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A review on bio-inspired nanoparticles and their impact on membrane applications

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Incorporation of nanoparticles into the membrane matrix plays a pivotal role in water purification and treatment. In this review, the recent advances in coupling green nanoparticles, encompassing diverse materials, such as metallic-, metal oxide-, and carbon-based nanoparticles, for tailoring NPs for specific membrane applications are elucidated. The green approach involves the synthesis of nanoparticles using plant extracts, enabling precise control over the size, shape, and surface properties of NPs. The incorporation of NPs improves the underlying hydrophilicity, antifouling properties, mechanical strength, and selectivity of the membrane matrix for various separations, including water purification, desalination, and wastewater treatment. This review also addresses the potential challenges in utilizing green-synthesized nanoparticles in membrane technology for targeted applications. Factors such as scalability, stability, and long-term environmental impact are assessed to ensure the practical viability and sustainability of this approach. In conclusion, the integration of green-synthesized nanoparticles in membrane applications represents a sustainable and innovative paradigm in the field of membrane technology. This approach not only augments the performance of membranes but also aligns with global efforts towards eco-friendly and sustainable practices in synthesis of materials and environmental remediation. This review encourages further research and development in this area, paving the way for greener and more efficient membrane-based separation processes.

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Sustainability spotlight

The increasing demand for clean water and energy-efficient processes has made membrane technology essential in filtration and purification applications. However, conventional membrane materials often encounter challenges such as fouling and limited lifespan. Thus, to address these issues, bio-inspired nanoparticles have emerged as a promising solution, which mimic the natural processes to enhance membrane performance, reduce fouling, and improve filtration efficiency. This sustainable advancement reduces the reliance on chemical treatments and extends membrane longevity, lowering the energy consumption and waste. The work aligns with several UN Sustainable Development Goals (SDGs), notably SDG 6 (Clean Water and Sanitation) by enhancing water treatment technologies and SDG 12 (Responsible Consumption and Production) through promoting sustainable material usage and offering a green alternative to conventional membrane systems.

1. Introduction

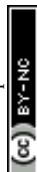
The green approach using plant extracts has been extended to the synthesis of a wide range of biomolecules, including amino acids, carbohydrates, enzymes, iridoids, proteins, polyphenylene, vitamins and polyphenols (flavonoids, non-flavonoids and phenolic acids). Among them, phenolic and terpenoids are essentially utilized as organic polymers in synthesizing nanomaterials (NMs) such as gold nanomaterials.¹ Further, phenolate ions, such as those in eugenol in clove

extract, can transfer electrons to metal ions during the formation of nanoparticles (NPs).^{2,3} Flavonoids, such as luteolin and apigenin in *Ocimum basilicum* plant extract, and amino acids, such as arginine, cysteine, lysine, and methionine, can help in NP formation.^{4,5} The synthesis of GNPs with the desired size and morphology depends on parameters such as pH and temperature.⁶

Despite the numerous studies demonstrating the role and impact of these biomolecules in reducing and stabilizing NPs during the green synthesis process, the synthesis of NPs from plant extracts still remains relatively obscure and complex.^{7–9} The biomaterial-based routes utilized for the synthesis of metal NPs have gained exponential interest as these green methods eliminate the use of harsh and toxic chemicals.⁸ Despite these advantages, as illustrated in Fig. 1, green synthesis of nanoparticles encounters several challenges, including low yield, poor size control, prolonged synthesis durations, stability

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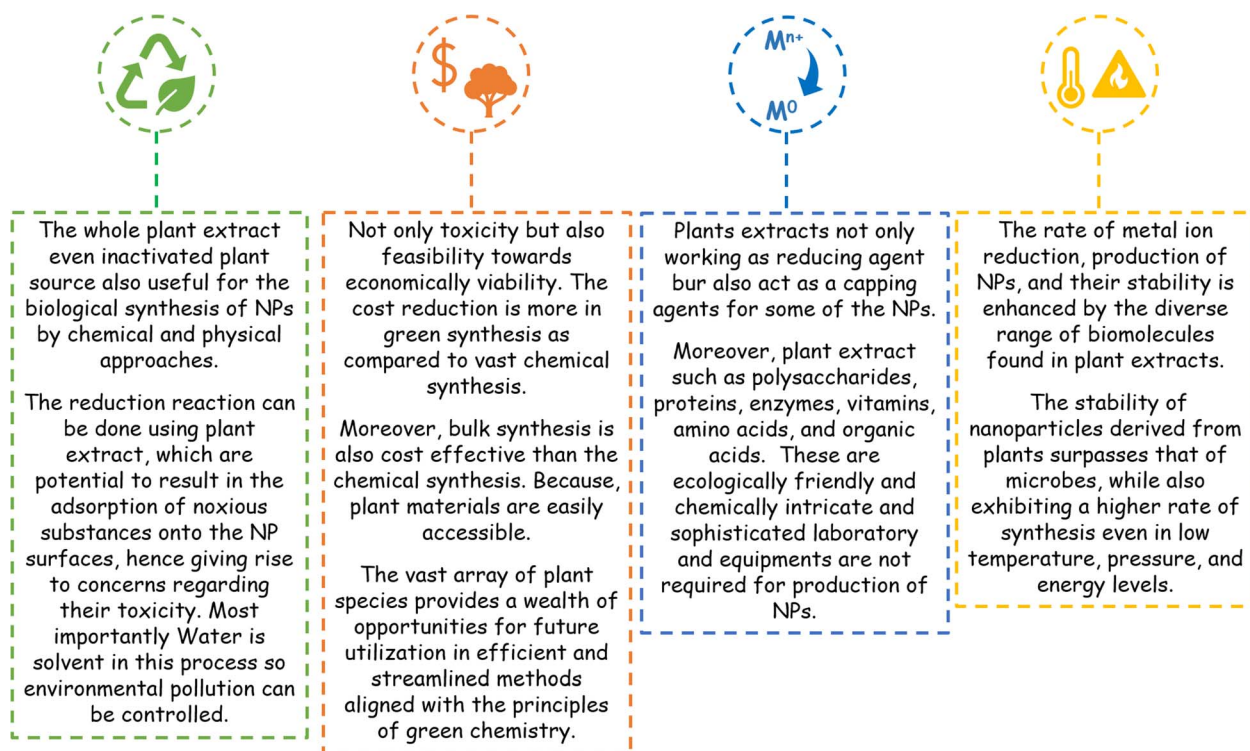
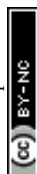


Fig. 1 Schematic of the advantages of green synthesis and green-synthesized NPs.

issues, and difficulties in purification.¹⁰ Furthermore, additional limitations such as variability, reliance on natural resources, undefined toxicity, and the absence of standardization hinder its scalability and industrial implementation.¹¹ Thus, addressing these challenges through focused research while retaining the eco-friendly advantages of green synthesis is essential.¹²

The symbiosis between both bio-materials and membrane-based materials has been found to contribute to the separation and purification of water. Membranes are thin films that function as selective barriers between distinct phases, facilitating the flow of substances between these phases. In the current era of nanotechnology, researchers have made notable advancements in the fabrication of mixed matrix membranes (MMMs), which have demonstrated considerable utility in separation processes and biomedical applications. The distinguishing characteristics that make MMMs highly favored materials among researchers include their favorable permeability to certain liquids or gases, selectivity, desirable mechanical strength, and effective resistance to fouling.¹³ The distinctive characteristics of MMMs arise from their deliberately engineered and customized structure, achieved through a controlled fabrication process that involves precise manipulation of the fabrication parameters and selection of appropriate materials. For instance, a polymeric membrane matrix containing well-dispersed NPs is chosen based on the specific requirements of the intended applications.¹⁴ Nevertheless, various conventional techniques have been employed for the production of MMMs, including co-casting, interfacial polymerization, phase-inversion method, electrospinning, and

coating. However, further advancements in technology for the fabrication of MMMs are necessary to achieve cost-effective and efficient processes suitable for large-scale industrial production as well as small-scale applications.¹⁵ Water and wastewater treatment plants face inherent limitations in dealing with contaminants, leading to difficulties in guaranteeing the provision of secure and safe water sources. In the contemporary context, membrane technology has emerged as a potential method for mitigating this growing difficulty. In the context of reverse osmosis (RO), forward osmosis (FO), membrane distillation (MD), nanofiltration (NF), and ultrafiltration (UF) membranes, it has been noted that these membranes have the capability to achieve the complete or almost complete removal of contaminants. Numerous membranes have been developed for commercial applications and meticulously engineered to serve a wide range of industrial purposes, including water treatment, gas separation, food processing, pharmaceutical production, and energy-related processes. Some of the commercially available membranes for water treatment are PVDF200, UV200,¹⁶ and NF90, NF270.¹⁷ Nanotechnology in alliance with membrane technology exhibits significant promise in the field of water purification and treatment. Thus, a wide range of nanoparticles has been extensively researched and developed to address water pollution. These NMs exhibit environmentally beneficial characteristics, and also economically viable options for water treatment. The primary types of NMs employed in water treatment include photocatalysts, nanomembranes and adsorbents. Nanomembranes are commonly employed in the field of nanotechnology for the



purpose of water softening and the removal of contaminants from the aquatic environment.¹⁸

Recently, the investigation and advancement of polymeric materials embedded with NPs, together with their utilization as membranes, have emerged as a captivating area of interest among researchers. Polymeric materials that contain NPs have been widely recognized for their essential compatibility with commonly used membrane matrices, adjustable physicochemical properties, and a diverse array of functions. The NP-embedded membranes that have been produced demonstrate significant potential for addressing the long-standing limitations encountered by the membrane-based separation sector. However, one of the primary obstacles in the advancement and application of membranes is achieving an optimal balance between membrane selectivity and permeability. The current progress in the preparation of polymeric materials, particularly NPs, has mostly focused on investigating techniques for the precise manipulation of the properties of both NPs and membranes. The objective of this endeavor is to further enhance the overall performance of membranes. The approaches designed to advance the performance of membranes containing NPs has been extensively integrated into their fabrication procedures. These strategies focus on leveraging the surface properties and pore and channel structures within nanoparticles. Anticipated breakthroughs in the development of enhanced membrane systems are expected due to the current degree of interest in the field of NP-incorporated polymeric materials.¹⁹ Hence, it has been firmly established that the selection of membrane materials holds paramount significance when evaluating the suitability of membrane separation technology for application in the treatment of consumable water and wastewater.²⁰ Photocatalytic membranes (PMs) offer energy-efficient water purification and wastewater treatment by integrating membrane filtration with photocatalysis. They have evolved from UV-responsive to vis-responsive membranes, with vis-PMs including $g\text{-C}_3\text{N}_4$, $\beta\text{-FeOOH}$, and $\text{TiO}_2/\text{ZnO}_2$ -based membranes. Their fabrication involves immobilizing photocatalysts onto or inside membranes.²¹ Metal or metal oxide nanoparticles can enhance the hydrophilicity, selectivity, strength, and permeability of polymer membranes. For example, silica NPs in polyvinylidene fluoride (PVDF) membranes improve their selectivity, thermal stability, and diffusivity. Silver NPs (AgNPs) are ideal for producing polymer nanocomposite membranes due to their antibacterial properties. Carbon nanotubes (CNTs) have excellent adsorption properties for water purification and have been incorporated into polymeric materials due to their high purity and low production cost. Graphene oxide (GO) is a hydrophilic and useful nanofiller in polymeric nanocomposite membranes, and can be combined with nanoparticles such as copper and silver for excellent antibacterial activity.²²

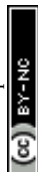
Herein, we critically review the ongoing developments in utilizing nanocomposite polymeric membranes embedded with biogenically synthesized nanofillers for improved antibacterial and antifouling activities. The future issues and challenges encountered in the use of green-synthesized NPs are also discussed. In recent years, the imperative to address

environmental challenges has spurred intensive research into sustainable technologies. Among them, the synthesis and application of green NPs have emerged as a groundbreaking approach, holding immense promise for membrane-based purification processes. This review delves into the pivotal role of green-synthesized NPs in revolutionizing membrane technologies, emphasizing their eco-friendly production methods and multifaceted applications in water and wastewater treatment. This review stands from its predecessors due to its comprehensive analysis of the latest advancements in green NP synthesis techniques. It provides a meticulous evaluation of the environmental impacts and potential toxicity associated with conventional NP production methods. Furthermore, it critically appraises the efficacy and scalability of green NP-incorporated membranes, highlighting their potential to outperform their conventional counterparts in terms of permeability, selectivity, and durability. This review also emphasizes the economic viability of green NP-based membranes, dissecting their cost-effectiveness and life-cycle analysis compared to conventional approaches. By juxtaposing the environmental and economic advantages, we provide a holistic perspective, underlining the potential of green NP-enhanced membrane systems for widespread adoption and commercialization. In summation, this review is a pioneering endeavor, offering a comprehensive and forward-looking assessment of the transformative impact of green NPs on membrane-based purification technologies. It not only consolidates the current state of knowledge but also charts a course towards a more sustainable and efficient future in water purification, underscoring the critical role of green-synthesized NPs in this endeavor.

2. Green synthesis of nanomaterials (GNP)

The biogenic transformation of metal salts to metal NPs using plant extracts is an ecologically benign and simple method involving oxidation-reduction processes.⁹ Plant extracts contain phytochemicals, which possess excellent reducing and capping activities. The phytochemicals such as alkaloids, terpenoids, flavonoids and saponins present in plant extracts (Fig. 1) act as excellent metal ion reducers.²³ Preclinical studies have provided evidence that NPs synthesized using plant extracts as reducing agents exhibit diverse beneficial properties. These properties include antibacterial, antifungal, anti-inflammatory, analgesic, and antioxidant activities. Besides, it has been shown that these NPs exhibit promising prospects in the field of ethnopharmacology. Green NPs produced using biological methods demonstrate biocompatibility, no toxicity, and offer potential for future utilization in therapeutic and biomedical research and developments (Fig. 2). The verification of the photocatalytic efficacy of various NPs has demonstrated their encouraging prospects for the advancement of entrepreneurial situations in the future.²⁴

The utilization of AgNPs derived from plant leaf extracts such as *Ocimum sanctum* has demonstrated considerable therapeutic promise. However, the use of silver NPs beyond the



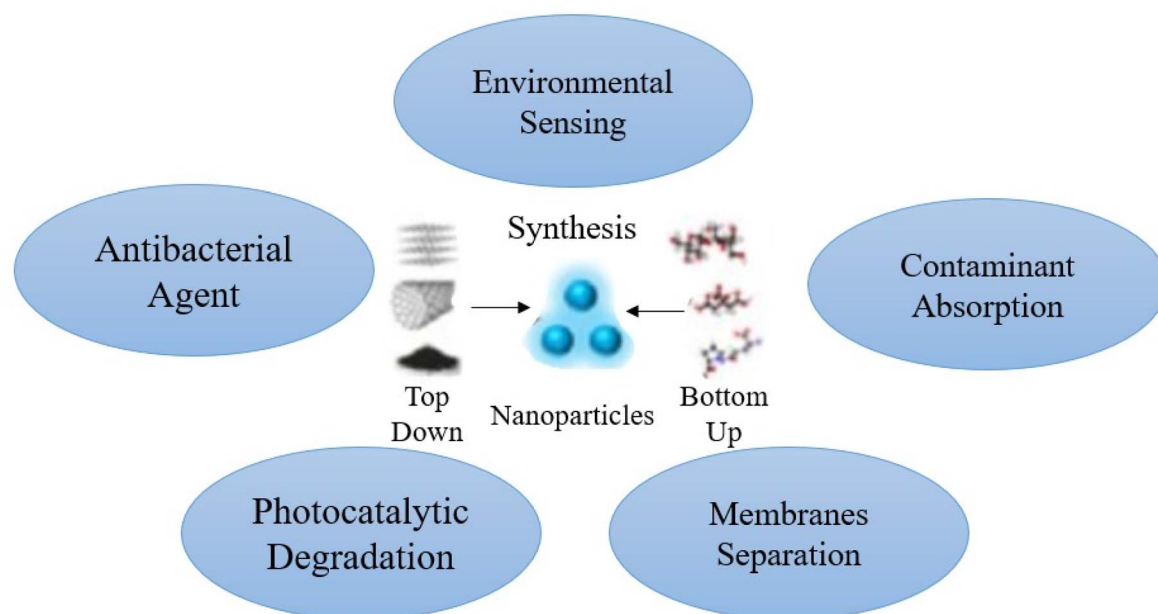


Fig. 2 Schematic of various applications of GNPs.

prescribed limit presents challenges when considering their application (Fig. 3) in the food and pharmaceutical sectors. Therefore, there has been a significant emphasis on the use of polymer metal complexes to promote the safeguarding of physiologically active chemicals through controlled drug release, degradation prevention, and better absorption of therapeutic agents.^{25,26} Further, *Azadirachta indica* leaf-derived Ag-Mo/CuO GNPs showed excellent results for the degradation of MB dye.²⁷

A previous study explored the synthesis of ZnO NPs using *Clerodendrum inerme*, *Abutilon indicum*, and *Clerodendrum infortunatum* leaves.²⁸ Undoped ZnO GNPs were produced using the green combustion method, while Cu-doped GNPs were synthesized using plant extract. Thus, the prepared Cu-doped ZnO GNPs demonstrated excellent photocatalytic and microbial activity.²⁸ In another study, flaxseed extract (FSE) was used to prepare TiO₂ nanoparticles, with titanium tetraisopropoxide added to the suspension. Further, a TiO₂/Fe₂O₃ nanocomposite

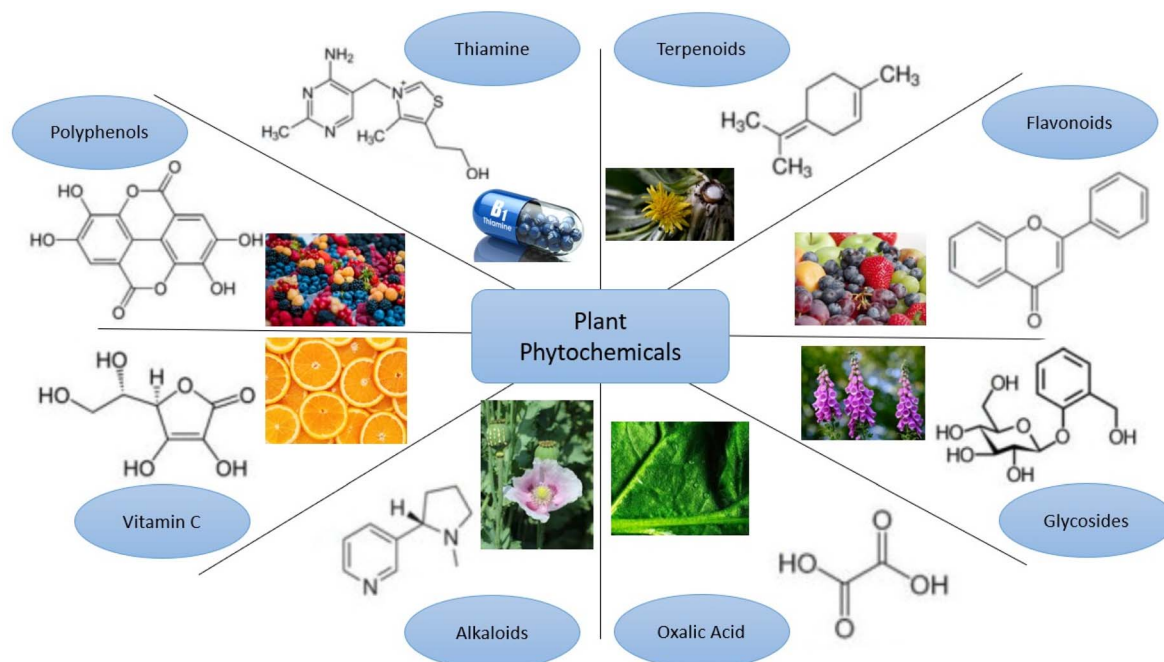
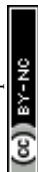


Fig. 3 Schematic of the library of phytochemicals extracted using different plant sources.



was obtained by hydrolyzing titanium(IV) tetraisopropoxide in an aqueous suspension of $\alpha\text{-Fe}_2\text{O}_3$ NPs. The prepared GNPs showed excellent photocatalytic activity for organic dye reduction.²⁹

2.1. Impact of pH on the synthesis of GNP

Chestnut shells were extracted in a 40% ethanol and water mixture and added to a solution containing 5% AgNO_3 by adjusting the pH in the range of 5.0–11.0. Lower pH values led to larger NPs, while higher pH values resulted in smaller NPs.³⁰ However, the Ag GNPs obtained at pH 9.0 exhibited excellent antimicrobial activity.³¹ The shape of NPs also depends on pH, where alkaline pH and surface functional groups resulted in smaller, decahedral NP.^{2,32}

2.2. Impact of concentration on GNP

A study demonstrated the impact of varying concentrations of *Hibiscus sabdariffa* flower extract on biogenically synthesized ZnO NPs for the photocatalytic degradation of methylene blue dye (MB). Extract concentrations of 1%, 4% and 8% were utilized, and zinc nitrate served as the source of zinc ions. Characterization methods confirmed the properties of the synthesized ZnO NPs, including their hexagonal crystalline phase, morphology, and chemical state. The band gap of the ZnO NPs decreased as extract concentration increased and these ZnO NPs exhibited excellent photocatalytic activity against MB dye.³³

2.3. Impact of temperature on GNP

The nucleation rate during the synthesis of GNPs also depends on the temperature. The shapes, sizes and rate of production of NPs vary with a change in temperature during their synthesis.³² The propagation temperature also affects the reduction process of metal ions and specifies changes in color owing to surface plasmon resonance. For example, due to a variation in temperature during the synthesis of gold NPs, changes in the color of the NPs were observed as yellow-brown, purplish pink and pinkish-brown at temperatures of 60 °C, 80 °C and 100 °C, respectively.³⁴ For example, according to an earlier report, maintaining the temperature equal to or greater than 30 °C during the synthesis of silver GNPs from *M. sativa* plant seed extract was a necessary criterion.² In addition, the structure of silver GNPs synthesized using *Cassia fistula* plant extract varied with temperature. At room temperature, silver GNPs accumulated linearly, causing recrystallization, which resulted in the formation of silver nanowires. However, at a higher temperature, such as 400 °C or above, Ag GNPs of irregular nanorods and spherical shapes were produced because of the changes in the interaction between the surface of the silver GNPs and biomolecules, due to which the amalgamation of the GNPs was hampered.³⁵ The reaction temperature also affects nucleation, for example, at higher temperature, the rate of action becomes high and the maximum gold ions are used to form nuclei, which prevents the nuclei from secondary nucleation at their surface. Generally, secondary nucleation occurs at low temperature.^{36–38} Considering the properties of green-synthesized NPs, they are

expected to have various applications in different fields. In this review, we have focus on the membrane applications of GNPs.

3. GNPs for membrane application

In recent years, membrane separation has gained attention in water purification. Among the various processes, polymeric membranes occupy a universal position in the water market. The integration of nanofillers into polymer matrices has attracted significant attention among academics due to their straightforward and efficient method of modification.

The utilization of polymeric membranes presents a viable solution for addressing the various challenges associated with flow, rejection, fouling, as well as chemical and mechanical stability.

3.1. Mixed matrix membranes

Mixed matrix membranes (MMM)³⁹ are composite materials used in membrane technology. These composite membranes provide multiphase features that offer increased flexibility in manipulating numerous interactions, customizing multiscale structures, and integrating different functionality, in contrast to pristine polymer membranes (Table 1). Typically, they consist of a polymeric matrix with embedded inorganic or organic fillers. These fillers are added to enhance the performance of the membrane, such as improving its selectivity, permeability, and stability. The combination of a polymeric matrix and filler materials allows the creation of a membrane with properties surpassing that its individual components. Currently, there is significant emphasis on the utilization of environmentally sustainable and ecologically friendly resources in scientific research. The whole plant of *Parkia speciosa* (*P. speciosa*) was used as a reducing agent for the synthesis of Ag/AgO NPs (Fig. 9). This process generated Ag/AgO GNPs with an average particle size of 35–65 nm, and then incorporated in the PSF polymer matrix, which increased the hydrophilicity. This led to greater productivity with a very high water flux rate of $393.3 \pm 19.7 \text{ L m}^{-2} \text{ h}^{-1}$ and rejection rate for humic acid of $98.6\% \pm 4.9\%$. The aforementioned discovery demonstrates that the inclusion of green Ag/AgO additives in porous PSf membranes enhances the efficacy of hybrid polymer-based ultrafiltration membranes as water separators, while also imparting antibacterial characteristics.^{22,54,68,69}

Green tea extract, a non-toxic, biodegradable, and “green” reducing agent, was used instead of sodium borohydride for the synthesis of Fe and Fe/Pd GNP. These GNP were incorporated in polymeric membrane composed of polyacrylic acid (PAA) and coated onto a polyvinylidene fluoride (PVDF) membrane. Also, the as-synthesized GNP were successfully used for the degradation of trichloroethylene (TCE), a common contaminant. In an Fe/Pd bimetallic system, it was seen that Fe is responsible for the generation of H_2 , while Pd functions as a catalyst.⁶⁰ In another study, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ GNP were synthesized by applying a coat of amorphous silica extracted from agricultural waste (namely, rice husk (Fig. 5)) onto Fe_3O_4 MNPs. This process is illustrated in Fig. 5. Additionally, the nanocomposite was



Table 1 Various green nanoparticles embedded in polymeric membranes for heavy metal ion adsorption, dye degradation and antibacterial applications

	Biogenic source	Nanocomposite	Membrane	Nanoparticle size/ shape (nm)	Application	Reference
1	Rice husk	$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$	PES-nanofiltration membrane matrix		Removal of MR dye (97%) and Cd(II) ions (93%)	40
2	<i>Scrophularia striata</i> extract	Nickel-bentonite nanoparticles (NBNPs)	(PES) nanofiltration membranes		Removal of Zn^{2+} (98.62%), Pb^{2+} (97.03%) and Cu^{2+} (97.88%)	9
3	<i>Lactobacillus fermentum</i> LMG 8900	Bio-Ag ⁰	Bio-Ag ⁰ /PES nanocomposites membrane	11.2 ± 0.9	(<i>Escherichia coli</i> and <i>Pseudomonas aeruginosa</i>)	41
4	<i>Paronychia argentea</i> Lam	(AgNPs)	Ultrafiltration polyvinylidene fluoride (PVDF) membrane		<i>E. coli</i> and <i>S. aureus</i> bacteria	42
5	<i>Ocimum sanctum</i> leaf extract	Silver nanoparticles	Polyvinyl alcohol (PVA) polymer matrix		<i>E. coli</i> and <i>S. aureus</i> bacteria	26
6	Leaf extract of <i>Amaranthus tristis</i>	Ag NPs	Ag/PVA nanocomposite membrane	20–40	<i>Pseudomonas fluorescens</i> and <i>Klebsiella pneumonia</i>	43
7	Medicinal plant <i>Mimosa pudica</i>	Ag NPs	Ag nanoparticle-incorporated PVA membranes	7.63 ± 1.2	Wound dressing application	44
8	<i>Catharanthus roseus</i> leaf extract	CuO NPs	CuO clay-alumina ceramic membrane		Chromium(VI) removal (88.08%)	45
9	Apple extract	AgNPs	AgNP-embedded PVDF nanofibre membrane	28.24 ± 1.15 and 22.05 ± 1.05	<i>Klebsiella pneumoniae</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> and <i>Geobacillus stearothermophilus</i>	46
10	Split pulse extract	(TiO ₂)	TiO ₂ /PDMS nanocomposite		Antibacterial activity	47
11	Clove extract	Iron NPs	PVDF-co-HFP membrane		Nitrobenzene reduction (89.92%), fluoride rejection	48
12	Plant extract of resveratrol	PdNPs	Polysulfone membrane		Crystal violet dye (99%)	49
13	Gomutra	AgNPs	CA/PES polymer composite membrane		Methylene blue dye (88%) and textile effluents (77%) removal	50
14	Glucose oxidase (GOx)	(rGO/PANI) composite	PSf-rGO/PANI composite membrane		NaCl rejection (82%)	51
15	Pomegranate peel	CrO and CuO nanoparticles	CrO@PA6 and CuO@PA6 nanocomposites		Uranium sorption from an aqueous solution	46
16	Orange peel extract	AgNPs	AgNPs/PS nanocomposite film	98.43	<i>Staphylococcus aureus</i> , <i>Klebsiella pneumoniae</i> , <i>Salmonella</i> , and <i>Escherichia coli</i>	52
17	<i>Pseudomonas aeruginosa</i>	AgNPs	(Na-Alg/poly-AAm) Ag NPs	24 to 58	Reduction of Fantacell dye (87%) and bromothymol blue dye (87%)	53
18	<i>Parkia speciosa</i> (leaves, pods and seeds)	Ag/AgO nanoparticle	PSf mixed-matrix ultrafiltration membrane	34.65	Inhibition ring (4.5 mm) (antibacterial), humic acid rejection (98.6%)	54
19	Bamboo leaves	Carbon quantum dots (CQDs)	(BPEI)-capped CQDs (BPEI-CQDs)	3.6	Detection of Cu^{2+} in river water	55
20	<i>Lavandula angustifolia</i> Mill	(AgNPs)	(Poly vinyl alcohol-graft-methyl acrylate) (PVA-graft-methyl acrylate) and silver nanoparticles (AgNPs)		Acetone optical detection	56



Table 1 (Contd.)

	Biogenic source	Nanocomposite	Membrane	Nanoparticle size/ shape (nm)	Application	Reference
21	<i>Diospyros lotus</i> fruit extract	Ag NPs	Ag/PVA/starch nanocomposites hydrogel membrane	40–80 nm	Wound dressing application	57
22	Dried chamomile flower extract	AgNPs	PEBAX/PVA/Ag hydrogel		<i>Escherichia coli</i> (antimicrobial activity)	58
23	Lime peel extract (LPE)	AgNPs	AgNP-Ppy nanocomposite		Low-cost conductive textile fabric	59
24	Green tea extract	(Fe and Fe/Pd)	(Fe and Fe/Pd) GNPs immobilized (PAA-coated PVDF) membrane		Trichloroethylene (TCE) degradation	60
25	<i>Ocimum sanctum</i> leaf extract	AgNPs	AgNPs in PVA matrix	20	<i>S. aureus</i> and <i>E. coli</i>	26
26	Curcumin	Curcumin boehmite nanoparticle(B-Cur)	B-Cur/PES membrane		Removal of Fe ²⁺ (99.88%), Pb ²⁺ (99.61%), Ni ²⁺ (99.11%), Cu ²⁺ (98.72%), Zn ²⁺ (99.51%), and Mn ²⁺ (99.31%)	61
27	Naringin	(γ -AlOOH@Nar) bionanocomposite	γ -AlOOH@Nar TFC NF membrane		Pharmaceutical waste rejection (99.8%)	62
28	Leaf extract of medicinal plant <i>Mimusops elengi</i> plant	AgNPs	AgNP-incorporated flat sheet PES membrane		Antibacterial activity against <i>E. coli</i>	63
29	<i>Lactobacillus fermentum</i>	AgNPs	PVDF membrane	11.2 $\pm$ 10.9	Inactivation of UZ1 bacteriophages (3.4 log decrease)	64
30	Cardamom extract	FeNPs	PVDF-co-HFP membrane	32	Nitrobenzene reduction	65
31	Rice husk ash	SiO ₂	PSf membrane		Humic acid rejection (96–98%)	66
32	Rice husk	CD/SiO ₂	PSf membrane		Tetrazine dye rejection (50.54%)	67

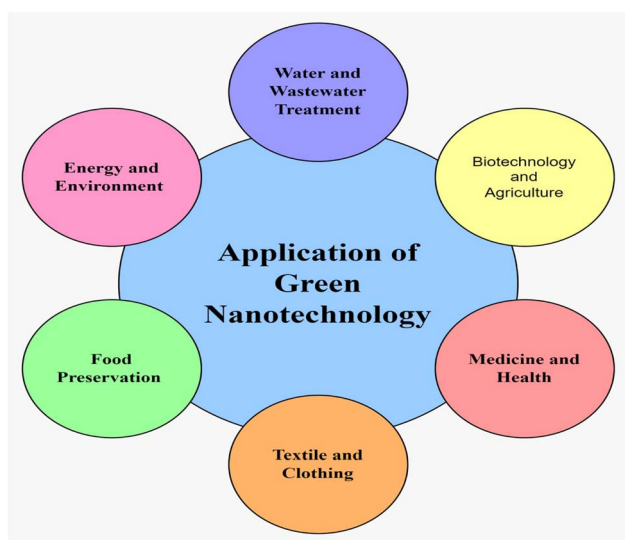


Fig. 4 Applications of green nanotechnology in the fields of energy, health and environment.

functionalized with amine functional groups. Polyethersulfone membranes were modified through the incorporation of Fe₃O₄@SiO₂-NH₂ GNP, which were synthesized and added using the phase inversion method. Different concentrations of the nanocomposite were utilized during the modification process. The modified membranes exhibited the most notable effectiveness in removing Cd(II) ions, with a removal rate of 93%, as well as in removing methyl red (MR) dye, with a removal rate of 97%. These results indicate that the modified membranes possess favorable characteristics for recyclable use and prolonged filtration applications. Furthermore, the modified membrane exhibited a gradual reduction in the flow of the dye solution by 7.5% over a period of 40 h of filtering, indicating its favorable anti-contamination property. The optimal membrane possessed 0.5 wt% of incorporated Fe₃O₄@SiO₂-NH₂, resulting in an improved performance in terms of pure water flux, salt rejection, elimination of Cd(II) ions, retention of MR dye, and fouling resistance. This enhancement makes this membrane well-suited for many environmental applications. NF membranes commonly exhibit rejection towards salts such as Na₂SO₄, MgSO₄, and NaCl, with a greater degree of rejection observed for divalent ions and a lower degree of rejection



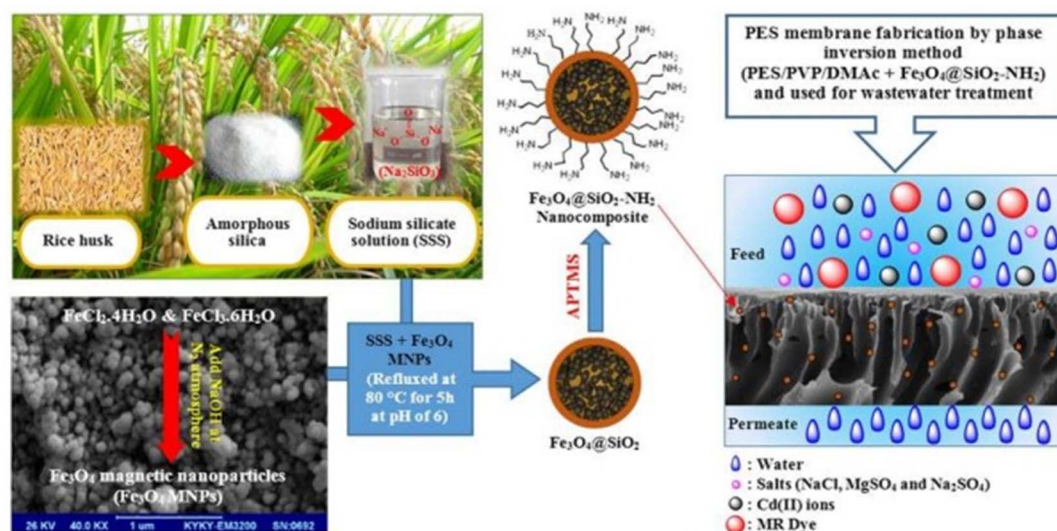


Fig. 5 Graphical representation of the fabrication of Fe₃O₄@SiO₂-NH₂-embedded PES membrane and its waste water treatment application.⁴⁰

observed for monovalent ions. The divalent anion SO₄²⁻ in Na₂SO₄ is rejected to a lesser extent compared to the anion in NaCl. The findings of this study indicated that the rate of Cd(II) removal from the fabricated membranes decreased significantly after a duration of 120 min compared to the unmodified membranes. This decrease can be attributed to the presence of polar primary amine groups and -NH₂ functional groups on the surface of the nanofiller. This study also revealed that an enhancement in dye removal efficiency was achieved by increasing the quantity of hydrophilic nanofiller particles, specifically Fe₃O₄@SiO₂-NH₂.³⁸ This water separation performance reported in this study was comparable to an earlier study on improving the characteristic properties and overall performance of porous PSf-green rice husk (GRH) additive MMMs. Previous studies show an increase in the hydrophilicity of membranes after the addition of silica, possibly due to the migration of green silica and hydroxyl group enrichment on the surface of SiO₂, enhancing the membrane hydrophilicity.⁶⁶

Further, zero valent iron GNPs (FeNPs) and their oxide were synthesized using clove extract as a reducing agent. The prepared composite membrane, PVDF-co-HFP, was highly pH-responsive and useful for the reduction of nitrobenzene. The flux of the membrane varied with a change in pH from 142 L m⁻² h⁻¹ at pH 3 to 58 L m⁻² h⁻¹ at pH 12. More importantly, the membrane was highly active at pH 3, with a greater yield in the production of aniline and fluoride detection. The pH responsiveness of the membranes also contributed to nitrobenzene reduction, with a variation in pore size with the solution pH, where with an increase in pH, de-protonation of COOH and C₆H₅OH occurs simultaneously, increasing the charge density and decreasing the pore size.⁴⁸ The obtained results were consistent with the findings reported in an earlier study.⁶⁵

The creation of a composite material composed of reduced graphene oxide and polyaniline (rGO/PANI) was previously demonstrated by the utilization of a unique enzymatic reaction-based technique. This approach was distinguished by its unique attributes, straightforward nature, and commitment to

environmental sustainability. The efficient application of glucose oxidase (GOx) as a catalyst in the presence of glucose resulted in the production of hydrogen peroxide. The hydrogen peroxide was later employed for the oxidative polymerization of aniline under standard atmospheric circumstances. The composite of reduced graphene oxide (rGO) and polyaniline (PANI) was dispersed in polysulfone (PSf), and subsequently the membranes were fabricated using the phase inversion polymerization technique. This study focused on evaluating the efficacy of the membranes in terms of their ability to selectively reject salt and facilitate the penetration of purified water. The introduction of reduced graphene oxide (rGO) into the membrane matrix resulted in the formation of a hydrophobic membrane surface, which demonstrated improved macrovoids. In contrast, the contact angle measurements indicated that the surface of the membrane possessing rGO/PANI demonstrated a certain level of hydrophilicity, which can be attributed to the presence of PANI fibers within the membrane. Furthermore, examination of the scanning electron microscopy (SEM) images of the membrane unveiled a significant increase in both the size and number of macrovoids observed on its surface. The integration of reduced graphene oxide (rGO) and polyaniline (PANI) doping in the membrane resulted in an enhanced salt rejection efficacy, and also membrane loading. Thus, the modified membrane with a loading of 0.5% rGO/PANI demonstrated the maximum effectiveness of 82% in rejecting NaCl when subjected to an applied pressure of 10 bar. This rejection rate exhibited a modest decline with an increase in pressure and working time; however, the decrease was not statistically significant. Additionally, the results revealed that the PSf-rGO/PANI composite membrane demonstrated the highest mean porosity and water flux.⁵¹

Alternative, CD/SiO₂ additives in a PSF MMM showed high water permeability. The modified membranes showed improved water permeability and better dye rejection output.⁶⁷ It is clear that GNP demonstrated a positive impact on the



membrane performance by enhancing its selectivity and improving its productivity across various applications.

3.2. Thin film composite membranes

Thin film composite (TFC) membranes⁷⁰ are a type of semi-permeable membrane widely used in various filtration and separation processes, particularly in reverse osmosis (RO) and nanofiltration (NF) applications. TFC are major components in the membrane market. They are known for their high rejection rates, allowing them to effectively remove a wide range of contaminants, including dissolved salts, organic compounds, and various microorganisms. Their design allows a balance between high permeability (allowing water to pass through) and high rejection (blocking contaminants), making them a popular choice in desalination, water purification, and other filtration processes. Recently, thin film nanocomposite (TFNC) membranes showed a remarkable impact on the existing commercial TFC membranes.

Green-synthesized NPs are of substantial consideration due to their non-toxic nature, biocompatibility, environmentally friendly nature and cost-effectiveness. Titanium dioxide (TiO₂)

NPs were synthesized using split pulse extract as a reducing/capping agent. These green-synthesized TiO₂ NPs were incorporated in a polydimethylsiloxane (PDMS) membrane to fabricate a nanocomposite using the solution casting technique. The TiO₂/PDMS nanocomposite showed excellent antibacterial activity compared to pristine PDMS. The nanocomposite film constructed with TiO₂ NPs in the polymer exhibited excellent antibacterial activity against Gram-negative and Gram-positive bacteria. At this point, to enhance the antibacterial activity of the TiO₂/PDMS nanocomposite, different loadings of TiO₂ NPs of 0 wt%, 7 wt%, 10 wt%, and 13 wt% were added to the PDMS surface (Fig. 6). Among them, the 13 wt% TiO₂-incorporated PDMS nanocomposite showed enhanced antibacterial activity against *E. coli* and *B. cereus*, suggesting its potential applications in marble, stone, and surface protection coatings with self-cleaning properties. This study found that the turbidity in the nutrient broth increased bacterial growth, while the 13 wt% TiO₂-coated PDMS showed excellent antibacterial effects. This is due to the synergistic effect of TiO₂ and PDMS, which increased the surface area of the nanocomposite thin film and decreased the aggregation of TiO₂ (Fig. 7).⁴⁷

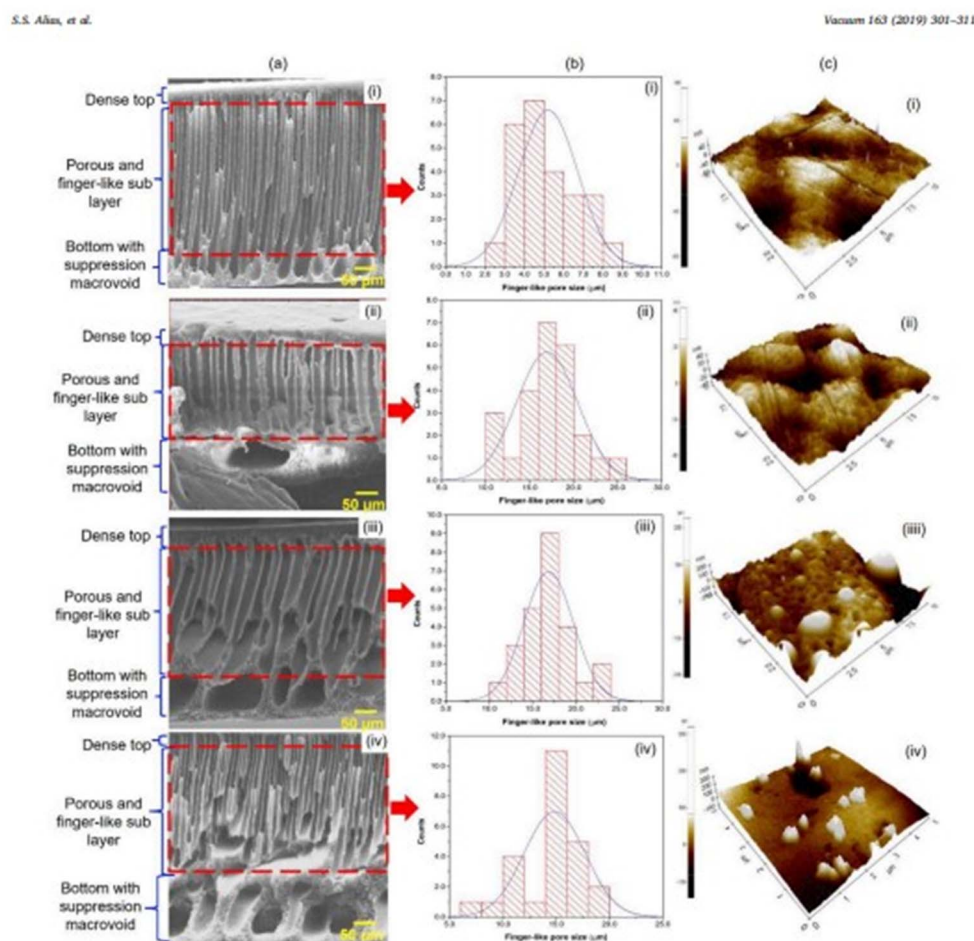


Fig. 6 (a) Cross-sectional images of SEM analysis. (b) Finger-like distribution of size of cavities. (c) AFM images of (i) PSf membrane and (ii) PSf-Ag/AgO membrane prepared using *P. speciosa* seeds, (iii) using pods and (iv) using leaves.⁵⁴



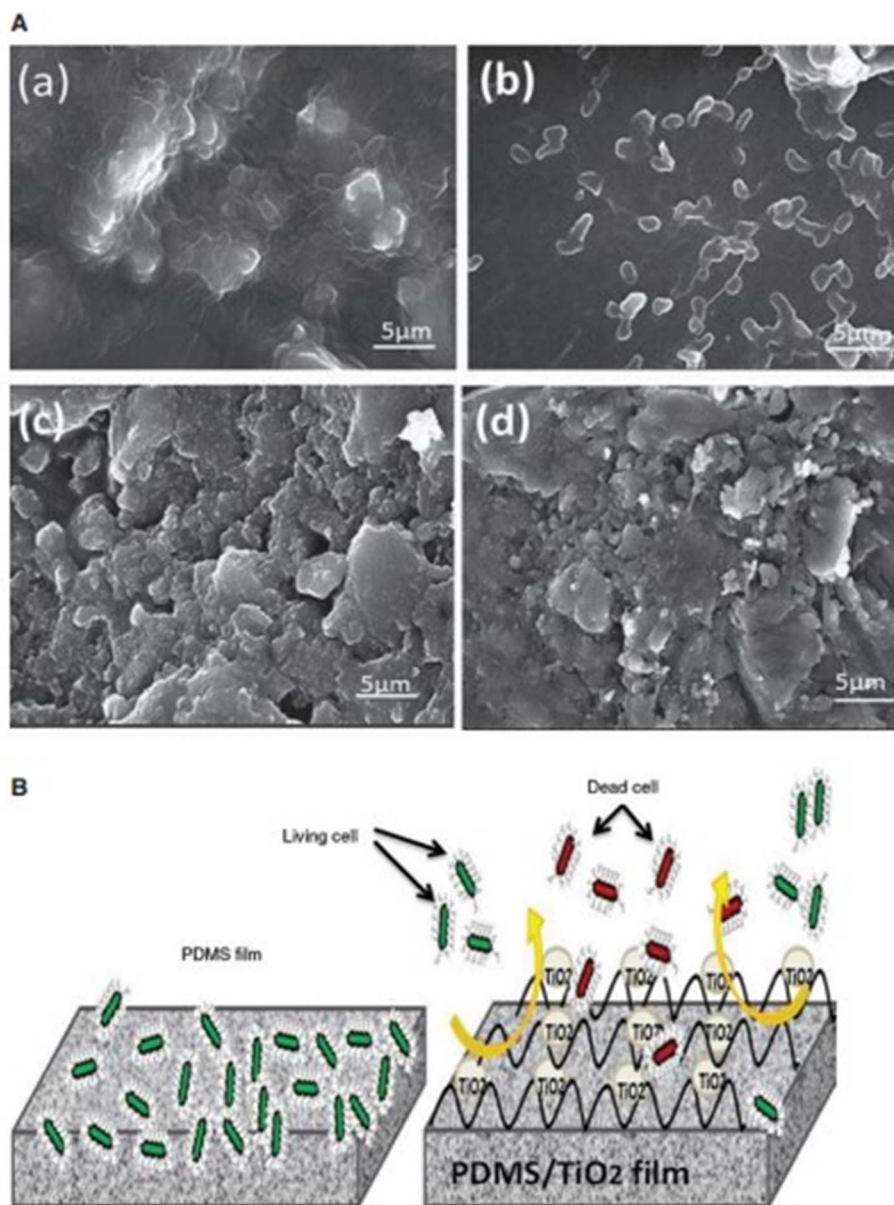


Fig. 7 (A) SEM images of the composite film at different concentrations of TiO_2 : (a) 0 wt%, (b) 7 wt%, (c) 10 wt%, and (d) 13 wt%. (B) Schematic of antibacterial mechanism of the composite film.⁴⁷

Biogenic synthesis was employed to create palladium (Pd) NPs, utilizing a plant extract derived from resveratrol and PdCl_2 . Subsequently, a thin film nanocomposite membrane was created by incorporating the aforementioned synthesized Pd NPs. The objective was to augment the characteristics and efficacy of the produced membrane with regards to salt rejection, dye rejection, flux, mechanical strength, hydrophilicity, and antifouling. The performance of the membranes was assessed using crystal violet dye. Therefore, an enhancement in the efficacy of the PSf membrane, which was augmented with PdNPs, was found in relation to its ability to reject salt and dye, its pure water flow rate, its resistance to fouling, its hydrophilic qualities, and its mechanical characteristics. The polyethersulfone (PES) membrane loaded with 2% Pd NPs exhibited

enhanced hydrophilic properties, achieving the greatest dye rejection rate of 99% alongside a breaking stress of 7.85 MPa. The optimization of the membrane performance was achieved by conducting permeation studies utilizing three distinct types of membranes with varying amounts of Pd NPs, namely 1%, 1.5%, and 2%. The concentration of the feed solution, operating pressure, and continuous flow rate were constant throughout the experiment. The flow of permeate and the percentage of dye rejection exhibited by the membranes were dependent on the concentration of NPs present in the polymer solution. The permeate flux exhibited a high value for low concentrations; however, the rejection of the dye consistently increased as the input concentration decreased, owing to the charged characteristics of the membrane. The permeate flux had a linear



relationship with the applied pressure, wherein an increase in pressure led to a proportional rise in flux. It is recommended to operate at a pressure of 2 bar for optimal performance. The observed rejection of crystal violet dye, held at a constant concentration of 0.1 mmol L^{-1} , was determined to be 99%. Furthermore, it was noted that the actual rejection of the dye increased marginally as pressure was applied, primarily as a result of the solute-membrane interactions. The membranes underwent testing to evaluate their salt rejection capabilities by subjecting them to a 1000 ppm NaCl solution under varying pressure conditions. The solute rejection exhibited an upward trend as the concentration of NPs increased, primarily attributed to the augmented hydrophilicity and enlarged surface area. The membrane composed of 2% Pd NPs had a peak NaCl rejection rate of 96% when subjected to a pressure of 2 bar. The study on salt rejection showed that the rejection of solutes was enhanced as the concentration of NPs increased, which is mostly attributed to the increased hydrophilicity and surface area of the membrane.⁴⁹

In another study, a bio-nanocomposite consisting of green naringin-functionalized boehmite ($\gamma\text{-AlOOH@Nar}$) to produce a thin film composite (TFC) polyvinylidene fluoride (PVDF)-based nanofiltration (NF) membrane was utilized. The resulting membrane exhibited improved antifouling capabilities and better rejection of medicinal compounds. To achieve this objective, the PVDF nanofiltration (NF) membrane was initially activated through the introduction of triazinyl groups. Next, the membrane surface was modified by the $\gamma\text{-AlOOH@Nar}$ nanocomposite at varying concentrations (0.2, 0.4, and 0.6 wt%). Furthermore, an investigation was conducted to assess the average pore radius, porosity, surface hydrophilicity, salt rejection, pure water flux, and antifouling capabilities of the membranes. The membrane denoted as TFC-0.4, consisting of 0.4 wt% $\gamma\text{-AlOOH@Nar}$, exhibited a pure water flux of $53.6 \text{ L m}^{-2} \text{ h}^{-1}$ and a fouling resistance ratio (FRR) of 95.4%. These values were approximately 2.3- and 2.4-times higher than that for the blank membrane, respectively. The TFC-0.4 membrane exhibited superior permeability and surface hydrophilicity.⁶² In addition to effectively reducing irreversible fouling, it demonstrated excellent rejection rates for pharmaceutical compounds, with a 99.8% rejection rate seen for both ceftriaxone (CTX) and cephalexin (CEX). The results of the pharmaceutical wastewater filtration experiment demonstrated that the $\gamma\text{-AlOOH@Nar}$ TFC membranes exhibited a significantly elevated normalized flow. Additionally, these membranes exhibited an impressive 89.8% removal of COD (chemical oxygen demand), complete removal of turbidity, and a moderate removal of TDS (total dissolved solids) (53.0%). In general, the $\gamma\text{-AlOOH@Nar}$ TFC membranes showed a notable capacity for effective separation and impressive resistance to fouling, indicating their considerable promise for application in pharmaceutical wastewater treatment facilities.

3.3. Nanofiber composite membranes

Nanofiber composite membranes⁷¹ are a type of membrane made from a combination of nanofibers and a supporting

matrix material. These membranes are engineered at the nanoscale, which provides them with unique properties and applications. The specific properties and performance of nanofiber composite membranes depend on factors such as the choice of nanofiber material, matrix material, and the manufacturing process used to create the membrane.

AgNPs derived from apple extract were synthesized using thermally-assisted and microwave-assisted methods. They were found to be uniformly distributed and had a faster reduction rate. These nanoparticles were embedded in PVDF nanofiber membranes, showing antibacterial activity against Gram-positive, *Staphylococcus aureus*, and Gram-negative bacteria. These membranes have potential for water purification systems. This study evaluated the antibacterial activities of the AgNP-embedded PVDF nanofiber membranes against mesophiles including *P. aeruginosa*, *K. pneumoniae*, and *S. aureus*, and the thermophile *G. stearothermophilus* using a modified disk-diffusion method. High-temperature-resistant bacteria are suggested to cause biofouling in thermally driven membrane processes, such as membrane distillation. This study found that the AgNP-embedded PVDF nanofiber membranes had a smaller inhibition zone than neomycin, given that the AgNPs were bound to the nanofiber membrane, preventing their diffusion within the culture media. This suggests that the AgNP-embedded PVDF nanofiber membrane can potentially prevent bacterial growth during water purification, reducing the formation of biofilms. The dynamics and succession of biofouling are not known, making it crucial to test the bacterial tactic response to AgNPs before real applications in membrane distillation systems.⁷²

3.4. Biodegradable polymeric nanocomposite membranes

Biodegradable membranes⁷³ are materials that possess the capability to break down naturally over time, ultimately returning to the environment as harmless substances. Thus, biodegradable polymeric nanocomposite membranes⁷⁴ represent an innovative class of materials that combine the benefits of biodegradability with the enhanced properties provided by NPs. Their versatility makes them a promising choice in various industries aiming for more sustainable and environmentally friendly solutions. Tables 2–4 provides a detailed literature on biodegradable membranes.

In the study by S. M. Albukhari *et al.*, they synthesized silver nanocomposites supported by cellulose acetate filter paper (Ag@CAF), and titanium dioxide (Ag@TiO_2) using *Duranta erecta* leaf extract, which demonstrated exceptional catalytic activity for reducing organic pollutants such as nitrophenols and dyes.⁷⁵ Ravikumar K. V. G., H. Kuberdiran, K. Ramesh *et al.* developed NiFe nanocomposite beads (GS-NiFe) using pomegranate peel extract and alginate, which effectively removed tetracycline (TC) from water, achieving 99% removal in batch studies and 487 mg g^{-1} capacity in continuous flow.⁷⁶ In another study, Reshmi C. R. *et al.* created a novel superhydrophobic, superoleophilic membrane of beeswax polycaprolactone (PCL-25BW), which demonstrated 98.1% oil-water separation efficiency, high oil sorption capacity ($16.95\text{--}31.05 \text{ g}$



Table 2 Green-synthesized nanoparticles in biodegradable membranes

	Biogenic source	Biodegradable polymer	Nanocomposite	Application	Reference
1	<i>Duranta erecta</i> leaf extract	Silver nanocomposites (synthesized using cellulose acetate filter paper as a support)	(Ag@CAF)	Unwanted dyes, nitro compounds	75
2	Pomegranate peel extract (<i>Punica granatum</i>)	NiFe immobilized into alginate	GS-NiFe beads	Removal of tetracycline (TC) (99%)	76
3	<i>Mukia maderaspatana</i> plant extract	Sodium alginate-based silver nanocomposite hydrogel	(SNC)	Methylene blue dye (MB) removal	79

Table 3 Biodegradable membranes

	Natural biodegradable membrane	Nanocomposite	Application	Properties	Reference
1	Beeswax and polycaprolactone nanofibrous membrane	(PCL-25BW)	Separation of oil-water mixture (98.1%)	Superhydrophobic, superoleophilic	77
2	Natural <i>Bombyx mori</i> silk fibers	Silk nanofibrils (SNFs)	The 64% rejection of rhodamine B	Ultrathin filtration membrane	78
3	Microalgal cells	Microalgae immobilized on chitosan nanofibers mats	Removal of around 87% nitrate	Electrospun chitosan nanofiber mats	80
4	Microalgae <i>Chlamydomonas reinhardtii</i>	Microalgae/PSU-NFW	Remazol black 5 and reactive blue 221 dye removal	Microalgae immobilized by PSf nanofibrous web	81

Table 4 Metal nanoparticles embedded in natural biodegradable membranes

	Metal nanoparticles	Biodegradable membranes	Applications	Reference
1	Silver nanoparticles	Carboxymethyl cellulose matrix (AgNPs/CMC)	Antibacterial properties toward <i>E. coli</i>	82
2	Silver nanoparticles	AgNP-embedded pectin-based hydrogel	Removal of metal ions Cu(II) and Pb(II) [99%], rejection of crystal violet (97%)	83
3	Ag NPs	Ag NP/wood membrane	<i>Candida albicans</i> , <i>Pseudomonas aeruginosa</i> , <i>Bacillus subtilis</i> , <i>Escherichia coli</i> , and <i>Staphylococcus aureus</i>	84
4	CuO-ZnO (CZ)	CZ-ESM nanocomposite (waste egg-shell membrane)	<i>E. coli</i> and <i>S. aureus</i>	85
5	Silver nanoparticles	Ag/Cs/PVA/PEG hydrogel nanocomposite	<i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	86
6	Pd NPs	(Pd NPs/wood membrane)	MB removal (>99.8%)	87
7	Silver (Ag)-nanoparticles	Guar gum/PVA composite	<i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> , and <i>Escherichia coli</i>	88

g^{-1}), and reusability for 15 cycles.⁷⁷ S. Ling *et al.* developed silk nanofibril (SNF) membranes derived from *Bombyx mori* silk, which were ultrathin (40 nm) with high water flux ($13\,000\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$) and efficient dye, protein, and nanoparticle colloid rejection, showing almost 64% rejection of Rhodamine B.⁷⁸ Nalan Oya San Keskin *et al.* developed microalgae-immobilized polysulfone nanofibrous webs (microalgae/PSU-NFW), which showed a significantly improved dye removal efficiency compared to pristine PSU-NFW, achieving 72.97% and 30.2% decolorization for RB5 and RB221 dyes, respectively.⁸¹

The significant properties of chitosan-based materials have been demonstrated through research on both synthetic and natural polymers.⁸⁹ Novel polymeric nanocomposite membranes, utilizing advanced chitosan, have been successfully engineered for the treatment of consumable water and

waste water. Biopolymers present eco-friendly and sustainable alternatives for membrane applications, offering excellent biocompatibility and low toxicity. These materials enhance the performance of membranes in water purification, gas separation, and biomedical applications by providing attributes such as selective permeability, antifouling properties, and structural flexibility.^{90–93} Biopolymers such as cellulose, chitosan, and alginate contribute significantly to environmental sustainability and foster the advancement of green technologies.⁹⁴ The biopolymers discussed herein are characterized by biodegradability, affordability, and lack of toxicity. Notably, these materials exhibit antioxidant and antibacterial attributes, making them very efficient in the elimination of pollutants such as dyes and heavy metals from aqueous environments.⁹⁵ Biopolymer materials possess several favorable characteristics, including



biocompatibility, cost-effectiveness, biodegradability, and renewability. Currently, scientists are utilizing NMs, specifically cellulose, to augment the characteristic properties and performance of biopolymeric membranes. The aforementioned membranes have found utility in various environmental applications for the remediation of hexane, crude oil, organic dyes, and medicinal compounds. These membranes are specifically designed to address concerns related to micropollutants, enhance resistance against fouling, improve rejection capacities, and enhance water permeability.⁷⁴

The inherent hydrophobicity of polymeric membranes is a notable obstacle in the context of water treatment applications, given that it leads to diminished membrane efficacy and performance during the separation procedure. This issue can be effectively addressed by utilizing an MMM comprised of polymeric substances, natural additives, and NMs. In this study, an MMM with hydrophobic properties was developed. The membrane was constructed using graphene oxide (GO) NM and PSf polymer, and the ecologically friendly gum Arabic (GA) as a natural additive. The construction of the membranes was achieved using the process of phase inversion, wherein the concentration of GO was modified while maintaining fixed quantities of GA (1.5) and PSf (18) wt%. The concentrations of GO utilized in the experiment were 0.2, 0.6, and 1.0 wt%. The characterization indicated that the MMM created using 0.6 wt% GO demonstrated the greatest degree of porosity, largest mean pore size, and improved hydrophilicity. The observed phenomena can be ascribed to the presence of oxygen-containing functional groups in both GO and GA. This particular factor exerted a substantial influence in attaining the highest water flux result, which had an average value of 63.55 L m⁻² h⁻¹ when operating at a pressure of 4 bar. Concurrently, this study exhibited a significant capability for the rejection of chemicals and enhanced resistance to fouling, as indicated by the humic acid rejection rate of 95% and flux recovery ratio of 88%. The findings of the study suggest that the incorporation of GO and GA can result in synergistic benefits, leading to improvements in the properties and functionality of membranes.⁹⁶

Cellulose acetate (CA) has been widely employed as one of the initial components in the production of filtration membranes.⁹⁷ In a study, a cellulose membrane with catalytic activity and high permeability⁹⁸ was produced using the vacuum filtering method, which involved the use of polydopamine (PDA) chemistry inspired by mussels. This study involved the fabrication of a membrane of nanocellulose fibers (NC) that were augmented with quasi-spherical AgNPs. The fabrication procedure entailed the reduction of silver salt *in situ*, namely on the surface of PDA covered nanometer-thick NC. This investigation focused on examining the permeability characteristics of the membranes through exposure to pure water in a gravimetric experimental setup. The evaluation of catalytic activity was conducted by means of the reduction reaction of 4-nitrophenol (4-NP), which is a prevalent contaminant found in water sources. The stacking membranes exhibited a conversion efficiency over 95% for the 4-NP compound when tested under gravimetric conditions. The investigation additionally encompassed an

analysis of the catalytic activity involved in the reduction of 4-NP within a batch reactor. The experimental results demonstrated that the full conversion of 4-NP could be accomplished within 8 min. The experiment yielded a turnover frequency (TOF) of 2.25×10^{-3} molecules per gram per minute for the process. The observed high water flux in the fabricated membrane can be ascribed to the inherent hydrophilicity of the PDA-coated nanocellulose (NC) and the hydrophobic repulsion induced by the presence of AgNPs. The observed catalytic activity of the AgNP membrane can be ascribed to the synergistic impact resulting from the combination of the PDA-coated NC and AgNPs. Furthermore, the enhanced catalytic reusability exhibited by the adhesive, specifically PDA, highlights the robust bonding capacity between NC and AgNPs. The produced AgNPs@NC membrane exhibits promising potential for utilization in industrial applications as a catalytic converter in the future.⁹⁹

A unique membrane type was described, utilizing a 3D web-like structure of bacterial cellulose (BC) modified with mussel-inspired dopamine (DA) in a liquid environment, combined with 2D graphene oxide (GO) nanosheets. This membrane showed excellent separation towards various dyes, oil/water, and water-immiscible organic solvents, and fouling parameter. However, in dye separation, size followed by charge separation was observed. Alternatively, in oil rejection for epichlorohydrin, with a modest enhancement in surface anti-oil-adhesion activity, 98% rejection of epichlorohydrin was observed.¹⁰⁰

Herein, a simple filtration process for the preparation of AgNPs decorated with cellulose nanofibrous (CNF) membranes was reported. CNFs were prepared *via* the oxidation process of 2,2,6,6-tetramethylpiperidine-1-oxyl. The Ag NP/CNF nanofibrous membranes on PVDF support showed excellent antibacterial properties, rejecting 12 nm ferritin and 5 nm NPs with 90% and 86% rejection, respectively, and exhibiting a water flux of approximately 1000 Liters per square meter per hour per bar, making them efficient to rapidly produce consumable water at the time of outdoor emergencies.¹⁰¹

The treatment of oily wastewater is being advanced by the utilization of emerging technologies, namely through the integration of ultrafiltration membranes that are augmented with hydrophilic nanoparticles. This integration aims to improve the overall effectiveness and efficiency of the treatment process. A previous investigation involved the fabrication of MMMs using CA and zwitterionic NPs, specifically polydopamine-sulfobetaine methacrylate (P(DA-SBMA)), by the wet-phase inversion method. The ratio of styrene butyl methacrylate (SBMA) to divinylbenzene (DA) monomers was manipulated to modify the dimensions of the poly(divinylbenzene-styrene butyl methacrylate) (P(DA-SBMA)) NPs. The introduction of P(DA-SBMA) into a CA solution resulted in thermodynamic instability, leading to instantaneous demixing during the phase separation process in water. The impact observed was advantageous in terms of the porosity of the membrane and the average radius of its pores. Additionally, the enhancement in membrane hydrophilicity can be attributed to the abundant presence of hydrophilic functional groups in the P(DA-SBMA)



nanoparticles. The CA membrane was modified by embedding P(DA-SBMA) nanoparticles in the CA matrix, achieving an ideal water flux of $583.64 \pm 25.12 \text{ L m}^{-2} \text{ h}^{-1}$. The size and composition of the NPs were carefully chosen to ensure the desired performance of the modified membrane. The improvement in flux recovery was seen to be 8.85%, while reversible fouling showed an enhancement of 11.10%. Alternatively, irreversible fouling exhibited a reduction of 8.85%. Various oil-in-water emulsions comprised of diesel oil, dodecane, food-grade oil, toluene, and hexane were examined through experimental analysis, resulting in notable separation efficiencies ranging from 95% to 99%. In general, the artificially produced membranes showed efficacy in the treatment of various forms of oily wastewater.¹⁰² An earth-abundant material, wood, is extensively used in daily life.¹⁰³ In addition to its mesoporous structure, natural wood contains numerous long, partially-aligned channels, as well as nanochannels that extend along its growth direction. This unique wood mesostructure is suitable for various emerging applications, particularly as a membrane or separation material. Together with its mesoporous structure, natural wood consists of several long, partially-aligned channels as well as nanochannels that stretch along its growth direction. This wood mesostructure is appropriate for a wide range of evolving applications, particularly as a membrane or a separation material.⁸⁷

The three-dimensional (3D) mesoporous structure of wood consists of diverse oxygen-containing functional groups, enabling it to effectively reduce metal NPs in its immediate surroundings. In a previous study, researchers successfully devised a novel wood filter membrane that was enhanced with silver AgNPs for the purpose of water filtering. The wood blocks were immersed immediately in a solution of silver nitrate (AgNO_3) to create the AgNP/wood membrane. Subsequently, these membranes were employed directly for the purpose of filter sterilizing. Moreover, the bacteriostatic impact of the AgNP/wood membrane was assessed through the filtration of river water. The experiment demonstrated the eradication of fungus and bacteria during the filtration process of 5 L of river water using three wood membranes simultaneously. The temporary bacteriostatic test was conducted to assess the sizes of the bacteriostatic circles formed by *Escherichia coli*, *Bacillus subtilis*, *Candida albicans*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*. The results indicated that all these bacterial strains exhibited bacteriostatic circles with diameters exceeding 1 cm. Thus, the AgNP/wood membranes demonstrated remarkable antibacterial efficacy and favorable filtering characteristics.⁸⁴

A recent study demonstrated the effectiveness of a mesoporous, three-dimensional wood membrane decorated with Pd NPs for the purpose of wastewater treatment. The remarkable efficacy of this substance can be ascribed to the synergistic impact of the evenly distributed catalyst particles at the nano-scale level and the distinctive channel configuration inherent in hardwood. Wood, which exhibits mesoporous properties, typified by partially-aligned yet uneven channels, possesses significant advantages across various domains. Firstly, it facilitates the creation of NPs within its structure. Additionally, it

facilitates the uninterrupted circulation and mobility of water. Finally, it facilitates the increased contact and interaction between pollutants and Pd NPs that are dispersed throughout its three-dimensional channels. The experimental methodology encompassed the utilization of a wastewater sample comprised of a solution containing MB and sodium borohydride (NaBH_4). The Pd NP/wood membrane exhibited a degradation efficiency of 99.8% for MB when the treatment flow rate reached $1 \times 105 \text{ L m}^{-2} \text{ h}^{-1}$. The results obtained from the experimental studies as well as computational modeling simulations provide evidence that the mesostructure of wood channels, which encompasses a range of characteristics including variable channel diameters, vessel pits, and spiral thickenings, plays a significant role in facilitating a high rate of degradation and efficient performance for MB. The prospective use of a 3D mesoporous wood membrane with partially aligned channels in water treatment is broad, encompassing many pollutants. The 3D wood membrane has characteristics of being both cost-effective and high-performance, hence possessing potential for future implementation in industrial-scale applications. The zigzag wooden jars enhance the cleanliness of wall surfaces by effectively segregating impurities from the fluid stream. As a consequence, there is a notable reduction in the concentration of soil at designated places further downstream. The presence of a zigzag pattern in the hardwood block results in a reduction in flow rate and an augmentation in surface area, hence facilitating the diffusion of dirt particles. Consequently, this leads to an improvement in the efficiency of dirt removal. The presence of a curved channel does not significantly impact the diffusivity of dirt. However, it leads to an increase in dirt residence time and an expansion of the wall surface area.⁸⁷

The synthesis of CuO-ZnO (CZ) nanocomposites was conducted by a biosynthetic method utilizing biowaste-derived eggshell membranes (ESM). The observed results provide justification for the preservation of the original structural properties of ESM in CZ-ESM nanocomposites, wherein the interlaced network is coated by tiny inorganic NPs. Furthermore, the materials exhibited exceptional catalytic, adsorptive, and bactericidal properties. The experimental results provided evidence that the adsorption kinetics and isotherm for Congo red (CR) dye were effectively described by the pseudo-second-order kinetics and Langmuir isotherm model, respectively. Also, the maximum adsorption capacity was determined to be 775 mg g^{-1} . The CZ-ESM nanocomposites exhibited a catalytic reduction efficiency of 98% for 4-NP within a 12 min timeframe at room temperature. Also, they exhibited the capacity to undergo several recycling cycles without encountering notable activity degradation. Moreover, the results obtained from the antibacterial investigations demonstrated that the CZ-ESM nanocomposites exhibited substantial inhibitory properties against both *S. aureus* and *E. coli*. The inhibitory zone diameter reached a maximum of 27.5 mm and 20.3 mm for *S. aureus* and *E. coli*, respectively. This study demonstrated the synthesis of nanocomposites, specifically CuO-ESM, CZ-ESM and ZnO-ESM, through the utilization of ESM-templated synthesis. The nanocomposite (CZ-ESM) exhibited an enhanced performance in comparison to individual components as a result of the



distinctive network structure, heterostructural attributes, and synergistic interplay between Cu^{2+} and Zn^{2+} ions. Additionally, the researchers showcased noteworthy antibacterial efficacy against both *E. coli* and *S. aureus*, hence indicating their potential applicability in environmental cleanup and water disinfection processes.⁸⁵

The aforementioned materials possess advantageous qualities such as non-toxicity and biodegradability, making them highly valuable. Currently, there is a heightened emphasis among researchers on the development of natural biodegradable goods for uses such as water filtration.

4. Impact of GNP on antibacterial and antiviral properties on membrane

Researchers have been exploring the integration of nanofillers into polymeric structures to overcome challenges related to chemical stability, mechanical stability, fouling, permeation flux, and rejection.¹⁰⁴ One of these methods involves the synthesis of nickel-bentonite NP (NBNPs)/PES membranes. This process involved adding bentonite powder to *Scrophularia striata* extract, adding Ni^{2+} solution, and centrifuging. The NBNP/PES membrane with a 0.5 wt% loading demonstrated the best practice in rejecting Pb^{2+} , Cu^{2+} , and Zn^{2+} ions. In this study, the Donnan exclusion principle primarily accounts for the efficient removal of the heavy metal ions. The 0.5 and 1 wt% (NBNPs/PES) membranes showed antibacterial rates of 68.1% and 90% and 66.9% and 88% against *Staphylococcus aureus* and *Escherichia coli* (Fig. 8), respectively, possibly due to the presence of nickel NPs and hydroxyl groups.⁹

In an alternative study, the biosynthesis of AgNPs was conducted utilizing *Amaranthus tristis* leaf extract. A nanocomposite membrane composed of Ag/PVA was crafted by incorporating biosynthesized AgNPs into the polymer matrix of polyvinyl alcohol (PVA). These crafted membranes were exposed in air to test their activity against airborne microbes and were compared with the pristine PVA membrane. The nanocomposite membrane composed of Ag and PVA in a 2 : 8 ratio exhibited outstanding effectiveness in inhibiting microbial growth. The

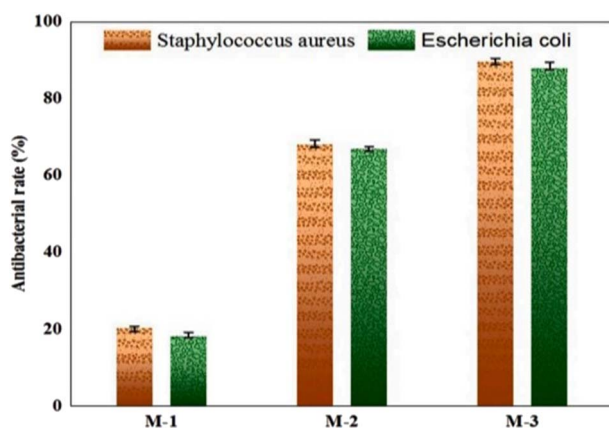


Fig. 8 Antibacterial reduction rate (%) of nanocomposite membranes.⁹

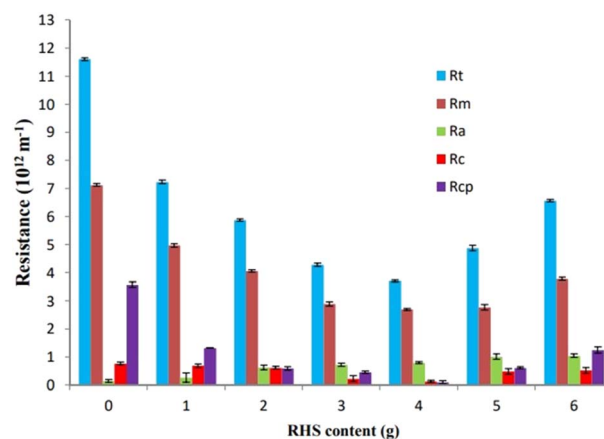


Fig. 9 Resistance, R_t : total; R_m : membrane; R_a : due to absorption; R_c : due to cake layer; R_{cp} : due to cake polarization.⁵⁴

AgNP and Ag/PVA nanocomposite membrane showed excellent antimicrobial activity against *Klebsiella pneumonia* and *Pseudomonas fluorescens*. The nanocomposite membrane could be used for the purification of harmful bacteria, such as infective microbes, to prevent respiratory diseases such as asthma, COPD, Legionnaire's disease, and flu fever. This nanocomposite membrane can help filter toxic gases in the atmosphere, protecting humans from hazardous respiratory diseases.⁴³

Ocimum sanctum leaf extract was employed as a source of Ag nanoparticles, which were prepared at room temperature and encased in a PVA polymer matrix. The antimicrobial efficacy of the PVA-encapsulated silver was evaluated against both Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria across various concentrations. It was observed that eugenol, an active component present in *Eugenol sanctum* leaves, exhibited sensitivity to AgNPs, aligning with the findings from prior research. The antibacterial effect of PVA-encapsulated silver was tested against Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria at different concentrations. Eugenol, an active constituent in *Eugenol sanctum* leaves, was found to be sensitive to AgNPs, which is consistent with previous studies.²⁶

The leaf extract of *Mimosa elengi* L was utilized to prepare AgNPs for the surface modification of ultrafiltration PES membranes, imparting antimicrobial properties. The resultant AgNP-incorporated membrane exhibited significant antibacterial activity against *E. coli*, underscoring the potential of biosynthesized AgNPs in creating ultrafiltration membranes with tailored antimicrobial characteristics.⁶³

Another study demonstrated the possible potential of biogenic silver (bio-Ag⁰) NPs in water disinfection. The bio-Ag⁰ nanoparticles were immobilized in a microporous PVDF membrane, resulting in the inactivation of UZ1 bacteriophages. The membranes showed a reduction of 3.4 log in viruses, with the silver concentration approaching the drinking water limit. This membrane technology has the potential for small-scale water disinfection, demonstrating the importance of innovative water disinfection strategies in preventing waterborne diseases. This study showcased the efficacy of PVDF membranes

featuring imprinted bio-Ag⁰ for the inactivation of viruses in water. The batch experiments revealed a 4-log reduction in phages upon incorporating 2500 mg of bio-Ag⁰ per square meter. AgNO₃ demonstrated effectiveness in inactivating MS2, T2, and monkeypox viruses as well. The antimicrobial action of AgNPs is not fully understood, but studies suggest that it is related to the release and interaction of Ag⁺ with bacterial enzymes and proteins. Comprehending the impact of the membrane structure on the release rate of Ag⁺ from bio-Ag⁰ can help reduce the concentration of Ag⁺ in the filtrate, thus controlling its depletion. Nevertheless, extended filtration practices are required to validate the antimicrobial effectiveness with time. This technique is suitable for treating limited polluted water volumes, but not appropriate for long-term consumable water production.⁶⁴

By considering these antibacterial and antiviral activities of membranes, it can be concluded that green-synthesized NPs can enhance the performance of membranes.

5. Antifouling properties of GNP on membranes

An aqueous extract obtained from the wild plant *Paronychia argentea* Lam (*P. argentea*) was employed to successfully synthesize AgNPs. The ultrafiltration PVDF membranes incorporated with these synthesized AgNPs showed excellent antifouling activity against both the bacterial strains. The BSA rejection rates were 99.4% for PVDF/NC and 98.7% for PVDF/PURE. In the study by Li *et al.* in 2013, AgNPs were employed to enhance the surface hydrophilicity and antifouling capabilities of a PVDF membrane. However, N. Alnairat *et al.* proved the permeability of Ag/PVDF-g-PAA was found to be less effective compared to the pure PVDF membrane.⁴² The issue of biofouling is a significant challenge in the utilization of membrane technology for the purpose of water and wastewater treatment. One effective approach for mitigating biofouling is the utilization of improved membrane materials specifically designed to resist and prevent the accumulation of biological organisms. The present investigation involved the incorporation of varying quantities of biogenic AgNPs (bio-Ag⁰) in PES membranes using the phase-inversion practice. This study examined biofilm formation on PES membrane surfaces in an anaerobic stimulated muck bioreactor. The bio-Ag⁰/PES composite membrane (bio-Ag⁰/PES), was characterized by low bacterial presence, successfully inhibited biofilm formation and demonstrated excellent resistance to biofouling. The increased bio-Ag⁰ loading decreased the membrane contact angle, resulting in enhanced hydrophilicity and Ag⁺ release, preventing bacterial attachment.⁴¹

The following study aimed to examine the impact of rice husk-derived silica (RHA) on a PSf membrane as an antifouling addition. The preparation of flat-sheet ultrafiltration (MMMS) PSf/RHS membrane was conducted using the phase inversion method, employing varying concentrations of silica. The composite membrane showed increased retrieval of flux after physio-chemical cleaning.⁶⁶

6. Future perspectives

Green chemistry is a discipline within the field of chemistry that is focused on reducing the utilization of harmful and dangerous chemicals to promote ecological sustainability (Fig. 4). There are various primary approaches to optimize the incorporation of ideologies of clean chemistry throughout all domains of human existence.^{38,105}

(1) In the framework of plant-mediated biosynthesis, it can anticipate that there will be variability in outcomes when utilizing extracts from the same plant species that have been gathered from diverse places across the globe, mostly due to the disparities in their chemical composition. This matter can be resolved through the accurate identification of a variety of biomolecules found in plant extracts, followed by an examination of their function in the processes of reduction and capping.¹⁰⁶

(2) The utilization of chemically manufactured NPs is associated with significant toxicity concerns. However, these adverse effects can be mitigated by employing metal GNPs. It is important to note that the latter still necessitates additional layering with biocompatible surface-active agents and polymeric materials. The utilization of advanced technology has significant promise in facilitating the advancement of innovative healing agents through the integration of medicinal plants, nanoparticles, and wound healing.¹⁰⁷

(3) The food business is greatly influenced by nanotechnology due to its ability to enhance the processing, packaging, and long-term preservation of food. As a result, there has been a significant surge in the food sector due to advancements that have enhanced the taste and consistency of food products. NMs and nanosensors contribute to enhancing security measures by facilitating pathogen detection, hence aiding customers in assessing the quality and nutritional state of food products. Due to the hydrophobic characteristics and limited bioavailability and stability of most of the consumable bioactives that fight countless ailments, the utilization of nanotechnology-based delivery approaches has shown effectiveness in augmenting the availability and targeted delivery of these bioactive complexes in food.¹⁰⁸

(4) The mechanism by which metal NPs exert their biotic properties remains unclear, highlighting a need to investigate this matter in future studies. The biological activities of NPs are believed to be influenced by various parameters, including their size and structure. Bioinformatics and modeling research can deliver insight into the actual impact of the aforementioned components.¹⁰⁹

To guarantee environmental preservation by legislative means.

To safeguard human health and mitigate adverse environmental impacts, it is imperative to employ inventive alternative approaches that minimize the production of undesirable chemicals. These approaches involve utilizing renewable sources for raw materials, using safer reagents, employing alternative solvents such as ionic liquids and water in organic synthesis, adopting “green” catalysts to minimize the utilization



of energy and production of waste, and also reducing energy usage throughout the industrial process stages. The widespread adoption of “green” chemistry in various sectors including food, energy, pharmaceuticals, cosmetics, plastics, and cleaning products will be essential for fostering industry advancements in the future.^{97,110}

7. Conclusions

The incorporation of green-synthesized nanoparticles into membrane applications presents a compelling and sustainable approach with significant potential for revolutionizing the field of membrane technology. Through eco-friendly synthesis methods utilizing plant extracts, microorganisms, and biomolecules, this approach addresses critical environmental concerns associated with conventional nanoparticle production. The nanoparticles obtained display improved compatibility with membrane materials and provide accurate regulation of their size, shape and surface characteristics. The advantages of utilizing green-synthesized nanoparticles in membranes are manifold. These nanoparticles impart improved hydrophilicity, antifouling characteristics, augmented mechanical strength, and heightened selectivity across a range of separation processes. From water purification and desalination to wastewater treatment, the impact of these sustainable nanoparticles is evident in their ability to enhance the separation efficiency and mitigate fouling. However, although this approach shows tremendous promise, it is essential to acknowledge its potential challenges. Scalability, stability, and long-term environmental impact must be carefully considered to ensure the practical viability of green-synthesized nanoparticles in large-scale membrane applications. Continued research and development efforts are crucial in addressing these challenges and further refining this sustainable approach. In conclusion, green-synthesized nanoparticles represent a pivotal advancement in membrane technology, aligning with global sustainability goals and pushing the boundaries of environmentally responsible materials synthesis. As this field continues to evolve, it holds the potential to revolutionize various applications, making them more efficient and environmentally friendly. The integration of green-synthesized NPs in membrane applications stands as a testament to the power of sustainable innovation in addressing pressing environmental challenges.

Data availability

The data that have been used are confidential. No persons/animals were included in our study.

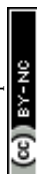
Conflicts of interest

There are no conflicts to declare.

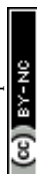
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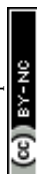
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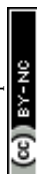
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