Design and Fabrication of Anti(-bio)fouling Nanostructured Membranes Using Responsive Microgels

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by

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Dedicated to
my supervisor
and
my family

CERTIFICATE

*This is to certify that the thesis entitled, "**Design and Fabrication of Anti(-bio)fouling Nanostructured Membranes Using Responsive Microgels**" being submitted by **Mrs. Supriya Maity** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Mrs. Supriya Maity has worked under my guidance and supervision and has fulfilled the requirements for the submission of her 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

In this present era of preservation and recycling of water, membranes have acquired a distinct place in research to tackle the demand and production ratio of drinkable water. Membrane processes effectively remove a variety of impurities, including particles, proteins, microbes, viruses, bacteria, ions, and other contaminants, to obtain pure water. However, existing membrane-based filtration technologies face considerable challenges, including elevated energy consumption, reduced flow rates, compromised separation efficiency, and improved affinity to fouling. Numerous technologies have been developed to prevent or mitigate the fouling process. Pre-modifications of the membrane, such as coating, blending, or grafting of antifouling components, are the most preferred approach in real-time applications due to their potential to extend the membrane's lifespan and improve performance by making them more resistant to fouling, scaling, or biological growth. Nanostructured membranes (NSMs) have recently emerged as a highly promising technology for advancing water purification. These membranes are specifically engineered to possess distinctive attributes and capabilities owing to their finely crafted nanoscale structure. This nanoscale design empowers NSMs to effectively eliminate contaminants from water, resulting in superior purification performance. These membranes are designed to have unique architecture, properties, and functionalities from conventional modified membranes or composite membranes due to their nanoscale structure (nanoparticles, nanofibers, nanotubes, or other nanoscale components), which enables them to achieve superior performance in removing impurities from water. Microgels have garnered much attention among various nanostructures due to their extraordinary properties. These 3D cross-linked polymeric particles swelled in a solvent, exhibit a tunable nature due to which their size, shape, and response to environmental triggers can be adjusted, making them fascinating for a wide array of applications. Despite the huge potential and diverse range of options delivered by microgel systems, their capabilities in membrane application remain predominantly unexplored.

Henceforth, this research aims to investigate the capabilities of microgels to obtain NSMs and mitigate fouling and bio-fouling issues with membrane technology and other processes related to water purification. The first chapter of this thesis provides the broader context of water scarcity, different treatment options, and membranes. In the second chapter, an anti(bio)-fouling membrane using antibacterial thermo-responsive zwitterionically functionalized core-shell microgels for a

well-controlled water purification application was developed. The synthesis of the zwitterionic poly(N-isopropylacrylamide)-polyethyleneimine-propane sultone ((PNIPAm-PEI)-PS) core-shell microgel comprised a dual-step method involving a method of grafting copolymerization of NIPAm, PEI, and MBA, followed by a subsequent post-modification using 1,3-propane sultone. Cross-linkable moieties on microgel's surface facilitate the construction of a thin and stable separation layer with tunable solute transportation characteristics. Additionally, the zwitterionic sulfobetaine groups on the polymeric chain of microgels imparted strong antibacterial and antifouling properties in the membranes. The pure water permeability and solute retention of membranes were strongly influenced by the microgel layer's thickness, trans-membrane pressure, and feed temperature. Most importantly, the microgel layer maintains its integrity during the long-term performance and delivers excellent separation results.

In Chapter 3, attempts were made to fabricate smart gating membranes with both antimicrobial and biocatalytic properties by utilizing unique core-shell microgels as building units. The microgels are prepared through grafting the short-chain poly(ethylenimine) (PEI) on the surface of poly((N-isopropyl acrylamide)-co-glycidyl methacrylate)) (P(NIPAm-co-GMA)) core microgel, followed by stabilizing silver nanoparticles (AgNPs) in the microgel matrix through an in-situ process. The AgNP-immobilized microgels were suction-filtered over support to fabricate a nanostructured microgel membrane. Subsequently, the laccase enzyme was immobilized on the microgel's surface covalently with aldehyde groups that were developed during the microgel cross-linking step in the membrane fabrication process. The incorporation of enzymes into membranes offers a beneficial approach to improve their real-time applicability by reducing the environmental impact of various water treatment and purification processes. The enzyme-immobilized membrane demonstrated promising bio-catalytic activity in terms of efficiency, stability, and reusability compared to the free form without compromising the membrane properties like thermo-regulated water flux and solute retention. The unique fusion of AgNPs and laccase in a membrane system led to the development of unique smart self-cleaning membranes with outstanding antibacterial and foulant degradation abilities for green membrane technology.

Contaminants like hazardous metal ions are also a pressing concern in drinking water today. Mercury, particularly in its organic forms, poses a significant threat to human health by causing damage to the kidneys, nerves, and other body systems. Thus, the detection and screening of

mercury is crucial for human health. Chapter 4 focused on developing a polymeric fluorescent microprobe with the "turn-off" sensing ability of mercury ions (Hg^{2+}). The fluorescent microgel was synthesized by emulsion co-polymerization of NIPAm and GMA monomers with MBA and SDS as a cross-linker and surfactant, respectively, followed by modification with 2-amino-4-(4-pyridyl) thiazole epoxy unit of PGMA. Under the irradiation process at 365 nm, the thiazole-based microgel emitted greenish-yellow fluorescence at 525 nm generated in the presence of aromatic heterocyclic pyridine and thiazole units. In presence of different metal ions, this microprobe only shows excellent sensitivity towards Hg^{2+} ions within 30 s through the quenching of fluorescence intensity, mainly from the interaction of metal ions and the heterocyclic thiazole group. With the rapid and precise Hg^{2+} ion detection abilities, the polymeric probe is anticipated to provide distinct platforms by integrating the sensing properties of microgel.

Finally, we describe the fabrication of a unique zwitterionic microgel-based anti-fouling membrane consisting of poly(*N*-isopropylacrylamide-*co*-*N*-(Acryloyloxy)succinimide) (P(NIPAm-co-NAS)) microgels, stabled by cross-linking with zwitterionic N, N, N-tris(2-aminoethyl)-3-sulfo-1-propanaminium salt (TRIPS). The cross-linker provides stability to the microgel layer and simultaneously imparts zwitterionic character via the NHS ester-amine reaction mechanism. This modification can reduce time and resource consumption, making the process more efficient than previous works. The microgel was synthesized by a surfactant-assisted precipitation copolymerization of NIPAm and NAS monomer. The prepared P(NIPAm-co-NAS)) microgel-based nanostructured microgel membranes displayed outstanding water permeation along with smart-gating properties due to the excellent water absorptivity and stimuli-responsiveness of the microgel. The nano-sized pores of cross-linked microgel layer enabled high rejection of dyes and proteins. Additionally, the pore size regulation by external stimuli offered the ability of the membrane to separate different-sized solutes in a stepwise manner. Overall, the microgel-based nanostructured membrane holds significant capability with combined membrane properties for applications in various environmental separation and water filtration processes.

सार

पानी के संरक्षण और पुनर्चक्रण के इस वर्तमान युग में, पीने योग्य पानी की मांग और उत्पादन अनुपात से निपटने के लिए झिल्ली अनुसंधान में एक विशिष्ट स्थान प्राप्त करती है। झिल्ली प्रक्रियाएं शुद्ध पानी प्राप्त करने के लिए कणों, प्रोटीन, रोगाणुओं, बैक्टीरिया, वायरस, आयनों और अन्य दूषित पदार्थों सहित अशुद्धियों की एक विस्तृत श्रृंखला को हटाने का एक प्रभावी तरीका है। हालाँकि, मौजूदा झिल्ली-आधारित निस्पंदन प्रौद्योगिकियों को काफी चुनौतियों का सामना करना पड़ता है, जिसमें बढ़ी हुई ऊर्जा खपत, कम प्रवाह दर, समझौता पृथक्करण दक्षता और फाउलिंग के प्रति बेहतर आत्मीयता शामिल है। प्रदूषण प्रक्रिया को रोकने या कम करने के लिए कई प्रौद्योगिकियाँ विकसित की गई हैं। झिल्ली के पूर्व-संशोधन, जैसे कोटिंग, सम्मिश्रण, या एंटीफाउलिंग घटकों की ग्राफ्टिंग, झिल्ली के जीवनकाल को बढ़ाने और उन्हें फाउलिंग, स्केलिंग के प्रति अधिक प्रतिरोधी बनाकर प्रदर्शन में सुधार करने की उनकी क्षमता के कारण वास्तविक समय के अनुप्रयोगों में सबसे पसंदीदा दृष्टिकोण है। , या जैविक विकास। हाल ही में, जल शोधन को आगे बढ़ाने के लिए नैनोस्ट्रक्चर्ड मेम्ब्रेन (एनएसएम) एक अत्यधिक आशाजनक तकनीक के रूप में उभरी है। इन झिल्लियों को विशेष रूप से उनकी सूक्ष्मता से तैयार की गई नैनोस्केल संरचना के कारण विशिष्ट विशेषताओं और क्षमताओं के लिए इंजीनियर किया गया है। यह नैनोस्केल डिज़ाइन एनएसएम को पानी से दूषित पदार्थों को प्रभावी ढंग से खत्म करने में सक्षम बनाता है, जिसके परिणामस्वरूप बेहतर शुद्धिकरण प्रदर्शन होता है। नैनोस्ट्रक्चर्ड मेम्ब्रेन (एनएसएम) को जल शोधन के क्षेत्र में एक आशाजनक तकनीक के रूप में डिजाइन किया गया है। इन झिल्लियों को उनकी नैनोस्केल संरचना (नैनोकण, नैनोफाइबर, नैनोट्यूब, या अन्य नैनोस्केल घटकों) के कारण पारंपरिक संशोधित झिल्लियों या मिश्रित झिल्लियों से अद्वितीय वास्तुकला, गुण और कार्यक्षमता के लिए डिज़ाइन किया गया है, जो उन्हें पानी से अशुद्धियों को हटाने में बेहतर प्रदर्शन प्राप्त करने में सक्षम बनाता है। . विभिन्न नैनोसंरचनाओं के बीच, माइक्रोजेल ने अपने असाधारण गुणों के कारण शोधकर्ताओं का बहुत ध्यान आकर्षित किया है। ये 3डी क्रॉस-लिंक्ड पॉलीमेरिक कण, एक विलायक में फूले हुए, ट्यून करने योग्य प्रकृति का प्रदर्शन करते हैं - जहां उनके आकार, आकार और पर्यावरणीय ट्रिगर्स के प्रति प्रतिक्रिया को समायोजित किया जा सकता है जो उन्हें अनुप्रयोगों की एक विस्तृत श्रृंखला के लिए आकर्षक बनाता है। माइक्रोजेल सिस्टम द्वारा प्रदान की जाने वाली विशाल क्षमता और विकल्पों की विविध श्रृंखला के बावजूद, झिल्ली अनुप्रयोग में उनकी क्षमताओं की पूरी सीमा मुख्य रूप से अज्ञात बनी हुई है।

अब से, इस शोध का उद्देश्य झिल्ली प्रौद्योगिकी और जल शुद्धिकरण से संबंधित अन्य प्रक्रियाओं के भीतर जैव ईंधन के मुद्दों को कम करने में माइक्रोजेल-आधारित नैनोस्ट्रक्चर की क्षमताओं की जांच करना है। पहले दृष्टिकोण में, हमने एक अच्छी तरह से नियंत्रित जल शोधन अनुप्रयोग के लिए जीवाणुरोधी तापमान-अनुक्रियाशील ज़्विटरियोनिकली कार्यात्मक गूदा-खोल माइक्रोजेल का उपयोग करके एक जैव प्रदूषण रोधी झिल्ली विकसित की। ज़्विटरियोनिक पॉली(एन-आइसोप्रोपाइलैक्रिलामाइड)-पॉलीइथिलीनमाइन- प्रोपेन सल्टोन ((PNIPAm-PEI)-PS) कोर-शेल माइक्रोजेल के संश्लेषण में एक दोहरे चरण की विधि शामिल है जिसमें एनआईपीएएम और पीईआई का एक-चरण ग्राफ्ट कोपोलिमराइजेशन शामिल है, इसके बाद बाद में संशोधन का उपयोग किया जाता है 1,3-प्रोपेन सल्टोन की। माइक्रोजेल की सतह पर क्रॉस-लिंक करने योग्य भाग ट्यून करने योग्य विलेय परिवहन विशेषताओं के साथ एक पतली और स्थिर पृथक्करण परत के निर्माण की सुविधा प्रदान करते हैं। इसके अतिरिक्त, माइक्रोजेल पर ज़्विटरियोनिक सल्फोबेटाइन समूहों की उपस्थिति ने झिल्लियों में मजबूत जीवाणुरोधी और एंटीफ्लिंग गुण प्रदान किए। पानी की पारगम्यता और झिल्लियों की विलेय अस्वीकृति माइक्रोगेल परत की मोटाई, ट्रांस-झिल्ली दबाव और फ़ीड समाधान तापमान से काफी प्रभावित थी। सबसे महत्वपूर्ण बात यह है कि दीर्घकालिक प्रदर्शन के दौरान, माइक्रोजेल परत अपनी अखंडता बनाए रखती है और पूरी प्रक्रिया के दौरान उत्कृष्ट पृथक्करण परिणाम प्रदान करती है।

अध्याय 3 में, निर्माण इकाइयों के रूप में अद्वितीय कोर-शेल माइक्रोजेल के उपयोग के माध्यम से रोगाणुरोधी और जैव-रासायनिक दोनों गुणों के साथ स्मार्ट गेटिंग झिल्ली बनाने का प्रयास किया गया था। माइक्रोजेल को पॉली ((एन-आइसोप्रोपाइल एक्रिलामाइड)-को-ग्लाइसीडिल मेथैक्रिलेट) (P(NIPAm-co-GMA)) कोर माइक्रोजेल की सतह पर छोटा-लंबाई पॉली(एथिलीनिमाइ) (PEI) ग्राफ्टिंग के माध्यम से संश्लेषित किया जाता है, इसके बाद इन-सीटू प्रक्रिया के माध्यम से माइक्रोजेल मैट्रिक्स में सिल्वर नैनोकणों (AgNPs) को स्थिर करना। AgNP-इमोबिलाइज्ड माइक्रोजेल को नैनोस्ट्रक्चर्ड माइक्रोजेल झिल्ली बनाने के लिए समर्थन पर सक्शन फ़िल्टर किया गया था। इसके बाद, लैकेस एंजाइम को एल्डिहाइड समूहों के साथ माइक्रोजेल परत की सतह पर सहसंयोजक रूप से स्थिर किया गया था जो झिल्ली निर्माण प्रक्रिया में माइक्रोजेल क्रॉस-लिंकिंग चरण के दौरान विकसित हुए थे। झिल्लियों में एंजाइमों का एकीकरण विभिन्न जल उपचार और शुद्धिकरण प्रक्रियाओं के पर्यावरणीय प्रभाव को कम करके उनकी वास्तविक समय प्रयोज्यता को बढ़ाने का एक आशाजनक अवसर प्रदान करता है। एंजाइम-स्थिर झिल्ली ने तापमान- अनुक्रियाशील जल पारगम्यता और विलेय अस्वीकृति जैसे झिल्ली गुणों से समझौता किए बिना मुक्त रूप की तुलना में दक्षता, स्थिरता और पुन: प्रयोज्य के संदर्भ में आशाजनक जैव-उत्प्रेरक गतिविधि का प्रदर्शन किया। एक झिल्ली प्रणाली में AgNPs

और लैकेस के अनूठे संलयन ने पर्यावरण-अनुकूल पृथक्करण प्रौद्योगिकी के लिए उत्कृष्ट रोगाणुरोधी और फाउलेंट क्षरण क्षमताओं के साथ अद्वितीय स्मार्ट स्व-सफाई झिल्ली का विकास किया।

पीने के पानी में खतरनाक धातु आयन जैसे संदूषक भी आज की दुनिया में एक गंभीर चिंता का विषय हैं। पारा, विशेष रूप से अपने कार्बनिक रूपों में, हमारे शरीर की किडनी, तंत्रिकाओर अन्य प्रणालियों को नुकसान पहुंचाकर मानव स्वास्थ्य के लिए एक महत्वपूर्ण खतरा पैदा करता है। इसलिए, पारे का पता लगाना और जांच करना मानव स्वास्थ्य के लिए महत्वपूर्ण है। अध्याय 4 पारा आयन (Hg^{2+}) की "टर्न-ऑफ" सेंसिंग क्षमता के साथ एक पॉलिमरिक फ्लोरोसेंट माइक्रो-जांच के विकास पर केंद्रित है। फ्लोरोसेंट माइक्रोजेल को क्रमशः एमबीए और एसडीएस की उपस्थिति में एनआईपीएएम और जीएमए के इमल्शन कोपोलिमराइजेशन द्वारा क्रॉस-लिंकर और सर्फेक्टेंट के रूप में संश्लेषित किया गया था, इसके बाद पीजीएमए की 2-एमिनो-4-(4-पाइरिडाइल) थियाज़ोल एपॉक्सी इकाई के साथ संशोधन किया गया था। 365 nm पर विकिरण प्रक्रिया के तहत, थियाज़ोल-आधारित माइक्रोजेल ने सुगंधित हेट्रोसाइक्लिक पाइरीडीन और थियाज़ोल इकाइयों की उपस्थिति में उत्पन्न 525 nm पर हरे-पीले प्रतिदीप्ति का उत्सर्जन किया। विभिन्न धातु आयनों की उपस्थिति में, सूक्ष्म जांच केवल प्रतिदीप्ति तीव्रता के शमन के माध्यम से 30 सेकंड के भीतर Hg^{2+} आयनों के प्रति उत्कृष्ट संवेदनशीलता दिखाती है, मुख्य रूप से धातु आयनों और हेट्रोसायक्लिक थियाज़ोल समूह की परस्पर क्रिया से। तीव्र और सटीक Hg^{2+} आयन का पता लगाने की क्षमताओं के साथ, पॉलिमरिक जांच से माइक्रोजेल के संवेदी गुणों को एकीकृत करके अलग-अलग प्लेटफ़ॉर्म प्रदान करने की उम्मीद है।

अंत में, हम अद्वितीय ज़िवटरियोनिक माइक्रोजेल-आधारित एंटी-फाउलिंग झिल्ली के निर्माण का वर्णन करते हैं, जिसमें पॉली(एन-आइसोप्रोपाइल एक्रिलामाइड-सीओ-एन- (एक्रिलोइलॉक्सी) स्यूसिनिमाइड) (P(NIPAm-co-NAS)) माइक्रोजेल शामिल है, जो क्रॉस द्वारा स्थिर है। -ज़िवटरियोनिक एन, एन, एन-ट्रिस (2-एमिनोइथाइल) -3-सल्फो-1-प्रोपेनामिनियम नमक (TRIPS) के साथ लिंक करना। क्रॉस-लिंकर न केवल माइक्रोजेल परत की स्थिरता प्रदान करता है, बल्कि एनएचएस एस्टर-अमीन प्रतिक्रिया तंत्र के माध्यम से माइक्रोजेल परत को ज़िवटरियोनिक भी बनाता है। इस संशोधन से समय और संसाधन की खपत कम हो सकती है, जिससे समग्र प्रक्रिया पिछले कार्यों की तुलना में अधिक कुशल हो जाएगी। माइक्रोजेल को NIPAm और NAS मोनोमर के सर्फेक्टेंट-असिस्टेड वर्षण कोपोलिमराइजेशन द्वारा संश्लेषित किया गया था। तैयार (P(NIPAm-co-NAS)) माइक्रोजेल-आधारित नैनोस्ट्रक्चर्ड माइक्रोजेल झिल्ली ने माइक्रोजेल की उत्कृष्ट जल अवशोषण क्षमता और उत्तेजना-प्रतिक्रियाशीलता के कारण, स्मार्ट-गेटिंग गुणों के साथ-साथ उत्कृष्ट जल

पारगम्यता प्रदर्शित की। क्रॉस-लिंक्ड माइक्रोजेल परत के नैनो- छिद्रों ने रंगों और प्रोटीनों की उच्च अस्वीकृति को सक्षम किया। इसके अतिरिक्त, बाहरी उत्तेजनाओं द्वारा छिद्र आकार विनियमन ने झिल्ली को चरणबद्ध तरीके से विभिन्न आकार के विलेय को अलग करने की क्षमता प्रदान की। कुल मिलाकर, माइक्रोजेल-आधारित नैनोस्ट्रक्चर्ड झिल्ली विभिन्न पर्यावरणीय पृथक्करण और जल निस्पंदन प्रक्रियाओं में अनुप्रयोगों के लिए संयुक्त झिल्ली गुणों के साथ महत्वपूर्ण क्षमता रखती है।

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LIST OF ABBRIVIATIONS

MF	Microfiltration	Cyt. C	Cytochrome C
NF	Nanofiltration	ZCP	zwitterionic colloid nanoparticles
UF	Ultrafiltration	ZNG	zwitterionic nanogels
FO	Forward osmosis	BG	bovine γ-globulin
RO	Reverse osmosis	BSA	Bovine serum albumin
PVP	Polyvinylpyrrolidone	PEI	Polyethyleneimine
PE	Polyethylene	4Vpy	4-vinyl pyridine
PA	Polyamide	AAm	Acrylamide
CA	Cellulose acetate	NIPAm	N-isopropyl acrylamide
PVA	Polyvinyl acetate	GMA	Glycidyl methacrylamide
PVDF	Poly(vinylidene fluoride)	AgNP	Silver nanoparticles
PES	Polyethersulfone	NAS	N-(Acryloxy)succinimide
PVCL	poly(N-vinylcaprolactam)	PAA	polyacrylic acid
PAH	Polyallylamine hydrochloride	PBI	Polybenzimidazol
PAN	Polyacrylonitrile	PC	Polycarbonate
PDMS	Poly(dimethylsiloxane)	PS	Polystyrene
PEEK	Polyetheretherketone	PP	Polypropylene
PSF	Polysulfone	PVC	Polyvinylchloride
PU	Polyurethane	PGMA	Polyglycidyl methacrylate
PET	Polyethylene terephthalate	PEG	Polyethylene glycol
TFC	Thin film composite	PAN	Polyacrylonitrile
PANI	Polyaniline	PDA	Polydopamine
NIPS	Nonsolvent-induced phase separation	TMC	1,3,5-benzenetricarboxylic chloride
POF	Porous organic framework	PVA	Polyvinyl alcohol
RhB	Rhodamine B	MO	Methyl orange
YS	Sunset yellow	CV	Crystal violate
MB	Methylene blue	CBB	Coomassie brilliant blue

PTFE	Polytetrafluorethylene	PC	Polycarbonate
CR	Congo red	OII	Orange II
RB	Rose bengal	DY	Direct yellow
HEMA	Hydroxyethyl methacrylate	BP	Benzophenone
MPC	Methacryloxyethylphosphorylcholin	PEth	Polyether
ADNP	Zwitterionic dopamine nanoparticles	MOF	Metal-organic framework
CMCNa	Sodium carboxymethyl cellulose	COF	Covalent organic framework
BNC	Bacterial nanocellulose	ChNC	Chitosan nanocellulose
CNC	Cellulose nanocrystals	GO	Graphene oxide
CNT	Carbon nanotube	CS	Chitosan
SDS	Sodium dodecyl sulfate	CNF	Cellulose nanofiber
NMR	Nuclear Magnetic resonance	FTIR	Fourier-transform IR
SEM	Scanning electron microscopy	TEM	Transmission electron microscopy
LCST	Lowest critical solution temperature	CMR	Catalytic membrane reactor
VPT	Volume phase transition	GS	Gas separation
ATRP	Atom transfer radical polymerization	CP	Concentration polarization
UV	Ultraviolet	VIPS	Vapor-induced phase separation
VIS	Visible		