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Grand Challenges in the Development of Nanomaterials-Incorporated Adsorptive Membrane for Water and Wastewater Treatment

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ABSTRACT

Integrating nanotechnology and membrane technology has resulted in the development of adsorptive nanocomposite membranes with exceptional properties for various applications, including water reclamation. The application of adsorptive membranes in wastewater treatment is a promising technology that combines the advantages of adsorption and membrane filtration techniques. Literature reviews reported that various adsorptive membranes were successfully developed and efficiently removed emerging contaminants such as heavy metals and persistent organic pollutants from water over the last decades. However, grand challenges in developing adsorptive membranes require more attention, such as aggregation and agglomeration of nanoadsorbents within membrane matrix, mechanical strength distortion, extreme water permeability, and alterations in surface charge. These challenges, as mentioned earlier, could deteriorate the performance of adsorptive membranes. Consequently, future research should focus on overcoming these challenges to employ adsorptive membranes to preserve the environment.

Keywords: Adsorptive membranes, membrane technology, heavy metals, wastewater treatment, adsorption

1.0 INTRODUCTION

Emerging pollutants such as heavy metals, endocrine disruptor compounds (EDC), synthetic dyes, and micropollutants in wastewater are significant issues that endanger public health. Currently, there are various wastewater treatment methods have been developed for the removal of emerging pollutants including ion exchange, chlorination, flocculation-coagulation, ozonation, and oxidation. However, most methods are inefficient, expensive and generate secondary pollution. For example, resin bead regeneration was necessary to remove pollutants using the ion exchange method, making it impractical when dealing with a substantial amount of wastewater due to its high operating costs [1]. Removing pollutants by coagulation and precipitation may produce hazardous bulk wastes. Additional post-treatment, such as separation and filtration, is necessary to eliminate waste [2]. The oxidation treatment method may yield toxic by-products since oxidation of organic pollutants from pharmaceutical and oilfield wastewater generates harmful intermediate by-products before they

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are completely removed from the water [3]. The complex reaction mechanism in the degradation of the organic pollutants reflected the generation of these harmful intermediate by-products.

Among those methods, adsorption by nanosized adsorbent is an efficient method for the removal of toxic pollutants present in water. Due to their vast surface area, great adsorption sites, and rapid kinetics, nanoadsorbents are promising for removing solutes with low molecular weights. Various nanosized adsorbents have been widely developed and used for the remediation of water and wastewater, such as metal oxides [4], carbon-based materials [5], metal-organic frameworks (MOFs) [6, 7], and zeolites [8]. Unfortunately, the nanoadsorbents are produced as fine powders, which causes problems with regeneration and separation, in addition to their high cost and potential toxicity hazards from leaching into water bodies. Due to their poor mechanical strength and high-pressure drop, utilizing nanoadsorbent in fixed column beds or any other flow systems is not the best approach [9].

Membrane technologies are frequently employed in water and wastewater due to their significant benefits over conventional treatment [10]. Recently, the incorporation of nanoparticles into polymeric membranes has been the trend in the field of membrane research [11–13]. Therefore, impregnating nanoadsorbent into membrane matrix to form adsorptive membranes is a promising tool to address the shortcomings of nanoadsorbents applications in wastewater treatment.

Adsorptive membranes are dual-functional membranes with specialized adsorption capability and filtration in the same chamber [14]. In the fabrication of adsorptive membranes, the nanoadsorbents are immobilized in the membrane matrix [15]. This membrane is based on the adsorption process, a standard mass transfer mechanism involving chemical or/and physical interactions that attract or attach the pollutants molecules. Most recently, adsorptive membranes also developed by integrating polyethyleneimine (PEI), tannic acid (TA), and metal ions like Fe^{2+} and Zn^{2+} into polysulfone (PSf) to form PSf/ PEI-TA/FeZn adsorptive membranes for removing three types of protein-bound uremic toxins in dialysis application [16]. Several works have been dedicated to the development of adsorptive membranes by incorporating nanosized adsorbents into polymeric membranes such as polyvinylidene fluoride (PVDF) [17–19], polyethersulfone (PES) [20–23], PSf [24–26], polycarbonate (PC) [27], and polyvinyl alcohol (PVA) [28–33]. Some of the developed adsorptive membranes are summarized in Table 1.

However, several challenges were identified in fabricating the nanomaterials-incorporated adsorptive membranes. Therefore, in this work, the grand challenges in the development of adsorptive membranes will be reviewed.

Table 1 Reported works on developed adsorptive membranes

Adsorptive membranes	**Nanoadsorbents loading (wt. %)**	**Pollutants**	**Feed concentration (mg/L)**	**Adsorption capacity (mg/g)**	**Kinetic model**	**Isotherm model**	**Water Flux (L/m^2.h)**	**Operating pressure (bar)**	**References**
PSf/PEI-TA/FeZn	1/2/1/8	Indoxyl sulfate (IS)	100	183	Elovich	Freundlich	69.0	0.3	[16]
		p-cresol sulfate (PCS)		134		Langmuir			
		Hippuric acid (HA)		78		Langmuir			
PSf/ HINM	1.50	As(III)	100	41.09	Pseudo-second order	Freundlich	173.8	1.0	[25]
PVDF/ TiO_2	1.00	Boron	8.2	0.43	-	-	223.0	3	[34]
PC/ HMO	15.00	Cd(II) Cu(II)	40	31.36 29.68	-	-	693.8	10	[27]
PES/ PANI-GO	0.25	Pb(II)	500	202.00	Pseudo-first order	Langmuir	5.5	4	[35]
PSf/ zeolite	10.00	Pb(II) Ni(II)	500 200	682.00 122.00	-	-	57.0	2.5	[24]
PSf/ GO	0.50	Pb(II) Cu(II) Cd(II) Cr(VI)	500	78.50 68.30 75.60 159.50	-	Langmuir	30.0	6.9	[36]
PET/ ACF-TiO_2	17.60	Bisphenol A	10	70.6	-	-	-	-	[37]

2.0 GRAND CHALLENGES IN THE DEVELOPMENT OF ADSORPTIVE MEMBRANES

The published works showed the great potential of adsorptive membranes as promising technologies to preserve the environment. Due to both adsorption and filtration synergistic effects, adsorptive membranes can potentially remove various types of emerging pollutants that cannot be eliminated using conventional approaches. However, **i**ntegrating the benefits of nanoadsorbents with membranes while overcoming their drawbacks in water treatment remains a challenge. The grand challenges in developing adsorptive membranes include aggregation and agglomeration of nanoadsorbent, mechanical strength distortion, extreme water permeability, and alterations in surface charge. Each of the grand challenges will be revealed in the following sections.

2.1 Aggregation and Agglomeration of Nanoadsorbents

Aggregation and agglomeration of nanoadsorbents within the polymer matrix membrane directly hinder the active surface area of the Nano adsorbents hence indirectly reducing the adsorption performance and physical properties of the adsorptive membranes. In addition, the active surface area of the nanoadsorbents may be diminished due to the interaction of the nanoadsorbent and the polymer membrane. A previous study reported the formation of agglomeration of HINM nanoparticles was observed in the hollow fiber PSf membrane as the loading of nanoadsorbent was 2.0 wt.% as depicted in Figure 1. The agglomeration of the nanoadsorbent produced undesirable voids and defects in the morphology of the membrane. Therefore, interfacial interactions between nanoadsorbents and the membrane matrix must be further studied to enhance their compatibility in the adsorptive membranes.

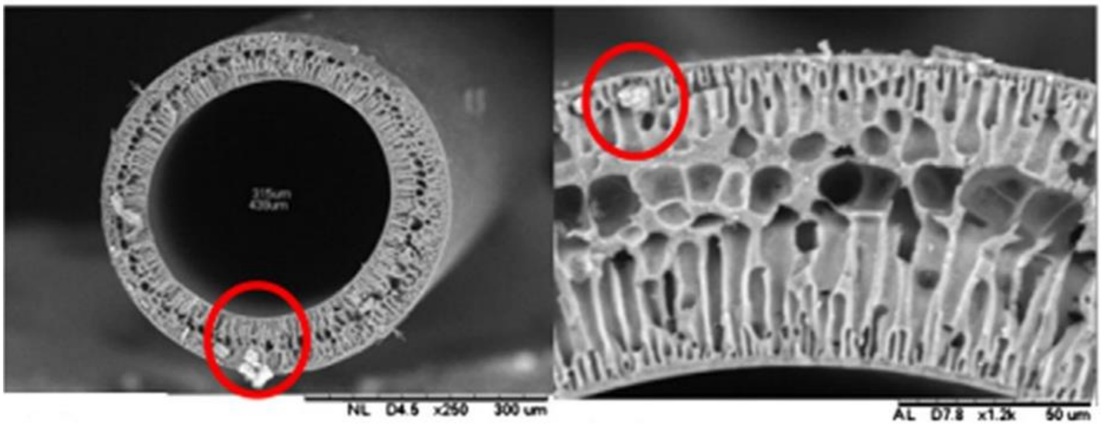

Figure 1 SEM image of cross-sectional morphology of PSF/HINM hollow fiber adsorptive membrane that contains nanoadsorbent agglomerates (in red circles)

Generally, many studies have shown that increasing the loading of nanoadsorbent in the adsorptive membrane could increase the adsorption performance. According to research by Gohari *et al*., increasing the ratio of TNT nanoadsorbent to PSf membrane matrix from 0.125 to 1.50 resulted in a remarkable increase in the adsorption capacity of arsenate from 21.7 mg/g to 124.9 mg/g [38]. The increase in active sites for pollutant adsorption at increased adsorbent loading into membranes has improved adsorption capacity. However, when excessive loading of nanoadsorbents was added into the polymer matrix membranes, the chance of the nanoadsorbents to aggregate and agglomerate by adhering together also increased.

An excessive amount of nanoadsorbents in the polymer matrix membrane could result in possible leaching of nanoadsorbents from the polymer membranes into the surrounding water. This occurred primarily during a long run of the adsorption-filtration process due to poor interaction or stability of nanoadsorbents in the membrane matrix. Some nanoadsorbents are harmful and dangerous since they contain toxic metals such as lead (Pb) and applying them in water treatment could result in secondary pollution [39]. Thus, it is essential to guarantee the nontoxicity and safety of the nanoadsorbents before being applied to the membrane. This can be achieved by performing toxicity and leaching studies to evaluate the stability of the adsorptive membranes and the quality of the treated water before disposal into the environment.

2.2 Mechanical Strength Distortion

As nanoadsorbents were introduced into the membrane matrix, the mechanical and structural properties of the adsorptive membranes definitely will change. The mechanical strength of adsorptive nanocomposite membranes has been recognized as a visual measure of long-term performance. Elongation at break, tensile strength, and Young's modulus offered a thorough understanding of the ability of adsorptive membranes to resist elastic deformation and stress when subjected to harsh operation circumstances [40].

According to earlier research, the mechanical strength of adsorptive membranes increases with an increase in nanoadsorbent loading up to a certain degree before it begins to decrease significantly. For example, Mukherjee demonstrated an enhancement in the mechanical strength of the PSf/graphene oxide (GO) nanocomposite membrane with an increase in GO loading from 0 to 0.1 wt.% in the PSf membrane [36]. However, as the loading of GO nanoparticles increased to 0.5 wt.%, the membrane matrix becomes spongy, resulting in increased pore density and reduced mechanical strength of the membranes. In another study, Razmjou *et al.* reported the higher loading of nanoparticles could significantly reduce the mechanical strength and elongation stress of the membranes [41]. They reported that there is a slight reduction in tensile strength and elongation at the break between the pristine PES membrane and TiO_2-loaded nanocomposite membrane [41]. This finding indicated that the TiO_2 nanoparticles were well dispersed in the polymeric matrix of the nanocomposite membrane. Nakamoto *et al.* reported that by increasing the loading of mordenite zeolite from 27.0 wt.% up to 69.0 wt.% into PES composite fiber, the tensile strength values decreased concomitantly [42]. The decrease in mechanical strength of the composite fiber might be due to the increased porous void space in PES/ mordenite fiber.

Adsorptive membranes that have optimum loading of nanoadsorbents boost the mechanical strength through the good interaction between nanoadsorbents and polymer matrix, formation of the thicker top layer, and suppression of microvoids which increase the rigidity and elasticity of the structure of the adsorptive membrane. Optimum loading of nanoparticles within polymeric membranes could often improve adsorptive nanocomposite membranes' elasticity behavior and mechanical properties.

2.3 Extremely High-water Permeability

Most of the studies reported water permeability of adsorptive membranes is highly dependent on the pore size, hydrophilicity, porosity, top layer thickness, and surface roughness. Rougher membrane surface led to higher water permeability due to the increase in the addition of hydrophilic nanoparticles. However, adsorptive membranes might experience extremely high-water permeability due to the addition of excessive hydrophilic nanoadsorbents. According to Abdullah *et al.*, by increasing the loading of hydrophilic hydrous ferrous oxide (HFO) nanoparticles, the porosity, hydrophilicity, water permeability, and membrane roughness were improved [26]. The membrane pure water flux significantly increased from 229.5 L/m^2h to 942.1 L/m^2h. From the FTIR analysis, when the loading of HFO increased, the amount of hydroxyl group interacted with PSf polymer also increased. These results triggered the membrane to become more hydrophilic, attracting more water molecules to the surface of the adsorptive membrane. This phenomenon raised the surface roughness and indirectly enhanced the water permeability of the membranes. The excellent water permeability in adsorptive membranes is mainly caused by larger pore sizes and high porosity

In another study, increasing GO concentration above 0.1 wt% increases the membrane permeability due to the solvent-nonsolvent demixing dominance, leading to a spongy and porous membrane matrix [36]. According to Mukherjee *et al.*, solvent-nonsolvent demixing refers to the process of exchanging solvents, specifically N, N- dimethylformamide (DMF), and nonsolvents like water during the formation of pores in a membrane through phase inversion. As DMF diffuses from the polymer-rich phase (membrane matrix) to the polymer-lean phase (water bath) during phase inversion, the water triggers phase inversion, leading to the creation of pores inside the membrane. Thus, this exchange of solvent, DMF, and nonsolvent; water, is considered a crucial mechanism for pore formation in membranes. The synergistic effect of the porous structure and the hydrophilic surface is responsible for better membrane permeability. During the phase inversion process, solvent from the casting solution diffused out, and the void space was replaced by non-solvent (water) from the coagulation bath. GO allowed more water to be attracted into the membrane matrix, increasing membrane porosity. However, pollutant rejection is reduced with increasing GO content in adsorptive membranes. Electrostatic interaction with the membrane surface and the pore size influence the solute rejection. Solute rejection decreases because the influence of pore size is dominant for adsorptive membranes with increasing GO concentration. Nevertheless, other researchers reported that the opposite observation that integrating functionalized GO nanoparticles in the polyaniline (PANI) membrane matrix had reduced its hydrophilicity, porosity, and permeability. This is due to an increase in casting solution viscosity, leading to a delay in the exchange rate of solvent and non-solvent during the phase inversion process [43]. Ghaemi *et al.* also reported by increasing the thickness of the membrane's top layer, membrane permeability will be reduced by creating a barrier against fluid passage. Hence, a decrease in water permeability of adsorptive membranes due to decreased hydrophilicity and porosity and a thicker top layer of membranes is reasonable.

Consequently, the membrane with excessive porosity and extremely high-water permeability is unsuitable for an efficient adsorptive membrane. This is because polluted water can easily pass through the pores of the membrane with no retention time for the adsorption process. The pollutants might be escaped without being adsorbed by the nanoadsorbent that is immobilized in the polymer matrix membrane. Therefore, moderate water permeability could provide enough retention time for the adsorption to take place within the adsorptive membrane.

2.4 Alterations in Surface Charge

One of the main challenges in developing adsorptive membranes is the alteration in the surface charge of the resultant adsorptive membranes. Impregnating nanoadsorbents into a polymeric membrane can alter the surface charge, which depends on the surface charge of the nanoadsorbents used in the process. Therefore, alteration in surface charge could be good in developing adsorptive membranes as it enables the design of membranes tailored to the specific surface charge requirements to remove pollutants with varying charges effectively.

The surface charge of the adsorbent is a leading indicator of the adsorption of charged pollutants such as heavy metals and organic pollutants. High surface charges, either positive or negative, in the resulting adsorptive membranes promote electrostatic attraction and increase the amount of charged pollutants such as heavy metal ions, that are adsorbed on the adsorption sites. Hence, high rejection and throughput can be attained in a single process. The surface charge of the adsorptive membranes is highly dependent on the surface charge of the nanoadsorbents and the membrane matrix. This can be observed by measuring the isoelectric point (IEP) or point of zero charges (PZC) of the adsorptive membranes. The PZC or IEP of nanoadsorbents, commonly metal oxides, is determined by protonation and deprotonation of surface hydroxyl groups, which they can show how a surface reacts to an electrolyte, usually water [44]. Since water is amphoteric, protonation and deprotonation reactions can produce positive or negative charges on the surface.

The IEP or PZC of the nanoadsorbent could be altered as it is incorporated into the membrane matrix. Karmakar *et al*. reported the IEP values of aluminum fumarate MOF and composite PAN/ aluminium fumarate MOFs [45]. They found that the IEP of aluminium fumarate was at pH 8.1. However, when the aluminium fumarate (3 wt.%) was impregnated into PAN membranes, the IEP value of the nanocomposite membrane decreased to around pH 7.0. The decrease in IEP values might happen due to the interaction of the negative charge of the cyanide functional group in the PAN structure with the positive charge of the aluminium fumarate MOFs. Cyanide functional group formed hydrogen bonding with the acidic hydrogen atoms attached to the axial oxygen atom in the aluminium fumarate structure. This reaction has partially neutralized the positive surface charge of aluminium fumarate hence reducing the positive IEP value when incorporated into PAN membranes. Adsorbent with negative surface charge is favorable for negatively charged heavy metal oxyanions such as As(V), Cr(III), and Cr(VI) which are mainly present in the typical pH of natural water.

Previously, Mondal *et al.*, studied the surface charges of nickel-iron oxide (NFO) nanoparticles and found that the zeta potential of NFO was 8.8 mV and -49.0 mV at pH 2.0 and pH 11, respectively [46]. They found that the IEP value of NFO nanoparticles was at pH 3.7 where the zeta potential is 0 mV. When NFO is impregnated into PSf membranes, the adsorptive membranes show a negative surface charge. This might be due to negatively charged NFO nanoparticles accumulating on the membrane surface at a pH ranging from 4 to 9. One possible mechanism is that during phase inversion, the hydrophilic NFO nanoparticles distributed themselves along the polymer-water interface to reach an equilibrium environment, making the adsorptive membranes' surface charge negative. The negatively charged PSf/ NFO membrane enhanced the adsorption of positively charged heavy metal ions such as Pb, Cu, Zn, Cd, Ni, and Cr.

To conclude, selecting the optimal nanoadsorbent with the required surface charge is a critical step, and it is essential to comprehend the surface charge characteristics of the nanoadsorbents after impregnation into the membrane matrix. Additionally, understanding the charge behavior of the pollutants targeted in the water system is equally crucial to ensure efficient adsorption.

3.0 CONCLUSIONS

Adsorptive nanocomposite membranes are a cutting-edge type of membrane that possesses the dual advantages of adsorption and separation exhibiting broad prospects in environmental preservation. Grand challenges in adsorptive membranes such as aggregation and agglomeration of nanoadsorbents, mechanical strength distortion, extreme water permeability, and alterations in surface charges could inhibit the performance of adsorptive membranes. Even though there are grand challenges in the development and application of adsorptive membranes, research over the past ten years has shown significant improvements in developing and implementing various types of adsorptive nanocomposite membranes. Future research should focus on maximizing the effectiveness of the adsorptive membranes by improving the compatibility and dispersion mechanism of nanoadsorbents and membranes matrix, especially through physicochemical modification. Optimization study of the dope formulation is very important to ensure optimum conditions and parameters in developing adsorptive membranes for targeted pollutants. In addition, future approaches should consider not just the aforementioned grand challenges but towards the use of green manufacturing methods for the development of adsorptive membranes that offer a safer and sustainable approach. Green production of nanoadsorbents and membrane materials based on microorganisms, plant extracts, or agricultural wastes should be explored further [48]. Adsorptive nanocomposite membranes are predicted to play a significant role and have a promising future in a wide range of applications by properly resolving the aforementioned grand challenges and exploring further research.

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