

THIN FILM NANOCOMPOSITE MEMBRANE INCORPORATED WITH  
PALYGORSKITE/CHITIN HYBRID FOR FORWARD OSMOSIS  
DESALINATION

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DESALINATION

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## ABSTRACT

Desalination technology has become more relevant as a result of increasing demands for clean water and shortcomings of surface water. In forward osmosis (FO) system, the difference in osmotic pressure resulting from the difference in concentration of feed solution (FS) and draw solution (DS) acts as the driving force of water molecules transportation across the membrane. FO membranes are faced with the issue of dilution of the DS which gives rise to internal concentration polarization (ICP) that results in the reduction of the osmotic pressure difference across the active layer of the membrane, hence leading to low water flux. Improving the hydrophilicity of the substrate of the FO thin film composite membranes has been proven as a feasible strategy to address this issue and enhance the desalination performance of the FO membranes. The objectives of the study are to synthesize PAL-CH based on different compositions of palygorskite and chitin and to characterize the material of the physic-chemico-chemical properties. Fabricate and characterize thin film nanocomposite (TFN) membrane with its substrate incorporated with synthesized PAL-CH hybrid, and evaluation of the TFN membrane performance in terms of rejection, flux and anti-fouling properties. To achieve these objectives, a thin film nanocomposite membrane incorporated with palygorskite/chitin (PAL-CH) hybrid nanomaterial had been successfully fabricated. The incorporation of PAL-CH material enhanced the hydrophilicity of the FO membrane, resulting in the formation of hydration layer at the membrane interface, thereby facilitating the transportation of water across the membrane. The PAL-CH hybrid nanomaterial was synthesized via ball milling method. The substrates were developed with 15 wt % of polysulfone (PSF) and various loads of PAL-CH hybrid nanomaterial (range 0 – 0.015 wt %). The first stage of this study was the synthesis of hybrid nanomaterial. At the second stage of this study, the synthesized hybrid nanomaterial was incorporated in the substrate of the TFN membrane and its performance was studied employing the reverse osmosis system. Water permeability of  $2.4 \text{ Lm}^{-2} \text{ h}^{-1}$  was achieved when 0.01 wt % of PAL-CH hybrid nanomaterial was incorporated into the substrate of the TFN membrane. The water permeability was approximately 192.7 % higher than that of pristine membrane. The sodium chloride rejection was 98.5 % and 98 % for PAL-CH hybrid incorporated membrane and pristine membrane respectively. At the final stage of the study, the fabricated PAL-CH based TFN membrane was subjected to FO performance test. The PAL-CH incorporated TFN membrane showed good FO performance with water fluxes of  $11.68 \text{ Lm}^{-2} \text{ h}^{-1}$  (in active layer facing FS mode) and  $34.39 \text{ Lm}^{-2} \text{ h}^{-1}$  (in active layer facing DS mode) while maintaining small structure parameter (S) and reverse solute flux (Js) value. The PAL-CH nanomaterial incorporation led to the formation of higher pronounced ridges in membrane which is a confirmation of improved surface roughness which facilitates higher degree of cross-linking. Besides, the modified membrane exhibited less severe membrane fouling and high pure water flux recovery which is an indication of a good quality FO membrane. The introduction of PAL-CH into the substrate enhanced the separation features of the membrane in terms of S parameter, rejection and water flux. The introduction of PAL-CH reduced the S parameter hence restricting the ICP phenomenon impact in the thin film composite FO process. It is concluded from the research findings that the addition of the PAL-CH hybrid nanomaterial within substrate has substantial effects on the performance of the TFN-FO membrane. The facile substrate modification promotes the applicability of this nanocomposite membrane for desalination application.

## ABSTRAK

Teknologi penyahgaraman telah menjadi lebih relevan hasil daripada peningkatan permintaan terhadap air bersih dan kekurangan air permukaan. Dalam sistem osmosis hadapan (FO), perbezaan tekanan osmosis yang terhasil daripada perbezaan kepekatan larutan suapan (FS) dan larutan luaran (DS) bertindak sebagai daya pacu pengangkutan molekul air merentasi membran. Membran FO berhadapan dengan isu pencairan DS yang menimbulkan pengutuban kepekatan dalaman (ICP) yang mengakibatkan pengurangan perbezaan tekanan osmosis merentasi lapisan aktif membran, seterusnya membawa kepada fluks air yang rendah. Peningkatan hidrofilik substrat membran komposit filem nipis FO telah terbukti sebagai strategi yang boleh dilaksanakan untuk menangani isu ini dan meningkatkan prestasi penyahgaraman membran FO. Objektif kajian adalah untuk mensintesis dan mencirikan sifat fizik-kimiko-kimia PAL-CH yang disintesis berdasarkan komposisi poligorskit dan kitin yang berbeza, fabrikasi dan pencirian membran komposit nano filem tipis (TFN) dengan substratnya digabungkan dengan hibrid PAL-CH yang disintesis dan penilaian prestasi membran TFN dari segi sifat penolakan, fluks dan anti-kotoran. Untuk mencapai objektif tersebut, dalam kajian ini membran nanokomposit filem nipis yang digabungkan dengan bahan nano hibrid poligorskit/kitin (PAL-CH) telah berjaya dihasilkan. Penggabungan bahan PAL-CH meningkatkan hidrofilik membran FO dan mengakibatkan pembentukan lapisan penghidratan pada antara muka membran, dengan itu memudahkan pengangkutan air merentasi membran. Bahan nano hibrid PAL-CH telah disintesis melalui kaedah pengilangan bebola. Substrat telah dibangunkan dengan 15 wt.% polisulfon (PSF) dan pelbagai muatan bahan nano hibrid PAL-CH (julat 0 – 0.015 wt.%). Peringkat pertama kajian ini ialah sintesis bahan nano hibrid. Pada peringkat kedua kajian ini, bahan nano hibrid tersintesis telah dimasukkan ke dalam substrat membran TFN dan prestasinya dikaji menggunakan sistem osmosis balikan. Kebolehtelapan air  $2.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  boleh dicapai apabila 0.01 wt.% bahan nano hibrid PAL-CH telah dimasukkan ke dalam substrat membran TFN. Kebolehtelapan air adalah lebih kurang 192.7% lebih tinggi daripada membran tulen. Penolakan natrium klorida masing-masing adalah 98.5 % dan 98 % untuk membran gabungan PAL-CH hibrid dan membran tulen. Pada peringkat akhir kajian, membran TFN berasaskan PAL-CH yang direka telah tertakluk kepada ujian prestasi FO. Membran TFN yang diperbadankan PAL-CH menunjukkan prestasi FO yang baik dengan kebolehtelapan air pada  $11.68 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (dalam mod lapisan aktif menghadapi FS) dan  $34.39 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (dalam mod lapisan aktif menghadapi DS) sambil mengekalkan saiz kecil parameter struktur (S) dan nilai fluks garam balikan (Js). Penggabungan bahan nano PAL-CH membawa kepada pembentukan rabung yang lebih jelas dalam membran yang menunjukkan kekasaran permukaan yang lebih baik dan memudahkan tahap pemautilangan yang lebih tinggi. Selain itu, membran yang diubah suai menunjukkan kekotoran membran yang kurang teruk dan perolehan fluks air tulen yang tinggi yang menunjukkan kualiti yang baik untuk membran FO. Penggabungan PAL-CH ke dalam substrat meningkatkan ciri pemisahan membran dari segi parameter S, penolakan dan fluks air. Penggabungan PAL-CH mengurangkan parameter S justeru menyekat kesan fenomena ICP dalam proses komposit filem tipis FO. Daripada penemuan penyelidikan dapat disimpulkan bahawa penambahan bahan nano hibrid PAL-CH dalam substrat mempunyai kesan yang besar terhadap prestasi membran TFN-FO. Pengubahsuaian substrat yang mudah menggalakkan kebolehgunaan membran nanokomposit ini untuk aplikasi penyahgaraman.

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## LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
AL-DS	-	Active layer facing draw solution
AL-FS	-	Active layer facing feed solution
ATR-IR	-	Attenuated total reflectance-infrared spectroscopy
A-PAL	-	Acid treated palygorskite
Aqp	-	Aquaporin
BSA	-	Bovine serum albumin
CA	-	Cellulose acetate
CH	-	Chitin
ChNF	-	Chitin nanofiber
CNTs	-	Carbon nanotubes
CP	-	Concentration polarization
DMAc	-	Dimethylacetamide
EPS	-	Extracellular polymer substance
FESEM	-	Field emission scanning electronic microscope
FO	-	Forward osmosis
FS	-	Feed solution
FTIR	-	Fourier transform infrared spectroscopy
HCl	-	Hydrochloric acid
HNT	-	Halloysite nanotube
HTI	-	Hydration technologies Inc.
ICP	-	Internal concentration polarization
IP	-	Interfacial polymerization
LBL	-	Layer by layer
MCDI	-	Membrane capacitive deionization
MED	-	Multieffect distillation
MFC	-	Microbial fuel cell
MEMO-PMMA-Br	-	methacrylate-polymethyl methacrylate-bromide
MPD	-	1,3-phenylenediamine

MMTs	-	Montmorillonites
MSF	-	Multi stage flash
MWCNTs	-	Multi-walled carbon nanotubes
NaCl	-	Sodium chloride
NaClO	-	Sodium hypochlorite
NaOH	-	Sodium hydroxide
NMP	-	N-methyl-2-pyrrolidone
NF	-	Nanofiltration
PA	-	polyamide
PAN	-	Polyacrylonitrile
PAL-CH	-	Palygorskite/chitin hybrid nanomaterial
PAL	-	Palygorskite
PEI	-	Polyethylenimine
PES	-	Polyethersulfone
PIP	-	Piparazine
PRO	-	Pressure retarded osmosis
PSF	-	Polysulfone
PVC	-	Polyvinyl chloride
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
RO	-	Reverse osmosis
RSD	-	Reverse salt diffusion
TEM	-	Transmission electron microscopy analysis
TEMPO	-	2,2,6,6-tetramethyl piperidin-1yl)oxyl
T-Chitin	-	TEMPO oxidized chitin
TFC	-	Thin film composite
TFN	-	Thin film nanocomposite
TGA	-	Thermogravimetric analysis
TMC	-	Trimesoyl chloride
TNTs	-	Titania nanotubes
UF	-	Ultrafiltration
VC	-	Vapor compression
XRD	-	X-ray diffraction

## LIST OF SYMBOLS

$A$	-	Water permeability coefficient ( L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )
$A_m$	-	membrane effective area (m <sup>2</sup> )
$B$	-	Solute permeability coefficient (m/s)
$C_P$	-	NaCl concentration in the permeate
$C_F$	-	NaCl concentrations in the feed
$C_t$	-	concentration of the salt measured at the start and at the end
$D$	-	Diffusion coefficient of solute
$J$	-	Water flux (Lm <sup>-2</sup> h <sup>-1</sup> )
$J_s$	-	Reverse salt flux (g/m <sup>2</sup> .h)
$M$	-	Molarity (M)
$\rho$	-	feed solution density
$p$	-	Pressure (bar)
$R$	-	Salt rejection (%)
$S$	-	Membrane structural parameter (mm)
$\pi$	-	Osmotic pressure
$\pi_{\text{draw}}$	-	Osmotic pressures of the draw solution
$\pi_{\text{feed}}$	-	Osmotic pressures of the feed solution
$\Delta P$	-	Hydraulic pressure difference (bar)
$\Delta V$	-	Difference in permeate volume (m <sup>2</sup> )
w/v	-	Weight over volume
$\Delta t$	-	Time for permeate collection (sec)
$V_t$	-	Feed volume measured at the start and at the end
$\delta$	-	Thickness of substrate
$W_w$	-	Weight of wet substrate
$W_d$	-	Weight of dry substrate
$WU$	-	Water uptake of the substrate



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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Fresh water is an important source for survival of life on earth and also essential feed in many key industrial operations such as pharmaceuticals industry, beverage and food industry, agricultural industry, electronics industry, petrochemical industry as well as the oil and gas industry[1]. As clean water is crucial for life as well for the economic and industrial growth, the world's clean water requirement has been increasing exponentially in the recent decade as a result of the population explosion and exponential industrialization in many developing countries of the globe. The pollution of available sources of water in addition to climate change has further increased the demands for fresh clean water supply [2]. According to the United Nation, by the middle of the 21<sup>st</sup> century two to seven billion people will face non availability of clean water[3]. Without the availability of clean water, the economic development and global health are affected while the industrial operations will be disrupted and supply of hygienic foods and beverages will be jeopardized. The World Health Organization endorsed a report in 2002 which stated that the shortage of safe and clean water resulted in 3.1% of death globally. This trend is predicted to increase over the periods of time [4].

Seawater desalination has been a great alternative to supply large volumes of clean water. According to statistics from the International Desalination Association (IDA), as in 2015, up to 16,000 desalination plants have been installed in more than 150 countries where the production of clean water has achieved 90 million m<sup>3</sup>/day globally [5]. Membrane-based desalination processes, like pressure driven nanofiltration (NF) and reverse osmosis (RO), osmotically driven membrane technologies such as forward osmosis(FO) and pressure retard osmosis (PRO), thermal processes such as membrane distillation (MD), as well as evolving technologies like

microbial fuel cell (MFC) and membrane capacitive deionization(MCEDI) are all acceptable solutions to sustainable clean and safe water supply and address the scarcity of water issue [6]. The conventional thermal desalination process is inefficient in terms of its energy consumption and liable to corrosion when compared to membrane desalination technology [7]. Hence, the membrane technology is preferable especially due to its lower consumption of energy and the simplicity of operation[8].

Among the membrane-based desalination technology, RO is a promising separation process to yield high quality pure water due to near complete rejection of most of the contaminants found in waste water [9]. Studies have shown the suitability of using RO to purify produce water for the past decades [10-11]. RO has been in the use for water desalination for fresh water requirement of the oil and gas industries. However, the accumulation of substances like dissolved and dispersed hydrocarbon, salts, clay particles and surfactant on the pores of the membranes has led to membrane fouling which in turn results in the deterioration of flux [12]. As the operating pressure and duration increase, the particle accumulation accelerates the formation of a layer on the surface of the membrane[13]. Cleaning or replacement of membrane is necessary hence more energy and chemical cost in addition to more downtime of the process installation are unavoidably imposed on the process. In addition, pollutants also decrease the available pore size by liquid liming formation within the pores which eventually lead to membrane fouling. When this phenomenon occurs, the membrane cleaning efficiency as well as the water flux is significantly affected. To tackle the fouling issue, RO process usually needs effective pre-treatment for better efficiency[9].

An alternative to conventionally pressure driven technology is FO. When compared with commonly used RO, osmotically driven process requires less energy with a better oil and salt rejection as well as lower tendency to fouling. FO is a membrane process that uses a semi permeable dense hydrophilic membrane that separates two aqueous solutions that are of different osmotic pressures. The difference in osmotic pressures is the driving force. Its principle is based on the osmotic transport of water across a semi-permeable hydrophilic membrane from a dilute feed solution into a concentrated draw solution [14]. For it to be competitively used in both

industrial and laboratory scale, there is a need to deal with the challenge of membrane performance and economic viability of the draw solution regeneration [9]. As a rule, a technological feasible draw solution should allow high water permeability and low reverse salt flux to reduce the leakage of salt to enhance the energy efficiency [15]. Currently a wide range of draw solutions with a promising FO performance and easy regeneration features have been explored [15]. Among the widely used draw solutions are low cost organic and inorganic salts with high osmotic pressure potential such as sodium chloride and ammonium bicarbonate[16].

One of the most significant challenges militating against osmotically driven membranes processes like FO is the occurrence of internal concentration polarization (ICP) due to the dilution of draw solutes or the accumulation of feed solutes in the substrate layer[17]. The former condition is known as dilutive ICP, whereas the latter is known as concentrative ICP. Due to the asymmetrical structure of TFC membrane, FO can be operated in two modes, i.e active layer facing feed solution (AL-FS) orientation and active layer is faced against the draw solution (AL-DS) orientation [18]. Fouling of membrane is a complex phenomenon which occurs due to the accumulation of different components on the membrane surface or deposits within the pores, this leads to pores blockage [19]. Although fouling in FO is less severe, it is still a major issue in FO. The fouling in the FO process is reversible due to induced cake-enhanced osmotic pressure and this is caused by reverse salt flux from the draw solution [20]. It then means that reverse solute flux may worsen the cake enhanced osmotic pressure in the fouling layer. The FO membrane improvement is faced with the challenge of design of thin film composite (TFC) and thin film nanocomposite (TFN) with the required characteristics. In the FO operation, the ICP induced water flux reduction is majorly affected by the tortuosity, porosity as well as the thickness of the support layer. Therefore, the morphology of the microporous substrate of TFC-FO membrane is one of the most vital factors to alleviate ICP and attain high FO flux [21]. A good FO membrane substrate should have characteristics of being very thin, highly porous, low tortuosity and has sufficient mechanical strength when hydraulic pressure is required [22].

Polyamide(PA) TFC membranes which typically consists of a microporous polymer membrane or polyester nonwoven fabric as support and an ultrathin PA barrier layer has been commonly applied for water desalination. This as result of their high water flux and excellent rejection capacities [23]. Despite the huge advancements in PA-TFC membranes, challenges like permeability and fouling are still shortcomings that need to be overcome by the desalination family. Presently, the major focus in FO membrane technology research for water treatment and desalination is related to the establishment of fouling resistant membranes through nanomaterial incorporation to form the so-called thin film nanocomposite (TFN) [24-25].

Nanomaterials have rekindled considerable interests in the application of water purification [26-27], owing to their exceptional properties such as; high surface area and hydrophilicity as well as tunable pore size and surface functionalities. Nanocomposite membranes inherit the fascinating properties of nanomaterials hence demonstrated enhanced physico-chemical properties which eventually contribute to improved performances. A wide range of nanomaterials have been explored for the preparation of TFN to improve the antifouling properties of FO membranes. A commercially attractive TFN membranes can give not only opportunities to address the permeability-selectivity trade-off but also enhancing fouling resistance and antibactericidal capacity. Chitin based nanomaterial have been used in different field of nanotechnology especially in the area of desalination [28].

Chitin has outstanding antifouling properties in water due to the hydrophilic nature of the shell, endowing it with an underwater superoleophobicity quality [29]. Being a major part of the shrimp shell, chitin might have the potential for self-cleaning, depending on the availability of many hydroxyl and acetylamino groups on chitin. It is worthy of mention that native chitin derived from shrimp shells is made up of bundles of crystalline chitin nanofibers and can be easily disintegrated sufficiently into individual chitin nanofibers [30]. Chitin nanofibers which have extremely high specific surface area can easily form a highly porous mesh [31]. Such a porous material would be beneficial for water permeation and salt/water separation. Besides, chitin nanofibers with high fracture and high young's modulus possess superior mechanical performance [32]. It is therefore no doubt that the combination of the

inherent hydrophilic feature and nanostructure of the chitin nanofiber would be a beneficial strategy to develop water separation membrane with high flux, high efficiency and antifouling properties.

Clays are also another ideal nanofillers for TFN membranes due to their high intercalation chemistry, inherent hydrophilicity and readily available properties [33-34]. Generally, clays are made up of silicates or alumina silicates, which are composed of silicon, aluminium or magnesium, oxygen and hydroxyl with other associated cations, which are joined together and stacked on top of each other with varied inter-layer distance to form the layered silicates frame work. As a result of their unique structure and properties, clay materials have been widely used in membrane water treatment. As an interesting material for construction of high performance ultrafiltration (UF) membranes, clay materials such as palygorskite (PAL), montmorillonites (MMTs) and halloysite nanotubes (HNTs) were added into mixed matrix membranes, which achieved an enhanced water flux and improved antifouling capability [35–37]. PAL is a low cost and environmentally friendly natural nanoclay material with tubular structure and excellent hydrophilicity. It is naturally available in 1D rod-like silicate clay mineral with high surface area and a large number of hydrophilic surface groups [38–40]. It has a tubular structure that promotes the movement of water molecules[41].

In this research, palygorskite-chitin hybrid is used as the nanofiller for TFN membranes to utilize the unique characteristic of both palygorskite and chitin nanofibers. Undoubtedly, the combination of the hydrophilic feature and the nanostructure of chitin nanofiber would be an advantageous strategy to fabricate water separation membrane with antifouling, high efficiency and high flux properties [42]. Besides, palygorskite is an efficient carrier to prepare nano composites with homogeneous dispersion of nanoparticles on its surface [43].

## 1.2 Problem Statement

At present, FO processes are faced with the issue of dilution of the DS which gives rise to ICP that results in the reduction of the osmotic pressure difference across the active layer of the membrane leading to low flux. In order to mitigate the ICP issue, the physic-chemical properties of the TFC FO membrane must be carefully tailored to address the inherent fouling [44]. One of the most applied strategies to tackle this issue is to modify the membrane substrate. Currently, many attempts have been reported based on incorporation of hydrophilic nanomaterials like graphene oxide. For instance, Lim et al mitigated ICP by modifying FO membrane substrate through the incorporation of graphene oxide leading to good performance of the membrane[45]. Darabi et al. reduced the ICP of FO membrane via the incorporation of  $\text{Fe}_3\text{O}_4$  in the substrate of the membrane [45]. Modification of membrane substrate by nanomaterial introduction can flexibly promote fabrication of favourable substrate properties in multiple ways. This includes improving the solvent exchange rate of the solvent and the nonsolvent, surface chemistry (wettability, hydrophilicity), microstructure (pore inter-connectivity, porosity) and mechanical stability of the substrates to increase rejection efficiencies and water permeability [46]. The current TFC and TFN membranes cannot sufficiently mitigate fouling as a result of the properties of the materials used for the fabrication of the membrane [47]. It is difficult to have a single material with both excellent hydrophilicity and anti-fouling properties. Therefore, it is desired to form a hybrid material which demonstrates synergetic advantages.

Notwithstanding the fact that ICP and fouling cannot be totally avoided in the FO process, modifying the surface and structural properties of the substrate can alleviate the adverse impacts of these phenomena. The negative effect of ICP could be minimized through alleviation of the S value of the membranes' substrates. The S parameter decreases proportionally as the porosity increases but increases with high thickness and tortuosity of the substrates. As a key step in controlling ICP, the substrates therefore need to be redesigned to introduce a mixture of qualities: high porosity, thinness, excellent hydrophilicity, and less pore tortuosity to reduce ICP and maximize water flux in FO. Xue et al. in their desire to mitigate ICP grafted titanium dioxide ( $\text{TiO}_2$ ) nanoparticle into two commercially available FO membrane, a

cellulose triacetate (CTA) membrane and aquaporin (AqP) membrane [48]. This was done via a specially designed 3-(trimethoxysilyl) propyl methacrylate–polymethyl methacrylate–bromide (MEMO–PMMA–Br) monomer chain to improve the filtration performance with regard to pure water flux and organic fouling resistance. Both membranes dramatically improved their pure water flux, with average flux increases of 73.4 % and 13.6 % for the modified CTA and AqP membranes, respectively. However, according to their report, there was adverse effect on the surface hydrophilicity of the modified Aqp which was attributed to obstruction of aquaporins from the feed solution due to the coverage of MEMO-PMMA-BR monomer and TiO<sub>2</sub> nanoparticles. This could be mitigated using other method of modification. Besides, grafting of nanoparticle unto membrane could be subjected to wash away over a period of time thereby limiting the performance of the membrane. This can be minimized through substrate modification via blending. Mengyuan et al. developed a thin film nanocomposite membrane through the incorporation of PAL nanorods during interfacial polymerization[49].The inclusion of PAL improved the porosity, surface hydrophilicity, surface pore diameter, mechanical strength, and thermal stability of the ultrafiltration membrane. As a result, the resultant membranes exhibited higher water permeability than pristine membranes. The water flux was 229.5 l m<sup>-2</sup>h<sup>-1</sup> which is 1.3 higher than the reference membrane. However, the salt rejection was only 92%, which indicates little compromise in salt rejection. The hybrid material demonstrated superior properties in terms of hydrophilicity or anti fouling than either of the constituent material of the hybrid.

PAL and CH have been separately used for modification of membranes for desalination. PAL has a better performance in terms of flux than CH while CH has a superior antifouling and mechanical properties than PAL, hence the motivation to form PAL-CH hybrid nanomaterial for FO membrane application. Using vacuum assisted filtration technology and PAL as the raw material, Yang et al. reported the simple construction of a superhydrophilic/underwater superoleophobic multifunctional separation membrane [50]. The membrane exhibited outstanding separation performance, with a permeation flux of 477.7 5.0 L. m<sup>-2</sup> bar<sup>-1</sup> and a high separation efficiency of up to 99.6 % . On the other hand, it has been reported that chitin nanofibrous membrane (CNM) developed via filtration of chitin nanofiber suspension showed salt rejection efficiency of >95% , water flux of >1500L.m<sup>-2</sup>bar<sup>-1</sup> and also



exhibited excellent mechanical strength, thermal stability, recyclable performance and pH-resistance [42]. In addition, Kai et al [51] reported that chitin nanofibers prepared by (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) mediated oxidation of chitin using one pot ball milling showed great potential in membrane applications. The oxidized chitin exhibited high hydrophilicity, biocompatibility and strong mechanical properties. From the above previous reports on PAL and chitin, it is obvious that PAL is more hydrophilic than chitin while chitin has a better anti fouling property. The shortcoming of each material can be addressed through the hybridization of chitin and PAL such that the resultant PAL-CH will be remarkably endowed with both desired properties.

This study aims to develop palygorskite-chitin (PAL-CH) hybrid membrane having both optimized PA layer and membrane support layer that address the limitations of both FO and RO membranes. Developing a membrane with PAL-CH nanofiber hybrid embedded within the thin substrate layer can improve the characteristics of membranes owing to their super hydrophilicity, high antifouling and strong mechanical properties. There has not been any report on the application of PAL-CH nanomaterial hybrid in TFN membrane but studies have been done on incorporation of some nano materials in TFN membranes. For instance, nanoparticle incorporation was reported to have been used to effectively improve water flux in a study by Ma et al. [52]. Also, Rajie et al. reported similar observation after incorporation of  $\text{TiO}_2$  into PA TFN membrane [53]. It is therefore hypothesized that TFN FO membrane consists of PAL-CH hybrid within the membrane supports could address the issues related to low FO water flux and, reverse solute diffusion from the DS into the feed. The suppression of nanomaterial agglomeration through modification can also reduce the tendency of the formation of defective membranes that would compromise the salt rejection performances.

### **1.3 Objective of the Study**

The aim of this study is to evaluate the potential of PAL-CH hybrid incorporated TFN membrane for desalination. Based on the aforementioned problem statement, the specific objectives of this study are:

1. To synthesize and characterize the physico-chemical properties of PAL-CH hybrid synthesized in different compositions of palygorskite and chitin
2. To fabricate and characterize TFN membrane with its substrate incorporated with different loadings of the synthesized PAL-CH hybrid.
3. To evaluate the TFN membrane performance in terms of rejection, flux properties through RO system and rejection, flux and anti-fouling properties through FO desalination system.

### **1.4 Scope of the Study**

To achieve the above objectives, the following scopes have been outlined:

1. Synthesis of PAL-CH hybrid via a ball milling synthesis method with PAL and chitin in the ratio of 3:1 (w/w). The ratio between PAL and chitin nanofiber suspension is 1:100 (w/v) with the predetermined concentrations of 1, 1.5, 2 and 5 mg ml<sup>-1</sup>.
2. Characterization of the synthesized PAL-CH hybrid using transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), spectroscopy and zeta potential analyzer for morphology, crystallinity, functional groups and surface charges respectively.

3. Fabrication of substrate layer by adding different loading of PAL-CH hybrid in a chosen range of 0-1 wt % (w/v) into polymer solution. The polymer is Polysulfone (PSF) while the solvent is N-methyl-2-pyrrolidone (NMP).
4. Preparation of TFN membranes over a fabricated membrane support with a top selective layer formed via interfacial polymerization of 1, 3-phenylenediamine (MPD) 2% (w/v) in aqueous solution and 1, 3, 5-benzenetricarbonyl trichloride (TMC) 0.1% (w/v) in n-hexane solution
5. Characterization of the fabricated TFN membranes using attenuated total reflectance Fourier transmission infrared spectroscopy (ATR-FTIR), field emission scanning electronic microscopy (FESEM), porosity test, atomic force microscopy (AFM), zeta potential, contact angle goniometer, for functional groups, surface morphology, surface roughness, surface charges, and surface wetting properties respectively.
6. Performance evaluation of the water permeability and salt rejection of the resultant TFC and TFN membranes in RO mode.
7. Performance evaluation of TFC/TFN membranes in terms of water flux and reverse salt flux in FO mode using RO water and aqueous NaCl solution as feed and draw solution respectively. Two FO operation modes, AL-FS and AL-DS are investigated.
8. Determination of S parameter values to evaluate the propensity of ICP in the synthesized TFC/TFN membranes.
9. Evaluation of PAL-CH membrane in terms of the anti-fouling and flux recovery of TFN membrane in FO application using 200 ppm of bovine serum albumin (BSA) as modal foulant.

## **1.5 Significance of the Study**

This study presents the first attempt to develop nanomaterial hybrid (PAL-CH) from a low cost, environmentally friendly nanoclay (PAL) and second most abundant biomass (chitin) via ball milling for incorporation into membrane fabrication for desalination application. Substrate modification through hybrid nanomaterial addition is a desirable strategy for preparation of an ultrathin composite membrane with tailored physicochemical. Through modification by nanomaterial incorporation, the substrate structure could be optimized in terms of its thickness, tortuosity, and porosity. Besides, the new features exhibited by PAL-CH hybrid nanomaterial could invigorate great interest in hybridization of nanoparticles and their utilization in TFC membrane modification. Thus, obtain a thin and high selective membrane with improved hydrophilicity, antifouling propensity and long period stability. This study also showcases the potential of PAL and chitin to be hybridized and used for industrial scale membrane substrate modification as it involves simple as well as straightforward method of membrane modification. The approach offers a solution to fabricate a green and sustainable engineering membrane that is promising for desalination application.

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## LIST OF PUBLICATIONS

1. **Stanley Chinedu Mamah**, P.S. Goh, A.F. Ismail\*, M.A.M. Amin, N.A. Ahmad, N.D. Suzaimi, Y.O. Raji,(2020). Facile preparation of palygorskite/chitin nanofibers hybrids nanomaterial with remarkable adsorption capacity, *Material Science and Engineering B*, 262 (Q1, IF: 4.051).
2. **Stanley Chinedu Mamah**, P.S. Goh, A.F. Ismail\*, N.D. Suzaimi, N.A. Ahmad, W.J. Lee, (2021). Flux enhancement in reverse osmosis membranes induced by synergistic effect of incorporated palygorskite/chitin hybrid nanomaterial, *Journal of Environmental Chemical Engineering* , 9: 25-37 ( Q1, IF: 5.909)
3. **Stanley Chinedu Mamah**, P.S. Goh, A.F. Ismail\*, T. El-badawy, A. Agi, F. Yakasai. (2021). Facile Purification of Palygorskite and Its Effect on The Performance of Reverse Osmosis Thin Film Nanocomposite Membrane, *Journal of Chemical Technology and Biotechnology*, 6744: 1-10 (Q2 , IF: 3.174)
4. **Stanley Chinedu Mamah**, P.S. Goh, A.F. Ismail\*, L.T. Yogarathinam, N.D. Suzaimi, A. C. Opia , S. Ojo, (2022). Bio-polymer modified nanoclay embedded forward osmosis membranes with enhanced desalination performance, *Journal of Applied Polymer Science*, 52473 (Q2 , IF: 3.125)
5. **Stanley Chinedu Mamah**, P.S. Goh, A.F. Ismail\*, A. C. Opia , S. Ojo, N. E. Ngwana, (2022). Performance evaluation of chitin as a nanofiller for reverse osmosis membrane development, *Nanotechnology for Environmental Engineering* (Scopus, submitted)