ABSTRACT

The presence of pharmaceutically active compounds (PhACs) in drinking water sources is a serious global challenge. Although several approaches have been made to overcome the challenge, unfortunately, most wastewater treatment processes still lack the capacity to provide water completely free of PhACs. This review reports the use of nanocomposite membranes as a promising material for the efficient removal of PhACs from the water system. The study revealed that fouling and high energy consumption—the major associative limitations of conventional membranes, can be circumvented by incorporating metal oxides and carbonaceous nanoparticles into nanocomposite membranes. Interestingly, photocatalytic nanocomposite membranes exhibited the additional benefit of complete degradation of PhACs. Therefore, it is essential to focus future studies on understanding the details of the photocatalytic nanocomposite membrane process. Furthermore, conducting more studies on a large scale, cost evaluation, and toxicity profiling of nanocomposite membranes is vital.

Keywords: nanocomposite membrane; water; PhACs; nanomaterials

1. Introduction

The continuous consumption of pharmaceutical products is the main contributor of pharmaceutically active compounds (PhACs) to the environment[1–4]. Although PhACs are found in small concentrations (ranging from ng L\(^{-1}\) to µg L\(^{-1}\)) in the environment, they may bioaccumulate to become toxic[5]. Their metabolites may be of serious health and environmental concern[6,7]. Table 1 presents the chemical profile of some selected PhACs.

Many of these PhACs have been detected in environmental water systems, effluents emerging from wastewater treatment plants (WWTP) and drinking water. The presence of PhACs could pose danger not only to public health but also aquatic system[16]. They are relatively stable and are not totally assimilated by the human and animal body system when used[17]. Therefore, they are not fully metabolized and are excreted from the body in body fluids and stools, from which PhACs get into the environment[18]. Other sources have been attributed to improper disposal of expired drugs and pharmaceutical wastes, run-off from veterinary and abattoirs, and domestic wastes[19–21]. Commonly used drugs like cotinine, caffeine, and acetaminophen have been reported in drinking water[22]. Studies have revealed that some of these PhACs may be linked to neurophysiological effects and mutagenic and carcinogenic consequences[23,24]. PhACs have been reported in drinking...
water sources with potential risks\cite{25–27}. The risk is higher in aquatic organisms than in humans because the concentrations reported in drinking water are trace amounts compared to those in environmental water systems\cite{28–30}. Some of the previously reported toxicological impacts of some PhACs are shown in Table 2. It is crucial to prevent PhACs from entering environmental water systems, especially drinking water sources, because of their associated risks.

### Table 1. Chemical profile of some selected commonly used PhACs.

<table>
<thead>
<tr>
<th>Class</th>
<th>PhAC</th>
<th>(pKa)</th>
<th>(m/z)</th>
<th>(\log K_{ow})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antibiotics</td>
<td>Levofloxacin</td>
<td>6.24, 8.74</td>
<td>362.143</td>
<td>−0.39</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>5.7</td>
<td>254.059</td>
<td>0.89</td>
<td>[8–10]</td>
</tr>
<tr>
<td></td>
<td>Norfloxacin</td>
<td>6.34, 8.76</td>
<td>320.141</td>
<td>0.46</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Ciprofloxacin</td>
<td>6.38</td>
<td>332.141</td>
<td>0.4</td>
<td>[8,10–13]</td>
</tr>
<tr>
<td></td>
<td>Erythromycin</td>
<td>8.8–8.9</td>
<td>734.5</td>
<td>3.06</td>
<td>[8,10–13]</td>
</tr>
<tr>
<td></td>
<td>Ofloxacin</td>
<td>5.97, 9.28</td>
<td>362.151</td>
<td>−0.39</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Azithromycin</td>
<td>8.74</td>
<td>749.519</td>
<td>4.02</td>
<td>[8]</td>
</tr>
<tr>
<td>Analgesic</td>
<td>Ibuprofen</td>
<td>4.9</td>
<td>207.138</td>
<td>3.97</td>
<td>[8–11,13,14]</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>4.2</td>
<td>229.085</td>
<td>3.18</td>
<td>[8,10,11,13,14]</td>
</tr>
<tr>
<td></td>
<td>Codeine</td>
<td>10.6</td>
<td>415.379</td>
<td>1.19</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Paracetamol</td>
<td>9.4</td>
<td>152.071</td>
<td>0.46</td>
<td>[8–11,13,14]</td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>4.2</td>
<td>296.024</td>
<td>0.70</td>
<td>[8–11,13,14]</td>
</tr>
<tr>
<td>Stimulant</td>
<td>Caffeine</td>
<td>10.4</td>
<td>194</td>
<td>−0.07</td>
<td>[8–11,15]</td>
</tr>
<tr>
<td></td>
<td>Paraxanthine</td>
<td>8.5</td>
<td>181.07</td>
<td>1.17</td>
<td>[8]</td>
</tr>
<tr>
<td>Hormones</td>
<td>Estriol</td>
<td>10.54</td>
<td>287.165</td>
<td>2.45</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>17-β Estradiol</td>
<td>10.46</td>
<td>271.170</td>
<td>4.01</td>
<td>[8–10,13]</td>
</tr>
<tr>
<td></td>
<td>Estrone</td>
<td>10.34</td>
<td>269.155</td>
<td>3.13</td>
<td>[8–10,13]</td>
</tr>
<tr>
<td>B-blockers</td>
<td>Diltiazem</td>
<td>8.06</td>
<td>415.169</td>
<td>2.70</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Atenolol</td>
<td>9.6</td>
<td>267.170</td>
<td>0.16</td>
<td>[8–10,13]</td>
</tr>
</tbody>
</table>

### Table 2. Toxicological impact of some selected PhACs.

<table>
<thead>
<tr>
<th>PhAC</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>Hinders the growth of human embryonic stem cells.</td>
<td>[31–33]</td>
</tr>
<tr>
<td></td>
<td>Toxic to aquatic systems</td>
<td></td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>Toxic to aquatic system</td>
<td>[33,34]</td>
</tr>
<tr>
<td>Caffeine</td>
<td>Promotes anxiety and panic disorders among humans.</td>
<td>[33,35]</td>
</tr>
<tr>
<td></td>
<td>May also cause cancer</td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>Causes cytological changes in the liver, kidneys, and \</td>
<td>[13,33]</td>
</tr>
<tr>
<td></td>
<td>gills of fishes. Reduces the hematocrit values of fishes.</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Hinders postembryonic development among amphibians.</td>
<td>[13,33,36,37]</td>
</tr>
<tr>
<td></td>
<td>Causes reproductive system of aquatic organisms.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Causes gastric ulceration, dyspepsia, bowel inflammation, mucosal \</td>
<td></td>
</tr>
<tr>
<td></td>
<td>damages, and cardiovascular dysfunction</td>
<td></td>
</tr>
<tr>
<td>Erythromycin</td>
<td>Causes damages to liver metabolic processes of fishes.</td>
<td>[38]</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>Causes cardiovascular and neural problems among humans.</td>
<td>[33,39]</td>
</tr>
<tr>
<td></td>
<td>Highly toxic to aquatic organisms.</td>
<td></td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>May damage immune system of humans and aquatic \</td>
<td>[33,40]</td>
</tr>
<tr>
<td></td>
<td>organisms</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. (Continued).

<table>
<thead>
<tr>
<th>PhAC</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraxanthine</td>
<td>Increases the diastolic blood pressure, free fatty acids, and plasma epinephrine levels. It stimulates the sympathetic nerves and hampers the sympathetic nervous system.</td>
<td>[41]</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Promotes the spread of antibiotic-resistant microorganisms.</td>
<td>[33,42]</td>
</tr>
<tr>
<td>Naproxen</td>
<td>Toxic to aquatic organisms</td>
<td>[13,33]</td>
</tr>
<tr>
<td>Codeine</td>
<td>Dangerous to aquatic organisms may cause increase in plasma concentrations</td>
<td>[43]</td>
</tr>
<tr>
<td>Estriol, Estrone and Estradiol</td>
<td>Manipulates the sexual and reproductive systems of fish and humans. Causes birth defects, abnormal sexual development, and cancer. Affects the nervous system and the immune system.</td>
<td>[33,44,45]</td>
</tr>
<tr>
<td>Paracetamol</td>
<td>Leads to the formation of hepatotoxic metabolites and affects the liver.</td>
<td>[13,33,40]</td>
</tr>
</tbody>
</table>

Despite the attempts by WWTP to remove impurities in water systems, most adopted methods still cannot effectively remove PhACs from water. However, membrane processes such as microfiltration (MF), nanofiltration (NF), reverse osmosis (RO), and ultrafiltration (UF) have been used extensively for purification of polluted water systems. These processes are preferred in water purification due to ease of operation, high separation efficiency, and space efficiency [17,46]. Previous studies revealed the suitability of RO and NF membranes for removing PhACs in water systems [47,48]. Unfortunately, fouling and high energy consumption have been the major limitations of using membranes in water treatment [48,49]. Efforts have been made to circumvent this problem, one of which is the inclusion of nanomaterials into the polymeric structure of the membranes. Including metal oxide-based materials and carbon-based nanomaterials can help improve the polymeric matrix and surface performance of membranes, making them favourable for removing PhACs during water treatment. A surface performance like the ability to function as a photocatalyst may be enhanced with metal oxides like TiO₂, ZnO, Fe₂O₃, MO₂, SnO₂, etc. Similar performance is also possible with the inclusion of carbon-based photocatalysts like graphitic carbon nitride (gC₃N₄).

Carbon-based materials like graphene, activated carbon (AC), carbon nanotube (CNT) and other functionalized materials have been used to improve the adsorption capacity, permeability and selectivity exhibited by membranes [50,51]. Zeolite nanoparticles have shown the ability to improve membrane performance for removing PhACs [50] while TiO₂ has demonstrated capacity towards metoprolol, sulfamethoxazole and triclosan removal [52]. A study also showed enhanced antifouling and photocatalytic tendencies towards diclofenac and ibuprofen [49].

Beyond any doubt, membrane technology has shown potentials for water treatment with the potential for removing PhACs in an aqueous solution. However, there is the limitation of fouling and high energy requirement, which is currently receiving attention with the development of methods to circumvent the challenge. One of the presently considered approaches is using nanocomposite membranes as an improved means of removing PhACs from the water system. Therefore, this study aims to understand and review the development of nanocomposite membranes that demonstrate good performance to remove pollutants particularly PhACs from water.

2. Conventional water treatment methods for PhACs

Methods involving wetlands treatment, biological treatment, adsorption, coagulation, flocculation, photocatalysis, oxidation, electrochemical, photolysis, and ozonation are conventionally used in water treatment [53]. Many of these methods need to be improved. For example, biological treatment cannot
completely biodegrade many of the PhACs such as carbamazepine, bezafibrate, and clofibric acid\textsuperscript{[17,29]}. Most wastewater treatment plants adopt adsorption as a posttreatment step after biological treatment, and in some cases, an advanced approach may be required for complete water purification. The cost of adsorbents and energy consumption limit the use of adsorption. The adsorption process has effectively removed polar PhACs\textsuperscript{[54]}; however, the efficiency is reduced in the presence of dissolved organic matters (DOMs) in a complex water matrix\textsuperscript{[17]}. Ozonation is considered a secondary treatment\textsuperscript{[55]}; unfortunately, ozonation of PhACs is challenged by the formation of toxic intermediates and high energy consumption. However, catalytic ozonation has been used as an efficient method to ensure an advanced oxidation process to achieve complete oxidation or conversion of any toxic intermediate to small molecules like CO\textsubscript{2} and H\textsubscript{2}O\textsuperscript{[56,57]}. Adding a catalyst to the ozonation process improves the degradation process by generating free radicals to facilitate the complete removal of organic substances.

Constructed wetlands approaches have served as practical means of water purification for years. Aquatic plant-based materials are used as alternatives to wastewater treatment plants for water purification. The process is inexpensive, easy to set up, eco-friendly and easy to maintain\textsuperscript{[58]}. The approach may involve biological and microbiological water treatments. Compared to other methods, the design and performance are highly varied based on simple models; unfortunately, most mechanistic models are limited. This approach has been used to treat wastewater contaminated with PhACs\textsuperscript{[59,60]}. It is mainly used as a secondary treatment step and sometimes called a black box without sufficient capacity to completely remove PhACs in water systems\textsuperscript{[60,61]}. With recent advancement in technology wetland approach now includes sorption, biological degradation, and photodegradation giving rise to efficiency that depends on the design and operational factors\textsuperscript{[58,62]}. Previous designs have shown higher efficiency for removing clarithromycin, ketoprofen, sulfamethoxazole, trimethoprim, and naproxen than ibuprofen and amoxicillin\textsuperscript{[60]}.

Membrane technology is commonly used as an effective separation process in water purification. Based on the process driving force, the membrane can be classified into pressure-driven, concentration-driven, electrical potential gradient-driven, and temperature gradient-driven operations, as shown in Figure 1.

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{membrane_operations.png}
\caption{Classification of membrane process operations.}
\end{figure}
\end{center}

This review is focused on pressure-driven membrane operations. Separation is achieved by making use of a pressure-driven filtration process. The membranes used for the separation process may be made of organic or inorganic materials or combined of both. The organic membranes may be produced from cellulose acetate (CA), polyethylene (PE), polypropylene (PP), polyethersulfone (PES), polysulfone (PSF), poly(vinylidene...
fluoride) (PVDF), polyamide (PA) and poly(vinyl alcohol) (PVA) while the inorganic membranes may be produced from silica, ceramics, metal oxides, zeolites, etc. The membrane process has shown high potential for removing PhACS from water systems\[63\]. The pressure-driven membranes are the most used in water treatment. The characteristics of the four most common types (MF, UF, NF, and RO) of pressure-driven membranes are shown in Table 3.

### Table 3. Some properties of pressure-driven membranes.

<table>
<thead>
<tr>
<th>Pressure-driven membrane type</th>
<th>Molecular weight cut off (kilo Dalton)</th>
<th>Pressure required (bar)</th>
<th>Average permeability (L m$^{-2}$ h bar)</th>
<th>Retained diameters (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>0.2–2</td>
<td>15–75</td>
<td>5–10</td>
<td>10$^{-4}$–10$^{-3}$</td>
</tr>
<tr>
<td>NF</td>
<td>2–20</td>
<td>5–20</td>
<td>10–20</td>
<td>10$^{-3}$–10$^{-2}$</td>
</tr>
<tr>
<td>UF</td>
<td>20–150</td>
<td>1–5</td>
<td>150</td>
<td>10$^{-3}$–1</td>
</tr>
<tr>
<td>MF</td>
<td>100–500</td>
<td>&lt;1</td>
<td>500</td>
<td>10$^{-1}$–10</td>
</tr>
</tbody>
</table>

RO is commonly used for water treatment, especially removing PhACs from the water system\[64,65\]. The different pressure-driven membrane processes are often combined in a treatment process to improve process efficiency. In most cases, MF, UF and NF are preferably used as pretreatment step before RO, which reduces fouling and help in maintaining constant flux\[63\]. The pretreatment approach is mainly referred to as multi-barrier treatment.

### 3. Membrane filtration for PhACs

The membrane filtration process requires low or no chemicals, which makes it a favourable potential technique that may bridge the present gap in water treatment processes\[66\]. Although there are still challenges to the high cost of a membrane with respect to UF, high energy consumption, irreplaceability of membrane (like in the case of RO) and fouling\[63,67,68\], membrane filtration remains a formidable technique for the removal of PhACs in water systems. The different types of membranes used in other countries are presented in Table 4.

### Table 4. Pressure-driven membranes used for water treatment in different countries.

<table>
<thead>
<tr>
<th>Type</th>
<th>Water source</th>
<th>Country</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity driven UF</td>
<td>Ground water</td>
<td>South Africa</td>
<td>[69]</td>
</tr>
<tr>
<td>MF</td>
<td>Black water</td>
<td>Egypt</td>
<td>[70]</td>
</tr>
<tr>
<td>UF</td>
<td>Reservoir</td>
<td>China</td>
<td>[71]</td>
</tr>
<tr>
<td>UF</td>
<td>Songhuajiang river</td>
<td>China</td>
<td>[72]</td>
</tr>
<tr>
<td>NF</td>
<td>Freshwater</td>
<td>Thailand</td>
<td>[73]</td>
</tr>
<tr>
<td>UF</td>
<td>Surface water and ground water</td>
<td>Malaysia</td>
<td>[74]</td>
</tr>
<tr>
<td>NF and RO</td>
<td>Pesticide contaminated surface water</td>
<td>India</td>
<td>[75]</td>
</tr>
<tr>
<td>NF</td>
<td>Ground water</td>
<td>Sri Lanka</td>
<td>[76]</td>
</tr>
<tr>
<td>RO and NF</td>
<td>Sea water</td>
<td>Turkey</td>
<td>[77]</td>
</tr>
<tr>
<td>RO</td>
<td>Brackish water</td>
<td>Brazil</td>
<td>[78]</td>
</tr>
<tr>
<td>UF and MF</td>
<td>Surface water</td>
<td>Netherland</td>
<td>[79]</td>
</tr>
<tr>
<td>MBR</td>
<td>Industry</td>
<td>Germany</td>
<td>[80]</td>
</tr>
<tr>
<td>UF and RO</td>
<td>Ground water</td>
<td>Australia</td>
<td>[81]</td>
</tr>
</tbody>
</table>

NF = nanofiltration, UF = ultrafiltration, RO = reverse osmosis, MBR = membrane bioreactor, MF = microfiltration.

NF and RO are the two most common membrane processes used globally for water treatment with respect to PhACs removal from water due to their small molecular weight cut-off (MWCO)\[82\]. Studies have shown
the use of membrane filtration to remove PhACs in water\textsuperscript{83–85}. The large MWCO limits the use of UF and MF to remove PhACs\textsuperscript{86}. Unfortunately, some authors argued that NF and RO membranes might not be so convincingly outstanding for removing PhACs from the solution. An example is the PES NF membrane’s inefficient performance in removing ibuprofen, carbamazepine, and diclofenac from drinking water\textsuperscript{87}. Furthermore, another study revealed that the charge and molecular size of PhACs and membranes have a role in the efficiency of membranes during the removal process\textsuperscript{87,88}. A previous study has shown that the performance of RO depends on the membrane used and the physicochemical properties of target PhACs\textsuperscript{89,90}.

Over time, process modification led to using a membrane bioreactor (MBR), a solid-liquid separation without a secondary clarifier. The process combines activated sludge treatment with UF or MF\textsuperscript{91}. The membrane is usually integrated or connected externally to the reactor. The process is challenged with fouling due to biofilm deposited on the surface of the membrane during the treatment process\textsuperscript{92}. MBR has brought tremendous improvement in removing PhACs in water; it remains a current method for water treatment and a method for the future that can be improved by a modification to enhance performance. MBR has shown high efficiency towards certain classes of PhACs\textsuperscript{93,94}. This is because MBR combines the biodegradation process and the activated sludge process. The biodegradation process depends on factors which may not be directly related to the design or configuration of the reactor\textsuperscript{91}. Most reactors are connected to RO or NF to boost performance\textsuperscript{84,95}. The kind of membrane connected to the reactor plays a vital role in the overall performance of the reactor. Despite the success achieved so far, there is a need to improve the performance of the membrane separation system in the MBR system. Several improvement techniques have been developed; however, nanocomposite membranes show outstanding performance and improvement\textsuperscript{96} that may be implemented along with MBR. Therefore, attention should be given to improving high energy consumption, fouling, selectivity, permeability, useability, and membrane modules.

Nanotechnology has shown the capacity to circumvent the challenges identified with the membrane filtration process. The approach has superior properties such as a large surface area for adsorption, tunable size to control fouling, high thermal and chemical stability, and functional groups that may enhance interaction with PhACs for removal via electrostatic interaction, \(\pi-\pi\) stacking, van der Waals interaction or hydrophobic interaction\textsuperscript{17,85,97}. Nanocomposite has been used as material for membrane modification to further improve membrane performance. The incorporated nanoparticles in the membrane may enhance permeability, fouling resistance, mechanical and thermal stability, and shelf life.

### 3.1. Nanocomposite membranes for PhACs removal in water

Nanoparticles are useful resources for the detection of PhACs in water\textsuperscript{98}. Different studies have reported the inclusion of nanocomposite in the membrane during preparation to improve efficiency\textsuperscript{96,99}. Many authors achieved this by increasing the amount of nanomaterial they include in the polymeric or inorganic structure of the membrane. Nanomaterials used in such cases include metal oxide nanoparticles (TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, ZnO, SnO\textsubscript{2}, CuO, zeolite, etc.) and carbonaceous nanoparticles such as graphene oxide (GO), gC\textsubscript{3}N\textsubscript{4}, AC, boron nitride (BN), etc.). When metal oxides are used, they help reduce fouling, improve surface hydrophilicity, and permeability\textsuperscript{100–102}. The inclusion of metal oxide further improves the thermal and electrical stability of the membrane as well as lowers the negative impact of heat and compaction on permeability\textsuperscript{101–104}. Most of the metal oxide nanoparticles are photoactive and may be photocatalytic; therefore, their inclusion in the membrane structure introduces photoactivity to the membrane, which is an additional benefit of photodegradation of PhACs during water treatment. Including carbonaceous nanoparticles such as functionalized nanomaterials improve the membrane’s surface and internal structure. The surface area is increased, enhancing the membrane’s adsorptive capacity. Selectivity and specificity of the membrane towards target PhACs are further improved.

Like metal oxide nanoparticles, very few carbonaceous nanoparticles are photoactive. Carbon-based nanoparticles like g-C\textsubscript{3}N\textsubscript{4} are photocatalytic\textsuperscript{66}. Effort has been made to develop photocatalytic membranes that
will ensure the complete elimination of PhACs in water systems; in this regard, TiO$_2$-modified membranes have been reported.[105] Imprinting photocatalytic properties into the membrane is an exciting technique receiving global attention. TiO$_2$ is a typical semiconductor metal oxide used, while g-C$_3$N$_4$ and metal-organic framework (MOF) are examples of carbon-based nanoparticles used as a photocatalyst to prepare nanocomposite membranes. When the nanocomposite membrane is exposed to light ($h\nu$), the composite metal oxide produces an electron/hole ($e^−/h^+$) pair that migrates to the surface of the membrane creating reactive oxygen species (ROS) such as hydroperoxyl radical (•OOH), hydroxyl radical (OH), and superoxide anion radical ($O_2^{−}$) in the water system as shown in Figure 2.

![Figure 2](image1.png)

**Figure 2.** Mechanism of photocatalytic degradation of PhACs by (a) metal oxides and (b) functionalized carbon-based nanoparticles.

The ROS promotes the degradation of the PhACs (Figure 2a). The $e^−/h^+$ is produced when $e^−$ is excited from the valence band (CB) to the conduction band (CB) to generate $h^+$. Similarly, $e^−$ may be promoted from the highest occupied molecular orbital (HOMO) of the carbon-based materials (g-C$_3$N$_4$ or MOF) to its lowest unoccupied molecular orbital (LUMO) to produce hole ($h^+$) as shown in Figure 2b, which is similar to the VB and CB of the metal oxides.[106–108]. The advantages and disadvantages of using nanoparticles in preparing nanocomposite membranes are shown in Table 5.

**Table 5.** Comparison of the advantages and disadvantages of some common nanoparticles for membrane modification.

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>High mechanical strength, selectivity, quick sorption kinetics and high capacity</td>
<td>Expensive, potential environmental risks from to leaching</td>
<td>[109,110]</td>
</tr>
<tr>
<td>CNTs</td>
<td>High mechanical strength, selectivity, sorption kinetics and capacity, high hydrophobicity and strong affinity to organic pollutants</td>
<td>Hard to recover, potential environmental risks, high cost</td>
<td>[111,112]</td>
</tr>
<tr>
<td>Metal oxides</td>
<td>High surface area, photocatalytic property, unique magnetic properties that facilitate their recovery, low toxicity</td>
<td>Low sorption capacity</td>
<td>[113]</td>
</tr>
</tbody>
</table>
Table 5. (Continued).

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>High adsorption capacity and kinetics</td>
<td>High cost, instability, potential environmental risks</td>
<td>[114]</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>High mechanical strength, high stability, good adsorption capacity</td>
<td>High cost and toxicity</td>
<td>[115,116]</td>
</tr>
</tbody>
</table>

Different nanoparticles have been identified; however, the nanoparticle used is determined by the desired membrane properties. Similarly, the different membrane modification methods are highlighted in Table 6.

Table 6. Techniques used in membrane modification.

<table>
<thead>
<tr>
<th>Material</th>
<th>Modification method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC/Polyvinyl formal (PVF)</td>
<td>Different concentrations of PVF with PVC dissolved in DMAc</td>
<td>[117]</td>
</tr>
<tr>
<td>PAN-MPDSAH</td>
<td>Acrylonitrile and MPDSAH randomly co-polymerized using AIBN as initiator to form PAN-MPDSAH</td>
<td>[118]</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Casting solution prepared from different blends of NOCC/CA</td>
<td>[119]</td>
</tr>
<tr>
<td>PAN-DMAEMA based zwitterionic copolymer in PAN</td>
<td>Reaction of DMAEMA radical with 1,3-propane sulfone to form zwitterionic copolymer with PAN</td>
<td>[120]</td>
</tr>
</tbody>
</table>

**Sol-gel modification method**

- **PVDF**: TEOS and DI water were added DMF at an adjusted pH to yield SiO$_2$ which was sol doped into PVDF-DMAc solution | [121] |
- **PES**: TET was added to DMAc with appropriate amount of HCl and DI water to yield TET sol-then added to PES-DMAc solution | [122] |
- **PVA**: TEOS added to HCl and DI water to get SiO$_2$ sol-then different concentrations of sol added to PVA/PEG aqueous solution | [123] |
- **PSF**: TBT added to NMP with appropriate amount of HCl and DI water to yield TiO$_2$ sol-then added to PS/PVP-DMAc/NMP solution | [124] |

**Surface modification method**

- **Polysulfone**: UV-initiated grafting polymerization with MPDSAH using benzophenone as photo-initiator | [125] |
- **PES**: ABS/CS polymer blend casted over PES substrate | [126] |
- **PP**: Grafting of ozone-treated PP membrane by HEMA | [127] |
- **Cardo-polyetherketone**: UV-induced grafting with acrylic acid monomer | [128] |

MPDSAH = ([3-(Methacryloylamino) propyl]-dimethyl (3-sulfopropyl) ammonium hydroxide), AIBN = azobis-isobutyro-nitrile, CA = Cellulose acetate, NOCC = N,O-carboxy methyl chitosan, PVDF = Polyvinylidene fluoride, TEOS = Tetraethoxysilane, DI = Deionized, DMAc = N,N'-dimethyl acetamide, TET = Tetraethyltitanate, PES = Polyethersulfone, PVA = Poly(vinyl alcohol), HCl = Hydrochloric acid, PEG = Polyethylene glycols, PSF = Polysulfone, TBT = Tetrabutyllitanate, NMP = N-methyl-2-pyrrolidone, PP = Polypropylene, HEMA = 2-hydroxyethyl methacrylate, PEK-C = Cardo-polyetherketone, ABS = Acrylonitrile butadiene styrene, CS = Chitosan, PVC = Polyvinyl chloride.

The modification methods include polymer blend$^{[129]}$, sol-gel$^{[130]}$, and surface modification$^{[131]}$. The previously reported modifications in the literature are summarized (Table 6). The type of desired membrane property determines the nanoparticle included in the membrane during modification and the modification process to use. Therefore, it becomes difficult to pinpoint the best modification process because the choice modification process depends on the desired membrane properties.

3.2. Metal oxide-based nanocomposite membranes

Metal oxide has played an essential role in the modification of membranes. Apart from the antifouling property, some metal oxides possess magnetic properties which positively impact the membrane, enhancing...
its water flux, and rejection capacity\textsuperscript{[132,133]}. Nanocomposite membranes have also been reported to show enhanced self-cleaning and low toxicity\textsuperscript{[134–137]}. Apart from the recorded achievement with metal oxides in the membrane, their inclusion may cause uncontrolled aggregation (at a high amount of loading into the membrane) because of inorganic-organic incompatibility or inorganic-organic incompatible interactions\textsuperscript{[138]}. Such incompatibility may negatively affect the surface area, permeability, and mechanical stability of the membrane, resulting in reduced effective pore size\textsuperscript{[139]}. Some selected metal oxides and inclusion method in the membrane is shown in Table 7. It is essential to moderate the inclusion of metal oxide in the membrane in the right proportion to avoid agglomeration while attaining maximum water flux and performance\textsuperscript{[138,140]}. It is paramount that the loaded metal oxide in the membrane should not leach out of the membrane during the water purification process. Leaching may cause serious environmental problems, which are undesirable. Currently, research is ongoing on understanding the inclusion process of metal oxide in the membrane and the development of a procedure that will not lead to the leaching of the metal oxide\textsuperscript{[141,142]}.

### Table 7. Selected metal oxide nanoparticles and methods for membrane modification.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>Product formed</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO modified</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethersulfone</td>
<td>Phase inversion</td>
<td>Polyethersulfone-ZnO</td>
<td>[143]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>Vacuum distillation</td>
<td>Poly(vinylidene fluoride)-ZnO</td>
<td>[144]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>Phase inversion</td>
<td>Poly(vinylidene fluoride)-ZnO</td>
<td>[145]</td>
</tr>
<tr>
<td>Polyvinylidene difluoride</td>
<td>Non-solvent induced phase separation</td>
<td>Polyvinylidene difluoride-ZnO</td>
<td>[146]</td>
</tr>
<tr>
<td>Polyethersulfone</td>
<td>dry/wet phase inversion</td>
<td>Polyethersulfone-ZnO</td>
<td>[147]</td>
</tr>
<tr>
<td>TiO\textsubscript{2} modified</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>Covalent bonding</td>
<td>Cellulose-TiO\textsubscript{2}</td>
<td>[148]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>Blending</td>
<td>Polyvinylidene fluoride-TiO\textsubscript{2}</td>
<td>[149]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>adsorption and filtration</td>
<td>Polyvinylidene fluoride-TiO\textsubscript{2}</td>
<td>[150]</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>Impregnation</td>
<td>GO-TiO\textsubscript{2}</td>
<td>[151]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>Impregnation</td>
<td>Polyvinylidene fluoride-TiO\textsubscript{2}</td>
<td>[151]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>Physical deposition</td>
<td>Polyvinylidene fluoride-TiO\textsubscript{2}</td>
<td>[152]</td>
</tr>
<tr>
<td>YSZ/silica</td>
<td>Sol-gel</td>
<td>YSZ/silica-TiO\textsubscript{2}</td>
<td>[153]</td>
</tr>
<tr>
<td>CuO modified</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethersulfone</td>
<td>Dispersion</td>
<td>Polyethersulfone-CuO</td>
<td>[154]</td>
</tr>
<tr>
<td>PSF</td>
<td>Dispersion in phase inversion</td>
<td>PSF-CuO</td>
<td>[155]</td>
</tr>
<tr>
<td>PES</td>
<td>Dispersion in phase inversion</td>
<td>PES-CuO</td>
<td>[156]</td>
</tr>
<tr>
<td>PES</td>
<td>Phase inversion-Immersion precipitaion</td>
<td>PES-CuO</td>
<td>[157]</td>
</tr>
<tr>
<td>PA/PS</td>
<td>Immobilization in PA layer</td>
<td>PA-CuO</td>
<td>[158]</td>
</tr>
<tr>
<td>Thin-Film Composite</td>
<td>Coating</td>
<td>Tin-Film Composite-CuO</td>
<td>[159]</td>
</tr>
<tr>
<td>PES</td>
<td>phase inversion</td>
<td>PES-CuO</td>
<td>[160]</td>
</tr>
</tbody>
</table>

PVDF = poly(vinylidene fluoride), PA = polyamide, PES = polyethersulfone, PSF = polysulfone, YSZ/silica = yttria-stabilized zirconia/silica.

### 3.2.1. TiO\textsubscript{2} nanoparticle incorporated nanocomposite membrane.

One of the advantages of incorporating TiO\textsubscript{2} into the composite membrane is that it is an excellent and low-toxic material for photocatalysis. The impacts of TiO\textsubscript{2} on the performance of nanocomposite membranes from some selected previous research studies are presented in Table 8.
Table 8. Impacts of TiO2 on the performance of nanocomposite membrane.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Fabrication method</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF and sulfonated PES blend membrane</td>
<td>Phase inversion</td>
<td>Enhanced hydrophilicity and antifouling. Agglomeration @ ≥ 4 wt.% loading</td>
<td>[161]</td>
</tr>
<tr>
<td>L-cysteine-surface in PES membrane</td>
<td>Phase inversion</td>
<td>Enhanced water flux, hydrophilicity and antifouling. Agglomeration @ 1 wt.% loading</td>
<td>[140]</td>
</tr>
<tr>
<td>PSF-based PANI-coated PA nanocomposite hollow fiber membrane</td>
<td>Coating</td>
<td>Enhanced hydrophilicity and antifouling. Agglomeration @ 1 wt.%</td>
<td>[162]</td>
</tr>
<tr>
<td>PSF membrane</td>
<td>Phase inversion</td>
<td>Enhanced hydrophilicity, high surface area, self-cleaning efficiency, antifouling activity</td>
<td>[163]</td>
</tr>
<tr>
<td>PSF UF membrane with PANI-coated PEG</td>
<td>Phase inversion</td>
<td>Enhanced porosity, permeability, hydrophilicity, water uptake and antifouling. Agglomeration @ 1.5 wt.% loading</td>
<td>[164]</td>
</tr>
<tr>
<td>PSF UF membrane</td>
<td>Phase inversion</td>
<td>Better porosity, hydrophilicity, and antifouling property. Aggregates @ 2.0 wt.%</td>
<td>[165]</td>
</tr>
<tr>
<td>Microporous PES membrane</td>
<td>Phase inversion</td>
<td>Enhanced hydrophilicity, mean pore size and permeation property, flux, mechanical strength, thermal stability. Agglomeration @ 4-5 wt.% loading</td>
<td>[166]</td>
</tr>
<tr>
<td>Electrospun nanofibers from a blend of PVP, and PVDF</td>
<td>One-step electrostatic spinning</td>
<td>Enhanced hydrophilicity, mechanical strength, chemical stability, and antifouling.</td>
<td>[167]</td>
</tr>
</tbody>
</table>

PANI: polyacrylonitrile; PSF: polysulfone; PEG: poly (ethylene) glycol; PVP: poly (1-vinylpyrrolidone); PVDF: polyvinylidene difluoride; UF: ultrafiltration; PA = Polyamide.

The presence of TiO2 improved the antifouling property of PVDF and sulfonated PES blend membrane\(^{[161]}\) and PSF-based polyacrylonitrile-coated PA nanocomposite hollow fibre membrane\(^{[162]}\). TiO2 enhanced hydrophilicity in all the membranes reported (Table 8). However, agglomeration occurred at a low loading weight. This was peculiar to PSF UF membrane with polyacrylonitrile-coated PEG\(^{[164]}\), PSF-based polyacrylonitrile-coated PA nanocomposite hollow fibre membrane\(^{[162]}\) and L-cysteine-surface in PES membrane\(^{[140]}\) where aggregation set-in at 1 wt.%. Attempt to go beyond 1 wt.% led to leaching of the TiO2 particles, unlike in the case of PVDF and sulfonated PES blend membrane\(^{[161]}\) and microporous PES membrane\(^{[166]}\), which could accommodate more of the nanoparticles. This indicates that it is essential to monitor the nanoparticle loading process to avoid aggregation, which limits the performance of the membrane.

The PVDF UF membrane was recently modified with TiO2 to remove sulfadiazine from water\(^{[168]}\). The process exhibited a high removal capacity of 91.40%, attributed to the photocatalytic activity of the incorporated TiO2. Similarly, a study reported the inclusion of TiO2 in a poly(vinylidene fluoride-hexafluoropropylene) matrix to remove metronidazole\(^{[169]}\). TiO2 supported on poly (vinylidenefluoride-co-hexafluoropropylene) membrane has been prepared to remove ciprofloxacin in solution\(^{[170]}\). The preparation steps produced a photocatalytic membrane with 80%–90% porosity, a promising membrane for removing ciprofloxacin in an aqueous solution.

Several studies have shown that the leaching of TiO2 from the membrane system varies. A study varied the doping of TiO2 in PVDF to form a hollow-fibre UF membrane via the sol-gel method\(^{[171]}\). At a loading of 1%, the UF membrane enhanced hydrophilicity, thermal stability, permeability, and mechanical strength. However, an attempt to go beyond 1% loading of TiO2 resulted in agglomeration. Interestingly, the loading of TiO2 in a UF membrane was up to 7%, while leaching set in at a loading of 10%\(^{[172]}\). Although the high loading of
nanoparticles into the membrane structure does not necessarily mean better performance, it is crucial to
determine the threshold for effectiveness while leaching is not undermined.

3.2.2. ZnO nanoparticle incorporated nanocomposite membranes

The inclusion of ZnO into the membrane is known for its antimicrobial activity. ZnO is low-cost,
environmentally friendly, and hydrophilic. Different methods have been used to include ZnO in membrane
preparation. However, phase inversion is commonly used. Hybrid PVDF-P(L-DOPA)-ZnO membrane has
been prepared by phase inversion to remove oxytetracycline in solution[173]. The process converted the
hydrophobic PVDF membrane to hydrophilic, having pores mean size of 1.5 µm. The membrane exhibited
high stability after 3 regeneration cycles. A facile synthesis involving incorporating ZnO in the PES membrane
matrix was reported with enhanced water flux (152 L m⁻² h⁻¹) and antifouling capacity that degraded
ciprofloxacin up to 95.1%[174]. Surface modification of the membrane with the incorporation of ZnO has shown
more remarkable improvement. The surface modification method may involve physical or chemical surface
coating[175,176], which introduces ZnO to the membrane surface allowing direct interaction with PhACs. PVDF–
ZnO composite membranes have been prepared by the blending method[145]; the inclusion of ZnO created
smaller water contact angles and an improved sublayer structure, enhancing membrane performance. A recent
study doped PSF and CA with 0.2 wt% ZnO to fabricate a membrane with super hydrophilic properties[177].
The composite membrane decreased the water contact angle from 72.86 to 13.17 °C and increased water flux
from 20 to 460 L m⁻² h⁻¹. Indeed, ZnO remains a promising metal oxide that can be used to improve the
capacity of filtration membranes as a sustainable means for removing PhACs from an aqueous solution.

3.2.3. CuO, SiO₂ and zeolite nanoparticle incorporated nanocomposite membranes

SiO₂ is often used in membrane modification because of its tremendous thermal, chemical, and structural
stability and superb facile suspension in solution[178,179]. CuO and SiO₂ have played essential roles in improving
the permeability and antifouling property of membranes; for example, including SiO₂ in PVDF improved
hydrophilicity, selectivity, and thermal stability[180]. A study has revealed that the presence of SiO₂ can help
unify the pore size distribution of nanocomposite membranes[181]. A PSF/PVDF/SiO₂ UF membrane was
synthesized to remove amoxicillin in an aqueous solution[182]. On increasing the loading of SiO₂ from 0 to 4
wt%, the membrane performance increased from 66.52% to 89.81%, suggesting the vital role SiO₂ plays in
ensuring enhanced membrane performance. CuO@CuS/PVDF composite membrane was also reported to be
able to remove tetracycline with a degradation capacity of 87.40%[183]. Poly(aniline-co-meta-
phenylenediamine) modified with Fe₂O₃/CuO was synthesized and used for removing ciprofloxacin from an
aqueous solution[184]. According to Aniagor et al.[185], CuO demonstrates potential as a nanoparticle that can
enhance the performance of membranes in water treatment. Zeolite-based nanocomposite membranes have
been reported for the removal of PhACs in water. Zeolite may be referred to as a green ceramic membrane
precursor[103,186]. They are the three-dimensional crystalline structure of aluminosilicates[187]. Several forms of
zeolite have different properties; therefore, the zeolite to improve the membrane’s or composite membrane’s
properties will depend on the desired membrane property. The well-defined structure, void, flow channels and
negative charges in zeolite have contributed significantly to its use in the water purification process and, by
extension, in improving the performance of nanocomposite membrane[188,189]. The silica-to-alumina (silica-
alumina) ratio in zeolite is critical in its application in water treatment. It plays a vital role in the zeolite’s
chemical stability and cationic exchange. When the silica content is high, the zeolite becomes hydrophilic and
is suitable for water treatment[187]. Different reaction mechanisms have been associated with using zeolite in
water treatment, such as molecular sieving, adsorption, charge exclusion and ion exchange[190,191]. A ceramic
MF membrane was reported to remove norfloxacin and ofloxacin from the aqueous solution[192]. The
membrane recorded a capacity of 98.70% towards norfloxacin and 94.61% towards ofloxacin. A study
provided an overview of nano-zeolite in water treatment, which shows its role in membrane activities[187].
Recently, a porous zeolite imidazolate framework-8 (ZIF-8) composite was reported to remove thymol in an
aqueous solution with high adsorption capacity[193].

11
3.3. Carbonaceous nanocomposite membranes for PhACs removal in water

Carbon-based materials have been used extensively as nanomaterials to modify membranes, especially in preparing nanocomposite membranes. This is possible because carbon-based nanoparticles can imprint functional properties on membranes by tampering with the membrane’s surface and internal structural identity. Their inclusion forms a complex matrix of polymeric structure with increased surface area and uniform porosity. The membrane’s thermal and chemical stability, surface reactivity and antifouling property are improved\cite{97,194,195}. They can be included as nanofillers to improve viscoelasticity and mechanical strength\cite{196,197}. Unfortunately, carbonaceous nanomaterial dispersibility is poor, making them agglomerate. It is necessary to consider this when selecting nano-carbonaceous materials to modify membranes. The agglomeration can be circumvented by surface functionalization, which in most cases is viewed as a pretreatment step for the carbon-based nanoparticles before incorporation into membranes.

3.3.1. CNT, GO, MOF-based nanocomposite membranes for PhACs removal

CNT is an allotrope of carbon of a two-dimensional structure known for its outstanding surface adsorption properties, thermal stability, and mechanical strength\cite{198}. It may be single (SWCNT) or multi-walled CNT (MWCNT). On the other hand, graphene is a one-dimensional carbon-based structure with a high surface area, excellent surface adsorptive properties, thermal stability, and mechanical strength. Graphene can be oxidized to form GO or reduced graphene oxide (rGO). The hydrophobicity and monoatomic thickness of graphene presents it as material for membrane separation\cite{199}; however, it exhibits a restricted permeability due to the \(\pi-\pi\) conjugation in its aromatic ring\cite{111}. Fortunately, the restricted permeability may be circumvented by enlarging its interlayer distance through intercalation\cite{200,201}, which may include processes like oxidation, exfoliation, and reduction to produce GO and rGO. Unlike graphene, GO has functional groups rich in oxygen (hydroxyl, epoxide, and carboxylic). The presence of the oxygen-rich groups makes it a two-dimensional structure, unlike graphene. It is hydrophilic, easily dispersed in solvents, has good permeability, and enhanced surface properties\cite{111,202}. Despite the improved permeability in GO, the thermal conductivity is poor, which may be partially improved by reducing GO to rGO\cite{203}.

Usually, CNT is hydrophobic; however, it can be pretreated via surface functionalization and used to prepare nanocomposite membranes. The inner diameter of CNT may be adjusted within the nano range to suit the required purpose or properties for enhanced membrane performance\cite{204}. Including CNT in membranes has shown better rheological properties\cite{205,206}. Unfortunately, the CNT may agglomerate if not appropriately functionalized, which is a limitation that must be carefully controlled\cite{207}. A nanocomposite membrane with improved mechanical and water flux properties has been synthesized by grafting PA with MWCNTs\cite{208}, similarly high porosity, better permeability and the antifouling property were attained when PA was incorporated with hydroxyl-functionalized CNT\cite{209}. A NF membrane with MWCNT interposed between GO has been reported to remove tetracycline hydrochloride from an aqueous solution\cite{210}. The study revealed a 99.23% removal of tetracycline hydrochloride by the membrane, exhibiting a high-water permeation of 16.12 Lm\(^{-2}\)h\(^{-1}\)bar\(^{-1}\). A study reported GO and AC membrane structure for removing tetracycline hydrochloride in solution\cite{211}. The membrane exhibited an adsorption capacity of 98.90% towards removing tetracycline hydrochloride in solution. The performance of membranes obtained from the inclusion of carbon-based nanoparticles is described in Table 9.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Fabrication method</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDA/RGO/(HNTs)-CA</td>
<td>Vacuum filtration</td>
<td>High antifouling property, high oil rejection (99.85%) and permeate flux (~60.3 Lm(^{-2})h(^{-1}))</td>
<td>[212]</td>
</tr>
<tr>
<td>Membrane material</td>
<td>Fabrication method</td>
<td>Performance</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------</td>
<td>---------------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>GO-HNTs</td>
<td>Vacuum-assisted filtration</td>
<td>High oil rejection (&gt;99%), fouling resistance and permeate flux (716 L m⁻² h⁻¹)</td>
<td>[213]</td>
</tr>
<tr>
<td>PEN/HNTs@GO-PDA</td>
<td>Vacuum filtration and electrospinning technique and hot-pressing process</td>
<td>Good thermally and chemically stable, high rejection (&gt;99.0%) and permeate flux (1130.56 L m⁻² h⁻¹)</td>
<td>[214]</td>
</tr>
<tr>
<td>RGO-coated wire mesh</td>
<td>Drop-coating</td>
<td>&gt;98%, excellent recyclability and high flux (1752 L m⁻² h⁻¹)</td>
<td>[215]</td>
</tr>
<tr>
<td>TiO₂/GO/recycled cellulose triacetate</td>
<td>Electrophoretic deposition method</td>
<td>High antifouling and self-cleaning ability and oil rejection (&gt;98%)</td>
<td>[216]</td>
</tr>
<tr>
<td>GO/g-C₃N₄/TiO₂</td>
<td>Vacuum-assisted self-assembly</td>
<td>Excellent antifouling, permeate flux (4536 L m⁻² h⁻¹) and oil rejection (&gt;99.9%)</td>
<td>[217]</td>
</tr>
<tr>
<td>F-rGO)-based coating</td>
<td>Dip-coating</td>
<td>High mechanical stability and recyclability and High flux (1395 L m⁻² h⁻¹)</td>
<td>[218]</td>
</tr>
<tr>
<td>RGO-silver (Ag)-TiO₂/CA</td>
<td>Vacuum filtration</td>
<td>Excellent oil rejection (~100%), antifouling capacity and recyclability; high water flux (191 L m⁻² h⁻¹) and stable oil rejection (~99%)</td>
<td>[219]</td>
</tr>
<tr>
<td>PVDF/RGO@SiO₂/PDA</td>
<td>Surface deposition and vacuum filtration</td>
<td>High FRR (87.2%), Flux (~125 L m⁻² h⁻¹) and oil rejection (~99%)</td>
<td>[220]</td>
</tr>
</tbody>
</table>

F-rGO = Fluorine-grafted reduced graphene oxide, rGO = reduced graphene oxide, HNTs = halloysite nanotubes, CA = cellulose acetate, PVDF = Polyvinylidene fluoride, PEN = Poly(arylene ether nitrile), g-C₃N₄ = graphitic carbon nitride.

The inclusion of carbon-based nanoparticles generally enhanced the antifouling property of the membrane. A microporous membrane was prepared by loading PSF with 0.5% CNT[221]. The approach increased the water flux from 268 to 342 L m⁻² h⁻¹ bar⁻¹; the surface porosity and the salt rejection were improved significantly. A photocatalytic g-C₃N₄/MnFe₂O₄/graphene nanocomposite membrane was designed to remove metronidazole, amoxicillin, tetracycline, and ciprofloxacin from aqueous solution[222]. The performance of g-C₃N₄/MnFe₂O₄/graphene is promising, with the highest performance for removing metronidazole (94.50%). To investigate the capacity of GO alone as material for water purification without inclusion in the membrane, GO nanoplatelets were examined for their capacity to remove carbamazepine from solution in a treatment process that revealed 99% carbamazepine removal[223]. It became evident that GO on its own, has the capacity to remove PhACs from solutions. However, its regeneration capacity for reuse may not be as outstanding as when incorporated into a nanocomposite membrane structure.

Other studies have reported the inclusion of MOF in the membrane has the potential for performance enhancement to remove PhACs. Powdered or monolithic MOFs have large surface areas that can improve the performance of the membrane[224]. MOFs exhibit higher surface area than GO, CNT, and AC[225]. A study incorporated MOF into UF, which showed improved performance compared to using UF[226]. Nanostructured membrane of the type ZIF-8 incorporated PSF membrane and layer-by-layer PA/ZIF-8 nanostructured membrane to remove acetaminophen from the solution[227]. In the MOF-based composite membrane, the MOF may serve as a filler to strengthen the structure of the composite membrane[228]. The MOF-based composite membrane is easy to scale up, cheaper and stable, and mainly prepared by blending method[229]. MOF is compatible with a polymeric structure, making it suitable and compatible when incorporated into a composite membrane[229]. The blending method involves three stages: (1) the MOF is mixed with polymer/matrix structure in a suitable solvent to form the composite membrane solution; (2) the composite membrane solution is cast on a porous substrate which may be by coating or casting and (3) evaporation of mixture solvent. A
nanocomposite membrane of enhanced performance has been prepared via this means combining super-
hydrophobic alkyl-functionalized nano-MOF (RHO-(Zn(eim)2)) (MAF-6) and polydimethylsiloxane (PDMS)
which was cast onto PVDF[231] similarly hydrophilic and hydrophobic nanoMOFs were incorporated into PES
matrix to improve performance[232]. The performance of different nanocomposite membranes towards different
classes of PhACs is shown in Table 10. The capacity varies; however, nanocomposite with zeolite
demonstrates a high capacity for removing PhACs from an aqueous solution. The inclusion of β-
cyclodextrin polymers in the composite structure showed a high performance of 99.90% towards propranolol and bisphenol A[233]. The presence of SiO$_2$ in the nanocomposites also showed significant contributions in the case of
acetaminophen[234], ibuprofen[235], and diclofenac[234].

Table 10. Removal of different class of PhACs from water system by nanocomposite membrane.

<table>
<thead>
<tr>
<th>Class</th>
<th>PhAC</th>
<th>Membrane process</th>
<th>Polymer</th>
<th>Nanomaterial</th>
<th>Removal Performance (%)</th>
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<td>UF</td>
<td>PES</td>
<td>HMCN</td>
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<td>PI</td>
<td>SiO$_2$</td>
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<td>inflammatory</td>
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PA$_{TF}$ = polyamide-thin-film membrane, CA$_{TF}$ = cellulose acetate-thin-film membrane, PES = polyethersulfone, PI = polyimide,
PVDF = Polyvinylidene fluoride, PVC = polyvinyl chloride, HMCN = mesoporous hollow carbon nanospheres, β-CDP = β-
cyclodextrin polymers, MWCNT = multi-walled carbon nanotubes, TF = thin-film membrane.

4. Trend and future prospects

Membrane technology has gained ground in water treatment processes. The use of nanocomposite membranes for treating PhACs contaminated water systems is receiving attention. Many wastewater treatment
plants are undergoing improvement to be able to handle emerging contaminants like PhACs. Most studies on nanocomposites are focused on dyes and heavy metals. There are very few studies on nanocomposite membranes focusing on PhACs, although there are studies using nanocomposites for water treatment but not as membranes. This area needs to be improved, and there is an urgent need for more studies to be conducted to understand the process better. Apart from this, it is rare to find studies on a large-scale using nanocomposite membranes for PhACs removal from water. Therefore, apart from conducting more studies, the studies should be more comprehensive than laboratory evaluations; there is a need to investigate applications on a large scale for industrial applications. There is no study on the cost evaluation of nanocomposite membranes, even where studies did not consider membrane activities. Future studies need to consider cost evaluation to understand the economic viability of the process.

Many studies pointed out fouling and high energy consumption as major limitations to using membranes in water treatment. Although most studies proffered solutions to fouling, such as including metal oxides and carbonaceous nanoparticles in nanocomposite membranes, most studies did not consider the high energy consumption issue, which was linked to pressure requirement and process time. It is essential to consider the challenge emanating from increased energy consumption during the process when designing a membrane process that is cheap, efficient and less energy-consuming. No study conducted a toxicity profiling of the membrane filters to confirm their level of safety. It is crucial to ascertain the safety of the nanocomposite matrix and what happens to them when they are completely spent in treatment cycle. Despite the success of using nanoparticles to improve membrane technology, studies have shown a limitation of incompatibility between organic-inorganic materials[240–242]. This limitation is a severe problem that requires urgent attention because it causes the leaching of nanoparticles from the surface or internal membrane structure. Such occurrence may lead to secondary pollution, and in areas where such materials are used, it may cause serious environmental hazards. Apart from leaching, incompatibility may cause high surface reactivity leading to agglomeration of the nanoparticles that may result in poor membrane performance[243,244]. It is expedient to develop a new method of incorporating nanoparticles in the membrane that will prevent the challenges faced by incompatibility.

The use of photocatalytic nanocomposite membranes should be encouraged. This will allow the complete breakdown of PhACs avoiding the generation of toxic side products that may be of environmental concern. Furthermore, the development of visible light active photocatalytic nanocomposite membrane should be preferred and encouraged as this will reduce process cost since a UV light source will not be necessary, which may be an additional cost. On the other hand, visible light is readily available at no cost, which makes the use of visible light-active nanocomposite membranes cheap. None of the studies considered checking the treated water to check whether a toxic product may have been produced during the treatment process. It is essential that studies in the future take this into consideration. In addition, many studies reported did not evaluate membrane regeneration for reuse. It is crucial to establish the reusability capacity of membrane filters before economic viability can be ascertained. Therefore, pilot studies in the future should take this into consideration, which is vital. The high cost of synthesis of MOF remains one of the drawbacks to using MOF-based nanocomposite membranes[228]. Developing a cheap reaction route for synthesizing MOF is necessary to make it affordable.

5. Conclusion

The contamination of water systems by PhACs is a severe challenge. Therefore, this review considers the development of nanocomposite membranes to remove PhACs in the polluted water system. Although several water treatment methods have been developed, membrane technology remains outstanding due to its properties and operation efficiency. However, the success with membrane technology, fouling and energy consumption are major challenges identified, which could be circumvented by including metal oxide and carbonaceous nanoparticles in nanocomposite membranes. Without any doubt, the nanocomposite membrane is a promising
solution for effectively removing PhACs in an aqueous system; however, there is an urgent need for more studies to be conducted on a large scale, which should cover cost evaluation and toxicity profiling.

Conflict of interest

The authors declare no conflict of interest.

References


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