



Advances in adsorptive membrane technology for water treatment and resource recovery applications: A critical review

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ARTICLE INFO

Editor: Dr. Zhang Xiwang

Keywords:

Adsorption
Membrane filtration
Refractory pollutant
Physicochemical treatment

ABSTRACT

The presence of recalcitrant contaminants in water bodies such as heavy metals, dyes, pharmaceutical compounds, and chemical residuals results in water pollution. This requires the development of seminal water technologies including adsorptive membrane filtrations. This article critically reviews recent advances in adsorptive membrane technology for wastewater treatment. Particular focus is given on its fabrication and classification, surface characterizations, and their practical applications in removing target pollutants from aqueous solutions. Their advantages and limitations in applications are critically evaluated and compared. Their operational conditions such as pressure, initial pollutant concentration, and treatment performance are presented. Research trends, challenges, solutions, and the way forward for adsorptive membrane filtration are also elaborated. It is conclusively evident from 280 published studies (1971–2022) that integrated adsorption and membrane filtration processes were highly effective in removing refractory pollutants from contaminated wastewater due to their rapid adsorption-desorption rates, low internal diffusion resistance, and high flow rates. The sulfonic groups of the Nafion 117 membrane have a good adsorptive capacity to metal ions such as copper (II), nickel, cobalt, lead and silver ions with their adsorption capacities of 66, 64, 60, 58, and 47 mg/g, respectively. It is important to note that technical applicability, treatment performance, and treatment cost are critical factors in determining the most suitable water technology for treating wastewater laden with recalcitrant contaminants. Further research should address technical bottlenecks such as membrane fouling and agglomeration formation during the adsorptive membrane fabrication and operation. The constraints can be tackled to improve the quality of the membranes fabricated.

1. Introduction

Attaining environmental sustainability through wastewater treatment is one of the priority lists in the UN's Sustainable Development Goals (SDG). However, water scarcity, water shortage, and water pollution induced by industrial activities have become serious global concerns in recent years. Climate change, rising global population, and rapid urbanization also have accelerated the increasing demand for clean water for domestic consumption over the past decades [1]. Therefore, water treatment operators have to ensure that treated effluents, discharged into the body of the environment, satisfy the

requirements of water quality set by local legislation.

To implement sustainable wastewater management, holistic and balanced approaches are important for water treatment operators to continuously improve the quality of wastewater effluents from the points of generation to its discharge. For this purpose, the application of safe, cost-effective, and practical water treatment is essential to achieve environmental sustainability. Therefore, state-of-the-art of water technologies has been developed to eliminate target contaminants effectively from contaminated water so that eventually, treated effluents can be safely discharged into the aquatic environment.

Depending on the physicochemical properties of contaminated

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<https://doi.org/10.1016/j.jece.2022.107633>

Received 13 January 2022; Received in revised form 10 March 2022; Accepted 27 March 2022

Available online 30 March 2022

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wastewater and target pollutants, the treatment techniques include chemical precipitation [2], coagulation-flocculation [3], adsorption [4], ion exchange [5], ultrafiltration [6], reverse osmosis [7], and electro-dialysis [8]. Meanwhile, biological process has more drawbacks than physicochemical treatment approaches. Not all starting compounds are rapidly biodegraded completely. As a result, their oxidation by-products become more toxic than starting compounds [9].

Unlike the other physicochemical treatments, ultrafiltration and microfiltration, which utilise a sieving process, have limited selectivity for metal cations and molecular pollutants in water. Through physicochemical interactions, the adsorbent can capture target pollutant in the solution based on attractive columbic forces during adsorption treatment [10].

Due to its simplicity, efficacy, and adaptability, adsorption has become a major technology for the separation of trace aquatic pollutants [11]. However, there are still certain drawbacks and bottlenecks such as a slow rate and a high internal diffusion resistance in adsorbents that need to be addressed. Therefore, further works have been directed toward uncovering cost-effective and efficient water technology to overcome the bottlenecks.

This shifts the focus from conventional adsorption to adsorptive membranes, capable of removing a variety of toxic pollutants that pose serious threats to public health and the environment. As reflected by its name, an integration of adsorption and membrane technology is one of the most promising options [12]. The application of adsorptive membranes offers solutions to address several bottlenecks such as membrane fouling, high energy consumption, regeneration costs, and selectivity.

As compared to conventional filtration membranes, the advantages of adsorptive membranes include superior contaminant ion retention, less energy consumption, and increased permeate flux. The membranes' process operation can also be expanded beyond simple filtration that includes adsorption. Moreover, its separation rate is faster than that of the conventional adsorptive beads because the removed contaminant ions can be transported via convective flow to both external and internal binding sites rather than through slow diffusion to either internal or external binding sites [13].

As the adsorptive membrane performs both adsorption and filtration functions, a mass transfer mechanism takes place, in which target pollutant is transferred to the surface of solid through physicochemical interactions using a porous membrane medium, which ultimately requires low pressure and less energy consumption. The common membrane separation removal of the same contaminants may require highly dense membrane such as nanofiltration and reverse osmosis, which eventually demand high energy consumption.

As a reversible process, the adsorbents may be regenerated using desorption. Their efficacy depends on morphology and target pollutants [14]. In spite of its technological strengths, this technique has inherent drawbacks such as agglomeration and costly operations in the case of granular activated carbon (GAC). Therefore, further research has intensified recently to develop cost-effective adsorbents [14].

Due to its different conformations, large surface area, spacious adsorption sites and varying fillers, adsorptive membrane technology is capable of removing a variety of contaminants from wastewater [11]. A low operating pressure, high permeability flux, regeneration, recyclability, compact size, and minimum space requirements also contribute to its technological prowess when polymers and/or particles with strong affinity for metal ions and molecules are incorporated into the membrane to cope with fouling issues [11]. For instance, the sulfonic groups of the Nafion 117 membrane have a good adsorptive capacity to heavy metals such as copper (II), nickel, cobalt, lead and silver with their adsorption capacities of 66, 64, 60, 58, and 47 mg/g, respectively [15]. Furthermore, within 30 min the adsorption achieved an equilibrium. Therefore, this technology has demonstrated significant advances in practical applications, including rejection rate, selectivity, permeability, and water flux.

In spite of its promising technological values in real application

settings, so far none has reviewed the technical applicability of adsorptive membrane for treatment of wastewater laden with refractory pollutants. To bridge the knowledge gap in the field of study, this article critically reviews recent developments in adsorptive membranes technology for water treatment. Particular focus is given on its fabrication and classification, fundamental theory, surface characterizations, and their practical applications in removing target pollutants from aqueous solutions. Their advantages and limitations in applications are critically evaluated and compared to each other. Their operational conditions such as pressure, initial pollutant's concentration, and treatment performance are presented. Research trends, challenges, solutions, and the way forward for adsorptive membrane are also elaborated.

2. Methodology

To provide an in-depth overview of the adsorptive membranes applicable for wastewater treatment operations and development, the authors analysed published journal articles within the scope and aim of this review using relevant keywords such as 'adsorptive membrane', 'wastewater treatment', 'adsorption', and 'resource recovery'. As statistical techniques have become a viable option for accumulating relevant articles on adsorptive membranes, the search for journal papers was conducted within the last 40 years (1971–2022). Selected journal articles were chosen based on their application of adsorptive membrane and technologies. Additional coverage on the applications of adsorptive membranes in diverse aspects was also extracted.

To synthesize a review article that encompasses a broad spectrum of conventional and recent technologies in adsorptive membranes used throughout the world, pertinent articles were selected based on their title and abstract to address the theme of this review. After preliminary screening, 280 journal articles were thoroughly analysed for this review. The references were classified into two categories: adsorptive membranes and water treatment. The vetted journal articles provided readers with pertinent information about the applicability of adsorptive membranes in water treatment. In addition, the disadvantages of both conventional and contemporary technologies for generating adsorptive membranes are critically evaluated and analysed. Subsequently, the review discussed the future development of adsorptive membranes for removing a variety of pollutants from wastewater.

To provide an overview about the scientific focus, tangible research outputs from a credible literature database were used to analyse the present trend of research work in the field of adsorptive membrane technology. Due to its reliability and consistency in citation records, the Thompson Reuter's Web of Science database was chosen to understand its research landscape systematically. The source provided a scientific tool of quantitatively analysing a dataset of appropriate articles related to the research trends on adsorptive membrane [16–18]. The need for bibliometric analysis to analyse emerging trends has grown in popularity across multiple fields. Despite the existence of review articles on the adsorptive membrane, none has reported statistical research-pattern information based on bibliometric analysis. Given the expanding scientific research in adsorptive membranes and their enormous potential in a variety of applications, this review assisted researchers to better understand the field, serving as a road map for present and future studies.

3. State of scientific focus on adsorptive membrane

About 280 journal articles related to "adsorptive membrane" using relevant keywords such as "adsorption", "membrane filtration", and "water treatment" were retrieved from the literature search and analysed consistently. The approach adopted in this study was water technology-driven [19–22]. Fig. 1 indicates that in recent years the number of journal articles concerning the subject has skyrocketed in the body of literature. By 2022, over 280 adsorptive membrane-related articles have been cumulatively recorded in the database of this subject.

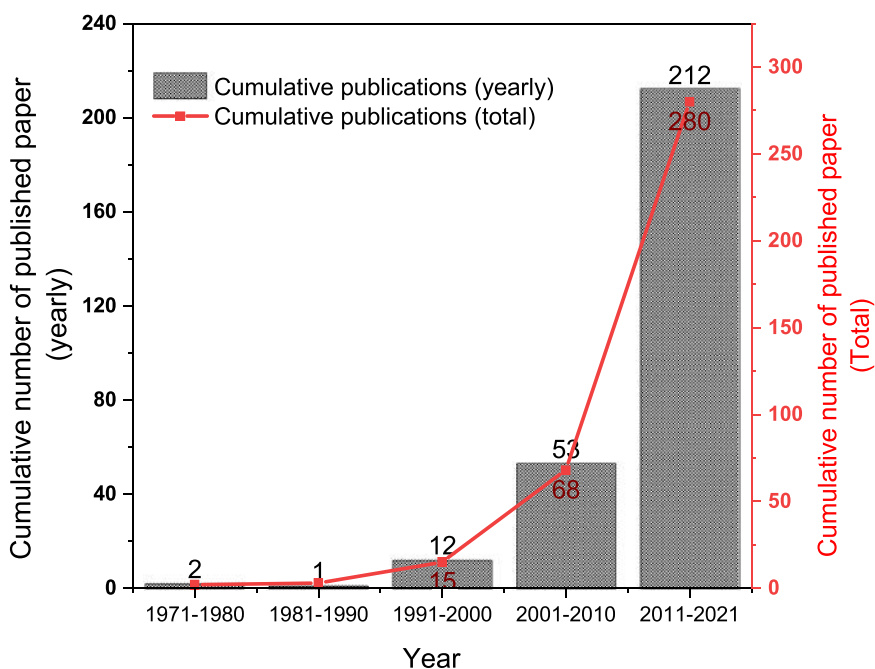


Fig. 1. Growth pattern of adsorptive membrane publications from 1971 to 2021. Source: Web of Science (2021).

This implies the novelty of adsorptive membrane technology in removing a variety of recalcitrant pollutants such as arsenic and heavy metal in contaminated wastewater [23–27].

Additional analyses from the literature search were also performed using VOS viewer software to construct a keyword co-occurrence network, which illustrates the relationship and relevance (weighting)

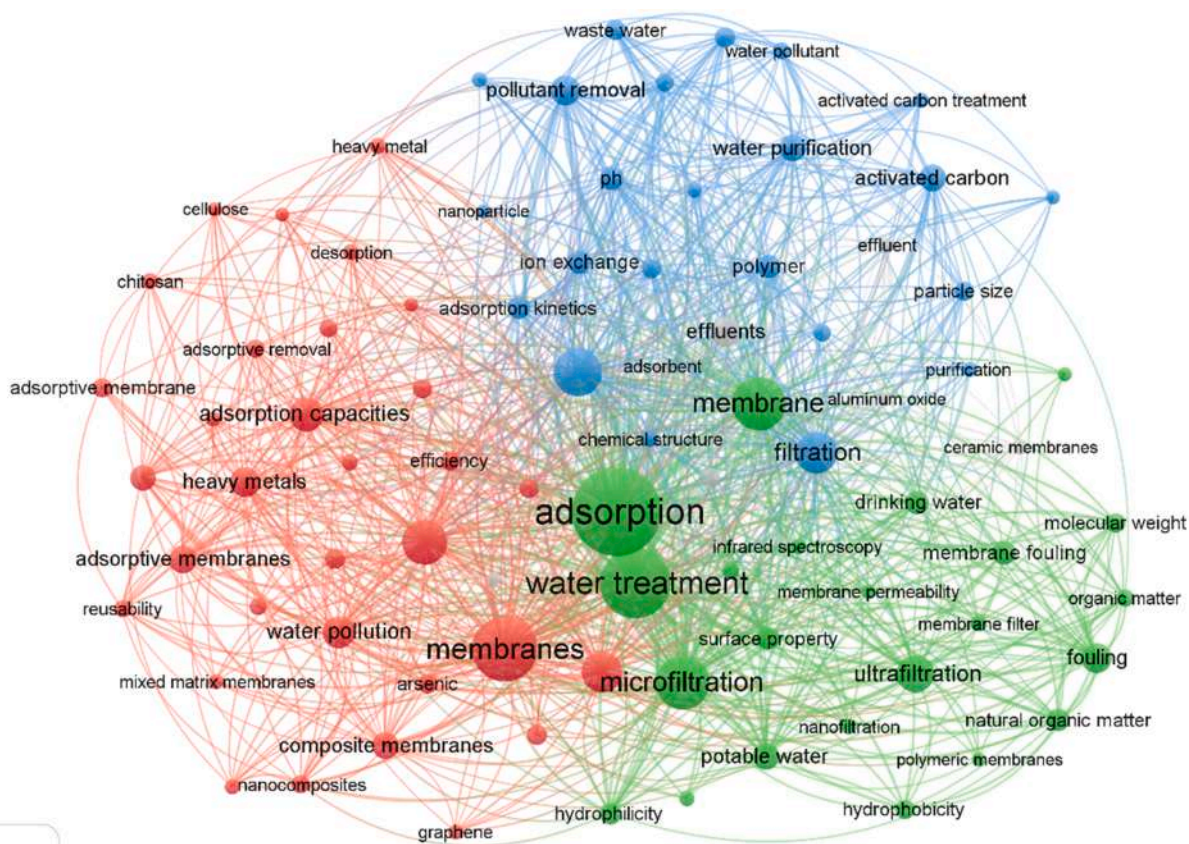


Fig. 2. Bibliometric map based on co-occurrence in network visualisation mode

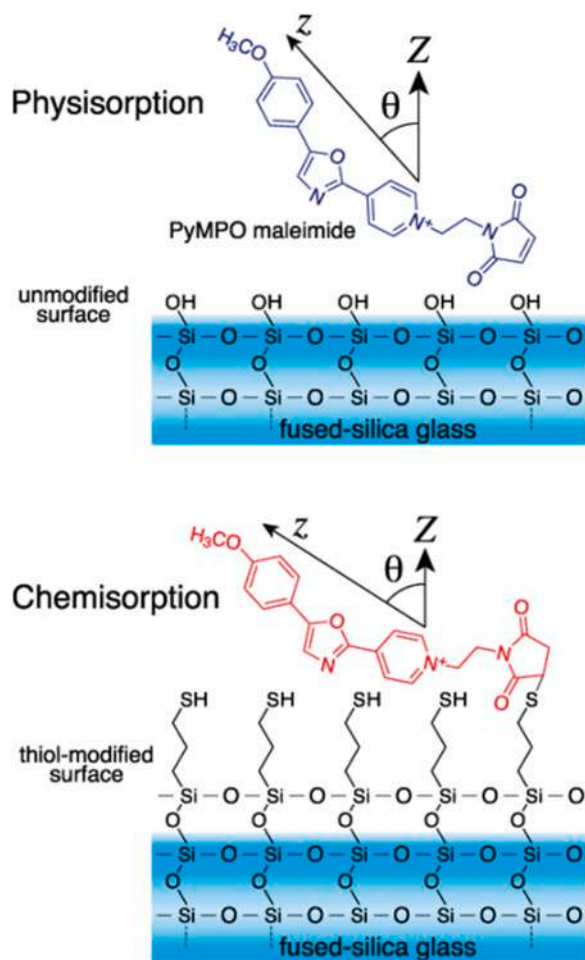


Fig. 4. Schematics of PyMPO physisorbed (blue) and chemisorbed (red) on the fused – glass surfaces [32]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

In adsorptive membrane, this process integrates the adsorption and filtration process in a single step. When the feed solution that contains the adsorbate passes through the membrane, the adsorbent's active binding sites capture the adsorbate's target components at a high adsorption rate because the contact distance between the adsorbent's active sites and the target adsorbate components is instantaneous and short, down to the submicron scale. The membrane's continuous filtering happened simultaneously with the adsorption of the target adsorbate [37].

Determining the major separation mechanism that occurred in the adsorptive membrane has gained popularity recently. The strategy can be determined from the membrane's pore size and the dynamic dimension of the adsorbed species. This indicator determines whether size exclusion is the main mechanism or not. If the saturated adsorptive membrane is regenerated using an efficient eluent and the target adsorbate is recovered, this implies that the target adsorbed species are adsorbed rather than sieved by the membrane.

In general, every membrane filtration operation, regardless of the predominant separation mechanism, is impacted by degradation over its lifespan. As a result, previous studies examined not only membrane performance, but also the augmentation of membrane endurance and the restoration of an inefficient membrane amortization, while operating. The approaches used to attain the desired efficiency are determined by the adsorption mechanisms either physical or chemical attachment of adsorbates to active sites.

Reusability of an adsorbent affects the economics of water treatment. By utilising reusable adsorbents, water treatment cost can be reduced.

As this represents the adsorbent's endurance, which refers to its resistance to thermal, chemical, and mechanical degradation throughout the course of a protracted process, membrane adsorbents are evaluated for their reusability during subsequent regeneration cycles [38].

The cost of the materials restricts the production of adsorptive membranes. As a result, regeneration of the membranes is a prerequisite of the production planning. Indeed, metal ions have a high propensity for forming coordination complexes with the functional groups of the adsorptive membranes' adsorbent [39]. If there are sufficient H^+ accessible, an acidic regenerant can substitute H^+ with positive metal ions in an occupying adsorption site and unleash the ion. Therefore, strong acid solutions (such as HNO_3 and HCl) could be used to regenerate active sites on the adsorptive membrane.

In certain research, a chelating agent was used to regenerate saturated adsorptive membrane. The hexadentate ligand, ethylene diamine tetra acetic acid (EDTA) is popular for its ability to robustly bind positively charged metal cations, particularly under alkaline environment. Due to its role in complexing metal ions, EDTA is an excellent option to be used as a regenerant [40]. The stability of metal-EDTA chelate is attributed to the formation of complexes that varies for monovalent, bivalent, and trivalent metal ions.

According to Ghaee et al. [38], the saturated adsorptive membranes employed to separate Ni^{2+} and Cu^{2+} were washed with distilled water and stirred in EDTA solution for three subsequent cycles. After the first cycle, the dissociation ratios of Ni^{2+} and Cu^{2+} from the adsorptive membranes were 46% and 69%, respectively. However, their efficiencies dropped throughout consecutive cycles due to less driving force and the emergence of irreversible adsorption.

5. Classification of adsorptive membranes

Based on their structure, adsorptive membranes can be classified into three broad categories: homogeneous membranes (organic and inorganic membranes), composite membranes (sandwich or surface composites), and mixed matrix membranes. Fig. 7 depicts the classification of the adsorptive membranes and their respective preparation techniques.

5.1. Homogeneous membrane

Unlike composite membranes, homogeneous membranes are composed of identical components in a single phase [41]. This means that they have no elements other than the primary constituent of the membrane. This membrane can be separated into two distinct sub-categories: inorganic and organic membranes. Organic membranes are composed of organic material either it is naturally or synthetically produced. The membranes are normally associated with the polymeric-typed membranes. Meanwhile, inorganic membranes can be divided into carbon, metal, glass and ceramic types. This review focuses on inorganic adsorptive membranes based on the ceramic membranes due to its extensive applications in adsorptive membrane.

5.1.1. Ceramic membranes

Ceramic adsorptive membrane consists of self-supported or multi-supported components. The most frequently applied support materials are microporous layers that consist of metals or oxides compounds. Inorganic materials such as alumina (Al_2O_3), zirconia (ZrO_2), titania (TiO_2), silica (SiO_2), magnesium oxide (MgO), silicon nitride (Si_3N_4) as well as ruthenium oxide (RuO_2) are used [42].

In addition, the fabricated ceramic adsorptive membranes are produced from low-cost materials such as clays and natural minerals [43, 44]. For instance, Ali et al. [45] fabricated ceramic membrane from local clay and incorporated it with different sawdust grades as an additive. They uncovered that the produced ceramic membrane could remove 99% of target metal including Cu^{2+} , Pb^{2+} , and Cd^{2+} with 15 mg/L of initial concentration. Apart from heavy metal, ceramic adsorptive

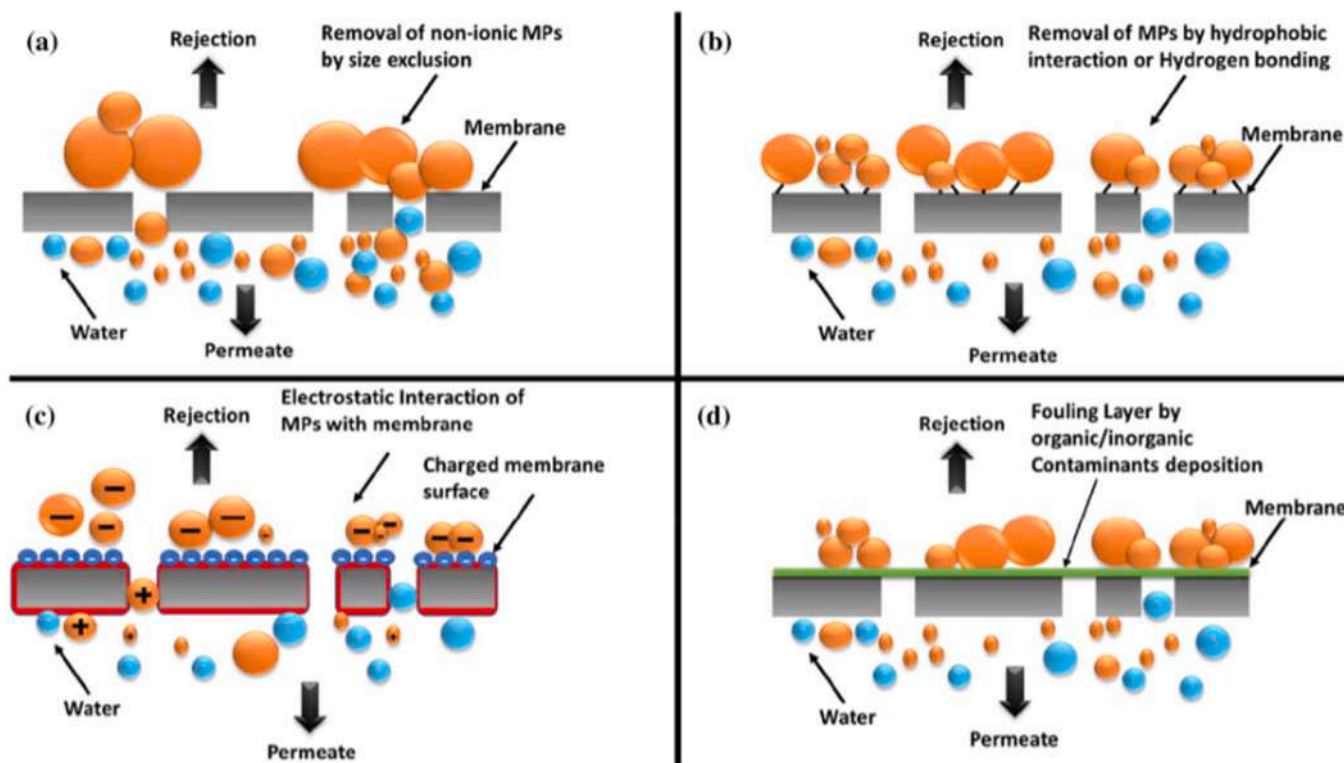


Fig. 5. Membrane filtration removal mechanisms (a) size exclusion; (b) hydrophobicity; (c) electrostatic interaction and (d) adsorption [33].

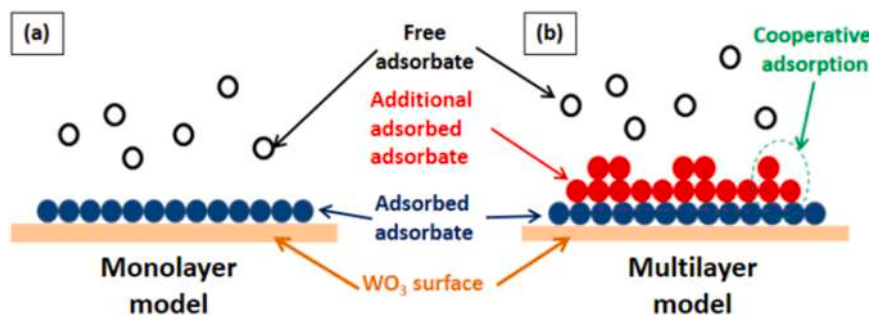


Fig. 6. Adsorption mechanism of (a) monolayer adsorption predicted by Langmuir interaction and (b) multilayer adsorption formation predicted by Freundlich isotherm model [36].

membranes also removed dye, ammonia, and other ceramic contaminants from wastewater [37,44,46–48].

Ceramic or inorganic membranes have gained popularity in recent years for their technological strength over polymer membranes in various environmental applications. The enhanced characteristics of these ceramic membranes might have contributed to their long life expectancy. The uniformity and integrity of the ceramic membranes reduce the need for repeated testing, maintenance, and membrane module replacement, which eventually decreases operational costs, justifying the adoption of the membranes [49].

However, due to the large size of the ceramic particle and the grain growth of the ceramic particle during sintering, majority of the ceramic membranes exhibits high flux, leading to low treatment efficiency. This restriction may be solved by the membrane's microporous layer coating. This alteration was done to improve the permeability and separation performance of a mesoporous-alumina membrane used in gas separation [50]. The layer of microporous silica was used as the top.

In addition, ceramic membranes are limited in applicability due to their high manufacturing costs, as a result of the utilisation of costly raw materials and extensive energy consumption during fabrication using

sintering techniques. Due to their low cost and mass manufacture, organic adsorptive membranes have gained popularity for adsorptive membrane applications.

5.1.2. Organic membranes

Organic adsorptive membranes are made up of polymers. This membrane type is often employed in microfiltration, ultrafiltration, and nanofiltration. The transition to polymer membranes is attributed to their ease of fabrication, attainable and adjustable pore size, and low cost of raw materials. Certain functional groups capable of behaving as an adsorbent such as carboxyl (C=O), amine ($\equiv\text{NH}$) and sulfonic acid (R-SO₃H) on the polymer structure [51]. These homogeneous organic adsorptive membranes can be synthesized via physical mixing, molecule grafting, and copolymerization approaches [52]. The techniques introduce reactive monomers such as acrylic acrylonitrile, acrylamide, acid, and those containing an epoxy group.

(a) Mixing.

The term 'mixing' or 'blending' refers to the assimilation of two or more homopolymers with different structures and functional groups. This approach improves the shortcomings of a homopolymer by

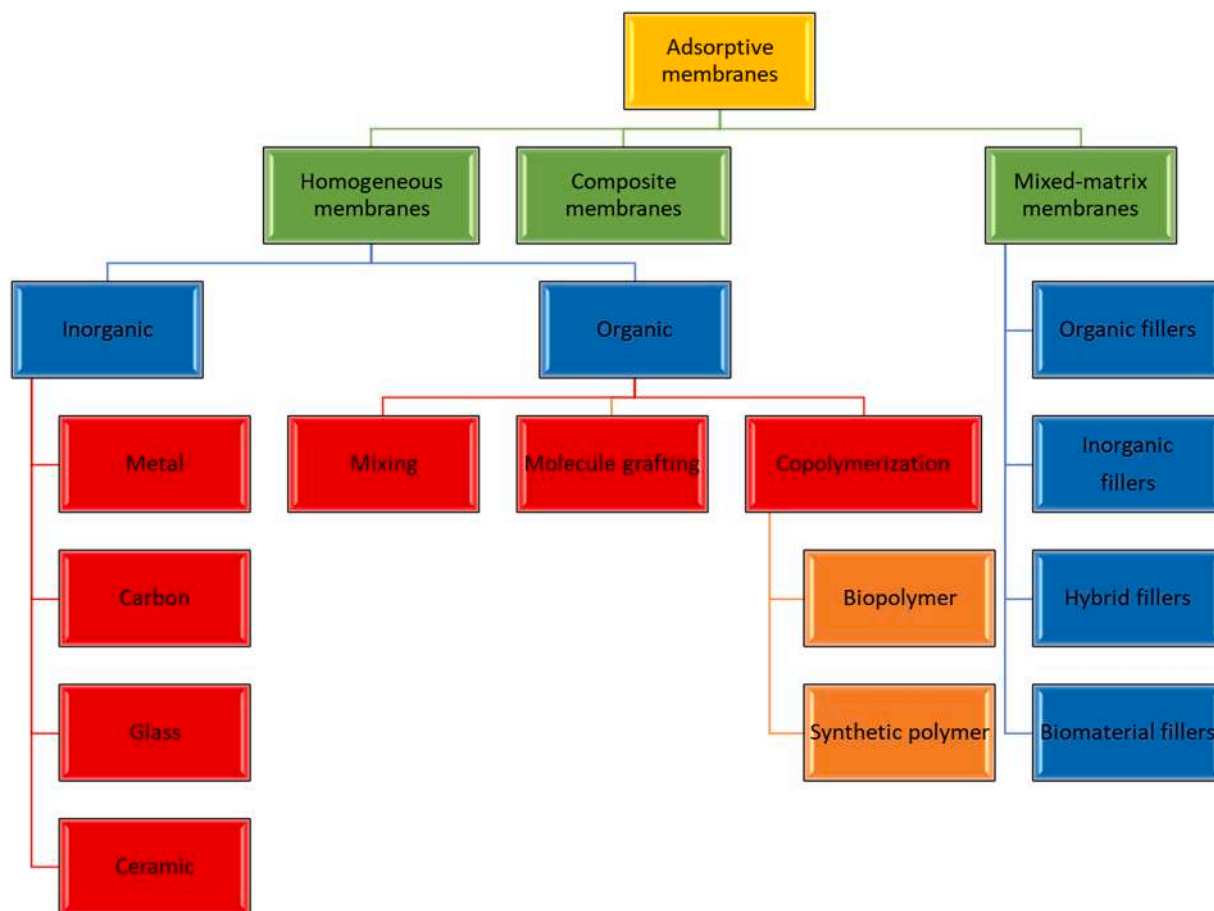


Fig. 7. Classification of adsorptive membranes and their preparation techniques.

amending them with another homopolymer. Chitosan adjustment is a common form of mixing. The adsorbent is popular for its high adsorption capacity, but has low mechanical strength. When chitosan is incorporated into polyacrylamide (PAAM), it forms a membrane with excellent adsorption capacity of 65.37 mg/g of Cu [53]. Chitin can also make a membrane for Hg^{2+} removal due to its strong affinity and huge surface area with the blended membrane [54].

(b) Molecular grafting.

In contrast to the physical mixing approach, molecular grafting entails the effective functionalization of polymeric compounds with a low affinity for target contaminant. The functionalized polymer attaches or grafts the metal cations with a high affinity onto it. Fig. 8 depicts the surface graft polymerization caused by UV irradiation that can be used to enhance the capabilities of hydrophobic membranes by introducing

hydrophilic group, demonstrating the grafted membrane's antifouling properties [55].

Hao et al. [56] grafted polyvinylidene difluoride (PVDF) molecule with caffeic acid using the same UV irradiation technique prior to thermal method. The grafted polymer membrane excellently adsorbed Cs^{2+} up to $0.23 \text{ mmol}\cdot\text{g}^{-1}$.

(c) Copolymerization.

Copolymerization technique involves the mixing of two or more monomers to make a copolymer. Copolymerization combines the outstanding qualities of one monomer with those of another polymer. Copolymerization is carried out prior to membrane fabrication. For example, Wei et al. [57] studied the electrospun adsorptive membrane of poly (butylene succinate-co-terephthalate) (PBST) for the removal of methylene blue. They found an increasing adsorption capacity from

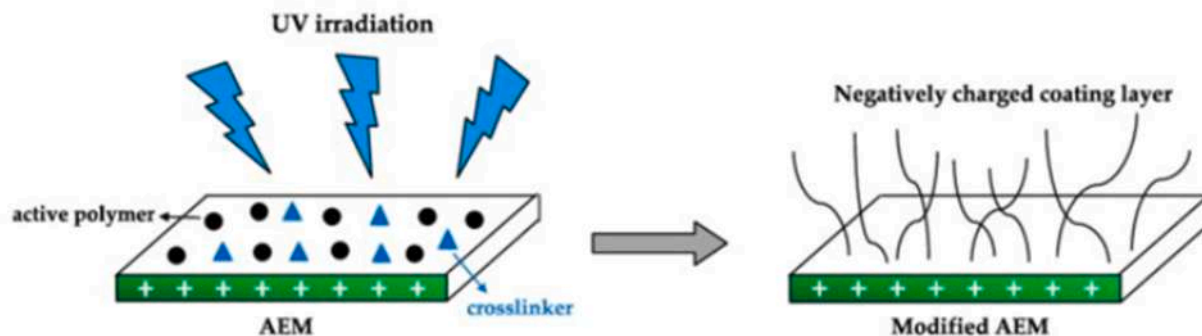


Fig. 8. Surface grafting polymerization of anion exchange membrane (AEM) via UV irradiation [55].

77 mg•g⁻¹ on individual PBTS membrane to 99 mg•g⁻¹ when being copolymerized with β-cyclodextrin polymer (CDP) for removing methylene blue with 10 mg/L of initial concentration [57]. Kumar et al. [58] prepared polyvinyl tetrazole-co-polyacrylonitrile (PVT-co-PAN) membranes via non solvent induced phase inversion (NIPS) and exhibited an outstanding Cu²⁺ removal up to 44.3 mg•g⁻¹ of Cu²⁺ for 8 h of treatment.

Another aspect that affects the membrane performance is the type of polymer employed to fabricate the membrane. In general, two distinct polymers are employed to produce adsorptive membranes: biopolymers and artificial polymers. Both the polymers influence not only the fabrication process, but also the membranes' adsorptive performance.

(i) Biopolymer.

Biopolymer has been widely used for adsorption process. The polymers have been utilized for the removal of various contaminants such as heavy metals and dyes. The fabrication of adsorptive membranes from the biopolymers can be achieved using biodegradable and renewable materials through the presence of oxygen and nitrogen in their chemical structures [59].

Chitosan is a common example for the utilization of biopolymers in the fabrication of adsorptive membrane. It is a polysaccharide biopolymer derived from chitin with amine and hydroxyl functional groups. The grafting of chitosan in the fabrication of adsorptive membranes has advantages such as easy availability, high binding capability, as well as distinctive properties [14]. The chitosan-based adsorptive membranes have excellent performance for heavy metal removal due to the presence of amine functional group capable of forming a surface complex with the metal ions [60]. Chitosan's effectiveness is restricted by the mechanical strength of the membranes. Coating with chitosan has a number of disadvantages such as insufficient coating of the membrane, as well as non-stick coated chitosan. As a result, it is conceivable to integrate other materials with chitosan for enhancing the mechanical strength and chemical stability of chitosan-based adsorptive membranes [61].

(ii) Artificial polymer.

Artificial polymer is beneficial for fabricating adsorptive polymer membranes on an industrial scale due to its technological benefits such as outstanding mechanical strength, high resistance to solvents, and cost-effectiveness. The choice of artificial polymers depends on their superior chemical properties. For example, cellulose acetate is a biopolymer frequently utilised in the production of membranes due to its resistance to fouling, high hydrophilicity, and low cost [62]. In spite of their advantages, there are a number of disadvantages such as low thermal, mechanical, and chemical resistance. As a result, artificial polymer such as polyurethane (PU) was used to compensate for the cellulose acetate's shortcomings in terms of thermal, mechanical, and chemical strength. The resulting membrane has exceptional physico-chemical properties of PU, such as high flux and fouling resistance due to the hydrophilic nature of cellulose acetate [63].

On the other hand, polyethersulfone (PES) is widely used for manufacturing large-scale polymeric membranes due to its thermal and chemical stability, resistance to extreme pH, and high mechanical strength. Nevertheless, this polymer has bottlenecks such as fouling caused by the adsorption of nonpolar solutes and the adhesion of bacteria and hydrophobic elements in feed wastewater. To mitigate the bottlenecks [64], one feasible approach is to introduce composite adsorptive membranes with filler materials to a modified homogeneous adsorptive membrane [65].

5.2. Composite membranes

While the homogeneous organic membrane is promising, its commercialization is limited. Inert polymers such as polypropylene, nylon, and polyethylene are the most prevalent. Therefore, it is critical to modify the surface of the inert polymer by introducing the inorganic and organic adsorbents to increase their affinity for removing target

pollutant [61].

Fig. 9 illustrates the formation of mixed matrix membrane and composite membrane [66]. In composite membrane formation, the adsorbent layer improves the adsorption capacity of the membrane [67]. The composite membranes can be developed by modifying the support membrane's surface. One of the feasible ways is by impregnating the adsorbent between the support membrane and the surface layer, widely known as 'sandwiched composite membranes'.

To modify the surface of composite membranes, each strategy utilises distinct approaches and formation techniques, while embedding the adsorbent onto the supporting membrane surface. The first method of surface modification is referred as 'in-situ'. The procedure is carried out in the location of the membrane surface. On the membrane surface, modifications were constructed or synthesized to increase the membrane's adsorption capability.

He et al. [68] produced a zirconia-metal organic framework (Zr-MOF) membrane through in-situ solvothermal synthesis. With the initial concentration of fluoride was 200 mg/L, the produced membrane had outstanding adsorption capacity of fluoride at 102.4 mg•g⁻¹ at pH 7 due to its large surface area (740.3 m²/g) and abundant hydroxyl functional group, which acted as the adsorption active sites [68]. It was also reported that the capability of the Zr-MOFs membrane to eliminate fluoride was governed by flow rate and initial fluoride concentration.

The second mode is deposition that utilizes physical processes such as vacuum filtration to deposit the adsorbent onto the membrane surface. Chen et al. [69] produced β-cyclodextrin modified with graphene oxide (GO) membrane through vacuum filtration by stacking the GO nanosheets onto the porous support β-cyclodextrin membrane. The modified GO layers were located on the membrane surface and capable of removing bisphenol-A (BPA) up to 25.5 mg/g from the feeding solution.

Surface grafting is another method of surface modification. This process attaches the organic group to the membrane surface. This approach entails the presence of a chemical initiator, followed by UV light or radiation [70,71]. Senna et al. [72] modified the high-density polyethylene (HDPE) with acrylamide via radiation-induced technique and followed by the chelation of Cu (II) on top of the modified membrane. The constructed membrane excellently removed phosphate ions (PO₄³⁻) up to 100 mg/g.

Surface molecular impressing is another way to modify the surface modification of the composite adsorptive membrane. In this process, the membrane is formed using a template structure. This process consists of three steps: (i) transferring the template molecule onto the membrane by electrostatic contact and hydrophilicity in a suitable solvent solution; (ii) polymerization reaction aided by a cross-linking agent; and (iii) removing the template molecule from the membrane. As a result, the produced membrane possessed a three-dimensional cavity to the functional group in the template. The cavity exhibited a memory effect, which allows the template molecules to be adsorbed. This improves mass transfer between the template site and the target molecules. This technique produced composite adsorptive membrane of chromium (III) - polyvinyl alcohol (PVA) – sodium alginate (SA) with excellent Cr(III) adsorption capacity of 59.9 mg/g [73]. Nevertheless, this particular membrane has a low flux disadvantage, which requires further investigation to address it.

Surface bonding technique utilises a membrane coupling approach in conjunction with affinity ligands that respond to the selectivity and adsorption of target pollutants. This surface alteration requires: (i) chemical activation of the membrane surface and (ii) ligands. The constructed membrane become activated and is capable of simultaneously separating and adsorbing target ions [74]. Fig. 10 depicts the surface modification of thin film composite membrane (TFC) with GO/Ag nanocomposites using a cysteamine solution [75]. The membrane surface was covalently bonded to the GO/Ag nanocomposites using the amine functional group of cysteamine via a chemical reaction. This formed strong amide bonds and supplied the membrane surface with

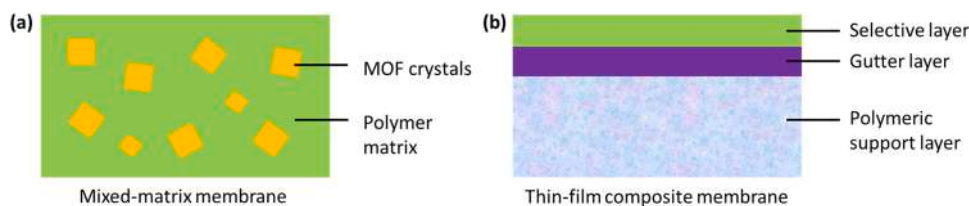


Fig. 9. Schematic illustration of mixed-matrix and composite membranes [66].

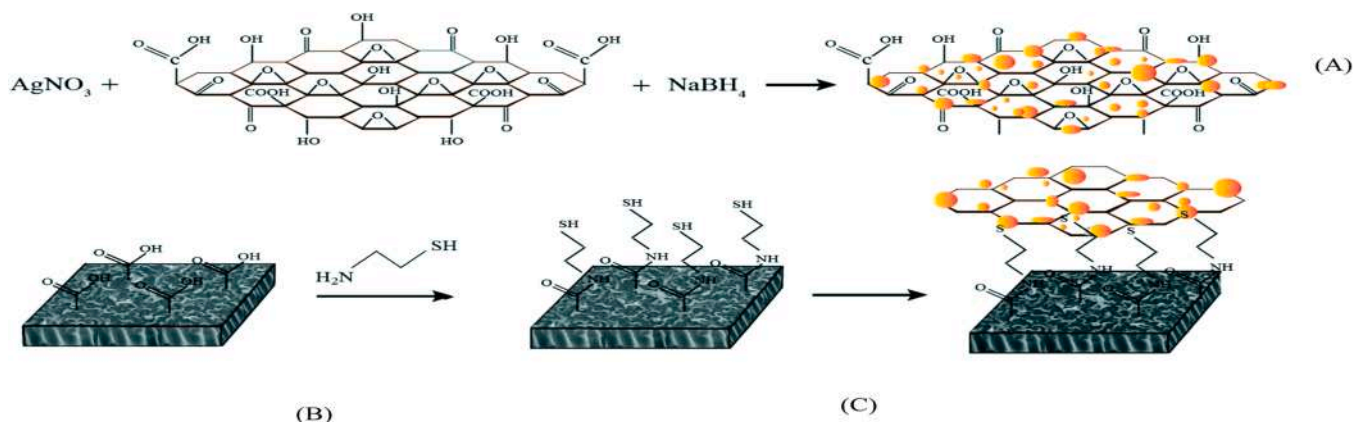


Fig. 10. Mechanistic steps description of covalently bonded AgNP-decorated GO nanosheets on TFC membranes: (A) in situ AgNPs synthesis on the GO nanosheets, (B) amide formation reaction and thiol functionalization, and (C) covalent bonding of the GO/Ag nanocomposites to the TFC membrane surface [75].

thiol functionality for covalent bond formation.

Unlike surface modified composite membranes, sandwiched composite membranes contain an adsorbent layer between the membrane support layer and the surface layer. Sandwiched membranes' unique structure enables the polymer solution on the surface layer to infiltrate the micropore structure of the substrate (support layer), hence increasing the membrane's stability and strength. Additionally, the asymmetric nature of the surface layer protects the membrane against clogging and fouling caused by smaller particles in the feeding solution [76]. This adsorptive membrane has a dynamic adsorption capacity towards the removal of contaminants. Prior to incorporating the sealant with dopamine as surface layer, Zhang et al. [43] uncovered that sandwiched adsorptive membrane derived from Fe_3O_4 microsphere on the supporting membrane layer removed bovine serum albumin (BSA) with adsorption capacity of 277.9 mg/g [43].

5.3. Mixed matrix membranes

The impregnation of an adsorbent into a polymer matrix results in the formation of mixed matrix membranes (MMMs). Like composite adsorptive membranes, MMMs combine polymer membranes with exceptional adsorption capacity, referred to as fillers [77]. The MMMs have advantages including their high reusability and permeability due to the filler types that have a high surface area on which the adsorption occurs. Meanwhile, MMMs can be categorized according to the type of filler such as organic filler, inorganic filler, hybrid filler, and biosynthetic filler.

5.3.1. Organic filler MMMs

The first kind of filler in MMMs is organic. Organic fillers such as chitosan beads, cyclodextrin, polyaniline (PANI), and polypyrrole are introduced to the membrane matrix via mixing followed by phase inversion. Organic fillers are advantageous for applications due to the functional groups, which makes them flexible and proficient at chemically bonding to the membrane matrix.

Another unique property of organic fillers is their capacity to attach

to hydrophobic membranes, resulting in a hydrophilic membrane with exceptional antifouling properties. Numerous attempts have been tested to create this membrane. One example is the incorporation of β -cyclodextrin polyurethane into the matrix of the polysulfone membrane [78]. The addition of the organic filler of β -cyclodextrin polyurethane eventually enhances the hydrophilicity and permeability of the adsorptive membrane due to the induced formation of pores on the surface. The adsorptive performance of the membrane has significantly increased up to 90% of Cd removal from contaminated water.

On the other hand, PANI nanofibers were used to fabricate MMMs when being mixed with polysulfone membrane matrix [79]. Several features of the adsorptive MMMs produced were enhanced, including increased permeability, water flux, and antifouling qualities. Additionally, the membranes demonstrated exceptional efficacy in the removal of bovine serum albumin (BSA). Nevertheless, MMMs constructed with the fillers have drawbacks such as a rough surface and poor mechanical stability of the membranes.

5.3.2. Inorganic filler MMMs

Unlike MMMs that contain organic fillers, those with inorganic fillers are synthesized using a variety of methods, including thermal plasma synthesis, sol-gel synthesis, flame synthesis, electrodeposition, ion sputtering, and mechanical milling/alloying. These inorganic fillers are covalently linked to the membrane matrix via H-bonds or van der Waals forces.

The inclusion of various fillers results in an increasing performance of the membranes. The incorporation of zinc oxide (ZnO) into the polyether sulfone (PES) matrix enhanced dye rejection rate to 82.3% with its initial concentration of 5 mg/L [80]. Graphene oxide (GO) on the polyetherimide (PEI) hollow fibre was utilized for the rejection of divalent ions and salts via instant dip coating approach [81]. Almost complete dye removal was successfully achieved when the GO was embedded into the PES matrix as nanoplates [82]. The improved performance of this membrane was attributed to the presence of acidic functional groups such as hydroxyl and carbonyl on its surface, which ultimately increased the membrane's hydrophilicity. This property also

enhanced the antifouling, flux, disinfection, and selectivity of the membrane [83].

5.3.3. Hybrid filler MMMs

Hybrid fillers MMMs are produced by adding two fillers as a composite or individually into the membrane matrix [84]. MMMs can be organic, inorganic, or a mix of the two. For example, a study on adsorptive MMMs was conducted using iron(II) and iron(III) in combination with PANI embedded in a PES membrane matrix. About 85% of Cu (II) removal with initial concentration of 20 mg/L was attained [84]. The produced membranes exhibited exceptional robustness and reusability. When a PES membrane matrix was implanted with a nanosheet of montmorillonite and chitosan [85], about 92% of dye removal was attained due to the adsorptive mechanistic of the adsorbent equipped with the robust MMMs that prolong the usability of the membranes.

5.3.4. Biosynthetic filler MMMs

To fabricate MMMs for adsorption studies, biosynthetic is used as filler or adsorbent due to its antifouling, enhanced mechanical strength, and high permeability. The biosynthetic was designed to remove target contaminants from wastewater by applying an amphiphilic triblock polymer vesicle as a filler [86]. Diverse biosynthetic sources, such as banana skin, tea waste, and pomelo peel, are used to fabricate adsorptive PES MMMs that achieved 95% of dyes removal [87].

To maintain the performance of the ultrafiltration adsorptive membranes, the adsorbent or filler loading should not exceed 6% (w/w) to avoid the formation of flaws and dripping interfacial cavities. Otherwise, the adsorptive membranes produced may exhibit poor performance due to limited adsorption capacity caused by the adsorbent's low loading. One of the primary drawbacks of adsorptive MMMs is that the rigid polymer layer impedes the adsorbent's active sites, hence reducing the adsorption capacity of the membranes [88]. As a result,

improvisations such as pore-filling and surface modification adsorptive membranes technology have been made. Others include surface coated, surface deposited, surface grafted, and surface assembled membranes. Table 1 outlines the procedures for fabricating adsorptive membranes and their features.

6. Applications of adsorptive membrane

In recent years, adsorptive membranes have been widely utilized due to its simultaneous dual functions of filtration and adsorption process. The application of adsorptive membranes includes environmental remediation such as heavy metal removal [95], dyes removal [96], separation of biochemical compounds [97], removal of pharmaceutical compounds [98], and solid phase extraction [99].

6.1. Heavy metals removal

The presence of heavy metal-laden effluent into water stream due to rapid industrialization has threatened public health and the environment. Heavy metals such as arsenic (As), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and chromium (Cr) are highly toxic even at trace concentration [13,100]. As the removal of heavy metals from water streams has become increasingly stringent, treated effluents have to meet the required discharge limit set by legislation.

Adsorptive membranes that possess reactive functional groups are capable of removing the metal ions via surface complexation or ion exchange. The functional groups that include -COOH, -SO₃H and -NH₂ can be modified into adsorptive membranes when being in contact with the membrane surface. To attach metal ions prior to adsorption, the pore size of the membrane needs to be larger than that of the metal ions [37].

Adsorptive membrane is normally constructed from porous membrane structure equipped with active functional group on its internal

Table 1
Adsorptive membranes fabrication techniques and their characteristics.

Technique	Characteristics	Procedures	Applications	References
Mixing and coating	Physical interaction of mixed polymer onto the membrane surface followed by deposition of hydrophilic layer	(i) Dispersion of adsorbent fillers into the solvent via ultrasonic or stirred with polymer (ii) The casted dope on a flat surface was dried via evaporation to remove solvent	Commonly used to produce mixed matrix membrane especially containing of chitosan	[89]
Surface molecular impressing	Generated membrane that owned the 3D cavity with the identical size, shape, and position of the functional group from the template of interested species of adsorbate. The cavity possessed the memory effect which can adsorbed the template molecules	(i) Templating molecule of interest with functional monomers onto the membrane via electrostatic interaction and hydrophilicity in suitable solvent system (ii) Polymerization reaction with the aid of cross-linking agent (iii) Removing the template molecule from the membrane.	Utilized for highly selective adsorptive membrane with specific binding capacity	[90]
Surface assembling	Produced by assembling layer by layer of anionic and cationic polyelectrolyte	The negative porous polymeric support layer adsorbed the cationic polyelectrolyte through electrostatic interaction	Fabricating adsorptive MMMs with enhanced hydrophilicity, porosity, and mean pore size thus, increasing the membrane permeability	[91]
Surface grafting	Attaching or grafting the targeted functional group that owned high affinity towards the contaminant ions onto the polymer molecule	(i) Grafted the functional groups onto the membrane's surface (ii) Followed by treatment using UV irradiation, plasma or ozone	Producing chelating membrane	[92]
Composite membrane	Involved the modification of support membrane on its surface by impregnating the adsorbent in between the support membrane and the surface layer	Dispersed the adsorbent fillers in the membrane matrix or added into the membrane's surface	Used to produce membrane with high adsorption capacity, high flexibility, and high antifouling properties	[93]
Electrospinning	Formed solid continuous nanofibers by electrostatic repulsion forces that break polymer surface tension and stretch out its droplet due to high voltage driven process	(i) The electric field created by a high voltage caused the droplet posited at the nozzle takes a cone-shaped deformation (ii) The charged dope rushes toward the collector, then evaporates the solvent, and the nanofibers produced	Applied to form nanofibrous membrane with improved removal capacity and efficiency	[94]
Phase inversion	Membrane synthesis via polymer-solvent mixture into homogeneous dope solution and solidified when contacted with non-solvent via solvent-non-solvent demixing process.	Evaporating the solvent or replacing with non-solvent from homogeneous solution via cooling a casting solution or solvent-non-solvent exchange.	Membranes produced with better dispersion of fillers, and enhanced uniform merging of fillers into polymer	[85]

and external surfaces. The functional groups are bounded to heavy metal ions through ion exchange mechanism and/or surface complexation [101]. The ion exchange mechanism occurs when the adsorbent has free electrons in the active site during physicochemical interactions between the adsorbent and the adsorbate electrostatically [61]. Therefore, when the heavy metal ions are attached to the membrane surface, they are removed from aqueous solution, although their size is less than the pore of the membrane. This method is chosen to remove tiny contaminants such as heavy metals according to their pores [101].

The applications of the adsorptive membranes include electrospinning nanofibers membranes, nano-enhanced membranes, polymeric membranes and polymeric-ceramic membranes [102]. For instance, polymeric membranes with active functional groups such as carboxyl, amine and sulfonic acid are beneficial for the adsorption of heavy metals due to their high adsorption capacity. Meanwhile, polymeric-ceramic membrane with inorganic materials such as natural clays are less favorable due to thermal stability and fouling constraints. Nanofibres fabricated using electrospinning nanofibres offers advantages such as practicability and high porosity membrane up to 90%. This technological strength is attributed to the long polymeric fibers that possess unique features such as high reactivity and large surface area [102].

The adsorption of heavy metals via polymeric-typed adsorptive membranes can be divided into natural and artificial polymeric membranes. The deployment of natural-originated polymer such as chitosan extracted from crustaceans' shells demonstrated an outstanding removal for heavy metals. The superior adsorptive performance of this polymer is attributed to the presence of hydroxyl and amine [101]. The removal of heavy metals such as Ni(II), Cu(II) and Cd(II) ions were undertaken by using chitosan-based adsorptive membranes blended with polysulfone polymer via phase-inversion technique.

For the removal of Cr(III), chitosan was synthesized with *N*-phthaloyl and blended with polyether imide prior to the fabrication of ultrafiltration membrane. The combination of the materials enhanced the content of the synthesized *N*-phthaloyl chitosan and ultimately reduced the membrane pore size, while increasing the permeate flux and hydrophilicity [103].

Likewise, artificial polymers have been utilized for the removal of Cu (II) using an adsorptive membrane fabricated by polyvinyltetrazole (PVT) -*co*- polyacrylonitrile (PAN) [104]. The main active binding sites possessed by the PVT and the membrane owned a high hydrophilicity due to the H-bonding interactions. The produced membrane demonstrated a higher selectivity towards Cu(II) when synthetic wastewater contained Cu(II) and Pb(II) ions. The saturated adsorptive membranes were regenerated using 0.25 mM ethylenediaminetetraacetic acid (EDTA) [104].

The membranes successfully retained Cu(II), while allowing Ni(II) to pass through. The instantaneous selectivity is calculated by dividing the Ni flux over the Cu flux. As the result, the selectivity of the membrane was obtained around 10 for the first 3 mL of permeate before declining to around 1.3, where it remained after the active sites have been saturated. The average selectivity for eluted quantities based on ion fluxes is 10.5, comparable to other membrane selectivity [105].

The heavy metals could be eliminated through non-specific adsorption on solid matrices through selective adsorption. The adsorbent contained a complexing or chelating agent that eventually reacts with target metal. This can be realized by combining the adsorbents to inorganic materials such as silica, aluminium oxide or glass, or organic materials such as polystyrene, polymethylmethacrylate, or cellulose as the supporting matrix.

The distinction between non-specific and specific adsorption could be explained by the fact that certain adsorbent contains a ligand that interacts with a specific metal ion. The PVA/SiO₂ composite membrane functionalized with thiol was electrospun and used for the removal of Cu (II). Wu et al. [106] reported an enhanced adsorption capacity over the pristine membrane. Such modification and functionalization of the adsorptive membranes resulted in the improvised performance due to

the highly reactive functional groups with metal cations. The modified adsorptive membranes showed excellent reusability, desorption rate and chemical stability under varying pH [107].

Apart from the modifications of the adsorptive membrane, dispersed nano-sized adsorbents were also studied in the fabrication of the mixed matrix adsorptive membranes embedded with nano-sorbent fillers under controlled conditions [19]. Table 2 summarizes the application of nano-sorbent filler in adsorptive membranes for heavy metals removal in aqueous solutions. The features of the nano-sorbent were presented based on the operating conditions of the adsorptive systems. Table 2 implied that the outstanding performance of adsorptive membrane depends on solution pH (acidic range). This is beneficial for eliminating the heavy metal ions by the composite membrane.

Adsorption capacity, mechanical strength, surface charge change, water permeability, ions selectivity and water flux need to be taken into account when determining whether an adsorptive membrane is appropriate. Adsorption capacity, affinity and selectivity for target metal species were enhanced when nano-sized adsorbents were incorporated into adsorptive nanocomposite membranes. By interacting with the polymer matrix, nano-sorbents boost the mechanical strength of the adsorptive membrane. This results in the formation of a thicker skin layer and the suppression of macrovoids, while increasing the stiffness and flexibility of the structure [29].

On the other hand, the removal of heavy metal from wastewater by conductive polymeric-based materials such as supporting beds and membranes [112] is attributed to their superior functionalization, mechanical stability, easy preparation, and high electrical conductivity. Polypyrrole, polyaniline and polythiophene are conductive polymers that can be coupled with other bio-based materials to treat contaminated wastewater.

6.2. Dye materials removal

Dyeing is the process of attaching chemical substances to surfaces or fabrics in order to add color. Dyes are composed of complex organic compounds resistant to detergents. Synthetic dyes and pigments are widely used in a variety of industries, including plastic, leather, textile, paper, paint, printing, cosmetics and food processing [113]. Azo, triarylmethane, and carotenoid are the most frequently used synthetic colors. There are about 100,000 types of dyes manufactured at annual rate of 9 million tonnes, contributing to water pollution [114].

There are two types of dye, namely anionic and cationic dyes. These dyes are utilized for different materials and applications, depending on the chemical composition. The major structures of dyes are heterocyclic and substituted aromatic compounds such as azo dye. The dye is popular due to the presence of azo compounds linked by azo bridge [115]. Most of the dye effluents are poisonous, carcinogenic, and constitute public health concern to aquatic life due to the depleted dissolved oxygen in water body [116]. As trace quantities of dyes in water are hazardous, unpleasant, and extremely difficult to remove, efforts have intensified recently to develop novel water technology to remove dye materials from contaminated wastewater [117].

The utilization of adsorptive membrane for this purpose has advantages such as insensitivity to toxic pollutant, high efficiency, and low energy requirement. This ultimately copes with the drawbacks of the conventional adsorption caused by costly adsorbent and inefficient regeneration of saturated adsorbents. The use of bio-sorbent materials may address drawbacks due to their low-cost and eco-friendliness.

For instance, chitosan-based membranes have gained popularity because of their chemical flexibility, as compared to cellulose and chitin. Their physicochemical qualities are influenced by molecular weight and degree of deacetylation. To access the structures generated from glucosamine and *N*-acetyl glucosamine residues, the main bottleneck was to create a deacetylated chitosan with a maximum molecular weight. This necessitated chitin extraction, while preserving its structure. The two crystalline allomorphs, α and β , found in biomass, were

Table 2
Heavy metals removal using nano-sorbent fillers in adsorptive membranes fabrication and their features.

Heavy metals	Membrane type	Nano-sorbents	Adsorption capacities (mg/g)	Operating conditions	Special Features	References
<ul style="list-style-type: none"> • Cu (II) ions • Pb (II) ions 	Composite membrane	Graphene oxide	<ul style="list-style-type: none"> • 72.6 • 250 	<ul style="list-style-type: none"> • 30 °C and pH 5.7 • 25 mg/L Pb (II) at 25 C and pH 6 	<ul style="list-style-type: none"> • Distinctive physicochemical properties 	[108]
<ul style="list-style-type: none"> • Hg (II) ions 	Composite membrane	Carbon nanotubes	<ul style="list-style-type: none"> • 181.8 	<ul style="list-style-type: none"> • Wastewater containing 1000 mg/L at pH 4 	<ul style="list-style-type: none"> • Excellent adsorption capacity 	[109]
<ul style="list-style-type: none"> • Cd (II) ions • As (III) ions • Hg (II) ions • Pb (II) ions 	Composite nanofiber membrane	Zeolites	<ul style="list-style-type: none"> • 838.7 	<ul style="list-style-type: none"> • 5 mg/L of Cd (II) at pH 5 	<ul style="list-style-type: none"> • Hydrophilic and high surface area 	[110]
<ul style="list-style-type: none"> • As (III) ions • Hg (II) ions • Pb (II) ions 	Composite membrane	Metal-organic framework (MOF) and metal oxides	<ul style="list-style-type: none"> • 49.5 – 123.0 mg/g of As(III) • 0.65 – 2173.0 mg/g of Hg(II) • 8.40 – 313.0 mg/g of Pb(II) 	<ul style="list-style-type: none"> • pH < 6 	<ul style="list-style-type: none"> • Outstanding performance in removing As (III), Hg (II) and Pb (II) ions 	[111]

linked to shrimp shells and squid pens, respectively [118].

Apart from being adsorptive, water solubility, high degree of shrinkage after drying, biodegradability, diversity of derivatives, and high polarity of chitosan biopolymer are crucial and affect elements in the membrane properties. With these properties, chitosan is likely to interfere with synthetic polymers commonly applied in membranes. This brings impacts on the chitosan's membrane production process, whether the sheets are free-standing or supported. Since chitosan-based membranes are dissolved in weak acidic environments, they are more difficult to fabricate than other polymeric membranes. Several innovative processes are used to create porous and dense composite or supported films. Recent research focus on improving the membrane's adsorptive properties, as well as its permeability and physicochemical stability.

Wong et al. [119] employed chitosan to absorb acid dyes. As a good bio-sorbent, chitosan was impregnated into electrospun PAN nanofibrous scaffolds with polyethylene terephthalate (PET) [120]. The adsorbent has a negatively charged surface density due to the presence of negatively charged functional groups COO^- and/or SO_3^- . Since the primary characteristics of adsorption is surface interaction, the functional groups on the surface of the chitosan, which play crucial roles in the removal of target compounds, affect the membrane's reusability, selectivity, and efficacy. Increased surface area and adsorption sites also improved the pollutant's removal from wastewater. For this reason, the functional groups of the chitosan contribute to dye removal via

attractive electrostatic interactions.

As a matrix, chitosan is primarily employed to remove negatively charged acidic dyes due to its functional group. When positively charged dyes such as methyl violet 2B, victoria blue 2B, and rhodamine 6 G are present in treated effluents, electrostatic interaction occurs between the positively charged target pollutants and the negatively charged membrane's surface. This contributes to electrostatic interactions between the dye molecules and the membrane surface, preventing the former from passing through the membrane.

Recently, chitosan-based membrane has also been utilized as adsorptive membranes by embedding it with natural fillers for dye removal. For instance, montmorillonite, originated from clay minerals, was used as a natural filler due to its biodegradability, biocompatibility and mechanical strength [121]. An integrated matrix of chitosan and clay may synergize the advantages of their treatment performance in adsorptive membrane, while overcoming their respective limitations. The removal of Bezactiv Orange V-3R dye by the integrated matrix was tested using varying ratio of montmorillonite to chitosan from 0.1 to 0.5 [115]. The adsorption capacity was enhanced as the montmorillonite dose in the adsorptive membranes increased.

Table 3 summarizes the operating conditions and removal efficiencies of dye using adsorptive membranes. In spite of its benefit for dyes removal from wastewater, chitosan has drawbacks. The performance of the membrane is dependent on solution pH. As a result, the pH of the wastewater has to be adjusted to acidic prior to treatment.

Table 3
Dye removal using adsorptive membranes.

Type of dye	Adsorptive membranes	Operating conditions	Removal efficiency (%)	Reference
<ul style="list-style-type: none"> • Reactive Black 5 • Acid Red 249 	Composite nanofiltration membrane that composed of TiO_2 nanoparticles and polysulfone (PSF) ultrafiltration support	<ul style="list-style-type: none"> • The membrane was prepared using a mixture of 1.5% (w/w) trimesoyl chloride (TMC), 0.9% (w/w) TiO_2, 0.3% (w/w) 2-hydroxypropyl trimethyl ammonium chloride chitosan (HACC) and 3% (w/w) polyethyleneimine (PEI) at 1 min at 20 °C. • The dye solutions were prepared using deionized water. 	<ul style="list-style-type: none"> • 93% • 99% 	[123]
<ul style="list-style-type: none"> • Reactive Red 49 • Reactive Black 5 • Direct Yellow 8 and 27 • Direct Red 75, 80 and 81 	Nanofiltration membrane that composed of chitosan-montmorillonite mixture nanosheet	<ul style="list-style-type: none"> • The dye solutions were prepared using deionized water at pH 5. 	<ul style="list-style-type: none"> • 92% • 92% 	[85]
<ul style="list-style-type: none"> • Direct Yellow 8 and 27 • Direct Red 75, 80 and 81 	Composite polyamide (PA) nanofiltration membrane	<ul style="list-style-type: none"> • The feed dye solutions were prepared at 1000 mg/L at room temperature. • The artificial dye solution containing dye, polyvinyl alcohol (PVA), Na_2SO_4 and NaCl as respective components. 	<ul style="list-style-type: none"> • ~ 100% of all dyes 	[124]
<ul style="list-style-type: none"> • Methylene Blue 	Commercial ultrafiltration polyvinylidene fluoride (PVDF) membrane coated with organoclay/chitosan composite	<ul style="list-style-type: none"> • The feed dye prepared with 1 ppm at neutral pH using distilled water 	<ul style="list-style-type: none"> • n/a 	[125]
<ul style="list-style-type: none"> • Direct Red 16 	Polyether sulfone (PES) nanofiltration membrane embedded with O – carboxymethyl chitosan/ Fe_3O_4 nanoparticles	<ul style="list-style-type: none"> • Filtration operated using dead-end stirred at pH 6 and 4 bar pressured 	<ul style="list-style-type: none"> • 99% 	[126]
<ul style="list-style-type: none"> • Rhodamine 6 G • Methyl Violet 2B • Victoria Blue 2B 	Chitosan mixed matrix membrane with cellulose nanocrystals	<ul style="list-style-type: none"> • Synthetic dye wastewater prepared at 1 ppm at pH 5.01 	<ul style="list-style-type: none"> • 70% • 84% • 98% 	[127]

Chitosan tends to swell when being exposed to water, resulting in the loss of its physical structure and low mechanical strength. To address these bottlenecks, chitosan needs to be used with a cross-linking agent to form covalent bonds, of which it reacts with amino groups [122].

6.3. Biochemical compounds separation

The other recalcitrant pollutants, which exist in the waste stream, is widely known as biochemical products. Compounds such as peptides, enzymes, amino acids, proteins, polysaccharides, hormones, nucleic acids and lipids are intricate due to the presence of intermediary metabolites, residuary soluble substrates, and mycelium [128]. Their concentrations were as low as 5% (w/v), posing obstacles to their refinement. Conventional purification techniques such as ion exchange, solvent extraction and precipitation processes are used for this purposes. However, the techniques have bottlenecks such as low rate of product recovery and high energy consumption [97].

Adsorptive membranes with functional groups such as selectivity membranes and molecularly imprinted membranes can be constructed and used to separate biochemical products. While the molecular design optimizes the selectivity of membranes in capturing target biomolecules, this raises the membranes' operational cost. Recently, an emulsion liquid membrane has been tested for the recovery of penicillin-2 from fermentation broth [129]. It was reported that about 76.5% of extraction rate with a molar ratio of 6.0 was attained. This shows that adsorptive membranes advanced the extraction and purification of biochemical products.

6.4. Pharmaceutical materials removal

The existence of 'emerging organic pollutants' (EOCs) in the environment, such as medications and personal care items (PPCPs) poses serious hazards to public health and the environment [130]. Pharmaceuticals, widely known as medications or drugs, are chemical substances used for medical purposes. The compounds are trace pollutants, which sparked public concern due to their massive presence in surface water via emission into the water bodies [131].

Pharmaceutical with a variety of chemical structures exist in wastewater treatment plants. Pharmaceutical pollutants such as acetylsalicylic acid, paracetamol, and ibuprofen could be effectively removed using physicochemical treatment such as activated carbon adsorption [132]. Nevertheless, such techniques have drawbacks since the pollutants are not digested by microbes as a carbon source, inhibiting their activity. The adsorbents have shortcomings such as uncertainty in the interactions, pathways, and kinetics, which precludes their industrial applicability [133].

To mitigate these bottlenecks, the application of adsorptive membranes for removal of medicines from wastewater appears to be a viable method. Raicopol et al. [98] reported that diclofenac sodium and tetracycline were removed from contaminated water using cellulose acetate/Mg-Al layered double hydroxide (LDH) nanocomposite adsorptive membranes. It was also found that the adsorptive membrane had an outstanding adsorption capability. The addition of nanofillers addressed the challenges, as the LDH has high specific surface area, stable thermal durability, and porosity when being integrated into the polymer matrices. The enhancement was caused by the electrostatic interaction between the negative charges of target pollutants and the positively charged Mg-Al LDH layers.

To remove 17-ethinyl estradiol and ibuprofen, an integrated metal organic frameworks (MOF) and ultrafiltration hybrid systems were utilised [134]. Ibuprofen is a commonly prescribed pain reliever, while 17-ethinyl estradiol (EE2) is an artificial hormone. MOFs have a high degree of adjustable porosity, and a low fouling rate in adsorbent-ultrafiltration composite membranes. Even if the pharmaceutically active chemicals are present in trace amounts in surface water, they are hazardous as they enter aquatic environment via

hydrological cycles. It was observed that the MOFs adsorbed target pharmaceuticals more consistently than UF at pH values of 3, 7, and 11, without experiencing fouling. This indicates that the MOFs captured them efficiently.

In comparison, the average of retention rate of pharmaceutically active compounds in the MOF-UF (53%) was higher than that of the UF neat membrane (37%). Meanwhile, the average of retention rate of natural organic matter in the MOF-UF (86%) was greater than that of the UF membrane (76%). Furthermore, the average of UF's normalised NOM flux for MOF (0.79) was higher than that of the UF itself (0.74). These findings showed that the adsorptive membrane could better perform than conventional membranes.

To justify their viability as effective adsorbents for water treatment, the performance of all adsorptive membrane needs to be compared. Table 4 summarizes the operational parameters and treatment performance of various adsorptive membranes for PPCP removal. This comparison is made based on different conditions (pH, wastewater composition), type of biomaterial, and methods.

6.5. Solid phase extraction

Solid phase extraction (SPE) is commonly used for pre-concentrating trace samples. This technique has been applied in a variety of applications for agricultural, environmental, and medicinal purposes. Out of the various technologies, SPE membranes have gained popularity in recent decades due to their abundance and consistency [137]. However, adsorbents may evaporate in the case of mixed matrix SPE membranes, leading to the production of secondary contamination as well as low recyclability.

A study undertaken by Hao et al. [138] developed sandwiched silica-based SPE membranes with octadecyl silyl bonds for the extraction of phenol from aqueous medium. A complete phenol extraction recovery was attained using portable SPE membrane for a rapid identification and removal of antibiotics, while the recovery of the spike ranged between 98% and 99%. On a SPE column, the membranes were produced by filtering it with silver nanoparticles-modified activated carbon (AgNPs/AC). The membranes demonstrated exceptional enrichment capability and a capacity to increase their detection accuracy.

As adsorbents, metal-organic frameworks (MOFs) have demonstrated promising uses. MOFs have a large surface area, superior and controllable porosity, and customizable surfaces. ZIF-8 is the most frequently used MOF for quantitative extractions due to its support in SPE. It has a persistent porosity, excellent resistance to water, a large specific surface area, and a hydrophobic nature.

In 2011, ZIF-8 was employed as an adsorbent to extract polycyclic aromatic hydrocarbons (PAHs) from aqueous systems [138]. The SEM micrographs demonstrated that the microstructure of ZIF-8 remained unaltered, providing insight into its water repellent design.

A further study using a ZIF-8-based SPE technique was performed to obtain oestrogens from water samples. Due to its hydrophobicity, coordination bonds, and π - π interrelations with oestrogens, it was found that ZIF-8 extracted oestrogens more efficiently than commercial SPE column such as HLB, C18 or MWCNTs [139]. In spite of its technological values, additional works on the newly structured membrane designs are required to boost its effectiveness.

6.6. Nutrient recovery from wastewater

Nutrients present in wastewater effluents include carbon, nitrogen, and phosphorus compounds (CNP). They are essential for the survival of living organisms such as food production. Nitrogen and phosphorus are crucial components of deoxyribonucleic acid (DNA), chlorophyll, and amino acids. Phosphorus serves as the "energy exchange" of eukaryotic cells in the form of adenosine triphosphate (ATP). Although N_2 is ubiquitous in the environment (78%), its presence in the soils is limited, as it is retained in amino acids, nitrate, and ammonia [140,141].

Table 4
Adsorptive membrane applications for pharmaceutical compounds removal.

Adsorptive membrane	Target pharmaceutical compounds	Removal efficiency (%)	Operating variables	Reference
PES nanofiltration membrane modified with organic acids	<ul style="list-style-type: none"> Xenobiotics p-nitrophenol (PNP) 	<ul style="list-style-type: none"> 85% 	<ul style="list-style-type: none"> Feed PNP solution of 0.1 mM was prepared using double distilled water at pH 8 	[135]
PVDF membrane embedded with multi-walled carbon nanotube (MWCNT) layers	<ul style="list-style-type: none"> Ibuprofen Acetaminophen Triclosan 	<ul style="list-style-type: none"> Ranged from 10% to 95% 	<ul style="list-style-type: none"> Samples were prepared using Suwannee River fulvic acid and ultrapure water to represent the real natural water containing natural organic matter pH values were varied from 4 to 10 that eventually affect the removal efficiencies by up to 70% when compared with removal at neutral pH 	[136]
Ultrafiltration membrane incorporated with metal organic framework (MOF)	<ul style="list-style-type: none"> 17α-ethinyl oestradiol Ibuprofen 	<ul style="list-style-type: none"> 53% 53% 	<ul style="list-style-type: none"> 10 μM of feed solution was prepared using deionized water at pH 3, 7 and 11 	[134]

To date, only a few studies have reported the application of adsorptive membrane for the recovery of phosphorus from wastewater. Ion exchange membranes (IEM) was applied during Donnan dialysis separation using semi-permeable IEMs [142]. As IEM-based techniques have shorter diffusion routes, they can be used in wastewater that consists of suspended particulates and dissolved organic.

Abetz et al. [144] reported the retrieval of ammonia gas from an acidic medium using a vacuum-operated gas-permeable membrane. On the permeate side of a macroporous hydrophobic membrane, their study explored the possibility of recovering ammonia as $(\text{NH}_4)_2\text{SO}_4$ [143]. A concentrated fertiliser with 13 g/L $\text{NH}_3\text{-N}$ was produced from liquefied animal manure using electrodialysis and RO [144]. Although this technique was effective, its limitations include high operational cost, high pressure requirement, and complex membrane preparation.

For nitrogen recovery, zeolite is widely used due to its tetrahedral structure with Al and Si atoms covalently linking to form interlinked cages and channels [145]. Each Si^{4+} atom is replaced with an Al^{3+} atom, resulting in a net negatively charged on the structure. The negatively charged within the pores are neutralized by charged cations on its surface, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . These cations are retained by weaker electrostatic interactions and exchanged for NH_4^+ .

The development of a mixed-matrix membrane using zeolite embedded into a PSU polymer matrix was reported by Ahmadiannamini et al. [146]. The membrane was capable of extracting over 90% of total ammoniacal nitrogen from treated effluents. Nonetheless, this technique has limitations such as membrane failure, leaching of inorganic fillers in

the membrane matrix, and poor membrane permeation. To mitigate the bottlenecks, ceramics - based adsorptive membrane needs to be introduced.

The production of an adsorptive hollow fibre ceramic membrane based on natural zeolite is attributed to its outstanding ammonia removal, inexpensive raw materials, and low sintering temperature [147]. Fig. 11 depicts the adsorption of ammonia by zeolite-based adsorptive hollow fibre ceramic membrane via ion exchange process [39]. The high ammonia adsorption by adsorptive ceramic membrane is attributed to its superior ion exchange characteristics. The substitution of Al^{3+} by Si^{4+} in the zeolite's lattice results in the generation of negatively charged adsorption sites. This active site migrates to the particle's surface, where it is neutralised by counter ions such as Na^+ , K^+ , and Ca^{2+} that are easily exchanged [148].

6.7. Drinking water purification

The increasing demand for clean water in energy, agriculture, municipalities and industries, along with the scarcity of fresh water, accelerated the development of water technology that provide safe drinking water from alternative sources. While secondary sources of water including seawater or brackish water may offer some options, this complex water contains high salinity and trace metal ions, which vary from one location to another [149]. As a result, emerging membrane technologies such as the extraction of particular ions from water distillation based on their selectivity has been recognized as one of the most

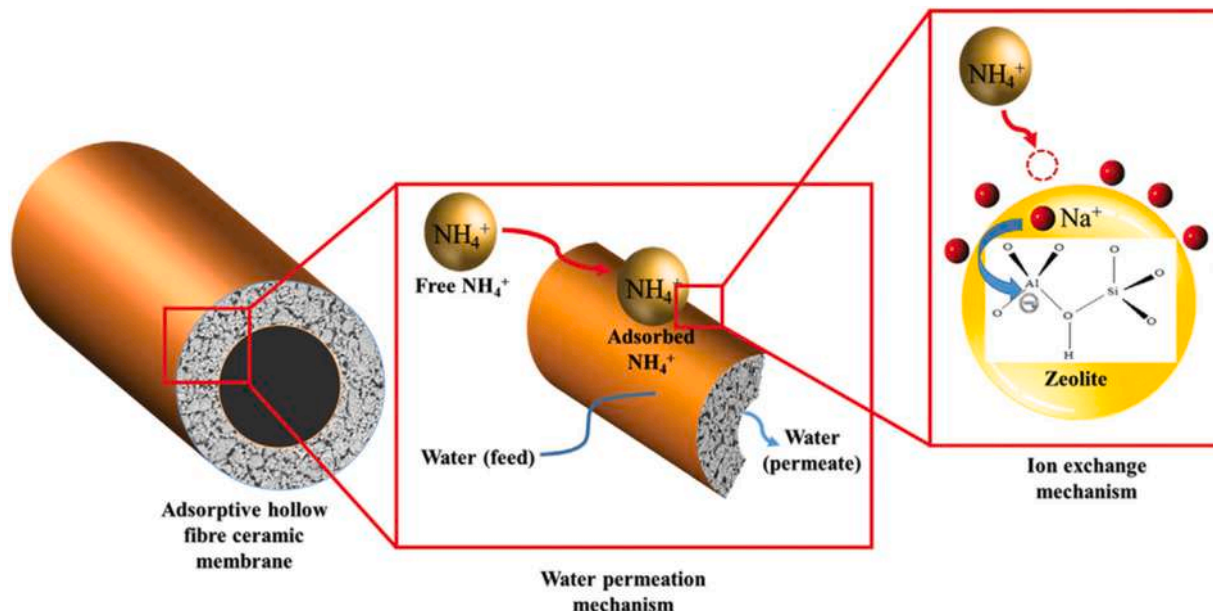


Fig. 11. Ammonia adsorption by natural zeolite – based adsorptive hollow fibre ceramic membrane mechanism via ion – exchange process [39].

promising options.

Adsorptive membranes have demonstrated their superior performance in various separation processes, as compared to conventional membranes. Several studies have shown the effectiveness of the adsorptive membrane utilization for water treatment process. Zhang et al. [43] successfully developed a new adsorptive membrane by modifying supporting layer with Fe₃O₄ microspheres for As removal. They created a novel adsorptive membrane for removing As by altering the porous supporting layer of a phase inversion. Reverse filtration was used to trap Fe₃O₄ microspheres in the membrane's support layer.

With respect to membrane morphologies and separation performance, the constructed adsorptive membrane was assessed by comparing its performance before and after incorporating Fe₃O₄ microspheres. This method produced an adsorptive membrane with rejection rate equivalent to the neat membrane without Fe₃O₄ microspheres, but demonstrated higher rejection rate than the conventional mixing method. The new adsorptive membrane was capable of treating over 2000 L of As-contaminated up to three regeneration cycles. During regeneration, one square m of the adsorptive membrane could purify almost 7 L of the contaminated water to meet the required standard for safe drinking water with respect to As concentration.

In addition to heavy metal, adsorptive membrane was utilized to eliminate ammonia. Ammonia level in surface water frequently exceeds the permitted effluent limit [37]. Although several ammonia removal methods have been widely employed, their removal efficiency for ammonia is not satisfactory. To cope with this bottleneck, Rohani et al. [150] utilized adsorptive membrane technology to remove ammonia from contaminated water.

The efficiency of a polyvinylidene fluoride (PVDF) flat sheet membrane including adsorbents (zeolite and gypsum) for ammonia removal was investigated by Rohani et al. [150]. The morphology of the blended PVDF membrane revealed the formation of an exceptionally wide finger-like structure at the membrane's bottom layer. The improved membrane has hydrophobic qualities with contact angles of $89.0 \pm 0.48^\circ$ for zeolite and $96.3 \pm 0.54^\circ$ for gypsum, respectively. Meanwhile, the crystallinity of the manufactured membrane rises from 20% for pure PVDF to 25.9% and 26.4% for gypsum and zeolite additives, respectively. They found that the presence of zeolite or gypsum in the manufactured PVDF membrane improved ammonia removal by acting as an adsorption material.

7. Challenges on adsorptive membranes applications

Membrane separation process depreciates over its lifetime. As a result, current works examine not only membrane performance, but also its durability and regeneration of saturated membrane during its operation. Adsorbent's durability refers to its resistance to chemical, thermal, and mechanical degradation throughout treatment. As reusability brings impact on the economics, membrane needs to be evaluated for their reusability during consecutive regeneration cycles [38].

For this reason, the mission of previous and future research is to determine the optimum operational parameters that maximize pollutants removal, while minimizing treatment costs. The conventional membrane separation and adsorptive membrane technologies have their own merits and drawbacks. As adsorption is an effective approach for removing target pollutant from wastewater cost-efficiently, this creates opportunity for its deployment in water treatment industry. This technology also enables ease of operation and operational conditions versatility.

Water treatment that requires operation at low or high pH demands the consumption of chemicals, increasing treatment cost over time. Although ideally adsorption could work without pH adjustment, conventional membrane separation is more costly than adsorptive membrane technique. While various projects focused on improving RO or NF that requires high energy consumption, UF system requires pressure source to function, unlike the adsorptive membrane.

A number of studies have reported the applicability of a PVDF-PFA/PEI membrane, which involve co-deposition of dopamine (DA) and polyethyleneimine (PEI) on a polyvinylidene fluoride (PVDF) micro-filtration membrane for dye removal [93,151,152]. The adsorptive membrane could be recycled for six cycles, while achieving 95% of dye removal [93]. Its exceptional regeneration was attributed to the deprotonation of imine and amine groups.

The primary drawbacks of adsorptive membranes are their high maintenance cost due to its reproducibility. To promote its commercialization, an efficient and cost-effective production of the adsorbent is required. Most of the research focused on laboratory scale studies that do not accurately reflect actual scenarios in wastewater treatment. As a result, wastewater operators are unable to optimize adsorbent's loading during adsorption treatment. While a high surface area is necessary to boost adsorption, a high loading of adsorbent results in leaching due to its instability in the membrane matrix. Therefore, the cost reduction of polymeric materials and their chemical stability, long-term stability, and reusability need to be investigated in further work.

Fouling has been another significant issue in the membrane over the past years. The addition of antifouling nanoparticles and surface modification contribute to solving this issue by enhancing their antifouling capabilities [153]. For this purpose, future work needs to limit microbial colonisation of the membrane surface and prevent fillers from leaching.

Adsorptive membranes could be used to integrate several processes into a single step of remediation strategy that integrates adsorption and filtration processes. The regeneration of adsorptive membranes evolves into a process for extracting the substances for environmental remediation. However, regeneration remains scarce in the body of literature. Operational pressure that demands backwashing needs to be addressed.

Overall, fouling and agglomeration represent key bottlenecks in the field of membrane technology. They prevent the use of nanoparticles in membranes applications. The development of adsorptive membranes with relevant compatibility and adsorptivity towards target compounds are economically attractive and technically promising. This provides definite solutions to address the main bottlenecks in the adsorptive membrane technology.

8. Perspectives on adsorptive membranes improvement

The emergence of new contaminants in wastewater has detrimental effects on the environment and exacerbates water shortage problems. Adsorptive membranes combine the technological advantages of adsorption and membrane separation for various environmental applications. This technology exhibited its effectiveness in removing heavy metal ions and dyes due to its selectivity, water flux, permeability, and rejection rates [154].

Nevertheless, there are bottlenecks of adsorptive membrane in their industrial applications. As current research remains laboratory settings, future work needs to focus on enhancing its adsorption capability, recyclability, manufacturing and operational costs, and antifouling qualities in the membrane matrix. Extensive research needs to be carried out to estimate water treatment cost at industrial scale.

9. Concluding remarks

This review has demonstrated recent advances in adsorptive membrane technology for water treatment and resource recovery applications. It is conclusively evident from 280 published studies (1971–2022) that integrated adsorption and membrane filtration processes were highly effective in removing refractory pollutants from contaminated wastewater due to their rapid adsorption-desorption rates, low internal diffusion resistance, and high flow rates. Technical bottlenecks of adsorptive membranes include maintaining a high membrane permeation rate for the substance to be separated, access to large membrane modules that can be produced with good reproducibility, cost-effective production, and long-term module consistency, as well as the potential

of repetitive membrane regeneration and technology for repairing defective membranes. It is important to note that the treatment cost of adsorptive membrane filtration varies, depending on local conditions. In general, technical applicability, treatment efficacy, and treatment cost are critical factors in determining the most suitable water technology for treating wastewater laden with recalcitrant contaminants. Further research should address technical bottlenecks such as membrane fouling and agglomeration formation during the adsorptive membrane fabrication and operation. The constraints can be tackled to improve the quality of the membranes fabricated. Indeed, adsorptive membranes are expected to play an important part in resistant contaminated water treatment and have a promising future.

Declaration of Competing Interest

There are no conflicts of interest to declare.

Acknowledgements

The authors wish to express their gratitude to the Ministry of Higher Education Malaysia for financial support through the Fundamental Research Grant Scheme (Project Number: R.J130000.7809.5F161) and the Higher Institution Centre of Excellence Scheme (Project Number: R.J090301.7809.4J430). Additionally, we would like to express our gratitude to JICA Technical Cooperation Project for ASEAN University Network/Southeast Asia Engineering Education Development Network (JICA Project for AUN/SEED-Net) via Collaborative Research Program (Project number: UTM CEP 2102a / R.J130000.7309.4B647) and UMW Corporation Sdn. Bhd. for the Contract Research (CR) DTD Grant (Project number: R.J130000.7609.4C471). Besides that, the authors wish to thank Universiti Teknologi Malaysia for the research funding through the Collaborative Research Grant (Project number: Q.J130000.2409.08G29), the Matching Grant (Q.J130000.3009.02M25), and the Professional Development Research University (PDRU) Grant (Project number: Q.J130000.21A2.05E04). Finally, the authors wish to express their gratitude to the Research Management Centre at Universiti Teknologi Malaysia for the technical assistance.

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