MOLECULAR FUNCTIONALIZED ANTIFOULING POLYMERIC MEMBRANES WITH TUNABLE WETTING FOR OIL-WATER SEPARATION

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by

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Submitted

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Dedicated to my family and my mentor

CERTIFICATE

This is to certify that the thesis entitled, "**Molecular Functionalized Antifouling Polymeric Membranes with Tunable Wetting for Oil-Water Separation**" being submitted by Ms. Kanupriya Nayak to Indian Institute of Technology Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Ms. Nayak has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

Increasing demand for and shortage of clean drinking water due to rapid urbanization, population growth, gross misuse, and climate change have become unprecedented urgent issues in this century. The direct discharge of polluted water containing harmful contents such as chemicals, industrial effluents, heavy metals, oils, biological reagents, and pathogens severely affects the marine ecosystem, human health, and the environment. Among different water polluting substances, oils released from petrochemical, food, metallurgical, and other industries, along with frequent oil spills, are difficult to separate from the oily wastewater. The membrane-based separation and filtration are superior to the traditional treatment methods because it does not require thermal or chemical treatment. Therefore, it is an aggressive approach for molecular separation. Besides, membrane separation offers other intrinsic merits, such as a smaller environmental footprint (no emissions), continuous operation, and great simplicity. However, current membrane based filtration technologies suffers from high energy consumption, low flux, compromised rejection, high organic and biological fouling, giving rise to a significant impetus to deliver new research for novel membrane development. To minimize the above problems, coating, blending, and grafting of hydrophilic polymers and nanomaterials are commonly used, which suffer from exclusion, phase separation, and leaching out from the matrix.

To address the above issues herein, a simple and straightforward method to modify and produce superhydrophilic and underwater superoleophobic membranes by molecular grafting and functionalization was targeted. Polyvinylidene fluoride (PVDF) and polysulfone (PSF) were used to fabricate the base membranes by non-solvent induced phase separation. In the first approach, the PVDF membrane was modified by molecular grafting of amino silanes with different amino groups on the polyvinyl alcohol primed surface. The molecular grafting followed by sol-gel imparted in-air superamphiphilicity and underwater superoleophobicity. Further, amino alkanes with varying chain lengths and amino groups were chosen and molecularly grafted on polydopamine coated PVDF membranes. The grafted amino alkanes were further functionalized with 1,3-propane sultone to obtain zwitterionic membranes. The zwitterionized membranes exhibited superhydrophilicity and underwater superoleophobicity. Both PVDF-amino silanes and zwitterionized PVDF membranes showed anti oil adhesion features under water. In the next work, a hydrophobic 1-Iodo-1H,1H,2H, 2H-perfluorodecane active molecule was grafted PSF base membranes by utilizing polydopamine surface chemistry. The prepared membranes showed in-air amphiphilicity, superhydrophilicity, and underwater superoleophobicity.

These molecules were chosen in such a way so that the surface should have either superhydrophilc/superoleophobic property or superamphiphilic property to impart strong antifouling behavior. The superhydrophilc/superoleophobic property along with zwitterionic functional groups led to substantial antifouling property towards BSA protein and oils and showed nearly complete flux recovery after multicycle filtration. All prepared membranes were thoroughly characterized using advanced tools and techniques such as ATR-FTIR, XPS, SEM, AFM, porometry, zeta potential, optical and fluorescence microscopy, etc., to establish the chemical and functional nature. The fully characterized membranes were tested for water permeation, solute/oil rejection, and flux recovery properties using pure water, BSA solution, and different oil-water emulsions (with and without surfactants). The molecularly grafted and functionalized membranes showed a manifold increase in water permeation compared to the neat membranes and high rejection of protein and oil emulsions. More than 95% flux recovery and very low irreversible fouling after a multicycle filtration operation confirm the usefulness of prepared membranes in separation, purification, and oily wastewater treatments. These findings indicate a promising and smart membrane surface modification technique that can be readily tailored for water filtration and separation applications. Moreover, the developed molecular functionalization strategy offers a simple and straightforward membrane modification methodology.

सार

तेजी से बढ़ते शहरीकरण, जनसंख्या वृद्धि, दुरुपयोग और जलवायु परिवर्तन के कारण स्वच्छ पेयजल की बढ़ती मांग और कमी इस सदी में अभूतपूर्व जरूरी मुद्दे बन गए हैं। अनेकों हानिकारक सामग्री जैसे कि विभिन्न प्रकार के रसायन, औद्योगिक अपशिष्ट, भारी धातु, तेल, जैविक अभिकर्मक और रोगजनकों से युक्त प्रदूषित पानी का सीधा निर्वहन, समुद्रीय पारिस्थितिकी तंत्र, मानव स्वास्थ्य एवं पर्यावरण को गंभीर रूप से प्रभावित करता है। विभिन्न जल प्रदूषणकारी पदार्थों में, पेट्रोकेमिकल, खाद्य, धातुकर्म और अन्य उद्योगों से निकलने वाले तेल, साथ ही बार-बार तेल टैंकरों के एक्सीडेंट और तैलीय अपशिष्ट को जल से अलग करना अत्यंत जटिल प्रक्रिया है। झिल्ली (membrane)-आधारित पृथक्करण और निस्पंदन को पारंपरिक उपचार विधियों से बेहतर बताया जाता है, क्योंकि इसमें थर्मल या रासायनिक उपचार की आवश्यकता नहीं होती है। इसलिए, यह आणविक पृथक्करण के लिए एक महत्वपूर्ण माध्यम है। इसके अलावा, झिल्ली पृथक्करण अन्य आंतरिक गुण भी प्रदान करता है, जैसे कि छोटा आकार एवं काम जगह लेना (बिना किसी अतिरिक्त उत्सर्जन के), निरंतर संचालन और साधारण प्रक्रिया, इत्यादि। हालांकि, वर्तमान में उपलब्ध झिल्ली आधारित निस्पंदन प्रौद्योगिकियों में उच्च ऊर्जा खपत, कम प्रवाह, बदलाव की कमी, उच्च जैविक और जैविक दूषण जैसे दोष के कारण, झिल्ली विकास के लिए नए शोध की आवश्यकता के लिए महत्वपूर्ण प्रोत्साहन को जन्म देता है उपरोक्त समस्याओं को कम करने के लिए, हाइड्रोफिलिक पॉलिमर और नैनोमैटेरियल्स के कोटिंग, सम्मिश्रण, और ग्राफ्टिंग का आमतौर पर उपयोग किया जाता है. पर इनमें आमतौर पर मैट्रिक्स से बहिष्करण, चरण पृथक्करण और लीचिंग की समस्या पायी जाती है। यहां उपरोक्त मुद्दे को संबोधित करने के लिए, आणविक ग्राफ्टिंग और क्रियाशीलता द्वारा सुपरहाइड्रोफिलिक और पानी में सुपरओलिओफोबिक झिल्ली को संशोधित

और उत्पादन करने के लिए एक सरल और सामान्य विधि को लक्षित किया गया था। पॉलीविनाइलिडीन फ्लोराइड (PVDF) और पॉलीसल्फोन (PSF) को लेकर गैर-विलायक प्रेरित चरण पृथक्करण द्वारा आधार-झिल्ली को बनाया गया है। प्रथम दृष्टिकोण में, PVDF झिल्ली को पॉलीविनाइल अल्कोहल से कोटिंग करने के बाद उसकी सतह पर विभिन्न अमीनो समूहों के साथ अमीनो सिलेन्स के आणविक ग्राफ्टिंग द्वारा संशोधित किया गया था। आणविक ग्राफ्टिंग के बाद सोल-जेल से उत्पन्न झिल्ली हवा में सुपरएम्फीफिलिसिटी और पानी में सुपरओलिओफोबिसिटी प्रदान करती है। इसके अलावा, अलग-अलग श्रृंखला की लंबाई और अमीनो समूहों के साथ अमीनो एल्केन को चुना गया और पॉलीडोपामाइन लेपित PVDF झिल्ली पर आणविक रूप से ग्राफ्ट किया गया। ग्राफ्टेड अमीनो अल्केन्स को 1,3-प्रोपेन सल्टोन के साथ क्रिया कराकर ज़्वीटरआयनिक झिल्ली प्राप्त बनाया गया था। प्राप्त किये गए zwitterionized झिल्लियों ने सुपरहाइड्रोफिलिसिटी और पानी के अंदर सुपरओलिओफोबिसिटी का प्रदर्शन किया। दोनों, PVDF-amino silanes और zwitterionized PVDF झिल्लियों ने पानी के अंदर तेल विरोधी विशेषताएं दिखाईं। अगले कार्य में, एक हाइड्रोफोबिक 1-Iodo-1H,1H,2H, 2H-perfluorodecane अणु को पॉलीडोपामाइन के सतह पर रसायानिक क्रिया का उपयोग करके PSF आधार-झिल्ली पर ग्राफ्ट किया गया था। इस प्रकार बनाये गए झिल्लियों ने हवा में रखने पर एम्फीफिलिसिटी, सुपरहाइड्रोफिलिसिटी और पानी के अंदर सुपरओलिओफोबिसिटी का प्रदर्शन किया।

उपरोक्त अणुओं को इस प्रकार से चुना गया था कि, सतह में या तो सुपरहाइड्रोफिलिक/ सुपरओलिओफोबिक अथवा सुपरएम्फीफिलिक गुण होनी चाहिए ताकि झिल्लिओं को एक प्रभावी एंटीफ़ाउलिंग व्यवहार प्रदान किया जा सके। ज़्वीटरआयनिक कार्यात्मक समूहों के साथ सुपरहाइड्रोफिलिक/सुपरओलिओफोबिक गुण ने बीएसए प्रोटीन और तेलों की ओर पर्याप्त

एंटीफ़ाउलिंग व्यवहार का प्रदर्शन किया और मल्टीसाइकिल निस्पंदन के बाद भी झिल्ली से लगभग पूर्ण पानी का प्रवाह बना रहा। रासायनिक और कार्यात्मक प्रकृति को स्थापित करने के लिए सभी तैयार झिल्लियों को उन्नत उपकरणों और तकनीकों जैसे कि एटीआर-एफटीआईआर, एक्सपीएस, एसईएम, एएफएम, पोरोमेट्री, ज़ीटा पोटेंशियल, ऑप्टिकल और फ्लोरेसेंस माइक्रोस्कोपी, आदि का उपयोग करके अच्छी तरह से उनके बिभिन्न गुणों को परखा गया था। शुद्ध पानी, बीएसए विलयन , और विभिन्न तेल-पानी इमल्शन (सर्फेक्टेंट के साथ और उसके बिना) का उपयोग करके पानी के पारगमन, विलेय / तेल पृथक्करण, और पारगमन स्तिथिरता का परीक्षण किया गया था। आणविक रूप से ग्राफ्टेड और कार्यात्मक झिल्ली ने अपरिवर्तित झिल्ली की तुलना में प्रोटीन और तेल इमल्शन की उच्च पृथक्करण और पानी के पारगमन में कई गुना वृद्धि दिखाई। एक बहु-चक्र निस्पंदन प्रक्रिया के बाद भी 95% से अधिक फ्लक्स रिकवरी और बाकि गुणों में बहुत कम परिवर्तन, पृथक्करण की छमता, बनाये गए झिलियों की शुद्धिकरण और तैलीय अपशिष्ट जल उपचार में उपयोगिता की पुष्टि करता है। ये निष्कर्ष एक आशाजनक और स्मार्ट झिल्ली के सतह को संशोधन करने की उपयुक्त तकनीक का संकेत देते हैं, जिसे जल निस्पंदन और पृथक्करण अनुप्रयोगों के लिए आसानी से उपयोग किया जा सकता है। इसके अलावा, विकसित आणविक क्रियाशीलता की रणनीति भविष्य में एक सरल और सामान्य झिल्ली संशोधन पद्धति को प्रदान करती है।

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LIST OF ABBREVIATIONS

4

4-(2-aminoethyl)benzene-1,2-diol
Dopamine 34

3

3-(2-aminoethylamino)propyl]trimethoxysilane
AEAPTMS 34
3-aminopropyl)trimethoxysilane
APTMS 34

A

Atomic force microscopy
AFM 41
Attenuated Total Reflectance-Fourier Transformed Infrared Spectroscopy
ATR-FTIR 40

B

Bovine serum albumin
BSA 24
BSA–fluorescein isothiocyanate conjugate
FITC-BSA 45

C

$CaSO_4$
Calcium sulfate 23

D

Dicholoromethane
DCM 74
Diethylene triamine
DETA 34
Dynamic light scattering
DLS 47

E

Energy dispersive X-ray analysis
EDX 41
Ethylene diamine
EDA 34

F

Field Emission Scanning Electron Microscopy
FESEM 40
First bubble point
FBP 64
Flux recovery ratio
FRR 46

H

Humic acid
HA 24
Hydrchloric acid
HCl 44
Hyperbranched fluoropolymer
HBFP 146

I

Isoelectric point
IEP 99

M

Mean flow pore size
MFP 64
Membrane bioreactors
MBR 23
Membrane distillation
MD 23
Microfiltration
MF 8

N

N^1-(3-trimethoxysilylpropyl) diethylenetriamine
N-TMSPDETA 34
Nanofiltration
NF 8
Nnitrogen
N 62
Nitrogen sulfur oxygen
NSO 5
N-Methyl-2-pyrrolidone
NMP 34
Non-solvent phase separation
NIPS 4

O

Oil contact angle
OCA 67
Water contact angle
WCA 67

P

Phosphate-buffered solution
PBS 45
Poly (dimethylsiloxane)
PDMS 14
Poly(ethylene glycol)
PEG 34
Poly(ethylene oxide)
PEO 50
Poly(ethylene terephthalate)
PET21
Poly(vinyl alcohol)
PVA 34
Poly(vinylidene fluoride)
PVDF 34
Polydopamine
PDA 85
Polysulfone
PSF38
Polyvinylidene fluoride-co-hexafluoropropylene
PVDF-HFP 22
Pottasium chloride
KCl 43
Pottasium hydroxide
KOH 44

R

Reverse osmosis
RO 8
Room temperature
RT 37
Root Mean Square
RMS 60

S

Silicon
Si 62
Silica
SiO_2 23
Sodium alginate
SA 24
Sodium dodecyl sulfate
SDS 47

T

Tetraethylene pentaamine
TEPA 34
Total organic carbon
TOC 149
Triethylene tetraamine
TETA 34

U

Ultrafiltration
UF 8
Ultrahigh molecular weight polyethylene
UHMWPE 18

X

X-ray photoelectron spectroscopy
XPS 40

LIST OF SYMBOLS

Symbol	**Meaning**
θ_Y	Young's angle
γ_{SV}	Solid vapor interface energy
γ_{SL}	Solid-liquid interface energy
γ_{LV}	Liquid-vapor interface energy
θ_W	Wenzel contact angle
R	The roughness factor
θ_C	Cassie-Wenzel contact angle
$\theta_{OW(Y)}$	Young's angle underwater oil contact angle
γ_{OV}	Surface tension at the oil-vapor interface
γ_{WV}	Surface tension at the water-vapor interface
γ_{OW}	Surface tension at the oil-water interface
α	Sliding angle
R	The liquid droplet radius
K	Proportionality constant
W_0	Dry weight of the membrane sample before modification
W	Dry weight of the membrane sample after modification
W_w	Wet weight
W_d	Dry weight
ρ_p	Density of polymer
ρ_s	Density of solvent
D	Diameter of cylindrical pore
Γ	Surface tension
Θ	Contact angle of Galwick™
P	Differential pressure across the membrane
θ_A	Advancing angle

θ_R	Receding angle
Z	Zeta potential
I_{str}	Streaming current
Δp	Hydrodynamic pressure difference
η	Viscosity of electrolyte solution
ε_e	Dielectric coefficient
ε_0	Vacuum permittivity
L	Streaming channel length
A	The streaming channel cross-section
V	Volume of the permeate
t	The permeate collection time
R, %	% Rejection
C_p	Amount of BSA in permeate
C_F	Amount of BSA in feed
J_{wi}	Pure water flux
J_{BSA}	BSA flux
J_{wr}	Remeasured pure water flux after cleaning the membranes
R_{t}	Total protein fouling
R_{r}	Reversible fouling
R_{ir}	Irreversible fouling
Ra	Average roughness
Rq	Root mean square roughness