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Recent progress and challenges on adsorptive membranes for the removal of pollutants from wastewater. Part I: Fundamentals and classification of membranes

Liyan Qalyoubi, Amani Al-Othman [*], Sameer Al-Asheh

Department of Chemical Engineering, American University of Sharjah, PO. Box 26666, Sharjah, United Arab Emirates

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ABSTRACT

The development of novel wastewater reuse technologies appears to be a thriving area of research. Adsorptive membranes are considered among the promising technologies that exhibited efficiency and competence in water reuse. They have the potential of removing different types of emerging pollutants from wastewater that cannot be removed via conventional methods. These membranes are attractive because of the dual advantage of adsorption/filtration mechanisms and by virtue of their various types and configurations. The use of adsorptive membranes tackles several issues including fouling, process cost, adsorbent regeneration, adsorption capacity, membrane permeability, rejection rates, and selectivity. This review is devoted to discussing adsorptive membranes and their fabrication techniques, as well as presenting their various types and classifications. The challenges associated with their application are also reviewed. Their classifications can be established based on either the type of the adsorbent used or their polymers matrix. The major challenges are fouling and identifying the right filling materials. The review also identified the great potential of using these membranes in removing emerging pollutants.

1. Introduction

Water is the essential element to human beings and the ecosystem lives. However, water scarcity is a major issue that concerns the world currently. This has triggered the search for good quality water resources to support the development of modern societies. For instance, water reuse has the potential to solve some of the existing problems in securing water. Therefore, the development of wastewater treatment technologies appears to be a thriving research topic to produce clean and drinkable water. Over the years, many conventional treatment methods were studied and implemented, e.g. coagulation, sedimentation, and adsorption. However, studies recently have been focusing on finding cost efficient and effective water treatment technologies that can overcome the limitations associated with the conventional methods. This brought the attention towards adsorptive membranes that can remove many types of emerging contaminants which threaten human's health and the aquatic organisms.

Adsorptive membranes are utilized to remove soluble micropollutants. A treatment method that combines between adsorption and membrane technology appears promising [1]. The use of adsorptive membranes has the potential of solving some of the existing problems in conventional water treatment methods like fouling, high pressure requirement, regeneration cost, and selectivity.

The adsorptive membrane has dual the function of adsorption and filtration. This membrane basically depends on the adsorption process which is typically a mass transfer process in which the substances are bounded by chemical and physical interactions to solid surfaces. Adsorption is an easy practical approach to perform, offering flexibility in the design and good resistance to toxic substances. Most importantly it is a reversible process, since the adsorbents can be regenerated by desorption processes which is considered cost efficient. The effectiveness of adsorbents used depends on their morphology and chemistry [2]. This process attracted researchers to study many types of adsorbents such as nano size adsorbents and bio adsorbents. The results showed their disadvantages such as agglomeration and difficulty in regeneration. The most used adsorbent is activated carbon. However, its regeneration is costly. This encouraged researchers to find alternative cost-efficient adsorbents [2].

The use of membrane technology via filtration received interest over the years. It is known that microfiltration (MF) and ultrafiltration (UF) can only eliminate some viruses and suspended solids, while nanofiltration and reverse osmosis can remove heavy metal ions and fluorides but with fouling problems and high operating pressure [3]. Since the

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[*] Corresponding author.
E-mail address: aalothman@aus.edu (A. Al-Othman).

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List of abbreviations

MF	Micro-filtration
UF	Ultra-filtration
PAN	Polyacrylonitrile
PES	Polyethersulfone
PVDF	polyvinylidene flouride
MWCNTs	Mulit-walled carbon nanotubes
FMWCNTs/CS	Fibrous mulit-walled carbon nanotubes/chitosan
PVT	Polyvinyl tetrazole
PVA	Poly (vinyl alcohol)
SEM	Scanning electron microscopy
PANI	Polyaniline
DFUF	Dual-functional ultrafiltration

conventional water purification methods have drawbacks and high cost, the investigation of more effective operations or even integration of alternatives has been a great area of research over the past years [2]. This resulted in the emergence of a combination between membranes and adsorption processes to overcome some of these drawbacks faced when the preceding approaches were used individually and exploit the benefits of both [1]. The membrane technology basically depends on three principles: adsorption, sieving and electrostatic phenomenon. The adsorption mechanism in the membrane separation process relies on the hydrophobic interactions of the membrane and the solute (analyte) [4].

Adsorptive membranes (can be also called modified membranes) have many advantages like the high removal rate and efficiency, low operating pressure, high permeability flux, regeneration, appropriate reusability, small footprint and less space requirements [5]. Polymers and powders with adsorption capability are installed in the membrane to reduce leakage and recovery problems. These adsorptive membranes are characterized by their high affinity for ions and molecules, as they combine ions by chelation bonding, complexion, or ion exchange [5]. Moreover, the large surface area and redundancy of adsorption sites are important factors for the efficiency of adsorption and removal of pollutants from wastewater. It is, therefore, the objective of this paper to outline and present the classifications, synthesis, and various types of adsorptive membranes. To the best of the authors' knowledge, this is the first comprehensive review that aims to discuss the preceding aspects as well as providing recommendations and future outlooks on the use of natural-based membrane bio-sorbents.

2. Mechanisms of solutes removal

Generally, the removal of solutes from wastewater by adsorptive membranes consists of two mechanisms: rejection and adsorption. Once the water-containing solutes contact the active layer of the membrane, the solutes with sizes greater than the membrane's pore size are rejected by molecular sieving. The solutes that have smaller sizes will pass through the active layer and reach to the support layer which acts as adsorption material microspheres. They will then react/attach and create a tight internal spherical complex and produce a permeate of filtered water from adsorptive membrane that satisfies the required standards [3]. Adsorptive membranes are modified to have reactive functional groups such as -NH_2 and -COOH that interact with the solutes by ion exchange or surface complexation [6]. Also, the system can differentiate both small and large solute molecules. For instance, in a study done by Xuan Zhang [3], arsenic contaminants were removed by an adsorptive polymeric membrane with iron oxide (Fe_3O_4) microspheres with its functional group and magnetic properties installed in the support layer. The small sized arsenic pollutants pass through the separation layer, reach the support layer, and react with Fe_3O_4 by chemical adsorption to form a tight internal spherical complex. As a result, filtered water permeate is produced. The selective removal of such pollutants by the adsorptive membrane is demonstrated in Fig. 1 [2].

Most commonly, MF and UF membranes are chosen because of their high permeability of water, low pressure requirement, and low cost. It was observed that enhancing the performance of the membrane can be done by increasing the functional adsorption sites reasonably. Therefore, adding hydrophilic nanoparticles can enhance the clean treated water flux efficiently [3]. However, addition of nanoparticles should not be done excessively to avoid damaging the membrane's structure and hindering its performance. Therefore, it is usually recommended to have less than 6 wt% of the adsorbent in the membrane matrix [3]. Below, the types of adsorptive membranes are discussed.

3. Classifications of adsorptive membranes

Adsorptive membrane technology can be an economic and efficient method for the treatment of different wastewater contaminants. More specifically for those contaminants which their removal efficiency depends on surface interactions controlled by the functional groups on the adsorbents' surface. The preceding properties play a crucial role in determining the capacity, efficiency, selectivity, and reusability of the adsorbent [7]. Hence, there are various types of adsorptive membranes, including the ion-imprinted membranes, where a particular ion is added as a template and then eluted out in the preparation procedure of the membrane. Other type of membranes includes polymer or inorganic particles in the matrix and called mixed matrix membrane (MMM). Adsorptive membranes are also found in ultrapure water production, and sulfur removal from fuel [5]. The pore size of adsorptive membranes comes in a range from nanofiltration to microfiltration scopes. The adsorbents used that have high adsorption capacity usually include hydroxyl, amino, carboxyl, and sulfonic groups [5].

Adsorptive membranes can be classified based on the type of polymer used or the type of adsorbent added to the membrane.

3.1. Classification based on the type of polymer used

Polymeric membranes are commonly utilized in microfiltration, ultrafiltration, and nanofiltration due to their low cost and ease of fabrication. It was found in a study that the cost of polymeric UF/MF membrane can be as low as 0.081$/GPD (gallon per day of water treated) [8]. This is a promising technology, however, commercialize practical adsorptive membranes are very limited and restricted to inactive polymers like nylon, polyethylene, and polypropylene. Therefore surface modification is needed to prepare the inert polymer, which can be done by the addition of inorganic and organic adsorbents to enhance their affinity to contaminants removal [6]. The organic adsorbents are

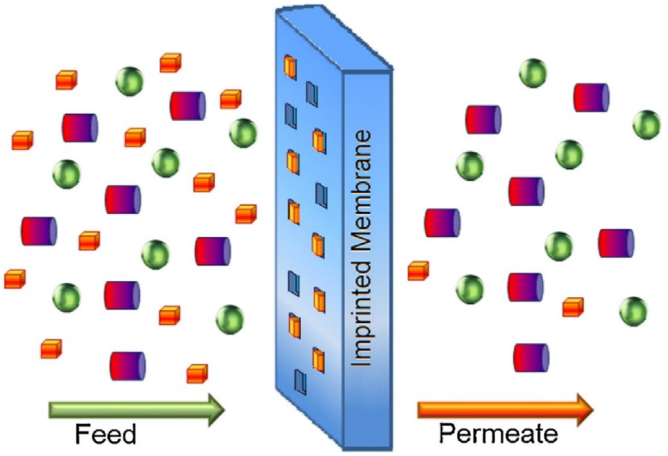

Fig. 1. Selective removal of multiple pollutants by adsorptive membrane [2].

introduced by grafting, blending, and assembling, while the inorganic adsorbents are added directly or after modification [5]. These methods are used to introduce the reactive monomers like acrylamide, acrylic acrylonitrile, acid, and those having the epoxy group. Other methods also include the attachment of several dye chemicals to hydrophilic polymeric membranes such as polyvinylbutyral and cellulose acetate membrane [6].

3.1.1. Natural polymers

Biopolymers or natural polymers are among the major used materials in adsorption of dyes, heavy metal ions, and other contaminants, even at low concentrations. They are fabricated using renewable and biodegradable materials which results from the presence of nitrogen and oxygen in their chemical structure [9]. For example, chitosan which is a polysaccharide biopolymer with high content of hydroxyl and amine functional groups derived from chitin, the natural biopolymer available in crustaceans shell, is widely used in adsorptive membranes. Its privilege comes from the high binding capacity, ease of accessibility, and unique properties [2]. A few concerns emerge when using it in an aquatic environment with a pH less than 6.5, therefore some reagents such as glyoxal and formaldehyde can be applied as cross-linkers to prevent any solubility problems and enhance the mechanical characteristics of chitosan with sorbents. Using chitosan-based membranes is a common practice as it is the most preferred way of adsorption due to excellent kinetics, improved reusability, and practicality of scaling up [2]. It has an excellent performance in heavy metals removal from wastewater because of the amine functional group that forms surface complexes with several metal ions [10].

Many previous studies used chitosan in powders, flakes, or gel beads forms [11]. However, the mechanical resistance of chitosan flat membranes needs to be improved. This can be done by applying chitosan as thin film composites to utilize a good support or it can be embedded in compatible nano biomaterials [2]. Moreover, other drawbacks are attributed to coating either nonuniform or incomplete coating of the membrane that can occur or non-stick coated chitosan. As a result, mixing other polymers with chitosan can be considered to overcome these issues, enhance the chemical stability and mechanical resistance [6].

3.1.2. Synthetic polymers

Polyacrylonitrile (PAN) is considered one of the preferred synthetic polymers for UF and MF adsorptive membranes manufacturing because of their cost-effectivity, outstanding solvent stability, and great mechanical resistance. This membrane can be synthesized by many methods. Some researchers successfully fabricated an adsorptive ultrafiltration membrane from synthesized polyvinyltetrazole-copolyacrylonitrile (PVT-*co*-PAN) via nonsolvent induced phase separation technique [12]. It has been proven that the PVT can change the pore size, charge, in addition to hydrophilicity of the membranes [18]. Thus, PVT makes the membrane more hydrophilic and negatively charged.

Other synthesized polymers include polyurethane with cellulose acetate in blended membranes, which are typically used to eliminate chromium (VI). Cellulose acetate is a common filtration membrane due to its hydrophilic nature, good fouling resistance, and cost efficiency [13]. Some disadvantages of using cellulose acetate-based membranes are low chemical, mechanical, and thermal strength. These properties can be improved by using polyurethane which provides good mechanical, chemical and thermal features. This polymer is a heterogeneous matrix consisting of an alternating array of soft and hard sections. The soft parts are flexible and soluble in water like polyether polyols, while the hard parts are rigid and non-soluble in water [14]. As a result, the synthetic polyurethane-cellulose acetate blend membrane appeared to be an effective costly efficient tool for contaminants removal from water. The scanning electron microscope (SEM) micrographs in Fig. 2 shows that the blend membranes have spongy structures, partly packed with dense cellulose acetate having various pores on the surface which facilitates the water flux rate [15].

Polyethersulfone (PES) is a widely used commercial material in manufacturing polymeric membranes due to its several outstanding characteristics such as: superior chemical and thermal stability, excellent mechanical strength, applicability in a broad range of pH (2–12). Despite all the wide uses of PES it has some disadvantages like fouling caused by nonpolar solutes adsorption, and by the hydrophobic particles or bacteria which leads to shorter membrane lifespan. Other problems are biocompatibility associated with aggregation, and its inert state in water. Therefore, membrane modification of common polymers or membranes to produce adsorptive membranes would be a reasonable alternative to overcome such constrains [16].

In the recent decades, significant effort on developing polymeric nanocomposites have resulted in nano-scale filler materials [17]. However, the composite is not necessarily in nanoscale, as it can be micro or macroscopic. Such advancement resulted in exceptional combination of the nanomaterial's properties which include the size, mechanical traits, low concentrations required to effect change in polymeric matrix, and ease of manufacturing since they can be manufactured as conventional polymer composite. Moreover, nanocomposite technology shows significant improvements in biodegradability, and great enhancement in mechanical, thermal, and electrical characteristics. However, implementing nanotechnology in mixed matrix membranes manufacturing has some challenges including the strong possibility of fine particles to agglomerate, and the difficulty in determining the composition, strength, and functionality of the interfacial area. Additional problems arise during processing the material such as degassing when the air gets entrapped while pouring the highly viscous material in the mold [17]. Therefore, this technology is a promising development in the adsorptive membrane field but still requires further investigations to benefit in water purification applications due to the above constrains.

Using nanoadsorbents is a promising technology for solutes removal with low molecular weights caused by the high surface area, plentiful adsorption sites, and fast kinetics [18]. Nevertheless, nanoadsorbents are

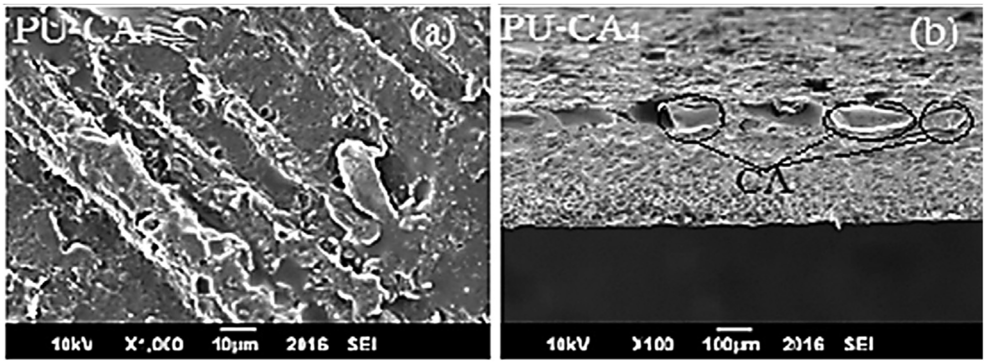

Fig. 2. SEM images of PU-CA blend membranes [21].

made as fine powders which results in issues in separation and regeneration, in addition to their high cost and some potential toxicity troubles from leaching into water bodies [19]. Combining the advantages of nanoadsorbents and UF membranes and overcoming their disadvantages in water purification remains a challenge.

3.2. *Classification based on the type of the adsorbent*

Adsorptive membranes are also classified into four main categories depending on the type of the adsorbent in the membrane including: inorganic fillers, organic fillers, biomaterials, and hybrid fillers-based membranes. These are mostly under the type of mixed matrix membranes (MMM). The MMM is a hybrid type of membrane developed from the single polymer membranes in which an inorganic material is fixed in the polymer matrix. In general, adsorbents in a polymer matrix type possess a lower adsorption capacity and a longer equilibrium time [5]. The MMM can have selective separation and filtration ability to remove suspended materials, microorganism, micro-contaminants in one step [20]. It can be applied in water purification and gas separation as well. This type of membrane can be applied in heavy metals removal from wastewater; for example removing lead and nickel cations using zeolite nanoparticle infused onto polysulfone membrane by hydrothermal process [21]. Thus, in principle these hybrid membranes are based on mixing the inorganic materials acting as adsorbents to the polymer membrane by certain methods. For example, two preparation techniques including the immersion of pre-treated polyvinylidene flouride (PVDF) films in zinc oxide (ZnO) suspension, and blending the ZnO nanoparticles with PVDF solution before the casting films process have been investigated [22]; the immersion method requires the need of surfactants as the pre-treatment of the PVDF films.

Polysulfone is a well-known polymer used in preparing MMM polymeric membranes because of its bright properties including the low cost, high mechanical strength, stabilitiy, resistance of pH range, practicality, and diversity of active functional groups. Usually, polysulfone is combined with nanomaterials or ceramic materials to enhance the properties of the membranes. For example, organoclay embedded polysulfone nanocomposite membranes were used for arsenate ion (AsO_4^{-3}) removal from polluted surface water [23]. This addition resulted in significant enhancement of pure water flux, roughness, surface hydrophilicity, and mechanical strength of the membranes which increased with increasing organoclay concentration from 0 to 2.0 wt% [23].

It important to mention that fabrication of mixed matrix membranes needs the use of an inorganic additive to the matrix in order to boost the selectivity of the membrane in the direction of a targeted species, reducing fouling, and increasing hydrophilicity. However, these additives should be selected wisely to avoid cost burdens or complexity in the manufacturing to satisfy the object of enhancing the membrane's properties. As a result, inorganics selection is done depending on their performance, size, complexity in production, and cost. Moreover, the selection of base polymer also plays a vital role in the performance of a membrane. As Polysulfone (PSF) is a thermoplastic polymer that is characterized with toughness and good stability at elevated temperatures, Polyvinyl-pyrrolidone (PVP) on the other hand is a pore former which creates a certain amount of diffusion and increases the mechanical stability [24]. Therefore, they are suitable candidates to be used as base matrix with additives.

Mixed matrix membranes propose alternate materials that merge both promising selectivity benefits of the inorganic particles and economical capabilities of polymers. Several studies have been conducted to predict their performance based on the ideal and the non-ideal MMMs models [25]. The ideal morphology model is composed of a system with two phases, with the inorganic fillers and the polymer matrix present without defects or distortion at the interface. However, it is hard to achieve this ideal model due to the imperfect filler−polymer adhesion that resulted in imperfect morphologies or three-phase systems. These membranes contain organic−inorganic interface flaws. Interface defects have three major categories: interface voids, rigidified polymer layer around the inorganic fillers, and particle pore blockage. As the polymer's chains cause clogging and blockage of the filler pores which prevents the passing of the material to be purified [25]. The models should be able to evaluate the permeability and selectivity for MMM morphologies. Other important parameters that affects the functioning of the mixed matrix membrane include: the particle pore size and distribution, particle dispersion, polymer characteristics, and interactions [26]. Fig. 3 shows the comparison of structures between an ideal MMM model which has the dispersed phase and the polymer matrix, and a nonideal structure.

In mixed matrix membranes, the polymer is the continuous phase, and the inorganic filler is the dispersed phase. The polymers in the continuous phase are typically characterized by their glass transition temperature and polarity, while the selection of the dispersed phase depend on the pore size, structure, and surface polarity. Block copolymers type is generally preferred as it offers advanced function and nanostructured membranes [27].

Depending on the physical state of the polymer, the MMMs can be also classified into three main categories, namely solid−polymer, liquid−polymer, and solid−liquid−polymer mixed matrix membranes. Solid−polymer MMMs are the most common type where usually zeolitic and nonzeolitic inorganic materials are used as fillers [26]. For fabrication of zeolitic MMMs, rubbery and glassy polymers were utilized as a polymer matrix. On the other hand, carbon molecular sieves, nonporous and porous silica nanoparticles, and metal oxide nanoparticles are known types of nonzeolitic fillers. Due to the recent advancements, many alternative fillers have emerged like: carbon nanotubes, graphene, layered silicates, and metal organic frameworks (MOFs) with numerous desired properties [26].

A new review done by Yin and Deng [28] specified four types of MMMs depending on the structure and filler location in the hybrid membrane structure; these include thin film nanocomposite, conventional nanocomposite, thin film composite with nanocomposite substrate, and surface located nanocomposite. In this context, the MMM will be discussed based on their filler type. In this regard, MMM have three main categories: inorganic filler-based MMMs, organic filler-based MMMs, biofiller-based MMMs and hybrid filler-based MMMs [29].

3.2.1. *Inorganic filler based MMMs*

In this case, the inorganic fillers get attached to the support materials via covalent bonds, van der Waals forces or hydrogen bonds. These fillers are made via processes like sol gel, ion sputtering, thermal plasma synthesis, flame synthesis, mechanical alloying/milling, and electrodeposition. These adsorptive materials significantly improve the performance of the membrane. For instance, it was shown that the addition of ZnO particles in polyether sulfone (PES) membranes improved dye rejection from 47.5% to 82.3% [30]. Also, Goh et al. [31] added graphene oxide layers on polyamide imide (PAI) or polyether imide (PEI) hollow fiber membrane through the instant dip coating technique for salt and divalent ions removal from water. In addition to using it with PES membranes as nanoplates for the removal of dyes with a rejection of 99% [32]. This high efficiency is due to the improved hydrophilicity because of the acidic groups (e.g., carboxylic acid and hydroxyl) affixed on the surface accompanied by adding graphene oxide to the polymer membrane [29]. The advantages of using this type of adsorptive membrane include improving flux, selectivity, disinfection purposes, and preventing membrane fouling [29].

3.2.2. *Organic filler based MMMs*

These advanced adsorptive membranes contain organic fillers like cyclodextrin, polypyrrole, polyaniline (PANI), and chitosan beads added by the methods of blending and phase inversion. They are more preferred than inorganics as they have more functional groups attached to them making them more adaptable and capable to attach themselves to the substrate through chemical reactions. Moreover, they successfully bound themselves with hydrophobic surfaces producing antifouling, highly

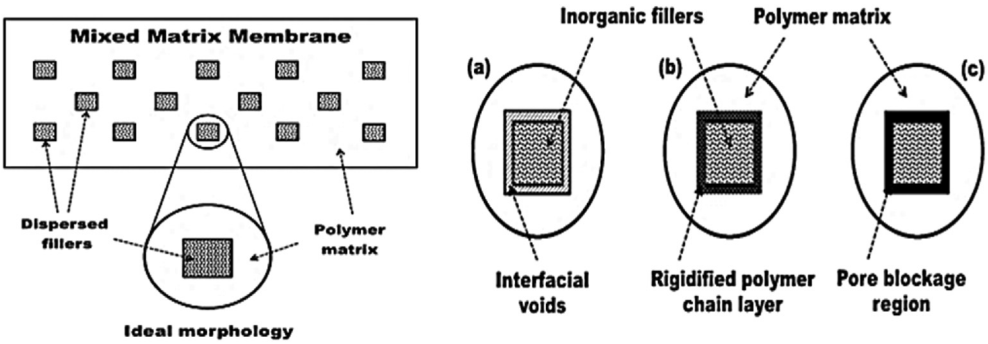

Fig. 3. Schematic diagram with ideal and non-ideal MMM structures [39].

hydrophilic adsorptive membranes. For example, PANI nanofibers were blended to produce synthesized nanocomposite membrane in polysulfone polymer, resulting in a membrane with better permeability, antifouling capacity, and water flux [33]. This type of membrane was successfully employed in the removal of certain types of proteins from water called BSA (Bovine serum albumin) [33].

In addition, an adsorptive membrane was prepared from blended β-cyclodextrin polyurethane into polysulfone matrix for removal of Cd^{+2} ions from water. The addition of this organic filler to the membrane increased the permeability by facilitating wider pores on the surface, higher hydrophilicity, and higher cadmium rejection that reached up to 90%. However, some drawbacks were reported in this technique due to the rougher and less mechanically stable mixed matrix membrane which should be avoided [34].

3.2.3. *Biomaterial-based MMMs*

Using biomaterials in adsorptive mixed matrix membrane is a new technology that has shown promising results due to high permeability, antifouling property, and mechanical reinforcement effect. Several biomaterials were considered for the removal of several pollutants from wastewater. For example, aquaporin filler in amphilic triblock polymer vesicles were investigated for the removal of urea, glucose, glycerol and salt from water [35]. The use of plant waste as biofiller in polyethersulfone to produce an adsorptive mixed matrix membrane used for the removal of cationic dyes from water was reported [36]. Three kinds of plant wastes, including tea waste, banana peel, and shaddock peel were used with a rejection that reached up to 95% [36].

3.2.4. *Hybrid filler based MMMs*

Hybrid filler based MMMs represent the latest mixed matrix membrane technology where two fillers (independently or in composite) are added to the continuous phase [37]. For instance, Daraei et al. [37] studied the combination of iron (II, III) oxide and polyaniline in polyethersulfone matrix to achieve 85% of Cu (II) removal from water with excellent reusability and durability. In addition, the novel hybrid material chitosan-montmorillonite was distributed in polyethersulfone matrix as nanosheets for the removal of dyes from wastewater discharge with high flux recovery that reached about 92% and enhanced mechanical properties [38].

As mentioned earlier, to maintain the UF performance, nanoadsorbents content in the matrix should be less than 6 wt % to prevent the formation of leaky interfacial voids and defects. However, the main problem was the unsatisfactory adsorption capacity. Another issue for the mixed matrix membrane was the rigidified polymer layer covering the surface of nanoadsorbents that can decrease the number of adsorption active sites and hinder the performance [39]. The preceding problems led to developing other type of adsorptive membranes following their preparation techniques, these membranes are discussed below.

4. New trends on adsorptive membranes preparation techniques

4.1. *Pore-filled adsorptive membrane*

This type was developed to overcome the disadvantages of the mixed matrix adsorptive membrane (MMM). It basically depends on trapping nanostructured adsorbents into the finger-like pores of UF membranes, instead of the membrane matrix blending. This resulted in simultaneous removal of several contaminants from water due to the dual functions of rejection and adsorption. For instance, in hollow porous Zr(OH)x nanospheres were added to the finger-like pores of polyethersulfone membrane preserved by polydopamine coating [39]. This membrane showed good adsorption efficiency for lead ions simultaneously with the removal of colloidal gold and polyethylene glycol (PEG). Moreover, it showed ease in reusability and regeneration with no comprising in the mechanical strength, yet lower permeability than MMMs [39]. This adsorptive membrane was synthesized by two processes: Firstly, the hollow porous nanospheres were inserted in the finger-like pores during reverse filtration, and secondly the polydopamine coating which was used to seal it in the cavities of the UF membrane. This results in a membrane with adsorption ability and ultrafiltration properties [39]. Fig. 4 compares schematically the blend membrane formed from nano adsorbents (hollow porous Zr(OH)x nanospheres (HPZNs) embedded in the membrane matrix (polyether sulfone PES), and the dual-functional ultrafiltration (DFUF) membrane of the type pore-filled adsorptive membrane. In addition, the figure presents the pure virgin PES membrane without the adsorbent, and after the loading.

4.2. *Surface adsorptive membrane*

Surface adsorptive membranes are the membranes in which the adsorbent particles are added to their surfaces by different means and can

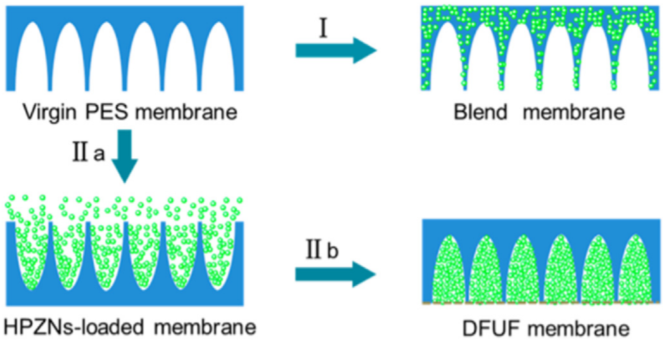

Fig. 4. Schematic representation of the two types novel adsorptive membranes. The UF membrane designs starting with Virgin polymer UF membrane (polyether sulfone-PES) and a traditional blend membrane are both synthesized through a one-step casting method (I) or a 2-step method (II) to form DFUF membrane [57].

be further subcategorized into four types. These methods include coating, depositing, grafting, and assembling. They are characterized by their excellent adsorption capacity and short equilibrium time [5].

The surface coated adsorptive membrane is prepared by two steps. Firstly, the adsorbent particles get stacked on the membrane surface by dipping and filtering, then coated by the polymer layer by crosslinking or coating [40]. This may provide better adsorption capacity and contaminants removal efficiency than MMMs. It also called the sandwich structure [41]. On the other hand, the surface-deposited adsorptive membranes can be produced by filtration deposition which leads to produce a highly ordered layered graphene oxide membrane [42].

The surface-grafted adsorptive membranes are fabricated by grafting or by the photo-induced postsynthetic polymerization technique which relies on immobilizing the adsorbents on the membrane surface by a covalent link. The photo-induced postsynthetic polymerization method has advantages such as enhancing the chemical and physical interface interactions between the material and the membrane. While avoiding the formation of voids is a big challenge in MMMs. This type of membrane was studied for the removal of Cr(VI) from water, as it improved the interaction between metal-organic framework particles and the polymer chains in the membrane [43]. However, it suffers limitations in applications, complications in the process, and harsh reaction conditions [5].

The surface assembled adsorptive membrane is fabricated by assembling polyelectrolyte using electrostatic interaction. This technique depends on alternating electrostatic adsorption of polyanions and polycations onto porous substrates utilizing the layer-by-layer approach [44]. For instance, polyethersulfone ultrafiltration membranes can be modified by a thin polyelectrolyte multilayer film via varying deposition of poly(allylamine hydrochloride) and poly(acrylic acid) [44]. This type can suffer from detachment of the assembly layer during functioning which is also a drawback of the surface-deposited adsorptive membranes [5]. To sum up the adsorptive membrane types mentioned, Fig. 5 illustrates schematic representation of the way the adsorptive material is added to the membrane.

5. Fabrication methods of adsorptive membranes

This section is devoted to describe the various fabrication methods of adsorptive membranes. It also gives detailed description of the main features and uses. Several examples and major findings in the literature are also presented. Table 1 shows detailed summary for these techniques, uses and examples.

6. Future trends and challenges

The use of adsorptive membranes' technology has some issues and challenges that need attention from the research community. These may include, but not limited to:

- Fouling has been a serious problem in the membrane industry for so long. Solutions to overcome this issue include incorporation of antifouling nanoparticles, surface modification, and processing (post or pre-treatment). As blending with nanoparticles, improves the antifouling properties significantly [57]. However, future research should focus on preventing the regeneration of microbial colonies on membrane surface and reducing the leaching of the filler.
- Identifying and developing new filler materials is still a challenge in adsorptive membranes industry. As the advancements in this field reached a high level and many filler materials are found and studied yet accompanying problems with that occur. For instance, their availability, usage practicality, cost, stability, agglomeration, and interfacial contact are always a great concern when putting these materials in application [29].
- Ensuring the safety and nontoxicity of the adsorptive material added to the membrane is a challenge. Some fillers have a toxic nature and applying them in water purifications results in toxic water. Therefore, any water treatment application should be free from any risk to humans or the environment. This can be done by conducting multiple tests and experiments to assess the quality of the water produced, its

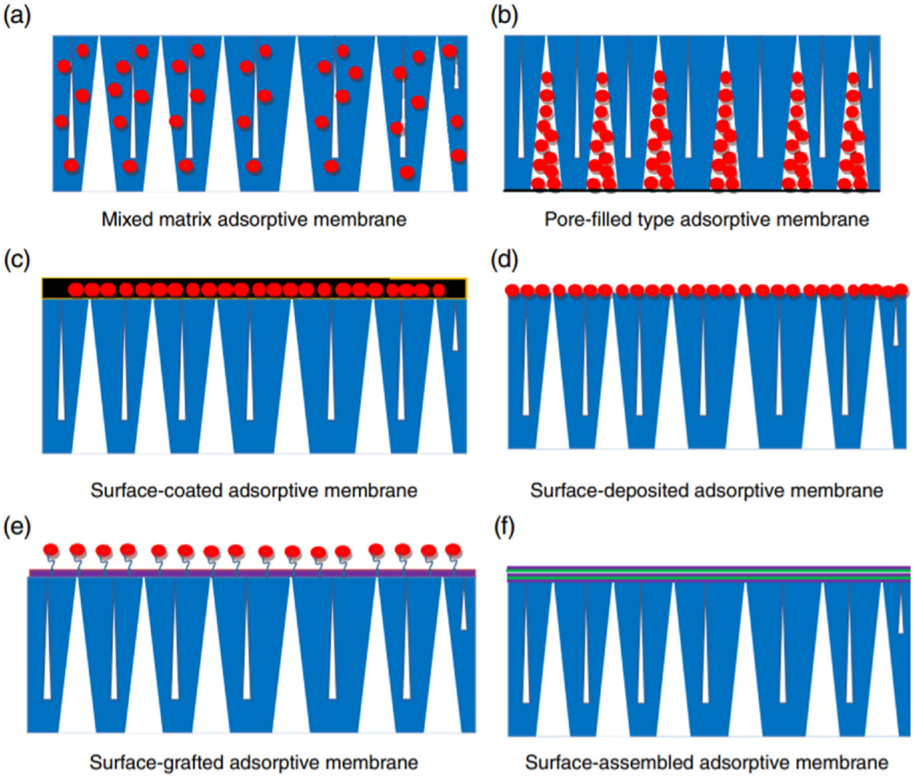

Fig. 5. Schematic representation of different types of adsorptive membranes [6].

Table 1
Summary for fabrication techniques.

Technique	Main Features	Uses	Description	Examples
Blending and Coating	Physical adsorption of blended polymer onto the surface and depositing the hydrophilic layers [45].	Used commonly in fabricating mixed matrix membranes especially chitosan membranes [45].	Done by dispersing the filler into the solvent using ultrasonic bath or with stirring where the polymer is added. Then the cast solution is cast on a flat surface and dried by evaporation of solvent [25].	1) N,O–carboxymethyl chitosan blended with cellulose acetate to fabricate nanofiltration membranes [46]. 2) Fe_3O_4 blended PES membrane [3].
Grafting	Fixing organic adsorbents on the polymeric membrane surface [5].	Used to prepare chelating microfiltration membranes [5].	Grafting on surfaces methods include: plasma treatment, UV irradiation and ozone [5].	1) Polypropylene hollow fiber membrane grafted with polyacrylamide polymer brush by surface-initiated atom transfer radical polymerization [47].
Assembling	Assembling layer by layer of cationic and anionic polyelectrolyte [44].	Fabricating mixed matrix membranes with improved permeability due to the increase in hydrophilic property, mean pore size, and overall porosity [48].	At normal conditions, the polymeric membrane is a negative porous support that adsorbs cationic polyelectrolyte by electrostatic attraction [44].	1) Ultrathin layer on a modified Torlons hollow fiber support was utilized with the layer-by-layer assembly to get the composite membrane used in removing Pb, Ni, and Zn ions [49].
Composite Membranes	A composite is a mixture of immiscible additives with polymeric components [50].	Used to produce membranes with high adsorption capacity, fast kinetics, reduced fouling, promising reactivity, and flexibility [51].	Adding micro or nanomaterial in membrane's structure on the surface or dispersed in the matrix [50].	1) A hybrid membrane fabricated by coating activated carbon fibers/chitosan/TiO_2 solution on a terylene fiber via a multi-step chemical grafting technique [51]. 2) A bio-composite membrane adsorbent synthesized by cellulose nanocrystals (CNCs) as functional sites in a chitosan matrix by freeze-drying technique [7].
Imprinting	Introducing synthetic receptor locations in membrane matrix that recognize, remember, and identify the target species among others available in the solution [2].	Used to obtain selective membrane adsorbents to overcome the issues in selectivity resulting from limited specific binding capacity [2].	Specialized configured voids are added to the polymer by inserting the target while preparing the membrane, then immediately leaching it to vacate the active sites [2].	1) Shawky [52] prepared ion-imprinted membranes from crosslinking chitosan (CS), PVA, and blend chitosan/PVA using glutaraldehyde (GA) as crosslinker for selective removal of Ag(I) ions.
Phase inversion and solution Casting	Membranes synthesis using polymer-solvent mixture to form a homogeneous solution at specific conditions of temperature and composition which separates if these conditions change [27].	Better dispersion of fillers, excellent interaction between the matrix and the filler, and uniform merging of polymer and adsorbent [53].	It can be done by evaporating a volatile solvent from the homogenous solution or via cooling a casting solution [27]. Phase inversion can entrap nanomaterials within the matrix where they get blended and dispersed in a polymer dope solution [54].	1) Chitosan–Montmorillonite nanosheets prepared by phase inversion with better antifouling nature and higher flux recovery ratio [38].
Electrospinning	A high voltage-driven process which creates an electric field that induces the electrostatic repulsion forces which shatters the polymer surface tension and stretches its droplets to form solid continuous nanofibers [55].	Used to synthesize Nanofibrous membranes with improved efficiency, and excellent removal capacity for heavy metals and organic pollutants [56].	Electrospinning is a high voltage-driven process which uses a pump equipped with a nozzle-fitted syringe, a spinneret, an electric current source, and a counter electrode or grounded target. Applying high voltage creates the electric field and the droplet at the nozzle takes a cone-shaped deformation. When the charged jet accelerates toward the collector, the solvent evaporates and the nanofibers [55].	1) Different fiber diameters for pure chitosan nanofibrous membranes were prepared to absorb acid blue-113 dye [56]. 2) Citosan/cellulose acetate blend hollow fiber adsorptive membranes were prepared by wet spinning [11].

eligibility to be consumed by humans, or its safety to be discharged to the aquatic environment.

- Developing novel materials for mixed matrix membranes is still a big challenge, as many materials so far have been only tested on a laboratory scale and need further investigation. Many novel materials could not penetrate to the market due to their high prices or expensive synthesis processes, hence, investigating cheaper materials for adsorptive membranes could be a potential research area. This is a great opportunity for agro-industrial waste, clays, and nanotechnology to be used for this purpose due to their high adsorptive capacity and excellent performance.
- Finding new processes for membranes fabrication: As many materials are being discovered and investigated, the limitation associated with fabricating the material is restricting the usage of many promising adsorptive membranes. Current processes are not capable of producing defect-free membranes even on laboratory scales, therefore new techniques to can be developed to attain the required interface and binding between the adsorptive material and the membrane without affecting the performance. In addition, to finding the required processes that enables the scaling up of novel membranes [58]. The work done on adsorptive membranes is still at the level of laboratory-based studies or targeted investigations, therefore finding fabrication techniques to produce adsorptive membranes on a larger industrial scale is still a challenge. In addition, challenges can be faced in approximating the lifespan of the adsorptive membranes, their reproducibility, reusability, and the adsorbent material regeneration.
- Developing models for the new adsorptive membranes, as thorough research is required to determine the morphology and unique characteristics of the filling adsorptive material in the membrane. Such models need to be developed to predict the membrane performance.

7. Conclusions

The use of adsorptive membranes in wastewater treatment is a promising technology that combines the advantages of adsorption and membrane filtration techniques. They have proved their efficiency in removing various emerging contaminants from water over the years. In addition, the diversity in the types and materials used is advantageous for adsorptive membranes application. However, applying adsorptive membranes have many challenges associated with fabricating them, ensuring their safety to humans and the environments, as well as scaling them up to industrial applications. Therefore, future research should be focused in overcoming these challenges to be able to utilize adsorptive membranes in the water treatment fields efficiently.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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