abstraction). Propagation is the next step in producing a graft copolymer via a free-radical polymer/monomer mechanism [125].

5- Ionic chain mechanisms

Ionic chain carriers, like radicals, can be generated by various mechanisms, and the key steps of initiation, propagation, and termination are applicable to them. Cations are suitable for polymerizing vinyl monomers containing an electron-donating group and epoxides. Unlike radicals, cations are generally generated singly, but this depends on the initiator. For example, when triarylsulfonium salts are photolyzed in the presence of a hydrogen donor species, two Brönsted acid initiating species are produced, along with free radicals. In many interpenetrating network syntheses, it is possible to simultaneously polymerize one species by cationic polymerization and another by radical polymerization using a single initiator. In "living" conditions, where chain terminators are excluded, the number of cationic charge carriers will increase during the initiation reaction, and no steady state will be achieved. One way to achieve grafted polymerization using cationic mechanisms is to use a polymer backbone with functionalities that can be easily converted to carbocations. Another method is to employ a "grafting to" mechanism where backbone functionalities can combine with polymer carbocations to create a covalent bond onto aminated cellulose [125], [131].

1.5.3. Redox grafting: benefits and applications

Grafting via redox reactions is a method employed to modify polymers by attaching various monomers or polymers to the primary chain through a chemical process involving oxidation and reduction. This approach offers several advantages over alternative methods, including:

1. Versatility in Functional Groups: One of the key advantages of redox grafting lies in its ability to introduce a wide range of functional groups onto polymers. This includes carboxylic acids, aldehydes, isocyanates, ferrocene, and more. These diverse functional groups can significantly enhance the properties and broaden the applications of the polymers, tailoring them to specific needs and industries [137].

2. Media Flexibility: Redox grafting can be performed in either aqueous or organic media, depending on the selection of redox initiators. This adaptability makes it a versatile and adaptable technique suitable for a wide array of polymer matrices and intended applications [138].

3. Energy and Environmentally Friendly: An additional benefit of redox grafting is its capability to operate at low temperatures and pressures. This feature not only reduces the energy consumption associated with the process but also minimizes its environmental impact. The method aligns with sustainability and environmentally conscious manufacturing practices [137].

4. Efficiency and Control: Redox grafting enables the achievement of high grafting efficiency and yield, while also providing precise control over grafting density and distribution. This control ensures that the desired modifications are consistently applied across the polymer matrix, resulting in a well-defined and designed material [139].

1.5.4. Surface grafting and antifouling mechanism

Polymeric membrane surface properties have been enhanced using surface grafting techniques where monomers are covalently bonded onto the membrane [140]–[142]. Surface grafting plays a fundamental role in reducing membrane fouling by bonding hydrophilic polymers onto the membrane's surface. These hydrophilic polymers work to enhance the membrane's hydrophilicity, resulting in improved antifouling properties [72]. Multiple studies have corroborated that an increase in surface hydrophilicity is associated with a decreased tendency for membrane fouling. Various grafting techniques, such as chemical, radiation, photochemical, plasma-induced, and enzymatic grafting, have been reported in literature (some studies employing various grafting methods are compared in Table 1-5) [116]. Control of the polymer grafting process is complicated by several parameters, including the backbone and monomer characteristics, solvent, initiator, additives, temperature, and degree of polymer graft yield. These parameters make it challenging to control the polymer grafting process, along with other variables involved in membrane fabrication.

Bernstein et al. [143], described the graft copolymerization of a strong polyelectrolyte hydrogel onto a PES ultrafiltration membrane using vinyl sulfonic acid (VSA) as the functional monomer and N,N'-methylenebisacrylamide (MBAA) as the cross-linker monomer. The effect of the polymerization conditions on the degree of grafting (DG) was investigated, and it was found that the cross-linker fraction affected the DG. The resulting membranes were tested under nanofiltration conditions and showed high Na₂SO₄ rejection, stable performance in a wide range of pH, and increasing salt rejection with increasing degree of cross-linking and VSA fraction.

In another study, Wavhal et al. [144], described a method to modify PES membranes by Argon-plasma treatment followed by graft copolymerization with acrylamide (AAm) in the vapor phase. The resulting modified membranes had highly hydrophilic surfaces, confirmed by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The grafting rate was dependent on plasma exposure time, and SEM analysis showed no surface damage or significant alteration in pore structure. The modified membranes had increased glass transition temperature and reduced susceptibility to BSA protein adsorption. The hydrophilic nature of the modified membrane also allowed for greater flux recoveries after cleaning, indicating reversible protein fouling.

Table 1-5: Grafted membrane comparisons: grafting methods, grafting materials, applications

Membrane/ Grafting materials	Grafting method	Application/ Performance	References
PVDF membrane/ PEGMA	• Surface-initiated radical graft copolymerization • Thermal-induced radical polymerization • ATRP	• Protein adsorption • Flux recovery ratio: 90.8%	[145]
PES hollow fiber membrane / acrylamide	• Graft polymerization	• Applications requiring both organic antifouling and antibacterial properties • BSA rejection: 90%	[24]
Nylon and polystyrene/ PNIPAM	• Atmospheric plasma treatment followed by free radical graft copolymerization	• Biomedical field, such as drug delivery, bioreactors, tissue engineering, and cell detachment control	[146]
PSF/PNIPM	• Atom transfer radical polymerization and click chemistry	• Forward osmosis filtration • Pure water permeability: 215 for grafted vs 79 for bare membrane (LMH/bar)	[147]

As depicted in Tables 1-5, the extensive range of applications for membranes grafted thermo-responsive polymer is quite evident. This diversity has stimulated the interest of numerous researchers, highlighting the attractiveness of thermo-responsive polymers as grafting agents for modifying membrane surfaces. Studying special polymers with a natural attraction to water and the ability to respond to temperature changes holds promise for reducing fouling on surfaces. These polymers have a strong affinity for water, discouraging contaminants from sticking to the surface. Additionally, they respond to temperature shifts by altering their hydrophilicity properties. This responsiveness can assist in keeping the surface clean, ultimately enhancing the membrane's performance and longevity [148].

1.6. Thermo-responsive polymers (TRPs)

Thermo-responsive polymers belong to the class of stimuli-responsive materials, which can alter their behavior according to different environmental conditions. They are also called temperature-responsive polymers or smart polymers. TRPs are types of polymers that can change their physical properties, such as solubility, shape, or size, in response to a change in temperature.

Water-soluble TRPs are of particular interest as water is an inexpensive and safe solvent, and also the solvent of living systems, making it suitable for a wide range of applications in biochemistry and environmental sciences [149]. Water soluble thermo-responsive polymers can be classified into two types based on their solubility behavior in a given solvent: those that have a lower critical solution temperature (LCST) and those that have an upper critical solution temperature (UCST). A polymer with LCST becomes insoluble when the temperature is above a certain point, while a polymer with UCST becomes insoluble when the temperature is below a certain point.

The majority of TRPs exhibit a change in hydrophilicity with temperature. This group of polymers is divided into two categories: those that phase separate from solution upon heating, and those that phase separate upon cooling. The former exhibit a lower critical solution temperature (LCST) in their phase diagram, while the latter exhibit an upper critical solution temperature (UCST), as shown in Figure 1-12 [150], [151]. The temperature at which the polymer undergoes a phase transition from a soluble to an insoluble state in a solvent is known as a cloud point of a thermo-responsive polymer. There are various methods to determine the cloud point of thermo-responsive polymers experimentally, such as UV-Vis Spectroscopy, differential scanning calorimetry (DSC), dynamic light scattering (DLS), nuclear magnetic resonance (NMR), and fluorescence spectroscopy [152]. UV-Vis Spectroscopy is one of the most common and simple methods, which measures the light transmittance or absorbance of a polymer solution as a function of temperature. The cloud point is defined as the temperature at which the transmittance or absorbance reaches a certain value, usually 50% or 90%. DSC measures the heat flow into or out of a polymer solution as a function of temperature. The cloud point is defined as the temperature at which an endothermic peak is observed, corresponding to the enthalpy change of the phase transition. DLS measures the size and distribution of polymer aggregates in solution as a function of temperature. The cloud point is defined as the temperature at which a sudden increase in aggregate size is observed. NMR measures the chemical shift and relaxation time of polymer protons in solution as a function of temperature. The cloud point is defined as the temperature at which a significant change in chemical shift or relaxation time is observed, indicating a change in polymer conformation or mobility. Fluorescence spectroscopy measures the fluorescence intensity or lifetime of a fluorescent probe

attached to or incorporated into a polymer chain as a function of temperature. The cloud point is defined as the temperature at which a significant change in fluorescence intensity or lifetime is observed, reflecting a change in polymer environment or dynamics [153].

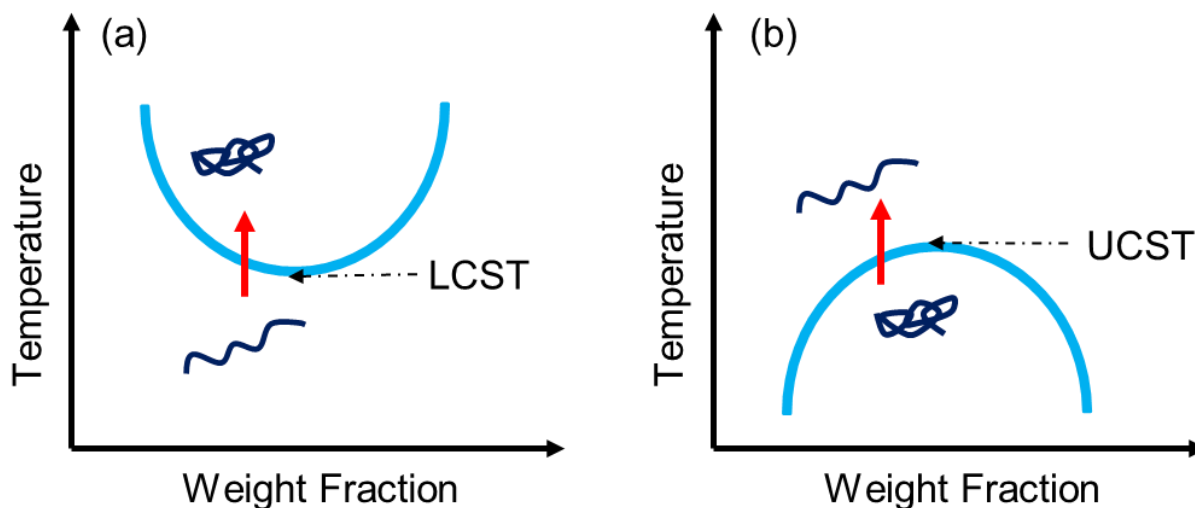


Figure 1-12: Temperature dependent phase transition of TRPs.

1.6.1. Thermodynamics of thermo-responsive polymers

The thermodynamics of thermo-responsive polymers can be understood by considering the Gibbs free energy of mixing (ΔG) of the polymer-solvent system. The ΔG is determined by the enthalpy of mixing (ΔH) and entropy of mixing (ΔS). The ΔH represents the change in intermolecular interactions between the polymer and the solvent, while the ΔS represents the change in disorder or randomness of the system.

For a polymer with LCST, the ΔH is positive, meaning that the polymer-solvent interactions are weaker than the polymer-polymer and solvent-solvent interactions. The ΔS is also positive, meaning that the system becomes more disordered when the polymer dissolves in the solvent. At low temperatures, the ΔS term dominates over the ΔH term, making the ΔG negative and

favoring dissolution. However, as the temperature increases, the ΔS term decreases faster than the ΔH term, making the ΔG positive and favoring precipitation. The temperature at which ΔG becomes zero is the LCST [154].

For a polymer with UCST, the opposite situation occurs. The ΔH is negative, meaning that the polymer-solvent interactions are stronger than the polymer-polymer and solvent-solvent interactions. The ΔS is also negative, meaning that the system becomes more ordered when the polymer dissolves in the solvent. At high temperatures, the ΔS term dominates over the ΔH term, making the ΔG negative and favoring dissolution. However, as the temperature decreases, the ΔS term increases faster than the ΔH term, making the ΔG positive and favoring precipitation. The temperature at which ΔG becomes zero is the UCST [155] [156].

The thermodynamics of thermo-responsive polymers can be influenced by various factors, such as polymer concentration, molecular weight, chemical structure, solvent quality, pH, salt concentration, and external stimuli. These factors can affect either the ΔH or ΔS terms or both, thus shifting or broadening the LCST or UCST values. For example, increasing polymer concentration can increase both ΔH and ΔS terms, thus lowering LCST or raising UCST values. Increasing molecular weight can decrease both ΔH and ΔS terms, thus raising LCST or lowering UCST values. Adding hydrophilic or ionic groups to the polymer can decrease ΔH term or increase ΔS term, thus lowering LCST or raising UCST values. Changing solvent quality can affect both ΔH and ΔS terms depending on whether it is a good or poor solvent for the polymer. Changing pH can affect both ΔH and ΔS terms depending on whether it changes the charge or polarity of the polymer. Adding salt can affect both ΔH and ΔS terms depending on whether it screens or enhances electrostatic interactions between polymer chains. Applying external stimuli such as

light or magnetic field can affect both ΔH and ΔS terms depending on whether they induce conformational changes or phase transitions in the polymer [157], [158].

1.6.2. Different thermo-responsive polymers, applications, and limitations

Thermo-responsive polymers have many potential applications in biomedical fields, such as tissue engineering, drug delivery, bioseparation, and liquid chromatography. For example, thermo-responsive polymers can be used to create cell sheets that can detach from a surface without using enzymes or mechanical force. Thermo-responsive polymers can also be used to deliver drugs that can be released at a specific temperature or location in the body. Thermo-responsive polymers can also be used to separate biomolecules that have different solubility or affinity at different temperatures. Thermo-responsive polymers can also be used to modulate the separation efficiency of liquid chromatography columns by changing the temperature of the mobile phase [154], [159].

There are various types of thermo-responsive polymers besides water-soluble thermo-responsive polymers. For example, thermo-responsive hydrogels. These are cross-linked polymer networks that can swell or shrink in response to temperature changes. They can be used for drug delivery, tissue engineering, or biosensors. Some examples of thermo-responsive hydrogels are poly (N-isopropylacrylamide) (PNIPAM), poly (ethylene glycol) (PEG), or poly (vinyl methyl ether) (PVME) hydrogels [154]. The other TRP category is thermo-responsive shape memory polymers. These are polymers that can memorize and recover their original shape upon heating or cooling. They can be used for smart textiles, self-healing materials, or biomedical devices. Some examples of thermo-responsive shape memory polymers are polyurethane (PU), poly (ϵ -caprolactone) (PCL), or poly (lactic acid) (PLA) polymers [159], [160]. The last type is thermo-responsive

magnetic polymers. These are polymers that contain magnetic nanoparticles that can generate heat under an external magnetic field. They can be used for hyperthermia therapy, drug delivery, or magnetic separation. Some examples of thermo-responsive magnetic polymers are poly (N-isopropylacrylamide-co-acrylic acid) (P(NIPAM-co-AA)) or poly (N-isopropylacrylamide-co-N,N'-methylenebisacrylamide) (P(NIPAM-co-BIS)) polymers [160]. Table 1-6 present the application and limitation of some of the thermo-responsive polymers studied in the literature.

Table 1-6: Comparison between different thermo-responsive polymers, applications, and limitations

Thermo-responsive polymer	Application	Limitation	Reference
Poly(N-isopropylacrylamide) (PNIPAm)	• Cell sheet engineering • Drug delivery • Water treatment	• Condition-dependent biocompatibility • Susceptibility to oxidation and hydrolysis • Difference between the transition temperatures during heating and cooling cycles	[154]
Poly(N-vinylcaprolactam) (PNVCL)	• Tissue engineering • Drug delivery • Wastewater treatment	• Low mechanical strength • Degradation by UV light • pH dependency • Ionic strength	[161]
Poly(ethylene glycol methacrylate) (PEGMA)	• Coating • Tissue engineering • Drug delivery	• Expensive • Complex monomer to synthesize • Degradation by UV light oxidation, and hydrolysis • Undesirable interaction with proteins, cells, or tissues	[162]
Polymethyl methacrylate (PMMA)	• Bone cement • Artificial teeth • Contact lenses	• Poor mechanical properties • High water absorption • High susceptibility to bacterial adhesion	[163]

1.6.3. Poly(N-isopropyl acrylamide)

Poly(N-isopropyl acrylamide) (PNIPAm) depicted at Figure 1-13 and its derivatives are extensively studied thermo-responsive polymers [164], [165]. Upon heating and cooling, PNIPAm undergoes a reversible phase transition from a hydrophilic coiled state to a hydrophobic globule state, exhibiting alterable water solubility and an LCST in the range of 30-35°C. Some of the reasons why PNIPAM is more popular than other thermo-responsive polymers are: (i) PNIPAm has a lower critical solution temperature (LCST) of about 32°C, which is close to the physiological temperature of the human body. This makes it suitable for applications that require temperature-triggered responses, such as drug delivery, tissue engineering, biosensors, and bio-separation. (ii) PNIPAm is biocompatible and non-toxic, which means it does not cause adverse effects on living cells and tissues. It can also be modified with different functional groups to enhance its biocompatibility and bioactivity. (iii) PNIPAm can form hydrogels that have high water content and elasticity, which mimic the properties of natural tissues. PNIPAM hydrogels can also be easily fabricated by various methods, such as polymerization, crosslinking, or laser processing. (iv) PNIPAm can be used to create smart surfaces that can control the adhesion and detachment of proteins and cells by changing the temperature. This allows for the fabrication of cell sheets, which are thin layers of cells that can be transferred to damaged tissues without using scaffolds or carriers [154], [166].

PNIPAm can be functionalized through replacing the isopropyl group with other functional groups such as a carboxyl group (2-carboxyl isopropyl acrylamide, CIPAM) [167], an amide group (2-amino isopropyl acrylamide, AIPAM) [168] or a hydroxyl group (2-hydroxy isopropyl acrylamide, HIPAM) [169] as well as copolymerization with functional monomers, allowing tuning

of the LCST to desired temperatures and responsiveness to properties such as temperature, pH, ion concentration, or salt concentration. These smart polymers have numerous applications in various fields, including biomedicine, biomaterials, water treatment, food, and cosmetics.

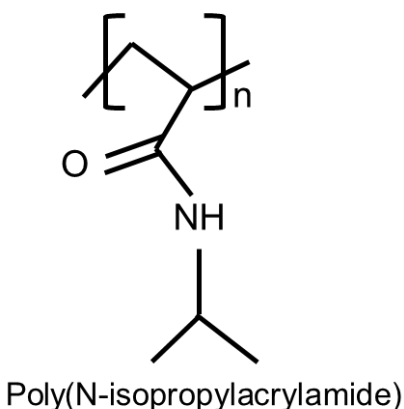


Figure 1-13: Chemical structure of N-isopropyl acrylamide.

1.6.4. Significance of PNIPAm in comparison to other TRPs

PNIPAm was chosen for our application based on its unique properties, including:

(1) A significant and reversible change in volume during the volume phase transition temperature (VPTT) at approximately 33°C. The swelling ratio (SR) is defined as the ratio of the mass of the swollen hydrogel to the mass of the dry hydrogel. The water retention ratio (WRR) is defined as the ratio of the mass of water in the swollen hydrogel to the mass of water in the collapsed hydrogel. The higher the SR or WRR, the more water the hydrogel can hold and the larger the volume change. Compared to other thermo-responsive polymers, such as Pluronics, elastin-like polypeptides (ELP), and poly(N-vinylcaprolactam) (PNVCL), PNIPAM has a higher water content and a lower swelling ratio (e.g., at 25 °C: ~2.2 for PNIPAM and ~4.5 for PNVCL) than these

polymers [170]. This means that PNIPAM has a larger volume change than these polymers when the temperature changes across their LCST or UCST values. Therefore, PNIPAM has more advantages and applications than other thermo-responsive polymers in bioengineering [171].

(2) A rapid phase transition process, with PNIPAm brushes displaying potential for rapid response times of less than one second to transition from a coiled to globular state; and (3) The ability to attach and detach living cells (such as bacteria) from the surface of PNIPAm-grafted substrates due to large changes in water contact angle (hydrophobicity and hydrophilicity) during the phase transition [172]. Compared to other thermo-responsive polymers, such as Pluronics, elastin-like polypeptides (ELP), and poly(N-vinylcaprolactam) (PNVCL), PNIPAM has a faster and sharper phase transition. This is because PNIPAM has a lower critical micelle concentration (CMC), a lower LCST range, a higher water content, and a lower swelling ratio than these polymers [173]. Regarding membrane technology, various forms of stimuli-responsive membranes have been thoroughly researched to enhance the antifouling properties and ease of cleaning associated with membranes. PNIPAm's hydrophilic nature plays a vital role in combatting membrane fouling by contributing to an increased surface energy facilitated by the hydration layer formed on the membrane's surface. This augmentation of surface energy substantially reduces the likelihood of deposition and adhesion, establishing it as an effective measure for mitigating fouling challenges. Consequently, the application of a hydrophilic membrane proves instrumental in minimizing flux deterioration, resulting in a higher recovery of flux during both filtration and subsequent cleaning processes [174]. According to a study conducted by Kajornprai et al. [175], the effect of PNIPAM grafting yield on fouling behavior of membrane was investigated. The study demonstrated the potential applications of thermo-responsive poly (N-isopropylacrylamide) (PNIPAm)-grafted

nylon membranes with different grafting yields and architecture. The thermo-responsive gating performance at temperatures below and above the lower critical solution temperature (LCST) of PNIPAm (32 °C) were demonstrated. The linear PNIPAm-grafted nylon membrane exhibited a sharp response over the temperature range 20–40 °C. The grafting yield of 25.5% and 21.9%, for linear and crosslinked PNIPAm respectively, exhibited highest thermo-responsive gating function for water flux and had a stable and repeatable “open-closed” switching function over 5 cycle operations. An excellent oil/water separation was obtained at $T < 32\text{ }^{\circ}\text{C}$, at which the hydrophilic behavior was observed. The O_2 and CO_2 transmission rates through the PNIPAm-grafted nylon membranes decreased when the grafting yield increased, showing the better gas barrier property. There isn't a substantial body of research focusing on the impact of PNIPAm grafting yield on membrane fouling behavior. Nevertheless, several studies have explored the influence of PNIPAm and its derivatives on the surface hydrophilicity and fouling characteristics of polymeric membranes.

For example in the study conducted by You et al. [176], modifications were made to a polyamide (PA) membrane by employing surface-initiated graft polymerization using pH, salt, and thermo-responsive polymers. The outcomes of a prolonged fouling-rinsing experiment demonstrated that the salt-responsive membrane exhibited the most effective anti-fouling and cleaning performance. The membrane experienced a minimal flux decline of merely 9% after 200 hours of testing and exhibited an impressive flux recovery of 88.1% following the initial rinse. This remarkable antifouling performance was attributed to several factors, including the lower surface roughness of the salt-responsive membrane, heightened hydrophilicity, and an accumulation of a more substantial negative surface charge.

In a separate study by Li et al. [177], copolymers P(NIPAm-co-Am) and P(NIPAm-co-GMA) (with GMA representing glycidyl methacrylate and Am denoting acrylamide) were grafted onto the surface of a PES membrane using electrochemical atom transfer radical polymerization. The results demonstrated notable flux recovery rates of approximately 70% after cleaning and exhibited a low total fouling (Rt) of about 50% for the P(NIPAm-co-Am) sample. This positive outcome was primarily attributed to the enhancement of hydrophilicity on the modified membrane, consequently reducing the water contact angle. Furthermore, it was also reported that at higher feed temperatures, there is a decrease in rejection rate. This decrease can be attributed to the enlargement of pore sizes resulting from the curling of TRP chains.

Additionally, Mao et al. [178], developed t-ATP (attapulgate modified with poly(N-isopropylacrylamide)) by modifying attapulgate (ATP) nanofibers with poly(N-isopropylacrylamide) (PNIPAm) and integrating it into the PVDF membrane structure. The inclusion of PNIPAm chains in t-ATP brought about alterations in the surface properties in response to temperature changes, consequently reducing adhesion between the membrane and biofoulants. This modification led to an enhanced biofouling resistance performance compared to a pristine PVDF membrane, mainly due to the hydrophilic nature of t-ATP and its stretchable surface chains. Notably, a significant portion of the biofouling (89%) on the membrane could be effortlessly removed through a simple temperature-based cleaning process coupled with ultrasonic treatment.

1.7. Functional group and metal nanoparticles as an effective strategy to mitigate biofouling

The integration of PNIPAm brushes has indeed showcased its prowess in enhancing fouling resistance, yet it's crucial to recognize that a singular antifouling surface can only effectively combat a limited range of foulants. Consequently, the amalgamation of multiple antifouling strategies stands as a promising approach to engineer innovative membranes endowed with durable and efficient antifouling properties. This multifaceted approach presents a highly promising avenue toward sustainable water purification for the future [178], [179], [180].

1.7.1. Acrylamide functional group

Numerous studies have documented the improvement in fouling resistance achieved through surface modification of porous membranes via the grafting of acrylamide (AAm) [181], [182]. These AAm-grafted membranes have demonstrated elevated hydrophilicity, heightened permeability, and markedly improved fouling resistance. In a noteworthy study, Hu et al. pioneered the creation of nanoporous membranes by combining photothermal-responsive ultrathin gold nanorods and a co-hybrid of poly(N-isopropylacrylamide-co-acrylamide) with single-walled carbon nanotubes (SWCNTs). This innovative combination led to exceptional separation efficiency exceeding 99.99%, coupled with enhanced antifouling and recyclability properties. The integration of PNIPAm-co-AAm was highlighted for conferring a highly hydrophilic surface to the ultrathin SWCNT network film, resulting in ultrafast separation of oil-in-water nano-emulsions while simultaneously bolstering antifouling capabilities. This research signifies a significant advancement in membrane technology, demonstrating the potential to

achieve superior filtration and antifouling efficiencies through strategic integration of complementary antifouling approaches [183] .

Despite the substantial benefits associated with integrating thermo-responsive polymers like PNIPAm and AAm to enhance a membrane's resistance to biofouling, there remains a critical imperative to amplify the incompatible interaction between foulant molecules and the membrane. This enhancement is particularly essential in the realm of biofouling mitigation, as it can effectively impede the regeneration of microorganisms, decelerate bacterial colony growth, and significantly decrease the concentration of live contaminants circulating within the feed water cycle [184].

1.7.2. Metal nanoparticles

Metal nanoparticles, including several nanostructured materials, have generated significant interest for their potential antibacterial effects on membrane surfaces [185]–[187]. Additionally, the morphological and physicochemical characteristics of these nanoparticles have been shown to have minimal impact on the membrane's filtration performance [18], [188]. Transition metals play crucial biological roles, such as hydroxylation, redox reactions, and electron transport. As such, transition metal nanoparticles can be considered potent biocidal agents, given their ability to generate reactive oxygen species (ROS) that attack the bacteria membrane and react with thiol (R-SH) groups in the amino acids' structure, ultimately leading to bacterial death [189]. The specific killing mechanism for the transition metal oxide is elaborated further in subsequent sections of this study. Furthermore, it is important to note that transition metal oxides can target both gram-negative and gram-positive bacteria, depending on their design and specifications, including factors such as size, shape, concentration, and surface charge. Of all the transition

metals, silver nanoparticles are likely the most used element for antibacterial treatment. Silver/silver oxide nanoparticles typically contain large number of silver atoms (20 to 15,000) with a diameter less than 100 nm. Low particle size lead to large surface-to-volume ratio which makes Ag nanoparticles a potent antibacterial agent even at low concentrations [190]–[192]. However, silver is expensive compared to other transition metals and is primarily used in medical specialty surgical devices [193]. Therefore, identifying a less costly biocidal element with high antibacterial activity is critical. Copper particles have shown promise as a potential candidate due to their low cytotoxicity, low cost, and strong antibacterial properties [194].

1.7.3. Copper oxide nanoparticles

Copper, an inexpensive and highly toxic inorganic agent, exhibits notable antibacterial properties, making it exceptionally effective against microorganisms and biofouling [195]. Copper oxide nanoparticles, for instance, have demonstrated the capability to enhance not only the flux rate and resistance to organic fouling but also exhibit antibacterial properties when seamlessly integrated into the matrix of poly(ether imide) (PEI) membranes [196]. The infusion of copper oxides into the membrane's active layers has yielded outstanding results, showcasing a remarkable rejection rate and flux recovery ratio (FRR) exceeding 97% for various organic foulants such as bovine serum albumin (BSA), humic acid (HA), and motor oil. Moreover, copper-based nanoparticles exhibit exceptional hydrophilicity, physical and chemical stability, and potent antibacterial properties [197].

In a notable study, Liu et al. [198] reported on the successful incorporation of copper nanoparticles into a polydopamine (PDA) coating immobilized on a thin film composite membrane through a mild reduction method. This integration resulted in a measured flux

reduction rate of 65% for the unmodified membrane, significantly reduced to 39% for the modified Cu/PDA-2/TFC membrane. Additionally, the biofilm thickness for the modified membrane was approximately 58% lower than that observed on the pristine membrane, demonstrating the potential for copper integration in inhibiting biofouling. Table 1-7 provide an overview of various research studies and their outcomes that utilized CuO nanoparticles in polymeric substrates to enhance antifouling or antibacterial performance.

In recent years, several studies have investigated the antibacterial properties of copper in composite materials [199], [200]. For instance, Wei et al. [201] studied the effects of copper nanoparticles (Cu NPs) loaded onto bacterial cellulose (BC) membranes, which were then utilized as wound dressings. The composite membranes exhibited effective long-term antibacterial activity against two different strains of bacteria, namely *Staphylococcus aureus* and *E. coli*, for up to 90 days of immersion. Rahimi et al. [202] conducted a study that examined the impact of cellulose/copper oxide nanoparticles on the structure of thin film composite membranes. The study aimed to evaluate the ability of these membranes to remove cadmium from water and to assess their antibacterial performance. Antibacterial tests showed that the modified membrane with 1 wt.% CuO concentration exhibited a significant inhibition zone against *E. coli* bacteria, demonstrating considerable antibacterial properties. Table 1-7 provides a summary of the applications and performance of membranes modified using CuO nanoparticles.

Table 1-7: Applications of CuO NPs as an antibacterial and antifouling agent in polymer membranes

Polymeric Substrate	Modification Technique	Application	Performance	Reference
PVC/PVDF	Laser ablation	Antibacterial	Max % Activity index =14 for <i>B. cereus</i>	[203]

Thin-film composite (TFC)	Nanoparticle entrapped to PA layers	Antibacterial	CFU= 60000 cell/ mm ²	[204]
Polyether sulfone (PES) and cellulose acetate (CA)	Wet chemical synthesis	Filtration and antibacterial	BSA rejection= 95% Bacteria growth inhibition= 85%	[205]
PVC-based membrane	Additive blending	Antibacterial	Optical density of E. coli: Modified membrane=0.5 Pristine membrane= 0.8	[206]
Thin film composite	Additive blending in PA membrane	Antibacterial	Decrease in CFU= 99% for modified membrane	[207]

1.7.4. Contact killing mechanism description in presence of CuO nanoparticles

Copper has been commonly utilized as an antibacterial or biocidal agent in various studies. It can contribute to bacteria-killing processes through a few mechanisms, such as (i) the production of hydroxyl radicals through the Fenton and Haber-Weiss reactions, which is a result of copper's high oxidation ability [208] [209], (ii) oxidation of the sulfhydryl groups, such as cysteine in proteins or the cellular redox buffer glutathione, [210] and (iii) inactivation of the protein by damaging Fe-S clusters in proteins [211].

(i) Reactive Oxygen Species (ROS)

Fenton reaction is one of the well-known chemical redox reactions that occurs between Cu²⁺ and Cu⁺ ions leading to the generation of reactive hydroxyl radicals (OH[•]) (reaction 1). These radical agents attack cellular molecules, such as DNA, proteins, and lipids [212], [213] and then run several reactions, including the oxidation of proteins and lipids [214].



However, it should be noted that the Fenton reaction may not be the primary toxic mechanism, as bacteria cells tend to maintain low levels of H_2O_2 at the expense of generating $\text{OH}^\bullet$ [213].

(ii) Oxidation of Sulfhydryl Groups

In addition to the Fenton reaction, copper ions can also catalyze the reduction of sulfhydryl bonds (bonds between sulfur and hydrogen atoms) and facilitate the formation of sulfinic and sulfonic acids (as depicted in Figure 1-14) [213], [215].

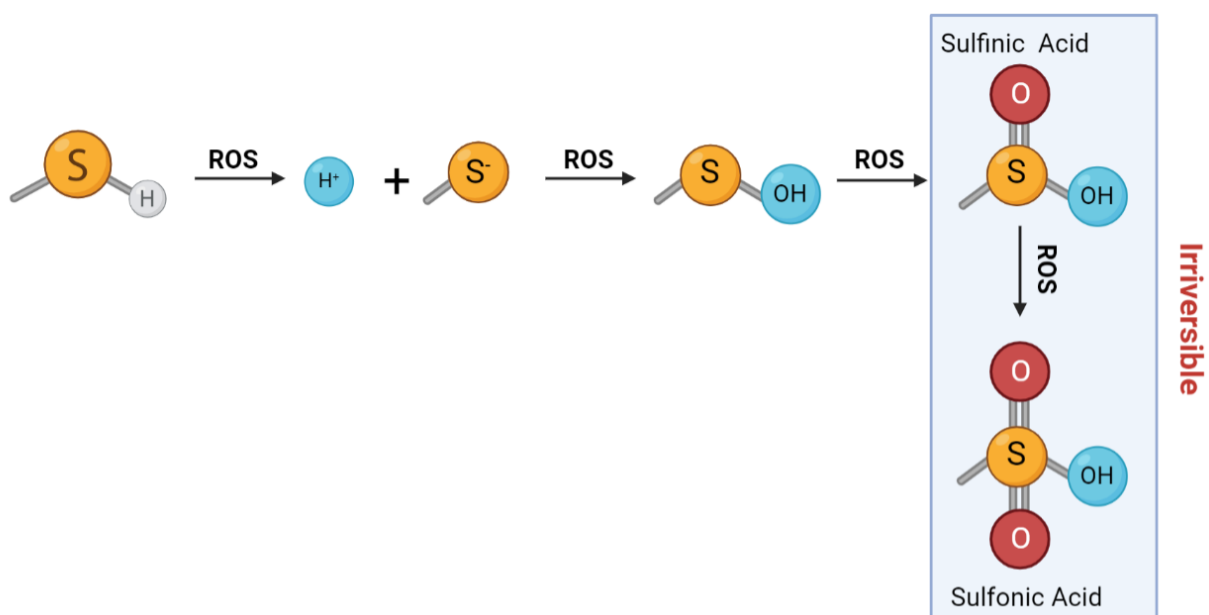


Figure 1-14: Schematic depicting the oxidation reaction of sulfhydryl groups.

Most living organisms contain high concentrations of thiols (e.g., cysteine) that serve as redox buffers providing a defense shield for the cells against a variety of reactive chemical species, such as reactive oxygen species (ROS), some antibiotics, and metalloids [216]. The formation of protein sulfenic acid has traditionally been viewed as undesirable damage resulting from ROS. However,

alterations in the redox state and the formation of sulfinic and sulfonic acid can also be associated with essential cellular processes, including proliferation, differentiation, and cell death.

The sulfhydryl bond is found in various components, including cysteines or glutathione, where it is referred to as a thiol group. Cysteine, with a chemical formula of $\text{HOOC-CH--CH}_2\text{-SH}$, is one of the most significant proteinogenic amino acids. Cysteine plays a crucial role in enzymatic reactions, including catalysis, structure stabilization, signal transduction, metal binding, protein splicing, and post-translational modifications [215]. When exposed to transition metal ions, such as Fe and Cu, cysteine is susceptible to an auto-oxidation reaction, in which oxygen (O_2) acts as an oxidant, generating hydroxyl radicals ($\text{OH}\bullet$) via the Fenton reaction (reaction 1) [217]. Several studies have shown that even at a concentration of $0.2\ \mu\text{M}$, Cu^{2+} or Cu^+ can oxidize half of the intracellular cysteine concentration within 60 minutes. Interestingly, the auto-oxidation of cysteine in the presence of copper has been observed to occur at a much faster rate than when in contact with other transition metals, such as iron [218], [219].

(iii) Damaging Fe-S clusters in proteins

The Fe-S cluster plays an essential role in both DNA replication by DNA polymerases and the repair processes necessary for genome maintenance [220]. An elevated concentration of oxygen, whether within the atmosphere or cellular environment, can pose a significant challenge to Fe-S clusters by rendering them susceptible to inactivation via cluster oxidation reactions. Furthermore, transition metals like iron and copper promote DNA damage through the Fenton reaction, which is a mechanism that gradually develops oxygen cytotoxicity and impairs genetic inheritance, thereby reducing the survival chances of bacteria [221], [222].

Fe-S clusters can be susceptible to ROS, but the Fe species can also be a source of ROS. Dehydratases, which include key enzymes in the biosynthesis of branched-chain amino acids, contain a complex of $[4\text{Fe}-4\text{S}]^{2+}$ clusters with one iron atom. The iron atom within the $[4\text{Fe}-4\text{S}]^{2+}$ clusters of dehydratases can be exposed to the solvent, leading to potential interaction with a superoxide anion [223]. Subsequent transfer of an electron to O_2^- can then result in the decomposition of H_2O_2 and the generation of hydroxyl radicals. Next, the cluster is targeted by the radical, resulting in the conversion of the $[4\text{Fe}-4\text{S}]^{2+}$ cluster into an unstable $[4\text{Fe}-4\text{S}]^{3+}$ form. This then leads to the formation of a $[3\text{Fe}-4\text{S}]^{1+}$ cluster by the loss of one Fe^{2+} , ultimately resulting in enzyme inactivation. According to this mechanism, any transition metal capable of generating ROS can initiate a similar reaction and deactivate the enzyme more rapidly than iron. Furthermore, the released transition metal such as iron or copper ion atom can bind to DNA and react with H_2O_2 , resulting in the generation of hydroxyl radicals ($\text{OH}\bullet$), which can directly cause damage to DNA (see Figure 1-15) [224], [225].

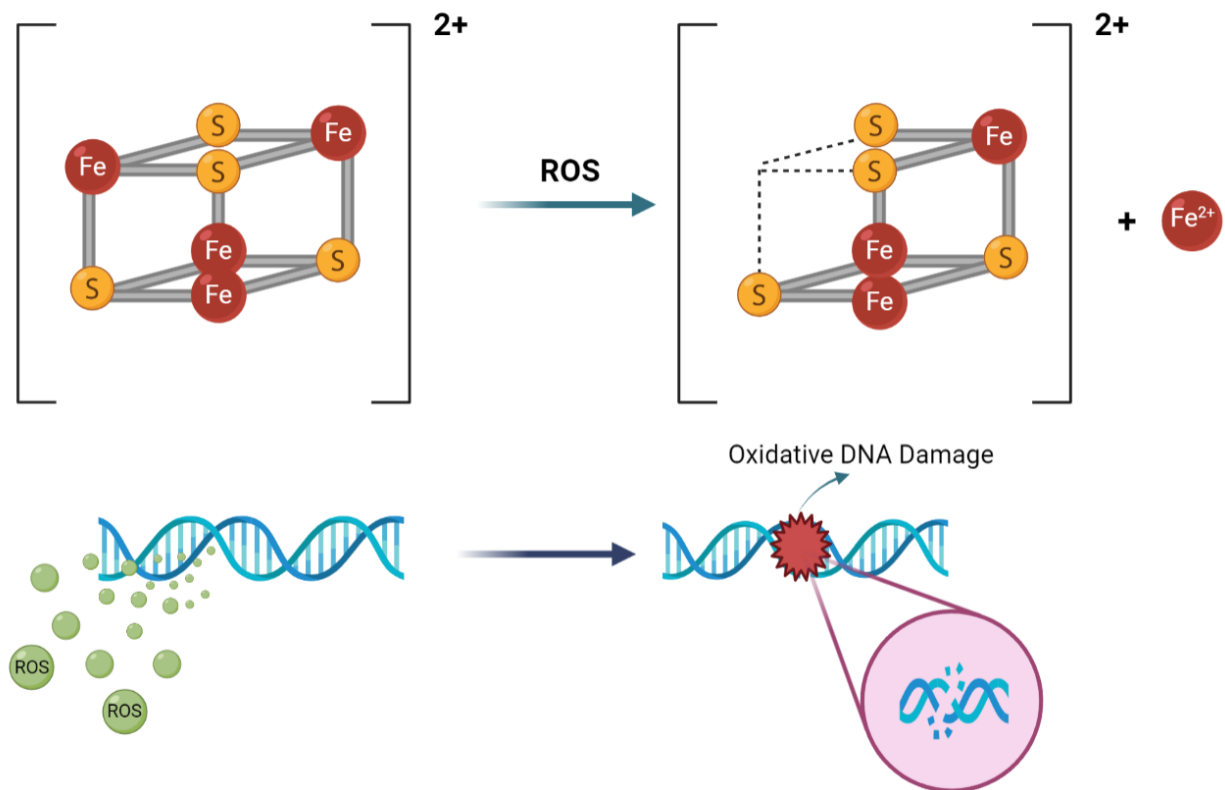


Figure 1-15: Schematic representation of Fe-S cluster damage following oxidative DNA damage.

1.7.5. Strengthening metal nanoparticle-membrane surface bonding via APTES ligand

The 3-aminopropyltriethoxysilane (APTES) is a potential candidate to create a strong bonding between organic and inorganic materials because it has both an amino group and a silane group in its structure. The amino group can react with various organic molecules, such as carboxylic acids, aldehydes, or isocyanates, to form covalent bonds. The silane group can hydrolyze and condense with metal oxides, such as silica or copper oxide, to form stable siloxane bonds. Therefore, APTES can act as a linker between organic and inorganic surfaces and provide functionalization and dispersion of nanoparticles in polymer matrices. APTES can also be used to

modify the surface charge and hydrophilicity of nanoparticles, which can affect their interactions with biopolymers, organic contaminants, and biological systems [226], [227].

1.7.6. The effect of environmental conditions on CuO bacteria killing properties

The effectiveness of metal oxide nanoparticles as antibacterial agents depends on various environmental conditions [228], [229], such as:

- The pH of the medium: The pH can affect the solubility, dissolution, ionization, and aggregation of the nanoparticles, which in turn can influence their antibacterial activity. For example, ZnO nanoparticles have higher solubility and ion release at acidic pH, which enhances their antibacterial activity, while CuO nanoparticles have lower solubility and ion release at acidic pH, which reduces their antibacterial activity.
- The temperature of the medium: The temperature can affect the kinetic and thermodynamic properties of the nanoparticles, such as the diffusion, reaction, and stability, which can affect their antibacterial activity. For example, CuO nanoparticles have lower ROS generation and antibacterial activity at higher temperatures.
- The presence of organic matter: The presence of organic matter, such as proteins, polysaccharides, or humic substances, can interact with the nanoparticles and form a coating or a corona, which can affect their size, shape, surface charge, and reactivity, which can affect their antibacterial activity. For example, the organic matter can reduce the ion release and ROS generation of the nanoparticles, which can reduce their antibacterial activity.

- The presence of other metal ions: The presence of other metal ions, such as Ca^{2+} , Mg^{2+} , or Fe^{3+} , can compete with the metal ions released from the nanoparticles for binding to the bacterial cell components, which can affect their antibacterial activity. For example, the other metal ions can reduce the toxicity of the metal ions released from the nanoparticles, such as Cu^{2+} , by forming complexes or precipitates, which can reduce their antibacterial activity.
- The size of copper oxide nanoparticles can also affect its antibacterial performance. Generally, smaller CuO NPs have higher antibacterial activity than larger ones, because they have larger surface area to volume ratio, higher dissolution rate of copper ions, and stronger interaction with bacterial cells. However, the size effect of CuO NPs may also vary depending on the bacterial strain, the medium composition, and the presence of other substances, such as proteins, organic matter, or metal ions.

1.8. Hybrid strategies (multi-functionalization) to mitigate biofouling

Hybrid strategies (multi-functionalization) aim to combine the advantages of different methods and overcome their limitations, to achieve a more effective and sustainable biofouling mitigation. For example, a hybrid strategy could involve the use of a physical method, such as ultrasound, to enhance the penetration and efficacy of a chemical agent, such as silver nanoparticles, on the biofilm. Alternatively, a hybrid strategy could involve the use of a biological method, such as bacteriophages, to selectively target and eliminate the biofilm, while preserving the beneficial microorganisms on the membrane surface. Another hybrid strategy could involve the use of a surface modification, such as a polyethylene glycol-silver nanoparticles (PEG-AgNPs) hybrid

material, to impart both hydrophilic and anti-microbial properties to the membrane surface [230]. Hybrid strategies (multi-functionalization) to mitigate biofouling are promising techniques that can improve the performance and durability of membrane systems. However, they also face some challenges, such as the cost, complexity, and compatibility of the methods, as well as the potential environmental and health impacts of the agents. Therefore, more research and development are needed to optimize and evaluate the hybrid strategies for different applications and conditions [231].

There are some studies that have explored the use of metal nanoparticles like silver nanoparticles functionalized with antimicrobial thermo-responsive polymers as a novel strategy to combat bacterial infections or antifouling membrane as presented in Table 1-8. For example, Gautam et al. [232] grafted thermo-responsive copolymers (p(NIPAAm-co-AEMA)) onto the surface of cellulose papers and immobilized silver nanoparticles (AgNPs) using electrostatic interactions to create smart antibacterial-cellulose papers with hybrid kill and release abilities. The modified cellulose papers were found to be effective in killing bacteria and releasing most of the dead bacterial residues from their surfaces after a hot and cold wash cycle.

There are three main strategies for preventing bacterial attachment and biofilm formation on membrane surfaces: (i) contact-killing, (ii) bacteria repelling (antiadhesion), and (iii) killing-release [233], [234]. Within a membrane possessing contact-killing surface traits, biocidal agents are incorporated onto the surface to eliminate bacteria that are attached. However, as dead bacteria accumulate, these agents can become deactivated over time, ultimately diminishing their efficiency [235], [236]. Bacteria-repelling surfaces rely on steric hindrance via: (i) surface hydration or (ii) charge repulsion to prevent bacterial adhesion, but these repellent agents can

lose their function over time, and the attachment of living cells to the surface becomes inevitable [237], [238]. A novel antibacterial technique, referred to as "kill and release," involves a reversible conversion between two modes: killing bacteria and the release of dead bacteria. This approach aims to minimize bacterial regeneration and increase the efficacy time of the antibacterial treatment [232], [239]. Smart surfaces that undergo chemical or physical changes in response to environmental stimuli, such as temperature, pH, or salt-responsive polymers, are often used in killing-release strategies [233], [240]. The "Kill and Release" application is one of the most significant and fundamental uses of membranes with hybrid modifications. Table 1-8 showcases the applications and performance of dual-functionalized membranes.

Table 1-8: A summary of dual-functionalized membranes for separation and antibacterial applications

Multi-function system	Application	Performance	Reference
• TFC • Silicon NPs • Hydroxyl functional groups	• Water vapor permeance	• Water vapor permeance in excess of 2200 GPU with vapor/N₂ selectivity of 501	[241]
• PVDF • Polyacrylic acid (PAA) • Titanium dioxide nanoparticles	• Antifouling membrane for organic materials (BSA) filtration	• Flux recovery ratio: 68% • Rejection rate: 90%	[242]
• Cellulose papers • (p(NIPAAm-co-AEMA)) • Silver nanoparticles	• Antibacterial-cellulose papers with hybrid kill and release abilities.	• Release almost all the dead bacterial debris from their surfaces after thermal stimulus wash	[232]

Chapter 2 – Research Goal and Objectives

2.1. Research Goal

The goal of this project is to make substantial enhancements in the antifouling efficiency and efficacy of polyethersulfone (PES) membranes specifically designed for water treatment applications. "Efficiency" in this context likely encompasses improvements in various aspects, such as the membrane's ability to effectively filter impurities, resist fouling or clogging, and resist bacteria growth during the water treatment process. The overarching objective is to enhance the performance and effectiveness of PES membranes, thereby improving their suitability for water treatment applications. This study outlines specific objectives aimed at achieving this goal. Upon completion, a comprehensive comparison between our study's outcomes and those of other published works will be presented confirming the effectiveness and success of our process in achieving our goal. This is evident in the accomplishment of a 100% reduction in bacteria within a 90-minute reaction period, showcasing remarkable bacterial eradication. When comparing this achievement to the recent progress of PES and polysulfone (PS) membranes modified with various biocidal agents, we observed an approximately 20% enhancement in antibacterial effectiveness [243], [244]. Additionally, noting a 30% improvement in cleaning ability over the bare membrane suggests that our approach is efficient compared to a bare membrane and other studies.

2.2. Research Objectives

By grafting TRP brushes onto the membrane surface and functionalizing these brushes with acrylamide and CuO nanoparticles, our goal is to enhance the membrane's antifouling properties, increase its ability to reject organic contaminants, improve cleaning performance, boost fouling

recovery rates, and enhance its antibacterial properties. The objectives of this project are to achieve the following:

1- Improve the antifouling properties/performance of PES membranes

Our first objective is to employ membrane modification techniques to enhance the antifouling properties of PES membranes. In this modification, we aim to:

- Graft thermo-responsive PNIPAm at varying grafting yields

Grafting polymers using a redox system presents a promising approach to achieve a high grafting density. Modifications with thermo-responsive polymer will not only enhance the membrane's surface hydrophilicity and resistance to fouling but also endow it with the ability to respond to temperature changes, thus improving its cleaning performance.

- Copolymerize the acrylamide functional group with PNIPAm

On the other hand, acrylamide, an organic agent with superhydrophilic properties, has the potential to improve the membrane's surface hydrophilicity.

- Incorporate copper oxide nanoparticles onto the membrane surface

Furthermore, the introduction of copper oxide nanoparticles onto the membrane's surface is expected to further enhance its hydrophilicity, complementing the effects of the thermo-responsive polymers and acrylamide on membrane surface properties.

With this approach, we anticipate a substantial:

- Improvement in water permeability, measured by flux rate
- Enhancement in antifouling properties, validated by a reduction in total fouling ratio

- Improvement in the cleaning ability of the membrane, evaluated by fouling recovery ratio

To assess the success of this objective, we will conduct a comparative analysis of the results obtained in our study in terms of:

- Total fouling rate
- Flux recovery ratio

Within this evaluation framework, we will utilize studies involving pristine and treated PES membranes as both a benchmark and a point of comparison. This comparison will be made with reference to findings from a closely related or similar study conducted within our research domain.

2- Improve the antibacterial properties/performance of PES membranes

In this section, we aim to capitalize on the distinctive characteristics of each modifier material to enhance the antibacterial performance of the membrane.

- Copper oxide is well-known for its potent antibacterial properties [195], [196]
- Thermo-responsive polymers are recognized for their phase transition behavior and ease of cleaning.
- Acrylamide functional groups are valued for their resistance to bacterial adhesion.

By incorporating CuO nanoparticles into the membrane structure, we aim to enhance the membrane's ability to eliminate various bacterial strains in the aqueous solution. This involves rendering the membrane more toxic to a wide spectrum of bacteria, including both gram-negative and gram-positive strains. This approach enables us to create a membrane that can disrupt bacterial structures, reduce the number of live microorganisms, and prevent the

regeneration of bacterial strains. Additionally, grafting thermo-responsive polymers and introducing acrylamide functional groups onto the PES membrane enhances the membrane's resistance to bacterial adhesion. The aim is to develop a surface that repels bacteria, thereby preventing them from adhering to the membrane. This is crucial for mitigating bacterial fouling, which could otherwise compromise the membrane's efficiency. With this approach, we anticipate a substantial:

- Improvement in the membrane's bacteria-killing ability, measured by CFU counting.
- Reduction in attached bacteria to the surface, qualitatively compared with others through surface imaging.

To evaluate the accomplishment of this objective, we will compare the results of bacteria eradication by comparing the followings with findings from similar studies:

- Reduction in number of gram-negative bacteria
- Reduction in number of gram-positive bacteria

This comparative analysis will enable us to gauge the effectiveness of our approach in relation to the outcomes observed in related research, thereby providing a comprehensive understanding of our contributions to the field.

3- Improve the membrane reusability and oil-water separation performance

The final objective of our study is to enhance the reusability of membrane and oil-water separation. To accomplish this goal, we will leverage the following features:

- Grafting PNIPAm and PNIPAm-co-AAm
- Utilizing APTES as a ligand

We leverage the membrane's phase transition behavior, enhancing its cleaning efficiency. This distinctive feature enables an increased number of membrane cleaning and reuse cycles. The application of APTES ligand enables chemical bonding between CuO NPs and the membrane, enhancing the stability and durability of CuO NPs, directly contributing to an extended number of membrane reuse cycles. With this approach, we anticipate a substantial:

- Improvement in oil-water emulsion separation, measured by rejection rate
- Extended number of membrane reuse cycles, validated by measurement of flux recovery ratio and rejection rate in each run

To evaluate the success of this objective, we will conduct a comprehensive assessment by comparing our results with relevant literature reports. This comparative analysis will include:

- The rejection rates
- Reusability runs and corresponding flux recovery ratios

In the context of this evaluation, we will include studies that focus on modified PES membranes as a benchmark. By contrasting our findings with these established references, we aim to gain a clear understanding of the advancements and improvements achieved through our modifications.

Chapter 3 – Approach and Novelty

In accordance with the specified objectives outlined in Chapter 2, our research project is dedicated to enhancing the antifouling performance of polyethersulfone (PES) membranes in four primary areas: weakening the bonding between the foulant and membrane surface, incorporating antibacterial capabilities to eliminate the regeneration of the attached bacteria, facilitating the removal of dead bacteria debris and other attached biofoulant (enabling easy cleaning), and improving the membrane's reusability.

To achieve these objectives, we have developed a novel methodology to graft polyN-isopropylacrylamide (PNIPAm) onto PES membranes using a redox initiator system, a method that has been novel in the context of PES membrane performance. This approach aims to boost the grafting yield of PNIPAm, capitalizing on its hydrophilic nature to improve the membrane's hydrophilicity and diminish the interaction of foulants with the membrane surface. Furthermore, the primary purpose of grafting PNIPAm onto the PES surface is to utilize its thermo-responsive behavior and enhance the cleaning efficiency of the membrane. By leveraging these properties of PNIPAm, we successfully modified the fouling behavior of PES membranes, achieving higher grafting yields and improved antifouling efficacy. Additionally, extending the membrane's reusability as a result of phase transition behavior of the membrane which enhances its cleaning efficiency, allowing for a higher number of membrane cleaning and reuse cycles.

Furthermore, acrylamide, known for its superhydrophilic properties, is introduced to further enhance the membrane's surface hydrophilicity. This addition improves water permeability and strengthens the membrane's resistance to fouling.

Next, we have introduced a technique for incorporating copper oxide nanoparticles onto the grafted membranes, offering a versatile solution for antibacterial applications. These

nanoparticles, stabilized by APTES ligands, enhance the antibacterial performance of PES membrane significantly. The potential bonding between APTES and CuO could possibly enhance stability to the CuO nanoparticles and prevents their aggregation or agglomeration. Without such stabilization, CuO nanoparticles tend to form larger clusters or precipitate, leading to reduced effectiveness in various applications. One crucial aspect of APTES's role is to inhibit the leaching of CuO from the nanoparticles.

The synergistic combination of these elements constitutes the primary novelty of this work, addressing gaps such as effective kill and release mechanism for both gram-negative and gram-positive bacteria and advancing the field of membrane technology.

Research Novelty

Based on the above explanation we claim that the novelty of this work is captured in the following aspects, none of which have been reported elsewhere while using PES membrane:

- Enhancing PNIPAm grafting yield on the PES membrane through stepwise addition of NIPAm monomer.
 - Here, for the first time, we enhanced the PNIPAm grafting yield on the surface of PES membrane from 5% to 25% by through stepwise monomer addition, minimizing reactions among the monomer molecules in the solution
- Dual-functionalization of PES membrane with P(NIPAm-co-AAm) and CuO-NPs
 - Through the functionalization of the PES membrane with P(NIPAm-co-AAm) and CuO NPs, we were able to leverage efficient cleaning ability as well as biocidal effectiveness toward a broad spectrum of bacterial strains

- Immobilization of copper oxide nanoparticles on the PES membrane surface using APTES ligand.
 - By utilizing the APTES ligand, we improved the stability of CuO nanoparticles on the membrane surface, thereby minimizing the leaching of Cu ions into the permeate water

Our research distinguishes itself from literature reports in several aspects: (i) We assessed the effect of PNIPAm grafting yield on PES membrane properties and performance. (ii) Our focus was on enhancing PES membrane surface hydrophilicity while preserving the structure and integrity of the membrane. (iii) We substantially improved the antibacterial properties of the PES membrane by introducing a biocidal agent. (iv) We emphasized the preparation of a membrane with low water ion toxicity, suitable for water filtration applications.

However, in the similar study by Li et al. [177], employed a novel approach to modify polyethersulfone membranes by grafting them with polymer chains consisting of PNIPAm, P(NIPAm-co-Am), and P(NIPAm-co-GMA) segments using electrochemistry atom transfer radical polymerization (e-ATRP) method. This variance in grafting methodology leads to fundamentally different outcomes in our membrane modification process. (ii) A significant difference is observed in the impact on the membrane's surface and pore structure. In the reference study, their grafting method results in a substantial deposition of polymeric materials covering the membrane surface, leading to alterations in both surface properties and pore structure. Additionally, our results showcase markedly higher durability and recovery in comparison to the reference study. While the reference study demonstrates enhanced flux recovery rates of approximately 19% after cleaning for the P(NIPAm-co-Am) sample over pristine membrane. Our

work achieves a significantly higher flux recovery rate resulting in 37% improvement over bare PES.

Adding copper oxide nanoparticles to the PES surface for its biocidal properties

Similarly in the study conducted by Gul et al. [205], the authors explore the eco-friendly synthesis of copper oxide nanoparticles (CuO NPs) through plant-mediated techniques. Subsequently, these nanoparticles are integrated into composite matrices composed of polyether sulfone (PES) and cellulose acetate (CA) using a solution casting process. Then, copper nanoparticles grow on the surface of the composite membrane in an aqueous solution. Here, our methodology involves dual functionalization, utilizing both thermo-responsive polymers and copper oxide nanoparticles, while their approach is limited to the incorporation of copper oxide nanoparticles alone. Our research employs APTES as a ligand to establish a chemical bond between CuO and the membrane (as observed by XPS analysis), providing a hydrogenic connection compared to the physical attachment between inorganic and organic compounds used in the reference study.

Dual-functionalized membranes for separation and antibacterial applications

In the other similar study, Gautam et al. [232] grafted thermo-responsive copolymers (p(NIPAAm-co-AEMA)) onto the surface of cellulose papers and immobilized silver nanoparticles (AgNPs) using electrostatic interactions to create smart antibacterial-cellulose papers with hybrid kill and release abilities. The modified cellulose papers were found to be effective in killing bacteria and releasing most of the dead bacterial residues from their surfaces after a hot and cold wash cycle. Despite variations in membrane type (PES vs. cellulose paper) and metal oxide nanoparticles (CuO vs. Ag), our most notable enhancement is the utilization of APTES for chemical bonding, in

contrast to the electrostatic bonding between Ag NPS and cellulose paper in the referenced study. The validity of this chemical bonding is confirmed through XPS analysis. Additionally, we assess the recyclability and reusability of the modified membrane toward killing bacteria and filtering organic contaminants, an aspect not explored in the reference article. Another improvement in our study is the notable biocidal effect of our membrane against both gram-negative and gram-positive bacteria. In contrast, the referenced study only demonstrated bacteria-killing performance against gram-negative bacteria.

Chapter 4 – Methodology

The methodology involves a multifaceted approach, encompassing membrane modification, surface functionalization, characterization techniques, and performance evaluation. The key steps involve grafting the PES membrane with thermo-responsive polymers, incorporating copper oxide nanoparticles, and evaluating the resulting membrane's performance in terms of antifouling properties, oil rejection, and antibacterial efficacy.

The process begins with the preparation of the base PES membrane, followed by the grafting of Poly(N-isopropyl acrylamide) (PNIPAm) polymer onto the membrane surface using a chemical redox initiator system. The degree of grafting is controlled by varying the grafting parameters to understand its effect on the membrane's behavior. Subsequently, the functionalization of the membrane with copper oxide nanoparticles is carried out through a two-step process to enhance antibacterial properties and membrane performance.

After the modification steps, extensive characterization is conducted. Various techniques, including surface analysis (e.g., contact angle measurements), structural analysis (e.g., scanning electron microscopy), and compositional analysis (e.g., Fourier-transform infrared spectroscopy), are employed to analyze the modified membranes' properties. These analyses provide critical insights into the modifications' success and the resulting changes in the membrane's properties. Following characterization, the membranes are subjected to performance evaluations. The evaluation involves testing the membranes for their antifouling capabilities, oil rejection rates, and antibacterial properties. These tests will help quantify the improvements achieved through the modifications and the potential of the dual-functionalized membranes for efficient water treatment applications.

In summary, the methodology for this research encompasses a systematic and comprehensive approach, starting from membrane modification and surface functionalization, proceeding to detailed characterization, and concluding with thorough performance evaluations. This structured methodology is designed to ensure the achievement of research objectives, generate reliable data, and contribute substantively to the advancement of membrane technology for water treatment and oil/water separation.

4.1. Materials

N-Isopropylacrylamide (NIPAM), Potassium persulfate ($K_2S_2O_8$), Potassium metabisulfite ($K_2S_2O_5$), Polyvinylpyrrolidone (PVP; Molecular weight: 25,000 g/mol), *N,N*-Dimethylacetamide, Acrylamide (AAM), (3-Aminopropyl)triethoxysilane (APTES), Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), and Sodium borohydride ($NaBH_4$), Bovine serum albumin (BSA), and Polysorbate 80 (tween 80) were purchased from Sigma Aldrich. PES (Ultrason E6020P, 58,000 g/mol) was received from BASF Company, Germany. All of the chemicals were used as received from the suppliers. Vegetable oil was purchased from a local store.

4.2. Characterizations

The fabricated membranes were characterized using various analytical techniques. Fourier transform infrared spectroscopy (FTIR) was conducted on the membrane samples (SHIMADZU ATR- FTIR Spectrometers Tracer 100) in a wavenumber range from 450 to 3500 cm^{-1} . To determine the chemical composition of the prepared copper oxide nanoparticles prior to immobilization process, powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8

Discover using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical surface properties of the membrane functionalized with copper oxide particles were analyzed using X-Ray Photo-Electron Spectroscopy (XPS PHI 5400) with a monochromatic and focused Mg K α X-ray source (1253.6 eV). For each sample, high-resolution core-level windows of carbon 1s, nitrogen 1s, oxygen 1s, silicon, and copper 2p levels were collected with a spot size of 600 μm , a resolution of 1 eV/step, and a pass energy of 89.45 eV. Prior to the XPS analysis, the membrane samples were pumped down in a vacuum chamber for 10 hours to eliminate any impurities attached to the surface. Additionally, thermogravimetric analysis (TA Instruments SDT650) was performed under air at a heating rate of 15 $^{\circ}\text{C}/\text{min}$. The elemental chemical composition and mapping of bare and modified membranes were determined using TopCon SM-300 Scanning Electron Microscope (EDS technique) by operating the microscope at an accelerating voltage of 15 kV and an acquisition time of 30 s. Scanning electron microscopy (SEM/EDS JEOL 6460LV) at 10 kV was used to analyze the morphologies (top surface and cross-section) of the samples. The roughness of the PES membranes was evaluated using atomic force microscopy (AFM, Agilent 5420) with a 5 $\mu\text{m} \times 5 \mu\text{m}$ scan area and 256 pixels of resolution. The hydrophilicity of the membranes was evaluated by measuring the water contact angle using a goniometer (Dataphysics OCA 15 Plus) based on droplet profiles captured on a membrane surface. The dynamic contact angle of bare and modified PES membranes was determined using a dynamic Wilhelmy plate method (Kruss K10T). The temperature of the test chamber, which had a volume of 100 mL, was carefully regulated by a thermostated circulator. The receding contact angles were measured while immersing the plate at a speed of 10 mm/min to a depth of 2 mm, and each data point represents the average of three consecutive measurements. The surface charge of the membranes was measured at pH 2,

7, and 10 using a Zetasizer instrument (Malvern Zetasizer). Hitachi S-4800 Ultra High-Resolution cold cathode Field Emission Scanning Electron Microscope (FE-SEM) was used to capture the remain bacteria on the membrane's surface.

4.3. Fabrication of PES membrane by phase inversion method

The fabrication of a pure PES flat-sheet membrane was done using the phase inversion method. Polyethersulfone (18 wt.%) and polyvinylpyrrolidone (2 wt.%) were dissolved into an 80 wt.% N,N-dimethylacetamide (DMAc) solution, and the mixture was stirred at 45 °C for 24 hours to form a uniform and homogeneous casting suspension. The casting solution was cast onto a glass plate using a 250 µm casting blade at room temperature and then immersed in a fresh DI water bath. After complete coagulation, the membrane was transferred to a fresh water bath and shaken for 24 hours at room temperature to remove all the remain solvent (DMAc). The water was changed after 6 hours to ensure effective removal of residual solvent from the membrane structure. The clarity of the water served as an indicator, with clear water suggesting the absence of any remaining DMAc in the membrane. Furthermore, the FTIR results presented in section 5.1.1.1 matches indicated the absence of DMAc residuals on the surface of membrane, with the peaks aligning perfectly with those of the PES membrane.

The membrane was then washed with ethanol and dried between two sheets of filter paper in air [245], [246]. The porosity (ϵ) of membranes was determined using Equation 4-1, which is based on the gravimetric method, as the following:

$$\epsilon (\%) = \frac{W_{wet} - W_{dry}}{\rho \cdot d \cdot A} \times 100 \quad (4-1)$$

In this equation, W_{wet} (g) represents the weight of the wet membrane and W_{dry} (g) refers to the weight of the membrane after it was dried in an oven at a temperature of 60 °C for at least 30 min. To ensure the membrane's thorough dryness, gravimetric weighing was performed. The weight reduction of the membrane was monitored every 10 minutes while in the oven. After three consecutive measurements with a consistent weight, we verified that the membrane had achieved almost complete dryness. The variables d , A , and ρ represent the thickness of the membrane (m), the area of the membrane (cm²), and the density of water (0.998 g/cm³), respectively [247].

4.4. Grafting of PNIPAm on the surface of PES membrane

The Design of Experiment (DOE) is a method where multiple factors are tested simultaneously, allowing the study of interactions between factors in a smaller number of optimized experiments.

In this project, initially, the DOE method was employed to achieve the following objectives:

- Reduce the number of experiments
- Generate correct and accurate results simultaneously
- Identify and control the main factors in the experiments and optimize them

To optimize the variables in the grafting reaction, a 3^3 full factorial design, based on 3 independent parameters with 3 independent values, was utilized to obtain an optimized formulation. The effects of the grafting conditions (e.g., NIPAm monomer concentration, grafting time and initiator ($\text{K}_2\text{S}_2\text{O}_5$: $\text{K}_2\text{S}_2\text{O}_8$) to NIPAm ratio) on grafting yield were investigated. Table 4-1 presents the complete experimental design for the grafting reaction.

Table 4-1: Experimental design based on 3³ full factorials for different variables of monomer concentration, redox system concentration and reaction time.

Run	[NIPAM] (mmol/L)	[Initiator]/[NIPAM]	Grafting Time (h)	Grafting Yield Wt.%
1	2	1:1	5	3.63
2	2	1:1	10	5.03
3	2	1:1	15	5.15
4	2	1:2	5	4.01
5	2	1:2	10	3.93
6	2	1:2	15	2.46
7	2	1:6	5	5.23
8	2	1:6	10	4.90
9	2	1:6	15	5.73
10	4	1:1	5	3.09
11	4	1:1	10	7.32
12	4	1:1	15	9.74
13	4	1:2	5	2.27
14	4	1:2	10	6.35
15	4	1:2	15	7.21
16	4	1:6	5	1.72
17	4	1:6	10	5.21
18	4	1:6	15	5.63
19	6	1:1	5	6.41

20	6	1:1	10	8.93
21	6	1:1	15	11.01
22	6	1:2	5	5.97
23	6	1:2	10	6.31
24	6	1:2	15	9.28
25	6	1:6	5	3.54
26	6	1:6	10	4.76
27	6	1:6	15	6.90

However, our results indicated that the maximum grafting yield achieved in this system is approximately 11%, falling short of our target grafting yield of above 15%. In response to this, we introduced a novel method that enhances the concentration of the monomer in the solution. This approach aims to minimize the reaction of radical monomer molecules with each other in the solution, rather than on the PES surface. The new graft polymerization process was carried out as follows: A 1:1 ratio of initiators ($K_2S_2O_5$: $K_2S_2O_8$) was dissolved in water in a three-necked flask containing a PES membrane sheet. The membrane was activated under an inert gas atmosphere for one hour, followed by the addition of 50 ml of a 1 mMol L⁻¹ of NIPAM monomer aqueous solution. To increase the grafting yield, the reaction temperature and concentration of NIPAM were gradually increased to 60 °C and 6 mMol L⁻¹, respectively. It is noteworthy that at temperatures exceeding 65 °C, the polymer solution underwent gelation, and polymerization occurred rapidly within the solution rather than grafting onto the membrane. The detail parameter is explained in Table 4-2. The flask was kept at 60 °C with slow stirring. Following a

suitable reaction time (6-24 h) , the membrane was removed and thoroughly washed with DI water for 24 hours to remove all unreacted monomer and homopolymer [246], [248]. Then the grafted membrane was dried in a vacuum oven at 50°C for 30 minutes. Figure 4-1 illustrates the schematic representation of the grafting process and the potential reactions that may occur with a PES membrane in the presence of a redox initiator system in the solution. Here, we used $K_2S_2O_5$ - $K_2S_2O_8$ which are salts of sulfurous acid and peroxydisulfuric acid, respectively. Those are commonly used as initiators for the grafting of polyethersulfone (PES) membranes, because they can generate free radicals under various reaction conditions. This makes them more convenient and versatile than other initiators that require more complex or harsh conditions, such as plasma treatment or radiation. Another advantage of using $K_2S_2O_5$ and $K_2S_2O_8$ is that they can be easily removed from the membrane surface after the grafting reaction by washing with water, which can reduce the risk of residual initiator contamination. Comparing $K_2S_2O_5$ - $K_2S_2O_8$ with other initiator system like $K_2S_2O_8$ - $NaHSO_3$, we can emphasize that $K_2S_2O_8$ - $NaHSO_3$ has a lower efficiency of free radical generation than $K_2S_2O_5$ - $K_2S_2O_8$, because the reaction between $K_2S_2O_8$ and $NaHSO_3$ is slower and less complete than the decomposition of $K_2S_2O_5$ or $K_2S_2O_8$ alone.

The redox initiator system generates aryl free-radicals on PES backbone which after reaction with the free-radical species of NIPAM monomer leads to grafting of PNIPAm brushes on the PES membrane (Figure 4-1b). The grafting yield was measured by weighing the membrane before and after grafting using the following equation.

$$Grafting\ Yield\ (\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (4-2)$$

Where W_0 and W_1 are the weight of PES membrane before and after grafting, respectively.

In order to validate the reproducibility of the grafting process, each set of conditions was replicated four times. This approach ensures that the observed results are consistent and can be reliably reproduced, contributing reliability of the grafting methodology.

Table 4-2: Redox reaction parameter for each grafting yield.

Grafting Yield (wt. %)	Grafting Time (h)	NIPAm Monomer Concentration mMol/L				Redox initiator: NIPAm Monomer
		Step1	Step 2	Step 3	Step 4	
3± 0.6	4	0.5	1	1.5	-	1:1
5± 1.1	6	1	1.5	2	-	1:1
10± 1.0	9	1	2	4	-	1:1
15± 1.3	15	1	2	4	-	1:1
18± 0.9	20	1	2	4	6	1:1
25± 2.6	24	1	2	4	6	1:1
15±1.7 (AAm)	15	1	2	4	-	1:1
15 ±0.8 (P(NIPAM-co-AAm))	15	1	2	4	-	1:1

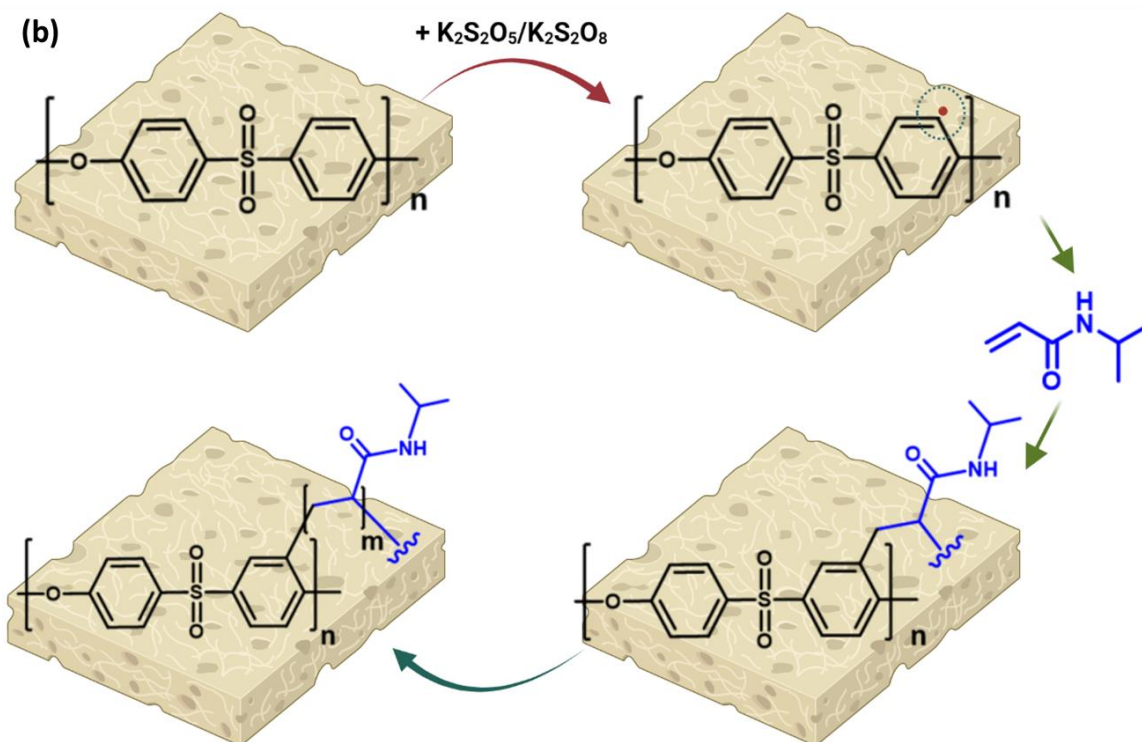
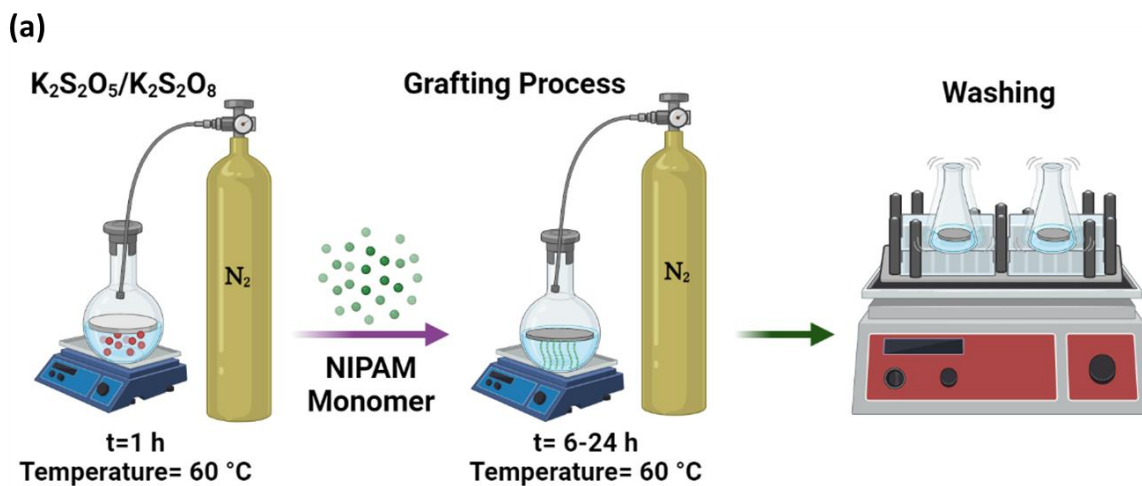


Figure 4-1: (a) Mechanism of PNIPAM grafting on surface of PES membrane using redox system. (b) Potential interactions between PES membrane, redox system, and NIPAM monomer.

4.5. Grafting of AAm and P(NIPAm-co-AAm) on the surface of PES membrane

The reaction parameters for the acrylamide functionalized membrane were set to achieve a 15% grafting yield, a target established based on our study regarding the influence of grafting yield on membrane properties. The membrane featuring a 15% grafting yield demonstrated high antifouling and filtration performance relatively comparable to a membrane grafted with 25% PNIPAm. This suggests a higher efficiency, demanding less energy and effort for comparable results. To carry out the graft polymerization process, a PES membrane sheet was placed in a three-necked flask containing a 1:1 ratio of initiators ($K_2S_2O_5$: $K_2S_2O_8$) dissolved in water. The membrane was activated for under an inert gas atmosphere for one hour before adding a 50 ml mixed solution of AAm and NIPAm monomers in a 1:9 ratio [249]. To increase the grafting yield to 15%, the reaction temperature and monomer concentration were gradually increased to 60 °C as described in table 4-2. The flask was kept at 60 °C with slow stirring for 15 hours under a nitrogen atmosphere. After the reaction, the membrane was removed and washed thoroughly with DI water for 24 hours to eliminate any unreacted monomer and homopolymer [246], [248], [250]. The selection of the ratio between the co-polymer of PNIPAm and AAm is based on extensive studies documented in the literature [249]. The higher amount of AAm in the structure of PNIPAm can increase the LCST of PNIPAm. Additionally, AAm can decrease the swelling ratio of PNIPAm hydrogels. This is because AAm can increase the crosslinking density and the rigidity of the polymer network, making it less responsive to temperature. However, AAm exhibits superhydrophilic properties, and even at low concentrations, it can markedly decrease the water contact angle. However, in future, exploring various grafting yields can offer additional insights into the impact of AAm incorporation on the phase transition behavior of PNIPAm.

To synthesize PES-g-AAm, the identical process was employed, utilizing a distinct monomer solution. The mixed NIPAm and AAm solution was replaced with a 1 mMol/L AAm solution, added to a three-necked flask containing a 1:1 ratio of initiators ($K_2S_2O_5$: $K_2S_2O_8$) dissolved in water. To achieve a 15% grafting yield, the reaction temperature and monomer concentration were incrementally raised to 60 °C and 4 mMol/L, respectively.

The selection of the ratio between the copolymers PNIPAm and AAm is based on extensive studies documented in the literature. However, accurately measuring the actual ratio of AAm and PNIPAm, particularly considering the presence of acrylamide groups in both chemical structures, proves challenging in practical terms. One potential method to determine the amount of AAm copolymerized on PNIPAm is through nuclear magnetic resonance (NMR) spectroscopy. NMR can offer insights into the chemical structure and composition of the copolymer by analyzing signals from different nuclei, such as hydrogen (H) and carbon (C). By comparing the peak areas or integrals of the signals corresponding to the NIPAm and AAm units, one can calculate the molar fraction of each monomer in the copolymer. However, it's important to note that this method is challenging and susceptible to potential errors.

4.6. Incorporation of CuO nanoparticles on the PES membrane surface

To synthesize copper oxide nanoparticles, the precipitation method was employed. Initially, 3 g of $CuSO_4 \cdot 5H_2O$ was dissolved in 600 mL of deionized (DI) water and stirred for 30 minutes. Subsequently, a 0.1 Molar $NaBH_4$ solution was added gradually to the mixture to increase the pH to approximately 10. The solution was stirred for an additional two hours, and the precipitated

materials were separated and washed via centrifugation. Finally, the materials were dried overnight in a 50 °C oven [251].

During the initial attempt to introduce copper oxide onto the membrane surface, we immersed the membrane in various concentrations of CuO suspension for 24 hours. However, SEM imaging results indicated a significant degree of nanoparticle agglomeration on the membrane, along with heterogeneous dispersion across the membrane surface as demonstrated in Figure 4-2. Consequently, we employed APTES as a ligand to facilitate reduce agglomeration and increase the likelihood of immobilization on the PES surface.

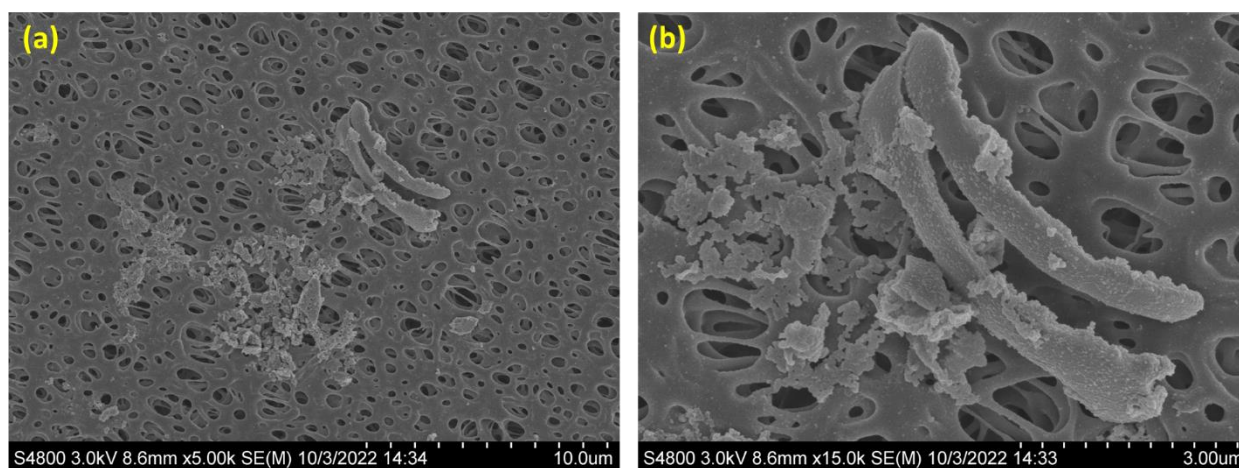


Figure 4-2: SEM imaging revealed a substantial agglomeration and heterogeneous distribution of copper oxide nanoparticles on the membrane surface in the absence of a ligand.

Our method includes the incorporation of CuO nanoparticles onto the surface of pristine and modified PES membranes, which involves using APTES (3-aminopropyltriethoxysilane) as a ligand to facilitate the organic-inorganic binding. The method involved the following steps: 0.02 g of copper oxide nanoparticles were added into 250 mL of anhydrous ethanol and dispersed via ultrasonication for 30 minutes. Then, the membrane sheets (both the pristine and the modified PES membranes) were immersed in the nanoparticle solution. 0.01 mL of APTES was added to the

solution and mixed at room temperature for 2 hours under a N_2 atmosphere. This facilitated the organic-inorganic bonding between the APTES ligand and the CuO nanoparticles. After 2 hours, the functionalized membrane was taken out of the solution and washed for 24 hours in deionized (DI) water to remove any unbound or loosely bound nanoparticles. Finally, the membrane was dried at 50 °C in an oven [252], [253].

This method can be helpful in creating membranes with improved properties, such as antibacterial or antifouling properties, depending on the specific application. The use of APTES as a ligand in this method helps to ensure that the nanoparticles are bound to the membrane surface, which is a critical factor in enhancing their performance and preventing the leaching of the nanoparticle, which is a limiting factor in the utilization of the nanoparticles in membranes in the desired application. Figure 4-3 demonstrates the schematic illustration of the process for incorporating copper oxide nanoparticles onto the surface of PES membranes. The figure highlights the key steps in the process, including using APTES as a ligand to facilitate the organic-inorganic bonding between the nanoparticles and the membrane surface.

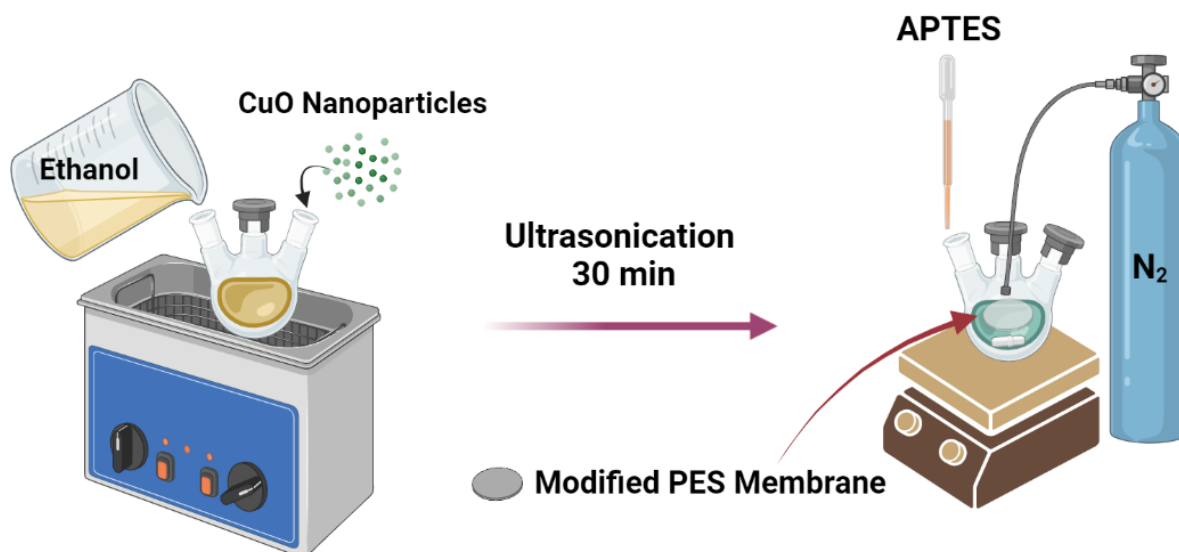


Figure 4-3: Functionalization process of PES membranes via copper oxide nanoparticles.

4.7. Evaluation of antifouling performance

The effect of PNIPAm grafting yield on the PES membrane's flux and fouling behavior was assessed using cross-flow filtration experiments. The measurement of the flux, flux recovery ratio (FRR), total fouling (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) was determined according to equations 4-3 to 4-7 [254].

$$J_{w1} = \frac{V}{A \cdot t} \quad (4-3)$$

Where J_{w1} is pure water flux, V is the volume of permeated water, A is the effective membrane area, and t is the time of the solution collection. After cleaning the membrane, pure water fluxes were measured as J_{w2} . BSA flux rate was also measured as J_p . Flux recovery ratio (FRR) was calculated using the following expression:

$$FRR = \frac{J_{w2}}{J_{w1}} \times 100 \quad (4-4)$$

Degree of total flux loss (R_t) caused by total fouling, reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) were also defined and calculated Based on Equation 4-5 to 4-8:

$$R_t = \left(1 - \frac{J_p}{J_{w1}}\right) \times 100 \quad (4-5)$$

$$R_r = \left(\frac{J_{w2} - J_p}{J_{w1}}\right) \times 100 \quad (4-6)$$

$$R_{ir} = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \times 100 \quad (4-7)$$

The experiments were performed using laboratory-made flat-sheet membrane with an effective area of 0.000225 m². During the tests, both permeate and retentate were sent back to the feed tank. The temperature of the feed was kept at room temperature, and the membrane flux was

recorded at 0.3 MPa pressure. A 1000 ppm oil emulsion and a 500 ppm BSA solution were used as a model contaminant and foulant, respectively. The oil solution was made using 1000 ppm vegetable oil and 0.1 wt.% polysorbate 80 (Tween 80) as a surfactant. The solution was sonicated for 30 minutes and mixed for 24 hours to produce stable emulsion [255], [256]. To evaluate the antifouling properties of the PNIPAm modified PES membranes, the following procedure was executed: (i) The membranes were compacted by using DI water as feed until a steady flux rate was achieved; (ii) The DI feed was replaced with a feed containing BSA as a model foulant and filtration experiment with BSA feed was continued for 300 minutes; (iii) The fouled membranes were cleaned with both cold (20°C), hot (45°C) and cold (20°C) water for a duration of 60 minutes (20 minutes for each cycle); (iv) The cleaned membranes were tested for flux recovery by using DI water as feed; and finally, (v) a second round of BSA solution filtration was performed to evaluate the membrane's reusability. The purification performance of each membrane was measured by determining the oil and BSA concentrations in the permeate. The rejection rate was calculated by measuring the signals of a UV-Vis spectrophotometer at 220 nm for oil and 278 nm for BSA and applying Equation 4-8.

$$Rejection\ Ratio = \left(\frac{C_0 - C_1}{C_0} \right) \times 100 \quad (4-8)$$

Where C_0 and C_1 are the contaminant (oil or BSA) concentration in feed and permeate solution, respectively.

4.8. Bacteria culturing and antibacterial testing

Tryptone Soya Broth (TSB) (Oxoid, CM129) was purchased from Thermo Fisher Scientific, while Sodium Chloride ($\geq 99.0\%$), Potassium Chloride (99.0-100.5%), Sodium Phosphate Dibasic

(≥99.0%), and Potassium Phosphate Monobasic (≥99.0%) were purchased from Millipore Sigma.

All the raw materials were used as received.

The antiadhesion and antibacterial efficacy of both the bare and functionalized membrane were assessed against both gram-positive and gram-negative bacteria. The gram-negative bacteria strain *Escherichia coli* (*E. coli*), isolated from the Point Beach environment in Wisconsin, USA, was employed, while the gram-positive bacteria strain *Bacillus cereus* (*B. cereus*) was utilized. To attain the overnight phase of the *E. coli* strain, it was cultured in a flask containing 30 mL of fresh TSB, followed by incubation in a shaker at 200 rpm and 37 °C for 24 hours. On the subsequent day, 1 mL of the overnight phase *E. coli* was poured into a sterile flask containing 30 mL of TSB. The mixture was once again placed in the incubator shaker at 200 rpm and 37 °C for a further 5 hours, to acquire the log phase of the bacteria. Antimicrobial agents are typically evaluated for their ability to kill bacteria during the log phase of multiplication, where cells undergo exponential growth and are most susceptible to bactericidal effects [257], [258].

To isolate the *E. coli* bacteria from the TSB solution following 5 hours of incubation, centrifugation was performed at 5000 rpm and 20 °C for 10 minutes. The resulting precipitate of *E. coli* was then dispersed and homogenized in a phosphate-buffered saline (PBS 1X) solution using a vortex. This mixture was then centrifuged again to isolate the bacteria from the PBS, and the centrifuge process was repeated three times to remove all the nutrient media (TSB). The growth of existing bacteria was stopped by washing off the nutrient media. Finally, the prepared bacteria were resuspended in 30 mL of PBS solution. To conduct the anti-bacterial and anti-adhesion tests, the prepared bacteria were diluted with the desired volume of PBS, thereby yielding a suspension with a concentration of around 1×10^7 CFU/mL.

Initially, bare PES (M₁), PES-g-PNIPAm (M₂), PES-g-P(NIPAm-co-AAm) (M₃), CuO@PES-g-PNIPAm (M₄), and CuO@PES-g-P(NIPAm-co-AAm) (M₅) membranes underwent anti-bacterial testing. Using a pipette, 100 µL of the pre-prepared *E. coli* suspension was placed onto a tryptone soya agar (TSA) plate (kept at room temperature) and then spread evenly across the surface. Subsequently, a 47 mm diameter round sheet of membrane was placed over the central region of the agar plate. The TSA plates were then placed in an incubator set at 37°C for 24 hours, following which the bacterial colonies located at the edges and beneath the covered area were visually inspected.

To conduct further antibacterial testing, each membrane was submerged in a sterile and sealed beaker containing 10 mL of *E. coli* suspension. After the mixture was prepared, it was agitated in an incubator shaker for 90 minutes at 200 rpm and 37°C. Once the incubation period was complete, the membranes were carefully extracted and rinsed three times with PBS for 10 minutes each, at temperatures of 20°C, 45°C, and 20°C [259]. To evaluate the anti-adhesion properties, the cleaned membranes were placed on fresh TSA plates and incubated for 24 hours at temperature of 37°C. The thickness of the bacterial layer developing at the edge of each membrane was measured to compare the number of live cells that adhered to the membrane [260].

After the incubation period of 90 minutes, the number of live *E. coli* bacteria was determined by counting the Colony Forming Units (CFUs) in the bacteria suspension. followed by pipetting 100 µL from each dilution onto freshly prepared TSA plates. The pipetted solution was then carefully spread over the entire plate using sterile inoculation loops. The TSA agar plates inoculated with the bacterial solution were then incubated overnight at 37°C [261]. Figure 4-4 demonstrates the

schematic of a bacterial study in terms of inhibition zones and bacteria killing. Finally, to prepare the adhered bacteria on the membrane for FE-SEM imaging, the membrane were immersed in a 3% (v/v) glutaraldehyde solution and kept at $T=4^{\circ}\text{C}$ for three hours to fix them in place. Next, the membrane was taken out from the glutaraldehyde solution and dehydrated through a series of ethanol concentrations of 25%, 50%, 75%, and 100%. Finally, the membrane was dried at room temperature for 24 h, prior to FE-SEM imaging.

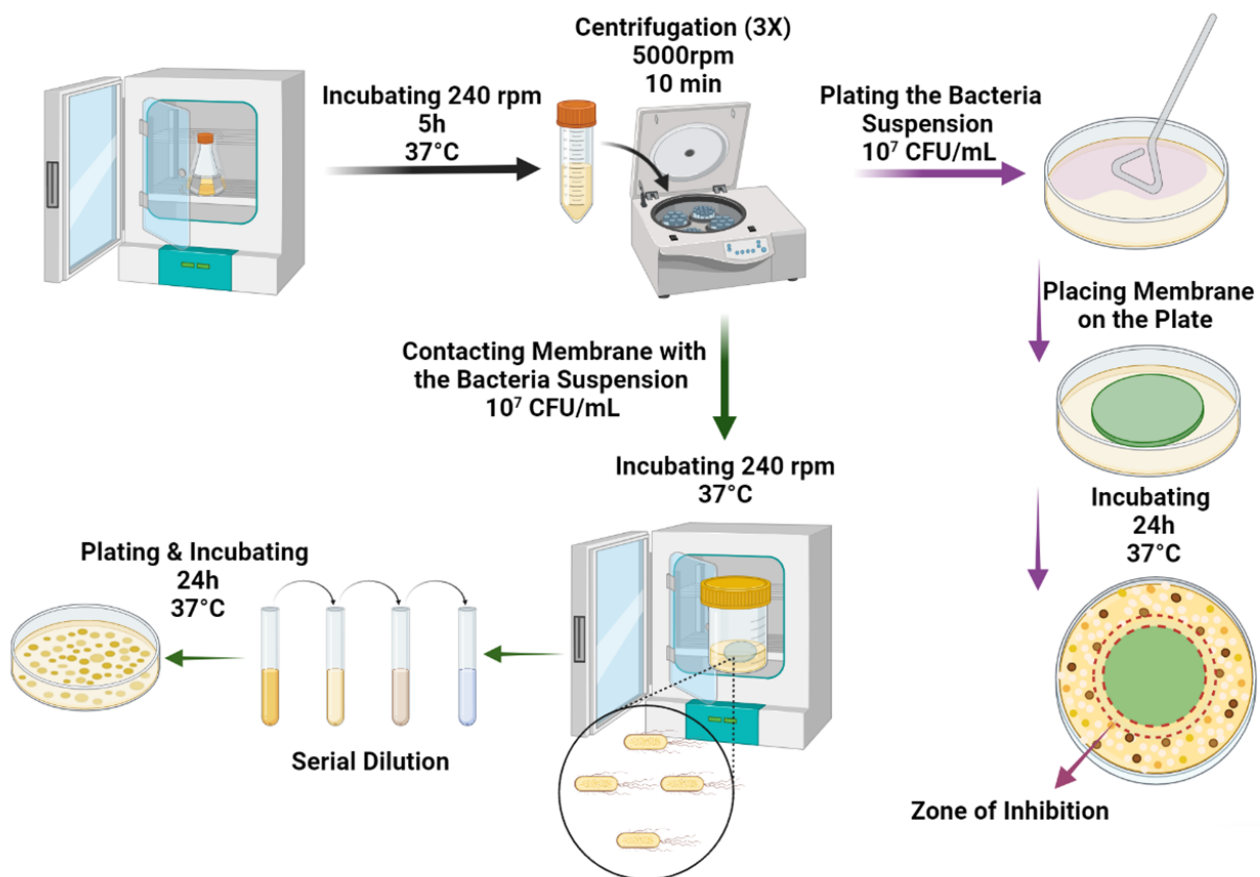


Figure 4-4: Schematics of bacteria culturing, inhibition zone test, and bacteria killing test.

Chapter 5 – Results and Discussion

5.1. Materials Characterization

In the materials characterization section, we have two main subsections. The first section involves a thorough characterization to examine the surface properties of the PES membrane with different degrees of Poly(N-isopropyl acrylamide) (PNIPAm) grafting yield. In the second section, we investigate the impacts of functionalization, with a specific focus on acrylamide functional groups and copper oxide nanoparticles, on the membrane structure.

5.1.1. Effect of thermo-responsive polymer grafting yield on the PES membrane characteristics

In this section, we focus on exploring the impact of different PNIPAm grafting yields (5%, 15%, and 25%) on our PES membrane, resulting in three distinct samples denoted as PES-g-5%PNIPAm, PES-g-15%PNIPAm, and PES-g-25%PNIPAm. The aim is to comprehensively understand how the varying degrees of grafting influence the membrane's properties.

The subsequent part of this section focuses on presenting the outcomes of material characterization. We delve into the chemical composition, surface morphology, roughness, and contact angle of each membrane, offering a comprehensive view of the structural and surface properties induced by the grafting process.

5.1.1.1. Chemical composition of PNIPAm-grafted membranes with different grafting yield

Figure 5-1 (a) shows the ATR-FTIR spectra of bare PES and PNIPAm-grafted PES membranes with grafting yields of 5% (PES-g-5%PNIPAm), 15% (PES-g-15%PNIPAm), and 25% (PES-g-25%PNIPAm). An increase in the graft yield to 25% resulted in the observation of a broad transmittance peak at 3433 cm^{-1} in PES-g-25%PNIPAm membrane, which is due to the presence of amine (N-H)

stretching vibrations. An additional peak was detected at 1642 cm^{-1} in the PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes, which is associated with the carbonyl group (C=O) and indicates the successful polymerization between the NIPAM monomers [262], [263]. The primary peaks of the PES membrane were also detected at 700, 800, 1240, 1489, 1577, and 3096 cm^{-1} due to the stretching vibrations of C-S, C-H, $-\text{SO}_2$, C-C and C-H in the aromatic skeleton of PES structure, respectively [264].

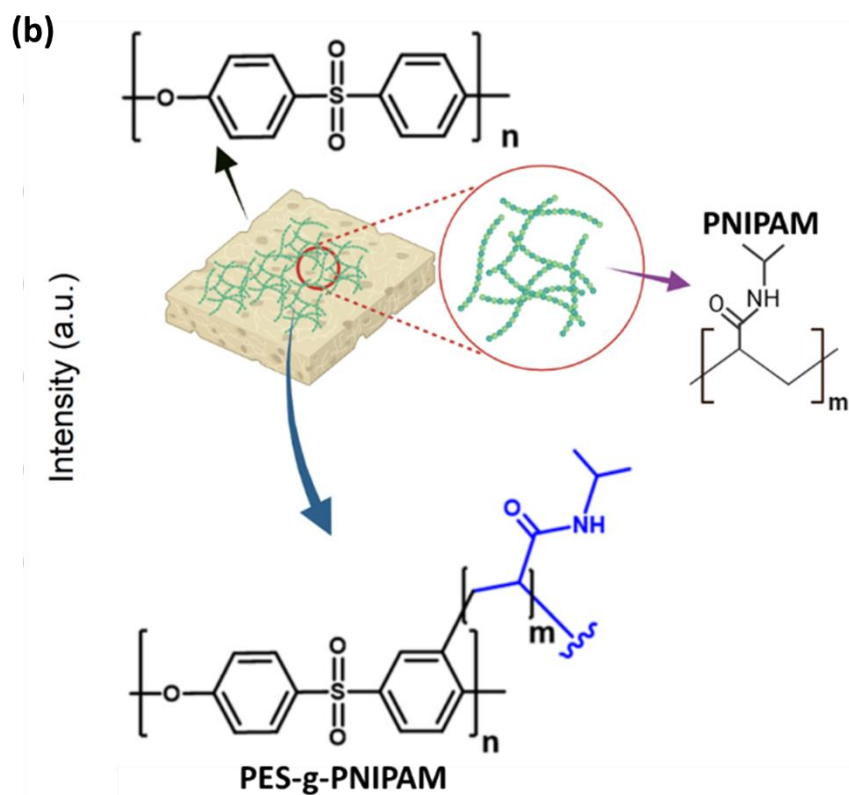
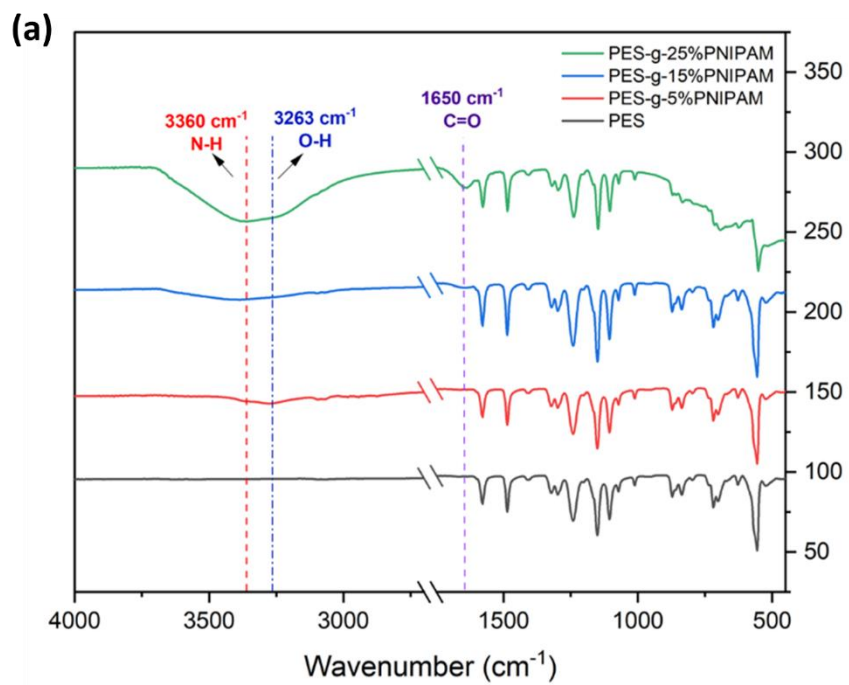


Figure 5-1: (a) ATR-FTIR spectra of bare PES and PNIPAm-grafted PES membranes (PES-g-5%PNIPAm, PES-g-15%PNIPAm and PES-g-25%PNIPAm). (b) The chemical structure and available bonding sites in PES, PNIPAm, and (PES-g-PNIPAm) grafted systems.

5.1.1.2. Effect of grafting yield on morphology of PNIPAm-grafted membranes

The surfaces (top and bottom) and cross-sectional morphology of the bare PES and PNIPAm-grafted PES membranes (PES-g-5%PNIPAm, PES-g-15%PNIPAm and PES-g-25%PNIPAm) were obtained using SEM analysis and are presented in Figure 5-2. The membranes were found to have highly dense, defect-free surfaces, while the bottom surfaces of bare PES membranes were very porous with an average pore size of $\sim 0.26 \mu\text{m}$. Spherical particles were observed on both sides of the PNIPAm-grafted PES membranes, and the concentration of particles increased with the increase in the grafting yield from 5% to 25%. The SEM images also indicated that the particles were uniformly distributed on the surface of PNIPAm-grafted PES membranes. The average particle size of the grafted polymer in the PNIPAm modified PES membranes was found to be $\sim 190 \text{ nm}$. Figure 5-2(d) shows (PES-g-25%PNIPAm membrane) that the PNIPAm particles +also grew inside the pores of the PES membrane, clogging many pores at the back side of the membrane. The cross-sectional SEM images of the PNIPAm-grafted PEM membranes reveal that the majority of PNIPAm particles did not penetrate the depth of the membrane and were merely grafted onto the surface. The morphology of the grafted PNIPAm polymer was found to be similar to previous studies [172], [177], [265]. The formation of clustered nanoparticles on the membrane surface is evident. Investigating the kinetics of polymerization and the associated

thermodynamics in future studies would be crucial steps to understand the process of cluster formation and determine their size.

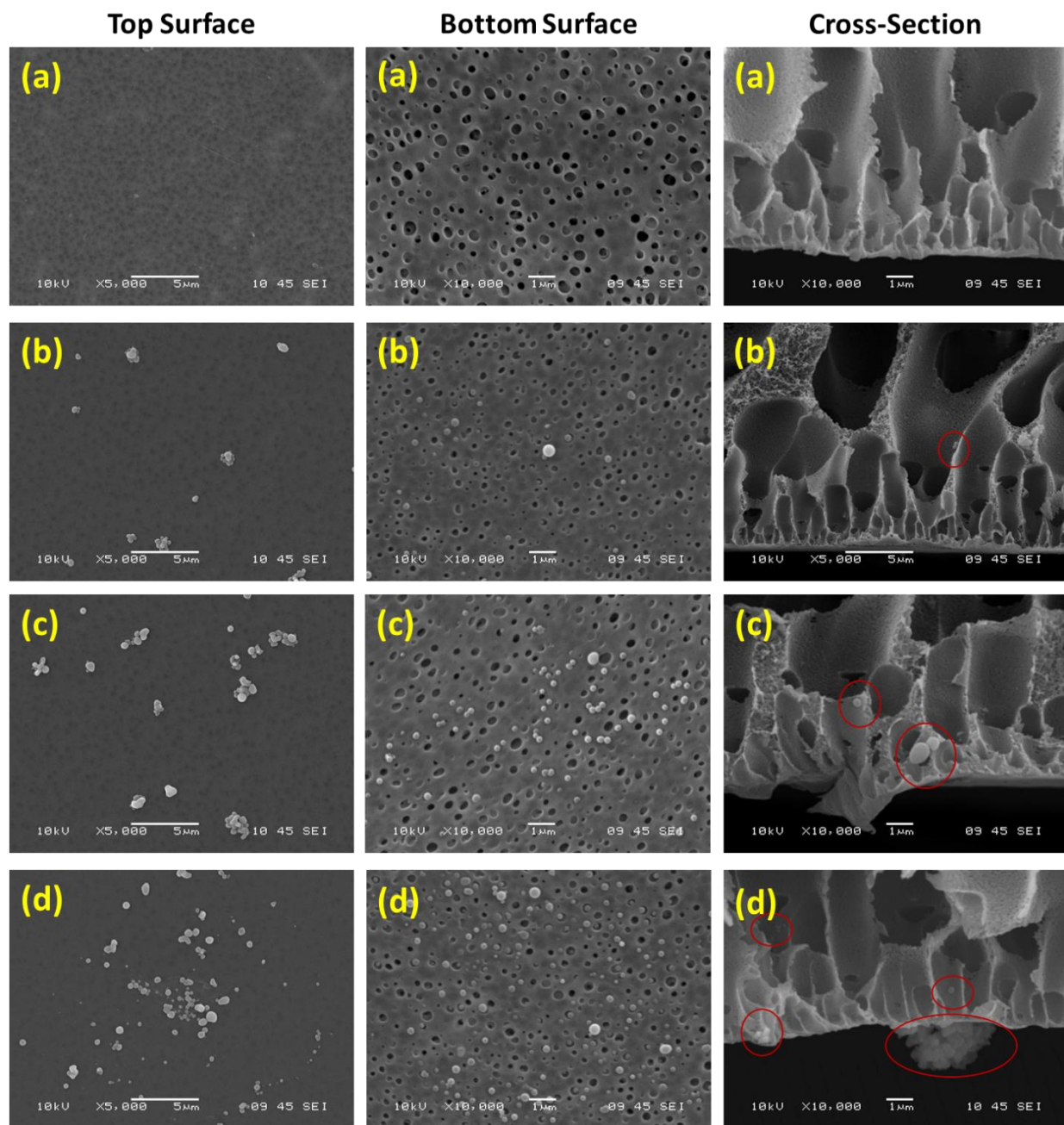


Figure 5-2: Top, bottom, and cross-sectional images of (a) bare PES, (b) PES-g-5%PNIPAm, PES-g-15%PNIPAm, and (d) PES-g-25%PNIPAm membranes. The red circles indicate the formation of PNIPAm nanoparticles with and without agglomeration.

To isolate the impact of the redox system from PNIPAm, we treated a PES membrane in the redox system (without the presence of NIPAm monomer) for 24 hours and examined its surface morphology. The results, presented in Figure 5-3, indicate that the redox system alone does not alter the surface, and no residual particles were observed. Putting the membrane in redox solution under the inert atmosphere does not cause the change in surface hydrophilicity. The membrane needs to be modified by some techniques to enhance its hydrophilicity. When a surface undergoes oxidation, in presence of air or other reactive gases such as CO₂, it often results in the formation of polar functional groups on the surface. These functional groups, such as hydroxyl (-OH) and carbonyl (C=O) groups, make the surface more hydrophilic. Basically, redox initiator cannot do anything on membrane without the presence of monomer. Redox initiator is a system that generates free radicals by a redox reaction between an oxidizing agent and a reducing agent. These free radicals can then initiate the polymerization of monomers by adding to their double bonds and forming new radicals. Without monomers, the redox initiator will not have any molecule to react with and will not produce any polymer. Therefore, redox initiator alone cannot modify the membrane surface by itself as it is indicated in Figure 5-3.

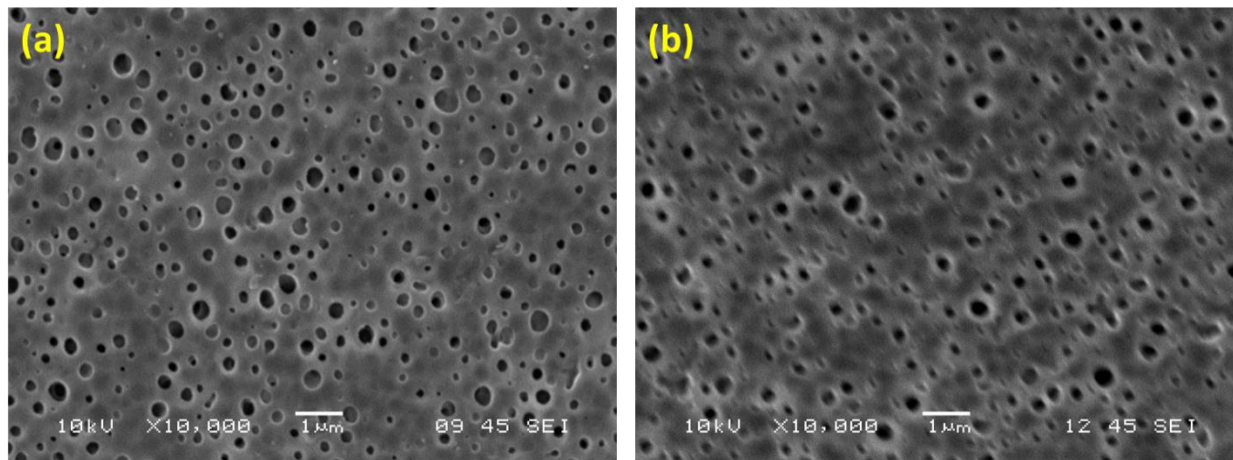


Figure 5-3 SEM image of (a) bare PES (b) PES treated with redox system.

5.1.1.3. Effect of grafting yield on surface roughness of PNIPAm-grafted membranes

AFM was used to examine the surface topography of bare and PNIPAm-grafted PES membranes, as shown in Figure 5-4. The surface roughness (S_q) of the bare PES membrane was 15.8 nm, which is typical for PES membrane surfaces. After grafting of PNIPAm polymer on the surface of PES membrane, the PES-g-5%PNIPAm, PES-g-15%PNIPAm, and PES-g-25%PNIPAm membranes showed slightly higher roughness, with S_q values of 21.8 nm, 22.1 nm, and 24.2 nm, respectively. This indicates that the presence of PNIPAm polymer on the surface of PES membranes can lead to a slightly rougher surface, but the increase in roughness was minor and still within the common range for PES membrane surfaces [266]. Additionally, brush-decorated samples revealed small island-like spots (<250 nm), likely caused by polymer chain aggregates in the grafted layer.

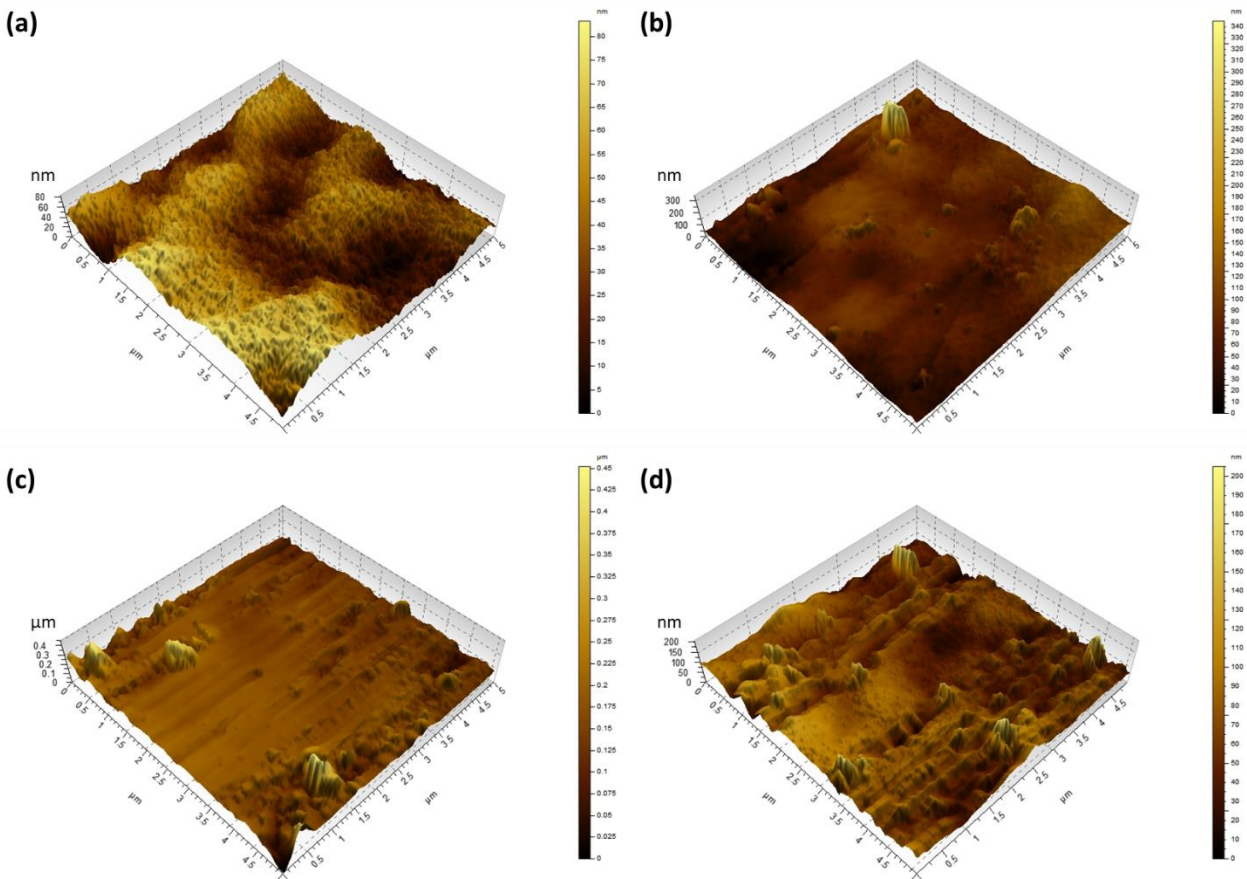


Figure 5-4: AFM images and surface roughness of (a) bare PES, (b) PES-g-5%PNIPAm, (c) PES-g-15%PNIPAm, and (d) PES-g-25%PNIPAm membranes.

5.1.1.4. Effect of grafting yield on surface hydrophilicity, and surface charge of PNIPAm-grafted membranes

All measurements in this section were conducted three times, and the reported values represent the average of these three measurements. This approach was employed to minimize the impact of experimental error.

-Surface hydrophilicity

The surface hydrophilicity of the membrane is a key factor that affects the membrane's permeation rate and antifouling behavior, and it is indicated by the contact angle. A surface that is more hydrophilic results in enhanced antifouling resistance and increased permeate flow [267].

Figure 5-5(a) displays the contact angle measurements for both bare PES and PNIPAm-grafted PES membranes at two different temperatures of 22 and 40 °C. The bare PES membrane had the highest contact angle ($59^{\circ} \pm 1.7$), which aligns with the reported contact angle of bare PES membranes [268]. The contact angle measurement results at room temperature were obtained for the sample subjected to a 24-hour treatment in the redox solution without NIPAm monomer. The results demonstrated that the water contact angle remained unchanged.

As PNIPAm grafting yield increased from 5% to 25%, the contact angle gradually decreased from $49^{\circ} \pm 1.5$ to $41^{\circ} \pm 2$. This decline can be attributed to the presence of more hydrophilic functional groups on the membrane surface, which are imparted by the hydrophilic nature of PNIPAm brushes [269]. In addition, the thermo-responsive behavior of the PNIPAm-grafted membrane could be indicated via the water contact angle at temperature below and above lower critical solution temperature (LCST). With a temperature above LCST (40 °C), the water contact angle increased from 41° to 69° for the 25% PNIPAm-grafted PES membrane (PES-g-25%PNIPAm), showing the phase transition behavior of PNIPAm. The change in contact angle was due to the transformation of PNIPAm chains from a coil structure to a globular structure, thereby exposing hydrophobic isopropyl groups on the membrane surface [180], [270].

- Dynamic contact angle

The impact of temperature on the surface properties of a PNIPAm-grafted PES membrane was further examined through dynamic contact angle measurements in an aqueous solution, and the

results are illustrated in Figure 5-5(b). The receding contact angle of the untreated PES membrane remained constant across varying temperatures as it lacks any thermal response. Conversely, the PES membranes that were grafted with PNIPAm displayed typical thermal response characteristics that aligned with the results of static contact angle measurements. The receding contact angle for the membrane with 25% PNIPAm grafting yield was significantly low ($\sim 10^\circ$) at a temperature below 33°C , but it increased to 37° when the temperature surpassed 40°C . A significant and abrupt change in surface wettability was observed in the temperature range of 33°C to 39°C , indicating the LCST point of PNIPAm. Below the LCST, the grafted PNIPAm layer absorbed water and swelled, enabling water to spread on the surface of the substrate, thereby lowering the contact angle of the membrane surface. Above the LCST, the PNIPAm shrank and became more hydrophobic, preventing water from spreading on the surface thereby increasing the surface contact angle [7].

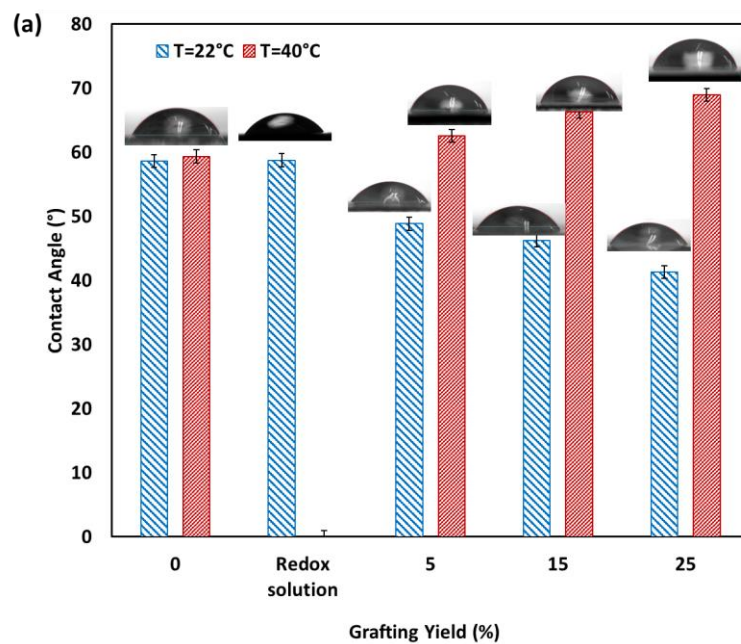
- Surface charge

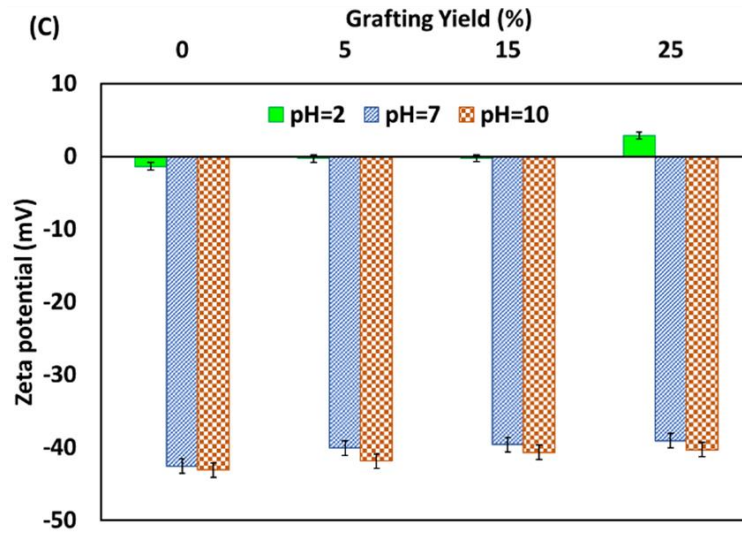
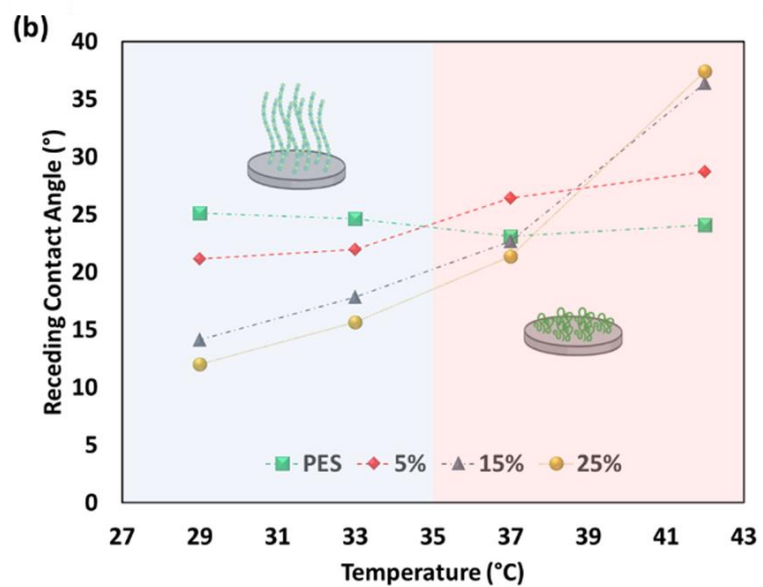
Along with the contact angle, the surface charge is a critical factor in determining the interaction between foulant molecules and the membrane surface. This is because the electrostatic forces resulting from the surface charge affect the attachment of foulants to the membrane. BSA protein, which serves as the model foulant in this study, is a type of amphoteric electrolyte. Its isoelectric point (pI) is around 4.8, which means that the protein is positively charged when the pH is below 4.8 and negatively charged when the pH is above 4.8. The electrostatic interactions between the protein and the membrane surface are affected by changes in pH, which can easily influence the repellence of foulants from the membrane [271], [272]. Therefore, we investigated the surface zeta potential of both bare PES and PNIPAm-grafted PES membranes at pH 2, 7 and

10 using a zetasizer. The results of zeta potential analysis of bare PES and PNIPAm-grafted PES membranes are displayed in Figure 5-5(c). At pH 2, the PES membrane was found to have a negative surface charge of -1.39 mV. However, grafting of PNIPAm on the surface of PES membrane affected the surface charge, where the membrane sample with the grafting yield of 25% (PES-g-25%PNIPAm) resulted in a surface charge of +2.82 mV. A similar pattern was observed at higher pH conditions, where an increase in the grafting yield from 0% to 25% resulted in a decrease in surface charge negativity from -42.6 to -39.1 mV at pH 7 and from -43.1 to -40.3 mV at pH 10. This suggests that the zeta potential of the PES-g-PNIPAm membranes increased after PNIPAm monomers were grafted onto the surface of the PES membranes, due to the electroneutral PNIPAm chains providing a shielding effect on the PES layer [180].

- Average porosity

Figure 5-5(d) shows the average porosity (ϵ) of each membrane, calculated using Equation 1. There is a slight decrease in membrane porosity (%) as the grafting yield increases. When the highest amount of PNIPAm was grafted, the porosity of the PES membrane decreased by only 5%, from approximately 72% for the bare PES to about 67% for the PES-g-25%PNIPAm membrane. This suggests that the PNIPAm has limited penetration into the bulk structure of the PES membrane and that the grafting process has a minimal effect on the pore structure.





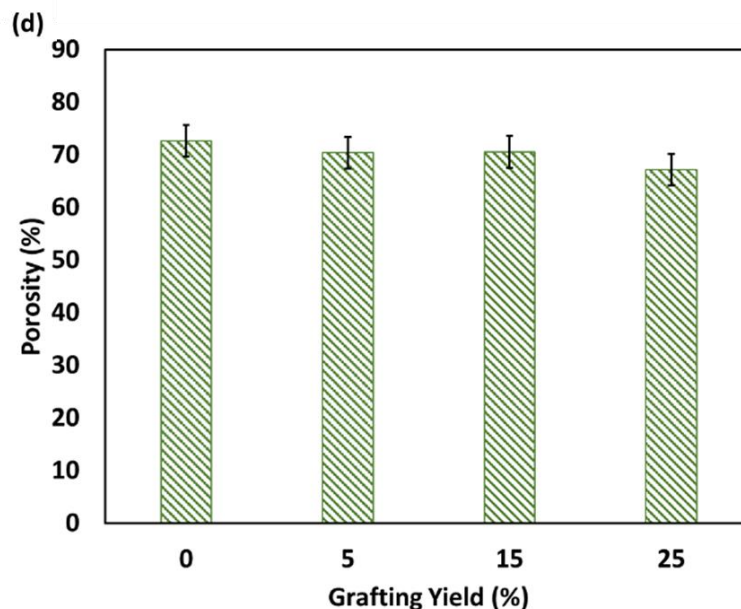


Figure 5-5: (a) Static water contact angles at temperatures of 22 and 40 °C, (b) effect of PNIPAm grafting yield on receding contact angle, (c) zeta potential of membranes at pH=2 and pH=7, and pH=10 and (d) the average porosity of bare PES and PES-g-5%PNIPAm, PES-g-15%PNIPAm, and PES-g-25%PNIPAm membranes.

5.1.2. The impact of surface functionalization with acrylamide and CuO nanoparticles on the grafted membrane characteristics

In this section, our focus shifts towards examining the impact of surface functionalization on the PES membrane's surface properties. Surface functionalization, incorporating acrylamide functional groups and copper oxide nanoparticles, represents a critical aspect of membrane modification. The focus here is to understand how these functionalizations alter the membrane's surface properties such as chemistry, hydrophilicity, roughness and surface charge and subsequently influence its performance in resisting fouling.

1. **PES-g-Functionalized Acrylamide (PES-g-AAm):** This sample with 15% grafting yield represents the membrane functionalized with acrylamide groups. We delve into the surface properties this functionalized membrane, aiming to understand the alterations induced by acrylamide functionalization.
2. **PES-g-Copper Oxide (CuO@PES):** Here, the membrane is functionalized with copper oxide nanoparticles.
3. **PES-g-Combined Functionalization CuO@PES-g-P(NIPAm-co-AAm):** This sample represents the membrane functionalized with a combination of thermo-responsive polymers, acrylamide groups (15% grafting yield) and copper oxide nanoparticles. We extensively analyze the surface properties and the synergistic effects arising from the combined functionalization.

5.1.2.1. Chemical composition of the functionalized PES membranes with acrylamide and copper oxide nanoparticles

- FTIR analysis

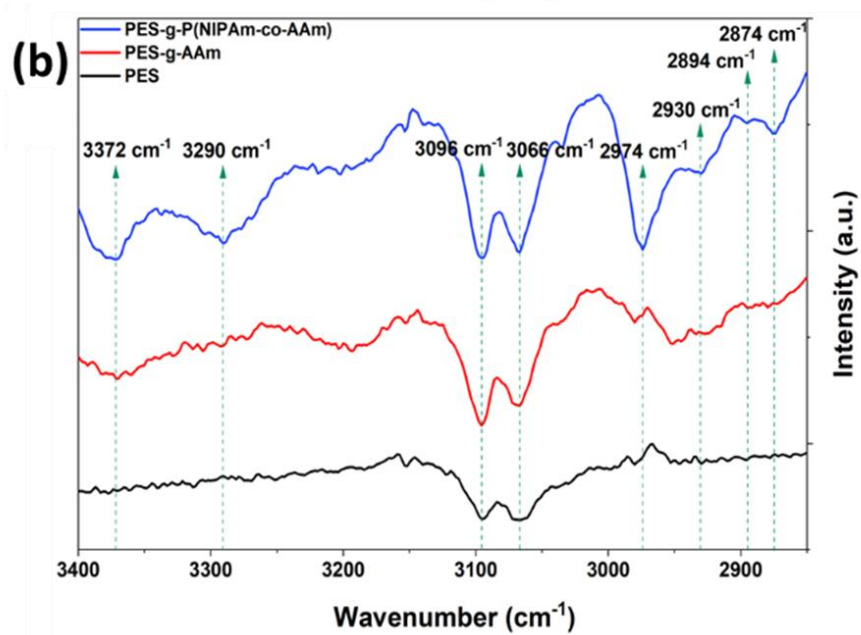
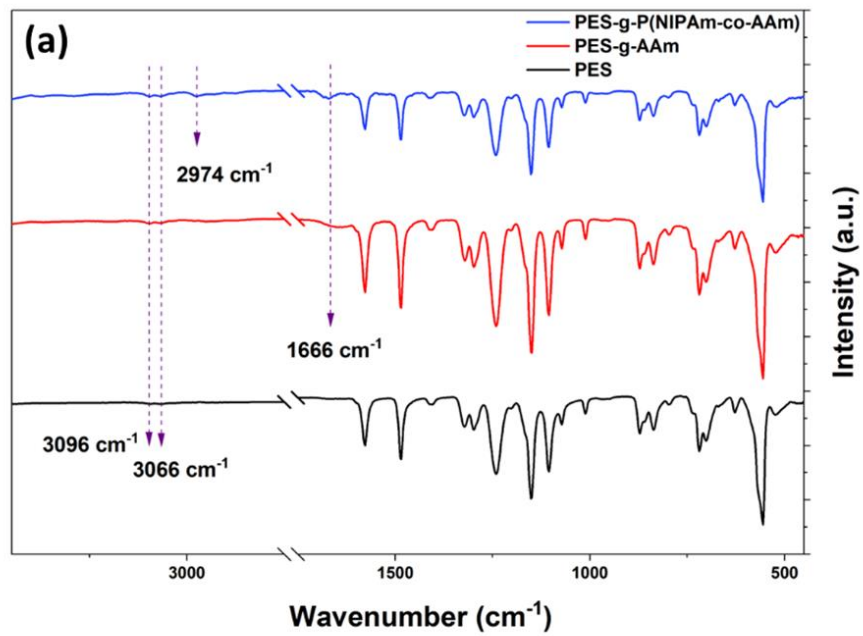
The chemical composition of the pristine and thermo-responsive polymer grafted PES membranes were thoroughly analyzed using FTIR and XPS analysis to investigate the presence of surface functionalities on the membrane surfaces. Figure 5-6(a) presents the ATR-FTIR spectra of bare PES, PES-g-AAm, and PES-g-P(NIPAm-co-AAm) membranes. The spectra reveal that all samples display primary peaks of the PES membrane at 700, 800, 1240, 1489, and 1577 cm^{-1} ,

which are attributed to the stretching vibrations of C-S, C-H, S=O and C-C in the aromatic skeleton, respectively [264]. The absorption band which appeared in the range of 3050-3100 cm^{-1} was assigned to the aromatic ring -CH stretching of PES. Obvious changes in the FTIR spectra of the polyacrylamide and P(NIPAm-co-AAm) grafted PES membranes were observed. In the PES-g-AAm and the PES-g-P(NIPAm-co-AAm) spectra, two new absorption bands appeared at 3290 cm^{-1} and 3372 cm^{-1} and were assigned to the -N-H vibrations of the primary and secondary amines groups present on the membrane surface, respectively. (see Figure 5-6(b)) [273]. This further supports the successful grafting of polymers in terms of PNIPAm, PAAm, and P(NIPAm-co-AAm)) on the surface of PES membrane. The absorption bands that appeared at 2974 cm^{-1} and 2894 cm^{-1} were assigned to the -CH asymmetric and symmetric stretching vibrations of -CH₃, whereas the absorption bands observed at 2930 and 2874 cm^{-1} were assigned to -CH stretching of methylene (-CH₂-) groups [274]. Furthermore, the FTIR analysis of the grafted membrane surfaces reveals the presence of the C=O group at 1666 cm^{-1} which was absent in the pristine PES, indicating the successful polymerization and grafting of AAm in PES-g-AAm and NIPAm/AAm in PES-g-P(NIPAm-co-AAm) membranes [262], [263]. The polyethersulfone polymer is a combination of an aromatic ring, sulfone group, and ether linkage, making it a stable polymer. Its overall reactivity is low due to the presence of stable groups; however, under certain conditions, the probability of the grafting of the reactive species is enhanced significantly. There are two possibilities of the grafting of the P(NIPAm-co-AAm) on the PES surface; (a) the first possibility is that the radical generated on the aromatic ring of the PES during the treatment with the KPS initiator, which results in the activation of the membrane surface, and it immediately interact to form a covalent bond as encountered the NIPAm and AAm. It results in the grafting of the P(NIPAm-co-Aam) on the surface

of the PES membrane; (b) the KPS is a potent initiator, and it immediately starts the polymerization of the NIPAm and AAm by generating the free radical. Some of the radical-containing chains of the P(NIPAm-co-AAm) attack the aromatic ring of the PES, and grafting has taken place on the PES membrane. Figure 5-6(c) illustrates the potential covalent interaction of the P(NIPAm-co-AAm) to graft on the surface of the PES from a thermo-responsive PES-g-P(NIPAm-co-AAm) membrane.

Quantifying the precise amount of AAm copolymerized with PNIPAm poses a significant challenge due to the structural similarity shared by the two monomers, with acrylamide existing in both PNIPAm and AAm. For future analyses, NMR could be used to potentially distinguish between different monomer units in a copolymer. Although each monomer contributes unique NMR signals, it may encounter difficulty distinguishing between the signals of AAm and NIPAm or may lack the accuracy needed to determine the mole fraction of each monomer.

An alternative approach involves utilizing a fluorescence labeling technique, wherein either the AAm or NIPAm monomer is labeled with a fluorescent dye, prior to copolymerization. The fluorescence intensity of the resulting copolymer can then be measured using a fluorescence spectrophotometer and correlated to the mole fraction of the labeled monomer. However, a noteworthy drawback of this technique is the introduction of impurities, which can adversely impact the properties of the copolymer.



(c)

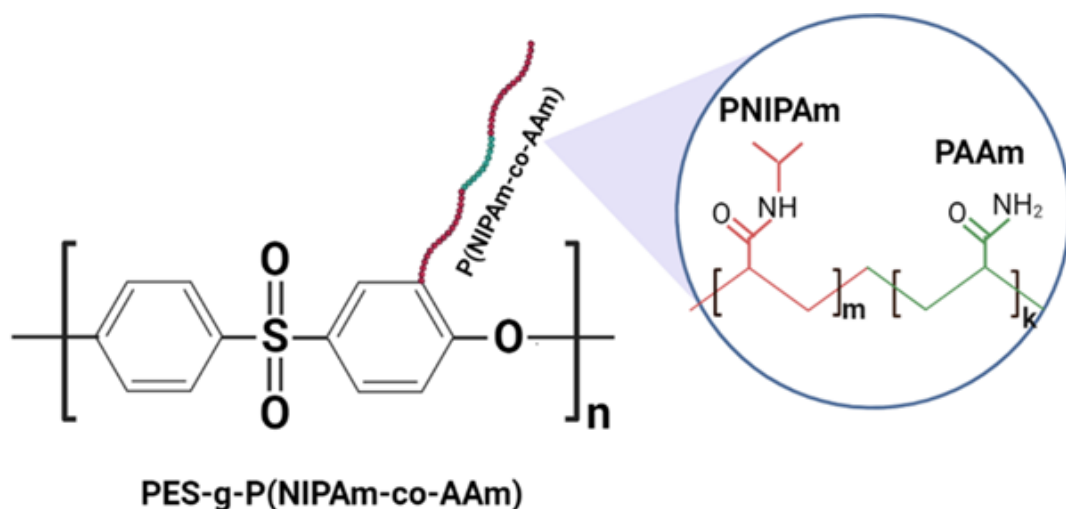


Figure 5-6: (a) ATR-FTIR spectra of bare PES, PES-g-AAm and P(NIPAm-co-AAm) grafted membranes at wavenumber 450-3500 cm⁻¹, (b) zoom-in from 2850-3400 cm⁻¹. (c) Proposed structure of PES-g-P(NIPAm-co-AAm).

- XRD analysis

Figure 5-7 depicts the XRD patterns of CuO nanoparticles synthesized prior to immobilization on the membrane surface, spanning 2θ from 30° to 80°. The sharpness of XRD reflections provides evidence of the crystalline nature of the synthesized nanoparticles. The well-matched peaks at 2θ values of 35.69°, 38.93°, 48.31°, 58.21°, 61.31°, 65.87°, 68.31°, and 75.39° correspond to ICSD No. 01-080-1916, thereby confirming the formation of CuO during the synthesis process [275].

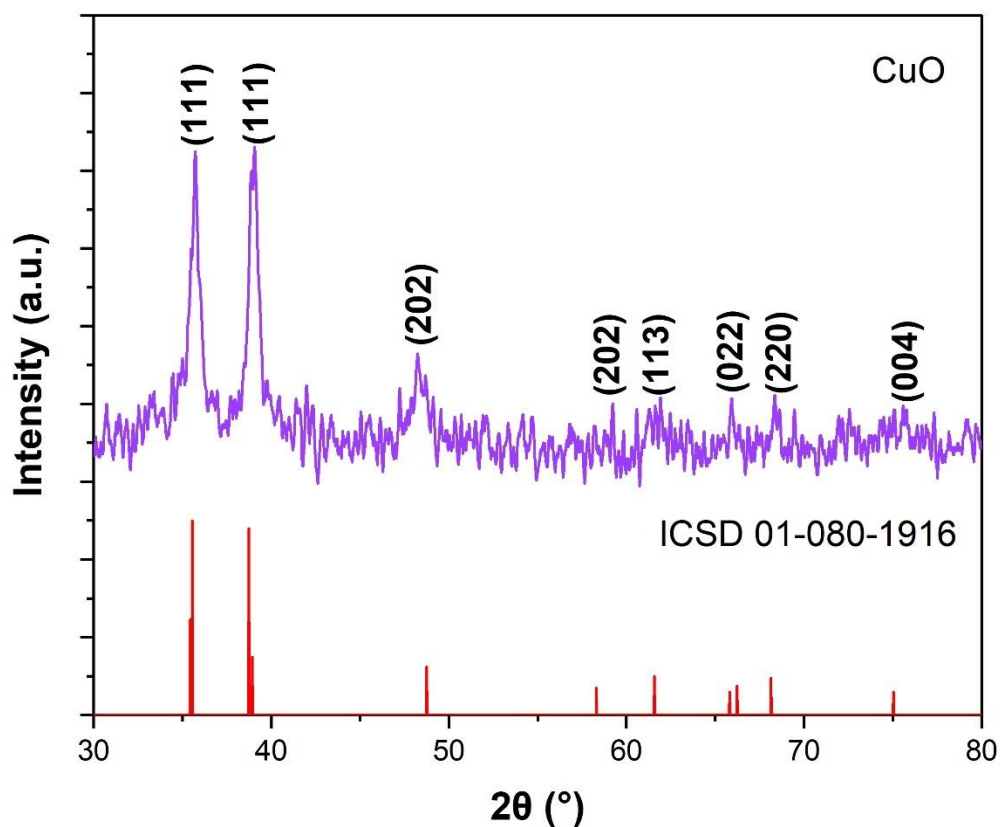


Figure 5-7: XRD-patterns of synthesized copper oxide nanoparticles prior to immobilization on the membrane surface.

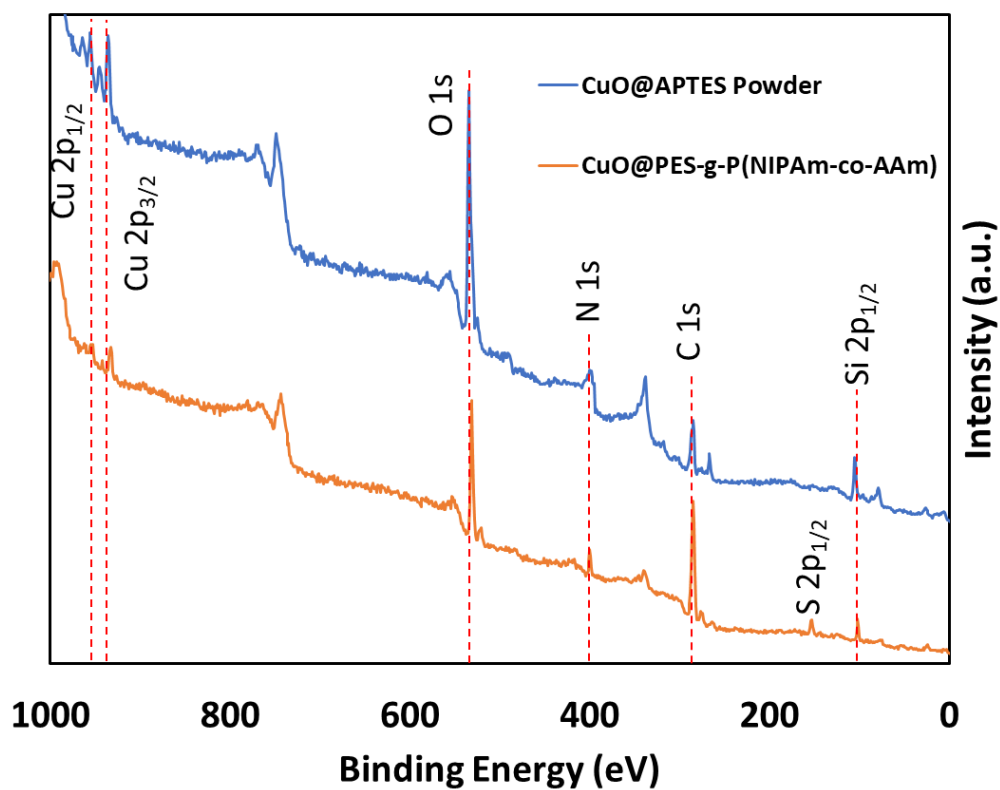
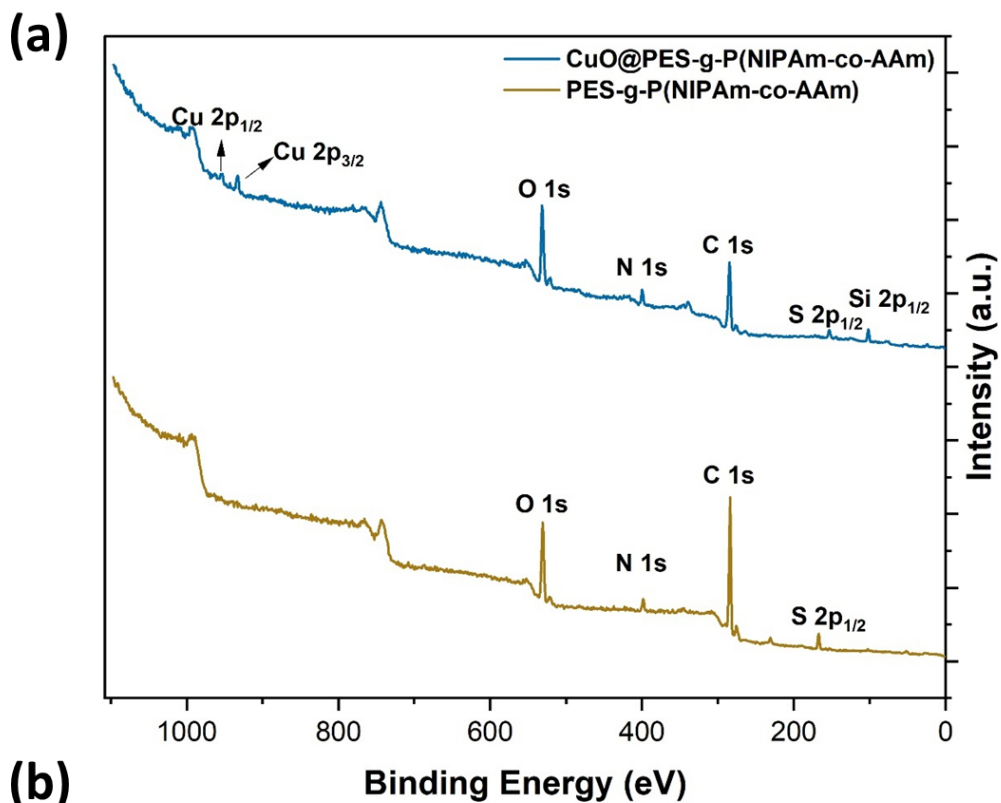
- XPS analysis, survey

The XPS survey results comparing CuO@PES-g-P(NIPAm-co-AAm) to PES-g-P(NIPAm-co-AAm) demonstrate the appearance of two new peaks in CuO@PES-g-P(NIPAm-co-AAm) at the binding energy of 933.7 and 953.7 eV, which correspond to the 2p_{3/2} and Cu 2p_{1/2} peaks. Additionally, peaks appear in CuO@PES-g-P(NIPAm-co-AAm) at 101.8 eV, corresponding to the Si 2p spectra, which confirms the presence of APTES in the dual-functionalized membrane structure as depicted at Figure 5-8. In both spectra, peaks at 167.6 eV, 284.6 eV, 399.2 eV and 531.8 eV correspond to

the presence of the basic elements of the grafted-PES membrane, including S 2p_{1/2}, C 1s, N 1s, and O 1s, respectively [276], [277].

To assess the bonding of APTES and CuO nanoparticles, the reaction solution underwent three rounds of centrifugation, supernatant removal, and washing with ethanol after immobilization. The resulting precipitated particles were separated and dried in an oven at 50°C overnight. Subsequently, the CuO nanoparticle powder was analyzed using the XPS method (Figure 5-8 (b)). The analysis revealed the presence of Cu²⁺ as indicated by the binding energies of 933.7 and 953.7 eV.

Moreover, peaks at 101.8 eV, 284.6 eV, 399.2 eV, and 531.8 eV corresponded to Si 2p, C 1s, N 1s, and O 1s, respectively. This indicates the presence of APTES on the nanoparticle powder. From these findings, we can possibly conclude that APTES chemically bonds with CuO during the immobilization process. Additionally, the EDS mapping analysis of agglomerated CuO@APTES particles on the surface of the PES membrane, as depicted in Figure 5-8(c), indicates a noticeably higher concentration of Si and Cu in the locations of the agglomerated particles compared to other areas on the surface. This observation could further provides support for the APTES-CuO interactions. However, to further investigate the bonding of APTES on the membrane surface, it would be highly beneficial to include a PES@APTES control sample and conduct XPS analysis to examine the bonding in this specific context.



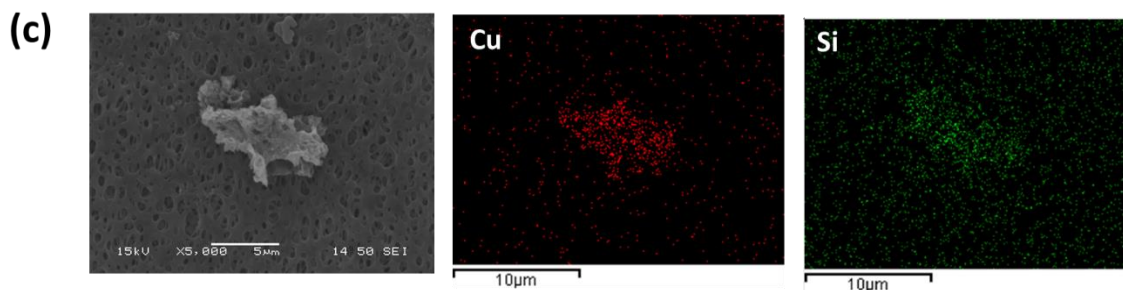
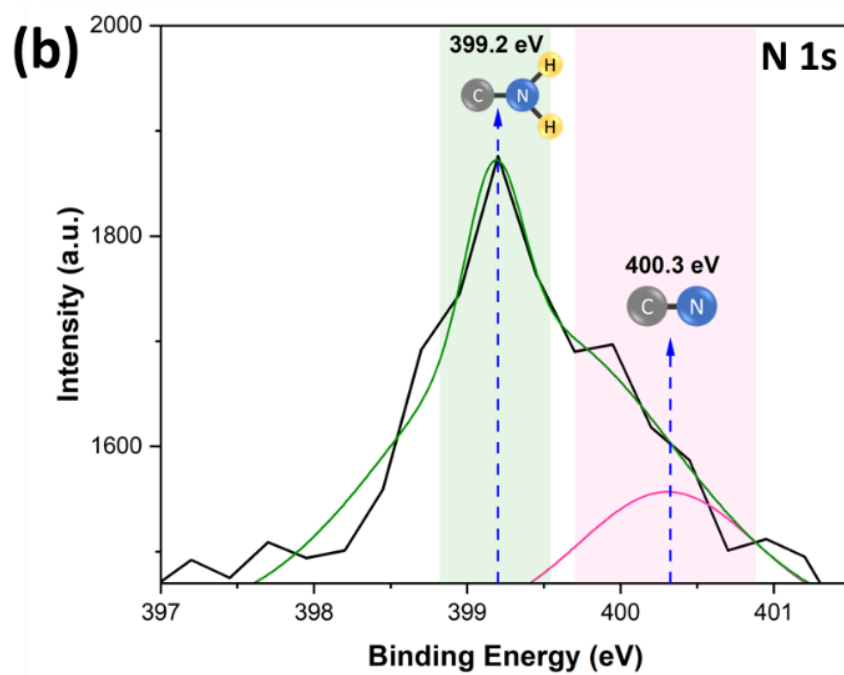
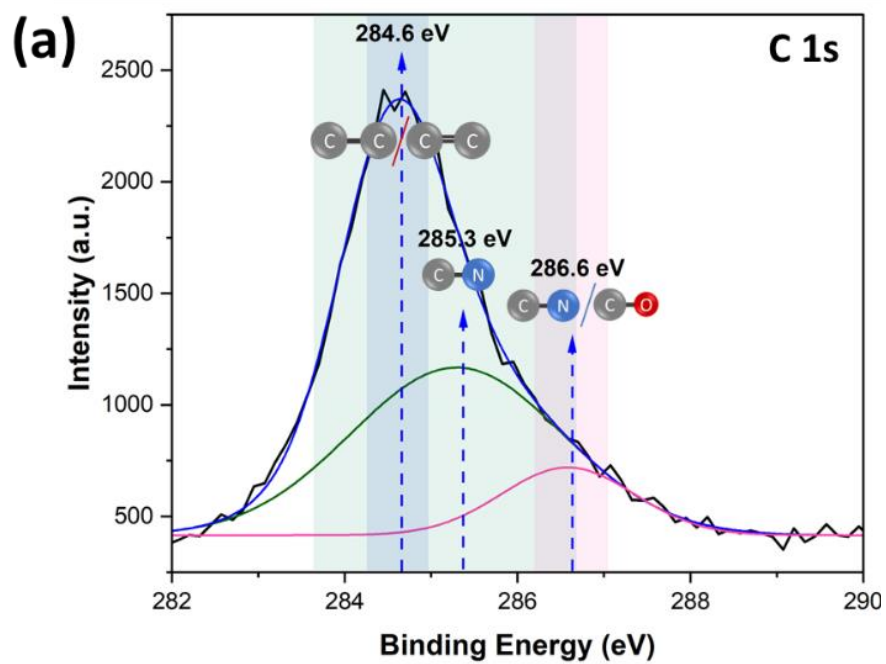


Figure 5-8: Wide XPS survey scan spectra of (a) grafted- (PES-g-P(NIPAm-co-AAm)) and dual-functionalized (CuO@PES-g-P(NIPAm-co-AAm)) membranes, and (b) CuO@APTES powder. (C) EDS elemental mapping analysis of agglomerated CuO@APTES particle on the membrane surface.

- XPS analysis, high-resolution

To gain a deeper understanding of the surface composition and chemical bonding pattern of PES-g-P(NIPAm-co-AAm) and the copper-functionalized P(NIPAm-co-AAm) grafted membrane, a high-resolution XPS analysis of carbon, nitrogen, copper, oxygen, and silicon was conducted (see Figure 5-9 and 5-10). The deconvoluted C 1s spectrum shows three contributions at 284.6, 285.3, and 286.6 eV, which correspond to the C-C/C=C, C-N, and C-N/C-O bonding, respectively [278]. Upon deconvolution of the N 1s XPS high-resolution peak, two components were identified. The component at 399.2 eV corresponds to the amine functional group C-NH₂, while the components at higher binding energies, 400.3 eV, are likely related to the C-N bonding [279]. Analysis of the O 1s spectra led to the identification of two sub-peaks at 531.3 and 533.0 eV, corresponding to the C-O and H₂O adsorbed water remaining in the membrane bonds, respectively [280], [281]. Based on the information extracted from FTIR and XPS analyses, we propose the chemical structure of the P(NIPAm-co-AAm) grafted PES membrane as demonstrated in Figure 5-9(d).



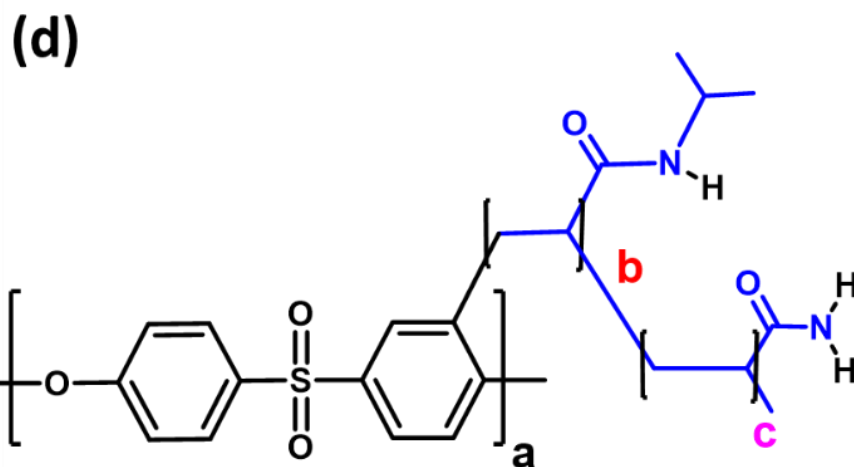
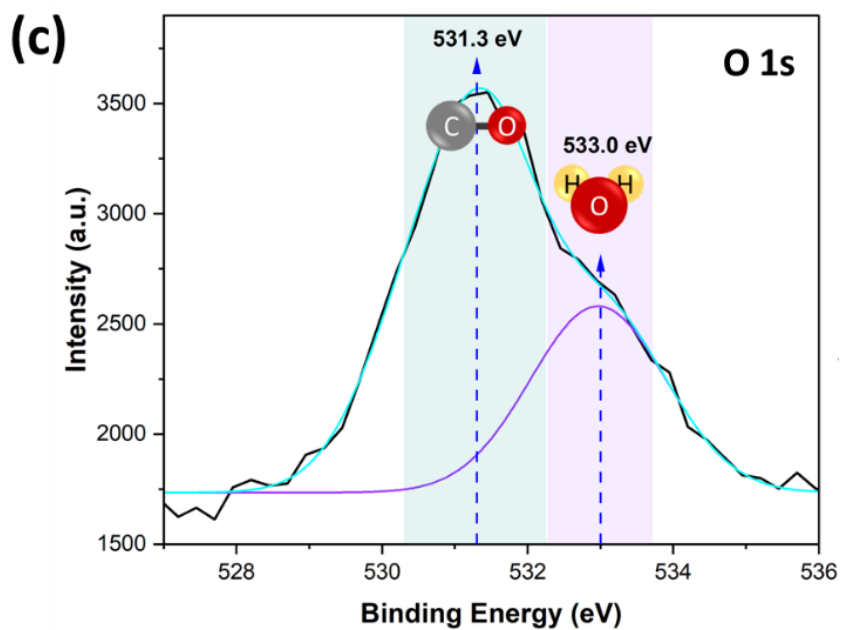
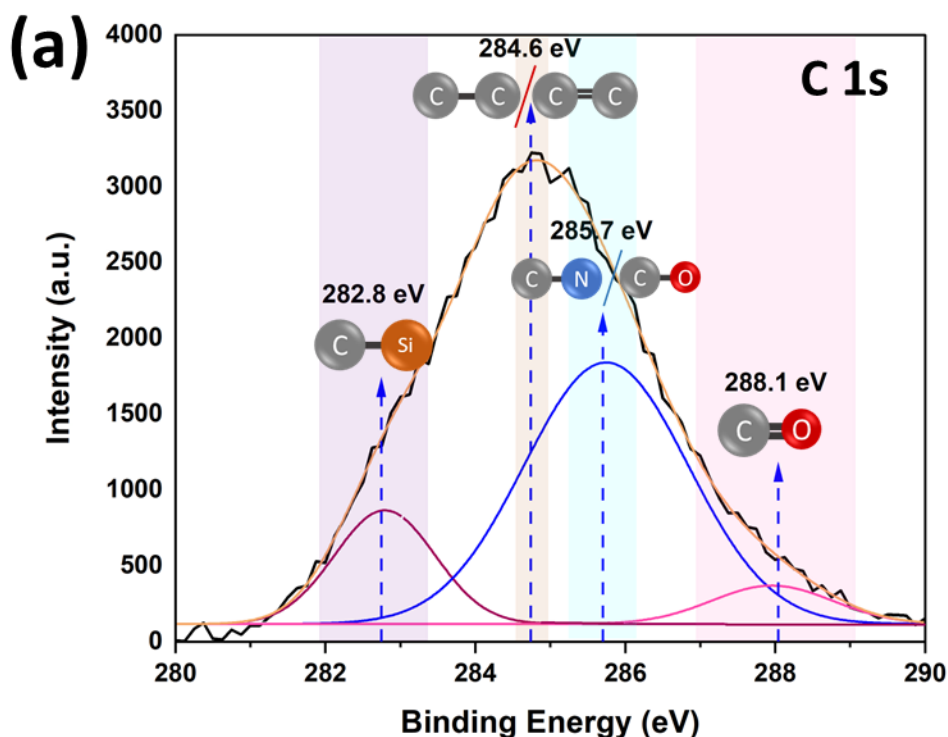


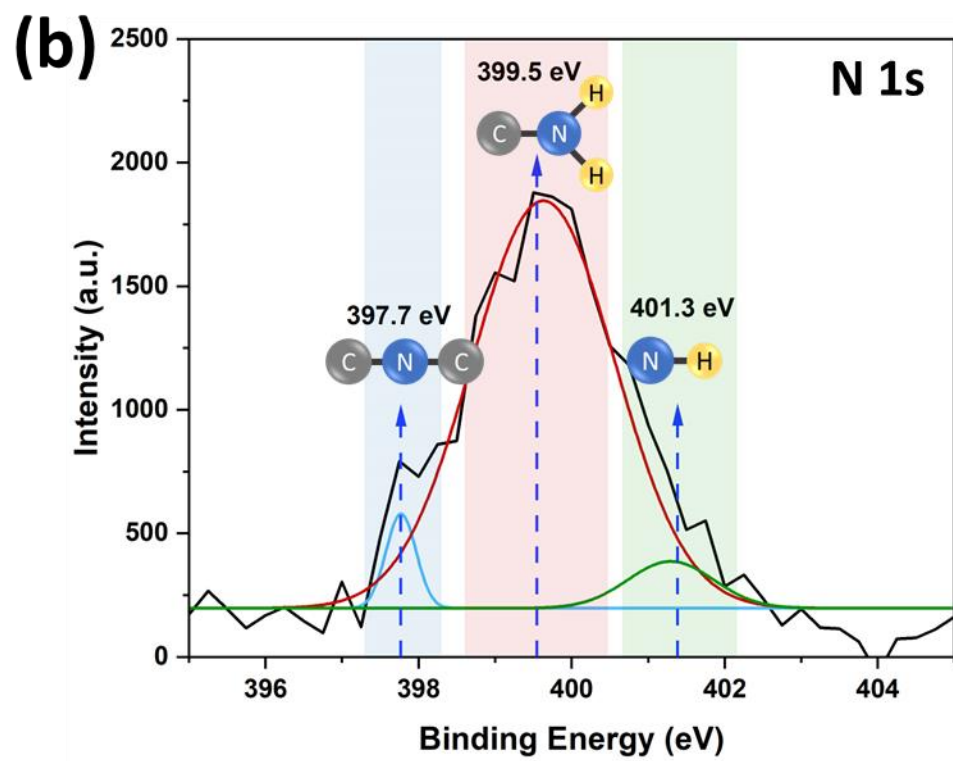
Figure 5-9: High resolution X-ray photoelectron spectroscopy (XPS) spectra of (a) C 1s, (b) N 1s, and (c) O 1s region for the PES-g-P(NIPAm-co-AAm). (d) proposed chemical structure for PES-g-P(NIPAm-co-AAm).

Figure 5-10 demonstrated the high resolution XPS spectra of C 1s, N 1s, Cu 2p_{1/2}/2p_{3/2}, O 1s, and Si 2p_{1/2} region for the CuO@PES-g-P(NIPAm-co-AAm). The deconvoluted C 1s spectrum exhibited four contributions at 282.8, 284.6, 285.7 and 288.1 eV, corresponding to the C-Si, C-C/C-H/C=C, C-N/C-O and -C=O functional groups, respectively [282]–[284]. Through deconvolution analysis of the N 1s XPS core level peaks, three distinct components were identified. The first component, observed at 397.7 eV, corresponds to the C-N-C bonding. The remaining two components, detected at higher binding energies of 399.5 and 401.3 eV, are likely associated with the C-NH₂ and N-H groups, respectively [285], [286]. Observation of the primary spectra of the copper 2p_{1/2} and 2p_{3/2} levels revealed peaks at 953.7 and 933.7 eV, respectively, accompanied by a shake-up satellite at approximately 962.6 eV and 943.5 eV. These features were attributed to the CuO chemical composition. As a result, the oxidation state of copper on the membrane's surface was identified as Cu²⁺ [287]. By analyzing Figure 5-10 (d), it was determined that the O 1s spectra could be primarily fitted using three sub-peaks positioned at 529.9, 531.9, and 534.4 eV. These sub-peaks correspond to the Cu-O, C-O, and Si-O bonds [280]. Additionally, the Si 2p spectra (Figure 5-10 (e)) exhibit two peaks at 101.8 and 104.7 eV, which correspond to the Si-Si/Si-C and Si-O bonds, respectively [280], [288].

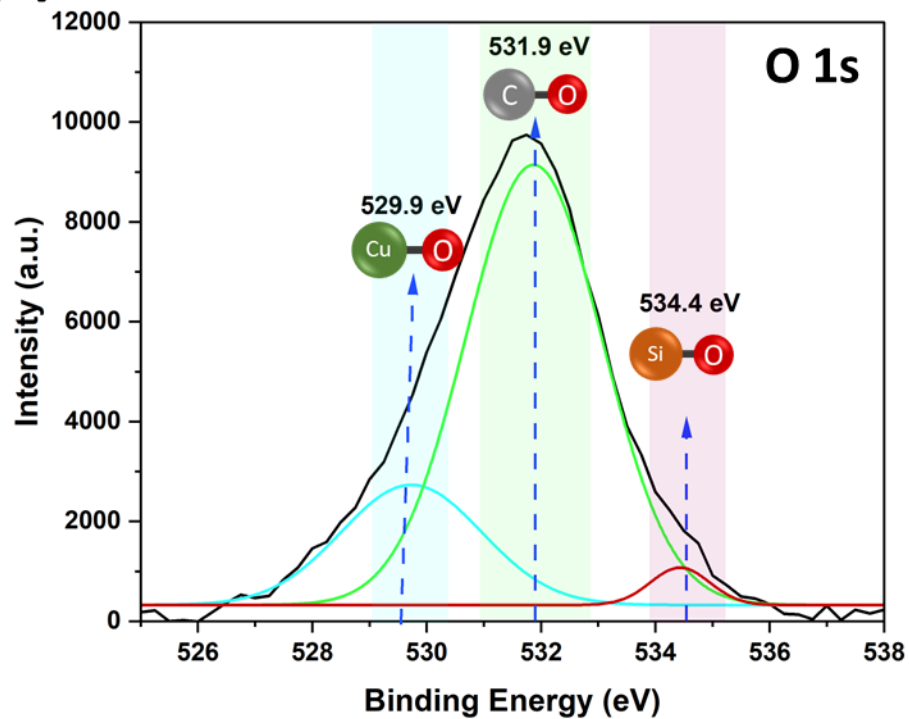
One of the concerns of metal oxide modified membrane is the contamination of the permeate by the disengaged nanoparticles from the membrane surface. However, the XPS results suggest the potential immobilization of CuO nanoparticles on P(NIPAm-co-AAm) grafted PES membranes. This possibility may arise from the hydroxyl groups present on the surface of CuO, which could potentially interact with the silane and form a covalent bond with APTES. Furthermore, the APTES-functionalized CuO particles may also be held on the surface of the P(NIPAm-co-AAm)

grafted membranes through a combination of physisorption, hydrogen bonding, and electrostatic attachment [289]. However, Further analysis on the PES@APTES is needed to define the bonding of APTES and PES membrane. The amino groups ($-NH_2$) present on the surface of $CuO-NH_2$ nanoparticles are both a hydrogen bond donors and acceptors which can develop considerable hydrogen bonding with amide groups ($-CONH$) of the P(NIPAm-co-AAm) grafted PES membranes. While hydrogen bonds are weaker than covalent bonds, but stronger than other intermolecular forces, such as van der Waals forces or electrostatic forces. These hydrogen bonds can create a network of interactions that can anchor the nanoparticles to the membrane surface and resist the detachment or leaching of the nanoparticles under external forces, such as water flow and temperature fluctuations [290].

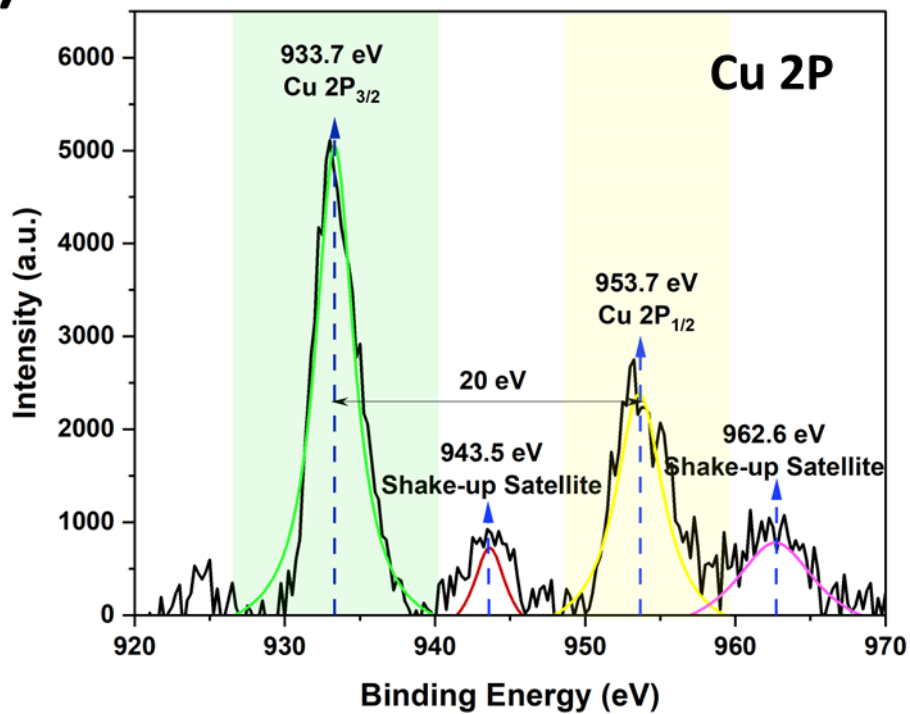




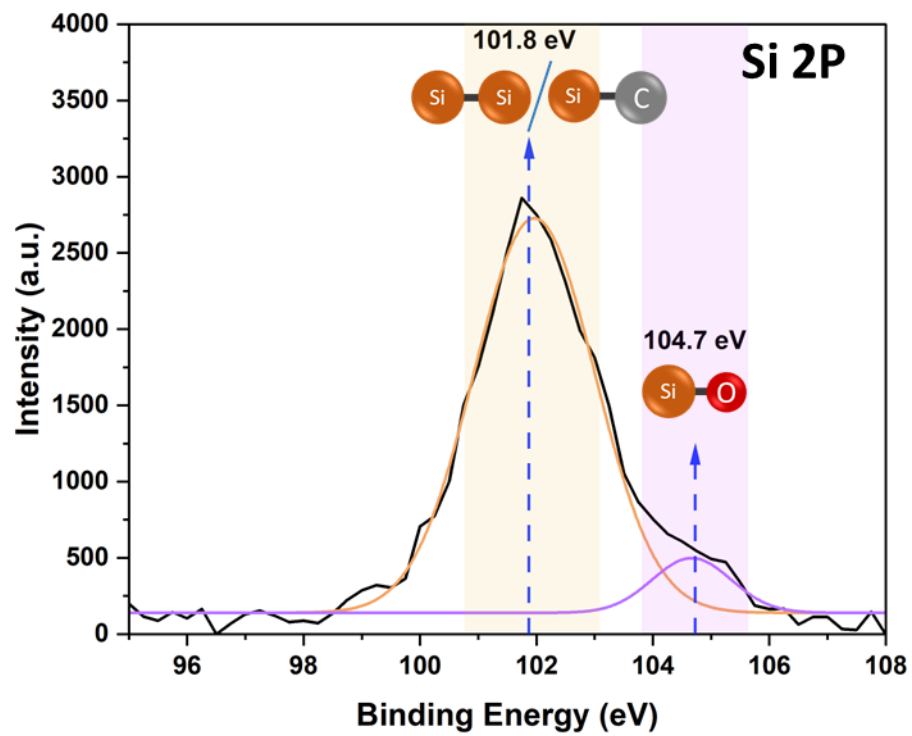
(c)



(d)



(e)



(f)

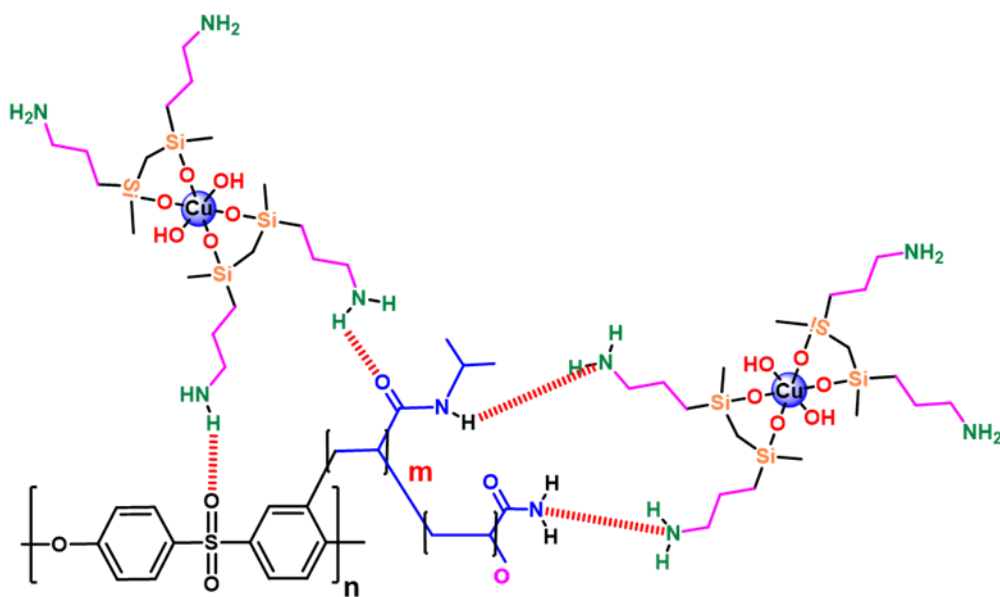


Figure 5-10: High resolution X-ray photoelectron spectroscopy (XPS) spectra of (a) C 1s, (b) N 1s, (c) Cu 2p_{1/2} and 2p_{3/2}, (d) O 1s, and (e) Si 2p_{1/2} region for the CuO@PES-g-P(NIPAm-co-AAm). (f) Proposed chemical structure for CuO@PES-g-P(NIPAm-co-AAm).

-Thermogravimetry analysis

The performance and antifouling characteristics of membranes are affected by the loading of inorganic nanoparticles. Hence, the weight loss in the TGA profile was examined to determine the CuO loading on the modified membrane as depicted on Figure 5-11. The analysis showed that the remaining inorganic content in CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm) membranes was 2.60 wt.% and 2.01 wt.%, respectively. the standard error of the mean (SEM) calculated to be approximately 0.3 wt.%. Given that wet chemistry was employed, this difference between inorganic content in the dual functionalized samples (2.6 wt.% and 2.01 wt.%,) is mostly considered within the experimental error range. However, future experiments are needed to fully answer the relationship between copper oxide concentration and AAm presence.

The TGA analysis was conducted twice for each sample, and the error function has been reported in. Moreover, based the weight ratio of APTES to CuO, the Si/(CuO+Si) ratio in the residue would be approximately 0.05 (see details in the footnote)⁶, assuming that all the APTES added into the solution attaches to the membrane surface. Therefore, an additional error function of 0.05 could contribute to the value of the standard error.

⁶ APTES density: 0.946 g/mL, volume of APTES added to the solution: 0.01 mL, weight of Si: 1.2 mg, weight of CuO: 20 mg.

The grafted and dual-functionalized membranes exhibited a weight reduction 100-370°C, due to the fracture and digestion of the terminal and side chain functional groups [291]. The weight loss of the blank PES membrane occurs around 450 °C, leaving approximately 93 wt% remaining. This can be attributed to sulfur dioxide cleavage and ether bond cleavage. At higher temperatures, the second thermal degradation stage initiates around 575 °C as the side chain groups and backbone (benzene ring) decomposes. [292], [293]. It should be mentioned that there was no substantial difference in weight loss pattern between the bare and modified membranes. Figure 5-11(b) illustrates the application of Differential Scanning Calorimetry (DSC) to characterize the thermal transition temperatures for various membranes, including bare PES, PES-g-PNIPAm, and CuO@PES-g-P(NIPAm-co-AAm) in the temperature range of 30-300 °C. The thermograms reveal that the glass transition temperature (T_g) of the bare PES occurs at around 230 °C [294].

Moreover, a subtle peak is observed between 30-50°C for PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm). This small peak could be indicative of the phase transition behavior of the PES membrane. However, the difference in the heat flow trend is marginal, making it challenging to conclusively correlate it with phase transition behavior. Further investigation may be required to establish a clearer understanding of this observed thermal behavior.

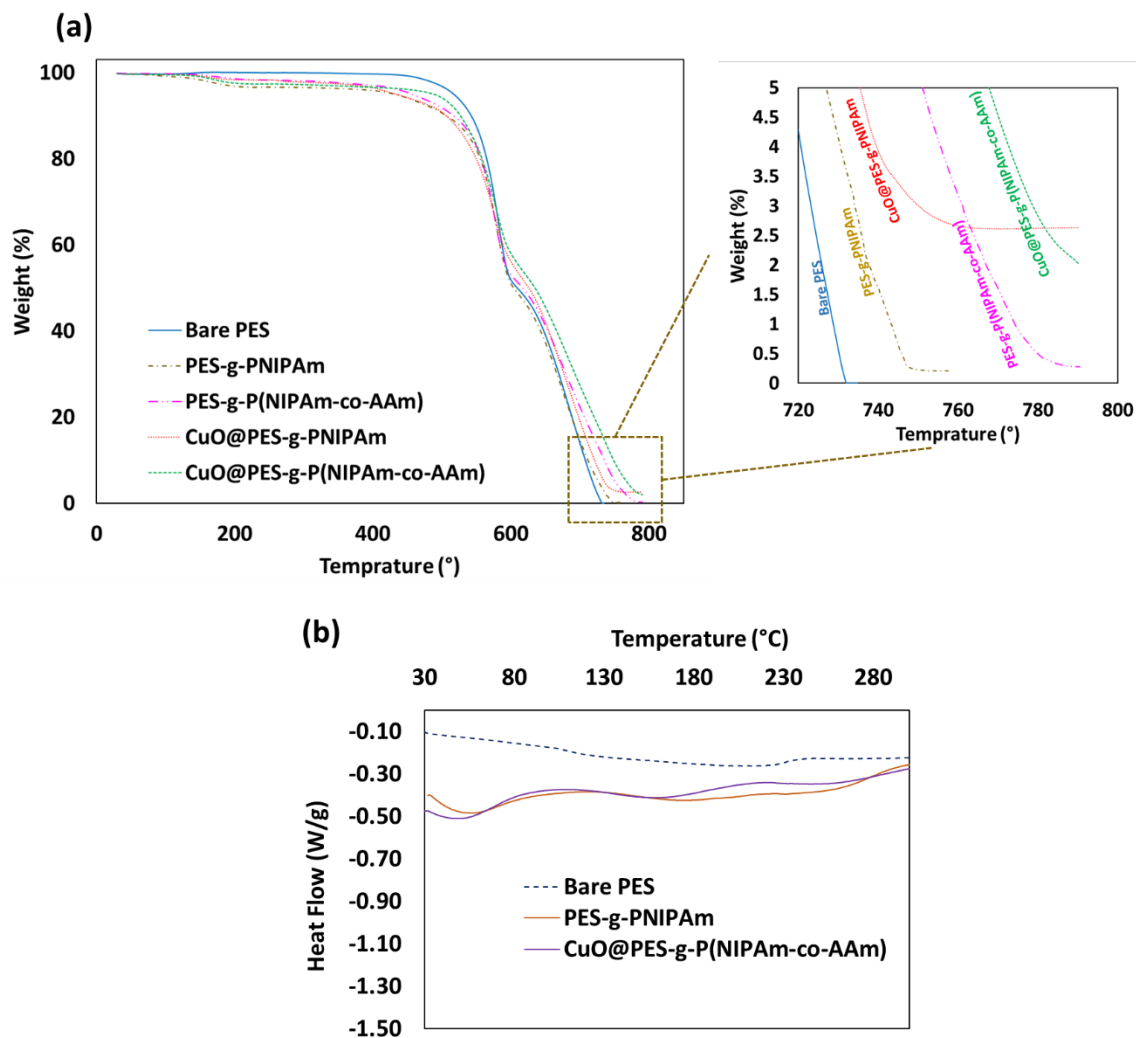


Figure 5-11: Thermogravimetric analysis (TGA) of bare PES, PES-g-PNIPAm, PES-g-P(NIPAm-co-AAm), CuO@PES-g-PNIPAm, and CuO@PES-g-P(NIPAm-co-AAm). (b) Differential scanning calorimetry (DSC) of bare PES, PES-g-PNIPAm, and CuO@PES-g-P(NIPAm-co-AAm) in the temperature range of 30-300 °C.

5.1.2.2. Surface morphology of the functionalized PES membranes functionalized with acrylamide and copper oxide nanoparticles

The pristine and modified PES membranes surfaces and cross-sectional morphology was scanned using SEM and are presented in Figure 5-12. The surface analysis of the pristine PES membrane has shown the uniform distribution of the tiny pores on the surface, whereas the bottom of the

PES membrane consists of different sizes of large-sized pores unequally distributed on the bottom surface. The impact of grafting can be observed on the active site of the membrane and the bottom of the membrane. A thin layer (~550 nm) can be observed after grafting AAm onto the PES membranes, the surface was covered with a thin layer, and some of the irregular particle materials can be observed at the bottom of the membrane. The surface of the P(NIPAM-co-AAm) grafted PES membrane appeared slightly different from the AAm grafted PES membranes. In P(NIPAM-co-AAm) grafted PES membrane, the spherically surface grafted polymers were observed on both sides of the membranes. The SEM images showed that the particles were uniformly distributed on the membrane surface, with an average particle size of less than 200 nm. The appearance of granules after grafting with the thermo-responsive polymers is according to the previously reported thermo-responsive polymer grafted membranes [172], [177], [265].

One of the main effects of cluster size on the phase-transition behavior of PNIPAM clusters is that smaller clusters have higher LCSTs than larger clusters. This is because smaller clusters have higher surface-to-volume ratios, which increases the entropy and solubility of the clusters at lower temperatures. Smaller clusters also have lower degrees of polymerization, which reduce the hydrophobic interactions and the cooperativity of the phase transition.

Another effect of cluster size on the phase-transition behavior of PNIPAM clusters is that smaller clusters have faster response times than larger clusters. This means that smaller clusters can swell or shrink more quickly in response to temperature changes than larger clusters. This is because smaller clusters have shorter diffusion lengths, which allow the water molecules to penetrate or escape the clusters more easily [295].

Determining the degree of polymerization for these types of copolymers presents significant challenges. While C-NMR could potentially aid in this measurement, the process involves dissolving the grafted membrane in a suitable solvent for analysis in the NMR cell. Unfortunately, this dissolution process can break the polymer chains, making the results unreliable. Furthermore, the complexity is compounded by the presence of two monomers in the solution, and the exact ratio of AAm to NIPAm in polymer chain is unknown. As a result, even obtaining an approximate estimate of the degree of polymerization in this case is challenging.

Functionalization of the bare and grafted membrane with copper oxide nanoparticles is shown in Figure 5-12 (d and e). The image demonstrates the formation of nearly spherical-shaped nanoparticles that are well dispersed on the surface of both bare and modified PES membranes.

The morphology of copper oxide nanoparticles agrees well with the previously reported literature [296], [297]. Additionally, a small concentration of these nanoparticles appeared to have formed large agglomerates, which is more prominent in the case of the CuO@PES-g-P(NIPAm-co-AAm) membrane. The prominent agglomeration in CuO@ PES-g-P(NIPAm-co-AAm) might be due to the interaction of the APTES functionalized CuO nanoparticles with the P(NIPAm-co-AAm). As many sides of the thermo-responsive polymer are available to interact with the APTES, which result into the agglomeration on the surface of the CuO@ PES-g-P(NIPAm-co-AAm) membrane. The cross sections of all the membranes have shown fingerlike projections that immediately start from the surface of the membrane and move towards the bottom. The fingerlike projections become broader as they move toward the bottom of the membrane. In the cross-sectional image, it can be observed that the added agents (AAm, P(NIPAm-co-AAm), and CuO) did not significantly penetrate the bulk of the membrane, and the microstructure of the membrane's porosity was

not altered after the modification. In material structures, surfaces and pore edges are generally considered as defects, and molecules located on these sites tend to possess higher energy. Consequently, during radical attacks, they are more susceptible to participating in the reaction and initiating nucleation processes [298]. As a result, we can expect to see the majority of particles form on the surface and do not penetrate deep into the bulk porosity.

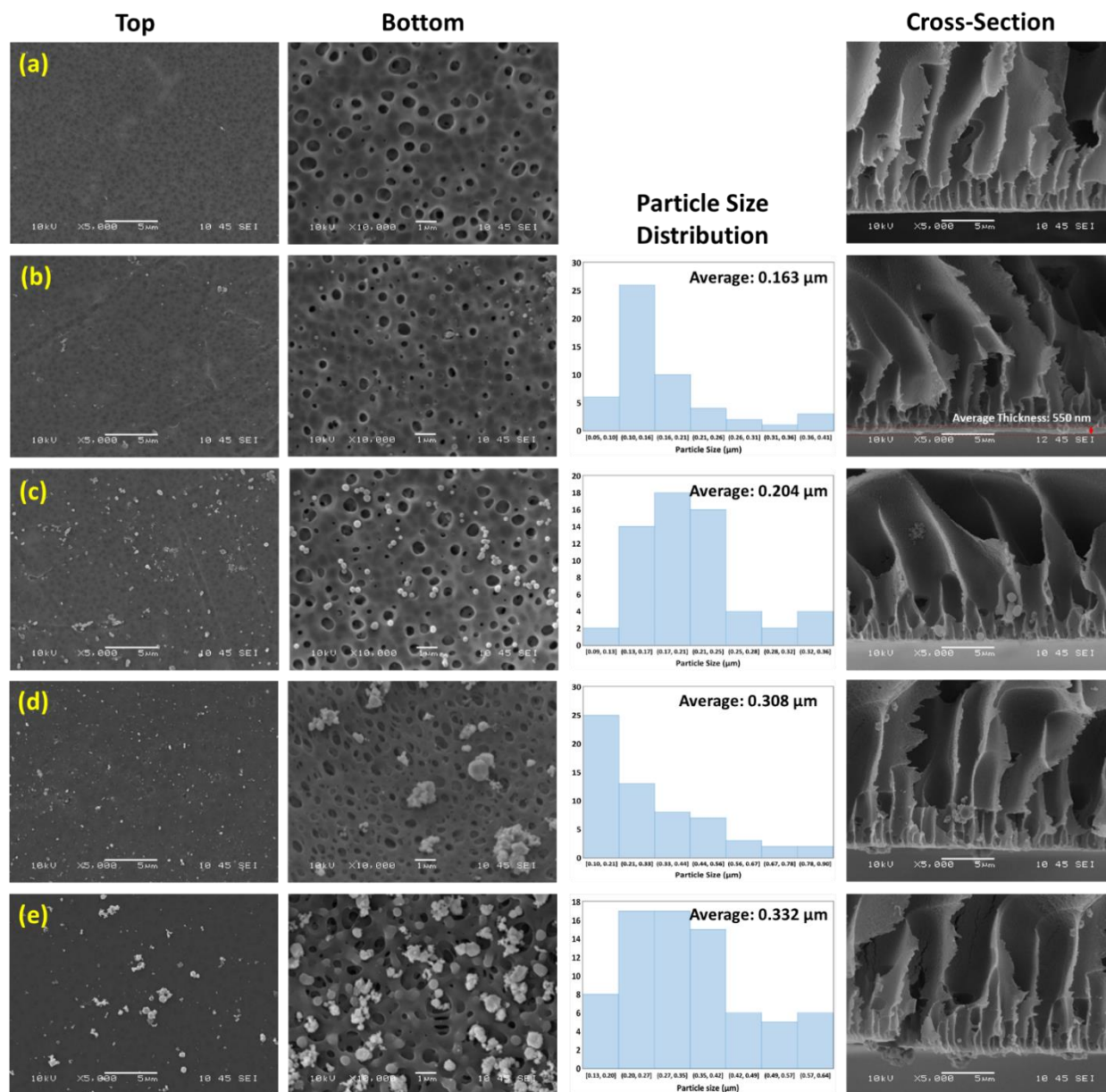


Figure 5-12: Top, bottom, and cross-sectional images of (a) bare PES, (b) PES-g-AAm, (c) PES-g-P(NIPAm-co-AAm), (d) CuO@PES, and (e) CuO@PES-g-P(NIPAm-co-AAm).

As shown in Figure 5-13, the bottom images reveal a consistent pore structure between the unmodified PES and modified membranes. The pore size distribution for the back porosity of both the modified and unmodified membranes was measured to be 0.2 μm . This uniformity can

be attributed to the non-destructive nature of the modification process. In the grafting process, the chemical reactions did not cause damage or deformation to the PES membrane. Moreover, the incorporation of copper oxide nanoparticles was limited to the membrane's surface and did not disrupt the pore formation process.

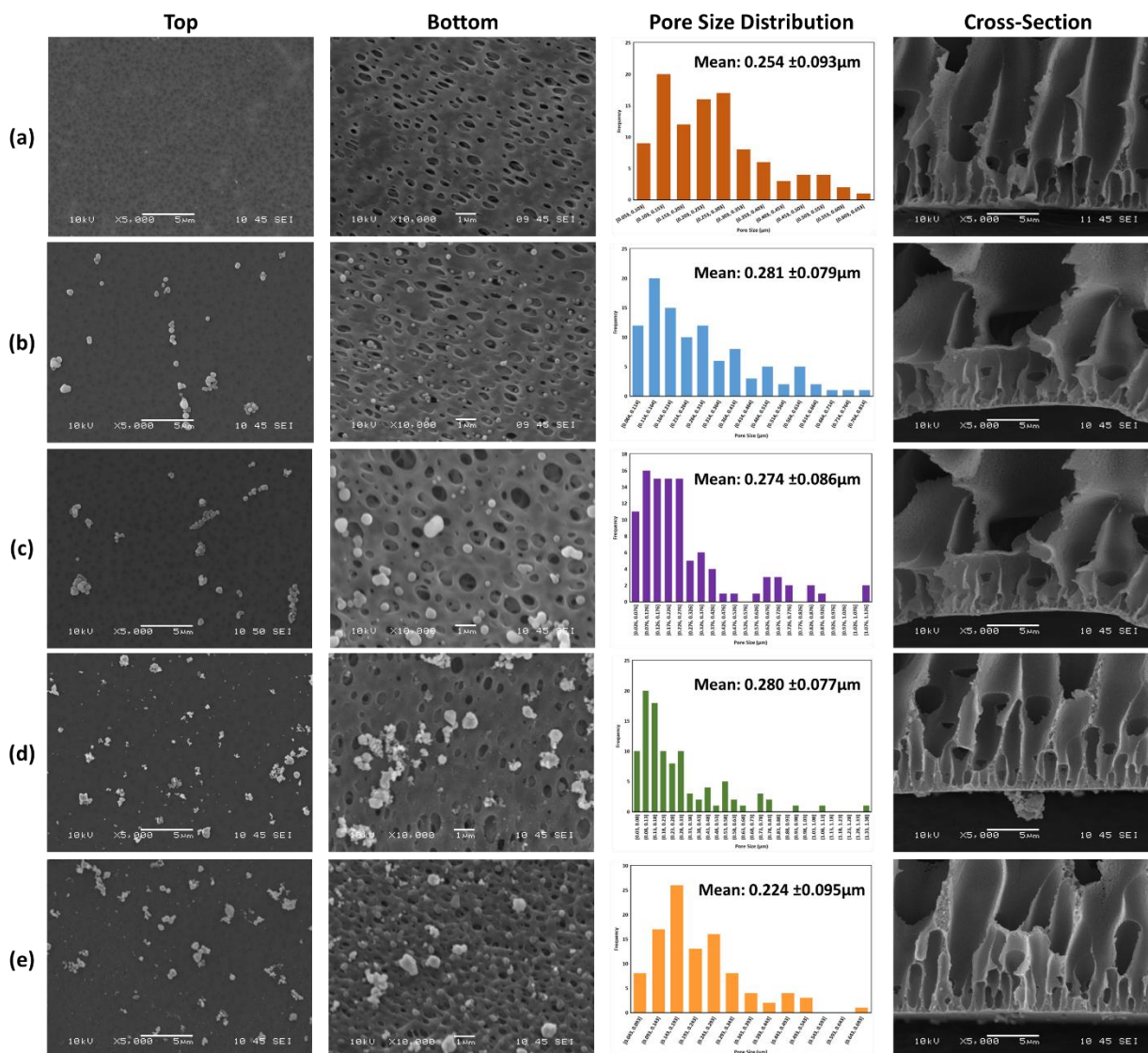
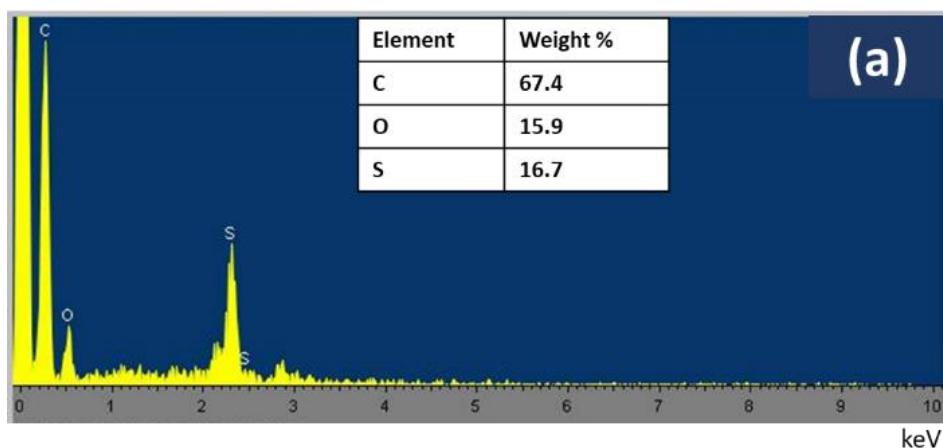


Figure 5-13: SEM images of bottom and pore size distribution of different PES membranes including (a) bare PES, (b) PES-g-PNIPAm, (c) PES-g-P(NIPAm-co-AAm), (d) CuO@PES-g-PNIPAm, and (e) CuO@PES-g-P(NIPAm-co-AAm) membranes in 5000 and 10000 X magnifications.

- EDS and elemental mapping analysis

Figure 5-14(a-c) depicts the SEM-EDS elemental analysis conducted on bare PES, PES-g-P(NIPAm-co-AAm), and CuO@PES-g-P(NIPAm-co-AAm) membranes. The analysis revealed the presence of nitrogen in PES-g-P(NIPAm-co-AAm) after grafting with P(NIPAm-co-AAm) and nitrogen, copper and silicon ions in the dual functionalized membrane CuO@PES-g-P(NIPAm-co-AAm). The fundamental elements of the PES membrane, namely carbon, sulfur, and oxygen were found in three samples. The elemental mapping results of CuO@PES-g-P(NIPAm-co-AAm) shown in Figure 5-14(d) revealed that copper, nitrogen, and silicon ions were uniformly distributed across the membrane surface, indicating that most copper oxide nanoparticles and thermo-responsive nanoparticles did not form very large agglomerates on the membrane surface and distributed uniformly on the surface.



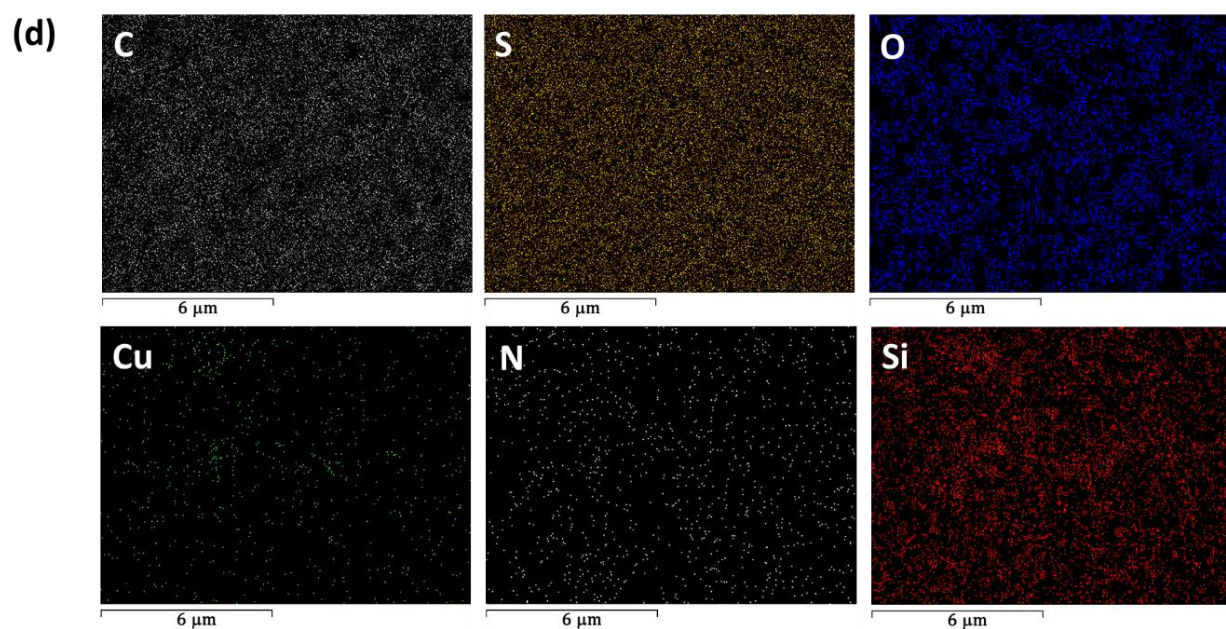
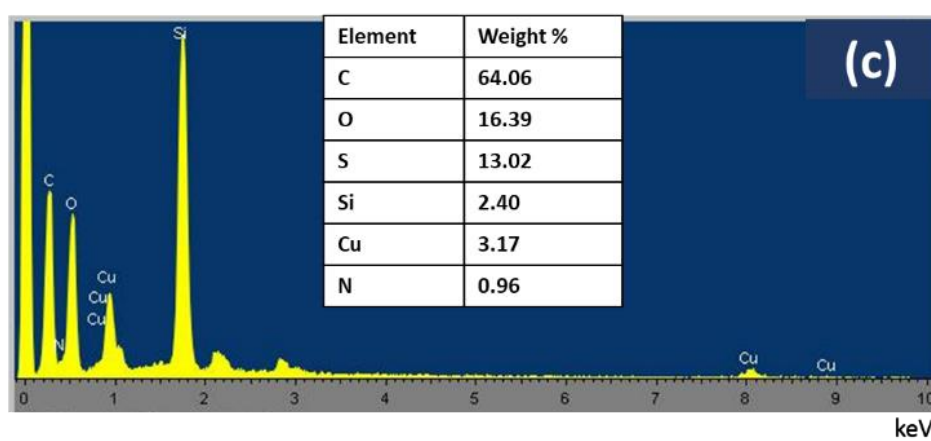
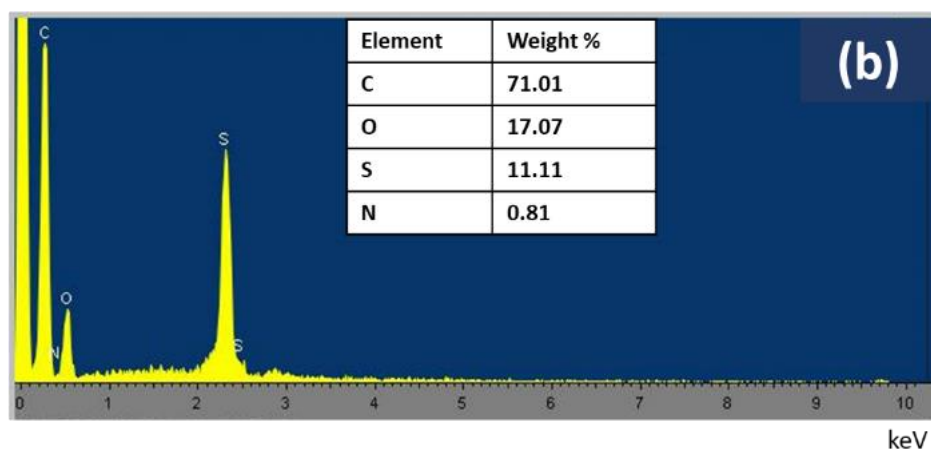
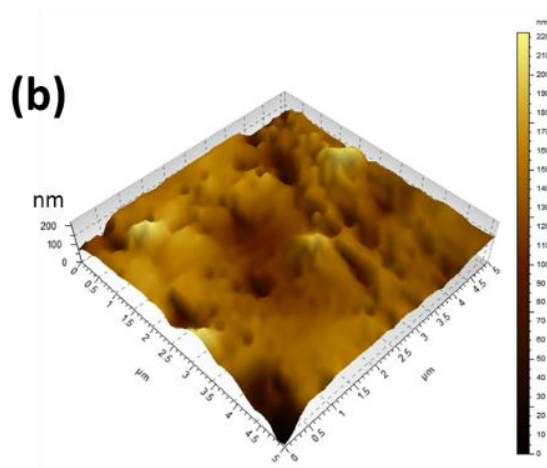
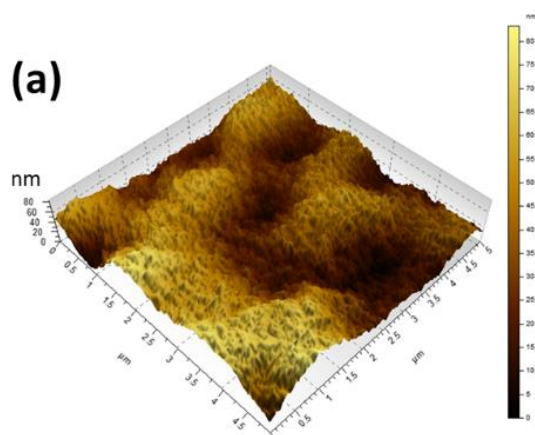


Figure 5-14: EDS elemental spectrum of (a) bare PES, (b) PES-g-P(NIPAm-co-AAm), and (c) CuO@PES-g-P(NIPAm-co-AAm). (d) EDS mapping analysis of CuO@PES-g-P(NIPAm-co-AAm) containing different elements of carbon, oxygen, copper, silicon, nitrogen and sulfur.

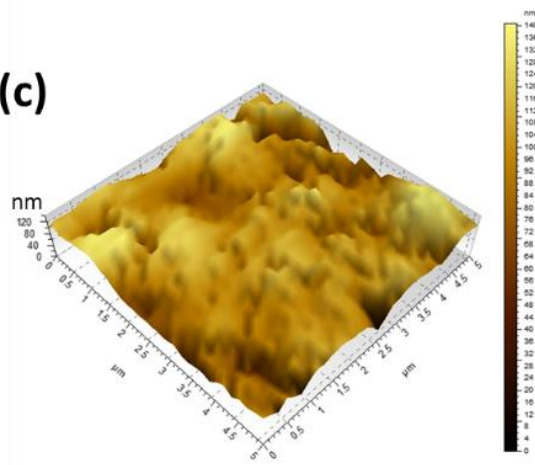
5.1.2.3. Surface roughness of the functionalized PES membranes functionalized with acrylamide and copper oxide nanoparticles

Various studies have indicated that the process of bacterial adhesion and accumulation is complex and can be influenced by several factors, including surface roughness. It has been found that a larger surface in rougher surfaces provide sufficient room for bacteria to attach and accumulate, thereby promoting bacterial accumulation [299]. In the case of PES membranes, the roughness data revealed that the surface functionalization with thermo-responsive polymers (such as PNIPAm and P(NIPAm-co-AAm)) and CuO nanoparticles led to a slight increase in surface roughness. Specifically, the root mean squared (Sq) values deduced from the AFM images increased from 15.8 nm for bare PES to 23.8, 16.8, 26.3, 31.7, 16.4, and 36.2 nm for PES-g-PNIPAm, PES-g-P(NIPAm-co-AAm), CuO@PES-g-PNIPAm, CuO@PES-g-P(NIPAm-co-AAm), PES-g-AAm, and CuO@PES, respectively. The presence of CuO agglomerates on the surface may have contributed to the higher surface roughness observed in CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm) (see Figure 5-15). It is important to note that although the roughness was slightly increased, it still remained within the normal range for PES membrane surfaces [266]. Based on the measurements of contact angle and surface roughness, we believe that the reduction in contact angle is primarily due to a change in surface chemistry, rather than the influence of surface heterogeneity on wettability in this specific case study. This is due to the fact that the surface roughness of PES membrane was slightly affected after surface functionalization

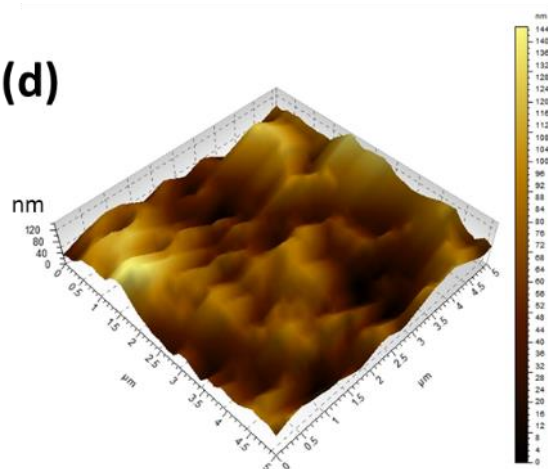
and the reported range for surface roughness is within reported values for bare PES membrane (~15-30 nm). These findings suggest that the alteration in surface chemistry plays a more significant role in determining the wettability behavior of the modified surface [300].



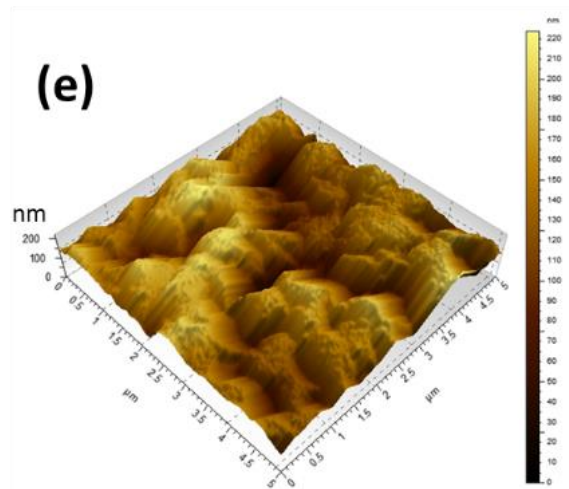
(c)



(d)



(e)



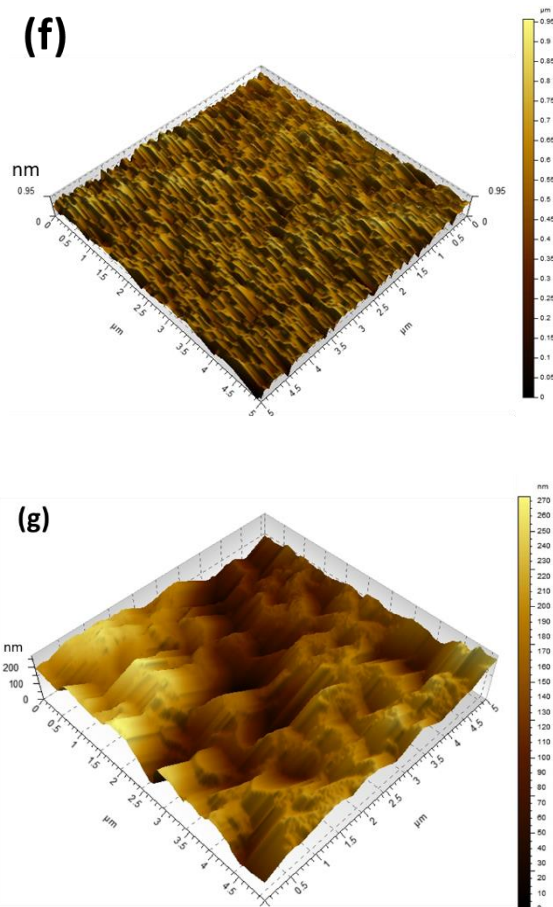


Figure 5-15: AFM images and surface roughness of bare and modified PES membranes. (a) bare PES, (b) PES-g-PNIPAm, (c) PES-g-P(NIPAm-co-AAm), (d) CuO@PES-g-PNIPAm, (e) CuO@PES-g-P(NIPAm-co-AAm), (f) PES-g-AAm, and (g) CuO@PES.

5.1.2.4. Surface hydrophilicity and surface charge of the functionalized PES membranes functionalized with acrylamide and copper oxide nanoparticles

In this section, for clearer visualization, each sample is represented in graphs using shorter names as follows: M_0 : bare PES; M_1 : PES-g-AAm; M_2 : PES-g-P(NIPAm-co-AAm); M_3 : CuO@PES; M_4 : CuO@PES-g-P(NIPAm-co-AAm), and M_5 : Cu@PES-g-PNIPAm.

- Surface hydrophilicity

Hydrophilicity is one of the critical factors that influence the permeation flux and antifouling properties of the membranes. In several studies it has been reported that, hydrophilic surface demonstrated the better antifouling properties and higher permeation fluxes [267]. In Figure 5-16(a), the contact angle measurements of bare and grafted membranes were taken at two different temperatures of 22 and 40°C. The bare PES membrane demonstrated the highest water contact angle ($59^\circ \pm 1.7$), which is consistent with the literature [268]. The contact angle gradually decreased to $46^\circ \pm 1.2$ and $42^\circ \pm 1$ with the grafting of AAm and P(NIPAm-co-AAm), respectively. The decline in water contact angle is due to the presence of hydrophilic functional groups on the membrane surface, imparted by polyacrylamide and hydrophilic part of PNIPAm polymer,[144], [269]. Moreover, introducing copper oxide nanoparticles further reduced the water contact angle compared to the bare membrane. At a temperature of 22 °C, the water contact angle for CuO@PES (M₃) and CuO@ PES-g-P(NIPAm-co-AAm) (M₄) were measured to be 35° and 34°, respectively. The CuO is hydrophilic and responsible for significantly enhancing the hydrophilicity of the membranes along with the APTES [301]. It is worth mentioning that the increase in surface roughness is minor for these samples compared to the substantial increase in surface hydrophilicity. The dynamic contact angle measurements reveal a notable change in contact angle that cannot be adequately explained by a mere alteration in surface roughness. Therefore, we can state that the enhancement in hydrophilicity is primarily a result of modification with various hydrophilic agents.

The PNIPAm-grafted membrane's thermo-responsive behavior can be analyzed by measuring water contact angle at temperatures above and below the lower critical solution temperature (LCST) of PNIPAm. In the case of M₂ and M₄, where PNIPAm is present in the modified membrane

structure, increasing the temperature above LCST (40°C) leads to an enhancement in the water contact angle. The contact angle increased from 42° to 58° for M₂, from 34° to 40° for M₄, and 37.9° to 47.2° for M₅. It indicates the phase transition behavior of PNIPAm with the change of temperature, which assists in controlling the fouling of the membranes. The increase in the contact angle can be attributed to the transformation of PNIPAm chains from a coil structure to a globular form, exposing hydrophobic isopropyl groups on the membrane surface [180], [270].

- Dynamic contact angle

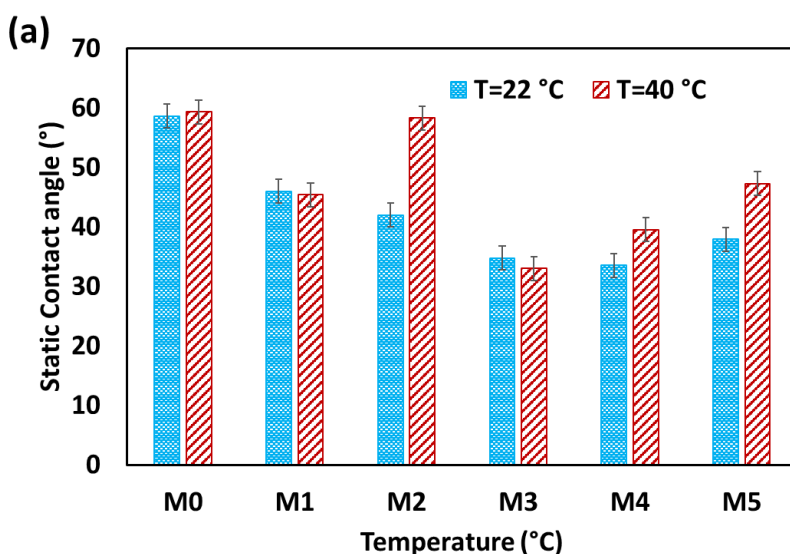
Dynamic contact angle measurements were conducted in an aqueous solution to investigate further the influence of temperature on the surface properties of pristine and grafted PES membranes. The behavior of the grafted membranes was entirely different from the PES membranes with the temperature changes. The analysis (Figure 5-16(b)), show that the receding water contact angle on the membrane surfaces without PNIPAm (M₀, M₁, M₃) remained constant across different temperatures due to the absence of thermal responsive moieties. On the other hand, surfaces grafted with PNIPAm exhibited distinctive thermal response characteristics consistent with the findings of static water contact angle measurements. At temperatures below 33°C, the receding contact angle for M₂, M₄, M₅ and was 13°, 10°, 11°, respectively. However, when the temperature exceeded 40°C, it increased to 28°, 21°, and 19°, respectively. A significant and sudden shift in surface wettability was observed in the temperature range of 33°C to 37°C, which reveals the LCST point of PNIPAm on the membrane surface. Below the LCST, the grafted PNIPAm layer absorbed water and swelled, allowing water to spread over the substrate surface, which decreased the contact angle of the surface. Above the LCST, the PNIPAm layer shrank and became more hydrophobic, preventing water from spreading over the surface and increasing

surface contact angle[7]. Comparing the dynamic contact angle change between PES-g-P(NIPAm-co-AAm) and PES-g-15%PNIPAm (13° to 27° vs. 14° to 36°), it is evident that the inclusion of AAm has an impact on the degree of hydrophilicity difference. This influence can be attributed to the effect of the molecular structure and conformation of PNIPAm after copolymerization with AAm. AAm has the potential to introduce more hydrogen bonds between polymer chains and water molecules, thereby enhancing the stabilization of the coil state of PNIPAm. Additionally, AAm can mitigate hydrophobic interactions between the isopropyl groups of PNIPAm, which play a role in the globule formation and aggregation of PNIPAm [274]. Hence, it can be concluded that the copolymerization of AAm in the PNIPAm structure affects its phase transition behavior. It is worth noting that gauging the degree of swelling for the grafted polymer on the membrane surface presents considerable challenges, given the potential for polymer hysteresis, dispersion, or aggregation during the phase transition. Therefore, it is challenging to measure the degree of swelling for PNIPAm accurately and reliably.

- Surface charge

The surface charge plays a critical role in deciding the antifouling behavior of the membranes. The Zeta potential of the pristine and grafted PES membranes is shown in Figure 5-16(c). The zeta potential of the copper oxide-functionalized membranes revealed an increase in negative charge at pH 7 and 10, and amazingly it was slightly positive at pH 2, whereas the rest of the membranes at pH 2 have demonstrated a negative zeta potential. The reason for appearing the +ve zeta potential of the M₃ and M₄ membranes at pH 2 is due to the functionalization of the copper oxide with APTES; the APTES contains the amine group, which is protonated at lower pH and results in the +ve zeta potential. However, in other membranes, M₀, M₁, and M₃, no such free amines are

present which can be protonated, and none of these membranes appear +ve at lower pH. The surface charge of the M₃, and M₄ membranes appeared more -ve compared to M₀ membrane at basic pH 10; the zeta potential of the M₀ membrane was observed as -44.1 eV and reached up to -59.3 eV and -56.1 eV for M₃ and M₄, respectively. As discussed the M₃ and M₄ membranes at lower pH get protonated, and as the pH increases, it may result in the deprotonation of the CuO containing membrane surface, resulting in a higher negative charge on the surface [8], [302]. In contrast, the samples that were grafted with both AAm (M₁) and P(NIPAm-co-AAm) (M₂) exhibited a different pattern of zeta potential. The negative surface charge density was decreased from -44.1 eV (M₀) to -40.9 eV (M₁) and -41.3 eV (M₂) after grafting with AAm and P(NIPAm-co-AAm). These finding suggest that the presence of electroneutral PNIPAm and non-ionic PAAm chains could potentially reduce the negative charge on the membrane surface [180] [303].



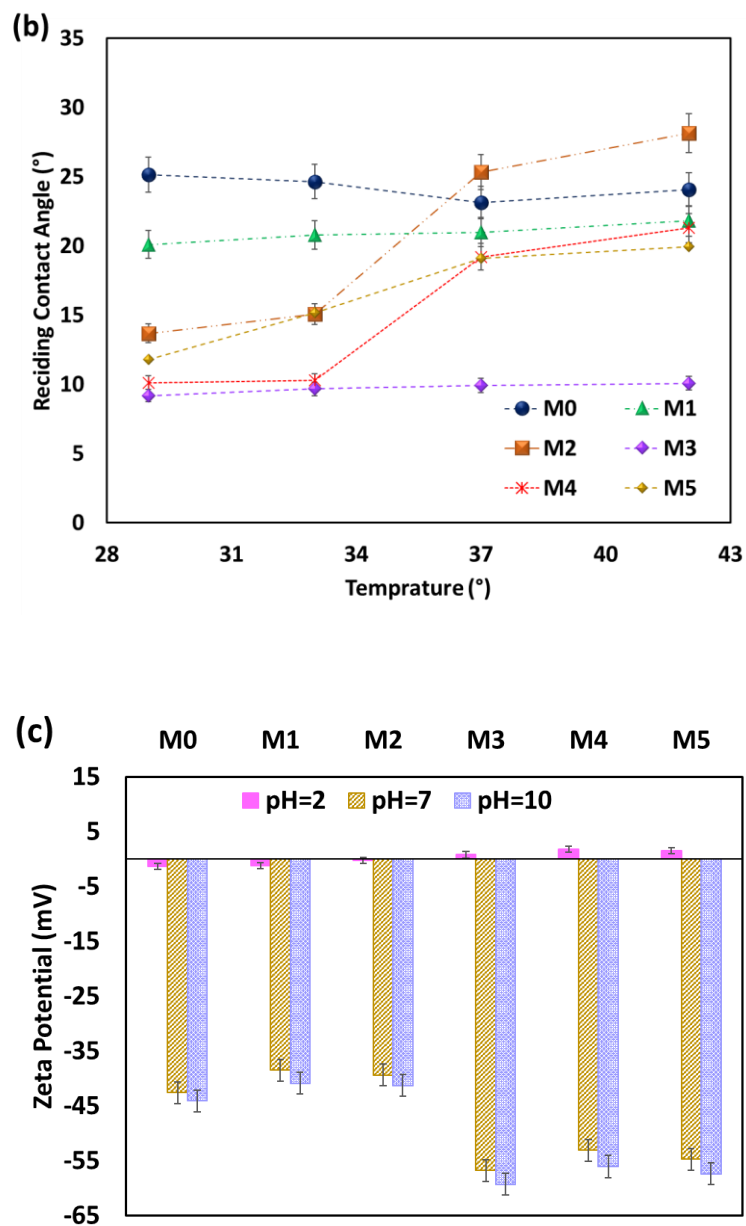


Figure 5-16: (a) Static water contact angles at temperatures of 22 and 40 °C, (b) effect of membrane's surface modification on the receding contact angle, (c) zeta potential of different membranes at pH=2, pH=7, and pH=10. M₀: bare PES; M₁: PES-g-AAm; M₂: PES-g-P(NIPAm-co-AAm); M₃: CuO@PES; M₄: CuO@PES-g-P(NIPAm-co-AAm), and M₅: Cu@PES-g-PNIPAm.

The summary of surface modification and alterations in surface properties is provided in Table 5-1.

Table 5-1: summary of surface modification and alterations in surface properties

Membrane	Static Contact Angle		Receding Contact Angle		Surface Charge			Surface Roughness
	22°C	40°C	29°C	45°C	pH=2	pH=7	pH=10	
Bare PES	59	59	25.1	25.9	-1.39	-42.6	-44.1	15.8
PES-g-5% PNIPAm	49	63	21.1	28.9	-0.319	-40.1	-41.9	21.8
PES-g-15% PNIPAm	46	66	14.1	36.1	-0.276	-39.6	-40.7	22.1
PES-g-25% PNIPAm	41	69	12.0	37.0	2.82	-39.1	-40.3	24.2
PES-g-AAm	46	45	20.0	21.6	-1.21	-38.5	-40.9	16.4
CuO@PES	35	33	9.1	10.6	0.759	-56.8	-59.3	32.3
CuO@PES-g-PNIPAm	38	47	11.7	20.0	1.47	-54.76	-57.4	26.3
PES-g-P(NIPAm-co-AAm)	42	58	13.6	27.6	-0.317	-39.4	-41.3	16.8
CuO@PES-g-P(NIPAm-co-AAm)	34	40	10.1	21.2	1.81	-53.1	-56.1	31.7

5.1.2.5. Effect of copper oxide concentration on PES membrane

To investigate the impact of copper oxide nanoparticles on the PES membrane surface, four distinct samples were prepared with concentrations of 1 wt.%, 2 wt.%, 5 wt.%, and 8 wt.% CuO. The preparation of these samples involved varying reaction conditions, including reaction time and CuO concentration, as detailed in Table 5-2. The outcomes indicate that an increase in both reaction time and CuO concentration leads to an increased amount of copper nanoparticles on

the surface of the PES membrane. We observed that when employing 0.005 g of CuO in the solution, even after a 6-hour reaction time, the weight percentage of CuO on the PES membrane is approximately 1 wt%. Interestingly, an increase in the amount of CuO in the solution from 0.005 to 0.02 g, even at a shorter reaction time of 2 hours compared to 6 hours, resulted in an increase in the weight percentage of CuO on the membrane surface from 1 wt% to 2 wt%. This suggests the importance of both the quantity of CuO and the reaction time in influencing the surface composition.

Furthermore, the results obtained from SEM imaging reveal a noteworthy observation (Figure 5-17). At higher concentrations of copper oxide nanoparticles, the membrane surface covered with higher metal nanoparticles concentration. This outcome deviates from the intended objective of the investigation, which is to solely modify the surface properties without altering the surface morphology or structure.

Table 5-2: Reaction conditions to achieve variable concentration of the CuO concentrations

Reaction time (h)	CuO amount in the reaction solution	Actual weight percentage of CuO on the surface
6	0.005 g	1 ± 0.1 wt.%
2	0.02 g	2 ± 0.3 wt.%
6	0.02 g	5 ± 0.2 wt.%
2	0.04 g	8 ± 0.4 wt.%

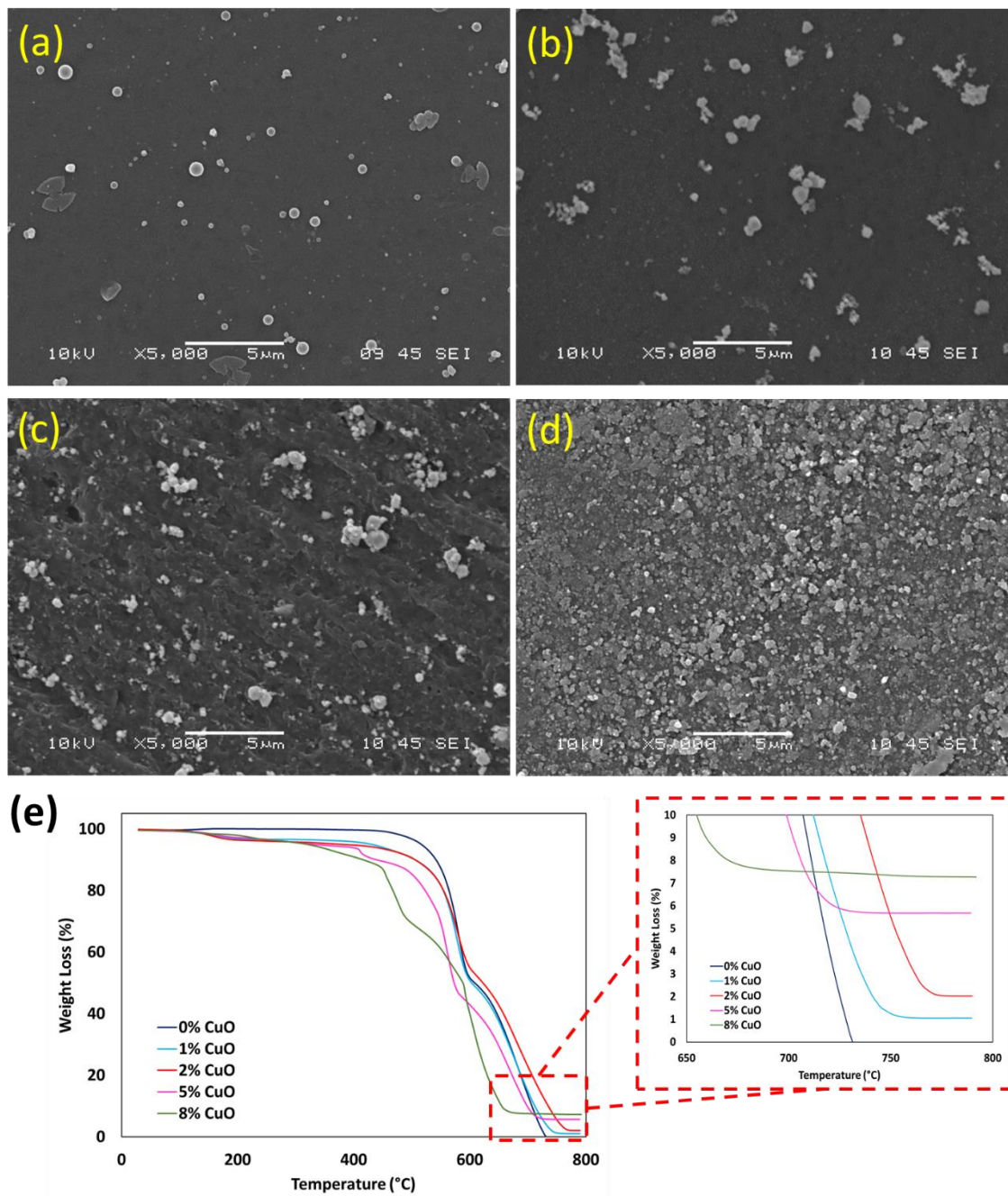


Figure 5-17: SEM image of PES-g-P(NIPAm-co-AAm) membrane functionalized with (a) 1 wt. %, (b) 2 wt. %, (c) 5 wt. %, and (d) 8 wt. % copper oxide nanoparticles. (e) Thermogravimetric analysis PES-g-P(NIPAm-co-AAm) membrane functionalized with 1 wt. %, 2 wt. %, 5 wt. %, and 8 wt. % copper oxide nanoparticles.

5.1.2.6. The effect of copper concentration on PES membrane surface roughness and water contact angle

Atomic force microscopy (AFM) was employed to investigate the surface roughness of membranes with bare PES, 1 wt.% CuO, and 8 wt.% CuO. In Figure 5-18(d), two-dimensional surface AFM images are presented with a scan size of $20\ \mu\text{m} \times 20\ \mu\text{m}$. The increase in the weight percentage of CuO nanoparticles on the surface resulted in higher surface roughness, measured as 78.2 nm for bare PES, 83.1 nm for 1 wt.% CuO, and 101.4 nm for 8 wt.% CuO. This increase in surface roughness suggests that the presence of copper oxide nanoparticles contributes to a more heterogeneous morphology, enhancing the overall roughness of the membrane surface.

In Figure 5-18(d), contact angle measurements were conducted on membranes functionalized with 1, 2, 5, and 8 wt.% CuO at two different temperatures, 22 and 40°C. The membrane with 1 wt.% CuO exhibited the highest water contact angle ($38^\circ \pm 0.9$). As the CuO percentage increased, the contact angle gradually decreased to $34^\circ \pm 1.3$, $23^\circ \pm 0.8$, and $14^\circ \pm 1.1$ for 2, 5, and 8 wt.% CuO, respectively. This decline in water contact angle can be attributed to the presence of hydrophilic CuO and APTES groups on the membrane surface.

Additionally, the results revealed that with an increase in CuO concentration on the surface, the change in contact angle with temperature alteration diminished. While the sample with 1 wt.% showed an increase in contact angle at a higher temperature ($38^\circ \pm 0.9$ vs. $49^\circ \pm 1.4$), the sample with 8 wt.% CuO demonstrated almost no change in surface contact angle ($\sim 14^\circ$). This observation indicates that the coverage of the surface with CuO nanoparticles significantly impacts the PNIPAm phase transition behavior, likely by reducing the water-PNIPAM interactions.

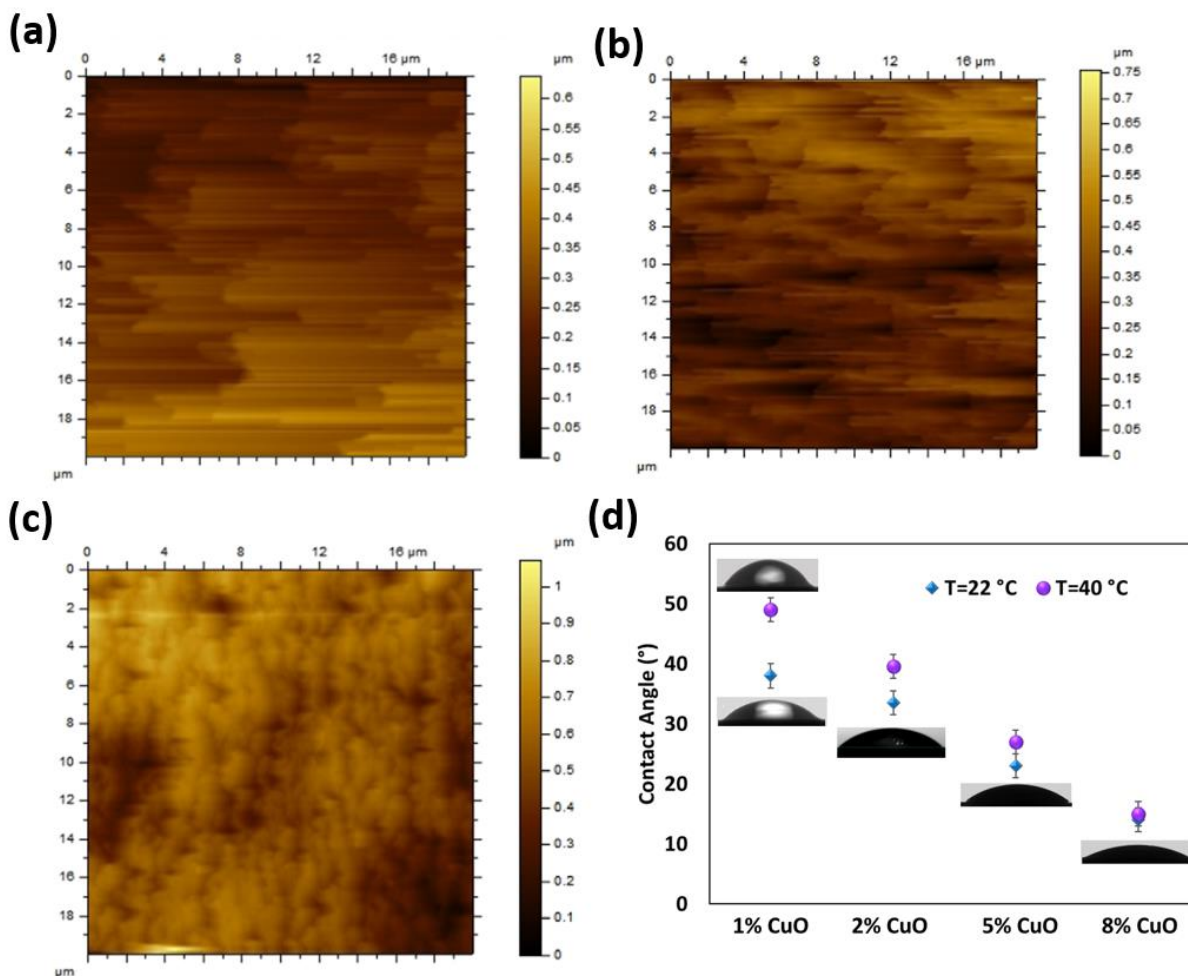


Figure 5-18: AFM images and surface roughness of bare and modified PES membranes. (a) bare PES, (b) 1% CuO, (c) 8% CuO. (d) Static water contact angles at temperatures of 22 and 40 °C.

5.2. Membrane fouling behavior

5.2.1. Effect of grafting yield on antifouling performance of PNIPAm-grafted membranes

The impact of grafting yield on the permeability of PES membranes were evaluated using cross-flow filtration system and depicted in Figure 5-19(a). The flux of pure water (J_{w1}) and BSA solution (J_p) was monitored during a 300-minute filtration process. Afterward, the membranes were subjected to 60-minutes of washing cycle with cold and warm water, and then again pure water

flux (J_{w2}) of the membranes were measured to assess the permeability and fouling resistance of the PNIPAN-grafted PES membranes [304], [305]. To determine its reusability, the membrane was subjected to five runs of 150-minute fouling test. To evaluate the antifouling performance, we conducted tests on three separate samples, and the reported results represent the average values obtained from these three samples. This approach ensures a more robust and reliable assessment, taking into account any potential variations between individual samples. It is important to note that our initial experiments were conducted using a 1000 ppm BSA solution (the results provided in Table 5-4 for comparison). Although we observed significantly high antifouling performance, we decided to shift our focus to a 500 ppm BSA solution. This adjustment is aimed at enhancing the relevance and reliability of the fouling study, as using a 500 ppm BSA solution is deemed more realistic. The lower concentration is preferred because using a 1000 ppm BSA solution could lead to severe, irreversible fouling and potential surface saturation on the membrane. This may not accurately represent the actual operating conditions of the membrane. Utilizing the lower concentration helps mitigate these issues, providing a more controlled and realistic experimental setup for evaluating antifouling properties.

The flux of pure water through the bare PES membrane was 68.3 L/m²·h, whereas the flux through the membrane with 5% PNIPAm grafting yield was slightly higher, at 73.1 L/m²·h. This improvement was mainly due to increased hydrophilicity of the membrane surface without significantly obstructing the pores of the PES membrane.

In a similar manner, as the PNIPAm grafting yield increased to 15% and 25%, the hydrophilicity of the modified PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes were also increased, leading to an increase in the flux rate to 78.4 and 80.0 L/m²·h, respectively. However, the PES-g-

25%PNIPAm membrane showed a minimal increase in the flux rate compared to the PES-g-15%PNIPAm membrane, which could be further attributed to clogging of the surface porosity as demonstrated in the SEM images. Furthermore, the impact of filtration time was evaluated, in which PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes showed a slower reduction rate in flux compared to the bare PES membrane, indicating lower foulant accumulation on the PNIPAm-grafted PES membrane surface.

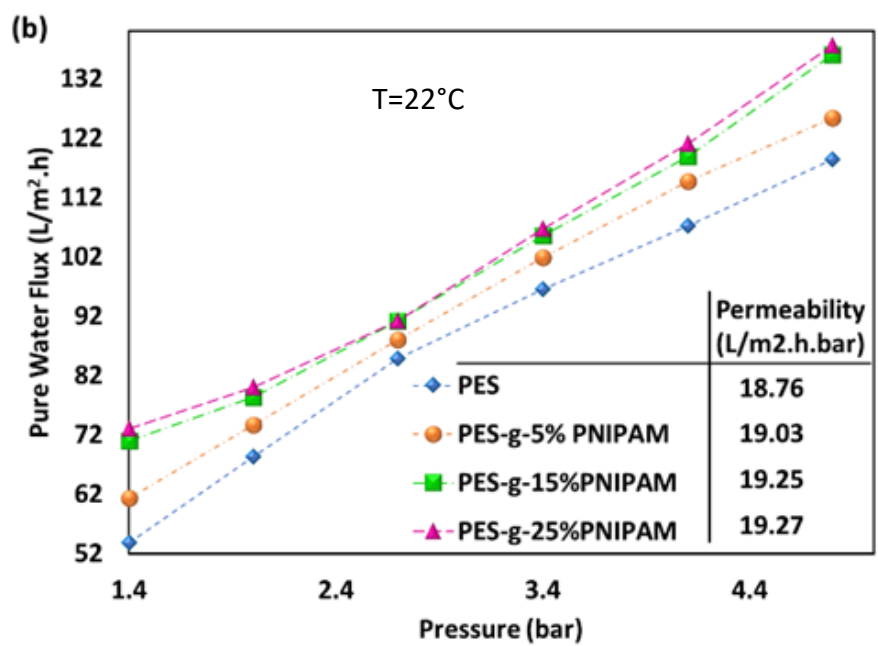
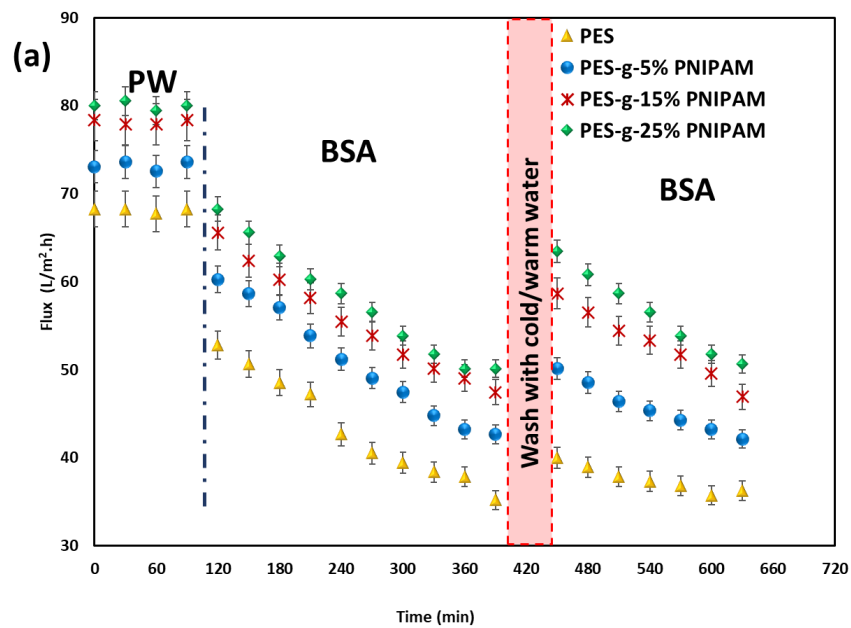
Figure 5-19(b) illustrates the effect of trans-membrane pressure on water permeation through the membranes. All the membranes exhibited a linear increase in pure water flux with increasing trans-membrane pressure, with the PES-g-25%PNIPAm membrane exhibiting the highest water flux (138 L/m².h at pressure of 4.8 bar). The water permeability was determined by calculating the slope of the trendline for each membrane. The results showed a slight increase in water permeability specifically, the water permeability was measured to be 18.76 ± 0.19 (L/m².h.bar) for the bare PES membrane and 19.27 ± 0.12 (L/m².h.bar) for the PES-g-25%PNIPAm membrane. When comparing the flux of water through membranes at 25°C and 45°C under the same operating pressures, it was observed that the flux is generally higher at the higher temperature regardless of the type of membrane tested. For the bare PES membrane, this increase in flux is due to a reduction in liquid viscosity coefficient as temperature increases, which can be explained by Equation (5-1) [306], [307].

$$J = \frac{n\pi d^4 P}{128 \eta l} \quad (5-1)$$

where J is the water flux, n is the number of pores per unit area, d is the effective pore size, P is the trans-membrane pressure, η is the viscosity of the flowing liquid (water viscosity at 22°C and 45 °C is 0.95 cp and 0.59 cp, respectively), and l is the membrane thickness. This equation shows

that, when other parameters remain constant, water flux is inversely proportional to liquid viscosity in which by increasing temperature from 22°C to 45°C the flux rate increases by 62%. To evaluate the temperature-related changes that occur solely due to the thermo-responsive nature of the membrane, the flux rate must be adjusted by multiplying the obtained values with the relative viscosity of water at the specified temperatures [308].

In contrast to bare PES membranes, PNIPAm-grafted membranes demonstrate a slightly greater increase in corrected flux rate at temperatures above the LCST. Specifically, while the increase in corrected flux with temperature was negligible for the bare membrane, it was approximately 9% for PES-g-25%PNIPAm membrane. This can be explained by the fact that, as temperature approaches PNIPAm's LCST, isopropyl groups in the PNIPAm chains begin to dehydrate and cause the chains to collapse, increasing the effective diameter and transmembrane flux. In other words, at the environmental temperature of 45°C, PNIPAm grafted in the membrane pores is in a shrunken state, which causes the membrane pores to be in an "open" state and have larger effective sizes [306], [309]. This phenomenon is illustrated in Figure 5-19 (c). It is worth noting that during the grafting processes, nano-sized monomers have the capability of attaching to the membrane surface and pores in the form of small chains. These may not be readily observable or quantifiable in SEM. Consequently, determining the exact amount of PNIPAM chains in the pores proves challenging. Nevertheless, even in low amounts, these chains can exert a subtle influence on certain properties.



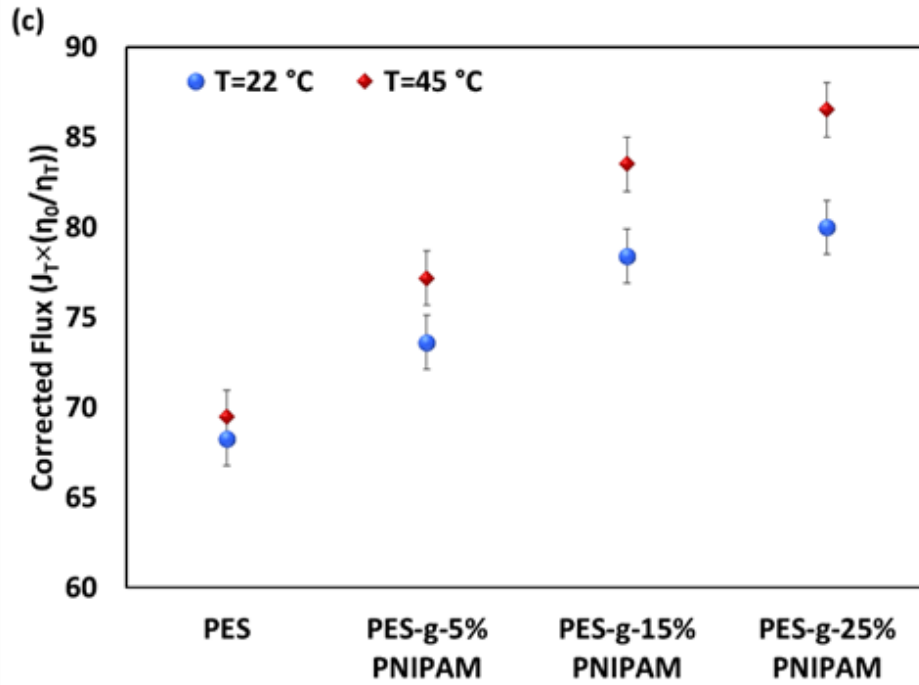


Figure 5-19: (a) Effect of grafting yield on membrane fouling resistance. (b) Pure water flux rate as a function of trans-membrane pressure. (c) Corrected pure water flux rate as a function of temperature.

Grafting PNIPAm onto the surface of the PES membrane can help mitigate fouling, but it may not entirely eliminate it during the filtration process. Therefore, it is crucial for the membranes to have the ability to regenerate for long-term filtration operations. After a 300-minute filtration of BSA, the membrane was cleaned using DI water at varying temperatures (20°C to 45°C). The membrane was then used for another round of filtration and the pure water and BSA flux rates were measured.

The results showed that the flux recovery ratio (FRR) of the PNIPAm-grafted PES membranes was greatly impacted by the grafting yield (refer to Figure 5-20(a)). The FRR of PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes (with 15% and 25% PNIPAm grafting yield) was higher compared

to that of the bare PES membrane and PES-g-5%PNIPAm membrane (with 5% PNIPAm grafting yield). This can be attributed to the hydrophilic nature of the PNIPAm-grafted PES membranes, at high grafting yield, which forms a hydration layer on the membrane surface, reducing the interaction between BSA and PES. As a result, BSA fouling can be removed more easily from the PNIPAm-grafted PES membranes during cleaning, compared to the bare PES membrane. Elevating the temperature can improve the mass transfer process and loosen the fouling layer on the membrane surface [178]. The highest FRR was approximately 97%, as obtained using PES-g-25%PNIPAm membrane (with 25% PNIPAm grafting yield).

During the membrane filtration and cleaning, the swelling of PNIPAm chains creates a hydration layer on the surface of the membrane. After filtration, BSA adsorption and deposition cause fouling of the membrane. In the washing process, raising the temperature of the solution to 45°C and agitating the fouled membrane solution leads to shrinkage of the PNIPAm chains. This process results in the release of H₂O molecules that interact with the membrane surface via hydrogen bonds, leading to a reduction in BSA adsorption. The agitation creates mechanical movements of H₂O that facilitate damaging the fouling layer. Lowering the temperature to 20°C causes the PNIPAm chains to swell again, reabsorbing H₂O and repelling BSA from the membrane surface and consequently breaking up the fouling layer [179], [310]. A higher PNIPAm grafting yield can result in greater removal of fouling material and flux recovery ratio as shown in Figure 5-20.

The resistance of bare PES and PNIPAm-grafted PES membranes to fouling was analyzed by determining the total fouling ratio (R_t), reversible (R_r), and irreversible (R_{ir}) fouling ratios using Equations 5-7. Based on the results, a more effective membrane for removing foulants would be

indicated by a lower R_t value and a higher R_r value. As shown in Figure 5-20(b), after 300 minutes of filtration with BSA solution, the total fouling ratio decreased from 48.4% for the bare PES membrane to 37.3% for the PES-g-25%PNIPAm membrane (with 25% PNIPAm grafting yield). Despite the small difference in total fouling ratio between the bare and modified membranes ($\sim 11.1\%$), the difference in reversible fouling ratio was much greater. The R_r significantly increased from 10.9% for the bare membrane to 26.8%, 33.3%, and 34% for the PES-g-5%PNIPAm, PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes (with the PNIPAm grafting yield of 5%, 15%, and 25%), respectively. A high reversible fouling ratio suggests a weak bond between the membrane and BSA molecules, making it easier to wash away foulants through cleaning with cold and warm water. This is demonstrated by the reduction in irreversible fouling ratio. The results suggest that the grafting of PNIPAm onto the PES membrane increases the surface hydrophilicity, resulting in enhanced fouling resistance [311].

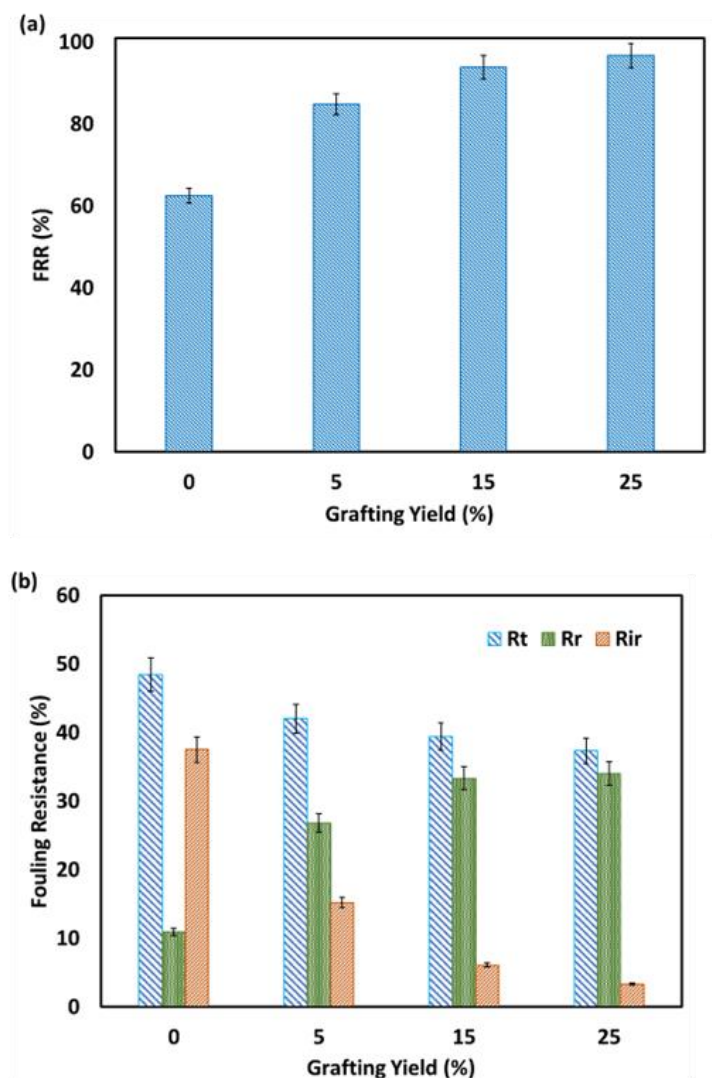


Figure 5-20: Results of the BSA fouling study, including (a) the flux recovery ratio and (b) the fouling resistance parameters (Rt, Rr, and Rir) of the bare PES and PNIPAm-grafted PES membranes.

5.2.2. PNIPAm fouling mitigation mechanism

The schematic diagram in Figure 5-21 shows the fouling and cleaning performance of PNIPAm-grafted PES membrane during the filtration test. During the fouling process, where the temperature of feed solution is below the lower critical solution temperature (LCST), PNIPAm chains are in the swollen state and make the membrane surface hydrophilic. On the contrary, washing the membrane using warm water ($T > \text{LCST}$) caused the PNIPAm chains to shrink thereby

making the membrane surface more hydrophobic [180], [312]. The phase transition behavior of PNIPAm can significantly affect the attachment and detachment of foulants on a membrane surface, ultimately impacting the cleaning performance of a modified membrane. To investigate this, we examined the fouling behavior of both bare PES and PNIPAm-grafted PES membranes after the cleaning process.

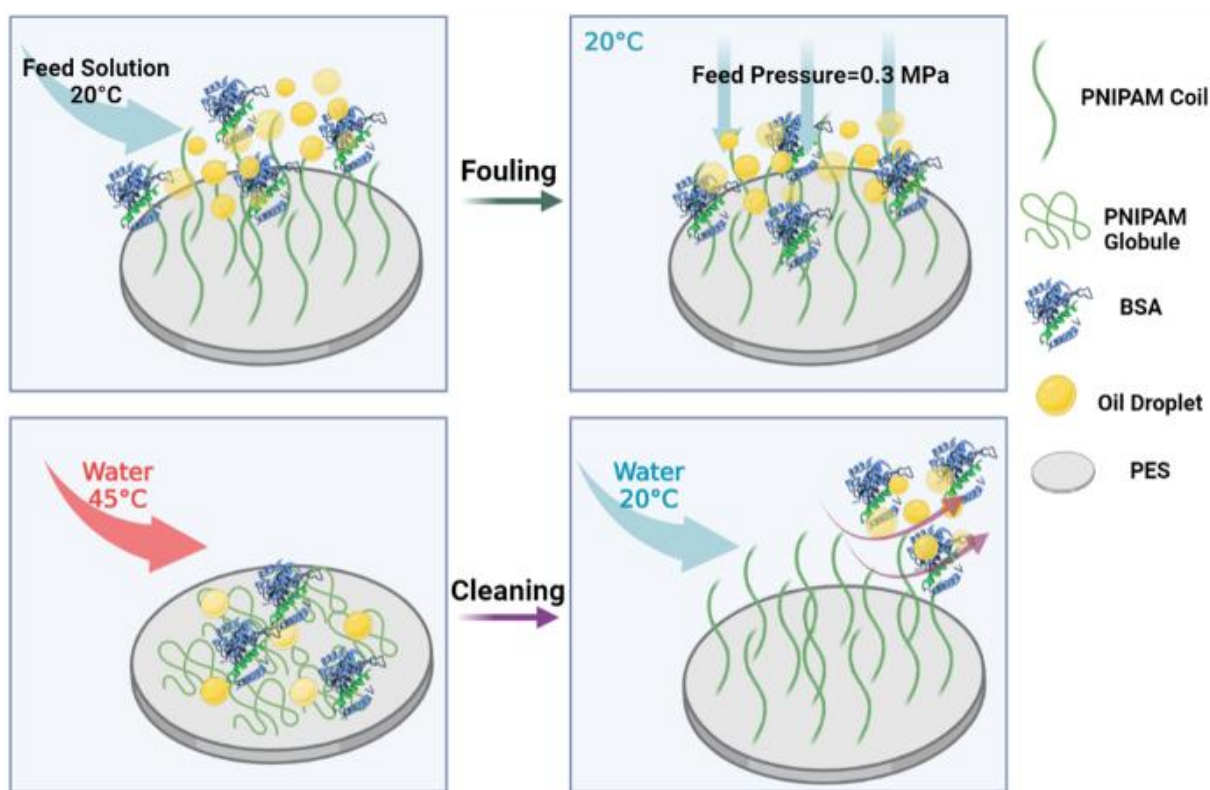


Figure 5-21 Schematic representation of thermo-response performance of PNIPAm-grafted PES membrane during filtration and cleaning experiments.

5.2.3. Effect of PES membranes functionalization with acrylamide and copper oxide nanoparticles on its antifouling behavior

In this section, for clearer visualization, each sample is represented in graphs using shorter names as follows: M_0 : bare PES; M_1 : PES-g-AAm; M_2 : PES-g-P(NIPAm-co-AAm); M_3 : CuO@PES; M_4 : CuO@PES-g-P(NIPAm-co-AAm), and M_5 : CuO@PES-g-PNIPAm.

The membrane's fouling has become a critical issue, and the operational cost of the membranes is significantly enhanced when the fouling is irreversible. The rational grafting and functionalization of the membranes can improve the membrane resistance to fouling and enhance the membrane's reversibility under a particular set of conditions. Figure 5-22(a) illustrates the analysis of the grafting impact on the permeability of PES membranes. The flux of pure water (J_{w1}), and BSA solution (500 ppm) as a foulant (J_p) was monitored until 300-minute of continuous filtration process under constant pressure of 0.3 MPa to assess the membrane's permeability and fouling resistance. Subsequently, the membrane underwent a 60-minute wash cycle with cold and warm water. After the cleaning process, the second pure water flux (J_{w2}) was measured. Additionally, another 150-minute fouling test was conducted to determine the membrane's reusability.

The bare PES membrane (M_0) had a pure water flux of $68.3 \text{ L/m}^2\cdot\text{h}$. In comparison with the bare membrane, the functionalized membranes PES-g-AAm (M_1), PES-g-P(NIPAm-co-AAm) (M_2), CuO@PES (M_3), CuO@PES-g-P(NIPAm-co-AAm) (M_4), and CuO@PES-g-PNIPAm (M_5) exhibited improved water permeation fluxes of 74.1, 78.9, and 71.5, 77.9, and $74.7 \text{ L/m}^2\cdot\text{h}$, respectively. This enhancement was mainly attributed to the increased hydrophilicity of all the modified membranes, as indicated before, without significantly obstructing the PES membrane's pores.

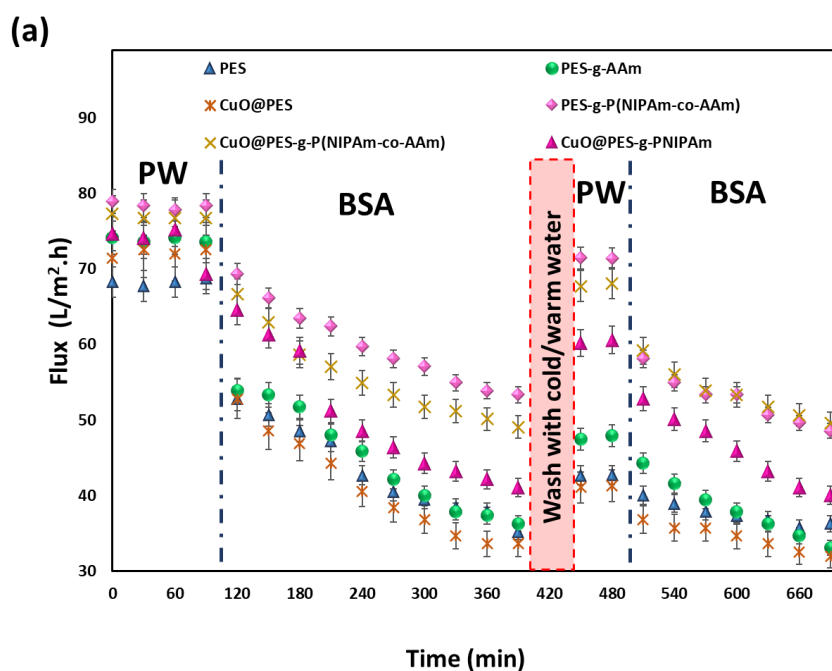
One of the primary reasons for utilizing thermo-responsive materials is to enhance the membrane's cleaning performance by using a simple washing procedure to regenerate the membrane for long-term filtration operations. Thus, after 300 minutes of BSA filtration, the membranes were cleaned using DI water at different temperatures (ranging from 20°C to 45°C). Subsequently, the membrane was used for another round of filtration, and the pure water and BSA flux rates were measured.

The results indicate that the presence of thermo-responsive polymer in the modified membrane significantly impacted the flux recovery ratio (FRR) of the membranes (see Figure 5-22 (b)). The FRR of M₂ and M₄, which contained PNIPAm, were higher than that of M₀, M₁, and M₃. This could be attributed to the phase transition behavior of the grafted PNIPAm. As discussed earlier, PNIPAm exists in a coiled shape at lower temperatures and is more hydrophilic, resulting in the formation of a hydration layer on the membrane surface that reduces the interaction between BSA and thermo-responsive polymer grafted PES membranes. As a result, BSA fouling can be more easily removed from the PNIPAm-grafted membranes during cleaning compared to those that do not contain PNIPAm. Elevating the temperature can improve the mass transfer process and loosen the fouling layer on the membrane surface [178]. The increase in temperature can weaken the fouling layer by increasing the foulant solubility, which can result in lower adsorption of BSA on the surface of membrane and higher foulant reversibility. The highest FRR was approximately 91% and 88% for M₂ and M₄ membranes, respectively. Additionally, it was observed that grafting polyacrylamide did not affect the cleaning performance of the membrane, as indicated by FRR value of 64% (62% for M₀ vs. 64% for M₂). However, surface functionalization with copper nanoparticles adversely affected the PES membrane cleaning performance, where the FRR

reduced from 62% for M_0 to 46% for M_3 . This could be due to the higher surface roughness of M_3 , (36.2 nm). Furthermore, BSA may interact with CuO nanoparticles, forming a complex that requires excess energy to detach the foulant from CuO@PES (M_3) membrane [313], [314].

The effectiveness of bare and modified membranes in fouling resistance was assessed by calculating the total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}) using Equations 4-6. A lower R_t value and a higher R_r value indicate a more efficient membrane resistant to foulant and easy to remove the foulants from its surface. As shown in Figure 5-22(c), membrane modification led to lower foulant accumulation on the membrane surface, where the total fouling ratio (R_t) for samples M_0 (bare membrane), M_2 and M_4 were 48.4%, 31.9% and 36.1%, respectively. More importantly, the reversible fouling ratio (R_r) increased significantly from 10.9% for the bare membrane to 23.13% for M_2 and 24.3% for M_4 . The weak adhesion between the membrane and BSA molecules allows for easier removal of foulants (i.e., BSA) from the surface through cleaning with cold and warm water. The decrease in irreversible fouling ratio further confirms the enhanced fouling resistance of the modified membranes due to the increased surface hydrophilicity resulting from the grafting of P(NIPAm-co-AAm) and incorporating CuO nanoparticles onto the membrane's surface [311]. In contrast, PES-g-AAm (M_1) and CuO@PES (M_3) exhibited lower fouling resistance than other modified membranes, with total fouling ratios of ~50% and 53%, respectively. This could be due to their higher surface roughness, which provides more accessible sites for foulants to attach. Additionally, the lack of phase transition behavior at different temperatures in these membranes results in lower cleaning efficiency and a lower reversible fouling ratio of ~15% for M_1 and ~10% for M_3 [315], [316].

Furthermore, Figure 5-22(d) depicts a schematic diagram that illustrates the fouling and cleaning performance of the PNIPAm-grafted membrane during the filtration test. During the fouling stage, when the feed solution temperature is below the lower critical solution temperature (LCST), PNIPAm chains swell, making the membrane surface hydrophilic. In contrast, using warm water ($T > \text{LCST}$) to wash the membrane causes the PNIPAm chains to shrink, resulting in a more hydrophobic membrane surface [14], [59]. The phase transition behavior of PNIPAm plays a crucial role in the attachment and detachment of foulants on a membrane surface, ultimately affecting the cleaning performance of a modified membrane [180], [312].



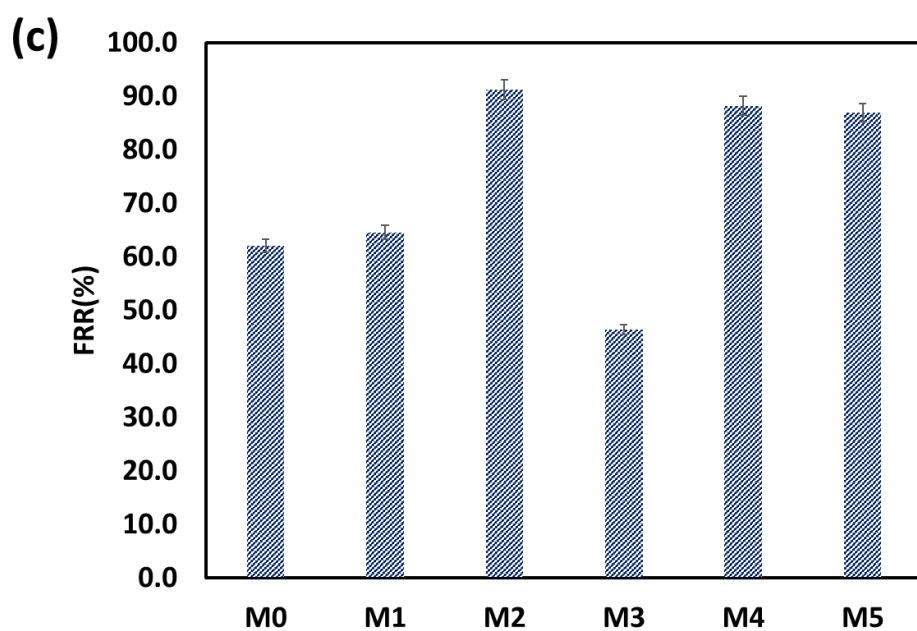
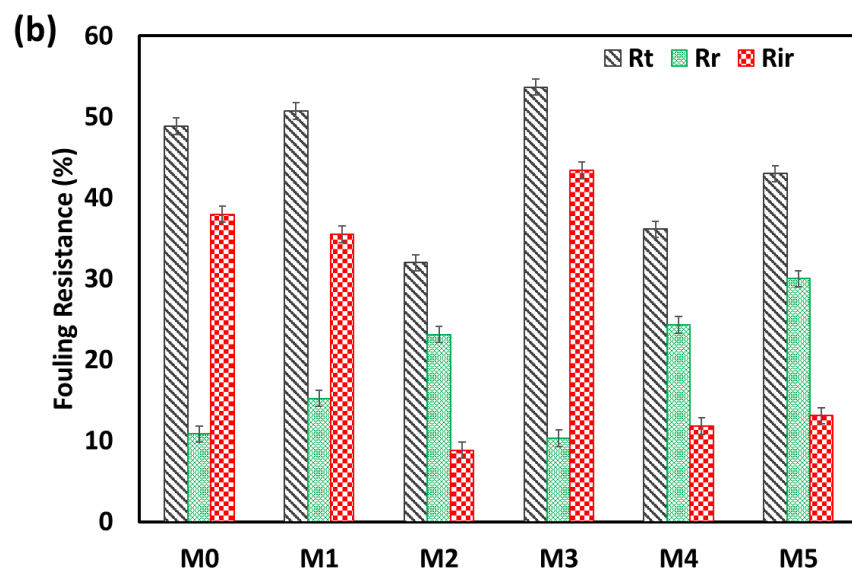


Figure 5-22: (a) Effect of surface modification on pure water and BSA solution flux rates and membrane fouling resistance. Filtration processes: (i) pure water was filtered until a steady flux rate was achieved; (ii) BSA was filtered for 300 minutes; (iii) The membrane was washed with cold (20°C) and hot (45°C) water for 60 minutes; (iv) pure water was filtered again to measure the second pure water flux rate; and (v) a second round of BSA filtration was

conducted to evaluate the membrane's reusability. (b) The flux recovery ratio, (c) the fouling resistance parameters (R_t , R_r , and R_{ir}) of the bare and modified membranes.

Summary of antifouling results for the bare and modified membranes in this study is provided in Table 5-3.

Table 5-3: Summary of antifouling results for the bare and modified membranes

Membrane	Water Flux L/m ² ·h	Flux recovery ratio (%)	Total fouling	Reversible fouling	Irreversible fouling
Bare PES	68.8±0.16	62.5	48.4	10.94	37.5
PES-g-5% PNIPAm	73.1±0.34	84.8	42.0	26.8	15.2
PES-g-15% PNIPAm	78.4±0.27	93.9	39.4	33.3	6.1
PES-g-25% PNIPAm	80.0±0.19	96.7	37.33	34.0	3.3
PES-g-AAm	74.1±0.45	64.5	50.7	15.2	35.5
CuO@PES	71.5±0.81	46.3	53.6	10.2	43.3
CuO@PES-g- PNIPAm	74.7±0.37	86.9	43.0	30.0	13.0
PES-g- P(NIPAm-co- AAm)	78.9±0.16	91.2	31.9	23.13	8.8
CuO@PES-g- P(NIPAm-co- AAm)	77.9±0.15	88.2	36.1	24.3	11.8

5.2.4. Comparing the antifouling performances of functionalized PES membranes with acrylamide and copper oxide nanoparticles with other modified PES membranes

The comparison of the antifouling performance of the designed thermo-responsive membranes with the previously reported PES membranes is shown in Table 5-4. Our comparative analysis reveals that our CuO@PES-g-P(NIPAm-co-AAm) membrane shows outstanding antifouling

performance in contrast to previous investigations. The findings in Table 5-4 demonstrate that surface functionalization is a viable approach to enhance membrane properties, especially to improve the flux recovery ratio.

The drawback of a PNIPAm grafted membrane with good performance at lower temperatures lies in its potential vulnerability to changes in weather conditions, particularly warmer temperatures. PNIPAm is a thermo-responsive polymer that exhibits a lower critical solution temperature (LCST) around 32°C. However, as the temperature rises above the LCST, PNIPAm becomes hydrophobic, leading to a collapse of the polymer chains. This transition may compromise the antifouling and separation performance of the membrane. In warmer weather, the membrane might lose its ability to resist fouling effectively, potentially resulting in reduced separation efficiency and increased susceptibility to fouling by contaminants.

Therefore, while PNIPAm grafted membranes demonstrate excellent performance in cooler conditions, their antifouling properties might be adversely affected as temperatures increase. Researchers and engineers need to consider these temperature-dependent characteristics when designing and implementing such membranes, taking into account the specific environmental conditions in which they will be used.

Table 5-4: Comparison of the antifouling performance of the CuO@PES-g-P(NIPAm-co-AAm) membranes with the previously reported functionalized PES membranes

Membrane	Grafting yield or weight ratio of antifoulant agent in blend	Feed Solution (ppm)	Feed Pressure (MPa)	Water Flux (L/m ² ·h ¹)	FRR (%)	Reference
PES/PDA/CuO/MPC	4 wt.% Blend	BSA (-)	0.24	106.4	64.5	[317]

0.1 wt% CuO/PES	0.1 wt% Blend	BSA (500)	0.3	673.9	59.2	[318]
SPDA/PES (SPM-2)	4 wt. % Blend	BSA (100)	0.2	515.8	75	[319]
Ni@MXene-PES(M ₄)	1 wt.% Blend	BSA (1000)	0.1	1181.1	64.6	[320]
PES-g-polyPEGMA	14%	BSA (1000)	0.1	163.3	90	[31]
HDT-2-Fe-5	0.9 wt.% Blend	Oil/water (1000)	0.1	682.48	92	[321]
(PES)/ SiO ₂ -g- (PDMAEMA-co- PDMAPS)	0.9 wt.% blend SiO ₂ -g- (PDMAEMA-co- PDMAPS)	Oil/Water (900)	0.1	64.10	84.26	[322]
PES/PDA/NMWCNTs	10 wt.% blend	Oil/Water (1000)	0.1	117	92.7	[323]
PES-g-SBMA	0.16 mg/cm ²	Oil/Water (3000)	0.15	771	87.5	[324]
CuO@PES-g- P(NIPAm-co-AAm)	15% grafting yield	BSA (1000)	0.3	90.7	85.4	This work
CuO@PES-g- P(NIPAm-co-AAm)	15% grafting yield	BSA (500)	0.3	90.7	88.1	This work
CuO@PES-g- P(NIPAm-co-AAm)	15% grafting yield	Oil/Water (1000)	0.3	90.7	88.1	This work

5.3. Membrane antibacterial performance

This section, aligned with our second objective, investigates the impact of surface functionalization on the PES membrane antibacterial performance. Through targeted surface functionalization involving acrylamide functional groups and copper oxide nanoparticles, we intend to enhance the antibacterial ability of the membrane utilizing a "kill and release" mechanism. This innovative approach holds promise for combating bacterial contamination and improving water quality.

5.3.1. Antibacterial properties of bare and dual-functionalized PES membranes

It is critical to discuss that the antibacterial activity of the pristine PES membranes is poor and its resistance to the feed containing the microorganisms such as bacteria is not strong enough to make them suitable for the wastewater streams. Therefore, in this work a significant effort has been made to improve the antibacterial efficacy of the PES membranes by grafting with strong antibacterial agents. The pristine PES and the surface grafted PES membranes antibacterial performance was assessed by exposing them to the model *E. coli* bacteria. The detail of antibacterial testing of the membranes using *E. coli* bacteria, discussed in the experimental section. In brief, first, a diluted *E. coli* cell suspension containing 10^4 cells/mL was spread on an agar plate, and then a membrane sample was placed on top of the inoculated plate. Following 24 hours of incubation at 37°C, the plate was examined for bacterial growth. The results in Figure 5-23 showed that the PES, PES-g-PNIPAm, and PES-g-P(NIPAm-co-AAm) membranes had no detectable antibacterial effects, as evidenced by the presence of *E. coli* colonies in the areas covered by these membranes. In contrast, the CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-

co-AAm) membranes demonstrated antibacterial properties, as evidenced by the absence of *E. coli* colonies in the areas covered by these membranes. Furthermore, a distinct inhibition zone was observed surrounding the edges of the CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm) membranes, where no *E. coli* colonies were present. This zone was not directly covered by the membrane disc, which further substantiates the antibacterial properties of the dual-functionalized membranes.

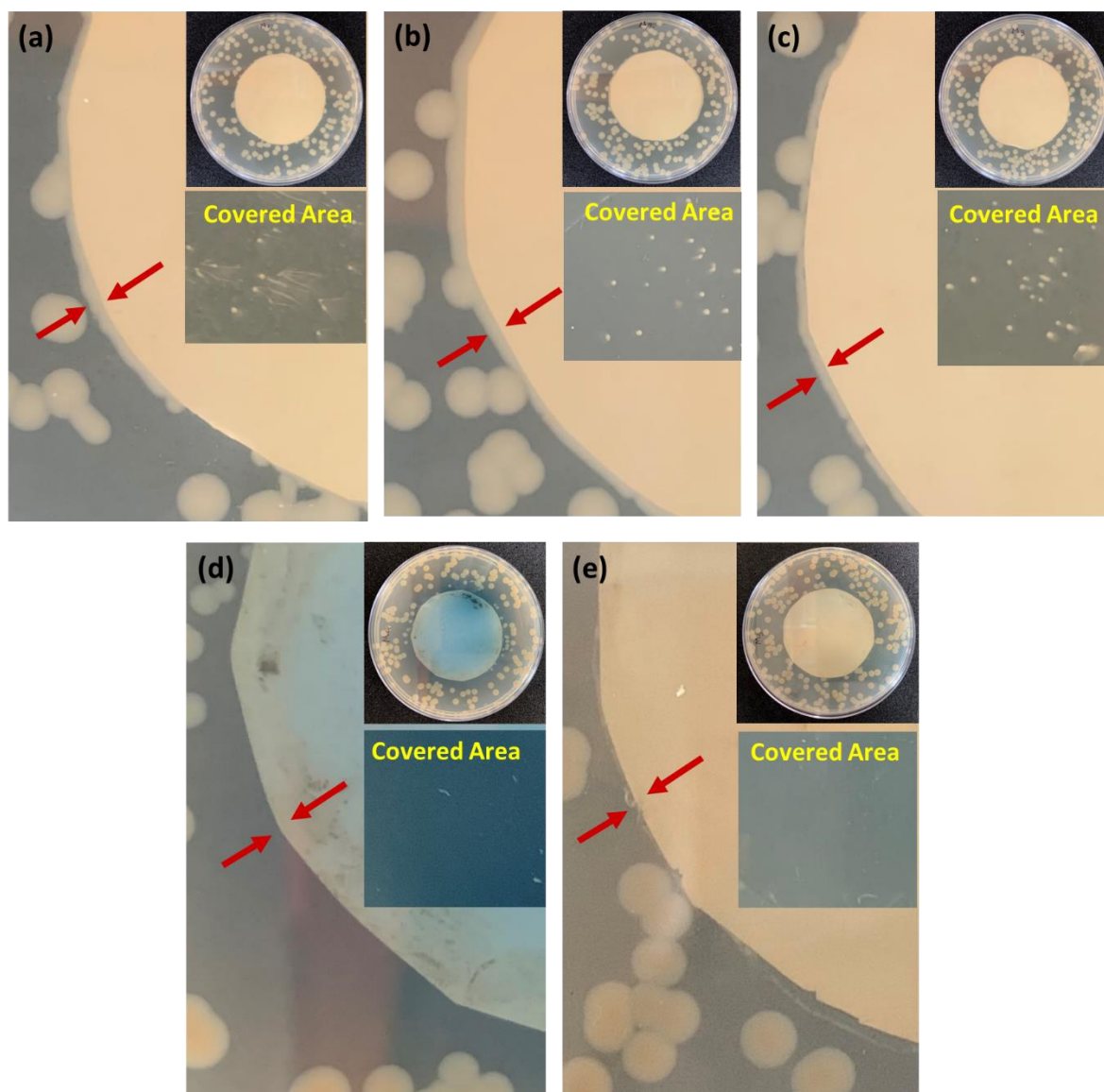


Figure 5-23: Photos showing inhibition zone and contact killing performance of (a) bare PES, (b) PES-g-PNIPAm, (c) PES-g-P(NIPAm-co-AAm), (d) CuO@PES-g-PNIPAm, and (e) CuO@PES-g-P(NIPAm-co-AAm). The membrane sample was positioned at the center of agar plates that were inoculated with *E. coli* bacteria and incubated at 37°C for 24 hours.

Figure 5-24 depicts the antibacterial efficacy of the bare membrane, grafted membranes (PES-g-PNIPAm and PES-g-P(NIPAm-co-AAm)) and the dual-functionalized membranes (CuO@PES-g-

PNIPAm and CuO@PES-g-P(NIPAm-co-AAm)), after 90 minutes of immersion in an *E. coli* suspension at 37°C. After the contact duration, the *E. coli* suspensions were serially diluted and cultured on agar plates. The results indicated that the suspension, which came into contact with the dual-functionalized membrane, did not yield any viable bacteria on the agar plates, suggesting that all the *E. coli* bacteria were killed during the contact time. However, the bare PES and grafted membranes (PES-g-PNIPAm and PES-g-P(NIPAm-co-AAm)) exhibited no antibacterial activity, implying that the antibacterial efficacy of PES, PNIPAm, and P(NIPAm-co-AAm) are not quite high, whereas the copper oxide loaded membranes (CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm)) demonstrated biocidal ability and toxicity for the microorganisms. The observations of this work are in agreement with the work of Pangilinan et al.[325], which reported the non-toxicity of PNIPAm brushes.

Literature reports revealed that copper and copper oxides have been commonly utilized as an antibacterial or biocidal agent. Copper can contribute to bacterial-killing processes through various mechanisms, including the production of hydroxyl radicals ($\text{OH}^\cdot$) via the Fenton and Haber-Weiss reactions. This is due to copper's high oxidation ability. [208] [209], (ii) oxidation of the sulfhydryl groups, such as cysteine in proteins or the cellular redox buffer glutathione, [210] and (iii) inactivation of the protein by damaging Fe-S clusters in proteins [211]. Fenton reaction is one of the well-known chemical redox reactions that occurs between Cu^{2+} and Cu^+ ions leading to the generation of reactive hydroxyl radicals ($\text{OH}^\cdot$). In addition to the Fenton reaction, copper ions can also catalyze the reduction of sulfhydryl bonds (bonds between sulfur and hydrogen atoms) and facilitate the formation of sulfinic and sulfonic acids [213], [215]. Furthermore, the released transition metal such as copper ion atom can bind to the bacteria DNA and react with

water molecules, resulting in the generation of hydroxyl radicals ($\text{OH}^\bullet$), which can directly cause damage to DNA [224], [225].

The results of the inhibition zone and contact killing analysis substantiate that our innovative dual-functionalized membrane has great potential as a biocidal/antibacterial surface. The rational grafting of the thermo-responsive polymer (PNIPAm or P(NIPAm-co-AAm)) and the CuO on the PES membranes work synergistically to enhance the antifouling characteristics of the membranes. From the antibacterial analysis of the various membranes, it has become clear that the CuO is playing critical role in killing of the bacteria and reducing the tendency of the formation of the biofilms. Apart from the inactivity of the PNIPAm, and P(NIPAm-co-AAm) grafted membranes against the bacterial which has shown that PNIPAm or P(NIPAm-co-AAm) have no significant role in it; however, the presence of the thermo-responsive polymeric brushes are highly effective in reducing the microorganism regeneration on the membrane by releasing the attached bacterial debris by switching the feed temperature. In order to understand the synergistic antibacterial and antifouling behavior of the thermo-responsive polymer along with the immobilized CuO nanoparticles the membrane study was performed by washing with hot (45°C) and cold (20°C) PBS solutions.

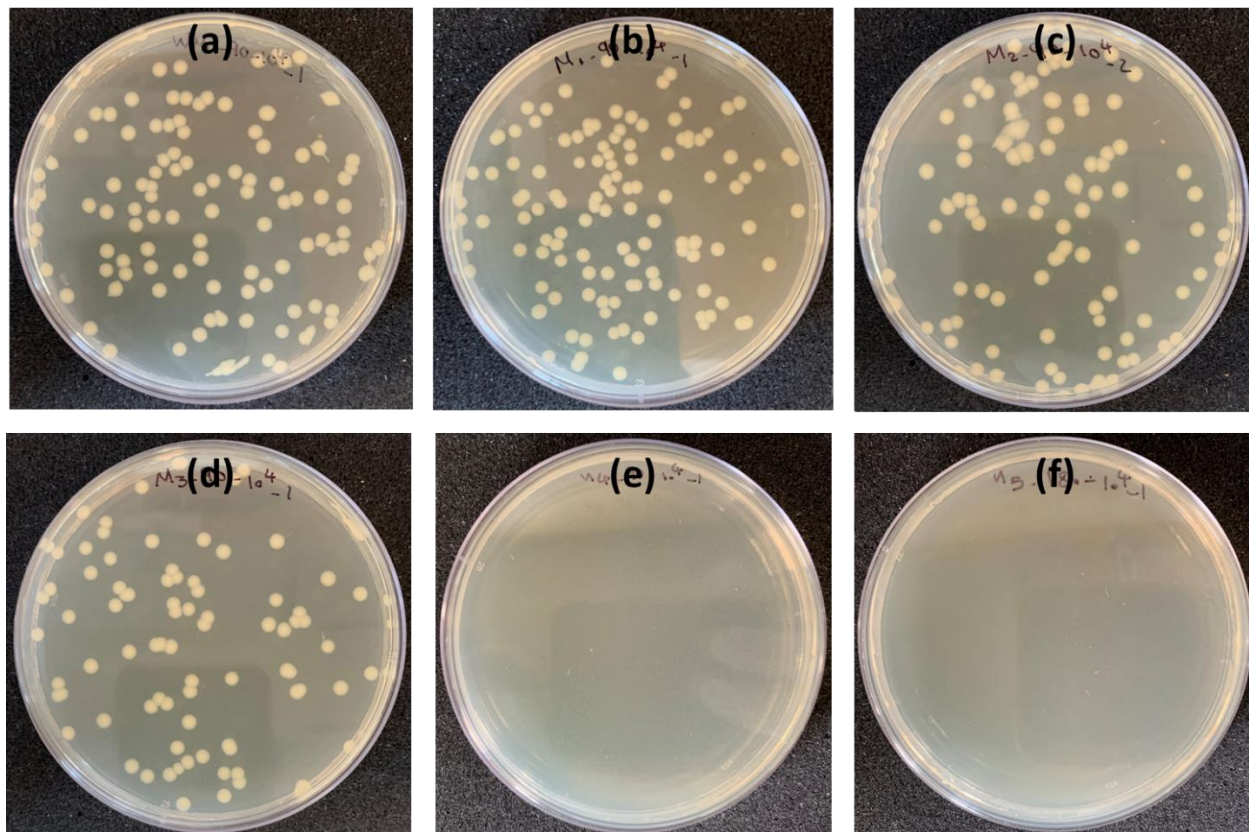


Figure 5-24: Bacterial killing results, plate count results of bacteria suspension in contact with (a) no membrane, (b) bare PES, (c) PES-g-PNIPAm, (d) PES-g-P(NIPAm-co-AAm), (e) CuO@PES-g-PNIPAm, and (f) CuO@PES-g-P(NIPAm-co-AAm). All membranes initially supplemented with 10^7 CFU/mL of *E. coli* for antibacterial study. Membranes photographs provide visual evidence of the bacterial growth.

5.3.2. Effect of contact time on Bacteria killing performance

To assess the impact of contact time on the bacteria-killing activity of the membrane, the bare PES, PES-g-P(NIPAm-co-AAm), and CuO@PES-g-P(NIPAm-co-AAm) were individually immersed in a 10^7 *E. coli* bacteria suspension and incubated at 37 °C. Samples were collected at 30-minute intervals from the bacteria suspension, serially diluted, and plated to determine the number of remaining viable bacteria for each membrane over time. Results of viable bacteria growth on

agar plates and CFU counting are presented in Figures 5-25. The thermo-responsive grafted membrane did not exhibit any bacteria toxicity, whereas the dual-functionalized membrane containing CuO killed 96% of live bacteria within the first 30 minutes and 100% of bacteria within the initial 90 minutes of contact time. As outlined in Chapter 1, within the contact time, the metal oxide nanoparticles engage with bacteria, inducing various damages that ultimately result in their demise. Some potential mechanisms include:

- The nanoparticles may attach to the bacterial cell wall or membrane and create pores or disrupt the integrity of the membrane, leading to leakage of cytoplasmic contents and loss of membrane potential.
- The nanoparticles may release metal ions that can bind to proteins, enzymes, or DNA and inhibit their functions, resulting in metabolic disruption, oxidative stress, or genetic damage.
- The nanoparticles may generate reactive oxygen species (ROS) such as hydroxyl radicals, superoxide anions, or hydrogen peroxide that can oxidize biomolecules and cause oxidative damage to the cell components.

The extent and rate of these mechanisms can vary over contact time. Therefore, the number of dead bacteria may increase with increasing contact time.

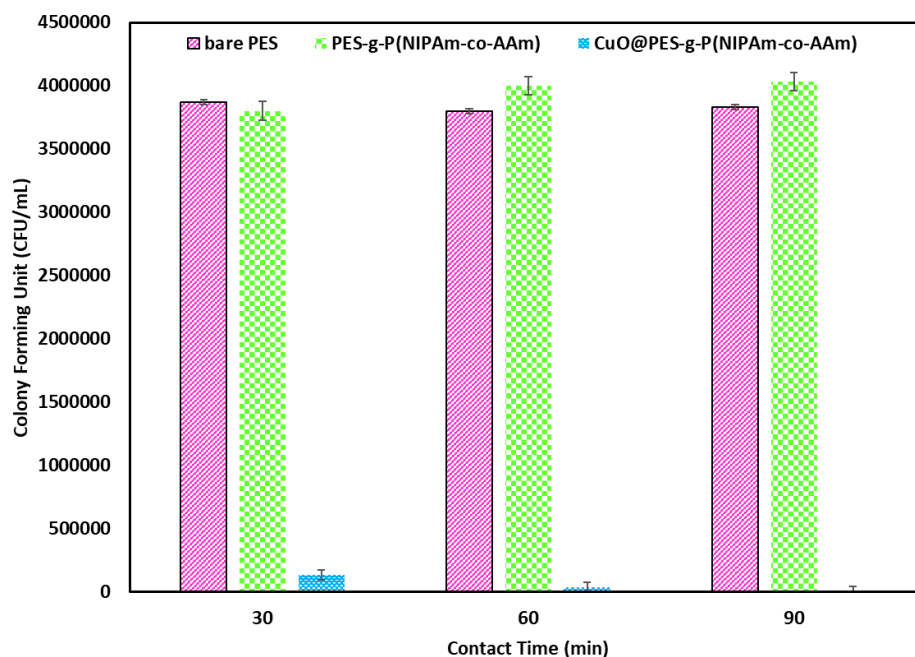


Figure 5-25- Survival of *E. Coli* bacteria after contacting the bacteria suspension with the bare PES, PES-g-P(NIPAm-co-AAm), and CuO@PES-g-P(NIPAm-co-AAm) membranes. Bacterial survival was measured using CFU counting method by plating the *E. coli* suspension on TSB agar plate and incubating at 37 °C for 24 h. (Dilution Factor: 10⁴)

5.3.3. Bacterial release performance of bare and dual-functionalized PES membranes

Bacterial adhesion test bare membrane, grafted membranes (PES-g-P(NIPAm-co-AAm) and CuO@PES-g-PNIPAm), and dual-functionalized membranes (CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm)) was carried out after 90 minutes of initial contact with an *E. coli* suspension, by washing the membranes with cold, hot and cold cycle with a PBS solution for 30 minutes (10 minutes each). It is quite clear from Figure 5-26, that the edges of the bare PES, PES-g-PNIPAm, and PES-g-P(NIPAm-co-AAm) membranes showed a layer of bacterial growth, whose thickness is the measure of the concentration of live colonies attached to the surface (presented in Table 5-5). The bare PES shows a bacterial thickness as high as 1.6 mm, whereas PES-g-PNIPAm and PES-

g-P(NIPAm-co-AAm) showed the thickness of 0.9 mm and 1.2 mm respectively. These findings suggest that during the washing process, PES-g-PNIPAm detached more bacteria due to the thermo-responsive properties of PNIPAm brushes that were grafted onto the surface of the PES membrane. It was reported that at 45°C, PNIPAm brushes tend to collapse on the surface, releasing the attached bacteria during the washing process [325] . The intermediate thickness of 1.2 mm in the case of P(NIPAm-co-AAm) could be due to a lower degree of temperature induced volume change, resulting in less detachment of bacteria from the membrane surface than the PNIPAm grafted membrane.

It is evident from Figure 5-26 (d and e), which demonstrates on the plates of CuO@PES-g-PNIPAm and CuO@PES-g-P(NIPAm-co-AAm), all the initially attached bacteria were killed during the first 90 minutes of contact due to the presence of a copper.

Table 5-5: Thickness of bacteria growth surrounding the membrane after washing cycle

Membrane	Thickness of bacteria growth after washing cycle (mm)
Bare PES	1.6
PES-g-PNIPAm	0.9
PES-g-P(NIPAm-co-AAm)	1.2
CuO@PES-g-PNIPAm	0
CuO@PES-g-P(NIPAm-co-AAm)	0

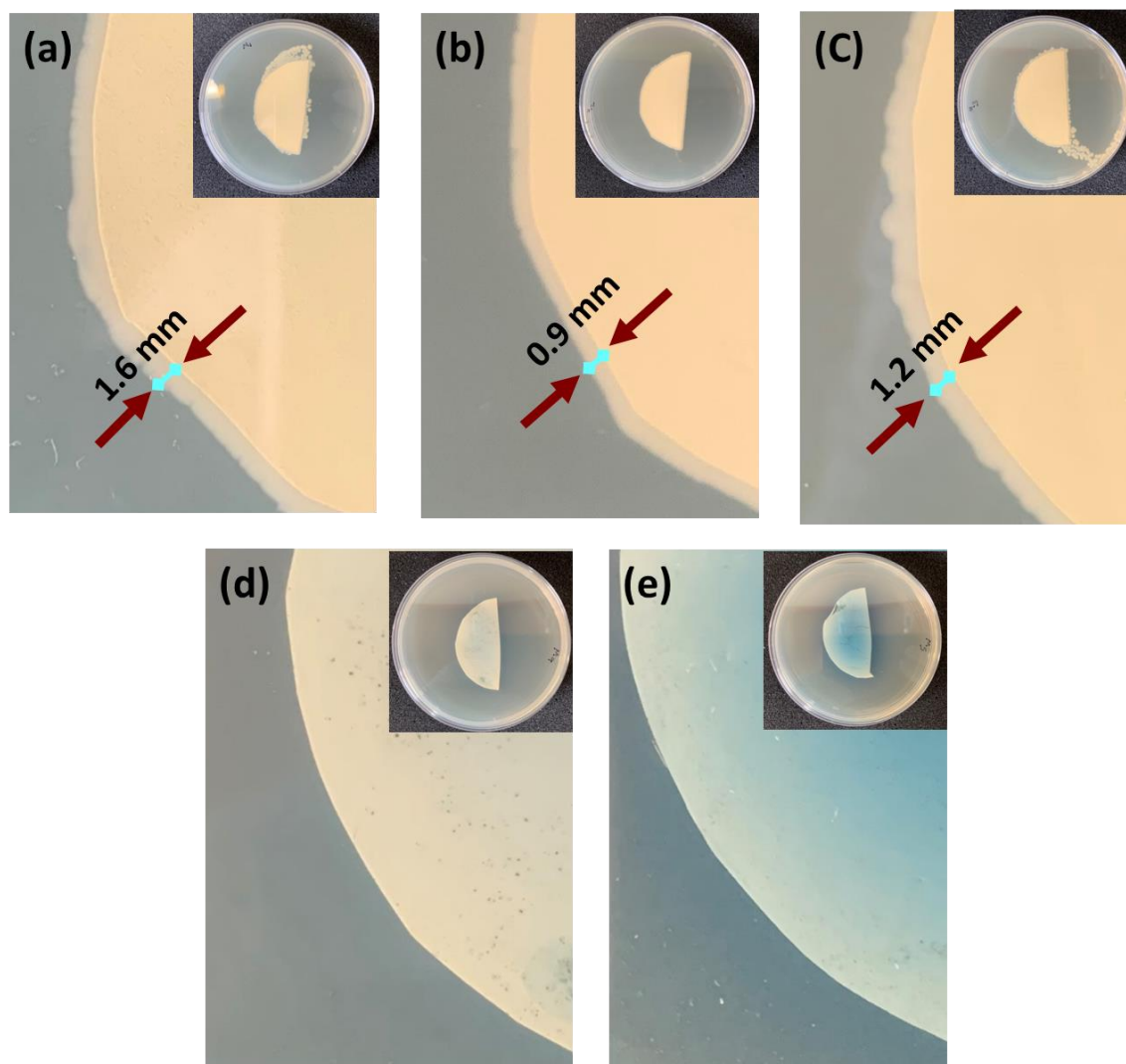


Figure 5-26: Bacteria antiadhesion results of (a) bare PES, (b) PES-g-PNIPAm, (c) PES-g-P(NIPAm-co-AAm), (d) CuO@PES-g-PNIPAm, and (e) CuO@PES-g-P(NIPAm-co-AAm). All membranes were initially supplemented with 10^7 CFU/mL of *E. coli* for antibacterial and antiadhesion studies. The membranes were washed with a hot (45°C) and cold (20°C) PBS solution after 90 minutes of contact time.

To delve deeper into the study of bacterial adhesion to the surface, we assessed the membranes that came into contact with bacteria via FE-SEM imaging. Our focus was exclusively on the surface of the membrane. This decision was based on the size difference between bacteria (0.5-75 μm diameter for *E. coli* [326] and 1-1.2 μm diameter for *B. cereus* [327]) and membrane pores (0.2

μm), given the bacteria cannot migrate to the bulk of the membrane through the pores. Figure 5-27 depicts the FE-SEM images of bare and modified membranes after cleaning them with hot (45°C) and cold (20°C) PBS solution, where, as earlier observed in Figure 5-27, the number of bacteria attached to the bare PES membrane is more than to the thermo-responsive grafted membrane. The attached bacteria on the bare PES and grafted membranes (PES-g-P(NIPAm-co-AAm) and PES-g-PNIPAm surface appeared smooth, suggesting that the bacteria cells were healthy and undamaged before fixation process. Alternatively, the dual-functionalized membrane CuO@PES-g-P(NIPAm-co-AAm) showed significant damage to the outer membrane, resulting in the loss of cellular integrity, which can be attributed to the presence of copper oxide groups. It has been suggested that copper oxide immobilized on a surface may attract bacteria through electrostatic interactions, leading to degradation of the cell membrane and destabilization of the intracellular matrix of the bacterium through contact mechanisms [328]. It is worth mentioning that no areas were observed on this membrane CuO@PES-g-P(NIPAm-co-AAm) with a significant number of dead cells attached to the surface. This indicates the membrane's ability to detach debris during the washing process. The antibacterial efficacy of metal oxide nanoparticles arises from a combination of various mechanisms that act synergistically or antagonistically, leading to bacterial death. The specific contribution of each mechanism may vary based on the unique conditions and parameters of individual cases. To discern these mechanisms, I employed two experimental methods:

1. **Quantifying the release of metal ions from the nanoparticles into the culture medium using ICP-MS:** The minimal release (4.5 ppb) of Cu ions in the bacteria suspension could indicate that leached ions is not primary mechanism for 100% killing ability. Considering

the fresh DI water which contained approximately 5 ppb Cu ions showed no toxicity toward killing *E. coli* bacteria (Figure 5-24(a)).

2. **Assessing damage to the bacterial cell wall or membrane through scanning electron microscopy (SEM):** Our results indicated bacterial attachment to CuO nanoparticles and damage to the bacterial cell, suggesting that interaction with the bacterial cell wall or membrane could be a possible mechanism contributing to the antibacterial activity of copper oxide nanoparticles.

However, additional information pertaining to the production of reactive oxygen species (ROS) is essential. Techniques such as fluorescence probes, electron spin resonance (ESR), or assessing damage to bacterial DNA and proteins using methods like gel electrophoresis and polymerase chain reaction (PCR) could be used in future for a more comprehensive understanding of the bacteria-killing mechanism. However, It should be noted that decoupling these effects are very challenging.

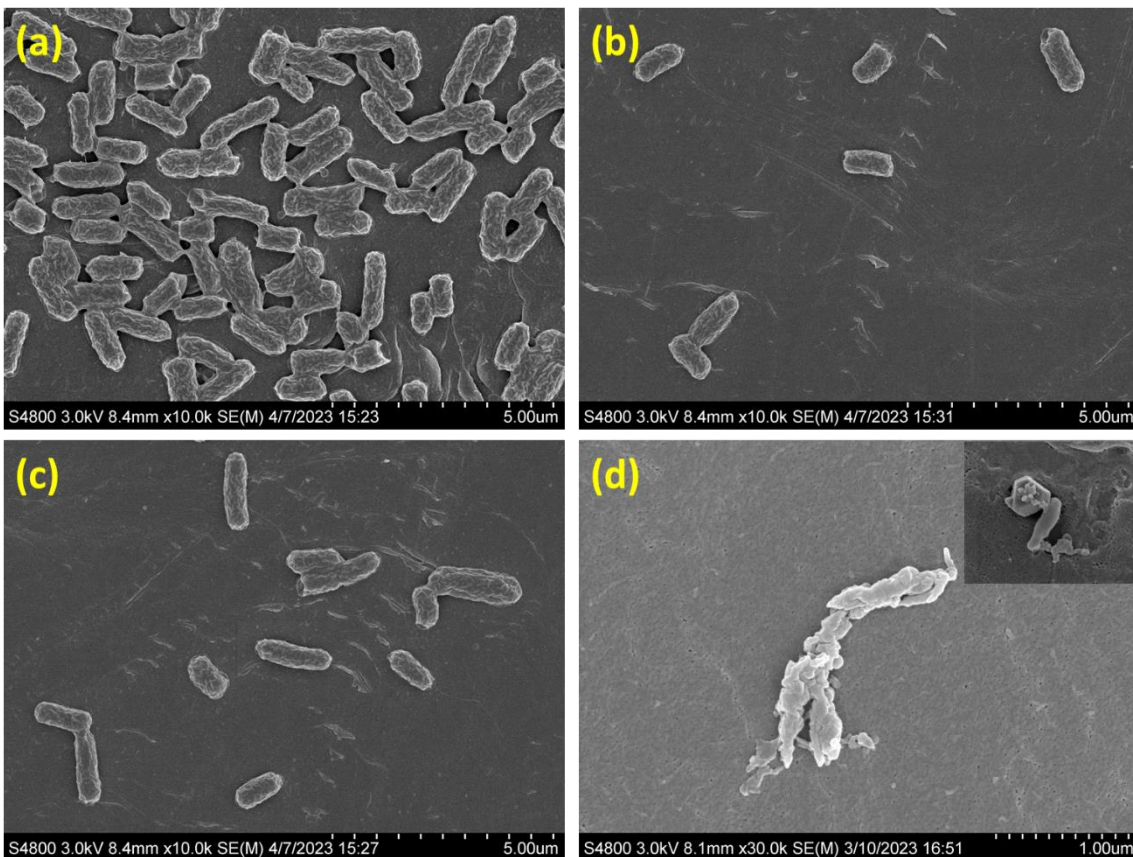


Figure 5-27: SEM images showing the adhesion of *E. coli* bacteria on the (a) bare PES, (b) PES-g-PNIPAm, (c) PES-g-P(NIPAm-co-AAm), and (d) CuO@PES-g-P(NIPAm-co-AAm) membranes after washing the membrane with hot (45°C) and cold (20°C) PBS solution.

5.3.4. Antibacterial properties of dual-functionalized membranes toward gram-positive bacteria

To further investigate the antibacterial properties of the dual functionalized membrane, bacteria killing experiment was conducted using gram-positive bacteria, *Bacillus cereus* (*B. cereus*). The experiment involved immersing bare and dual functionalized membranes CuO@PES-g-P(NIPAm-co-AAm) in a sterile and sealed beaker containing 10 mL of *B. cereus* suspension with a cell

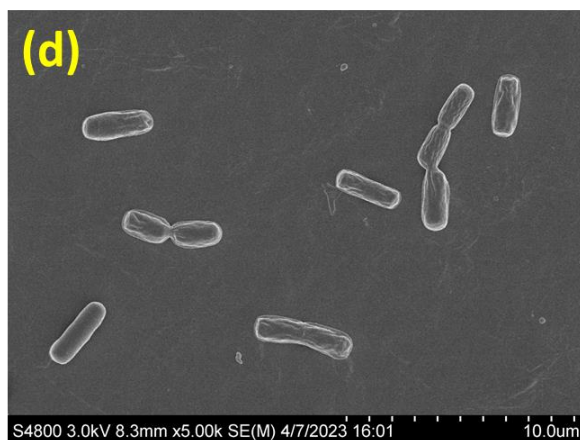
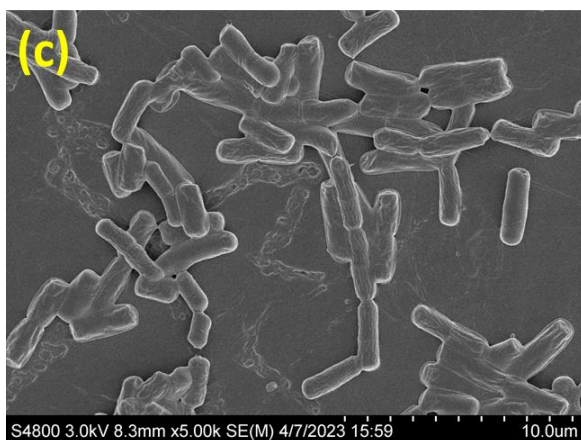
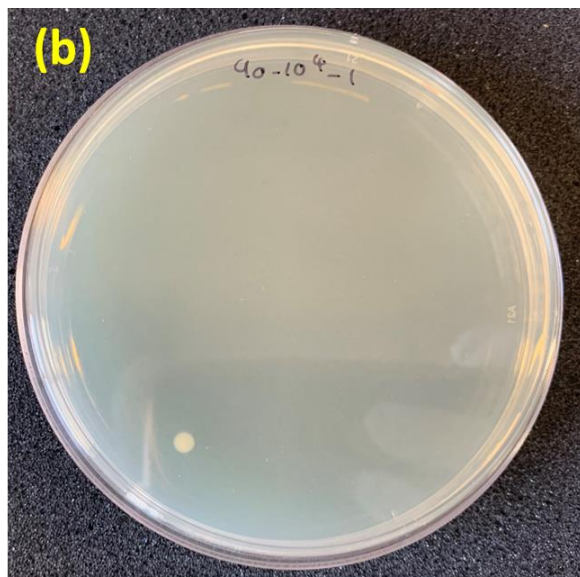
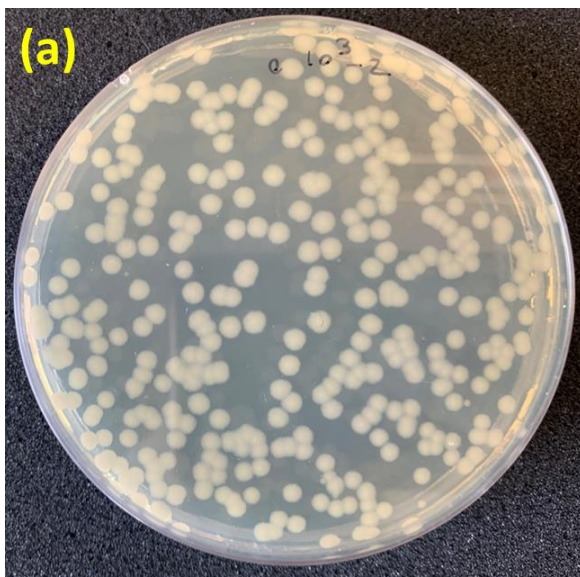
concentration of 10^7 cell/mL. The mixture was agitated in an incubator shaker at 200 rpm and 30°C for 90 and 180 minutes.

The results of the experiment showed that the number of live *B. cereus* cells remained the same compared to the initial bacterial concentration when using the bare membrane. However, when using the dual functionalized membrane CuO@PES-g-P(NIPAm-co-AAm), the number of live bacteria remaining in the solution was significantly reduced to approximately 10^4 cell/mL after 90 minutes, as depicted in Figure 5-28 (a, b, and e). Furthermore, increasing the contact time did not show any change in the number of remaining live bacteria, suggesting that the maximum biocidal activity of the dual functionalized membrane can be attained within 90 minutes.

Overall, copper oxide has been shown to have biocidal properties against both gram-positive and gram-negative bacteria. However, some studies suggest that gram-negative bacteria may be more susceptible to copper's antimicrobial effects than gram-positive bacteria. This is because gram-negative bacteria have a thinner cell wall that is more vulnerable to damage from copper ions. For instance, the cell wall thickness of gram-positive bacteria such as *B. cereus* ranges from 20 to 80 nm [329], whereas for gram-negative bacteria like *E. coli*, this value is approximately below 4 nm, as reported in the literature [330].

The effectiveness of the PNIPAm-grafted membrane in detaching gram-positive bacteria cells was evaluated through an anti-adhesion test, which was confirmed by FE-SEM imaging. As shown in Figure 5-28 (c and d), the bare membrane allowed a large number of bacteria to attach to the surface even after washing with hot (45°C) and cold (20°C) PBS solutions. In contrast, the images revealed that a significantly lower number of bacteria attached to the PES-g-PNIPAm membrane

surface after the washing process. These results clearly demonstrate that the incorporation of a thermo-responsive membrane effectively reduces the number of adhered bacterial cells during the washing process.



(e)

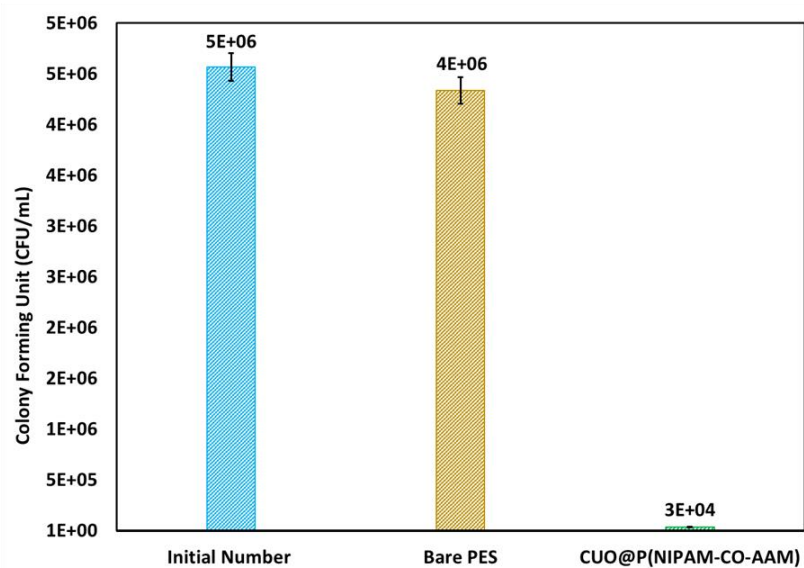


Figure 5-28: Bacterial killing results, plate count results of *B. cereus* bacteria suspension in contact with (a) no membrane, (b) CuO@PES-g-P(NIPAm-co-AAm). SEM images showing the adhesion of *B. cereus* bacteria on the (c) bare PES, (d) PES-g-PNIPAm membranes. (e) Graphical representation of colony counts (CFU/mL) for suspension in contact with bare and dual-functionalized membranes.

5.3.5. Effect of CuO concentration on antibacterial performance of modified PES membrane

To assess the influence of copper concentration on the bactericidal activity of the membrane, PNIPAm-co-AAm grafted membranes were functionalized with 1, 2, 5, and 8 wt.% of copper oxide nanoparticles. Subsequently, each modified membrane was individually immersed in a suspension of 10^7 *E. coli* bacteria and incubated at 37 °C. After four hours, samples were collected from the bacterial suspension, serially diluted, and plated to determine the number of viable bacteria for each membrane. The results, including viable bacteria grown on agar plates and CFU counting, are depicted in Figures 5-29.

The antibacterial membrane containing 1 wt.% copper exhibited partial efficacy, unable to completely eradicate all bacteria during the four-hour exposure time. The initial count of 1×10^7 living cells significantly decreased after exposure to the antibacterial membrane with 1 wt.% copper, leaving only $12.3 \pm 1.8\%$ detectable live bacteria after the 4-hour exposure period. In contrast, membranes with 2, 5, and 8 wt.% concentrations demonstrated 100% bactericidal effectiveness against *E. coli* after 4 hours of exposure. In future research, exploring various ratios of APTES to CuO and adjusting reaction temperatures can provide insights into controlling the size and agglomeration of CuO nanoparticles and their impact on antibacterial performance.

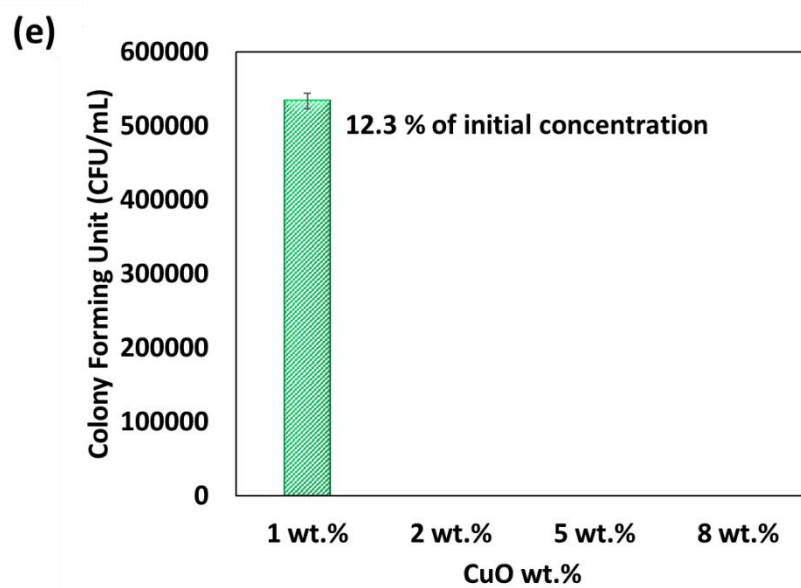
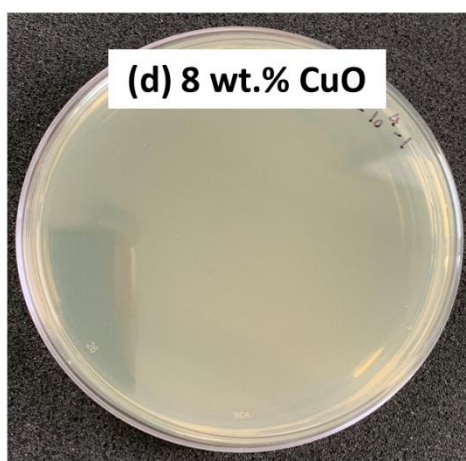
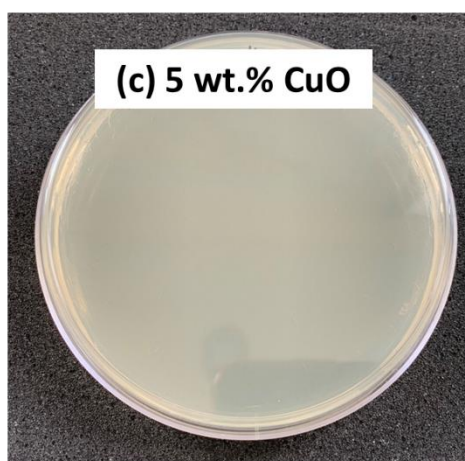
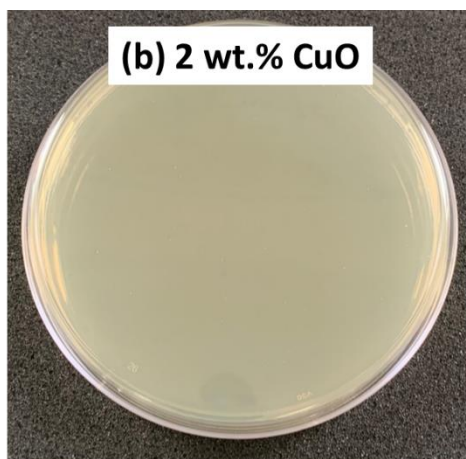
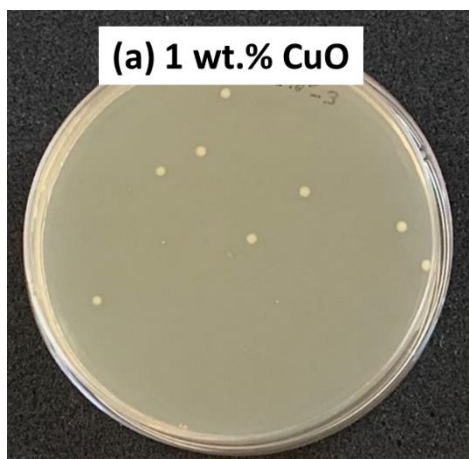


Figure 5-29: Bacterial killing results, plate count results of bacteria suspension in contact with (a) 1 wt.%, (b) 2 wt.%, and (c) 5 wt.%, (d) 8 wt.%. All membranes were initially supplemented with 10^7 CFU/mL of *E. coli* for antibacterial study. Membranes photographs provide visual evidence of bacterial growth. (e) Graphical representation of colony counts (CFU/mL) for suspension in contact with membranes 1, 2, 5, and 8 wt.% CuO.

5.3.6. Comparing the antibacterial performances of functionalized PES membranes with acrylamide and copper oxide nanoparticles with other modified PES membranes

The antibacterial performance of the thermo-responsive membranes we designed is compared with previously reported PES membranes in Table 5-6. Our analysis indicates that the CuO@PES-g-P(NIPAm-co-AAm) membrane exhibits exceptional antibacterial efficacy against both gram-negative and gram-positive bacterial strains compared to prior studies. The results in Table 5-6 underscore the effectiveness of surface functionalization as a viable approach to enhance membrane properties, particularly in terms of increasing membrane toxicity to bacteria and improving bacteria-killing efficiency.

Table 5-6: Comparison of the antibacterial performance of the CuO@PES-g-P(NIPAm-co-AAm) membranes with the previously reported functionalized PES membranes

Membrane	Weight ratio of antibacterial agent	Contact Time	Bacteria Killing (Gram-negative)	Bacteria Killing (Gram-positive)	References
HPEI-GO/PES	5 wt. %	24 h	74.88%	Not studied	[331]
SLS-CNT/PES	2.5 wt. %	3 h	not significant	Not studied	[332]
cellulose-p(NIPAAm-co-AEMA)-AgNPs	Not provided	24 h	Less than 100%	Not studied	[232]
PES-Ag2.0P360	2 wt. %	24 h	100%	Studied, but numerical results were not provided.	[333]

COL/PGT/PES	COL: 1 wt.% PGT: 3 wt.%	24 h	98%	98%	[334]
CuO@PES-g-P(NIPAm-co-AAm)	2 wt.%	90 min	100%	99%	This work

5.4. Membrane separation performance and reusability

5.4.1. Effect of grafting yield on separation performance of PNIPAm-grafted membranes

The efficiency of bare PES and PNIPAm-grafted PES membranes in removing persistent organic foulants such as BSA and oil from water, and the results were demonstrated in Figure 5-30. All the membranes displayed excellent performance in rejection of oil from oil-in-water emulsions. However, the PNIPAm-grafted PES membranes showed a slightly better performance toward oil rejection, with a measurement of $96.9 \pm 0.71\%$ for the bare PES membrane and $98.4 \pm 0.63\%$ for the PES-g-25%PNIPAm membrane. In general, the oil-in-water emulsion separation capability in membrane filtration is determined by two mechanisms, namely size exclusion and hydrophobic/hydrophilic interactions between the feed solution and the membrane surface. The hydrophilic nature of the membrane surface plays a crucial role in regulating the water/oil attraction. Therefore, a membrane surface with increased hydrophilicity will easily form a hydration layer to impede oil passage, resulting in improved water permeability and higher oil rejection rate [255], [335].

The time-based evolution of membrane separation performance has been investigated and demonstrated in Figure 5-30 (b), revealing a consistent increase over time until reaching equilibrium. This phenomenon is attributed to the interaction of contaminant molecules with the membrane's active sites, causing these sites to become adsorbed with particles or molecules. This leads to a gradual enhancement in separation efficiency until saturation is attained. As the

system stabilizes, separation performance may continue to improve until it reaches a steady state [336]. Consequently, moving forward, our study will exclusively report on the equilibrium separation conditions.

Furthermore, the experimental results demonstrate that increasing the PNIPAm grafting yield on a PES membrane leads to an increase in BSA rejection. A bare PES membrane has a BSA rejection of $90 \pm 0.78\%$, while the BSA rejection increases to $91.3 \pm 0.46\%$, $94.9 \pm 0.83\%$, and $96.4 \pm 1.01\%$ for PES-g-5%PNIPAm, PES-g-15%PNIPAm and PES-g-25%PNIPAm membranes, respectively. This improvement in BSA rejection may be attributed to several factors. The electrostatic repulsion of negatively charged proteins from PNIPAm-grafted PES membrane surface is one possible mechanism. During the initial phase of a filtration experiment, the membrane surface becomes coated with a monolayer of protein, acquiring electrostatic charge in the process. Based on the zeta potential measurements, both bare and grafted PES membranes exhibit a negative charge at pH = 6, which is attributed to an increase in the number of $(-\text{OH}^-)$ groups on the membrane surface due to the higher pH. This increase in the negatively charged groups enhances the electrostatic repulsion between the membrane and BSA, which can contribute to a reduction in fouling [267], [337]. Additionally, the inter-protein interactions in the solution can often result in the agglomeration of BSA, which can obstruct the passage of proteins and therefore enhance rejection in the grafted membrane [338].

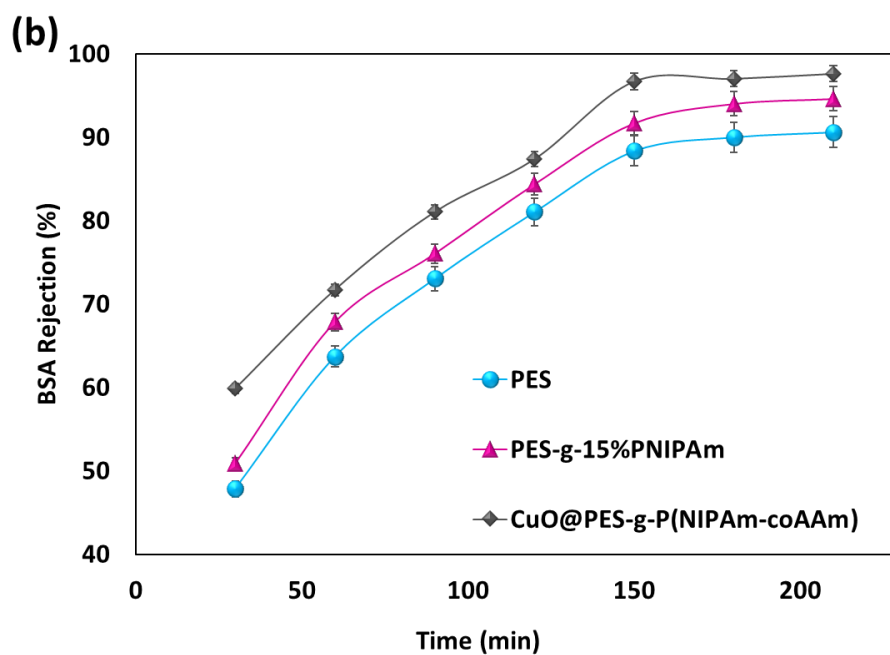
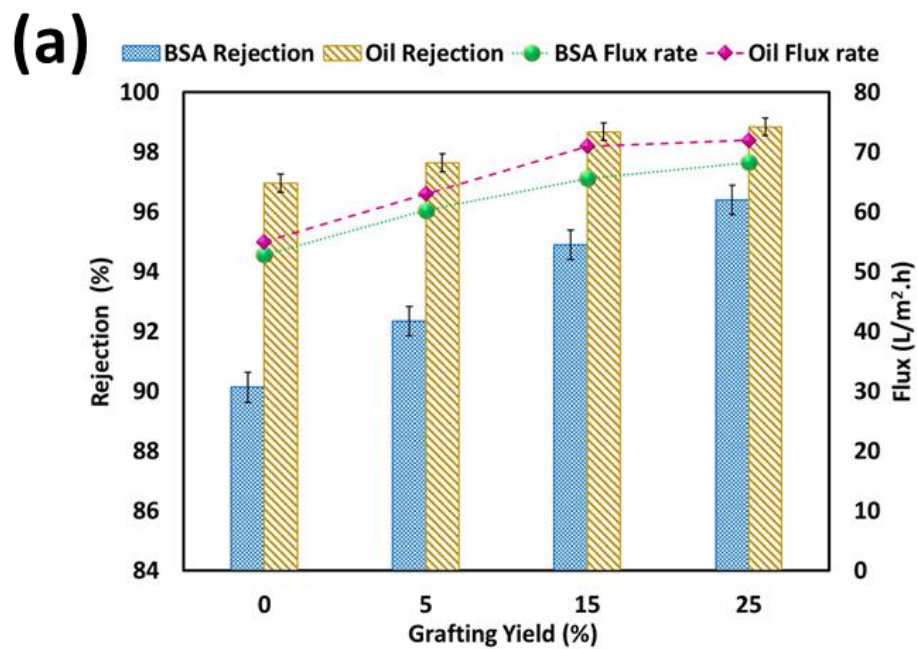


Figure 5-30: (a) Rejection rate of BSA and Oil after filtration using bare PES and PES-g-5%PNIPAm, PES-g-15%PNIPAm, and PES-g-25%PNIPAm membranes (b) Effect of time on the BSA rejection rate of the modified membrane.

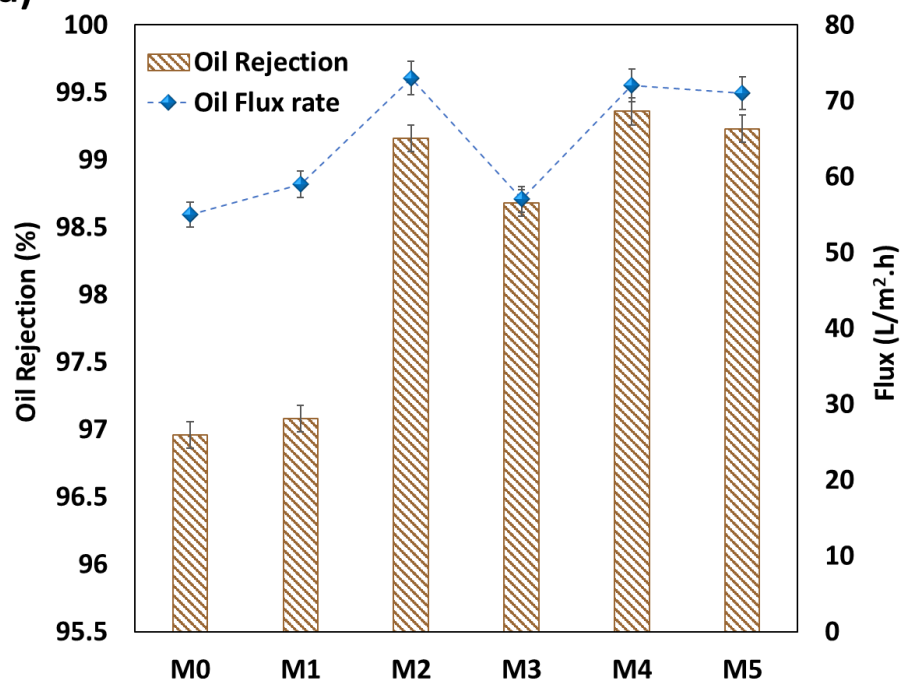
5.4.2. Separation performance of the functionalized PES membranes with acrylamide and copper oxide nanoparticles

In this section, for clearer visualization, each sample is represented in graphs using shorter names as follows: M₀: bare PES; M₁: PES-g-AAm; M₂: PES-g-P(NIPAm-co-AAm); M₃: CuO@PES; and M₄: CuO@PES-g-P(NIPAm-co-AAm), M₅: CuO@PES-g-PNIPAm.

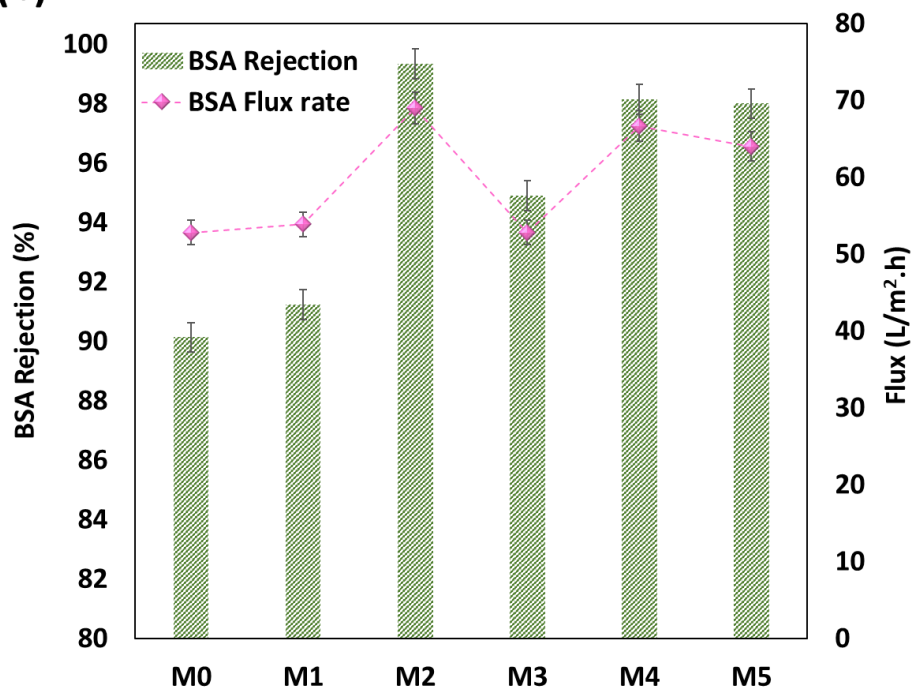
The modified and thermo-responsive polymer grafted membranes' separation performance was evaluated by separating the BSA and oil-in-water emulsions. All membranes showed good performance in removing oil-water emulsions (1000 ppm), but the membrane containing copper oxide nanoparticles performed exceptionally well compared to the other membranes, with a separation efficiency of > 99% for CuO@PES and CuO@PES-g-P(NIPAm-co-AAm) membranes. The pristine membrane has shown the lowest separation efficiency during the oil-in-water emulsion separation, and separation efficiency was observed about $\sim 97 \pm 0.68$ % as shown in Figure 5-31 (a and b). In general, the effectiveness of oil-water separation in membrane filtration is influenced by: (i) size exclusion and (ii) hydrophobic/hydrophilic interactions between the feed solution and the membrane surface. The hydrophilic nature of the membrane surface is crucial in separating the oil-in-water emulsions. The membranes with better hydrophilic surfaces showed better attraction towards the water, resulting in the formation of the hydration layer on the surface of the membranes and the developed hydration layer along with the polar groups, strongly repelling the oil, resulting in the demulsification of the oil-in-water emulsion with improved water permeability and oil rejection [255], [335]. Figure 5-31 (c) demonstrates the optical microscope images of an oil-in-water emulsion before and after the filtration process. As shown in the images, a significant portion of the oil droplets was separated during filtration.

Furthermore, the experimental findings indicate that the addition of copper oxide to a PES membrane increases BSA rejection. While a bare PES membrane has a BSA rejection rate of 90%, the BSA rejection rates for CuO@PES and CuO@PES-g-P(NIPAm-co-AAm) were $99.3 \pm 0.51\%$ and $98.1 \pm 0.32\%$, respectively. This enhancement could be attributed to two potential mechanisms: (i) a decrease in the passage or penetration of BSA molecules due to size exclusion and (ii) a possible interaction between the copper oxide nanoparticles and BSA, leading to the formation of a complex that reduces the passage of BSA molecules through the membrane pores [339], [340]. In addition, our observations showed that surface treatment of PES through grafting of P(NIPAm-co-AAm) or AAm slightly enhanced BSA rejection, with rates of $91.2 \pm 0.45\%$ and $94.9 \pm 0.67\%$ for PES-g-AAm and PES-g-P(NIPAm-co-AAm), respectively. This enhancement could be attributed to the electrostatic repulsion between negatively charged proteins and the modified membrane in a neutral pH environment ($\text{pH} > \text{BSA isoelectric point}$). Additionally, the grafting of P(NIPAm-co-AAm) onto the surface of the PES membrane can decrease the membrane surface pore size, impeding the passage of BSA molecules and resulting in an increased rejection rate [341].

(a)



(b)



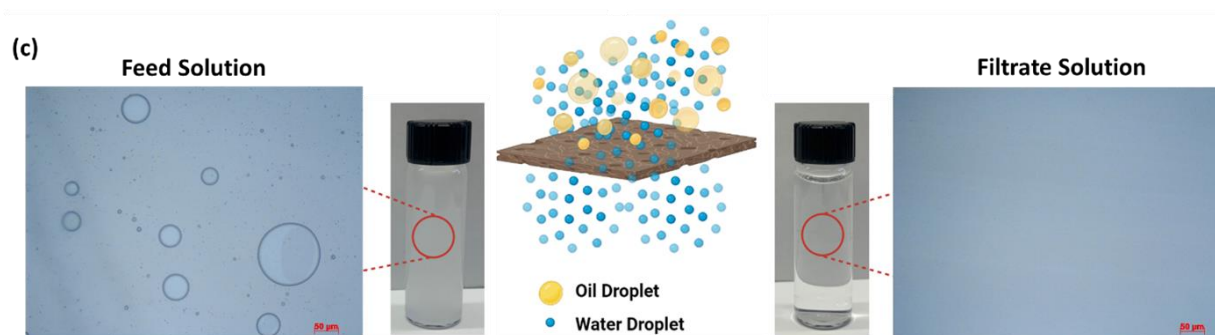


Figure 5-31: Results of the (a) oil (1000 ppm) and (b) BSA (500 ppm) rejection study for bare and modified membrane.

M_0 : bare PES; M_1 : PES-g-AAm; M_2 : PES-g-P(NIPAm-co-AAm); M_3 : CuO@PES; M_4 : CuO@PES-g-P(NIPAm-co-AAm), M_5 : CuO@PES-g-PNIPAm.

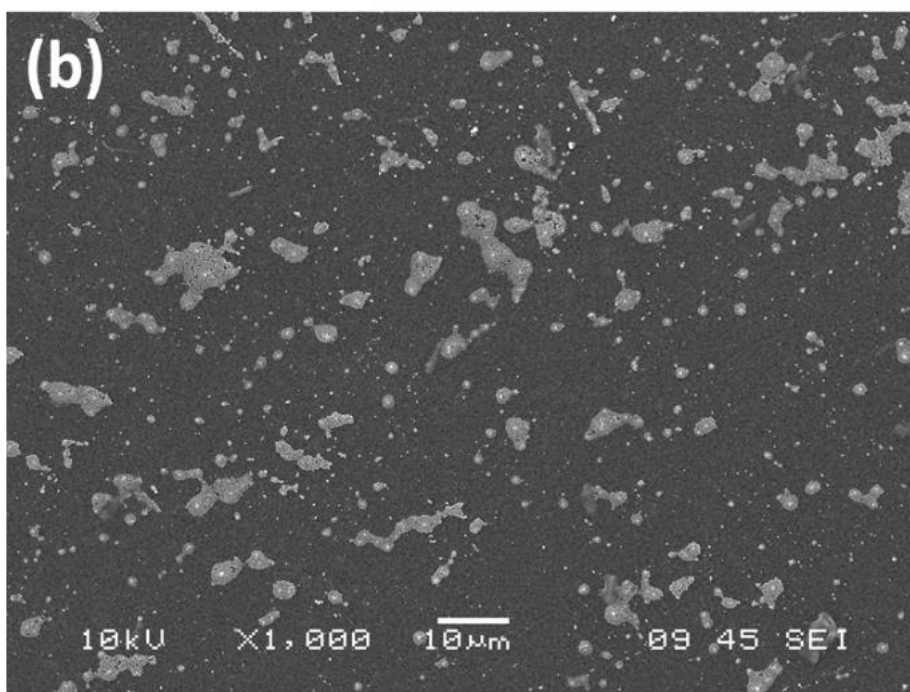
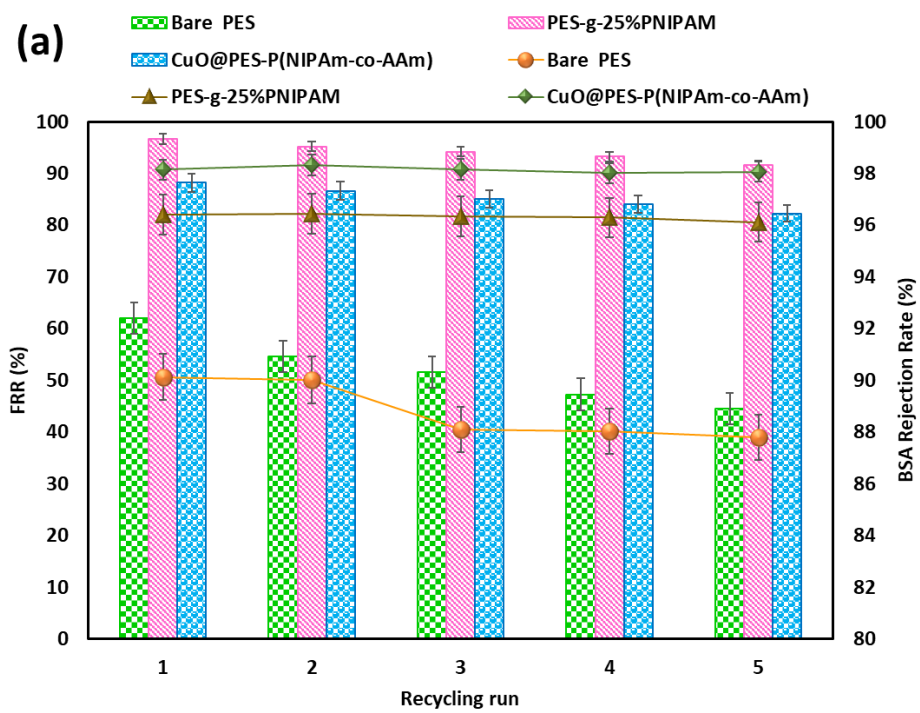
5.4.3. Reusability/stability of the functionalized PES membranes with acrylamide and copper oxide nanoparticles for water treatment application

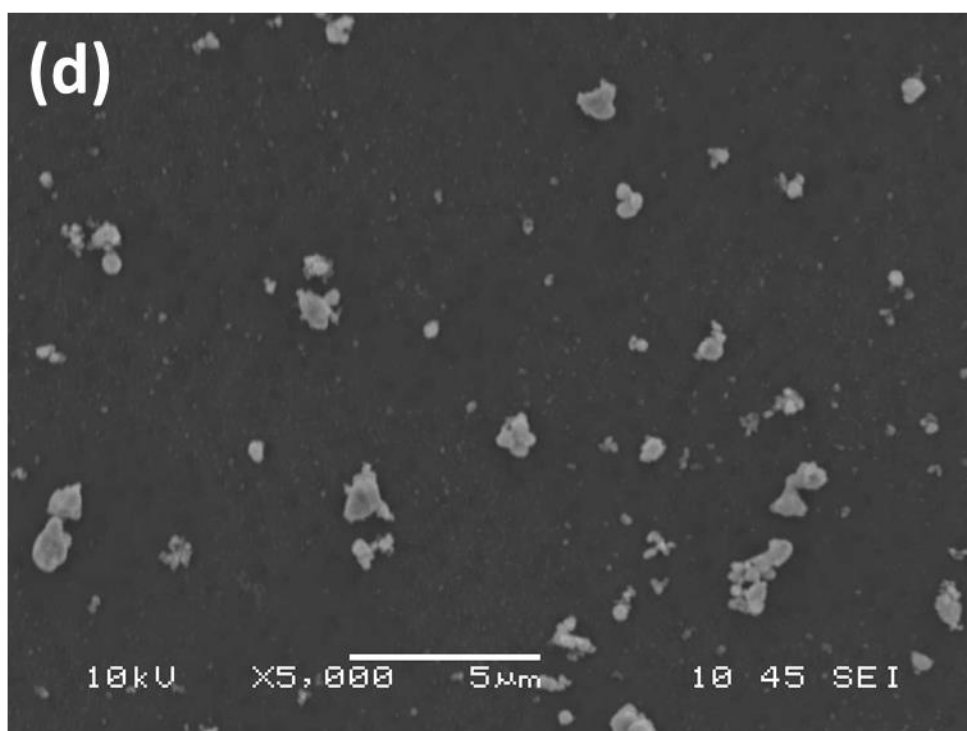
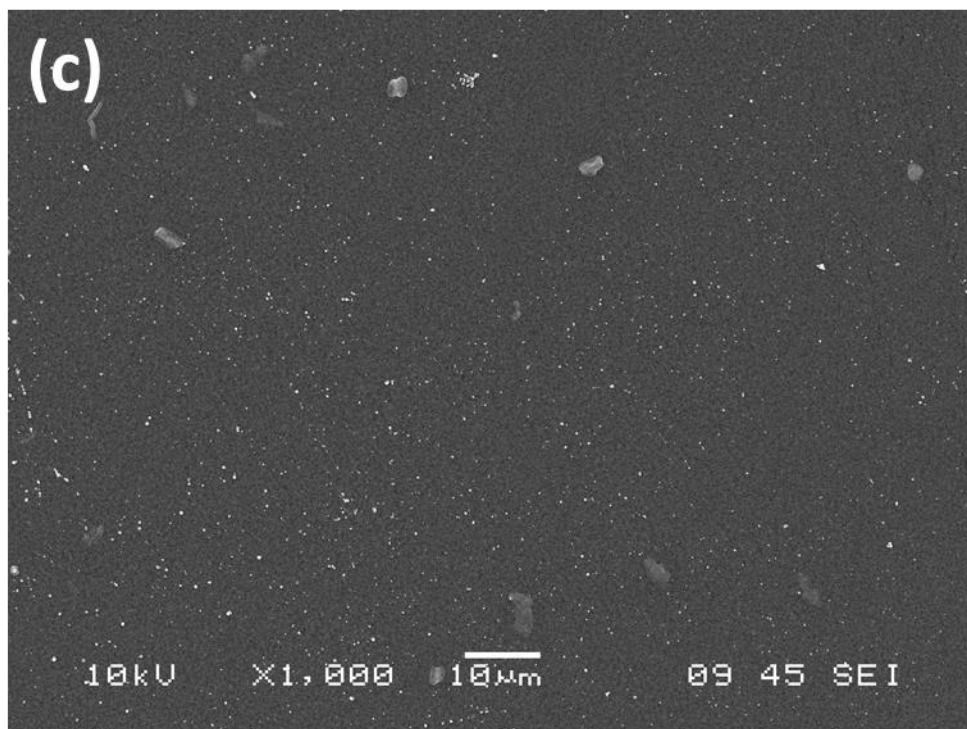
To assess the reusability of the membrane, the flux of the BSA solution was measured during a 150-minute filtration process. Subsequently, the membranes underwent a 30-minute washing cycle with both cold and warm water. Following this, the pure water flux of the membranes was measured to evaluate the flux recovery rate (FRR) and overall fouling resistance of the modified PES membranes. This entire process was repeated five times to assess the reusability. Table 5-7 briefly summarized the results for bare PES, PES-g-25% PNIPAM, and dual functionalized membrane CuO@PES-g-P(NIPAm-co-AAm). The results, presented in Figure 5-32 (a), illustrate a decline in flux recovery values over five cycles, decreasing from 88.19% to 82.27% for CuO@PES-g-P(NIPAm-co-AAm). Interestingly, the BSA rejection rate remains remarkably high at approximately 98% even after five filtration runs. Additionally, in the case of PES-g-25%PNIPAm a

decline in flux recovery values over five cycles, decreasing from 97.0% to 91.3%. The 25% PNIPAm grafted membranes exhibited excellent separation performance, maintaining a consistently high BSA rejection rate of approximately 96% even after undergoing five filtration runs. Compared to the bare membrane, both of these modified membranes exhibited excellent reusability. In contrast, the bare PES membrane experienced a noticeable reduction in fouling resistance ratio (FRR) from 62.02% to 44.53% after five recycling runs, indicating a significant accumulation of irreversible foulants on the surface.

Moreover, examination of the SEM images taken before and after the cleaning process reveals that the P(NIPAm-co-AAm) and CuO nanoparticles remain attached to the membrane's surface, as shown in Figure 5-32(b). These findings indicate that reversible fouling constitutes the majority of the overall fouling, and the cleaning process maintains high efficiency even after multiple filtration runs.

Additionally, the concentration of copper ions leached during cross-flow filtration into the permeate water was quantified using ICP-MS. Following the first and fifth recycling runs for CuO@PES-g-P(NIPAm-co-AAm), the filtered pure water was collected and analyzed to assess the Cu ion concentration. The results revealed a remarkably low concentration of copper ions, measuring 9.5 (ratio of leached Cu ions to total CuO on the membrane= 1.58%) ppb and 14.5 (ratio of leached Cu ions to total CuO on the membrane=2.40%) ppb for run 1 and 5, respectively. This underscores the pivotal role played by the APTES ligand in immobilizing copper oxide nanoparticles onto the membrane surface.





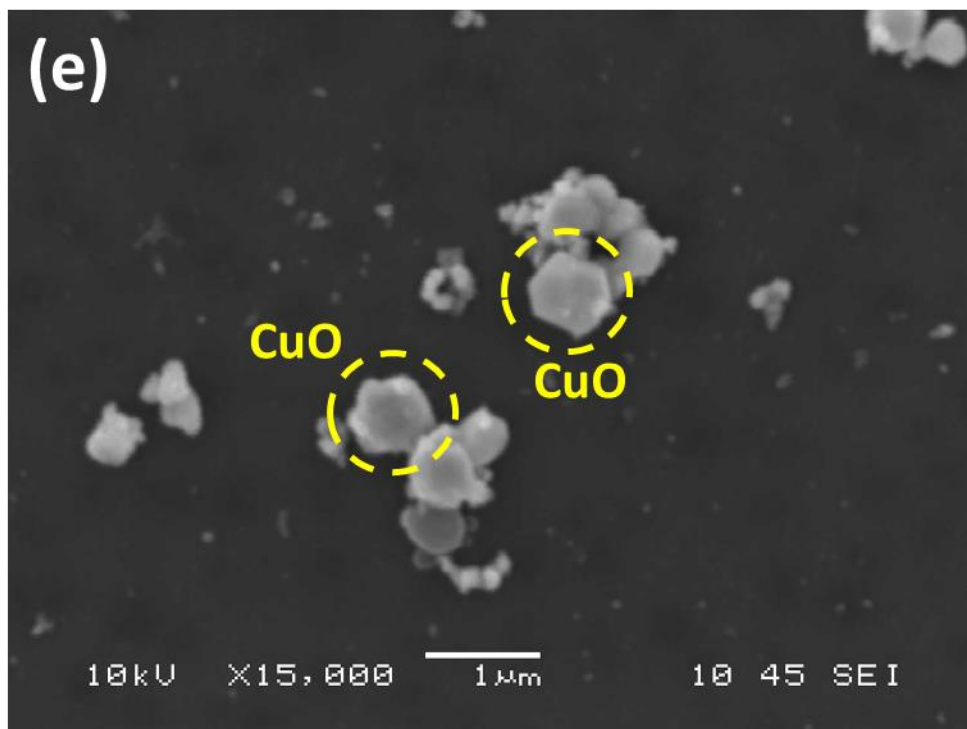


Figure 5-32: Results of the (a) BSA (500 ppm) fouling and rejection study for bare PES, 25% PNIPAM grafted PES, and dual functionalized membrane CuO@PES-g-P(NIPAm-co-AAm), the line plot depicts the rejection rate, and the column bar illustrates the FRR. SEM images captured from the top surface of CuO@PES-g-P(NIPAm-co-AAm) after (b) fouling, (c) after cleaning with cold and warm water cycle, (d) after cleaning Mag: 5000X, and (e) after cleaning Mag: 15000X.

Table 5-7: Summary of reusability results for bare PES, PES-g-25% PNIPAM, and dual functionalized membrane CuO@PES-g-P(NIPAm-co-AAm)

# Run	Bare PES		PES-g-25%PNIPAM		CuO@PES-P(NIPAm-co-AAm)	
	FRR	BSA Rejection	FRR	BSA Rejection	FRR	BSA Rejection
1	62.02	90.13	96.67	96.4	88.19	98.14
2	54.61	90.01	95.21	96.4	86.65	98.32
3	51.63	88.1	94.16	96.4	85.03	98.15
4	47.28	88.02	93.28	96.3	83.98	98.01
5	44.53	87.8	91.60	96.1	82.27	98.07

Furthermore, to ascertain the presence of copper oxide and polymers on the surface, we conducted an analysis of the membrane surface using EDS elemental mapping. The results (Figure

5-33) indicate the presence of Cu and N elements after washing process on the surface, representative of copper oxide, APTES, and P(NIPAm-co-AAm) presence after washing cycle.

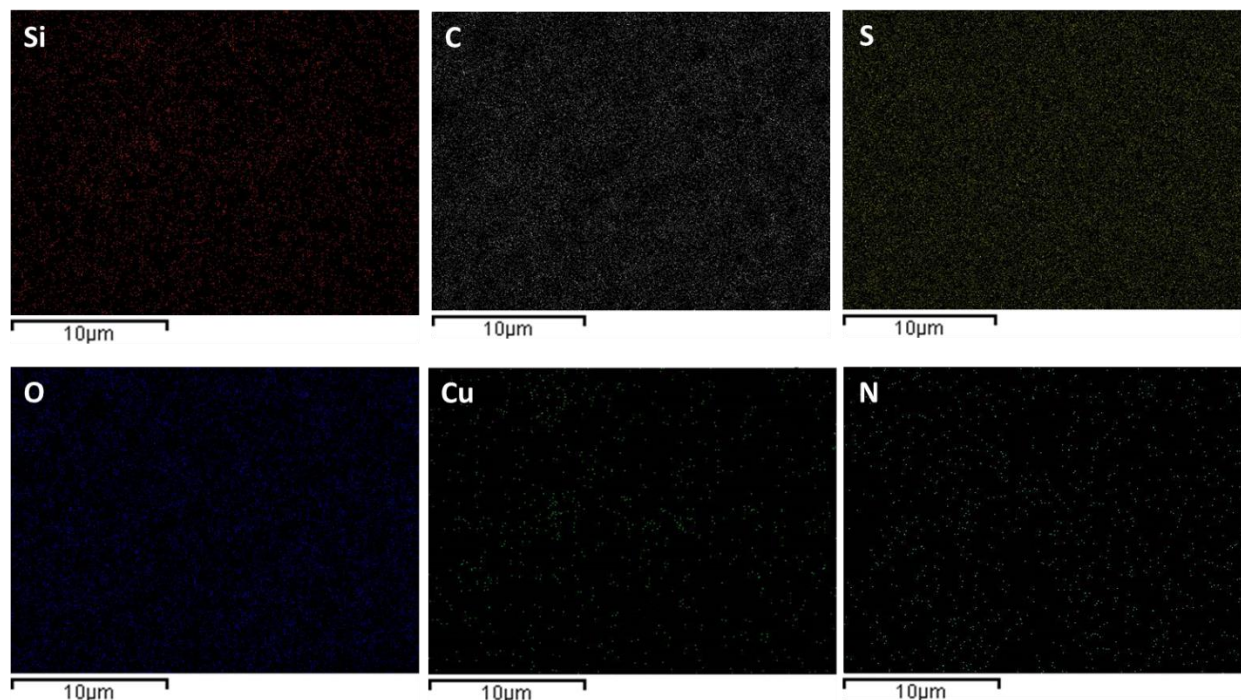


Figure 5-33: EDS mapping analysis of CuO@PES-g-P(NIPAm-co-AAm) after washing process containing different elements of carbon, oxygen, copper, silicon, nitrogen and sulfur.

5.4.4. Reusability/stability of the functionalized PES membranes with acrylamide and copper oxide nanoparticles for antibacterial application

Surface modification of membranes using metal oxide nanoparticles presents a significant challenge due to the stability of nanoparticles during the filtration process. Extensive research has been conducted to evaluate nanoparticle stability in various studies [342]. In this study, we aimed to assess the stability of copper oxide nanoparticles and grafted thermo-responsive polymers. To achieve this, we conducted antibacterial testing on three separate antibacterial run. Our findings reveal that even after the third test, the dual functionalized membrane, incorporating copper oxide nanoparticles, exhibited remarkable effectiveness in eradicating *E. coli* bacteria, as illustrated in Figure 5-34 (a and b). Two sets of experiments were conducted to

assess both the stability of copper oxide nanoparticles and the reusability of the membrane in the process of bacteria killing. (i) CuO@PES-g-P(NIPAm-co-AAm) membrane was submerged in a sterile and sealed beaker containing 10 mL of *E. coli* suspension (10^7 cell/mL). After the mixture was prepared, it was agitated in an incubator shaker for 90 minutes at 200 rpm and 37°C. After the incubation period of 90 minutes, the number of live *E. coli* bacteria was determined by counting the Colony Forming Units (CFUs) in the bacteria suspension followed by pipetting 100 μ L from each dilution onto freshly prepared TSA plates. The pipetted solution was then carefully spread over the entire plate using sterile inoculation loops. The TSB agar plates inoculated with the bacterial solution were then incubated overnight at 37°C [261]. This process was repeated three times to evaluate the reusability of membrane. (ii) Using a pipette, 100 μ L of the pre-prepared *E. coli* suspension was placed onto a tryptone soya agar (TSA) plate (kept at room temperature) and then spread evenly across the surface. Subsequently, a 10 mm $\times$ 10 mm square sheet from the used membrane was placed over the agar plate. The TSA plates were then placed in an incubator set at 37°C for 24 hours, following which the bacterial colonies located at the edges and beneath the covered area were visually inspected.

The dual functionalized membrane demonstrated a complete absence of surviving bacteria upon contact. Furthermore, concerns often arise regarding the immobilization of metal nanomaterials, primarily due to the potential leaching of ions during the contact time. To address this concern, we utilized ICP-MS to measure the concentration of copper ions leached from CuO@PES-g-P(NIPAm-co-AAm) into the bacteria solution after 90 minutes. However, to enhance the antibacterial performance of the membrane in an actual filtration process, it is imperative to conduct a study evaluating its efficiency under a constant concentration of bacteria. This involves

prolonged contact with a suspension containing 10^7 cell/mL bacteria, allowing us to determine the membrane's real-life longevity. The results demonstrated a significantly low concentration of copper ions, measuring less than 4.5 ppb in the bacteria solution. This observation confirms the role of APTES ligand in immobilizing the copper oxide nanoparticles onto the membrane surface.

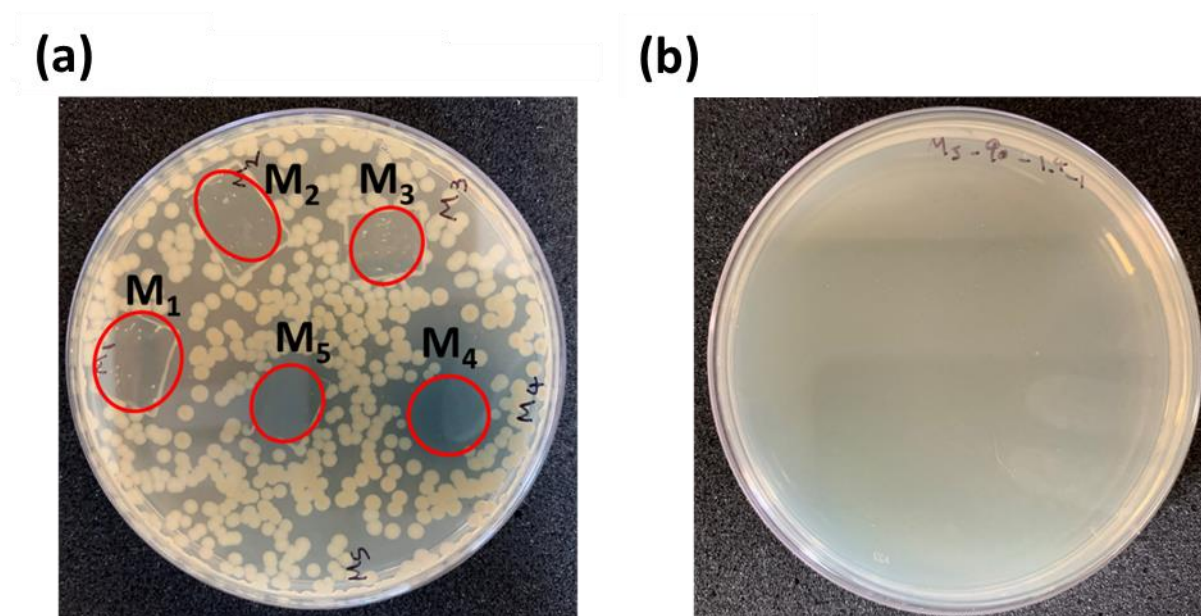


Figure 5-34: (a) Photos displaying inhibition zones and contact killing performance of all membranes after the third anti-adhesion run (bare PES (M₁), (b) PES-g-PNIPAm (M₂), (c) PES-g-P(NIPAm-co-AAm) (M₃), (d) CuO@PES-g-PNIPAm (M₄), and (e) CuO@PES-g-P(NIPAm-co-AAm) (M₅)). (b) Plate count results of *E. coli* bacteria suspension in contact with CuO@PES-g-P(NIPAm-co-AAm) for the third run.

5.4.5. Comparing the separation performances of grafted and functionalized PES membranes with other modified PES membranes

The separation performance and reusability of the thermo-responsive membranes we designed are compared with previously reported PES membranes in Table 5-8. Our analysis indicates that the CuO@PES-g-P(NIPAm-co-AAm) membrane demonstrates exceptional separation efficiency in

removing oil-water emulsion and BSA protein compared to prior studies. Furthermore, this comparison reveals that the modified membrane benefits from prolonged durability, maintaining a high FRR% even after five successive runs, while other studies typically assess lower FRR% for only three cycles. The findings in Table 5-8 underscore the effectiveness of surface functionalization as a viable approach to enhance membrane reusability and separation performance.

Table 5-8: Comparison of the separation performance and reusability of the CuO@PES-g-P(NIPAm-co-AAm) membranes with the previously reported functionalized PES membranes

Membrane	Grafting yield or weight ratio of antifoulant agent in blend	Feed Solution (ppm)	Flux Rate L/(m ² ·h)	Rejection (%)	Reusability (#Run-FRR%)	Reference
PES/PDA/CuO/MPC	4 wt.% Blend	BSA (-)	106.4	99.29	3 cycles - 76.25%	[317]
PES-0.5 TiO ₂	0.5 wt.% Blend	Wastewater (COD) (1000)	Microfiltration 1181.1	88.7 %	3 cycles - 46%	[320]
Polyampholyte hydrogel grafted 3:1 [VSA:METMAC] PES	250 µg/cm ² degree of grafting	EPS (10)	87	93%	3 cycles - 80%%	[343]
PES-g-polyPEGMA	14%	BSA (1000)	57	90%	3 cycles - 63.4%	[31]
CuO@PES-g-P(NIPAm-co-AAm)	15%	BSA (500)	90.7	98	5 cycles - 82.27%	This work
CuO@PES-g-P(NIPAm-co-AAm)	15%	Oil/Water (1000)	90.7	99	N/A	This work

Chapter 6 – Summary

The aim across these investigations was to significantly improve the efficiency and efficacy of polyethersulfone (PES) membranes for water treatment applications through various surface modifications. Each approach targeted unique enhancements, resulting in membranes with advanced properties and potential applications.

Firstly, the grafting of Poly(N-isopropyl acrylamide) (PNIPAm) onto polyethersulfone (PES) membranes significantly influenced surface hydrophilicity and antifouling efficacy. The grafting process imparted thermo-responsive behavior to the membranes, leading to altered surface properties depending on temperature.

In the second step, we explored the effects of incorporating acrylamide functional groups and copper oxide nanoparticles onto PES membranes. The resulting membranes exhibited enhanced surface hydrophilicity and demonstrated thermo-responsive characteristics. The summary of surface modification and alterations in surface properties is provided in Table 6-1.

Table 6-1: summary of surface modification and alterations in surface properties

Membrane	Static Contact Angle		Receding Contact Angle		Surface Charge			Surface Roughness
	22°C	40°C	29°C	45°C	pH=2	pH=7	pH=10	
Bare PES	59	59	25.1	25.9	-1.39	-42.6	-44.1	15.8
PES-g-5% PNIPAm	49	63	21.1	28.9	-0.319	-40.1	-41.9	21.8
PES-g-15% PNIPAm	46	66	14.1	36.1	-0.276	-39.6	-40.7	22.1
PES-g-25% PNIPAm	41	69	12.0	37.0	2.82	-39.1	-40.3	24.2
PES-g-AAm	46	45	20.0	21.6	-1.21	-38.5	-40.9	16.4

CuO@PES	35	33	9.1	10.6	0.759	-56.8	-59.3	32.3
CuO@PES-g-PNIPAm	38	47	11.7	20.0	1.47	-54.76	-57.4	26.3
PES-g-P(NIPAm-co-AAm)	42	58	13.6	27.6	-0.317	-39.4	-41.3	16.8
CuO@PES-g-P(NIPAm-co-AAm)	34	40	10.1	21.2	1.81	-53.1	-56.1	31.7

The dual-functionalized membrane showed significant improvements in flux and flux recovery ratio, underlining the synergistic effect of combined functionalization.

Next, our study focused on incorporating thermo-responsive polymers and copper oxide nanoparticles to develop antibacterial PES membranes. The functionalized membranes exhibited heightened surface hydrophilicity, showcasing enhanced anti-adhesion properties and bacteria-repelling performance. The dual-functionalized membrane, enriched with copper oxide nanoparticles, demonstrated excellent bacteria-killing activity against both gram-negative and gram-positive bacteria. This outcome signifies the effectiveness of the developed antibacterial approach, establishing these membranes as highly efficient in removing harmful microorganisms from aqueous feeds.

The separation performance of the modified membrane was also investigated. The PNIPAm grafted PES membrane demonstrated higher BSA and oil-water rejection rate than the bare PES. Moreover, functionalized PES membranes with acrylamide and copper oxide nanoparticles exhibited superior contaminant rejection and antifouling capabilities, positioning it as an ideal choice for the separation of oil-water emulsions and wastewater treatment.

Tables 6-2 and 6-3 summarizes the list of achieved improvements in this study and comparison with relevant literature reports. Collectively, these approaches in membrane modification demonstrate promising advancements in membrane technology, extending their potential applications to diverse domains, including water treatment, oil-water separation, and combating bacterial contamination. These findings contribute substantively to the ongoing progress in membrane research and open avenues for the design of next-generation smart membranes tailored to specific environmental and biomedical needs.

Table 6-2: List of improved surface properties in this study and comparison with relevant literature reports

List of properties	[Ref]	Our work	[31]	[324]	[177]
Surface contact angle		59° vs. 34°	67° vs 37°	73° vs 35°	90° vs 60°
Surface roughness		15 vs. 31	Not provided	Not provided	Not provided
Surface charge at pH 7		-42 vs. -53	Not provided	Not provided	Not provided

Table 6-3: List of achieved improvements in this study and comparison with relevant literature reports

List of improvements	Modification			Parameters (tests) used for evaluation	Benchmarked against relevant studies		
	PNIPAM	PNIPAM-co-AAm	CuO		PES vs. CuO@PES-g-P(NIPAm-co-AAm)	Modifies PES, -Its bare PES, [Ref]	Modifies PES, -Its bare PES, [Ref]
Enhanced antifouling	X	X		Total fouling (R_t %)	48% vs. 36%	83% vs. 59% [31]	72% vs. 55% [177]
Enhanced antibacterial	X	X	X	Reduction in number of CFU	0% vs.100%	0% vs. 74.88% [331]	22% vs. 96% [334]
Enhanced cleaning	X			Flux recovery ratio (FRR%)	62% vs. 88%	52% vs 77% [177]	52% vs. 87% [324]
Enhanced permeability	X	X	X	Flux rate (L/m^2h)	68 vs 77	N/A*	N/A*

Contaminant separation (BSA)	X	X	X	Rejection ratio(%)	90% vs. 99%	90% vs. 90% [31]	92% vs. 97% [324]
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*Flux rate cannot be directly compared to other studies since it depends on factors such as pore structure, pore size, operational pressure, and flow direction. Therefore, we can only compare these results with the bare PES membrane.

However, there are certain limitations associated with this study. For instance, the experimental setup lacks the capability to assess membrane fouling under a continuous flow of fresh solvent (as opposed to a closed loop). This limitation prevents us from measuring the total loss of CuO over the filtration time. In our closed-loop setup, the mass balance effect helps mitigate the leaching of copper into the solution after equilibrium is reached. Another limitation to consider is the potential detachment of the thermo-responsive polymer in a real-life application. The force required to detach dead bacteria from the surface may also remove the polymer chain. In conclusion, a commercial evaluation of these new samples is essential to precisely define their potential cost benefits. The current scale of our samples is too small to offer a sufficient justification regarding the operating cost of the modified membrane.

Chapter 7 – Conclusions and Future Directions

1. Concluding remarks

This chapter describes the scope and focus of the research presented in a dissertation on PES membrane surface modification with thermo-responsive polymers and metal oxide nanoparticles. The dissertation aims to provide a comprehensive understanding of how such modifications impact the membrane's surface properties, filtration, fouling, and separation performance. Additionally, the dissertation presents practical solutions to address the challenges in the field of membrane filtration, including altering surface hydrophilicity, surface charge, and introducing stimuli-responsive characteristics. The main conclusions of this research work are summarized and provide insight into the findings and contributions of the dissertation.

1. The effectiveness and durability of polymeric membranes for oil/water separation and wastewater treatment are determined by their surface chemistry, morphology, and roughness.
2. PNIPAm grafting onto the membrane surface as a thermo-responsive layer occurs via a covalent bond in the presence of a redox system ($K_2S_2O_5$ and $K_2S_2O_8$)
3. The membranes grafted with thermo-responsive materials showed an increase in surface hydrophilicity. The highest degree of grafting yield resulted in the highest degree of hydrophilicity.
4. The receding contact angle of the thermo-responsive grafted membrane changed with variations in solution temperature. In contrast, this value remained constant for the

pristine PES membrane and those that were not modified with TRPs, indicating the phase volume transition behavior of PNIPAm in this study.

5. The incorporation of acrylamide functional group (AAm) into the PNIPAm structure led to a reduction in volume phase transition, which was evident from a smaller change in the receding contact angle as the feed solution temperature changed.
6. The immobilization of copper oxide (CuO) nanoparticles onto the membrane surface was facilitated using an arganosilane ligand (APTES).
7. The incorporation of CuO@APTES nanoparticles onto the surface of the PES membrane resulted in a significant decrease in surface hydrophilicity, which can be attributed to the hydrophilic nature of CuO and APTES.
8. The functionalization of PES membrane with thermo-responsive polymers and copper oxide nanoparticles affected the water flux of the membrane, enhancing it due to the increased surface hydrophilicity and wettability of the modified membrane.
9. Surface modification of the PES membrane resulted in an improvement in the membrane's fouling behavior, as evidenced by a significant increase in both the flux recovery ratio and the reversible fouling ratio. The enhancement in flux recovery ratio was solely attributed to the presence of PNIPAm on the surface, which undergoes a shape change from coil to globule in response to the cleaning solution temperature. This change in shape alters the surface hydrophilicity, facilitating the detachment of foulants from the membrane.
10. The rejection rate of BSA was enhanced for membranes functionalized with copper oxide nanoparticles. This enhancement could be attributed to two potential mechanisms: (i) a

decrease in the passage or penetration of BSA molecules due to size exclusion and (ii) a possible interaction between the copper oxide nanoparticles and BSA, leading to the formation of a complex that reduces the passage of BSA molecules through the membrane pores. In the case of oil-water emulsions, the modified membrane showed a slight enhancement in the rejection rate. The primary mechanism for oil separation was size exclusion. Therefore, it can be concluded that the incorporation of copper oxide slightly reduced the surface pore size, resulting in a slight enhancement in the oil-water rejection rate.

11. The thermo-responsive grafted membrane exhibited higher bacteria detachment during washing with both cold (20°C) and warm (45°C) solutions, indicating its anti-adhesion properties and easy-cleaning ability as a smart membrane.
12. The copper oxide-functionalized membrane demonstrated 100% bacteria killing ability, while the thermo-responsive grafted membrane showed no toxicity towards killing *E. coli* bacteria. The morphology of the bacteria on the surface of both membranes further confirmed these results. Significant damage to the outer shell was observed in bacteria attached to the CuO-functionalized membrane. In contrast, the bacteria attached to the bare or thermo-responsive grafted membrane were generally smooth and intact, indicating that the cells were normal and healthy.

2. Future direction

In the next section of this dissertation, relevant scientific suggestions and recommendations are provided to offer guidelines for future work.

2.1. Optimizing the PNIPAm grafting condition on PES membrane

In this study we already evaluated the effect of **Processing** (reaction time, temperature, and monomer concentration) on **Structure** (PNIPAm grafting yield), **Properties** (hydrophilicity, surface roughness, morphology, and surface charge), and **Performance** (phase transition behavior, water flux, and membrane reusability). To complement this work, the following studies need to be evaluated: **Processing** (ratio of monomer:reducing initiator, increase of monomer concentration), **Structure** (agglomeration size and distribution), **Properties** (hydrophilicity, surface roughness, morphology, and surface charge, phase transition behavior in the solution using thermal analysis methods like DSC and light scattering), and **Performance** (phase transition behavior, water flux, and membrane reusability).

2.2. Optimizing the grafting conditions for copolymerization of PNIPAM with AAm on PES membrane

Studying the copolymerization of PNIPAM with AAm involves a systematic approach, covering processing, structure, properties, and performance. Here's a step-by-step guide on how to conduct this study:

Design the experiment to evaluate the effect of the temperature range for the copolymerization reaction, the reaction time, concentrations of NIPAM, AAm, and the concentration of the initiators. Define the desired ratio of PNIPAm: AAm based on the application and vary the ratio to

observe its impact on copolymer composition. Use techniques like dynamic light scattering (DLS) or transmission electron microscopy (TEM) to study agglomeration size and distribution. Analyze the copolymer composition using techniques like NMR or MALDI. Use DLS or TEM for agglomeration studies. Assess hydrophilicity, surface roughness, surface charge, and pore characteristics through contact angle measurements, AFM, zeta potential measurement, and SEM. Examine the copolymer's phase transition behavior in the solution using thermal analysis methods like DSC and dynamic light scattering. Perform filtration tests to evaluate water flux and stability. By comparing the results of these experiments, we can understand how the PNIPAm:AAM ratio influences the copolymer characteristics and performance, and optimize the copolymer composition for desired application.

2.3. Grafting of salt responsive polymer on the surface of PES membrane

Salt responsive polymers are a class of smart polymers that undergo a reversible change in their physical or chemical properties in response to changes in salt concentration in their environment. They are also known as ion-sensitive or ionotropic polymers and have applications in various fields, including drug delivery, tissue engineering, and water treatment. Examples of salt responsive polymers include poly(acrylic acid), poly(methacrylic acid), and chitosan. One of their key applications is in the development of smart membranes that can respond to changes in salt concentration. For example, poly(acrylic acid) and its derivatives can be grafted onto the surface of commercial membranes to create salt-responsive surfaces that can selectively filter ions based on changes in the salt concentration of the feed solution. One advantage of salt responsive polymers over thermo-responsive polymers is that they can respond to changes in salt concentration, which is a common stimulus in many industrial and environmental applications.

Salt responsive polymers can also be used to create ion-selective membranes for water treatment applications, whereas thermo-responsive polymers are less well-suited for this purpose.

2.4. Using the thermo-responsive polymer as an additive, blend it with the polymer mixture solution

While grafting offers advantages such as precise control over resulting material properties, the ability to create more stable bonds between polymers, and selective surface property modification, blending provides several benefits:

1. **Flexibility:** Blending allows for a wide range of combinations, making it possible to create materials with a range of different properties.
2. **Scalability:** Blending can be easily scaled up for mass production, making it a cost-effective approach.
3. **Compatibility:** Blending can be used to create materials with improved compatibility, making it possible to mix polymers that might otherwise be incompatible.

The results of our study have indicated that grafting can have a slight impact on the permeation rate while significantly affecting the antifouling behavior of the material. However, it is equally important to consider the effect of blending on these properties. Blending polymers allows for a more flexible approach in tailoring the properties of the resulting material. It is possible to create a range of materials with varying degrees of permeation rate and antifouling behavior through blending. Further investigation into the effect of blending on permeation rate and antifouling behavior is warranted to fully understand its potential benefits.

Chapter 8 – References

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