

**Development of Thin film nanocomposite-supported membranes for
Highly Efficient Water Purification**

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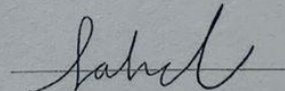
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Dedication

[This work is dedicated to my beloved parents, late. Alh Adamu Abdullahi Danjuma and Haj Maimuna Adamu, for their tremendous support, prayers, and guidance may Allah bless and grant them Al-Jannatul Firdaus, Ameen.]

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LIST OF ABBREVIATIONS

TFN-1: Tested Thin Film nanocomposite (Si-PDA-MM)

TFN-2: Tested Thin Film nanocomposite (Si-APTES-TA-MM)

APTES: (3-aminopropyl)triethoxysilane

TA: Trimesic Acid

MM: Melamine

TMC: Trimesoyl chloride

PDA: Polydopamine

PVDF: polyvinylidene fluoride

Si-NPs: Silica nanoparticles

Si-PDA-MM@PVDF: Si-NPs-PDA-MM Coated PVDF with nanocomposite

Si-APTES-TA-MM@PVDF: Si-NPs-APTES-TA-MM Coated PVDF with nanocomposite

TFN: Thin film nanocomposite

AFM: Atomic Force Microscopy

I.P: Interfacial polymerization

FESEM: Field emission scanning electron spectroscopy.

EDX: Energy dispersive spectroscopy.

|

ABSTRACT

Full Name : [Abbas Adamu Abdullahi]
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Water treatment has become more important in most societies due to the expansion of most economies and significant advances in industrialization. Due to ongoing water problems such as pollution, many parts of the world will suffer from a shortage of drinking water. Nanofiltration membranes are often used in wastewater and pretreatment due to their surface pore size and distinctive functions, enabling them to selectively separate ions from equivalence wastewater and different types. This makes it necessary to quickly create solutions to meet the growing global demand for clean water. Here, the proposed research demonstrates the use of 3-aminopropyl triethoxysilane modified silica nanoparticles, polyamide and functional polyphenylacetyl fluoride chloride (PVDF) for wastewater treatment. The developed thin film nanocomposite was thoroughly investigated through electronic microscopy for field emission survey, contact angle measurement, X-ray diffraction technology, filtration test, atomic force microscope, and infrared spectrometry of Fourier conversion. The nanocomplex of modified thin films was used to investigate and evaluate organic pollutants which include hydrocarbons, heavy metals and salt ions from wastewater. The flow from the membrane reached 27.77 LMH 30 minutes after the initial ultrafiltration test of the nanocomplex, when tested with fresh water, at an applied pressure of 300 kPa, 400KPa, and wastewater was introduced at a stable flow of 18 LMH with Si-APTES-TA-MM@PVDF. Nanofilms with modified thin films > 90% rejection of magnesium, sulfate, cobalt ions and lead ions when tested with the Si-g-Pam nanocomposite and 100% Hydrocarbons (pentanes, isooctane, toluene, hexadecanes).

ملخص الرسالة

الاسم بالكامل: عباس آدم عبد الله
عنوان الرسالة: تطوير الأغشية المدعومة بالمركب النانوي الرقيق من أجل تنقية المياه عالية الكفاءة
تاريخ الدرجة: مايو 2023

أصبحت معالجة المياه أكثر أهمية في معظم المجتمعات بسبب توسع معظم الاقتصادات والتقدم الكبير في التصنيع بسبب مشاكل المياه المستمرة مثل التلوث، ستعاني أجزاء كثيرة من العالم من نقص مياه الشرب. غالبا ما تستخدم أغشية الترشيح النانوي في مياه الصرف الصحي والمعالجة المسبقة بسبب حجم مسام سطحها ووظائفها المميزة، مما يمكنها من فصل الأيونات بشكل انتقائي عن مياه الصرف الصحي المكافئة وأنواع مختلفة. وهذا يجعل من الضروري إيجاد حلول بسرعة لتلبية الطلب العالمي المتزايد على المياه النظيفة. هنا، يوضح البحث المقترح استخدام جسيمات السيليكات (PVDF) النانوية المعدلة 3-أمينوبروبيل تريثوكسيسيلان والبولي أميد وكلوريد فلوريد البوليفينيلسيل الوظيفي لمعالجة مياه الصرف الصحي. تم التحقيق بدقة في المركب النانوي للأغشية الرقيقة المطورة من خلال الفحص المجهر الإلكتروني لمسح الانبعثات الميدانية، وقياس زاوية التلامس، وتكنولوجيا حيود الأشعة السينية، واختبار الترشيح، ومجهر القوة الذرية، وقياس الطيف بالأشعة تحت الحمراء لتحويل فورييه. تم استخدام المركب النانوي للأغشية الرقيقة المعدلة للتحقيق في الملوثات العضوية وتقييمها والتي تشمل الهيدروكربونات والمعادن الثقيلة وأيونات بعد 30 دقيقة من اختبار الترشيح الفائق LMH الملح من مياه الصرف الصحي. وصل التدفق من الغشاء إلى 27.77 الأولى للمجمع النانوي، عند اختباره بالماء العذب، عند ضغط مطبق قدره 300 كيلو باسكال، 400 كيلو باسكال، وتم تم إدخال Si-APTES-TA-MM@PVDF مع LMH إدخال مياه الصرف الصحي عند تدفق مستقر قدره 18. أفلام نانوية ذات الهيدروكربونات (البنتانات والإجوكتان والتولوين والهيكساديكان).

CHAPTER 1

INTRODUCTION

1.0 Background

The need for freshwater is under tremendous strain due to the growth of industries such as petrochemicals, textiles, agrochemicals, and mining industries. The scarcity of water due to its limited supplies in so many locations has created a serious threat to human survival, therefore recycling the effluent must be done properly (Seah et al., 2022). A major environmental problem is the presence of pollutants in water and wastewater streams, including drugs, dyes, heavy metals, hydrocarbons, and salts. Most of these pollutants are hazardous and harmful to humans and aquatic. The concentrations of organic micropollutants are frequently found in the nanogram to microgram per liter range. They could pose significant health concerns to both people and aquatic habitats. They can be discovered in soil sediments, freshwater reservoirs, natural bodies of water, and water treatment effluents (Yousaf et al., 2022). Because of population increase, droughts, and pollution brought on by the expansion of industry, the availability of fresh water is limited (Mohammad Mehrabi et al., 2022). Water is an essential resource for many economic sectors, including health, industry, and household use. Scientists have been searching for better water sources and the replacement of hazardous water due to the rising demand for fresh water and its rapid depletion (Deepa Suresh et al., 2022). Heavy metals such as strontium, lead, and magnesium are present in significant amounts in the wastewater discharged by metallurgical industries, alloys-smelting, and naturally occurring minerals processing industries. Unfortunately, the accumulation of these metal ions over time has a detrimental effect on the environment and biodiversity and puts human life at risk for major adverse health effects later in the food chain because they are persistent and not biodegradable (C. Liu et al., 2017). Another prominent component that contaminates water is sulfur-containing compounds. Although these compounds are typically found in low concentration, they can nonetheless have an impact on safety, cause equipment to corrode, and have an unpleasant odor. Since sulfur diffuses into groundwater aquifers, it affects biomes and aquatic habitats, making sulfur toxic from an environmental standpoint (Azizi Namaghi et al., 2019). Salts and heavy metal ions, including chloride, mercury, sulfate, lead, strontium, calcium, and potassium, are found in large quantities in seawater. During desalination, the scaling of pipes is caused by calcium, chloride, magnesium, and sulfate ions. Scaling or pipe fouling can be avoided by removing these divalent ions. The development of novel membranes with enhanced permeating flux has profited immensely from

the discovery of nanostructured materials. Polymeric membranes have been surfaced and functionalized to provide properties like hydrophilicity and toughness to increase membrane water permeance.

Contamination of water is a serious environmental challenge that has terrible consequences for both humans and aquatic life. Oil and organic spills are the main causes of water pollution (Kabiri et al., 2014). The industrial revolution in the 18th century shows that there has been an upsurge in the demand for fossil fuels and by-products of crude oil. As a result, the oil must now be often transported offshore from the site of production to the point of demand (Aguilera et al., 2010). The water quality is being destroyed by the frequent oil spill incidents and the massive oily wastewater discharge from sectors such as petrochemicals, textile and leather, lead, cadmium, metal finishing, oil, and food. Contamination of water is not only harmful to human health but also has a destructive effect on aquatic life and almost individual species across the marine food chains are affected (Gupta et al., 2017). Water treatment has turned out to be more important in most societies due to the expansion of most economies and the considerable advancement of industrialization (P. Gao et al., 2021).

Currently, there are millions of people without access to clean water who suffer from illnesses brought on by contaminated water (Mruthunjayappa et al., 2020). A serious threat to humanity is the conflagration of "water pollution." A hazardous and cancer-causing metalloid called arsenic enters the water supply from both natural and man-made sources. The largest case of "mass poisoning" in the world is unquestionably arsenic pollution. It can exist in natural water in many forms, including As^{3+} and As^{5+} (A, 2018a). Natural occurring contaminant such as lead, nickel, and cadmium's concentrations rely on the geological materials' composition through which the groundwater flows and the recharge's quality water. flowing through sedimentary rocks with groundwater. Soils may absorb a variety of substances, including Arsenate, fluoride, magnesium, calcium, and chloride. The impact of these natural contaminations varies on their types and amounts of nitrate, iron, and other contaminants (Sharma & Bhattacharya, 2017a). The fundamental component of membrane processes, which determines how effectively oily wastewater is separated overall, is the membrane (Ahmad et al., 2018).

This study will use the sol-gel method to synthesize various types of surface-coated Si-NPs incorporated with PDA-MM-MPD-TMC and in comparison, with APTES-TA-MM-MPD-TMC via in-situ for thin film nanocomposite nanofiltration membrane to further improve the quality and intrinsic properties of nanoparticles and nanomaterials for thin film nanocomposite membranes. By utilizing the SterlitechTM thin film cell tester machine, it is interesting to examine the interactions between the two superhydrophilic surface coatings on the

Si-NPs and how the surface chemistry modifications may impact the properties of thin film nanocomposites that were suggested for the treatment of synthetic water or brine, it is intended to compare the rejection efficiency and the flux of the two thin film nanocomposites membrane for removal of lead, cobalt, sulfur, strontium, and hydrocarbons under an applied pressure of 300 KPa.

1.1 Nanofiltration

Membranes for nanofiltration (NF) are frequently employed in wastewater and pre-treatment because of their surface pore volume and distinctive functionality, which enable them to selectively separate ions from wastewater of different valences and species. This makes it necessary for solutions to be created quickly to meet the growing worldwide demand for clean water. (Cheng et al., 2022). Hoek was the fore-fronter that was successful in the inclusion of NaA zeolite NPs in a Polymeric nanostructured layer and, the TFN membrane considerably increased with the minimal depreciation in salt ions rejection (Gong et al., 2020). Therefore, more research into membrane surface modification which does not only improve water filtration and separation performance but simultaneously imparts antibacterial characteristics for antifouling purposes, thereby surface modification provide low resistance to water permeation. Yang describes a simple process for creating an innovative high-performance thin film composite membrane, they produce nanovoids by etching nanoparticles embedded in the Polyamide-Polysulfone interface. When the membrane was tested with an applied pressure of about 10-25 bar, the etched thin film composite portrayed a huge flux of about 2.6 times compared to the unetched TFC, with a 70% rejection for chloride ion. The flux and the applied pressure gotten from the etched TFC showed a linear relationship which was in line with other reported literature (Yang et al., 2019).

1.2 Statement of the problem

Water purification has turns out to be more important in most society due to expansion of most economy and the considerable advancement of industrialization. Because more pollutants, including dyes, pharmaceutical wastes, organic pollutants, and heavy metal components, are contaminating fresh water, which are generated by industries, urban, and mining processes, all these are the primary causes of drinking water shortages. Various regions of the planet will suffer drinking water shortages because of ongoing water issues such as pollution. **Thin film nanocomposites such as nanofiltration membranes** have recently been used in the treatment of wastewater (Gao et al. 2021).

1.3 Objectives of the study

The aim of the proposed work is to synthesize a new set of inexpensive, highly effective ***in-situ* Si-g-Pam TFN nanocomposite membranes for wastewater treatment**. The specific objectives of this research are :

- Synthesizing silica, graphene oxide nanoparticles modified with APTES-TA-MM, MPD-SA and will be used in functionalizing PVDF substrate.
- Characterizing the prepared nanocomposites by field emission scanning electron microscopy- energy dispersive spectroscopy, contact angle measurement, X-ray diffraction, Fourier transform infrared spectroscopy, and atomic force microscopy.
- Investigate the TFN membrane's efficiency and flux of the wastewater using SterlitechTM membrane Test Cell Machine.

1.4 Significance of the study

The most effective membranes for desalination and organic pollution removal are thin film nanocomposite membranes. These membranes improve productivity and selectivity while using less energy than conventional asymmetric membranes.

1.5 Scheme of research findings reporting

Below is a summary of the order of this thesis report which was organized and arranged in chronological manner into five chapters for easy reading and comprehension:

Chapter 1: Comprises of a general introduction on wastewater, and the causes of contamination of freshwater. Specific objectives of the study was highlighted and a brief significance of the study.

CHAPTER 2: Provides a brief literature review on the basic considerations in freshwater treatment, several studies that have been carried out on coating materials as well as their efficiencies with respect to wastewater treatment.

CHAPTER 3: Describes a detailed studies between two novel thin film nanocomposite membrane which were prepared using *in-situ* sol-gel one pot method and were fabricated using Silica nanoparticles alongside with modification using, polydopamine, melamine, Trimesic acid, m-phenylene diamine and trimesoyl chloride on polyvinylidene fluoride substrate.

CHAPTER 4: Illustrates the preparation of Silica nanoparticles functionalized with 3-(aminophenyltrioxysilane), incorporated Trimesic acid and melamine on polyvinylidene substrate for retrieval of freshwater from contaminated water.

CHAPTER 5: Describes the preparation of nanocomposites of reduced graphene oxide functionalized with 3-(aminophenyltrioxysilane), incorporated Trimesic acid and melamine on polyvinylidene substrate for the treatment of wastewater.

Chapter 6: Gives the summary and the conclusion of the work.

|

CHAPTER 2

LITERATURE VIEW

Sahoo developed a switchable wettability hierarchical bead-like porous fibrous membrane for oily sewage treatment, and this was achieved using nonsolvent-induced phase separation. The membrane's flux stretched out to be around $186.80 \text{ L/m}^2\text{h}^1$ with a separation efficiency of 99.20% (Sahoo & Balasubramanian, 2015), (Mruthunjayappa et al., 2020), (Low et al., 2015). In another study, Gao and Y. Chen designed an interlayer-controlled nanofiltration membrane by incorporating an MXene/CNC framework with high heavy metal ions and permeability-selectivity upper-bound breaking capabilities. They found a significant increase in water permeability of about ($31.68 \text{ LMH bar}^{-1}$) when the membrane was tested (H. Gao & Chen, 2022). Also, R. Joshi *et al.*, utilized micro-fibrillated cellulosic membranes as a scaffolding material, in demonstrating a novel superhydrophobic hybrid cellulosic membrane system with a dual-layered hydrophilic and hydrophobic structure. The membrane was tested for brackish and seawater, and the membrane was found to maintain surface hydrophilicity when tested for hydrocarbons and water separation (Joshi et al., 2022), (Chen et al., 2018). Gao, P, and co-workers successfully synthesized a high-flux fine hollow fibre nanofiltration membrane, in which a polysulfone-ultrafiltration membrane with an external diameter of around 425.00 m was used as the substrate to create a high-flux membrane using the process of interfacial polymerization (IP) for the purification of wastewater. Trimesoyl chloride was anchored as the organic monomer, and piperazine (PIP) aqueous phase solution was reinforced with poly (vinyl alcohol) (PVA) to minimize surface imperfections and to improve the nanofiltration membrane's separation capabilities. When tested, the membrane's flux stretched out to be around $34.19 \pm 1.5 \text{ LMH/Bar}$ (P. Gao et al., 2021). Also, Guzman used interfacial polymerization in fabricating a TFN nanofiltration membrane, while experimenting with three diamines to see which would result in the best-performing composite membrane, the chemical structure of the trimesoyl chloride and m-phenyldiamine was changed. He found out that this class of thin film composite class of membrane is most effective for wastewater treatment and industrial gas separations and many more. The composite membrane showed a flux of about (J_w) of $18.24 \pm 1.33 \text{ L m}^{-2} \text{ h}^{-1}$ and a reverse salt flux (J_s) of $5.75 \text{ G m}^{-2} \text{ h}^{-1}$. (de Guzman et al., 2021). (Ong et al., 2020).

Another study uses methyltrichlorosilane to modify a polyamide thin film nanocomposite and this was used for nanofiltration. When the nanocomposite was tested, the composite revealed an increase in flux and water-salt separation, with a maximum flux increase of about $4.70 \text{ L/m}^2\text{h}^1\text{bar}$, and 99% increase in water

permeability (Shen et al., 2019). Yuling and co-workers highlighted the synthesis of high-operational thin film nanocomposite for water treatment, the composite was formed by o-Porous organic polymers. The interfacial polymerization process was used in adding o-hydroxy porous organic polymer nanofillers to give the proposed TFN membrane. After testing it, the result reveals that the TFN has an excellent bivalent salt ions rejection of about 97% for sulfate ion with a flux of about 30 LMH/bar which was three folds compared to commercial film membrane (Ren et al., 2019). Butler reported the synthesis of TFC and TFN membranes for nanofiltration application, they compared the permeability of poly(m-phenylenediamine trimesamide)-TFC and that of MIL-101 loaded on poly(piperazine trimesamide), these polymers were used to produce a thin film nanocomposite while using NO₂-benzene as the organic phase. It was found that the latter has a high surface roughness than TFC, and the TFN shows a permeance of about 1.9 folds than TFC for methanol, with a rejection of 90% (Butler et al., 2020). A TFN was prepared by Li, and covalent organic frameworks watershed as a surface modification, by incorporating it with a polyamide substrate, it turns out that the observed flux showed a solute rejection for solvents from organic constituents, there was an increase in the rejection of Rhodamine B reaching 99.4%, with an observed flux of 79.80 LMH megaPa⁻¹ with an increase in ethanol rejection, and this increase in rejection for ethanol was due to the surface modification of the substrate layer making it more hydrophilic (Li et al., 2019). Also (Mengjiao Xia et al., 2022) designed a high-performance polyamide membrane with an interlayer of ZIF-8 NPs, and was also used for divalent ions filtration. The proposed membrane exhibited rejection of about 96.6 % for divalent SO₄²⁻ with a 20.70 LMH/Bar.

In a different study, a metal-organic framework was incorporated with a PSF substrate with MOFs nanosheets to form a TFN membrane. The membrane was utilized for salt ions separation. The rejection for Na₂SO₄ reached 99.7% which was due to the membrane's high selectivity with a permeate flux of 32.7LMH/Bar in comparison to when MoS₂ was used as the surface functionalization agent. Recently, a study revealed that amorphous perfluoro polymers can be used to synthesize a hydrophilic ultra-TFC membrane with a highly selective layer for water and salt separation, the composite shows a filtration property for Li⁺, hydrocarbon (methanol), Na⁺, and dyes. The proposed membrane has a rejection of about 95.2 % for Na₂SO₄ compared to commercial membranes in terms of nanofiltration test, with one of the proposed membranes tagged PES1K having a lower flux of about 0.07 LMH/bar when tested theoretically for water permeance filtration test (Ameya Manoj Tandel et al., 2022).

2.1 Membrane

Membranes can be considered hydrophilic or hydrophobic based on how they interact with water.

- **Hydrophobic membranes**

- Water is repelled from pores and droplets form spherical shapes on the membrane surface.
- Used for air/gas filtration & Venting, with the contact angle $> 90^\circ$

- **Hydrophilic membranes**

- Water is spontaneously drawn into pores and saturates the membrane
- Used for filtering water-based fluids, with the contact angle $< 90^\circ$

2.2. Various materials used in coating membrane for water treatment purpose from the Lit.

Coating Materials	Membrane	Contaminant removal	Rejection rate %	Flux (LMH)	Refer.
TFN-ZIF-8@TA1.0	NF	Na ₂ SO ₄	96.6	20.7	(Mengjiao Xia et al., 2022)
COFs-TFN	NF	Rhodamine B (479 Da)	99.4	79.8	(Li et al., 2019)
PA/TiO ₂	NF	Sulfur	97	16.3	(Azizi Namaghi et al., 2019)
MIL-101	NF	MeOH	95.7	4.9	(Butler et al., 2020)
POPs	NF	Na ₂ SO ₄	97.5	29.9	(Ren et al., 2019)
MWCNT	NF	MgCl ₂ , Co ²⁺ , Zn ²⁺	95, 80, 73	18	(Liu et al., 2017)
<i>p</i> -aminophenol modified GO	NF/RO	NaCl	99.7	23.6	(Yan Zhang et al., 2020)
PA/UIO-66-NH ₂	NF	Na ₂ SO ₄	97.1	46	(Gong et al., 2020)
PES/PVDF/GNPs	NF	Phenol	80	30	(Salawudeen et al., 2019)
MeSiCl ₃ -Pam	RO	Bovine serum albumin (BSA), sodium alginate (SA),	96	18.5	(Shen et al., 2019)

Table 2.1 Coating materials and rejection efficiency used for various nanofiltration studies

CHAPTER 3

***IN-SITU* Si-PDA-MM AND *IN-SITU*-Si-ATES-TA-MM**

CHAPTER 3

3.1 Introduction

This study uses the solution-gelation method in synthesizing various types of surface-coated Si-NPs incorporated with PDA-MM-MPD-TMC and in comparison, with APTES-TA-MM-MPD-TMC via *in-situ* for thin film nanocomposite nanofiltration membrane to further improve the quality and intrinsic properties of nanomaterials for thin film nanocomposite membranes. By utilizing the SterlitechTM thin film cell tester machine, it is interesting to examine the interactions between the two superhydrophilic surface coatings on the Si-NPs and how the surface chemistry modifications may impact the properties of thin film nanocomposites that were suggested for the treatment of synthetic water or brine. It is intended to compare the rejection efficiency and the flux of the two thin film nanocomposites membrane for removal of lead, cobalt, sulfur, strontium, and hydrocarbons under an applied pressure of 300 KPa.

3.2 Experimental section.

3.2.1 Materials and chemicals used for the study.

The chemicals that were utilized for the study were gotten from Sig-ma Aldrich, some of them includes polydopamine (PDA), n-hexane (C_6H_{14}) 99.0% purity, DCC, m-phenylenediamine (MDP) ($C_6H_8N_2$, 99 % purity), melamine MM, trimesoyl chloride (TMC), dimethylformamide DMF, silica nano powder). The base material which was used as the substrate was a powder made of polyvinylidene fluoride $M_w 25 \times 10^3 \text{ g mol}^{-1}$), Nice Chemicals provided the following chemicals for the process: ethanol, hexadecane, toluene, pentane, strontium sulfide, lead (II) nitrate, isooctane, and nitric acid. All of these chemicals are of analytical grade and require additional treatment or purification. Polyvinylpyrrolidone PVP (molecular weight of $25,000 \text{ g mol}^{-1}$) was from Merck and was employed as an additive for substrate synthesis. Deionized water was produced from a real-time Milli-Q Ultrapure water system that was used for the reaction.

3.2.2 Preparation of the Nanocomposites.

1.5g of Silica powder was weighed and poured into a 300ml round bottom flask and was dissolved by the introduction of 50ml ethanol, the solution was ultrasonicated for 45 mins to make it homogeneous. 5ml of ammonium hydroxide was added to the solution dropwise to initiate OH bond formation forming the $Si(OH)_4$. Furthermore, 0.5g of PDA was added to the $Si(OH)_4$ and was ultrasonicated for 1 hour and later refluxed for 5 hours at a temperature of 70°C . A slightly pale brown solution was acquired and the mixture was later reacted with 0.2g of Melamine (MM), under nitrogen gas intake for about 10 minutes to remove water

bubbles and form an inert environment, this resultant solution was refluxed for about 22 hours , the PDA hydroxyl layer is oxidized in the process with a trace amount of sulphuric acid giving the melamine's amine branch to bind with the host molecule, in which the electronegative oxygen atom donates it lone pair to the deficient N-atom of the melamine, which formed a new bond --O-NH-. Then modified composite was then dried under vacuum for about 2 days at room temperature to form the nanocomposites (Si-PDA-MM), as shown in the figure below:

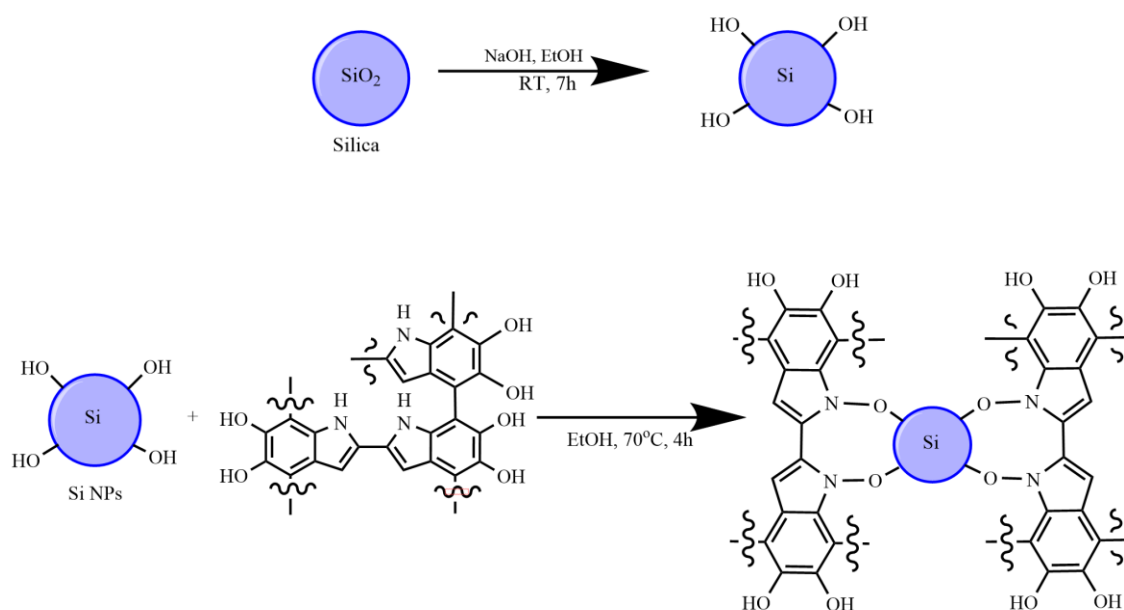


Figure 3.1. Preparation of (a) Silica nanoparticules (Si-NPs), (b) Si-PDA

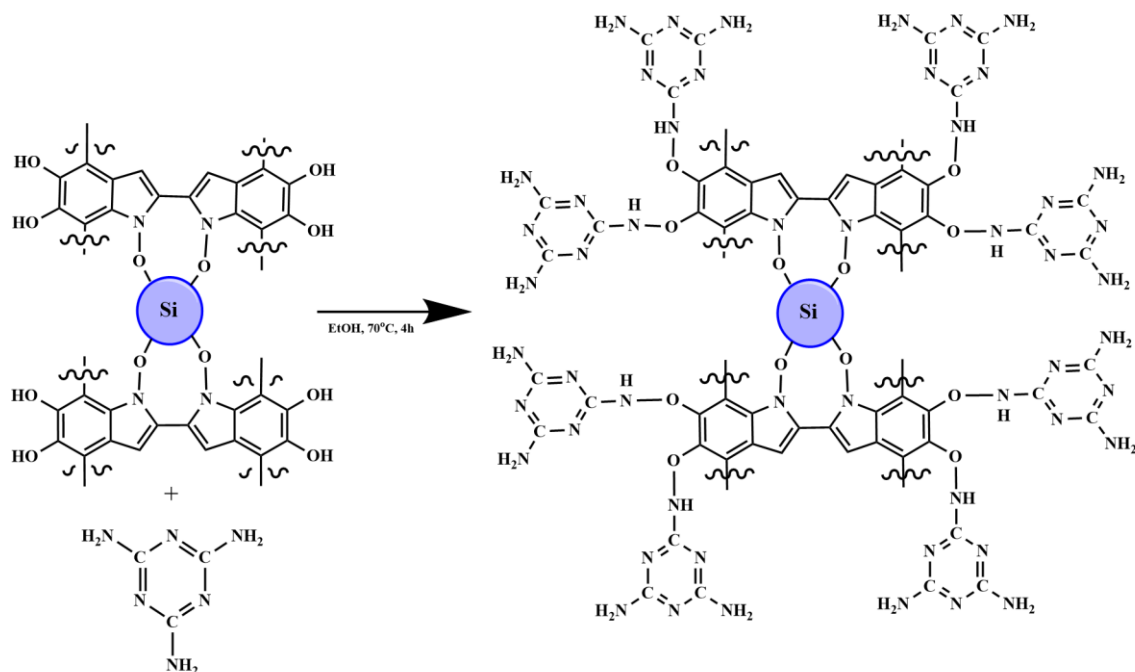


Figure 3.2. Si-PDA-MM nanocomposite.

Also, Si-APTES-TA-MM nanocomposite was synthesized using the method used by/in ([Abbas et al.,](#)). Chapter 4, experimental section.

3.2.3 Measurements and Characterization

The surface morphologies of the functionalized *in-situ*-Si-PDA-MMF@PVDF membranes were studied using the FESEM-EDX at a voltage of 20kV. Chemical compositions of the TFN were characterized by high-resolution XRD D8 Advance, Bruker, Germany) with Cu, K radiation at a continuous scanning mode (40 kV, 40 mA, and $\lambda = 0.15418$ nm) and a scanning rate of 5 deg./min and a range 3 - 90 ° was used to determine the crystalline and amorphous phase. The functional groups that took place during the interfacial polymerization and in the nanocomposite fabrication was investigated using a smart iTR Nicolet is10 FT-IR spectrophotometer. While the nanocomposite morphology and elemental composition was accessed using FESEM-EDX.

3.2.4 TFN permeability and separation efficiency test.

Table one below shows the contaminants and their concentrations as used during the study, and **figure 5** shows the crossflow of the cell tester used, which has a cross sectional area of 36 cm² for membrane test. A pressure of about 300 KPa was used in determining the flux capability of the fabricated membrane as well as the separation efficiency of the TFN, this test was done at 25 °C. Prior to the filtration test, portion of the membrane was sliced and placed in the cell of the machine and ran with 2L of distilled water for about 4 h before introducing the brine solution. The purpose was to achieve a stable condition before the filtration process. A chosen interval of 30 mins consecutively was used in collection of the permeate solution in a 10 ml graduated cylinder, thereby accessing the permeate and the rejection ability of the Si-PDA-MM-TMC@PVDF, and Si-APTES-TA-MM@PVDF composites as well as the flow rate. The contaminants that were determined were hydrocarbons which consist of isooctane, hexadecane, pentane, and toluene, while the heavy metals were strontium, lead, cobalt and magnesium and the salt was sulphate. Sulphate salt ion was considered for this study this is because, in the middle east there is high concentration of sulphate ion dissolved in the water body and therefore there is need for a sustainable solution, this is why the concentration was about 4000 ppm compared to other contaminant's concentration accessed in the study. Inhibition of salts, heavy metals, and organic molecules was measured by keeping track of changes in the permeate water concentration both before and after treatment with the membrane, using the equation below, the permeability of the TFN was determined.

$$J_w = \frac{V_w}{A_M \Delta t} \quad (\text{Eq. 1})$$

Where:

J_w = permeate flux (L m⁻² h⁻¹),

V_w = change in the volume of the permeated water (L),

A_M = effective area of the inserted membrane (m²), and

Δt = time of collecting the permeated water (h).

Also, the following formula was used to determine each contaminant's percentage rejection,

Equation 2:

$$\% R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100 \quad (\text{Eq. 2})$$

Where:

C_{feed} = concentration of the feed tank (ppm) and $C_{permeate}$ = concentration of the permeated solution (ppm).

N ₀	Samples	Concentration (ppm)	D ₀ Tank	Bulk Compound
1.	SO ₄ ²⁻	4000	4000	MgSO ₄
2.	Pb ²⁺	208	208	Pb(NHO ₃)
3.	Co ²⁺	100	100	CoCO ₃
4.	Sr ²⁺	100	100	SrCO ₃
5.	Mg ²⁺	250	250	MgSO ₄
6.	Hexadecane	500	500	-
7.	Pentane	500	500	-
8.	Toluene	500	500	-
9.	Isooctane	500	500	-

Table 3.1: The constituent's composition.



Figure 3.3. wastewater and permeate water.

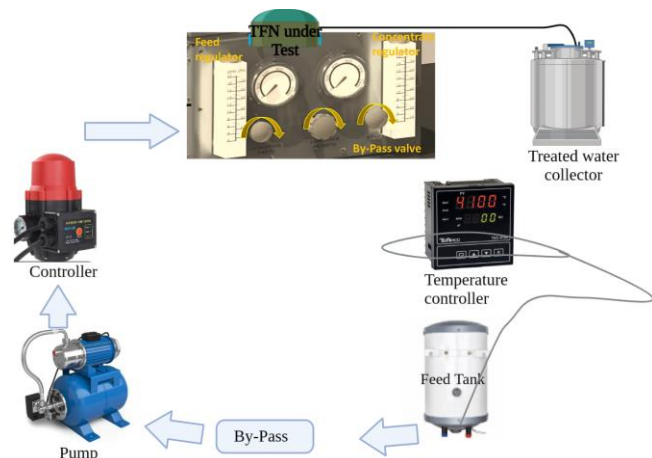


Figure 3.4. Sterlitech TM cell test machine arrangement as used for the study purpose.

3.2.5 Substrate preparation

The PVDF substrate was synthesized by dissolving 0.2g of PVP in 10ml DMF , followed by ultrasonication for 10 mins. Then 2.2g of PVDF powder was also dissolved in a separate beaker in the presence of 20ml DMF, and the solution was stirred to attain a homogenous mixture. Then the PVP was added to the to the PVDF solution and furthermore about 200 mg of Si-PDA-MM was added to the above solution which gave rise to an *in-situ* nanocomposite solution and, the resultant solutions were stirred for 20 hours (500 rpm @ room temperature). PVP was used in other to create a self-assembly of the nanocomposites by acting as a surface directing agent (Koczur et al., 2015). The mixture was then casted using the glass plate casting knife method and after 2-5 mins of casting the produced support was dipped into 450 ml double distilled water for about 20 hours, to form polymerization. Following the next day , To eliminate contaminants, Deionized water was used to clean the PVDF support before it was submerged in 300ml 0.1M HNO₃ to remove impurities and to attain 100% purity of the support (Aya Y Ibrahim et al., 2022), after soaking, the PVDF was stored under vacuum until when used.

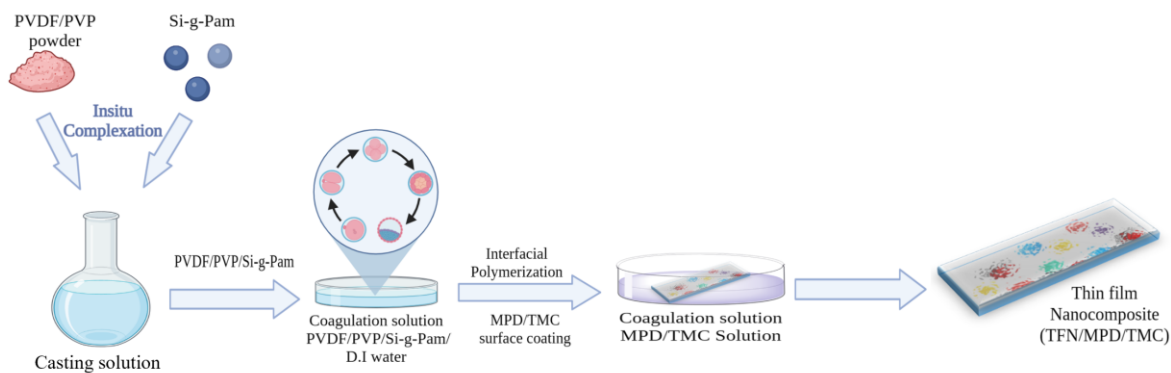


Figure 3.5. Representation of the synthesized TFN which was used for the studies.

3.2.6 Modified PVDF (nanocomposite) preparation

About 36cm² area of the produced PVDF was sliced and immersed in a diluted HNO₃ solution to moisten the pores and activating the active phase of the functional groups in the surface of the PVDF, and this process was followed by further rinsing with distilled water and subsequently coated with 0.6 wt. % of trimesoyl chloride/n-hexane, followed by 0.3 wt. % of MPD, allowing just the surface portion of the PVDF substrate to get in contact with the TMC/MPD solution, while excess TMC was removed using a rubber roller. And the thin film nanocomposite was allowed to dry under vacuum for about 2 hours before testing with the sterlitechTM cell tester membrane machine. The coagulation solution of MPD/TMC was used in the study to make the TFN surface more superhydrophilic, as was depicted in figure 3.2 above.

3.3 Results and Discussion.

3.3.1 PVDF substrate Functionalization.

The substrate was coated with Si-PDA-MM nanocomposite and further incorporated with TMC. TMC was used to increase the hydrophilic behavior of the TFN and as well as the surface wettability. Due to the polydopamine and melamine functional groups. The functionality of the substrate shows a tremendous behavior towards the filtration mechanism and inhibiting the passage of contaminants species, which includes -OH, NH₂, Cl⁻, and -COOH. A dense cross-linked polyamide layer of PDA-MM-TMC was formed after the

primary and secondary NH_2 reactions with the acyl chloride, making the layer extremely hydrophilic. The reaction mechanism and the conditions used for the study were given in **Figure 3.2** above.

3.3.2 FT-IR Results of the nanocomposites and the thin film nanocomposite used for the study.

After successfully incorporating the Si-PDA-MM@PVDF membrane, functional groups elucidation of the TFN membrane was done to scientifically establish the chemical attachment that forms the interfacial polymerization process and as well as the cross-linking of PDA-MM with the TMC. ATR-FTIR was used for exploring different functionalities present for the active layers which were contributed in the process as shown in **Figure 3.6**. The FTIR spectral from the PDA and MM showed the characteristics bands which portrayed the primary and secondary group of the Amine. For MM, the two bands in the region of 1632cm^{-1} and 1650 are attributed to the amine functionality from the melamine. However, the Si-PDA-MM also showed a peak for the amine group around $3490.70/\text{cm}$ and $3450.41/\text{cm}$ which is due to $-\text{NH}_2$ from melamine, a slight obstruction was observed in the bands for MM and that of Si-PDA-MM which was due to PDA incorporated with the MM, that is an amidation reaction took place causing a shift in the band of the observed bands. Also, for the Tested TFN (Si-PDA-MM) spectrum shows peaks around 3500 cm^{-1} portraying the aromatic $-\text{NH}$ bond in the nanocomposite. Moreover, the FT-IR results obtained for the nanocomposite and the fabricated TFN show the peaks obtained in the MM and Si-PDA-MM, confirming the successful interfacial polymerization between the nanocomposite species. As evidence, the active superhydrophilic layer was made, by the reaction of the monomers under different reaction conditions as shown in **Figure 3.6** where the coated layer is visible as a TFN within the interface of the aqueous and the organic phases of the active monomers. Upon establishing this, the fabricated Si-PDA-MM@PVDF before test and after test was recorded as depicted in **Figure 3.6**, the Tested TFN was observed to have a broad band from $3700/\text{cm}$ to $3200/\text{cm}$ which infer the presence of $(-\text{CO}-\text{H}-)$ bond of Si-PDA-MM as shown in **Figure 3.6**. Interestingly, the fingerprint region obtained from the FTIR elucidated the characteristic bands of PVDF substrate and the Si-PDA-MM@PVDF thin film nanocomposite which was used for the study.

3.3.3 FT-IR Results of the nanocomposites and the thin film nanocomposite used for the study (Insitu-Si-APTES-TA-MM).

Also, for Si-APTES-TA-MM in **figure 3.7**. FTIR characterization was done to investigate how the membrane and nanocomposite with functional group appearances were prepared. As seen from the created composite's FTIR spectra, which are shown in Figure 7a. In contrast, in **Figure 3.7b's** Si-APTES-TA-MM, a (-NH) band occurred at 3700 cm^{-1} , indicating a stretching vibration emanating from APTES and Si-NPs due to the presence of highly condensed silica, which has a symmetric siloxane (Si-O-Si) network mix (-NH₂). As well as the weak absorption band at 1020 cm^{-1} for the (C-O) and (C-N) stretching vibrations, the absorption band at 1200 cm^{-1} was attributed to the (aminopropyl)triethoxysilane chain's -C-C- stretching vibration mode. In addition, a second band of 1700 cm^{-1} for (C=N) stretching vibrations from melamine was seen in **Figure 3.7c**. Additionally, after being combined with the composite, the modified PVDF membrane generated a number of main bands. The -OH stretching vibration absorption band was sighted at $3650/\text{cm}$, and it is noteworthy to note that the PVDF chain caused the -CH stretching vibration absorption bands at 2920 cm^{-1} to remain continuously strong. The absorption bands depicted from the modified TFN can be remarkably compared with those observed from the TFN that had been tested, demonstrating the effective incorporation of the composite on the outer layer of the PVDF membrane to provide superhydrophilic behavior.

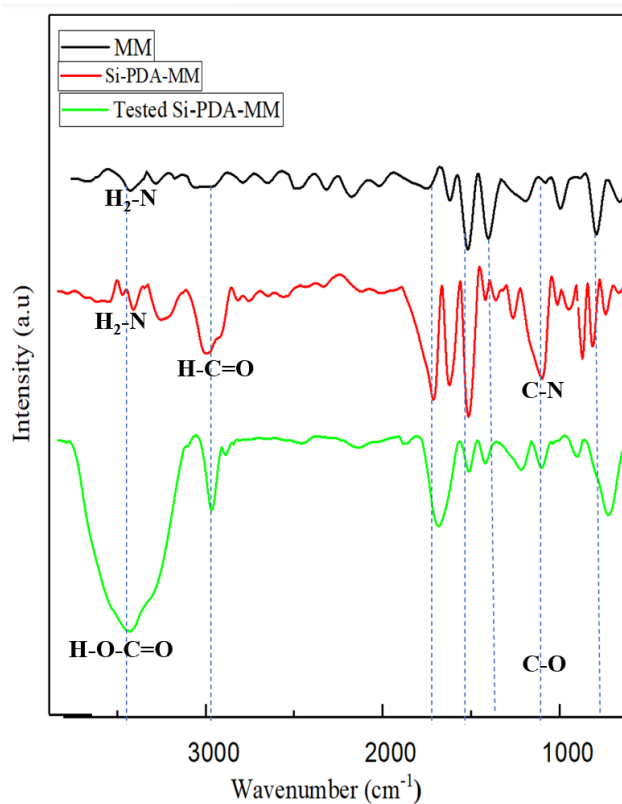


Figure 3.6. FTIR result of the Si-PDA-MM nanocomposite and that of Tested TFN.

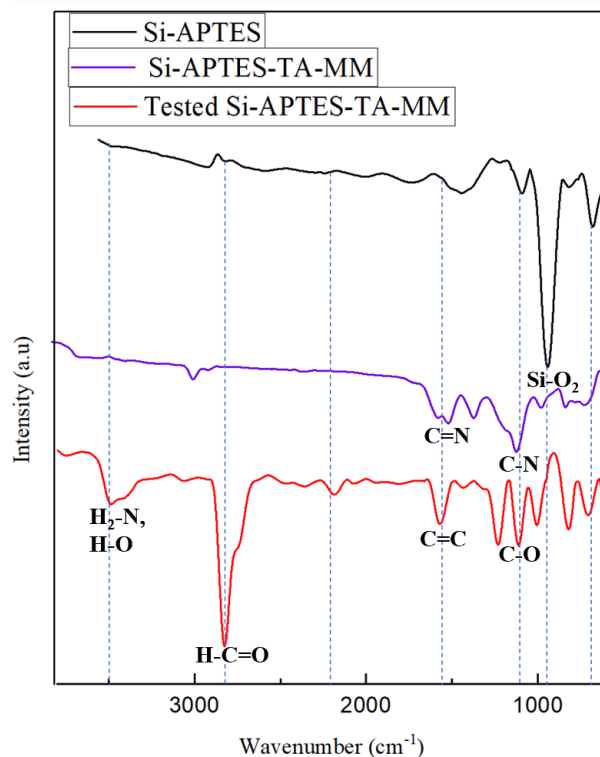


Figure 3.7. FT-IR result of Si-APTES-TA-MM and Tested TFN.

3.4 FE-SEM and EDX of the nanocomposite and thin film nanocomposites were used for the study.

Field Emission Scanning Electron dispersion spectroscopy was used in depicting the elemental composition of the nanocomposite and TFN morphology, as shown in **Figure 3.8**. (**Figure 3.8a**) SEM image of synthesized *in-situ*-Si-PDA-MM nanocomposite. (**Figure 3.8b**) depict the clear EDS of the various elemental composition found on the nanocomposite's surface, with nitrogen having a peak wt. % of 48.2% which is due to the amine group found in both PDA and MM of the nanocomposite, also carbon appeared to be 35.7% which is from the aromatic -C=O and oxygen which was found to be 14.7 % which was from the SiO₂ NPs and lastly Si which is due to the initial nanoparticles of the SiO₂ starting compound. While (**figure 3.8c**) shows the mapping of the nanocomposite, with Nitrogen having a homogenous dispersion than other species with a higher percentage which was about 48.2 %. (**Figure 3.9d**) shows the tested TFN Si-PDA-MM@PVDF, the *in-situ*-Si-PDA-MM@PVDF nanofiltration support showed a uniform distribution of the microporous active phase of the nanocomposite as shown in (**Figure 3.9d** and **Figure 3. 9f**) mapping of the tested TFN. This was achieved due to the successful phase inversion efficiency of dimethyl formamide with

the individual monomers that were used in the support, that is the starting materials (PVP and PVDF powder). However, the interfacial polymerization brought about the deposition of the ***in-situ*-Si-PDA-MM** active layer, covering the PVDF support with a highly dense uniform dispersion. It was observed that (**Figure 3.9d**) appeared rough, which is due to the inhibition of contaminants which were examined for the study. Furthermore, EDX of the Tested TFN in (**Figure 3.9e**) confirms the inhibition of the salts, percentages of heavy metals inhibited with 18.5 % for Pb^{2+} , 8.5 % for Sr^{2+} , 3.3% for S which was from the SO_4^{2-} . The mapping in (**Figure 3.9f**) shows the effectiveness of the rejections and inhibition of the contaminant's species indicated by the percentage increase as shown in the figure:

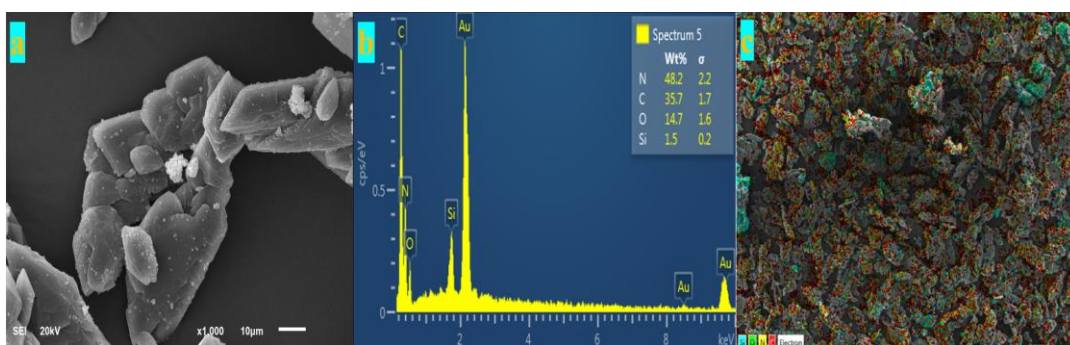


Figure 3.8. a) *Insitu*-Si-PDA-MM nanocomposite b) Nanocomposite EDX c) Nanocomposite Mapping.

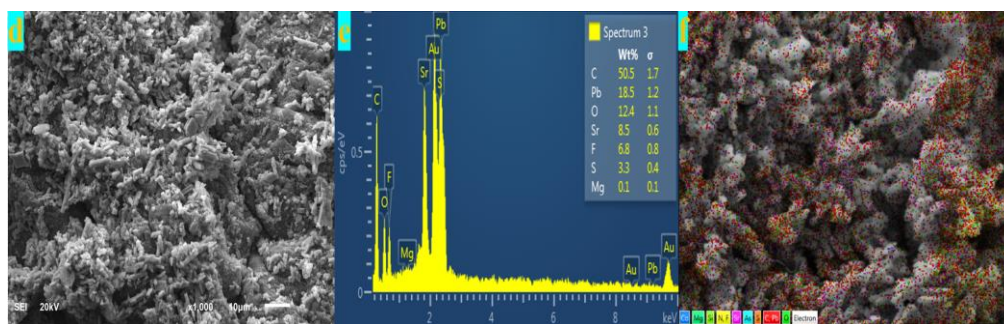


Figure 3.9. d) Tested TFN *Insitu*-Si-PDA-MM e) TFN EDX f) TFN Mapping

3.4.1 FE-SEM and EDS of the nanocomposite and thin film nanocomposites used for the study (*Insitu*-Si-APTES-TA-MM).

In comparison with the ***Insitu*-Si-APTES-TA-MM** nanocomposite, the dispersion of the APTES-TA-MM on the mesoporous silica forms a dense active layer which contributed to the support efficiency. The

modification of the SiO₂ with other nanomaterials gave a homogenous dispersion as depicted in the micrograph in **Figure 3.10g**. Moreover, (**Figure 3.10h**) shows the EDS of the observed nanocomposite, there was an increase in **carbon % from 35.7 % to 58 %** when compared to that of *in-situ*-Si-PDA-MM which was due to the presence of functionality of the **-C=O from the TA and the -CH₂- aliphatic chain** from the APTES, also for the oxygen and nitrogen, the nitrogen was due to the repeated nitrogen species in the melamine, while the Si was due to the functionalization of Si-NPs with APTES, and this was achieved in the presence of ETOH, 70°C. (**Figure 3.10i**) shows the mapping of the *in-situ*-Si-APTES-TA-MM and some important elemental dispersion. It was observed that **Figure 3.11j appeared** rough, which was due to the inhibition of contaminants in the surface of the tested TFN which were examined for the study. Furthermore, EDS of the tested TFN in **Figure 3.11k** confirms the ionization of the salts, percentages of heavy metals inhibited, it was observed that there was an increment in the inhibition of the heavy metals and CO₃²⁻ in trace when **tested with the *in-situ*-Si-APTES-TA-MM** compared to the *in-situ*-Si-PDA-MM. Pb (from 18.5 % to 22.5 %), Sr (from 8.5% to 11.3%), S (from 3.3% to 3.4 %), the sulfur was due to the presence of SO₄²⁻. The mapping in **Figure 3.11l** shows an effectiveness of the rejections and inhibition of the contaminant's species indicated by the percentage increase as shown in the figure, for a clearer understanding, **table 2 and 3 shows the comparison between the two TFN and the nanocomposite used for the study.**

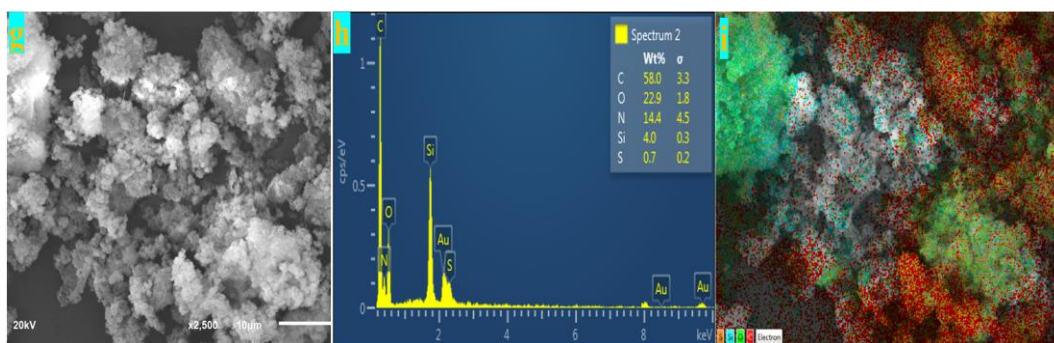


Figure 3.10. g) *In-situ*-Si-APTES-TA-MM nanocomposite h) Nanocomposite EDX i) Nanocomposite Mapping.

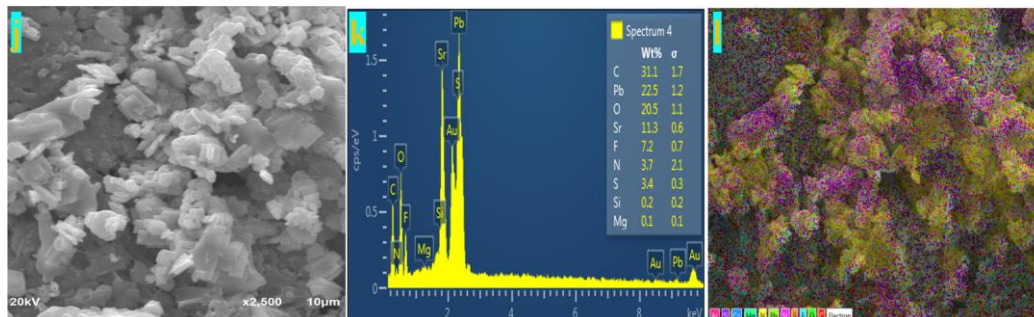


Figure 3.11 j) Tested TFN Si-APTES-TA-MM k) TFN EDX l) TFN Mapping

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Nanocomposite
C	K series	16.77	0.16771	35.67	1.74	C Vit	<i>Insitu-Si-PDA-MM</i>
	“”	31.25	0.31250	57.99	3.30		<i>Insitu-Si-APTES-TA-MM</i>
N	K series	35.37	0.06297	48.15	2.22	-NH ₂	<i>Insitu-Si-PDA-MM</i>
	“”	8.85	0.01576	14.42	4.48		<i>Insitu-Si-APTES-TA-MM</i>
O	K series	3.96	0.01331	14.72	1.57	SiO ₂	<i>Insitu-Si-PDA-MM</i>
	“”	11.98	0.04030	22.93	1.84		<i>Insitu-Si-APTES-TA-MM</i>
Si	K series	1.89	0.01494	1.46	0.16	SiO ₂	<i>Insitu-Si-PDA-MM</i>
	“”	7.59	0.06018	3.95	0.30		<i>Insitu-Si-APTES-TA-MM</i>
Total:				100.00			

Table 3.2. Comparison between the EDS of the *Insitu-Si-PDA-MM* and *Insitu-Si-APTES-TA-MM* with respect to the elemental compositions of C, N, O, Si.

It was depicted that there was an increase in amount of C, N, Si, O on the active surface of the nanocomposite which contributed in the inhibition of the contaminants.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Standard Calibration Date
O	K series	4.50	0.01514	12.37	1.14	SiO ₂	<i>Tested-Si-PDA-MM</i>
		9.09	0.03059	20.45	1.10		<i>Tested-Si-APTES-TA-MM</i>
S	K series	3.04	0.02615	3.29	0.40	SO ₄ ²⁻	<i>Tested-Si-PDA-MM</i>
		3.29	0.02831	3.44	0.35		<i>Tested-Si-APTES-TA-MM</i>
Sr	L series	8.39	0.07378	8.48	0.56	SrCO ₃	<i>Tested-Si-PDA-MM</i>
		11.69	0.10286	11.27	0.59		<i>Tested-Si-APTES-TA-MM</i>
Pb	M series	15.59	0.14508	18.47	1.22	Pb(NO ₃) ₂	<i>Tested-Si-PDA-MM</i>
		19.68	0.18312	22.47	1.16		<i>Tested-Si-APTES-TA-MM</i>

Table 3.3. comparison between the EDX of the *Tested Si-PDA-MM* and *Tested-Si-APTES-TA-MM* with respect to the rejection of the contaminant's species (**Pb, Sr, S**).

It was observed that there was an increase in the removal of Pb, Sr, S by the Tested TFN (**Si-APTES-TA-MM@PVDF**), in comparison to Si-PDA-MM@PVDF, that is the second TFN (Si-APTES-TA-MM@PVDF) inhibition to the contamination of the synthetic water was higher and this is due to the surface functionalization and as well as the elemental composition was attributed due to the active phases in the nanocomposite as shown in **table 2** which was used in the coating of the support, this active phases took part in the rejection and separation mechanism and thereby inhibiting the passage of Pb^{2+} , Sr^{2+} , and as well as the salt ion SO_4^{2-} .

3.5 XRD of the nanocomposites and the thin film nanocomposites

The diffractograms obtained from the powdered XRD of the proposed nanocomposite and the tested TFNs are presented below **figure 3.12**. The XRD of the *in-situ-Si-PDA-MM* and the tested *Si-PDA-MM@PVDF* (the diffractogram are black and orange). The typical Si-NPs without any functionalization is 31° , the XRD pattern for Si-NPs incorporated with PDA typically displays a continuous diffraction that corresponds to the crystalline phase of modified silica nanoparticles. The small size and incomplete inner structure of the Si particles contribute to this broadness, showing a high percentage that results in the diffractogram at an angle of (31°) to the 2θ axis, (Dubey et al., 2015). An intense diffraction at around 31° of the *in-situ-Si-PDA-MM* was due to the incorporation of the PDA-MM into the Si-NPs. The peak at $\sim 31^\circ$ is most likely a mixture of (111) and (220) peaks of the Si-PDA-M, which appeared to be very close and distinct. The diffractogram observed with 2θ at $\sim 28.5^\circ$, 31° , 43° is probably from (111), (220), (311) which is due to reflections of silicon (JCPDS card no. 27-1402) that were observed for Si-PDA, (Z. Liu et al., 2019). The most interesting feature of the XRD is the sharp diffractogram with spikes at $\sim 41^\circ$ of Si-PDA-MM which shifts to $\sim 48^\circ$ as observed in the tested *Si-PDA-MM@PVDF*.

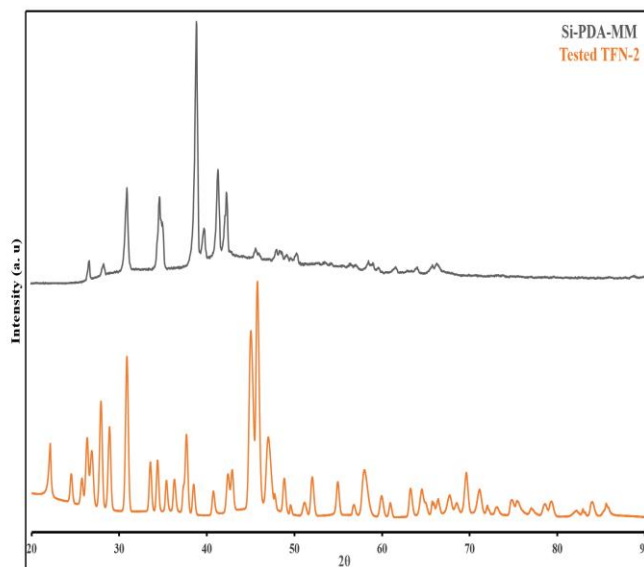


Figure 3.12. Shows the diffractograms obtained from the powdered XRD of the proposed nanocomposite (**Si-PDA-MM**) and the tested TFN-2 (**Si-PDA-MM@PVDF**).

3.5.1 XRD of the nanocomposites and the thin film nanocomposite. (**Si-APTES-TA-MM**).

In comparison to the diffractograms obtained from the powered XRD of the *Si-APTES-TA-MM* and tested *Si-APTES-TA-MM@PVDF* in **Figure 3.13** below. Broad intense diffraction at around $\sim 22^\circ$ of the **Si-APTES-TA-MM** was observed which was due to the incorporation of the APTES to the Si-NPs. All other diffractograms were not intense enough and were found around 2θ axis with 30° - 50° . The most interesting feature of the XRD when compared to that of the modified PVDF was, the diffractogram peak at $\sim 22^\circ$ of Si-APTES was still observed and in addition to that other peaks resulting from the inhibited contaminants species which causes the diffraction of other peaks and were also observed, diffraction around 2θ axis at 32° , 36° signifies a peak from Pb with (111), (200) diffraction (Banerjee et al., 2012), the diffractogram with 2θ around 42° , 44° , 47° are due to Co^{2+} (Chung et al., 2007). Also, the diffractogram with 2θ around 25° (111) (021) diffraction peaks match with the database (JCPDS file #6-520) which corresponds to $\text{Sr}(\text{OH})_2$ with cubic structure, for the inhibited Sr (Alimuddin et al., 2021), and 22° for Sulphur, the typical pattern of sulfur with JCPDS card number 77-0145 and pure sulfur are well in agreement. Figure 13 demonstrates that the F_{ddd} orthorhombic structure of sulfur was found in the finished product and correlates to the significant peak at $2\theta = 23^\circ$ (Radhika et al., 2018), which were all observed in the powered XRD of the tested Si-PDA-MM@PVDF.

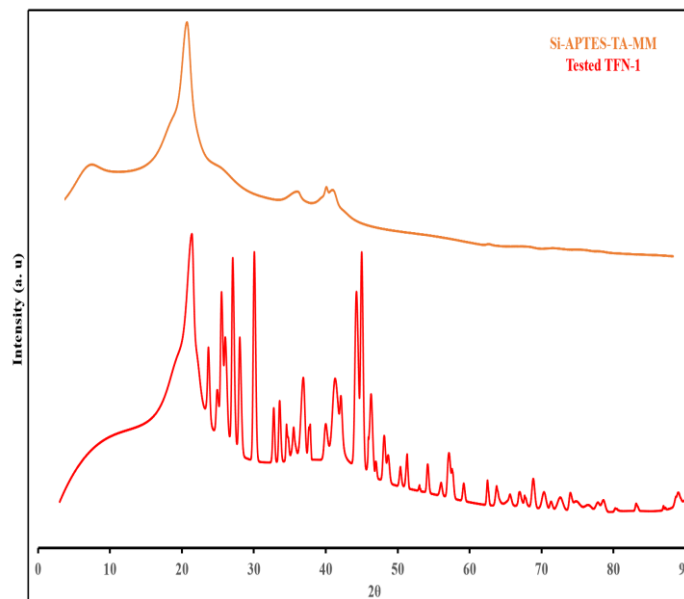


Figure 3.13. Shows the diffractograms obtained from the powered XRD of the *Si-APTES-TA-MM* and *TFN-1* tested *Si-APTES-TA-MM@PVDF*.

3.6 Atomic Force Microscopy (AFM)

The figures obtained from the AFM instrumentations show surface roughness for both the pristine PVDF substrate and the TFN before and after the filtration test, the 2-D and 3-D micrographs were taken in micrometer scale for the different samples characterized as shown in fFigure14, and 15 and 16. The Ra, Rq, Rv, and other important parameters were summarised in Table 4 below for the unlayered PVDF and Figures 14a and 15b show the pristine and the modified PVDF substrate. However, the pristine PVDF substrate shows a lower Ra, Rq, Rv, and other parameters in the trend which was due absence of surface functionalization. Also, the presence of the mountain-like shapes, valleys, and depths observed for the coated and tested TFN was due to the surface functionality with the Si-PDA-MM. and even after testing, the TFN-2 was an increment in the surface roughness and other parameters as shown in Figure 16c, and this was due to the inhibited salts ions and heavy metals and oils from the feed water.

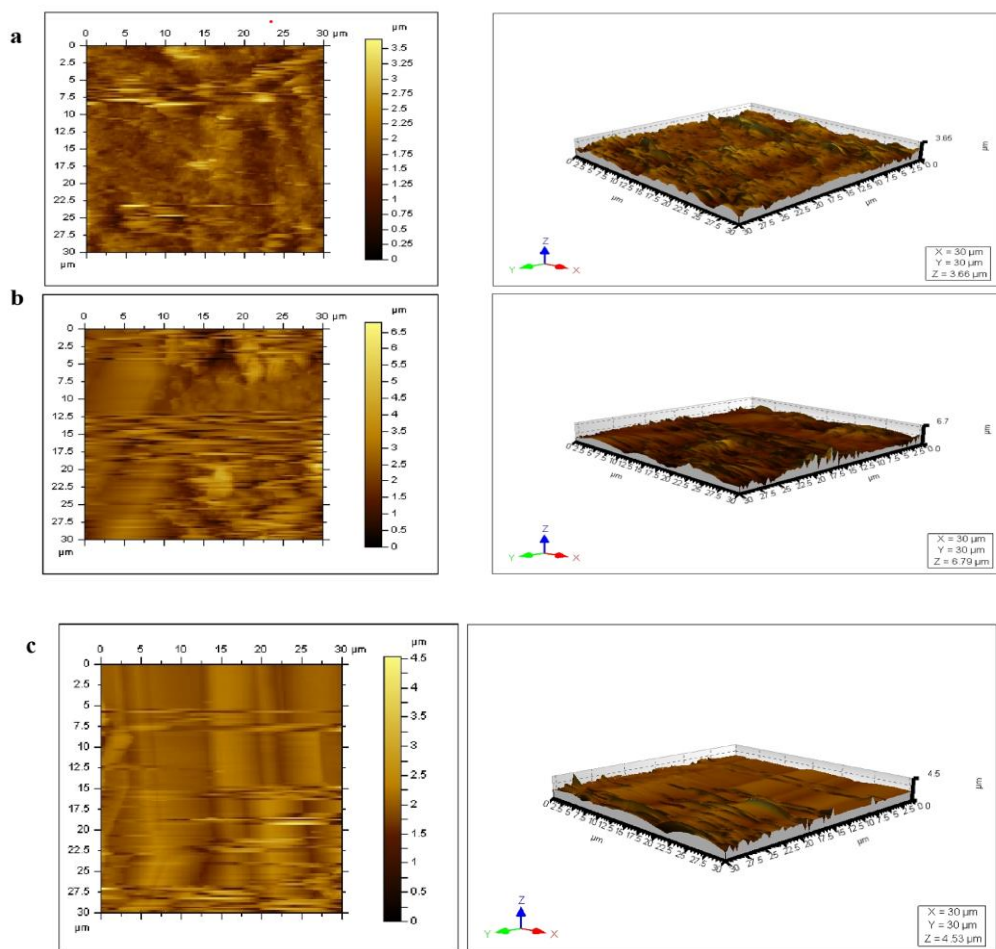


Figure 3.14 (a) PVDF (b) TFN-1 (Si-APTES-TA-MM) (C) TFN-2 (Si-PDA-MM)

3.6.1 Parameters obtained from AFM.

S/N	Parameters	Definitions	PVDF	TFN-2 (Before)	TFN-2 (After)
1.	z	The lower and upper threshold below and above the mean line	3.65	6.7	9.8
2.	Rc	The mean height of profile elements	0.31	0.625	0.83
3.	Rq	Root mean square deviation of heights in a line/area profile. Another common roughness parameter.	0.13	0.326	0.655
4.	Rsk	The skewness of the height data distribution within a line profile/area. The measure of the symmetry of heights is about the mean height. This can be indicative of anomalous frames.	0.119	0.395	1.18
5.	Rku	The kurtosis of the height data distribution within a line profile/area. Kurtosis indicates the strength of the tails in a height distribution. Can be quite a strong	2.28	3.04	3.55

		indicator of excessively high peaks (or deep valleys) and can be used to identify images with tip scarring or contaminant particles.			
6.	R _T	Total height of profile	0.502	0.83	1.08
7.	R _{DQ}	Root mean square slope	21.4	28.8	31
8.	P _{MR}	Load Length Ratio	85.2	94	100
9.	P _{DC}	Profile cut level difference	1.18	1.38	1.526
10.	R _a	Average roughness on the surface.	0.108	0.259	0.497
11.	R _q	The standard deviation of the surface height	0.13	0.326	0.0655
12.	R _v	Maximum profile valley depth.	0.259	0.967	1.266
13.	R _z	Maximum height or height range , the difference between the highest peak and the deepest valley in a line/area profile. A large height range can be indicative of large contaminant particles or	0.502	1.33	1.508

		excessive tip scarring.			
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Table 3.4: AFM parameters for the unlayered PVDF and TFN-2 before and after the filtration test.

3.7 Flux Evaluation of thin film nanocomposites.

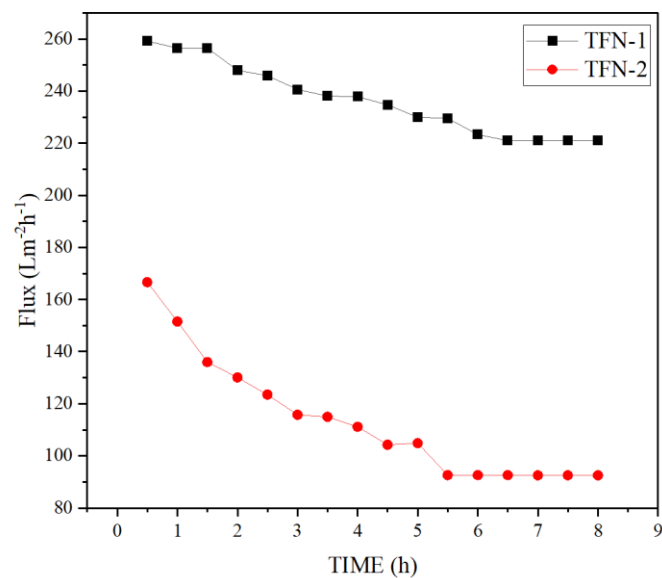


Figure 3.15: The Flux of the proposed TFNs were investigated by using synthetic water as the feed solutions.

The TFNs illustrated a stable flux with double distilled water but on running with the proposed synthetic water, TFN-1 showed a decrease in flux after 5.5 h, on comparison with TFN-2, there was a continuous trend from the starting of the test down to the final time attaining a minimum flux of $90 \text{ L m}^{-2} \text{ h}^{-1}$. It was so amazing that after long-run experiments, the TFN-2 was fouled more compared to TFN-1. The decline in the flux was due to TFN surface fouling on exposure to the synthetic water. Moreover, the increased fouling performance of TFN-2 can be explained by two promising factors, which include, an increase in surface roughness of the TFN-2 compared to TFN-1 which was confirmed by **AFM**. And the other factor is , the surface functionality of TFN-2 was found to be more hydrophilic and shows high surface charge density. The presence of $-\text{COOH}$ and $-\text{C-O}$ found on the surface of surface TA, and $-\text{NH}_2$ amine group in MM have been examined (Ang et al., 2019). The active layer of the TFN-2 also took part in increasing the hydrophilicity as confirmed by the decline when tested for water contact angle measurements. The decrease in the water contact angle leads to an increase in the flux. The presence of the functionality of the TFN-2 shows maximum rejection for SO_4^{2-}

which was attributed due to the active layer. The presence of the functionality has been confirmed by various characterization techniques including FT-IR, FE-SEM, and elemental mapping. Additionally, the TFN-2's rejection of salt may potentially be influenced by the electrostatic repulsion of salt ions from the membrane surface. Additionally, the TFN-2's rejection of salt may potentially be influenced by the electrostatic repulsion of salt ions from the membrane surface.

3.8 TFN Filtration Test

Filtration experiments were performed utilizing TFN-1 and TFN-2, and that of the pristine polyvinylidene fluoride membrane from the experimental setup to compare the water components and permeate flux of the membranes.

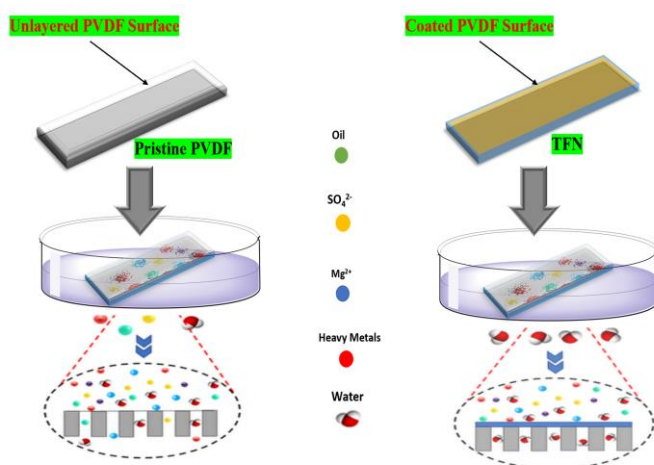


Figure 3.16. Filtration tests were performed using membranes made of pure polyvinylidene fluoride (PVDF) and modified polyvinylidene fluoride (TFN-1 and TFN-2)

3.9 A TFN Separation Efficiency and Rejection Analysis.

A study was carried out on TFN-1 and TFN-2 capacity in rejecting salt ions, heavy metals, and hydrocarbons from wastewater. **Figure 3.17-3.19** depicts the results of the thin film nanocomposites' performances toward the removal of the contaminants. The TFN-1 that is (Si-PDA-MM-TMC-MPD) filtered $> 62\%$ for SO_4^{2-} , Mg^{2+} after 1 h filtration While TFN-2 showed the maximum rejection for all the contaminants, with over $> 70\%$ for SO_4^{2-} , Mg^{2+} and 100% for pentane, isooctane, hexadecane, and toluene. An effect negative separation of inorganic salts such as Sr^{2+} , Co^{2+} , Pb^{2+} Mg^{2+} was 2^{+} was achieved, have a significant impact on the rejection. Furthermore, the heavy metals were seen to be eliminated after 0.5 h by both TFNs. And there was a steady rejection for the rest of the experiment accompanied by a gradual increase with time, the proposed TFNs displayed an appreciable rejection for salt ions at the time of the test. In terms of the thin film

nanocomposite, TFN-2 performance was higher and the heavy metals and the oils were inhibited with an efficiency of about 98% compared salt ions, with that of TFN-2 with a less flux compared to TFN-1, as depicted in the figures below.

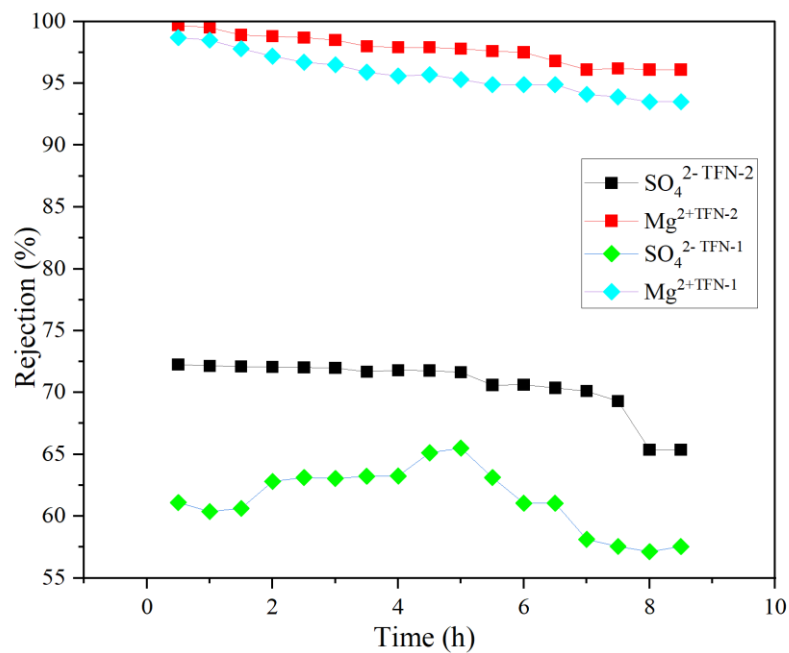


Figure 3.17. Rejection patterns of the thin film composite for the salts in both TFN-1 and TFN-2.

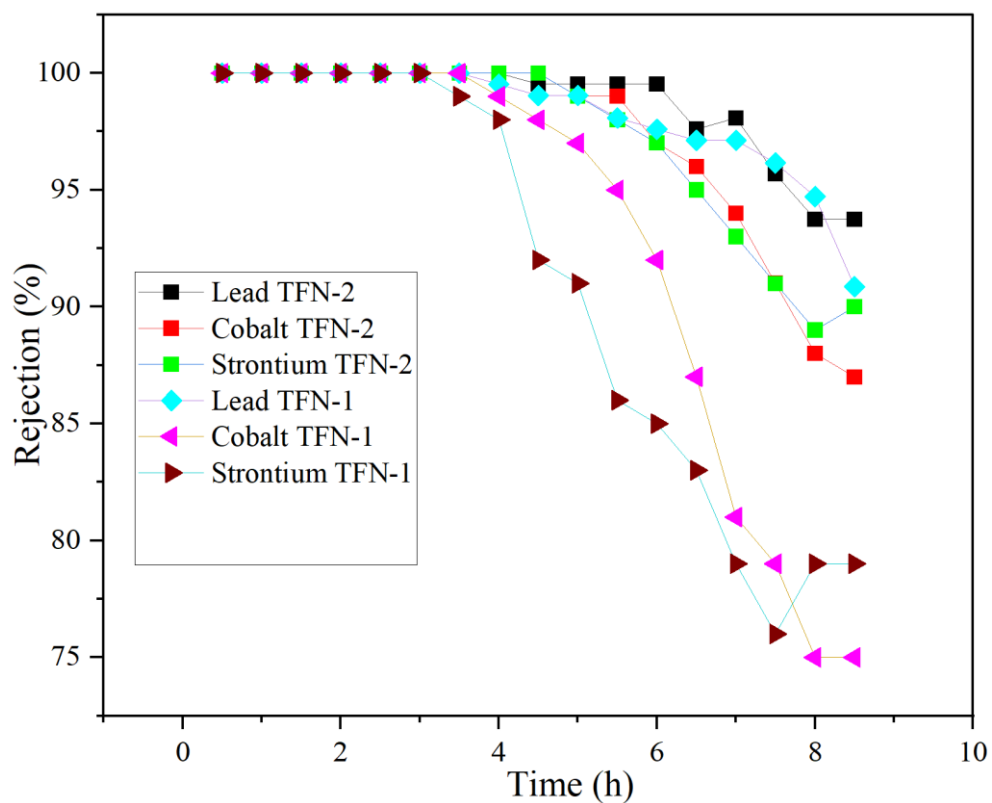


Figure 3.18. Rejection patterns of the thin film composite for the heavy metals in both TFN-1 and TFN-2.

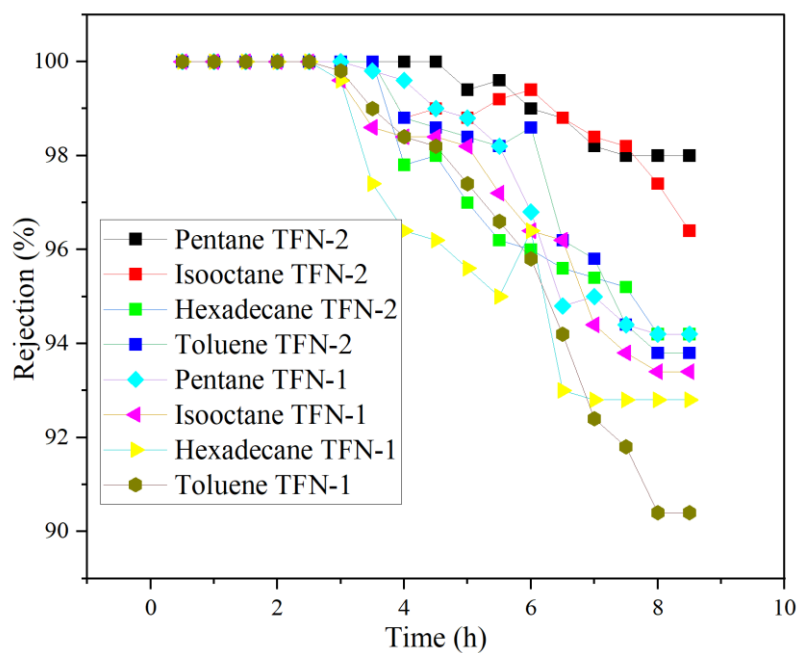


Figure 3.19. Rejection patterns of the thin film composite for the hydrocarbons of both TFN-1 and TFN-2.

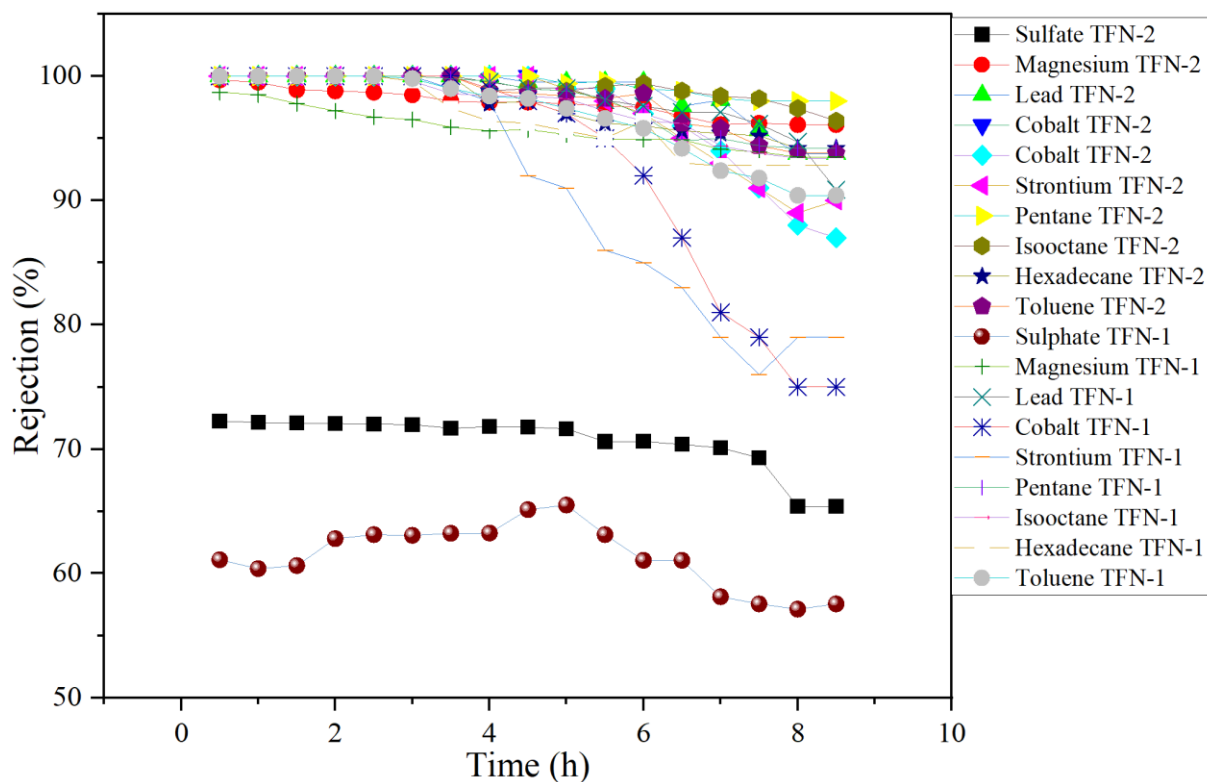


Figure 3.20. Shows the rejection after treatment with the TFNs for an applied pressure of about **300 kPa** and there were 100 % rejection for Pb^{2+} , Co^{2+} , Sr^{2+} , Pentane, Isooctane, Hexadecane, and Toluene, which was higher in TFN-2 compared to TFN-1.

3.10 Water filtration mechanism

Possible interactions of the TFN during the filtration process with water, oil, heavy metals, and anions from salts. When pressure is applied, the negatively charged functional group that holds the positive charges for metals is further pushed away, causing the metal components to go to the rejection site. The membrane's modest pore size may also help to explain these. Anions are driven to the rejection sites by the negatively charged carboxylate and NH_2 functional groups at the membrane's surface. Oils are recognized to be non-polar in nature, with regard to hydrocarbons, polarity differences underlie the rejection process, which causes the polar membrane to reject the non-polar oil contents in the feed.

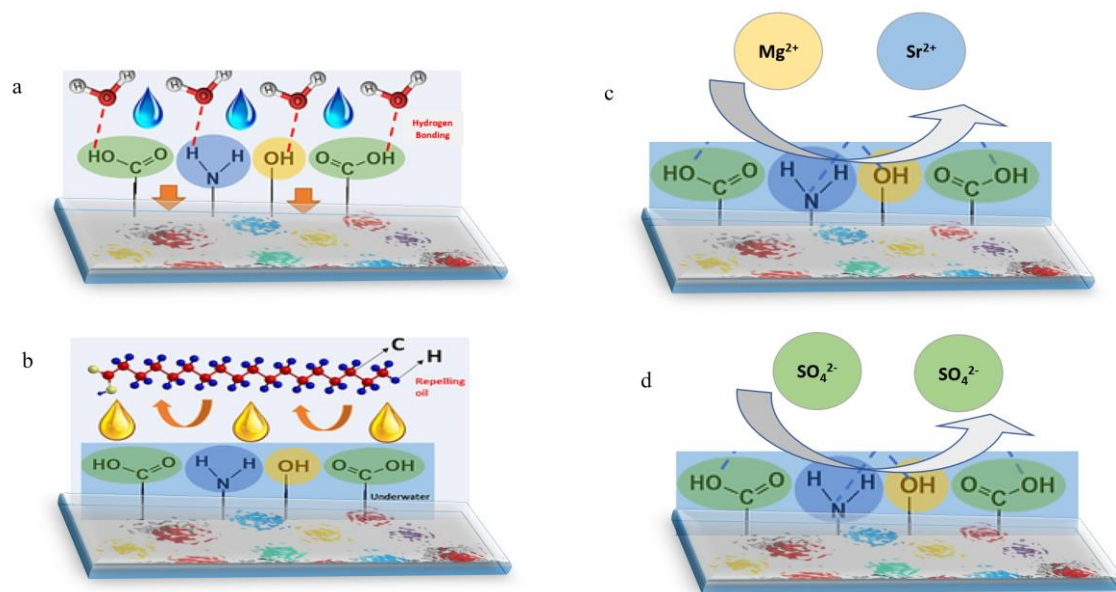


Figure 3.21. During the filtration process, there was a mechanism between the modified polyvinylidene fluoride membrane and (a) water, (b) hydrocarbons (c) heavy metals, and (d) anions from salts.

Coating Materials	Membrane	Contaminant Removal	Rejection rate (%)	Flux (LMH)	Refer.
TFN-AA/GO(3)	NF	Na ₂ SO ₄ , NaCl, Dye	95, 20, 99	11.34	(Seah et al. 2022)
TA/Fe-Ag	NF	NaCl	98	34.5	(Gao et al. 2022)
MTPCS PVA/GA	NF	trimethylbenzene	98	—	(Yousaf et al., 2022)
2D MOFs (Cu-TCPP)	NF	Na ₂ SO ₄	99.7	32.7	(Cheng et al., 2022)
MIL-101(Cr)-Pyz-SO ₃ H	NF/RO	NaCl	98.05	41.4	(Mehrabani et al., 2022)
PES10k-	UF	Li ₂ SO ₄	94.4	0.37	(Ameya Manoj Tandel et al., 2022)
TFC-SDS	NF	MgCl ₂ , MgSO ₄ , Na ₂ SO ₄	95, 41, 36	44.8	(Ang et al., 2019)

Si- APTES- TA-MM	NF	Co ²⁺ , SO ₄ ²⁻ , Pb ²⁺ , Sr ²⁺	96, 98, 98	18	This work
<i>In situ</i> -Si- g-Pam	NF	Pentane, toluene isooctane, decane,		100, 100, 100, 100	This work

Table 3.5. Coating materials and rejection efficiency were used for various nanofiltration studies in comparison to the recent work.

CHAPTER 4

Si-APTES-TA-MM

CHAPTER 4

4.1 Introduction

In this study, silica (Si) nanoparticles modified with three potent hydrophilic agents 3-(aminopropyl)triethoxysilane (APTES), trimesic acid (TA) incorporated melamine (MM), meta-phenylenediamine (MPD) and trimesoyl chloride (TMC) were used to modify the polyvinylidene fluoride (PVDF) support. In order to create the best 3D ordered and rough designs for high-resolution observation, silanization insertions were extensively exploited (Duțu et al., 2014). The substrate was functionalized using the straightforward 3-(aminopropyl)triethoxysilane, trimesic acid-melamine-meta-phenylenediamine, and trimesoyl chloride, the attachment comprising amine, carboxylic, hydroxyl functional groups. Overall superhydrophilic characteristics of the TFN on the membrane have been identified by the increase of the rejection efficiency based on their reactivity to external stimuli. As a result of the successful preparation of the modified PVDF substrate coated with Si-APTES-TA-MM-MPD and TMC composite material, an easy-to-follow technique was used in the interfacial polymerization process, the response time of water wettability as well as oil and solute rejection for water treatment application was enhanced.

4.2 Experimental Section

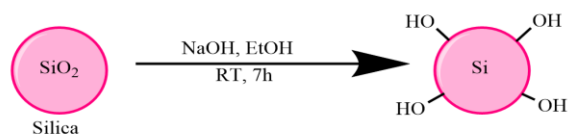
4.2.1 Materials and Chemicals

Most of the chemicals used in most of the research were sourced from Sigma-Aldrich, which includes n-hexane (C_6H_{14}), m-phenylenediamine (MDP) ($C_6H_8N_2$, 99 % purity), trimesoyl chloride (TMC), isooctane (C_8H_{18}), hexadecane ($C_{16}H_{34}$), silica nanoparticle, 3-(aminopropyl)triethoxysilane (APTES, 99.0%). The substrate employed was a powder made of polyvinylidene fluoride, $MW\ 25000\ g\ mol^{-1}$, (Satria et al., 2022) and (P. Gao et al., 2021). Nitric acid (HNO_3 , purity 65%), magnesium sulfate ($MgSO_4$, purity 99.5%), lead (II) nitrate ($Pb(NO_3)_2$), pentane (C_5H_{12}), m-phenylenediamine (MDP) and toluene (C_7H_8) were all the analytical grades. Sodium hydroxide and dimethylformamide (DMF) were obtained from BDH Chemicals, England. Polyvinylidene fluoride powder (PVDF, $M_w\ 25 \times 10^3\ g\ mol^{-1}$) was provided by Alfa Aesar Co. (Germany), and all these were utilized in the studies. Polyvinylpyrrolidone (PVP, $MW\ 25000\ g\ mol^{-1}$) was from Merck and was employed as an additive. Deionized water was produced from a real-time Milli-Q Ultrapure water system (Millipore, USA)

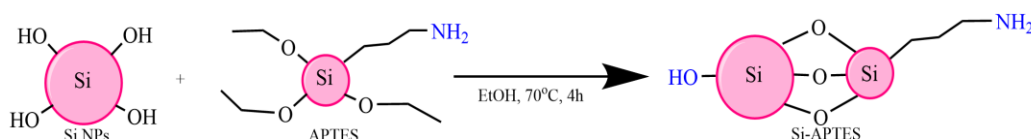
4.2.2 Silica Nanocomposite (Si-APTES-TA-MM) synthesis.

1g of silica nano-powder was carefully measured and transferred into a 250 ml round bottom flask, 50 ml of ethanol was added, then ultrasonicated for 30 mins. Then followed by the addition of NH_4OH in a dropwise manner. NH_4OH was added to serve as a surfactant and to make a basic condition, thereby initiating the hydroxyl formation to produce $\text{Si}(\text{OH})_4$. The reaction mixture was slowly stirred before being allowed to dry and turn into a white powder. After that, 2.5 mL of APTES was added and ultrasonicated for 3 hours, furthermore, the resultant solution was refluxed at 50°C . To obtain the white Si-APTES, the mixture was then allowed to dry at 70°C (Arribas et al., 2020). After being acquired, the Si-APTES composite was further modified by reacting with 2.2 g of Trimesic acid (TA) in 30 mL of ethanol under acidic conditions (H_2SO_4 drop-wise), with a minute amount of DCC, under nitrogen (N_2) gas intake for 5 minutes to eliminate any water droplets. The reaction mixture was gradually agitated at 120°C for 15 hours after integration, allowing the melamine's (MM) organic branch to bind to the TA as a host molecule via an amide bond, this is because the nucleophilic acyl substitution reaction results from the interaction of TA with MM. A new bond between the carbon and nitrogen atoms is created when the oxygen in the acid donates its lone pair to the amine's electron-deficient nitrogen atom (Park et al., 2020), (Chong & Wang, 2019). The modified nanocomposite was then dried for a further 10 h at 50°C to form a composite called Si-APTES-TA-MM, as shown in **Figure 4.1(c-d)**.

a



b



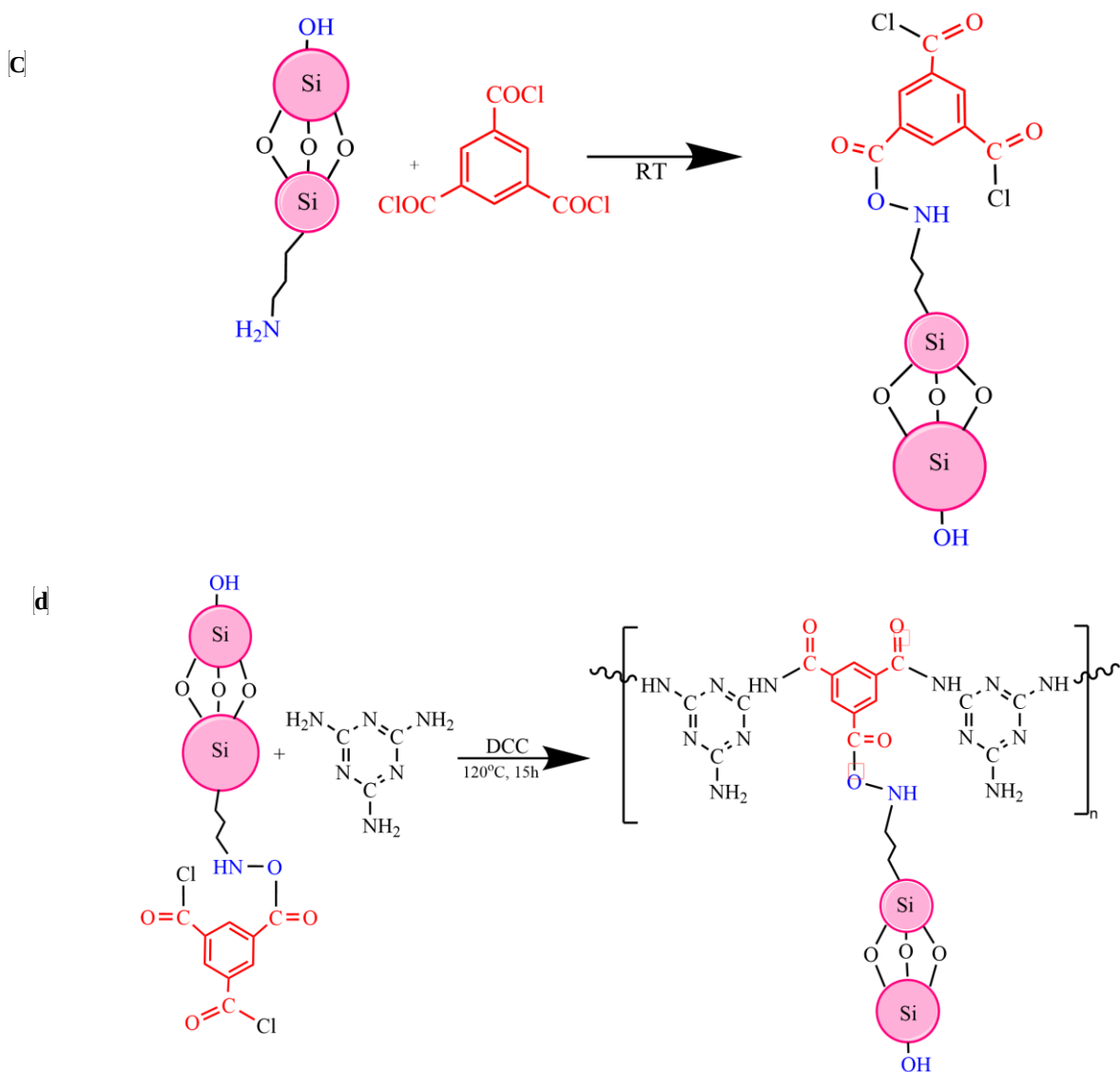


Figure 4.1. Preparation of (a) Silica nanoparticles (Si-NPs), (b) Si-APTES (C-d) Si-APTES-TA-TM nanocomposite.

4.2.3 Preparation of the modified PVDF membrane

36 cm² section of polyvinylidene fluoride substrate layer as shown in **Figure 4.2** was cut and immersed into a 0.1 M HNO₃ solution, and then rinsed with double distilled water for 24 hours to completely activate the substrate's surface and wet all its pores, and then allowed to dry for 2.5 hours. The PVDF substrate was then submerged for 5 minutes at room temperature in an N₂-purged solution of 0.2 weight % Si-APTES-TA-MM

composite, allowing just the top of the PVDF substrate to absorb the solution. The Si-APTES-TA-MM@PVDF was then coated with a 0.3 wt. % trimesoyl chloride (TMC)/n-hexane solution and allowed to interact with the PVDF for about 10 minutes before being re-coated with a 1.5 wt. % m-phenylenediamine (MPD). The interaction between the TMC@Si-APTES-TA-MM/PVDF and MPD was fast, which is due to interfacial polymerization between the TMC and MPD, the nanocomposite membrane was twisted on the glass plate in different directions to evenly distribute the solution on the surface, and a rubber roller was used to equally disperse the solution on the surface, and extra solutions was removed using the rubber roller. The membrane was then heated for a further 5 minutes at 50 °C to facilitate cross-linking, and it was then dried in the air for roughly 30 minutes. The membrane was then stored in a glass plate until needed after being cleansed with distilled water (Satria et al., 2022).

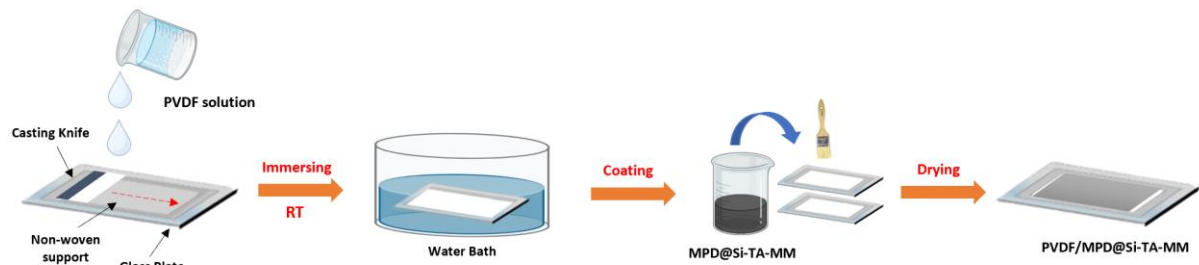


Figure 4.2. Preparation and Coating of the PVDF.

4.2.4 Characterizations

To analyze the modified nanocomposite membrane for the wastewater purification test, some characterization measurements were made. Field scanning electron microscopy FESEM with an Energy Dispersive X-ray spectrometer (EDX) at a voltage of 20 kV was utilized to analyze the elemental compositions, morphology, and dispersion of the modification at different magnifications. Furthermore, an X-Ray Diffractometer (XRD D8 Advance, Bruker, Germany) with Cu, K radiation at a continuous scanning mode (40 kV, 40 mA, and $\lambda = 0.15418$ nm) and a scanning rate of 5 deg./min and a range 3 - 90 deg was used to determine the crystalline/amorphous phase and average crystalline size of the modified nanomaterial. Fourier Transform Infrared spectra (Smart iTR NICOLET iS10) were carried out in the 350–4000/cm wavelength range with 64 scans and a resolution of 32 cm^{-1} to analyze the material and charged membrane functional groups. Without producing any pellets, because the sample to be analyzed is a thin film composite.

4.2.5 Membrane permeability and test for the separation capacity

The modified membranes' performance parameters, such as flux and the refutation of various organic contaminants, heavy metals, and inorganic salts, are shown in **Table 1**. The flux was tested using a Sterlitech™ crossflow cell tester, with an area of 36 cm² of the TFN membrane placed in the cell. The separation test was applied at a pressure rate of 400, 800, 1000, and 1500 kPa, and an ambient temperature was used in the process. The membrane was compacted with distilled water for approximately 4 h until achieving a stable condition before the testing measurements, and a pressure of 400 kPa (3.99 bar) was used to test for the flux during the duration of the filtering test. By collecting the permeate solution in the graduated cylinder at a chosen interval, the flux and rejection of the membrane were, the solution comprising of lead, strontium, cobalt, magnesium sulfate, and hydrocarbons such as pentane, isooctane, hexadecane, and toluene at the given concentrations were employed to examine the filtration capabilities of the modified membrane. Also, by monitoring the variations in the concentration of the permeate flux, it was possible to quantify the retention of inorganic salts, heavy metals, and organic molecules. Using Equation 1, the flux of the produced membrane was determined.

$$J_W = \frac{V_W}{A_M \Delta t} \quad (\text{Eq. 1})$$

Where:

J_W = permeate flux (L m⁻² h⁻¹),

V_W = change in the volume of the permeated water (L),

A_M = effective area of the inserted membrane (m²), and

Δt = time of collecting the permeated water (h).

Also, the following formula was used to determine each contaminant's percentage rejection, **Equation 2**:

$$\% R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100 \quad (\text{Eq. 2})$$

Where:

C_{feed} = concentration of the feed tank (ppm) and

$C_{permeate}$ = concentration of the permeated solution (ppm).

Table 4.1. The brain solution's composition.

Sample	SO ₄ ²⁻	Mg ²⁺	Pb ²⁺	Co ²⁺	Sr ²⁺	Pentane	Isooctane	Hexadecane	Toluene
	10 ³ ppm	250 ppm	208 ppm	100 ppm	100 ppm	500 ppm	500 ppm	500 ppm	500 ppm
D ₀ (tank)	1000	250	208	100	100	500	500	500	500

4.3 Results and Discussion

4.3.1 Surface Coating of the PVDF

PVDF membrane was coated using Si-APTES-TA-MM, MPD, and TMC to form a superhydrophilic active surface and a good wettability composite as depicted in **Figure 4.3** below. More interestingly, because the produced membrane has a lot of hydrophilic functional groups on the top membrane surface, it exhibits excellent superhydrophilicity. The most prevalent functional groups that show excellent surface wettability toward water include -OH, COO⁻, -NH₂, and Cl⁻, (Ma et al., 2018). In the functionalization of the PVDF surface, trimesic acid - melamine (TA-MM) and APTES were attached to the hydrolyzed Si-NPs via amidation and carboxylation process between the -OH in TA and -NH₂ in MM under an acidic condition. Moreover, the nanocomposite (Si-APTES-TA-MM-MPD) could also be made to react with TMC via the H-bond in MPD and the Cl⁻ bond in TMC in order to produce the dope solution of Si-APTES-TA-MM-MPD-TMC, which is then used in coating the thin layer on the surface of the pristine PVDF substrate. When these typical functional groups were added to the membrane surface, the surface energy of the modified membrane increased.

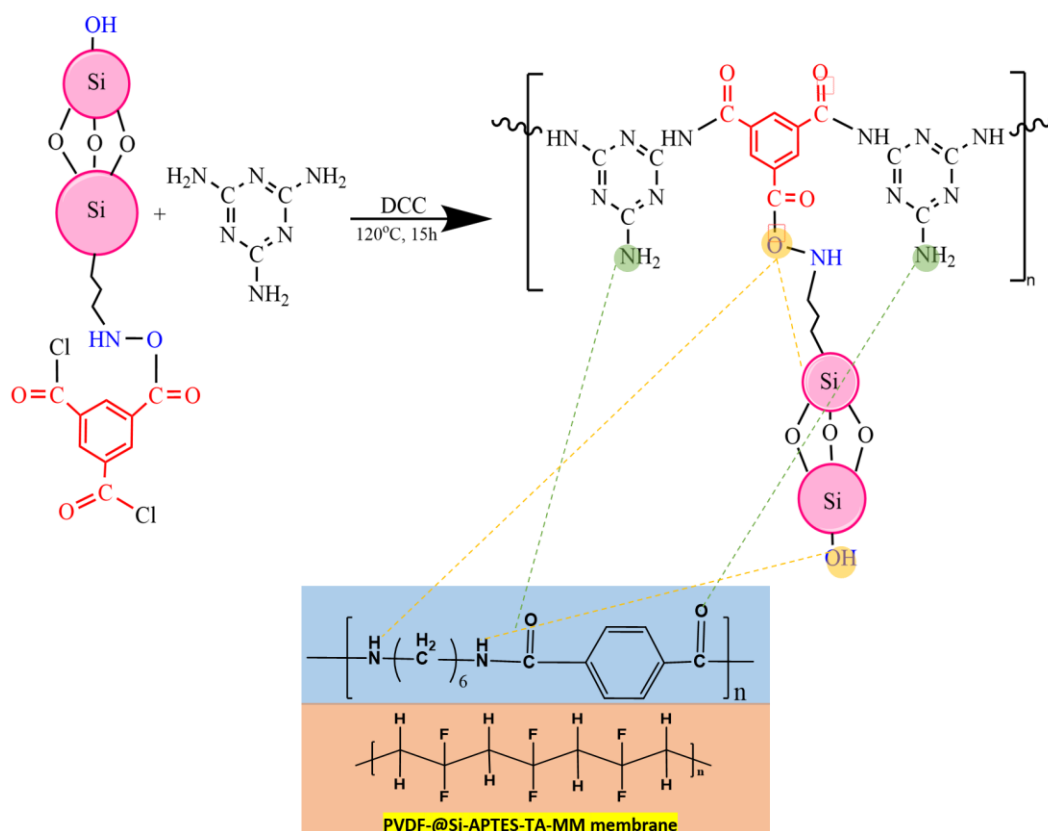


Figure 4.3. PVDF@Si-APTES-TA-MM nanocomposite chemical mechanism.

4.3.2 Membrane Characterization Results

To investigate the presence of the functional groups in both the prepared membrane and nanocomposite, FTIR characterization was performed. As observed from the FTIR spectrum in **Figure 4.4a**. The absorption bands at around 780 cm^{-1} indicate the presence of highly condensed silica which contains a symmetric siloxane (Si–O–Si) network mixture, (Al-Gamal et al., 2021), while in **Figure 4.4b**, that is the nanocomposite (Si-APTES-TA-MM), an (–NH) band appeared at 3700 cm^{-1} which shows a stretching vibration coming from APTES and Si-NPs due to the presence of (–NH₂). The absorption band at 1200 cm^{-1} was attributed to the –C–C– stretching vibration mode from the (aminopropyl)triethoxysilane chain. (Rubio, R. Pena-Alonso, Rubio F, Rubio J, Oteo, 2007) .The other bands observed are attributed due to the weak absorption band around 1020 cm^{-1} for (C–O), and (C–N) stretching vibration-(Farahmandjou & Golabiyani, 2015). Also, **figure 4.4c** shows an additional band of 1700 cm^{-1} for (C=N) stretching vibrations from melamine. In addition to this, several primary bands were produced by the modified PVDF membrane after being incorporated with the composite. It is interesting to see that the PVDF chain caused the –CH stretching vibration absorption bands

at 2920 cm^{-1} to remain consistently strong (Satria et al., 2022), and the broad absorption band of hydroxyl (-OH) stretching vibration was observed at 3650 cm^{-1} . **Figure 4.4d** depicts the absorption bands from the modified TFN, which can be remarkably compared with those observed from the tested TFN, demonstrating the effective incorporation of the composite on the outer layer of the PVDF membrane to provide superhydrophilic behavior.

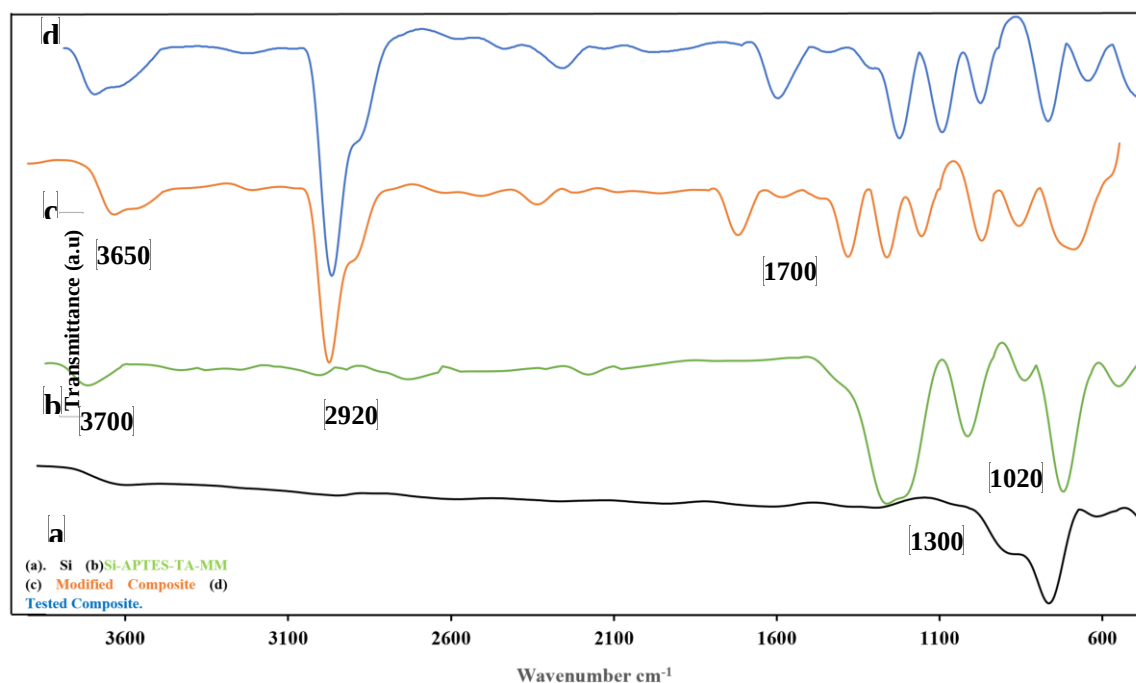


Figure 4.4. Fourier-transform infrared spectroscopy result of (a). Si (b)Si-APTES-TA-MM (c) Modified Composite (d) Tested Composite.

4.4 XRD

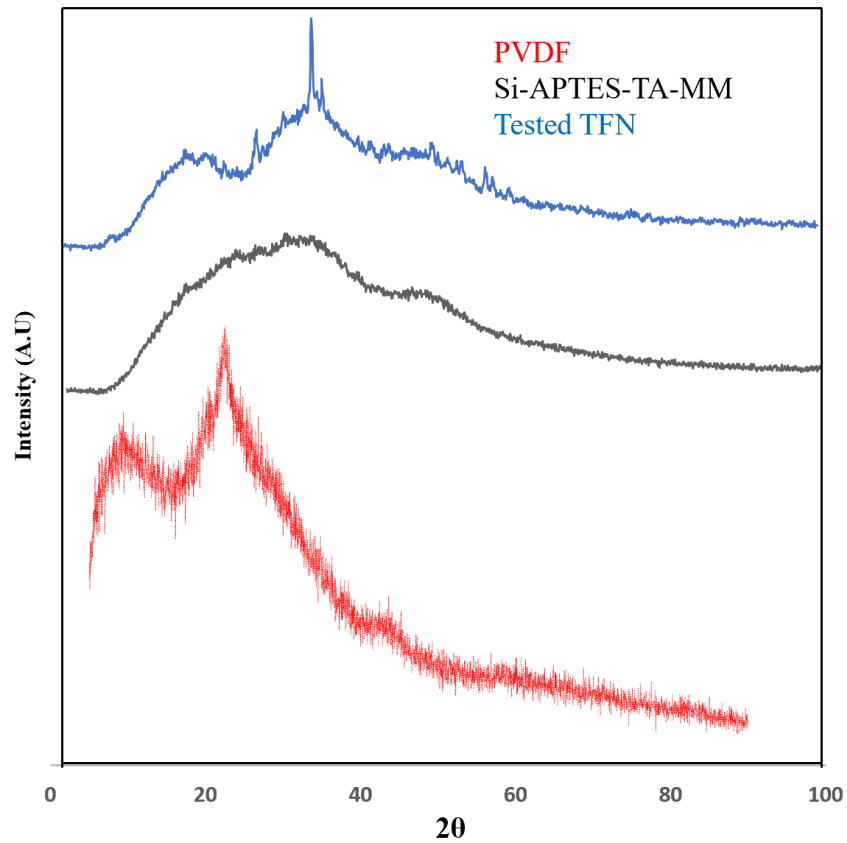


Figure 4.5. XRD patterns (a) Pristine PVDF (b) Modified polyvinylidene fluoride membrane with Si-APTES-TA-MM. (C) Tested membrane.

The XRD pattern of the pristine PVDF appeared amorphous with a slightly sharp diffraction at around 22.36° . The distinct diffraction was identified in the diffractograms as being at $2\theta = 22.3$ (110) after a thorough investigation. This diffraction was the primary peak in every diffractogram, indicating the development of β -phase in the PVDF Support. Its peak strongly overlapped with the remaining α -phase (Abdullah et al., 2015). The molecular interaction between the PVDF and DMF is one of the crucial factors to improve the β -phase of PVDF crystallization. The molecular interactions in DMF as a solvent include the dipolar interactions between CO and $\text{CH}_2\text{-CF}_2$ in DMF and PVDF, respectively, both of which cause the inter-chain forces of solid PVDF to be disrupted and ultimately cause the PVDF to dissolve. Whereas for the modified silica composite nanomaterial, an overall amorphous phase of the synthesized material was observed with two broad humps, the first hump was due to the SiO_2 nanoparticle functionalization with APTES which moves the peak from normal 22° to 27.2° (Dubey et al., 2015), showing a successful silica universal dispersion on

the PVDF support following the international center of diffraction data (ICDD) (Tabatabaei et al., 2006). While the tested membrane was a mixture of both amorphous and crystalline which was due to the attachment of the pollutant's species and the salts on the surface, given a slight shift of the 2θ when compared to that of the modified membrane (Si-APTES-TA-MM) from 27.2° to around 33.2° .

4.4.1 Morphology

The modified membrane and the nanocomposite material's SEM and EDX micrographs are shown in **Figure 4.6**. **Figure 4.6 a**, the SEM images of the Si-APTES-TA-MM as a host material which have a sizes ranging from $5\mu\text{m}$ - $10\mu\text{m}$. After being modified by APTES, TA, MM, MPD, and TMC, the Si-APTES-TA-MM composite was observed with different shape made up of different sizes, consisting of cylindrical, and semi-cylindrical size distribution ranging from $5\text{--}10\mu\text{m}$ (**Figure 4.6 b-c**). Additionally, SEM analysis was used to examine both the original PVDF membrane and the modified PVDF membrane before and after the filtration test. A rough, thick, microporous support layer made up of an asymmetric surface structure was discovered on the morphological surface of pristine PVDF (**Figure 4.6 c**). (Bai et al., 2012) It was clear from EDX spectra that the main elements (F and C) peaks appeared in a high percentage around 52 % and 47 % respectively (**Figure 4.6 f**). The PVDF membrane surface was explored with a new surface hydrophilicity property forming a homogeneous layer after being coated, forming PVDF@Si-APTES-TA-MM membrane, these added layer makes the membrane surface denser and coarser in structure (**Figure 4.6 c**). (Safarpour et al., 2014; Saleh et al., 2017) .From EDX spectra, the additional constituents from the synthetic wastewater solution were deposited on the thin film membrane surface, and the following elemental composition percentages were observed, Nitrogen 13.8%, Oxygen 13.7%, Silica 1.8%, as illustrated in **Figure 4.6 f**. Interestingly, the F atom percentage was extremely decreased from 50.9 % to 7.1 % due to the atom replacement with the N and O atoms after the chemical reaction It's interesting to note that after the chemical reaction, the N and O atoms replaced the F atoms, drastically reducing their fraction from 50.9 to 7.1 % (Bai et al., 2012; Bazargan et al., 2009). Following the filtration test, the evaluation of the changed membrane surface confirmed the salt particles' appearance and their extremely rough structure (**Figure 4.6 f**). In the EDX result, small percentages of extra heavy metal atoms produced by the ionization of salts were examined, such as Sr^{2+} , Pb^{2+} , Co^{2+} , and Mg^{2+} (**Figure 4.6 f**). These outcomes proved the effectiveness of the membrane filtering and modification, as indicated by the percentage increases.

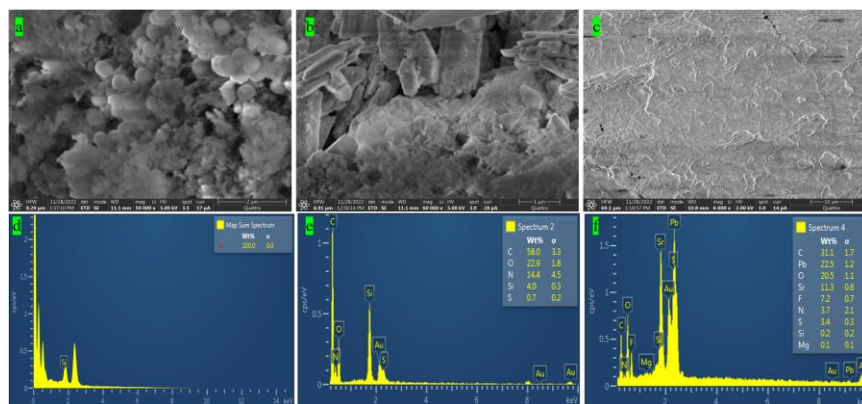


Figure 4.6. SEM images of the (a) Si-APTES-TA-MM (b) Modified PVDF/Si-APTES-TA-MM nanocomposite before testing, (c).Modified PVDF/ Si-APTES-TA-MM after filtration test. Elemental composition of (d). Si-APTES-TA-MM, (e-f). Modified PVDF/ Si-APTES-TA-MM before filtration test, and after filtration test (Atoms from salts were detected).

4.4.2 Water Flux Evaluation of the thin film nanocomposite.

Figure 4.7 depicts the flux of the modified PVDF substrate. According to the data, the flux reached $27.77 \text{ L m}^{-2} \text{ h}^{-1}$ during conditioning with fresh water after 30 minutes (0.5 h) of the membrane test. After that, the performance of the flux dropped substantially to $23.37 \text{ L m}^{-2} \text{ h}^{-1}$ after 240 minutes (8 h) and continued for 2.5 hours of filtering operation. With a consistent flux value of about $18 \text{ L m}^{-2} \text{ h}^{-1}$ attained, at this time, the brine solutions containing the contaminants were introduced, and the performance of the membrane was shown to be stable over time at around 8 h. Previous FESEM and EDX tests demonstrated the membrane's outstanding stability, which is a vital component of the steady flow. The elemental content of the membrane significantly altered before and after the treatment. This phenomenon supports and explains the results of the silica-based nanocomposite membrane. The greater flux may also be related to the thinner MPD layer and better hydrophilicity that was produced after embedding with silica nanoparticles, according to a study of water contact angles. This occurs because of the primer of nanomaterials; this improved the membrane's surface with several hydrophilic functional groups and caused the surface charges to change to a negative state. Surface charges are a few factors that affect the flux performance of the membrane's hydrophilicity. (Sarkar et al., 2010), (Zhu et al., 2020), (Moradi et al., 2020), (Deng et al., 2020).

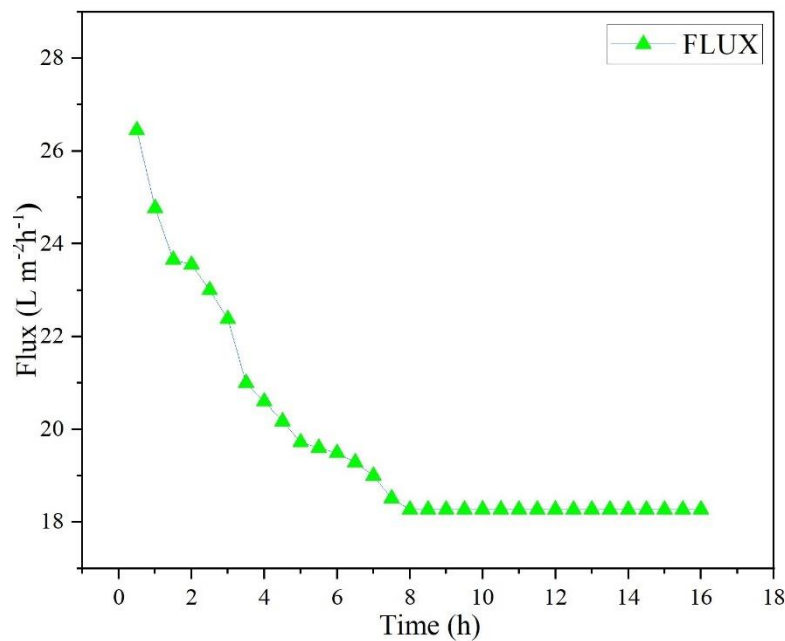


Figure 4.7. Water permeability of the functionalized PVDF substrate.

4.4.3 Filtration Test

To compare the water constituents of pristine and modified membrane, filtration tests were accessed using the Polyvinylidene fluoride membrane and modified Polyvinylidene fluoride membrane from the experimental setup, **Figure 4.8**.

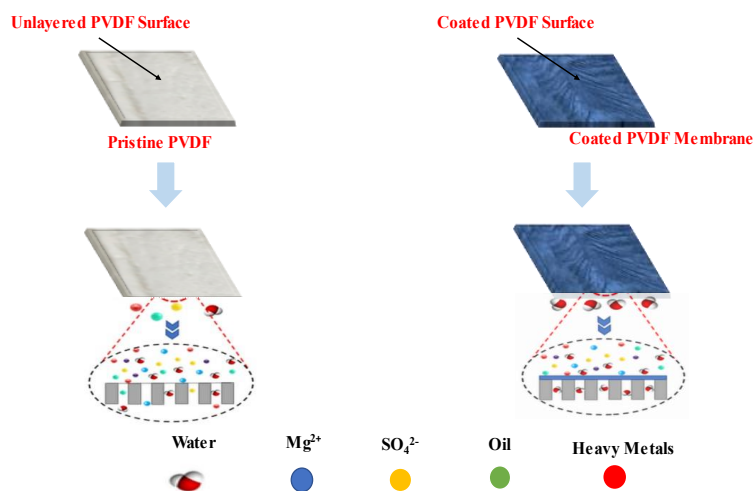
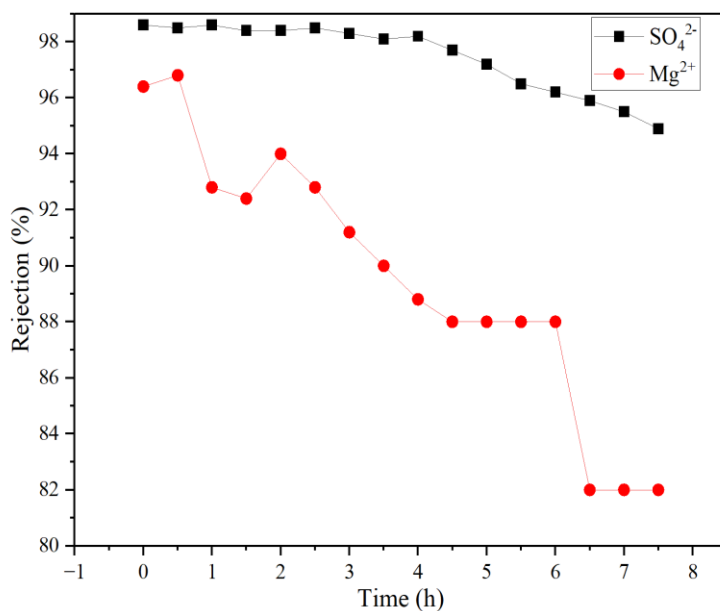


Figure 4.8: Filtration test using pristine and coated Polyvinylidene fluoride (PVDF) membrane.

4.4.4 Proposed Thin film composite Separation Efficiency

Investigations were made on the functionalized PVDF substrate's capacity to reject salt particles, hydrocarbons, and heavy metals from the synthetic wastewater. **Figure 4.9** shows the results of the membrane performance towards rejection of heavy metals, and separation of environmental organic contaminants from industries and urban settlements. The membrane had filtered and cleared **>92% of the salts' ions (Mg^{2+} and SO_4^{2-}) after 3.5 hours** of filtration. The separation effectiveness against inorganic salts decreased with the increase of time.(Al-Gamal et al., 2021; Jahanshahi et al., 2010; Najafi et al., 2020; Soyekwo et al., 2017) . The atomic and ionic size of the investigated contaminants was shown to have an impact due to the time the membrane was accessed in the following order: SO_4^{2-} , and Mg^{2+} . Additionally, Pb^{2+} , Sr^{2+} , and Co^{2+} were all eliminated after 5 hours by the modified membrane. Following that, the rejection behavior **increased** steadily for the rest of the experiment. Even though the efficiency gradually **increased** with time, the developed membrane displayed an appreciable rejection of salts in 6 hours. In terms of membrane performance, hexadecane, pentane, toluene, and isooctane all behave similarly.

a



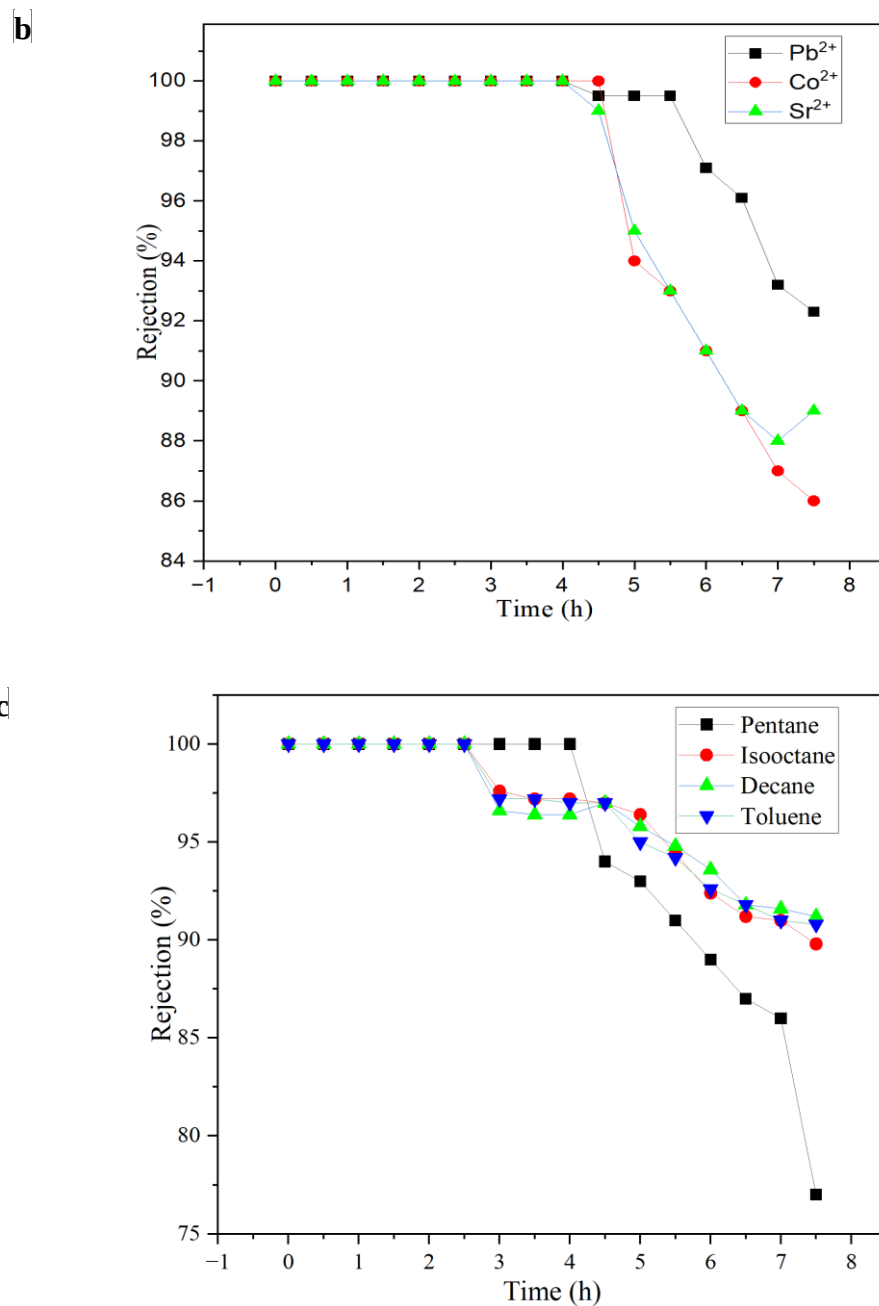


Figure 4.9. Rejection patterns of the thin film nanocomposite for the (a) salts, (b) heavy metals, and (c) hydrocarbons.

At 6 and 8 hours, **Figure 4.10 a-b** shows the Concentration behavior after treatment (ppm) in comparison to the analyzed contaminants. It can be proven that salt separation is more effective than separating organic species and heavy metals. Additionally, the membrane retained more than 90% of the magnesium contaminant after 6 hours of filtering testing. The separation of salts is demonstrated to be more effective than that of organic species and heavy metals. As a result of 6 hours of filtering testing, more than 90 % of

all evaluated contaminants were retained by the membrane. Following an hour of filtration, contaminants will ultimately breach the membrane because the detached solutes and contaminants will aggregate on the superficial layer, increasing the ionic pressure. (Lai et al., 2016) Furthermore, continuously applying pressure to a membrane may cause its pore properties to change. By eliminating a variety of environmental toxins often found in actual wastewater, the created composite membrane shows remarkable durability and effectiveness.

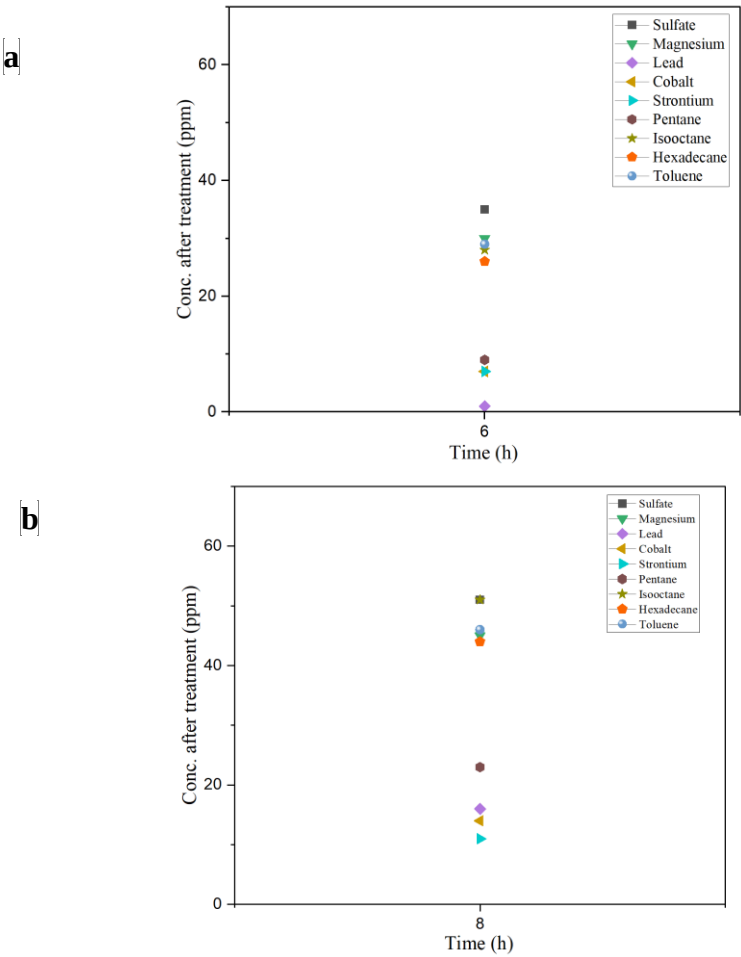


Figure 4.10. Analysis of the Concentration behavior after treatment (ppm) in comparison to the analyzed contaminants at (a). 360 mins (6 hours) and (b). 480mins (8 hours).

4.4.5 Rejection Analysis.

The rejection was high for Lead, Isooctane, and Cobalt at all the flow rates, around 400 kPa the rejection showed about 99 %, showing a 0 ppm concentration after treatment with the membrane.

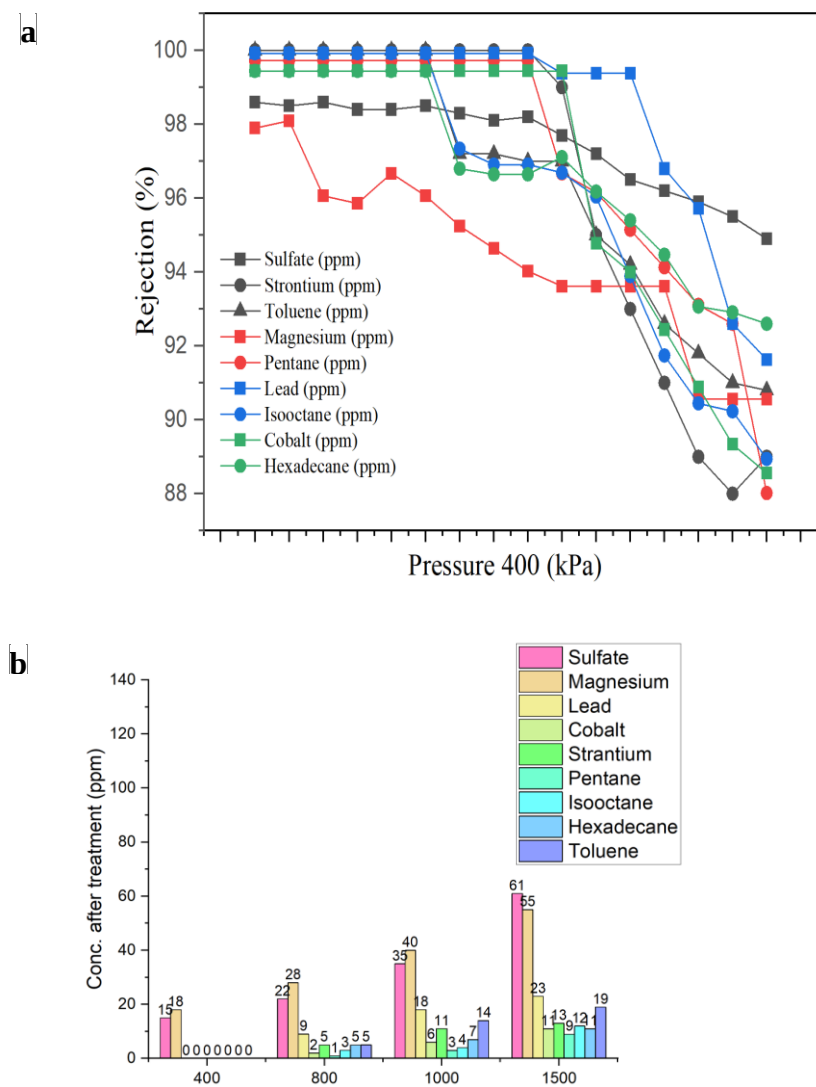


Figure 4.11 (a) Shows the Rejection removal after treatment for all the applied pressure 400 kPa but at around 400 kPa there was 100 % rejection for Pb^{2+} , Co^{2+} , Sr^{2+} , pentane, isooctane, hexadecane, and toluene. (b) Shows the highest concentration removal after treatment for all the applied pressures 400, 800, 1000, and 1500 kPa respectively.

4.4.6 Water Filtration Mechanism

Possible interactions between the modified Polyvinylidene fluoride membrane with water, oil, heavy metals, and anions from salts during the filtration process. For the metals, the positive charges are held by the negatively charged functional group, which is further pushed away by the applied pressure, moving the metal constituents to the rejection site. These could also be explained by the small pore size of the membrane. While the anions are repelled by the negatively charged carboxylate and amine functional group at the surface of the membrane thereby pushing the anions to the rejection sites. For the hydrocarbons, oils are known to be non-polar in nature. The mechanism of rejection is based on polarity differences, in which the polar membrane rejects the non-polar oil contents on the feed.

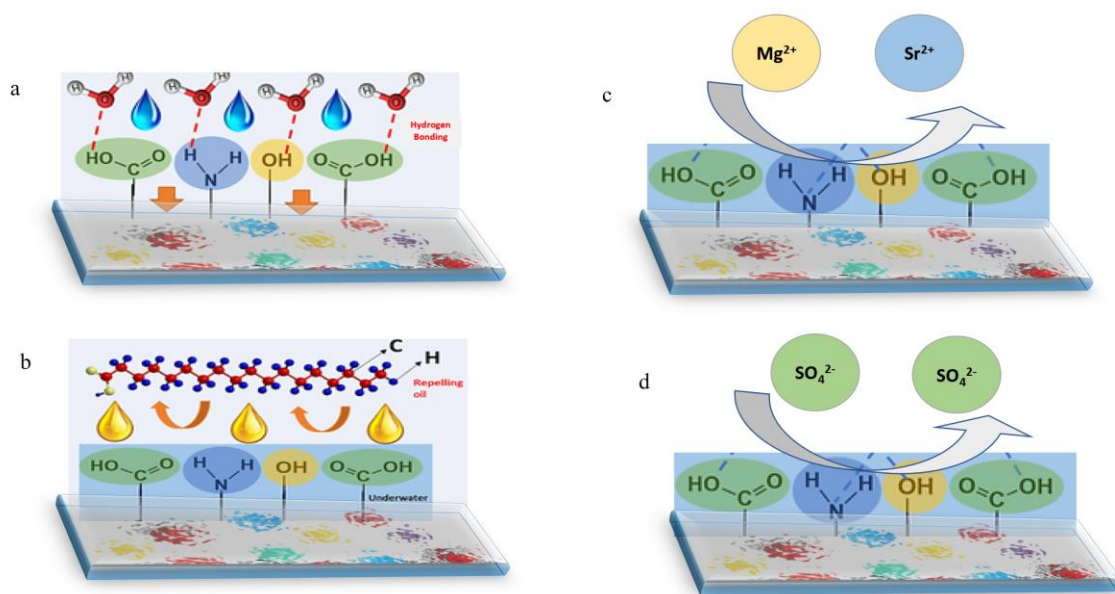


Figure 4.12: Mechanism between the modified Polyvinylidene fluoride membrane and (a) water, (b) oil, (c) heavy metals, and (d) anions from salts during the filtration process.

4.4.7 Contact Angle Measurement.

To further explain the surface hydrophilicity of the membrane, a contact angle measurement was done. By measuring the water contact angle on the modified membrane surface, it was possible to determine the major impact of MPD-TMC@Si-APTES-TA-MM composite deposition on the polyvinylidene fluoride surface. After letting around 6 μL of water droplets settle on the pristine PVDF and modified PVDF, the findings were obtained. As illustrated in **Figure 4.13a**, the initial water contact angle for the pristine PVDF membrane was investigated at 95° indicating the hydrophobic feature of the pure PVDF. When a water droplet was made to contact the surface of the membrane after the PVDF had been modified with the nanocomposite, it revealed a contact angle of around 37° , indicating that the membrane's wettability had changed to be more hydrophilic than before. The water contact angle decreased till it reached 0° , after then the water droplet of water was quickly absorbed into the modified membrane surface after a few seconds. The pristine PVDF composition, which has a high concentration of hydrophobic Carbon and Fluorine atoms, produced this initial superhydrophobic characteristic resulting in 95° when contacted with the water droplet. Additionally, following coating with nanocomposite on the PVDF, the water contact angle decreased to 0° , showing that the membrane's wettability had been significantly improved as shown in **Figure 4.13(b-d)**. As a result, it can be inferred from both wettability processes that when the water contact angle is greater than 90° , the Δp -value must > 0 , indicating the presence of a hydrophobic surface allowing the PVDF membrane to withstand a specific amount of water droplet pressure (**Figure 4.13e**). However, when the water contact angle was less than 90° , and the Δp -value was less than zero, this indicated a superhydrophilic surface which means the thin film nanocomposite was not able to support water pressure (**Figure 4.13f**). These results illustrated that the water contact angle on the membrane surface after interacting with the thin film nanocomposite can produce superhydrophilicity on the membrane surface, which enhances the negative charge and makes it easier to absorb water, attract salt ions, and repel hydrocarbons. It showed that the modified PVDF membrane was successful in reducing the permeability of salts and oils, allowing the freshwater to be easily absorbed.

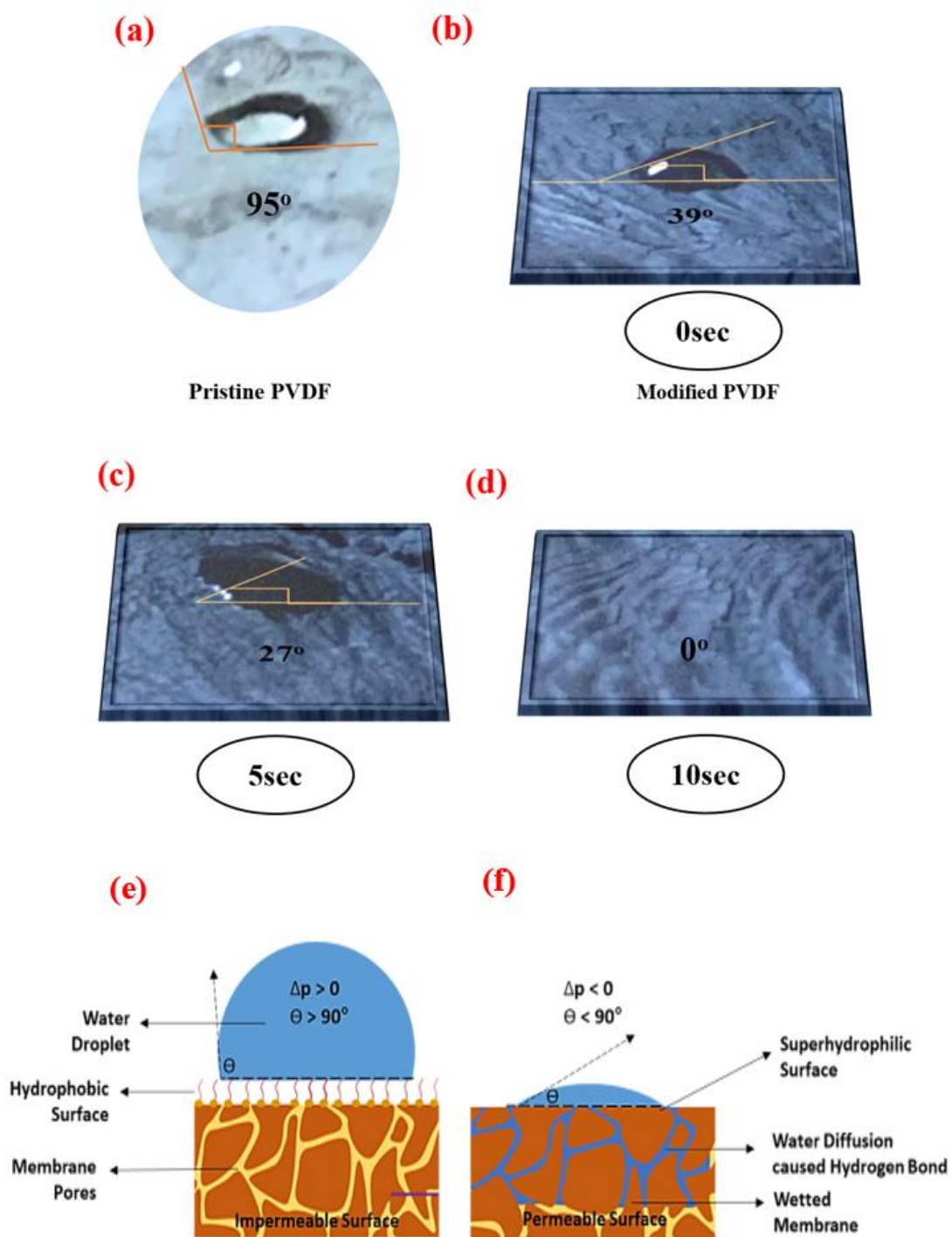


Figure 4.13. Water contact angle measurement (a). uncoated PVDF, (b). Modified PVDF/MPD-TMC@Si-APTES-TA-MM membrane after 0 sec, (c). After 5 sec, (d). After 10 sec, and (e-f). Surface mechanism of the droplet.

Table 4.2. Coating materials and rejection efficiency were used for various nanofiltration studies in comparison to the recent work.

Coating Materials	Membrane	Contaminant removal	Rejection rate (%)	Flux (LMH)	Refer.
TFN-ZIF-8@TA1.0	NF	Na ₂ SO ₄	96.6	20.7	(Mengjiao Xia et al., 2022)
COFs-TFN	NF	Rhodamine B (479 Da)	99.4	79.8	(Li et al., 2019)
PA/TiO ₂	NF	Sulfur	97	16.3	(Azizi Namaghi et al., 2019)
MIL-101	NF	MeOH	95.7	4.9	(Butler et al., 2020)
POPs	NF	Na ₂ SO ₄	97.5	29.9	(Ren et al., 2019)
Si-APTES-TA-MM	NF	Na ₂ SO ₄	98	18	This Work

CHAPTER 5

GO-APTES-TA-MM

5.1 Introduction

Herein, a high-performance GO-g-PA/TFN membrane was fabricated using the incorporation of 200mg of APTES-TA-MM as nanofillers. The APTES-TA-MM nanofillers were synthesized via the sol-gel method at high temperatures and were characterized. In-depth analysis was done to determine how nanofillers affected the thin film nanocomposite membrane's physical and chemical characteristics, and these nanofillers were successfully included using graphene oxide's surface exfoliation and interfacial polymerization with the monomers. The performance of the newly proposed thin film membrane was examined, and the flux in terms of separation and antifouling behavior was examined using a sterlitechTM membrane cell tester machine, FESEM-EDX was used to determine the morphology of the nanocomposite and thin film nanocomposite, as well as the percentages of the elemental compositions, and average roughness of the nanocomposite and the TFN was determined using the Atomic force microscope. The mapping was studied using the FESEM-EDX to determine the quantitative percentages of removal of the contaminants inhibited by the proposed thin film nanocomposite.

5.2 Experimental Section

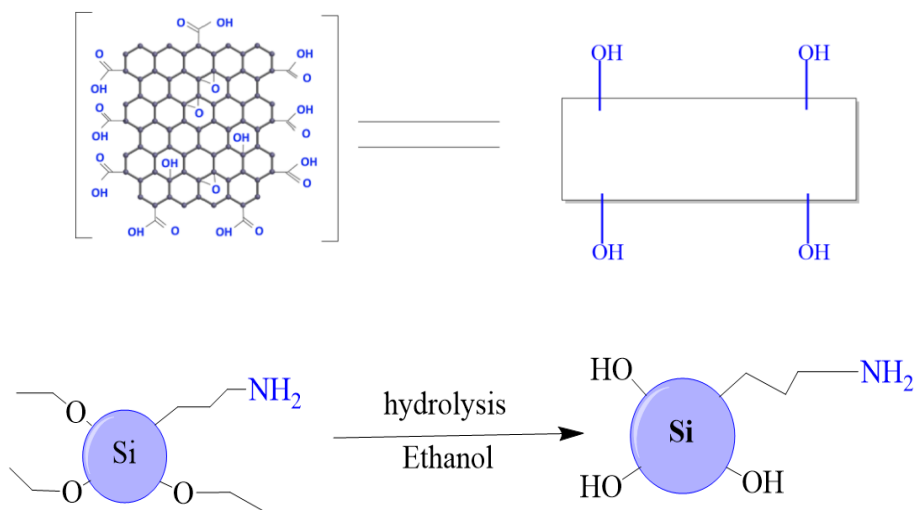
5.2.1 Materials and Chemicals

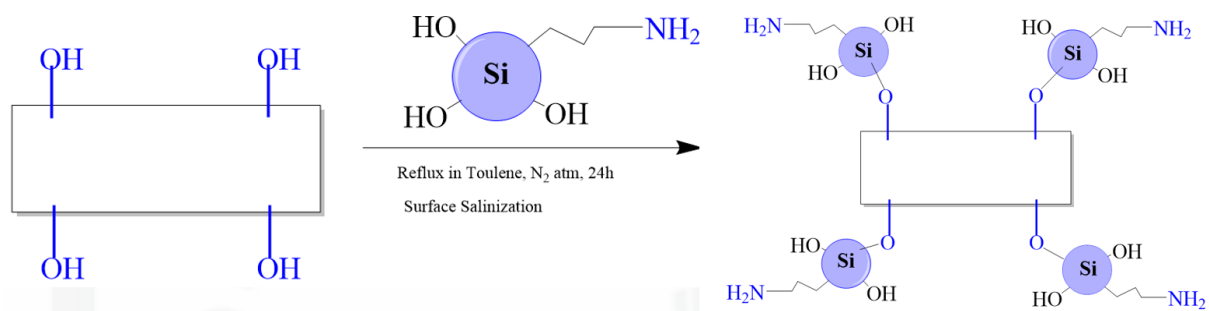
Polyvinylidene fluoride (PVDF, $M_w = 25,000 \text{ g mol}^{-1}$, Veradel ® 3000P, Solvay) was used to prepare the substrate. The PVDF powder was dissolved in dimethylformamide (DMF, Merck). PVP (PVP $M_w 1000 \text{ g mol}^{-1}$, Sigma-Aldrich), M-phenylenediamine (MPD = 99%) and trimesoyl chloride (TMC = 98%) Sigma-Aldrich. The PVP and PVDF powder were used as the monomers for the nanofiltration membranes. However, 3-(aminophenyltrimethoxysilane) APTES 99% Sigma-Aldrich were introduced into the phase via interfacial polymerization. The TFN were tested using MgSO_4 , $\text{Pb}(\text{NO}_3)_2$, and SrCO_3 sourced from Sinopharm chemical reagent Co., Ltd). Double distilled water was used throughout the experimental procedures.

5.2.2 APTES-TA-MM and Graphene oxide preparation.

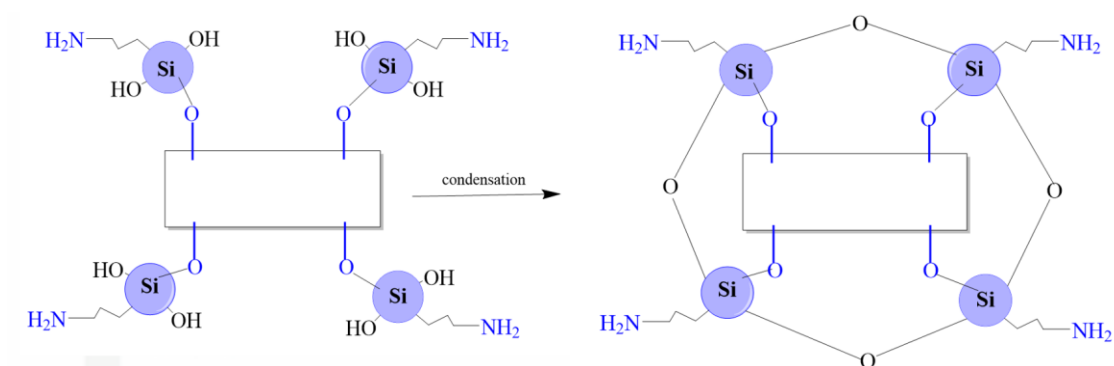
Graphene oxide was synthesized from graphite flakes using the modified Hummer's method. On the other hand, APTES was dispersed in toluene before the chemical grafting of graphene oxide at the N₂ environment refluxed for 24 h, this was tagged as solution A. Meanwhile, TA-MM aqueous solution was prepared under high temperature by first addition of melamine at a round bottom flask followed by the addition of solvent the resultant solution undergoes ultrasonication for 1 h for the solution to be uniformly dispersed, this process was followed by transferring the aqueous MM to a hot-plate at a temperature of 115 °C followed by reflux for 2 h, the solution was made acidic before the introduction of TA, and this process was tagged as solution B. The resultant mixtures (solutions A and B) were further ultrasonicated for 7 h to form a uniform dispersion and a homogenous mixture (Prasenjit Mandal & Hari Shankar Biswas, 2022). **Figure 5.1.** Furthermore, the resultant solution was mixed with TMC at room temperature and was rigorously stirred at room temperature. The solution was further reacted with melamine in the presence of DCC, at 70 °C for about 8 hours and later the temperature was brought to 25 °C and stirred for an additional 14 hours to form the GO-APTES-TA-MM nanocomposite.

(a)

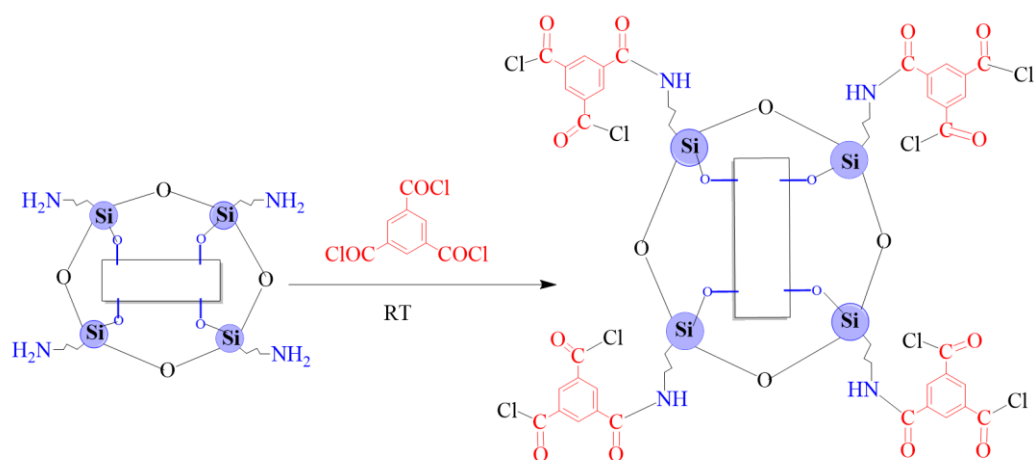




(b)



(c)



(d)

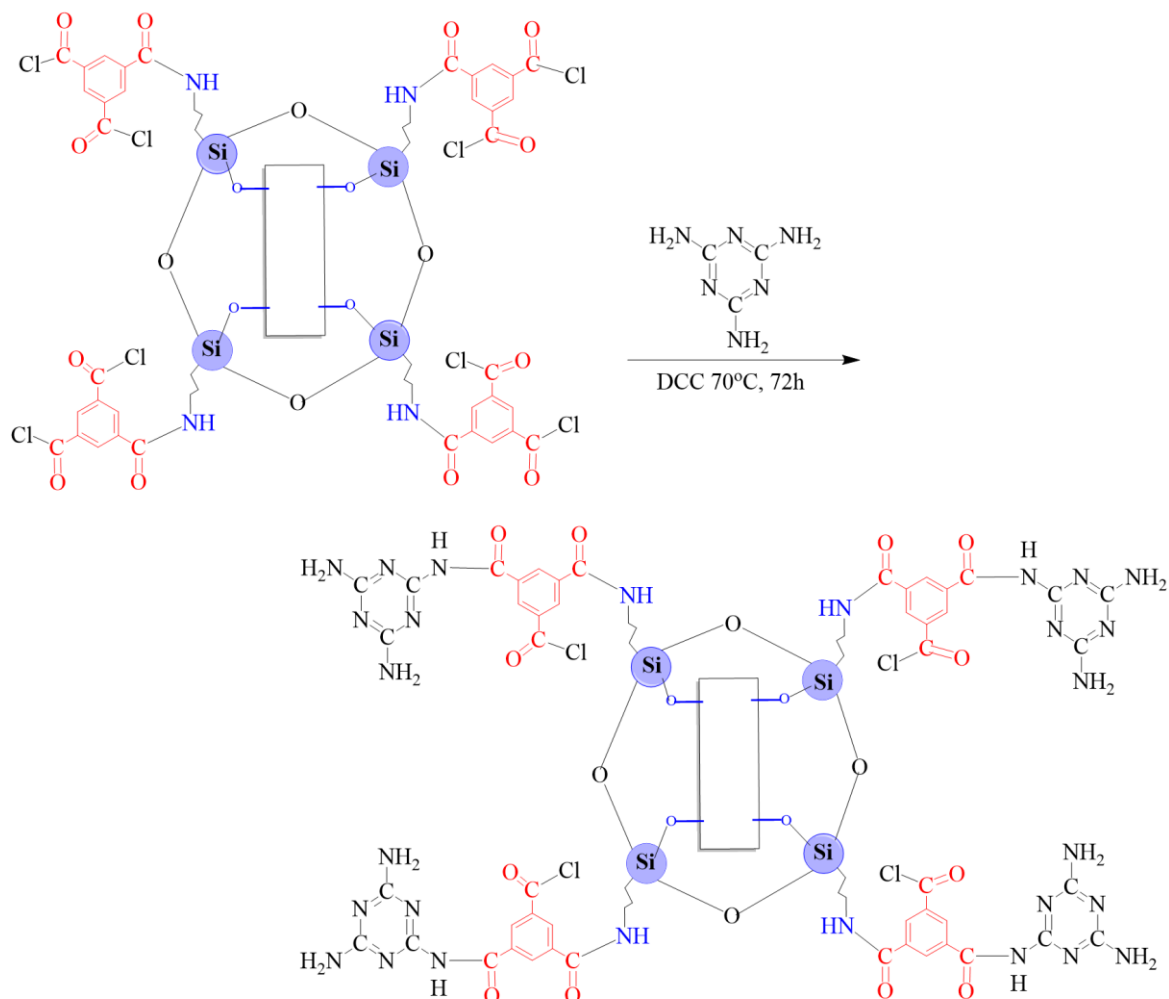


Figure 5.1. Preparation of (a) GO/APTES hydrolysis (b) GO-APTES, (c) GO-APTES-TA (d) GO-APTES-TA-MM nanocomposite.

5.2.3 Measurement and Characterization

Surface and cross-sectional morphologies of thin film nanocomposite membranes were investigated at 20 kV using FESEM-EDX, Hitachi SU802, the thin film nanocomposite surface was coated with thin platinum sputtering on the surface to avoid a charging effect. Atomic force microscopy (AFM) was conducted to determine the surface roughness of the proposed thin film nanocomposite membrane. The scanning area of the TFN was set at 3 micrometers x 30 micrometers. The TFN membrane was accessed by an Attenuated total reflectance-FTIR (Smart iTR NICOLET iS10) spectrometer was used to analyze the functional groups

on the thin film nanocomposite membrane active layer for the wavenumber ranging between 400–4000 cm^{-1} . The crystalline/amorphous phase and average crystal size of the changed nanomaterial were determined using XRD coupled with Cu, K radiation in a continuous scanning mode (40 kV, 40 mA, and $\lambda = 0.15418 \text{ nm}$), scanning was carried out at an average rate of $5^\circ/\text{min}$, and a range of 3° – 90° . (XRD D8 Advance, Bruker, Germany).

5.2.4 Surface Modification of the Thin-film Nanocomposite

Interfacial polymerization technique was used in the preparation of thin film nanocomposite membrane which was like the previously discussed in **section 4.2.3**. After the production of the nanocomposite as stated above, the GO-APTES-TA-MM@PVDF substrate was cut into an area of 18 cm^2 by 18 cm^2 and was dipped into 300 mL 0.1 M HNO_3 for a period of 2 hours, the dipping was carried out to remove trace impurities and to activate the pores. The PVDF was further rinsed with double distilled water to remove any impurities which may form from the initial dipping to make sure it's $\sim 100\%$ pristine. This process was followed by placing the PVDF in a glass and sticking the sides of the GO-APTES-TA-MM@PVDF. The GO-APTES-TA-MM@PVDF was placed on a glass plate and then coated with 0.6 weight % Trimesoyl chloride/n-hexane for 15 minutes. To initiate the I.P process, the thin film was further coated with 1.5-weight % M-phenylenediamine. To create the active layer, the final two procedures were carried out eight times, only enabling the TFN membrane surface to get in contact with the solution. After that, a rubber roller was used to remove the extra solution on the surface of the TFN membrane. The membrane was dried for around 30 minutes while being heated to 55°C for cross-linking.

5.2.5 GO-APTES-TA-MM performance evaluation (permeability) and separation effectiveness.

A commercial stainless-steel filtration SterlitechTM membrane cell tester machine was used in carrying out these studies to access the flux and filtration performance of the proposed TFN membrane (Rayat, 2011). The table below gives information about most of the contaminants there were utilized for the determination of the membrane efficiency, and also the figure shows the cross-section of the membrane cell tester which was used to test the flux and it has a cell area of $36 \times 10^{-4} \text{ m}^2$. A permeated pressure of about **400 KPa** was used when carrying out the flux test at a regular time interval of about 30 mins, the test was carried on at room temperature and was tested for a total of 10 hours. Before the filtration process begins, the modified membrane (GO-APTES-TA-MM@PVDF) was sliced into an area of about 36 cm^2 and was placed in the

Sterlitech cell membrane tester and ran with about 2000mL of doubled deionized water for a maximum of 5 hours, after this process, 4000mL of the prepared synthetic wastewater solution was introduced. The rationale for running the machine for 5 hours with the double deionized water is to achieve a stable condition for the filtration test. During the test, Hydrocarbons comprising of isooctane, pentane, hexadecane, and toluene were used in addition to strontium carbonate, lead nitrite, cobalt carbonate, and magnesium sulfate were all used in producing the synthetic wastewater. While the concentrations that were used are discussed in the table below. The flux of the TFN membrane was assessed by monitoring variations in the change of the flux and measuring the permeated water after treated with the membrane. $F(\text{L m}^{-2} \text{ h}^{-1})$ was used to symbolize the flux of the TFN membrane and was calculated using eq (1) and (2) respectively.

$$F = \frac{V}{A \cdot T} \quad (\text{Eqn. 1})$$

Where:

F = permeate flux ($\text{L m}^{-2} \text{ h}^{-1}$),

A = effective area of the inserted membrane (m^2),

V = change in the volume of the permeated water (L),

T = time of collecting the permeated water (h). and

Additionally, the following equation was used to calculate the percentage rejection of each contaminant,

Equation 2:

$$\% R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100 \quad (\text{Eqn. 2})$$

Where,

C_{feed} = stands for the feed tank's concentration (ppm), and $C_{permeate}$ = for the permeated solution's concentration (ppm).

Table 5.1: The constituent's composition.

N ₀	Samples	Concentration (ppm)	D ₀ Tank	Bulk Compound
1.	Hexadecane	500	500	-
2.	Pentane	500	500	-
3.	Toluene	500	500	-
4.	Isooctane	500	500	-
5.	SO ₄ ²⁻	4000	4000	MgSO ₄
6.	Pb ²⁺	208	208	Pb(NHO ₃)
7.	Co ²⁺	100	100	CoCO ₃
8.	Sr ²⁺	100	100	SrCO ₃
9.	Mg ²⁺	250	250	MgSO ₄
10.	SO ₄ ²⁻	1000	1000	MgSO ₄

5.3 Results and Discussion

5.3.1 FT-IR result of the incorporation of Trimesic acid to melamine (TA-MM), GO-APTES-TA-MM, and the proposed GO-APTES-TA-MM@PVDF (TFN).

The incorporation of Trimesic acid and melamine was established by exploring the functional groups that are -COOH and -NH₂, while the GO-APTES-TA-MM@PVDF was cross-linked with the TMC and MPD via interfacial polymerization process. Attenuated reflectance Fourier transformation infrared spectroscopy was used in elucidation the presence of the functionalities that took place in the active layers of the nanocomposite as shown in the figure below. The spectral obtained from the TA-MM band was attributed to the secondary amide group of melamine and the carboxylic acid from the trimesic acid. Before the incorporation of MM into TA. The broad band around 3490 cm⁻¹ was due to -NH from the MM, while the band around ~ 2200 cm⁻¹ is due to The -C band. While to observed band around ~1490 cm⁻¹ was due to aromatic C=C, also the peak around 1200 cm⁻¹ is due to the presence of -C-N. However, for the GO-APTES-TA-MM nanocomposite,

an amine peak was observed around 3600 cm^{-1} but slightly above that observed in the TA-MM, and this was due to the incorporation of the APTES, this peak was attributed due to the presence of -NH_2 from the MM via amidation reaction thereby shifting the peaks as observed in the FT-IR spectrum below. Furthermore, after modifying the thin film nanocomposite, it was also investigated to elucidate the presence of the functional groups of the GO-APTES-TA-MM@PVDF and the TMC-MPD. The FT-IR results obtained for the nanocomposite and the fabricated TFN show the peaks obtained in the GO-APTES-TA-MM and GO-APTES-TA-MM@PVDF, confirming the successful interfacial polymerization between the nanocomposite species. As evidence, the active superhydrophilic layer was made, by the reaction of the monomers under different reaction conditions as shown in **Figure 5.2**, the modified layer is visible as a TFN membrane within the interface of the aqueous and the organic phases of the active monomers. Upon establishing this, the fabricated GO-APTES-TA-MM@PVDF before the best was characterized and showed a broad band spanning from $3300/\text{cm}$ to $3450/\text{cm}$ which gives an absorption band for the (-CO-NH-) bond of the GO-APTES-TA-MM@PVDF as shown in **Figure 5.2**. Interestingly, the fingerprint region obtained from the FTIR elucidated the bands of the support and as well as the GO-APTES-TA-MM@PVDF thin film nanocomposite which was used for the study.

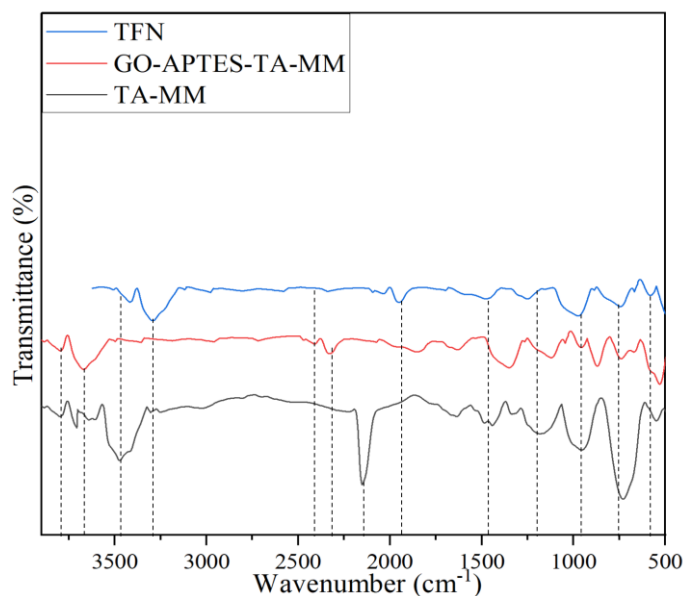


Figure 5.2. FT-IR Results of the incorporation of Trimesic acid to melamine (TA-MM), GO-APTES-TA-MM, and the proposed GO-APTES-TA-MM@PVDF (TFN).

5.3.2 FE-SEM AND EDX of the nanocomposite, and TFN after testing.

FE-SEM was used to determine the surface morphology of the nanocomposite and the tested membrane. **Figure 5.3** below is an SEM image taken at 20 micrometers, 5 micrometers, and 1 micrometer. That of the 1 micrometer shows the dispersion of the nanocomposite. Also, for the TFN, the resolution was taken from 100 micrometers to 1 micrometer, in other to show the interactions of the contaminants to the modified layers on the surface of the tested thin film as illustrated in **Figure 5.3** below. The FESEM-EDX was also taken in other to determine the percentages of the various elemental compositions, with carbon having a wt. % of 60.8 %, followed by 30.2 % of nitrogen, then 8.5 % of oxygen, and trace percentages of fluorine and silica.

The FESEM micrographs show the prepared nanocomposite, modified membrane, and tested thin film membrane. **Figure 5.3 a-b** show the nanosheet and the wrinkles features of the GO-APTES-TA-MM nanocomposite with different magnification, in other to see the incorporation of the TA-MM with the GO-APTES, the different morphologies were observed in 5b which was due to TA-MM grating in GO-APTES. **Figure 5.3 c** shows the universal dispersion of GO-APTES-TA-MM on the PVDF layer, and the SEM-EDX analysis of the nanocomposite membrane showed most of the expected element's composition is ascertained. While **Figure 5.4 a**, FESEM of the tested TFN, the morphology observed at 100 micrometers shows some cracks on the surfaces of the TFN, this was due to the inhibition of the constituents by the membrane. **Figure 5.4 b**, the magnification at 10 micrometers further shows the cracked surfaces clearer which was due to the permeating synthetic water constituent when the pressure was applied. While figure 6c shows the different morphology of the constituents such as Pb^{2+} crystals, Co^{2+} , and Sr^{2+} ionic crystals which were observed from the FESEM-EDX elementals composition when the tested TFN was analyzed using the instrument (Zamarripa–Cerón et al., 2016), (A. Akinterinwa et al., 2023)

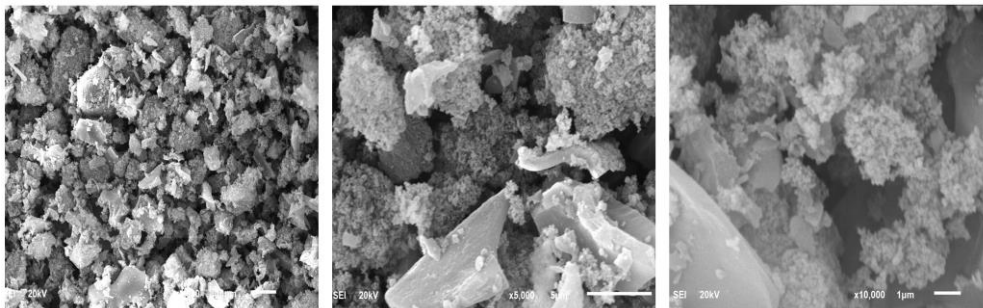


Figure 5.3. SEM image of the GO-APTES-TA-MM Nanocomposite

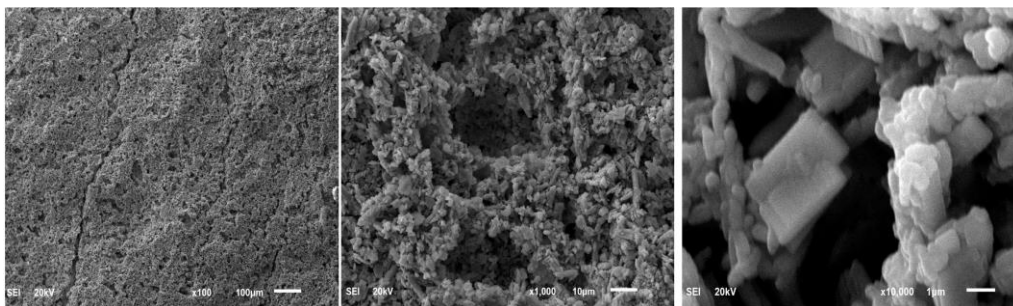


Figure 5.4. SEM image of the Tested TFN (GO-APTES-TA-MM@PVDF) Nanocomposite

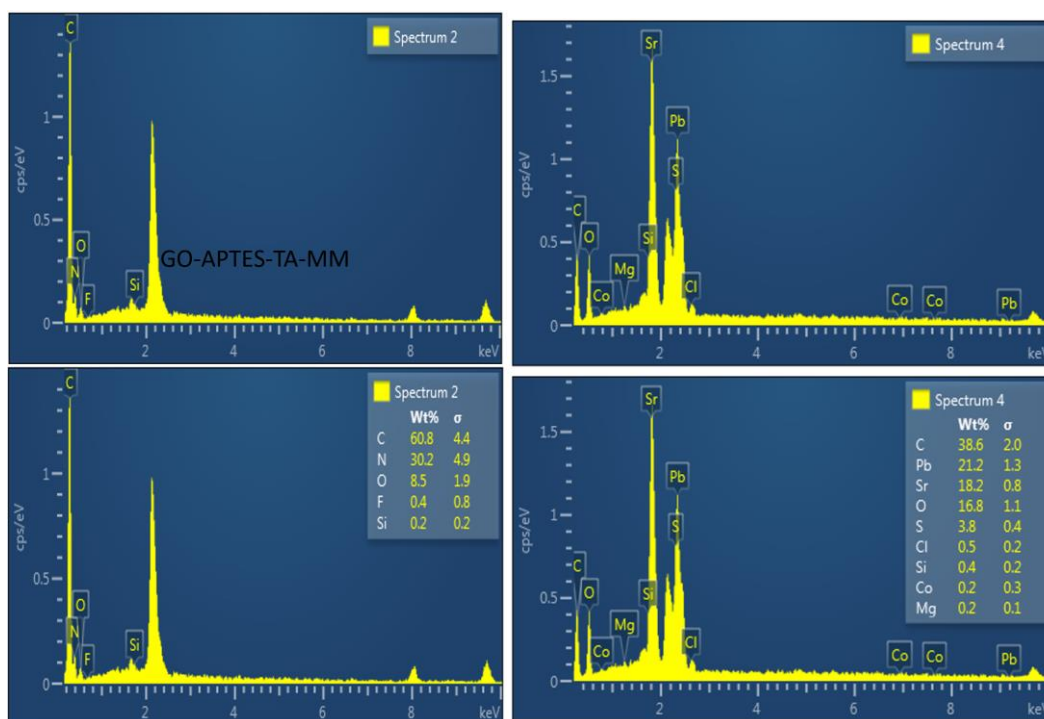


Figure 5.5 . FESEM-EDX image of the Nanocomposite and the Tested TFN (GO-APTES-TA-MM@PVDF) Nanocomposite.

Figure 5.6 shows the mapping of the nanocomposite and the tested TFN. It was observed that when the mapping was taken the composition of carbon was universal due to the contribution of the monomers and also the nanocomposite's species. Also, **Figure 5.7**, shows the mapping obtained from the FESEM-EDX of the tested thin film nanocomposite after passing synthetic water through the membrane.

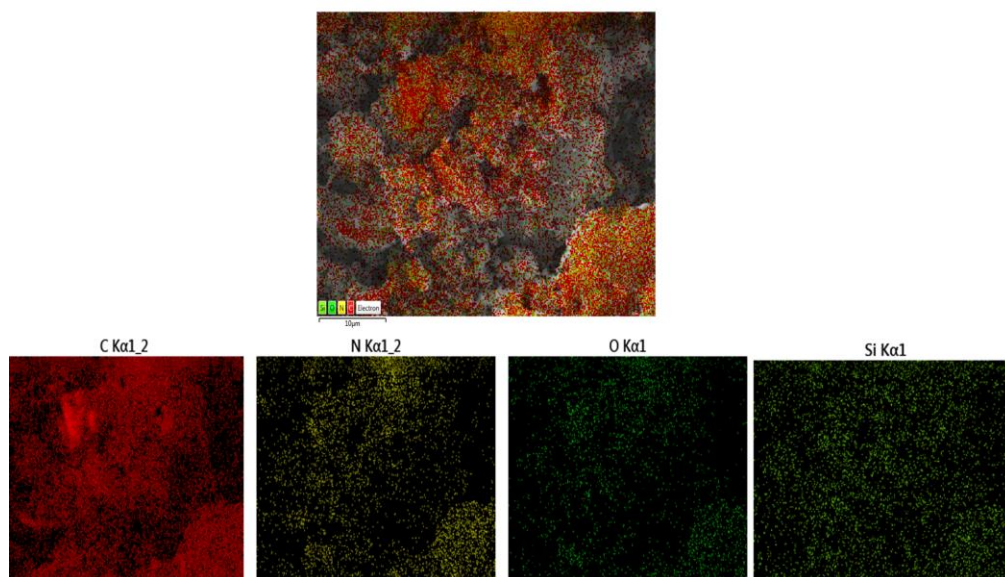


Figure 5.6. Mapping image of the Nanocomposite

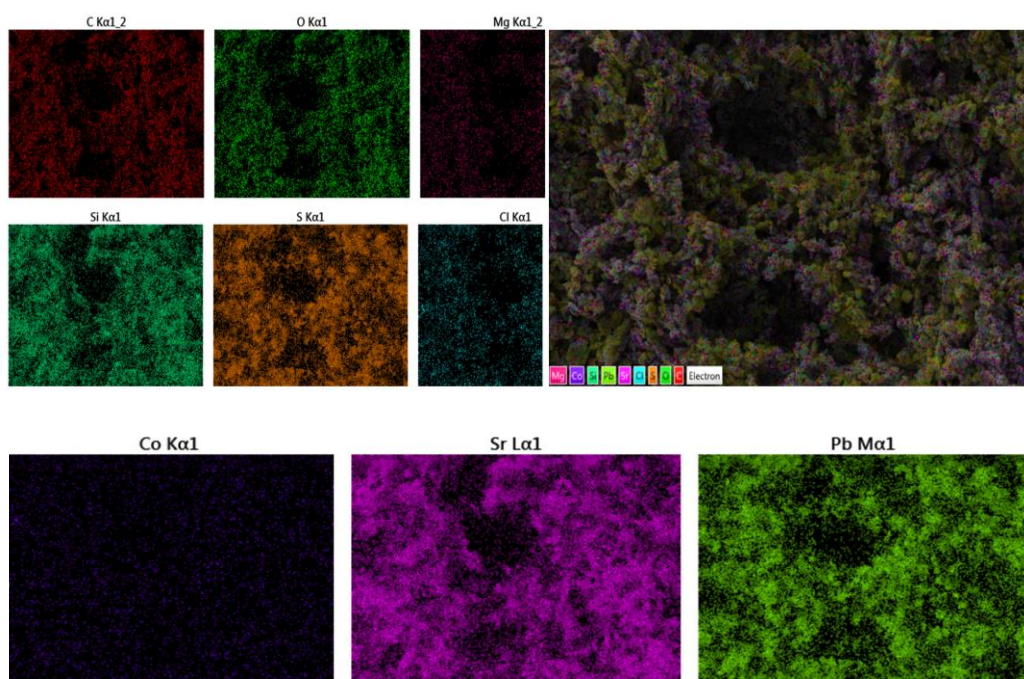


Figure 5.7. Mapping image of the Tested TFN (GO-APTES-TA-MM@PVDF) Nanocomposite.

Coating Materials	Membrane	Contaminant removal	Rejection rate (%)	Flux (LMH)	Refer.
MWCNT	NF	MgCl ₂ , Co ²⁺ , Zn ²⁺	95, 80, 73	18	(Liu et al., 2017)
<i>p</i> -aminophenol modified GO	NF/RO	NaCl	99.7	23.6	(Yan Zhang et al., 2020)
PA/UIO-66-NH ₂	NF	Na ₂ SO ₄	97.1	46	(Gong et al., 2020)
PES/PVDF/GNPs	NF	Phenol	80	30	(Salawudeen et al., 2019)
MeSiCl ₃ -Pam	RO	Bovine serum albumin (BSA), sodium alginate (SA),	96	18.5	(Shen et al., 2019)
GO-APTES-TA-MM	NF	Hexadecane, isooctane, toluene, Pb ²⁺ , Co ²⁺ , SO ₄ ²⁻	95	70	This Work

Table 5.2. Coating materials and rejection efficiency were used for various nanofiltration studies in comparison to the recent work.

Constituents	TFN-1 and TFN-2	Si-APTES-TA-MM	GO-APTES-TA-MM
Pentane	100 %	100 %	100 %
Isooctane	100 %	100 %	100 %
Hexadecane	100 %	100 %	100 %
Toluene	100 %	100 %	100 %
SO ₄ ²⁻	61.1 % 72.2 %	98.6 %	86.4 %
Mg ²⁺	98.7 % 99.7 %	96.8 %	41.6 %
Pb ²⁺	100 % 100 %	99.5 %	92.8 %
Co ²⁺	100 % 100 %	99.5 %	81 %
Sr ²⁺	100 % 100 %	99.5 %	81 %

Table 5.3. General comparison between the materials used for the studies.

CHAPTER 6

6.1 Conclusion

In conclusion, the present work demonstrates the advancement of a new composite for water treatment which shows superb water permeability. The thin film composite-based filtration process was carried out under the pressure of 400 kPa (nanofiltration) which is a good concept of nanocomposites that are restrained in a very stable hybrid network showing very great potential for pollutant removal in wastewater. The result showed an increase in rejection of salts ions; Mg^{2+} , SO_4^{2-} , (>90% at a stable flux of **18 L m⁻²h⁻¹**) and organic pollutants such as pentane, isooctane, toluene, hexadecane (100% rejection from the water sample) for material in section 4. Also, the modified membrane showed >98% rejection for heavy metals such as Sr^{2+} , Pb^{2+} , and Co^{2+} at a flux of **18 L m⁻²h⁻¹**. The proposed membrane's capacity to remove sulfate, even in high quantities, along with the functionalized membrane's good reusability, revealed the membrane's promise for treating industrial wastewater. In general, the excellent separation capacity for heavy metals such as lead, strontium, and cobalt, alongside hydrocarbons like pentane, isooctane, hexadecane, and toluene using a constant-pressure approach and an environmentally friendly functionalized silica thin-film composite could have great potential in dealing with wastewater.

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PROFILE

I have experience both in learning, character and at new technologies as needed. Excellent communication skills, ability to work with little or no supervision, a team player, a young man with can-do attitude. I believe that the combination of my academic and professional experiences has provided me with the organizational, interpersonal, and analytical skills that will enable me to make a significant contribution to the Support Services.

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Institutions attended (with dates – starting with the latest)

Schools	Date
King Fahd University of Petroleum and Minerals	2021- 2023
Bayero University Kano	2015 – 2019
Nasara Science Academy	2009 – 2015
Nasara Primary School	2003 – 2009
Demonstration Staff School, Federal College of Education, Kano	2002– 2003

Pure Academic Qualifications (with dates – starting with the latest)

Certificate	Date
M.Sc Analytical Chemistry	In View
Bachelor of Chemistry (Second Class Upper Division)	2020
Quadcore computer Institute (Distinction Class)	2017
Senior Secondary Certificate Examination (SSCE)	2015
Junior Secondary school Cert	2013
Primary School Leaving Certificate	2009

Professional Qualifications and Membership (with dates – starting with the latest)

Certificate	Date
National intellectual Property Awareness Mission Certificate (NIPAM)	2022
Member at the Institute of Chartered Chemists of Nigeria.	2021
Certificate in Business Achievement and Start-up (TEF)	2019
Certificate in Career Dev.	2019
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Hobbies:

- Cooking
- Watching Documentaries
- Cycling

Work Experience (General and Specific Experience Starting with the Latest)

Dates	Position & Place	Responsibilities & Duties
2021 to 2023	King Fahd University of petroleum and minerals (Teaching Assistant)	• Guide students to carry out physicochemical Analysis in the lab. • Lead students to understand basic Safety precautions in the lab. • Organise a case study for student to understand the objectives of the practical. • Leads students to identify chemical apparatus and how to utilize them for qualitative and quantitative analysis.
2020 to 2021	NYSC. Chemistry and Civic Education Teacher	☐ Teaches Secondary Students General Chemistry. ☐ Lead students to understand several topics that has to do with practical in the lab. ☐ Leads students to identify chemical apparatus and how to utilize them for qualitative and quantitative analysis. ☐ Guide students to carry out physicochemical Analysis in the lab such as Gravimetric, titrimetric measurements. ☐ Lead students to understand basic civic human right in civic society • Expose students to how to resolve conflict and stay in peace.
2017 to 2019	Quadcore computer Institute	Facilitator– teach senior secondary how to utilise computer for CBT exams. <i>Duty Manager</i> – register new intakes, process records, issuance of receipt, collect and collate lists of debtors, and management of financial statements, organize, manage and report duty. <i>Tutor</i> – teaches OTM Courses for O' Level Students

Research Interests

Projects: Research Interest

- Bioanalytical Chemistry
- Wastewater Treatment Using Functionalized Membranes
- 2d-Energy Storage Devices.

Completed Projects BS (Starting with the Latest)

Date	Title
2019	Production of biogas from rumen content by catalytic activity of ZnO ₂ and ZrO ₂ catalyst.

Works Completed in MS

Date	Title and Organization
2022	Wastewater Treatment Using Functionalized Membranes
2023	Development of thin film nanocomposite supported membrane for Highly efficient water purification.

Publications and Conferences

- Production Of Biogas From Rumen Content By Catalytic Activity Of ZnO_2 And ZrO_2 Catalyst (Final Year Degree Project Unpublished)
- Synthesis Of Aminopropyl Triethoxysilane/Melamine Incorporated Superhydrophilic Membranes For Simultaneous Removal Of Oil, Metals, And Salts From Water. (Under Review)
- American Chemical Society End Of 2021 Chemistry Conference (Online)
- Green Sciences For Sustainable Development Foundation, GSSD Foundation Venice Italy.
- ACS Fall Online Conference:
Paper Id: 3889259
Paper Title: Smart Superhydrophilic Thin Film Nanocomposite Supported Si-G-Polyamide For Highly Effective Water Treatment

Paper presented:

- Production of biogas from anaerobic digestion of cow dung and rumen content. 2019
- Comparison between the thermodynamic characteristics of corrosion inhibition efficiency using green leaf of *moringa oleifera* and fruit leaf of *carica papaya* in 1.0M Sulphuric acid on Al. 2021
- Titania based Nanomaterials for energy production 2022

Service to the Community (with Status and dates)

- Computer training on office packages at Quadcore computers Duties: Staff 2019
- Voluntary Mathematics teacher at Nusratul islam Girls 2016
- Senior secondary school, Gwale LG, Kano