

# Chemosphere

## Ongoing progress on novel nanocomposite membranes for the separation of heavy metals from contaminated water

--Manuscript Draft--

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<b>Abstract:</b>	Membranes, as the primary separation element of membrane-based processes, have greatly attracted the attention of researchers in several water treatment applications, including wastewater treatment, water purification, water disinfection, toxic and non-toxic chemical molecules, heavy metals, among others. Today, the removal of heavy metals from water has become challenging, in which chemical engineers are approaching new materials in membrane technologies. Therefore, the current review elucidates the progress of using different concepts of membranes and potential novel materials for such separations, identifying that polymeric membranes can exhibit a removal efficiency from 77 up to 99%; while novel nanocomposite membranes are able to offer complete removal of heavy metals (up to 100%), together with unprecedented permeation rates (from 80 up to 1, 300 L m <sup>-2</sup> h <sup>-1</sup> ). Thereby, the review also addresses the highlighted literature survey of using polymeric and nanocomposite membranes for heavy metal removal, highlighting the relevant insights and denoted metal uptake mechanisms. Moreover, it gives up-to-date information related to those novel nanocomposite materials and their contribution to heavy metals separation. Finally, the concluding remarks, future perspectives, and strategies for new researchers in the field are given according to the recent findings of this comprehensive review.
<b>Opposed Reviewers:</b>	

**Professor Jacob de Boer**  
**Editor-in-Chief for Chemosphere**  
**Free University of Amsterdam Department of Environment and Health, De**  
**Boelelaan 1085, 1081 HV, Amsterdam, Netherlands**

We are herewith submitting the manuscript “Progress and current updates on the application of polymeric and nanocomposite membranes for the separation and recovery of heavy metals from metal-contaminated wastewater” for Chemosphere. This work is an original contribution that has not been published previously and it is not under consideration for publication elsewhere. The novelty of the contribution is focused on the recent development works towards the new concepts of membranes (e.g. polymeric and nanocomposite) for the efficient separation and recovery of heavy metal ions from wastewaters. The current challenges on research and development deal with development of new membranes with enhanced adsorption capacity for heavy metals separation. Its publication is approved by the authors: Roberto Castro-Muñoz \*, Luisa Loreti Gonzalez-Melgoza, Octavio García-Depraect.

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“Ongoing progress on novel nanocomposite membranes for the separation of heavy metals from contaminated water”

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## Abstract

Membranes, as the primary separation element of membrane-based processes, have greatly attracted the attention of researchers in several water treatment applications, including wastewater treatment, water purification, water disinfection, toxic and non-toxic chemical molecules, heavy metals, among others. Today, the removal of heavy metals from water has become challenging, in which chemical engineers are approaching new materials in membrane technologies. Therefore, the current review elucidates the progress of using different concepts of membranes and potential novel materials for such separations, identifying that polymeric membranes can exhibit a removal efficiency from 77 up to 99%; while novel nanocomposite membranes are able to offer a complete removal of heavy metals (up to 100%), together with unprecedented permeation rates (from 80 up to 1, 300 L m<sup>-2</sup> h<sup>-1</sup>). Thereby, the review also addresses the highlighted literature survey of using polymeric and nanocomposite membranes for heavy metal removal, highlighting the relevant insights and denoted metal uptake mechanisms. Moreover, it gives up-to-date information related to those novel nanocomposite materials and their contribution to heavy metals separation. Finally, the concluding remarks, future perspectives, and strategies for new researchers in the field are given according to the recent findings of this comprehensive review.

**Keywords:** *Heavy metals; water treatment; membrane-based technologies, water purification, novel composite materials.*

## Highlights

The novel breakthroughs in new concepts of membranes have been reviewed and analyzed

A *last 5 years* comprehensive review of nanocomposite membranes is addressed

Nanocomposite membranes display the highest separation efficiency toward heavy metals

Polymers filled with inorganic materials result in enhanced adsorption of metal ions

## Response to Reviewers' comments

Chemosphere

Ms. Ref. No.: CHEM78274R1

Dear Editor,

Please find enclosed the revised manuscript “*Ongoing progress on novel nanocomposite membranes for the separation of heavy metals from contaminated water*”, by Roberto Castro-Muñoz\*, Luisa Loreti González-Melgoza, Octavio García-Depraect for publication in Chemosphere as review paper.

We thank the reviewers and editor for their careful and thoughtful comments on our draft. We have carefully taken their comments into consideration in preparing our revision, which has resulted in a paper that is clearer and more compelling. Below are our responses to the comments raised by both the Editor and Reviewers, which are highlighted in yellow color.

In any event, thanks in advance for your kind consideration. I look forward to hearing from you soon.

Yours sincerely,

Roberto Castro-Muñoz

## Comments from the editors and reviewers:

### -Reviewer #4:

#### *Specific remark 1*

1) Introduction lacks of state of the art applied in the field and the NOVELTY of "novel nanocomposite membranes",

*Response: We thank the reviewer for her/his effort revising our manuscript and hope to be able to improve it by following her/his remarks. The state-of-art in the field, as well as novel composite materials, are included in revised manuscript:*

*On lines 146-154...As a current trend in the field of development of new membrane materials, the merging of both materials to produce nanocomposite membranes is also a promising tool for the efficient removal of heavy metals. However, there is a lack of reviewing the progress and latest nanocomposite membrane concepts and their role in water treatment and separation of heavy metals. Very recently, novel breakthroughs in tailoring nanocomposite materials have been released, such as nanoscale zerovalent iron impregnated biochar entrapped in calcium-alginate matrix (Wan et al., 2019), MnO<sub>2</sub>/chitosan (Dinh et al., 2020), core-shell structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe<sub>3</sub>O<sub>4</sub>/GO composite introduced into graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> (Dai et al., 2020), to mention just a few of them.*

#### *References:*

*Zhou, N., Gong, K., Hu, Q., Cheng, X., Zhou, J., Dong, M., ... Guo, Z. (2020). Optimizing nanocarbon shell in zero-valent iron nanoparticles for improved electron utilization in Cr(VI) reduction. Chemosphere, 242, 125235.*

*Wan, Z., Cho, D. W., Tsang, D. C. W., Li, M., Sun, T., & Verpoort, F. (2019). Concurrent adsorption and micro-electrolysis of Cr(VI) by nanoscale zerovalent iron/biochar/Ca-alginate composite. Environmental Pollution, 247, 410–420. <https://doi.org/10.1016/j.envpol.2019.01.047>*

*Dinh, V. P., Nguyen, M. D., Nguyen, Q. H., Do, T. T. T., Luu, T. T., Luu, A. T., ... Tan, L. V. (2020). Chitosan-MnO<sub>2</sub> nanocomposite for effective removal of Cr (VI) from aqueous solution. Chemosphere, 257, 127147. <https://doi.org/10.1016/j.chemosphere.2020.127147>*

*Dai, Z., Sun, Y., Zhang, H., Ding, D., & Li, L. (2020). Photocatalytic reduction of U(VI) in wastewater by mGO/g-C<sub>3</sub>N<sub>4</sub> nanocomposite under visible LED light irradiation. Chemosphere, 254, 3–9. <https://doi.org/10.1016/j.chemosphere.2020.126671>*

#### *Specific remark 2*

2) More feedback concerning emerging membrane technologies (FULL SCALE) is required, especially for resource recovery.

*Response: We thank the reviewer for the comment. We added a feedback on emerging membrane technologies used at a large scale for resource recovery, as follows:*

*On lines 105-109... Membranes are involved in various prominent large-scale advanced treatment approaches applied worldwide for artificial groundwater recharge, indirect potable reuse, and industrial process-water production. Particularly, ultrafiltration, nanofiltration and reverse osmosis are among the emerging membrane technologies used at a large-scale for resource recovery (i.e. water) from wastewater treatment plants (Kehrein et al., 2020).*

#### **References:**

*Kehrein, P., van Loosdrecht, M., Osseweijer, P., Garfi, M., Dewulf, J., Posada, J. (2020). A critical review of resource recovery from municipal wastewater treatment plants – market supply potentials, technologies and bottlenecks. *Environmental Science Water Research & Technology*, 6, 877-910.*

#### **Specific remark 3**

3) Discussion could include more comparisons with the results of relevant studies.

**Response:** *We thank the reviewer for the comment. More discussion has been added including new relevant studies, as follows:*

*On lines 644-665... Most of the nanocomposite materials and membranes tend to display impressive metal ion uptake, and more importantly, some composites can concurrently remove more than one type of ion. However, to core the complete resource recovery (i.e. water), it is important to consider the synthesis of nanocomposite membranes which may offer the simultaneous removal of heavy metal ions and organic contaminants, e.g. Zhang et al. (2020) developed composite membranes filling polydopamine-coated ferric oxide (Fe<sub>3</sub>O<sub>4</sub>@PDA) in PES. In addition to the higher permeabilities of the composite membranes (e.g. over 2600 L/m<sup>2</sup> h bar corresponding to 20wt.% Fe<sub>3</sub>O<sub>4</sub>@PDA PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive removal of Pb<sup>2+</sup> and catalytic degradation of methylene blue, e.g. acceptable Pb<sup>2+</sup> removal efficiency (above 80%) together with high methylene blue degradation (above 90%). In this case of study, the authors strategically designed the composite to display a synergistic effect. For example, the phenolic hydroxy and amino groups on the surface of PDA were able to chelate the cations to promote the adsorption of heavy metal ions, while the electron transfer in the Fenton-like reaction was promoted due to the phenoquinone structure of the surface of the PDA, boosting the catalytic reaction. With a similar scope, Fan et al. (2019) documented the simultaneous and rapid removal of organic micropollutants (bisphenol) and metal ions (Pb<sup>2+</sup>) using an electrospun β-cyclodextrin/chitosan/polyvinyl alcohol nanofibers. These novel nanocomposites exhibited a large number of adsorption sites, e.g. the cyclodextrin owed a featured molecule structure with a hydrophilic outer surface and hydrophobic inner cavity for binding organic contaminants while chitosan has plenty of hydroxyl and amino groups to form complex with metal ions and thus remove them. Both authors concluded that their nanocomposites represent a new pathway to deal with hard-to-be-treated wastewaters (e.g. paper making, leather, textile, etc.)*

#### **References:**

*Fan, J., Luo, J., Zhang, X., Zhen, B., Dong, C., Li, Y., Shen, J., Cheng, Y., Chen, H. (2019). A novel electrospun β-CD/CS/PVA nanofiber membrane for simultaneous and rapid removal of organic micropollutants and heavy metal ions from water. *Chemical Engineering Journal*, 378, 122232.*

*Zhang, L., Liu, Z., Zhou, X., Zhang, C., Cai, Q., Xie, R., Ju, X., Wang, W., Faraj, Y., Chu, L. (2020). Novel composite membranes for simultaneous catalytic degradation of organic contaminants and adsorption of heavy metal ions. *Separation and Purification Technology*, 237, 116364.*



***Guest editors comments:***

- Kindly check the formatting, spacing and spelling mistakes and please submit within the next 15 days so that a final decision can be taken by the editors.

***Response:*** *We thank the editor for the comment. We have carefully double checked the grammar over the revised manuscript, fixing all spacing and spelling mistakes.*



1 **Ongoing progress on novel nanocomposite membranes for the separation of heavy metals**  
2 **from contaminated water**

3  
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## 26 **Abstract**

27 Membranes, as the primary separation element of membrane-based processes, have greatly  
28 attracted the attention of researchers in several water treatment applications, including wastewater  
29 treatment, water purification, water disinfection, toxic and non-toxic chemical molecules, heavy  
30 metals, among others. Today, the removal of heavy metals from water has become challenging, in  
31 which chemical engineers are approaching new materials in membrane technologies. Therefore,  
32 the current review elucidates the progress of using different concepts of membranes and potential  
33 novel materials for such separations, identifying that polymeric membranes can exhibit a removal  
34 efficiency from 77 up to 99%; while novel nanocomposite membranes are able to offer complete  
35 removal of heavy metals (up to 100%), together with unprecedented permeation rates (from 80 up  
36 to 1, 300 L m<sup>-2</sup> h<sup>-1</sup>). Thereby, the review also addresses the highlighted literature survey of using  
37 polymeric and nanocomposite membranes for heavy metal removal, highlighting the relevant  
38 insights and denoted metal uptake mechanisms. Moreover, it gives up-to-date information related  
39 to those novel nanocomposite materials and their contribution to heavy metals separation. Finally,  
40 the concluding remarks, future perspectives, and strategies for new researchers in the field are  
41 given according to the recent findings of this comprehensive review.

## 43 **Keywords**

44 *Heavy metals; water treatment; membrane-based technologies, water purification, novel composite*  
45 *materials.*

## 47 **Abbreviations:**

48 Ag: silver

49 As: Arsenic

50 APTS: 3-Aminopropyltriethoxysilane

- 51 CA: Cellulose acetate
- 52 Cd: Cadmium
- 53 CNT: Carbon Nanotubes
- 54 Co: Cobalt
- 55 Cr: Chromium
- 56 Cu: copper
- 57 DCMD: Direct contact membrane distillation
- 58 ESPM: Polymer Mixed e-spinning Membranes
- 59 Fe: Iron
- 60 f-GO: functionalized Graphene Oxide
- 61 GO: Graphene Oxide
- 62 IPDI: Isophorone diisocyanate
- 63 MD: Membrane distillation
- 64 MF: Microfiltration
- 65 MMGO: Modified magnetic Graphene Oxide
- 66 MMM: Mixed Matrix Membranes
- 67 MOF: Metal-Organic Frameworks
- 68 MWCNT: Multi-walled carbon nanotubes
- 69 NF: Nanofiltration
- 70 Ni: Nickel
- 71 NPs: Nanoparticles
- 72 nZVI: nano– Zero Valent Iron
- 73 PAH: Poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated
- 74 PAN: Polyacrylonitrile

- 75 PBI: Polybenzimidazole
- 76 PES: Polyethersulfone
- 77 PMVEMA: Poly(methyl vinyl ether-alt-maleic acid)
- 78 POSS: Polyhedral Oligomeric Silsesquioxane
- 79 PSF: Polysulfone
- 80 PSS: Poly(sodium 4-styrenesulfonate)
- 81 PV: Pervaporation
- 82 PVA: Polyvinyl alcohol
- 83 PVP: Polyvinylpyrrolidone
- 84 PVDF: Polyvinylidene fluoride
- 85 RO: Reverse Osmosis
- 86 TCE: Trichloroethylene
- 87 UF: Ultrafiltration
- 88 VFM: Vacuum filtered membranes
- 89 ZIF: Zeolite imidazolate framework

90  
91  
92

### 93 **1. Introduction**

94 The removal of pollutants (including metal ions) from water has been approached using several  
95 traditional treatments and protocols, such as chemical precipitation (Chabot et al., 2014), microbial  
96 decomposition (Yang et al., 2016), and physical adsorption (Kumar et al., 2013). Inherently, these  
97 pollutants represent strong issues to the environment (i.e. plants, animals, ecology climate) and  
98 humans. However, the removal of heavy metals through conventional protocols (such as flotation,  
99 chemical precipitation, ion exchange, adsorption, and electrochemical deposition) is still

100 challenging, requiring further efforts to circumvent the production of a high amount of toxic sludge  
101 and liquid waste, long time consumption, and extreme use of supplies (e.g. solvents, resins, among  
102 others), together with poor separation efficiency.

103 Currently, according to the scarcity of drinking water and the increasingly serious water pollution  
104 (Marousek et al., 2019), water treatment with membrane-based processes has potentially attracted  
105 the attention of the research community. Membranes are involved in various prominent large-scale  
106 advanced treatment approaches applied worldwide for artificial groundwater recharge, indirect  
107 potable reuse, and industrial process-water production. Particularly, ultrafiltration, nanofiltration  
108 and reverse osmosis are among the emerging membrane technologies used at a large-scale for  
109 resource recovery (i.e. water) from wastewater treatment plants (Kehrein et al., 2020). To date,  
110 polymeric membranes are likely the most used membranes for water treatment applications  
111 (Castro-Muñoz et al., 2018a), including treatment of agro-food wastes (Castro-Muñoz et al., 2016),  
112 textile (Chao et al., 2016), petroleum industry streams (Alzahrani and Wahab, 2014), acid mine  
113 waters (Lopez et al., 2019), and seawater desalination (Castro-Muñoz, 2020a). Membranes are  
114 capable to separate the compounds from aqueous streams and thus reduce the contaminants  
115 contained in wastewater (Castro-Muñoz et al., 2018b). Extensive sources and a large number of  
116 molecules, as well as ions contained in polluted water, challenge the effective purification and  
117 separation of water by membranes. The membranes, based on their intrinsic properties, can be  
118 implemented among different types of membrane-based technologies including pressure-driven  
119 membrane processes, such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and  
120 Reverse osmosis (RO). These are potentially recognized as excellent candidates for the removal  
121 of large amounts of organic macropollutants; in which NF and RO membranes are among the  
122 barriers with the highest efficiency in withdrawing micropollutants (Castro-Muñoz et al., 2017).  
123 Other membrane technologies, e.g. membrane distillation (MD) (Criscuoli and Carnevale, 2015),

124 membrane bioreactors (Santos and Judd, 2010), membrane contactors (Bey et al., 2010), have also  
125 been proven to remove **specific** heavy metal ions, such as arsenic (As), fluoride (F) and uranium  
126 (U). In particular, As is a natural tasteless and odorless element **that** may be highly toxic to humans  
127 exposed to it from air, food and water. It is known that this element exists in the earth's crust at  
128 average levels between 2000–5000 µg per kg (Figoli et al., 2010).

129 In this way, membranes have shown to be **efficient** in removing different metal ions (e.g. Cd<sup>2+</sup>,  
130 Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Al<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>4+</sup>) from water streams. A large number of studies has  
131 been now devoted to the manufacture of synthetic membranes for these particular separations,  
132 demonstrating compelling benefits, such as permeability, selectivity, enhanced chemical and  
133 physical properties within the removal of metal ions. When dealing with the removal efficiency of  
134 such membranes, the material properties, including chemical, physical, mechanical, play an  
135 important role in their efficiency, but also the membrane preparation protocols are crucial. In this  
136 context, several techniques **have been used in membrane manufacture**, such as stretching, track-  
137 etching, sintering, electrospinning, phase inversion (Lalia et al., 2013), and interfacial  
138 polymerization (Peydayesh et al., 2018), **in which** plenty **of** organic and inorganic materials have  
139 been proposed and used in tailoring membranes (Castro-Muñoz et al. 2020). Polymers have been  
140 the most used organic materials in membrane preparation, followed by the inorganic ones (e.g.  
141 ceramics, metals and glass) (Ulbricht, 2006). Polymer membranes tend to present great design  
142 flexibility, while the advantages of inorganic membranes, e.g. ceramic membranes, compared with  
143 polymeric ones comprise their higher thermal, mechanical and chemical stability (Castro-Muñoz  
144 et al. 2018c). Also, the hydrophilicity and the surface charge in ceramic membranes are higher.  
145 Ceramic membranes can also be operated under extreme conditions of pH, temperature and high  
146 oxidizing environment (Yong et al., 2013). **As a current trend in the field of development of new**  
147 **membrane materials, the merging of both materials to produce nanocomposite membranes is also**



148 a promising tool for the efficient removal of heavy metals. However, there is a lack of reviewing  
149 the progress and latest nanocomposite membrane concepts and their role in water treatment and  
150 separation of heavy metals. Very recently, novel breakthroughs in tailoring nanocomposite  
151 materials have been released, such as nanoscale zerovalent iron impregnated biochar entrapped in  
152 calcium-alginate matrix (Wan et al., 2019), MnO<sub>2</sub>/chitosan (Dinh et al., 2020), core-shell  
153 structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe<sub>3</sub>O<sub>4</sub>/GO composite  
154 introduced into graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> (Dai et al., 2020), to mention just a few of them.  
155 Thereby, this review paper aims at providing the ongoing progress of using different concepts of  
156 membranes (polymeric, composite and nanocomposite) and potential novel materials for removing  
157 heavy metals. Herein, a highlighted literature survey of using polymeric and nanocomposite  
158 membranes for heavy metal removal from water is provided. Ultimately, the current advances and  
159 future trends of nanocomposite membranes in the field are also given.

160

## 161 **2. Metal ions removal using pristine polymeric and chemically modified polymeric** 162 **membranes**

163 Polymers are probably the most widely applied membrane material for wastewater treatment. Due  
164 to their advantages including facile pore-forming mechanism, low cost and high flexibility (Yong  
165 et al., 2013), polymers are leading as the main material for membrane manufacture for different  
166 membrane-based technologies, such as electrodialysis, UF, NF and RO. Experimentally,  
167 polymeric membranes can remove different types of contaminants, such as organic matter, organic  
168 and inorganic compounds (e.g. heavy metal ions), and suspended pollutants (Wieszczycka and  
169 Staszak, 2017).

170 Polymeric membranes are typically manufactured from natural or chemically-synthesized  
171 polymers. The membranes are creating a selective interface barrier between two adjacent phases

172 (feed and permeate) which governs the transport behavior of species between them. In general,  
173 the separation performance of the membrane depends on the properties of transported species (e.g.  
174 molecule size, shape and chemical nature), as well as **physicochemical** properties  
175 (**hydrophilicity**/hydrophobicity, surface charge, roughness) of the polymer membrane, especially  
176 porous structure. For **instance**, **Table 1** enlists some of the reported studies in which the removal  
177 of heavy metal ions has been performed by means of different polymeric membranes and  
178 processes. It can be seen that the removal efficiency towards metal ions using polymer membranes  
179 has been reported between 77 **to** 99%.

180

181 **Table 1.** Polymeric membranes used for the removal of metal ions.

182

183 For instance, Qdais and Moussa (2004) evaluated the separation performance of the RO and NF  
184 technologies using polyamide spiral wound membranes for the removal of copper (Cu) and  
185 cadmium (Cd) metals from industrial wastewater. While the RO process showed Cu and Cd  
186 removal efficiencies of about 98 and 99%, respectively, the NF process exhibited more than 90%  
187 of Cu ions. Interestingly, the membranes were able to concurrently treat wastewater containing  
188 more than one heavy metal ion. As an example, these membranes reduced the ion concentration  
189 from 500 ppm to 3 ppm, meaning a removal efficiency **of** over 99%. Another typical polymeric  
190 membrane material is polyethersulfone (PES), which has been successfully consolidated in  
191 membrane preparation owing to its high thermal and mechanical stability, physiological and  
192 chemical neutrality and wide range pH resistance. PES, however, tends to present a hydrophobic  
193 nature which results in high membrane fouling when applied for organic aqueous filtration. Thus,  
194 with the aim of improving its separation performance and properties, efforts have been proposed  
195 to shift the surface properties of this hydrophobic polymer. It is known that hydrophobic polymers





196 are more prone to membrane fouling due to the particles contained in the feed bulk tend to  
197 accumulate on hydrophobic and rough surfaces, minimizing the interfacial tension between water  
198 and membrane (Pichardo-Romero et al., 2020). Therefore, the on-going strategies are aimed at  
199 mitigating the interaction between the foulants and the barrier layer. For example, an easy approach  
200 is to chemically modify the surface properties of the membrane by immersing it in a polyelectrolyte  
201 solution. It has been found that the polyelectrolyte adsorbed onto the membranes may significantly  
202 improve the membrane performance in terms of metal ions removal due to the presence of  
203 chelating functions in their structure. In this way, Mokhter et al. (2017) performed the chemical  
204 modification of PES membranes by polyelectrolyte multilayers, made of poly(allylamine  
205 hydrochloride) with poly(styrene sulfonate). The resulting membranes were employed to treat  
206 aqueous solutions containing single or mixed heavy metals,  $\text{Cu}^{2+}$ , zinc ( $\text{Zn}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ), at  
207 various concentrations (50–1200 ppm). The tested membrane was efficient in separating all the  
208 tested metals either alone or mixed with high long-term stability and removal efficiencies over  
209 90%. Similarly, polyacrylonitrile (PAN) membranes were modified by Qin et al. (2013), who  
210 synthesized positively charged membranes by depositing polyelectrolytes. Researchers used PAN  
211 membranes modified by the layer-by-layer assembly of polyethyleneimine (PEI) and poly(sodium  
212 4-styrenesulfonate) (PSS), to successfully separate  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  aqueous solutions,  
213 achieving removal efficiencies in the range of 95–98%. Particularly, the NF tests showed that the  
214 removal efficiency of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions increased with the number of bilayers, but a decrease in  
215 permeate fluxes was observed. The usage of additional polymeric layers could also be applicable  
216 in the case of hollow fiber membranes. The great benefit of multi-layer materials lies in the fact  
217 that a relatively cheap material could be used as a support while a high-performance material  
218 (commonly a more expensive material) can be used as the selective layer. For instance, Zhu et al.  
219 (2014) tailored a high-performance dual-layer NF hollow fiber membrane and tested for the



220 removal of  $\text{Cd}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pb}^{2+}$  salts from model wastewater, attaining removal efficiencies  
221 above 95%. Herein, researchers applied polybenzimidazole (PBI) as the outer selective layer while  
222 the blend of PES and polyvinylpyrrolidone (PVP) was implemented as the support layer. Thanks  
223 to the unique charge characteristics and high chemical resistance of PBI, the novel developed dual-  
224 layer NF membrane demonstrated a great salt rejection value due to the Donnan exclusion effect  
225 enhancement and low adsorption of heavy metal ions on the PBI surface.

226 Polyvinylidene fluoride (PVDF) is **definitely** another hydrophobic polymer that remains popular  
227 in **a** wide number of water treatment applications (Gontarek et al., 2019; Xia & Ni, 2015). PVDF  
228 membranes are well recognized **for** their multiple advantages including high chemical tolerance,  
229 good mechanical and thermal properties. Tzanetakis et al. (2003) have proved that the performance  
230 of chemically sulfonated PVDF membrane in the electro dialysis process can be comparable with  
231 the one given by a perfluorosulfonic Nafion 117 commercial membrane. The sulfonated PVDF  
232 membrane has displayed removal efficiencies towards Co and Ni ions of about 90% and 69%,  
233 respectively. In addition to this, a meaningful enhancement of the amounts of transported metal  
234 ions was seen while using corrugated membranes, which resulted in an increase in membrane area  
235 of 60% compared with those using flat membranes. Wang et al. (2017) have developed the  
236 modification of PVDF membrane for post UF testing. In general, the results **revealed** that the  
237 interaction by blending of PVDF with 2-aminobenzothiazole conducted to **the** efficient removal of  
238 chromium (Cr) from the wastewater. As a disadvantage of such membrane preparation, the  
239 membranes showed a low permeate flux when compared with the typical UF membranes. Since **a**  
240 long time ago, it is documented that one of the simplest approaches to improve the water flux in  
241 hydrophobic polymeric membranes, like PVDF, is to mitigate the membrane fouling, which can  
242 be reached through hydrophilicity enhancement. For instance, Pereira et al. (2014) combined  
243 PVDF polymer matrix with polyaniline nanofibers, which was, in this case, proposed as a

244 hydrophilic agent to fabricate enhanced hydrophilic membranes. The authors described that the  
245 resulting membranes exhibited better hydrophilicity and better membrane properties, as well as a  
246 relatively high rejection toward heavy metal ions, such as  $Pb^{2+}$  and  $Cd^{2+}$ , e.g. around 98.5% and  
247 97.3%, respectively.

248 Cellulose acetate (CA), originated from natural sources and feedstocks, is a polymer material  
249 widely used in UF membrane manufacture. Such a polymer combines the advantages to have low  
250 cost and high biocompatibility with other materials. Unfortunately, this polymer does not reveal  
251 high enough fluxes, and it can allow preparing low porous sub-layers, as well as easy fouling issues  
252 (Combe et al., 1999). However, the blending of CA with hydrophilic agents may result in  
253 membranes with a superior antifouling property. This has been indeed demonstrated by Lavanya  
254 et al. (2019), who carried out the blending of CA with poly(methyl vinyl ether-alt-maleic acid)  
255 (PMVEMA). The generated membranes displayed enhanced antifouling capacity in the blend  
256 membranes in comparison with the pristine CA membrane. When dealing with their separation  
257 performance, the flux recovery ratio was reached up to 95%. Importantly, the pure water fluxes  
258 of such blend membranes were raised with the content of PMVEMA, since PMVEMA conducted  
259 to higher porosity and hydrophilicity. Concurrently, the blend membranes were also more efficient  
260 for the removal of heavy metal ions compared to pure CA membrane.

261 Taking into account the advantages and disadvantages of polymeric membranes, the popularity of  
262 their use and implementation for removing heavy metal ions is also attributed to their low  
263 manufacture costs and ease of modification. However, such polymeric membranes still lack  
264 different desired properties for membrane separation processes, including the ones that required  
265 high selectivity towards low solutes and species. To date, many works have been done at aiming  
266 the enhancement of the separation performance of the polymeric membranes (as listed in **Table**  
267 **1**). Nevertheless, the membrane fouling and low mechanical strength in polymeric membranes are



268 recognized as the most relevant issue in limiting their application. The development and  
269 manufacture of membranes with high selectivity, permeability, rejection, and superior antifouling  
270 properties are the biggest challenges among scientists who work on membrane development and  
271 separation processes. Despite these drawbacks, the membranes have shown interesting results  
272 during the removal of heavy metal ions. For example, Uddin et al. (2007) analyzed the removal  
273 capacity of two commercial NF polyamide membranes (NF90 and NF200) towards As (III) and  
274 As (V). The effect of the operating conditions on the rejection performance was investigated in the  
275 study. As set by authors, the feed stream contained mainly in tap water together with arsenate and  
276 arsenite. In all tests, As (V) was generally rejected better than As (III), and the membranes offered  
277 the high removals over 98% and 65% for As (V) and As (III), respectively.

278 Amy et al. (1998) previously designed a bench-scale RO process implementing a commercial  
279 membrane (DK2540F manufactured by DESAL) for As removal. The experiments comprised the  
280 single element testing in flat sheet membrane for lake water and deionized water filtration. The  
281 findings demonstrated high removal efficiency towards arsenate (up to 96%), and acceptable  
282 removal efficiency for arsenite (60–85%).

283 More recently, using a different membrane process, i.e. membrane distillation (MD), it has been  
284 demonstrated its ability to effectively separate specific heavy metal ions. For example, direct  
285 contact MD (DCMD) technology can be feasible in removing up to 99.95% arsenic molecules,  
286 like As (III) and As (V), from a contaminated water model solution. Interestingly, this process was  
287 operated for 250 h containing  $500 \mu\text{g L}^{-1}$ , the process did not evidence any change in the permeate  
288 fluxes and As content (Pal and Manna, 2010). Similarly, Manna and Pal (2016) used a similar  
289 DCMD unit, but in this case possessing a hydrophobic flat sheet membrane (nominal pore size  
290  $0.13 \mu\text{m}$ , thickness  $150 \mu\text{m}$ , porosity 70–75%). As a result, the systems proved an As removal of



291 about 100% from contaminated groundwater, and no flux decline was recorded during 4 days of  
292 operation.

293 Today, the most important approach in obtaining **membranes** with exceptional separation  
294 performance and properties relies on the synthesis and preparation **of** nanocomposites. This  
295 concept of membranes **is** well defined together with their features in the following section, and  
296 finally, the progress and latest development works in manufacturing such membranes for heavy  
297 metals removal.

298

### 299 **3. Beginnings of nanocomposite membranes for the removal of heavy metal ions**

300 Polyethersulfone (PES), polysulfone (PSF), PAN, polytetrafluoroethylene, polypropylene, and  
301 PVDF are among the main polymer materials used in the manufacture and production of  
302 membranes for pressure-driven membrane processes. It is known that most of these materials have  
303 excellent permeability, selectivity, and acceptable chemical, mechanical and thermal stability  
304 when used in water treatment applications. Particularly, PSF and PES membranes are the most  
305 used materials for manufacturing UF membranes. Such standard chemically synthesized polymers  
306 are also involved within the fabrication of NF and RO membranes, while polypropylene and PVDF  
307 are more exploited in MF membranes production (Pendergast, & Hoek, 2011). However, it is still  
308 challenging the optimization and enhancement of the separation performance of these pristine  
309 polymeric membranes (Alzahrani& Wahab, 2014), as well as the improvement of some other  
310 physicochemical properties, such as stability, hydrophilicity/hydrophobicity, fouling resistance,  
311 among others (Hana et al., 2016).

312 The enhancement of such properties has been recently breakthrough by using nanotechnology,  
313 which has been extended in a wide range of applications into membrane-based technologies, e.g.  
314 to enhance the membranes' efficiency for the removal of heavy metals, which is a relevant matter



315 within water treatment (Ursino et al., 2018). Nanocomposite membranes are recognized as “*the*  
316 *next generation of membranes*”. In theory, a typical nanocomposite membrane includes the  
317 dispersion or deposition of nanosized filling materials into polymer matrices (Castro-Muñoz et al.,  
318 2018d; Castro-Muñoz et al., 2018e; Song et al., 2012). This concept of membranes can be  
319 implemented in different membrane-based separations, including gas–gas, liquid–liquid, and  
320 liquid–solid separation. In the early 1990s, nanocomposite membranes were initially developed  
321 for membrane gas separation processes (Ahmadizadegan et al., 2018; Robeson, 1991), where  
322 selective zeolites were embedded into polymers to improve both permeability and selectivity (Li  
323 et al., 2017). Due to such success on gas separation approaches, nanocomposite membranes were  
324 then initiated to be explored in other fields of applications and processes, such as sensor  
325 applications (Jiang et al., 2004; Pandey et al., 2018), direct methanol fuel cells (Chen et al., 2006),  
326 lithium-ion battery (Li et al., 2008), proton exchange membrane fuel cells (Boaretti et al., 2017;  
327 Jalani et al., 2005), pervaporation (PV) (Castro-Muñoz et al., 2018e; Yang et al., 2009), organic  
328 solvent nanofiltration (Sorribas et al., 2013), water treatment, to mention just a few.

329 Nanocomposite membranes, also known as mixed matrix membranes (MMM), are not only  
330 tailored by embedding nanosized materials into a continuous matrix phase, nanoparticles or fillers  
331 can also be coated onto the membrane surface, which is actually well denoted as a nanocomposite  
332 membrane. Currently, the preparation and implementation of these membranes are a current trend  
333 in the nanotechnological field for water treatment, especially in the separation of metal ions  
334 (Marino et al., 2017). Importantly, such nanosized filling materials not only possess exceptional  
335 features that may be provided to the primary element (e.g. polymer) but also good compatibility  
336 when embedded. Nanocomposite membranes have concurrently revealed low-fouling issues when  
337 embedding the inorganic materials (Kim and Bruggen, 2010), together with improved permeability  
338 and selectivity, compared with polymeric membranes (Madaeni et al., 2015). To date, plenty of

339 nanosized fillers have been utilized in the preparation of nanocomposite membranes, such as  
340 titanium dioxide (TiO<sub>2</sub>) (Zhang et al., 2013), silver (Ag) (Prince et al., 2014), carbon nanotubes  
341 (CNTs) (Celik et al., 2011), zinc oxide (ZnO) (Balta et al., 2012), copper oxide (CuO) (García et  
342 al., 2017), graphene-based materials (e.g. graphene, graphene oxide or reduced graphene oxide)  
343 (Gontarek et al., 2019; Kashyap, Pratihari and Behera, 2016; Xia and Ni, 2015), alumina (Al<sub>2</sub>O<sub>3</sub>)  
344 (Arsuaga et al., 2013), silica (SiO<sub>2</sub>) (Yu et al., 2009), magnetite (Fe<sub>3</sub>O<sub>4</sub>) (Alam et al., 2016), cobalt  
345 (Co) (Gzara et al., 2016), zirconium dioxide (ZrO<sub>2</sub>) (Maximous et al., 2010), clay (Mierzwa et al.,  
346 2013) and zeolites (e.g. NaX) (Fathizadeh et al., 2011), among others. For instance, **Table 2**  
347 summarizes recent studies in which such inorganic fillers have been filled among several polymers  
348 and then applied in different applications of water treatment, wastewater treatment, toxic and metal  
349 ions removal from water.

350

351 **Table 2.** Different filling materials embedded into nanocomposite membranes for different water  
352 treatment applications.

353

354 Specially, these nanocomposite membranes have shown valid insights during the removal of  
355 **metal** ions. For example, Bahadar et al. (2015) developed and tested ZnO-filled CA nanocomposite  
356 membranes for the separation of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup>, Sb<sup>3+</sup>, and Sr<sup>3+</sup>,  
357 concluding that these membranes were highly selective towards Fe<sup>2+</sup>. Furthermore, the developed  
358 membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>. Some  
359 authors have tailored nanocomposite membranes based on functionalized multi-walled carbon  
360 nanotube (MWCNT)/polysulfone (Shah and Murthy, 2013), which also has demonstrated ability  
361 for heavy metal removal (up to 98%). In this study, the percent of rejection towards heavy metal  
362 was noted to increase by increasing the MWCNTs amount due to MWCNTs reduced the



363 membranes' pore size, the best nanocomposite performances were about 94.2% and 78.2%  
364 removal for Cr(VI) and Cd(II), respectively. It is important to mention that pristine polymer offered  
365 only 10.2% and 9.9% removal, respectively. Here, the use of inorganic materials is showing  
366 remarkable enhancement of polymeric membranes towards heavy metal ions retention. Therefore,  
367 the research community is today putting big efforts into the development of novel nanocomposite  
368 membranes that may efficiently separate heavy metal ions from several aqueous streams. Herein,  
369 the following section provides the progress, latest developments and breakthroughs in the field.

370

371

#### 372 **4. Progress in nanocomposite membranes for heavy metal ions separation**

373 To date, different categories of fillers and additives have been involved in the manufacture of  
374 nanocomposite membranes. Graphene oxide (GO) is likely one of the main materials that has been  
375 fully explored. GO has attracted the attention of the research community, especially for the  
376 separation of toxic ions and organic molecules in polluted water (An et al., 2016). GO has proven  
377 its excellent separation ability towards different molecules (e.g. water molecules) and ions. GO  
378 possesses interlayer nano-capillary networks that are formed thanks to their connected interlayer  
379 spaces, together with the gaps between edges of non-interlocked neighbouring GO sheets (An et  
380 al., 2016; He et al., 2015), facilitating the transport of molecules or ions through the GO membrane.  
381 At this point, multiple factors, including molecules' size or ions, the charge of ions, and numerous  
382 interactions (such as electrostatic interaction, metal coordination, and cation- $\pi$  interaction between  
383 ions and GO sheets) strictly influence the separation performance of the GO. These properties  
384 make to consider GO as a promising candidate material within the removal of pharmaceutical  
385 traces from water and wastewater (Sophia et al., 2016). More interestingly, the embedding of GO  
386 can also bring some benefits to the properties of the polymeric membranes, e.g. thanks to the high





387 hydrophilicity of GO, the change of the hydrophobic to hydrophilic nature of polymeric  
388 membranes has been done, resulting in enhanced permeation fluxes (Xia et al., 2015). As an  
389 example, Chang et al. (2014) analyzed the synergistic effect of GO and PVP on the performance  
390 of PVDF UF membranes. The study found out that the membrane's hydrophilicity and anti-fouling  
391 properties were enhanced by the addition of both GO and PVP. The authors concluded that this  
392 enhancement could be associated with the possible formation of hydrogen bonds between PVP  
393 and GO. Recognizing the multiple benefits that GO has given to polymeric membranes,  
394 researchers have initiated the improvement of the structural features of GO, e.g. the chemical  
395 modification has been an alternative in the field. According to researchers' insights, the chemical  
396 modification (to a positive charge) of GO is suggested for better metal ions removal efficiency (Yu  
397 Zhang et al., 2015). In this sense, Xu et al. (2014) performed the chemical functionalization of  
398 graphene oxide (f-GO) through a simple covalent functionalization with 3-  
399 aminopropyltriethoxysilane (APTS). The resulting organosilane-GO was then filled in PVDF UF  
400 membranes (Xu et al., 2014), the PVDF/ f-GO membranes had higher hydrophilicity, water flux,  
401 and protein rejection than pristine PVDF membranes and conventional PVDF/GO membranes. For  
402 instance, the membranes, containing 1wt.% f-GO, released a high permeate flux of about 401.3 L  
403 m<sup>-2</sup> h<sup>-1</sup>, a higher value compared to the one provided by the pristine PVDF (ca. 240 L m<sup>-2</sup> h<sup>-1</sup>)  
404 and PVDF/GO membranes, pointing out that these composite membranes also had better anti-  
405 fouling properties due to their higher hydrophilicity (Xu et al., 2014).

406 More recently, Zhang et al. (2017) carried out the cross-linking procedure in GO composite with  
407 isophorone diisocyanate (IPDI), later coated on PVDF membrane. Basically, the cross-linking  
408 methodology helped to improve the removal of dyes (over 96%) and heavy metal ions (Pb<sup>2+</sup>, Cu<sup>2+</sup>,  
409 Cd<sup>2+</sup>, Cr<sup>3+</sup>) (between 40-70 %) in the MF membrane compared to the pattern GO-PVDF  
410 membrane. It is worth mentioning that these composite membranes also showed high permeation



411 rates between  $80\text{-}100\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$  under low external pressure (i.e. 1.0 bar). By embedding  
412 modified magnetic GO (MMGO), it was also eventuated a significant increase in the pure water  
413 flux due to changes in surface roughness and hydrophilicity of PES NF membranes. Regarding the  
414 copper and dye removal ability of the membranes remarkably increased thanks to the presence of  
415 hydrophilic functional groups on the surface of MMGO hybrid. The prepared NF membrane,  
416 containing 0.5 wt.% MMGO hybrid, demonstrated the highest copper ions removal (ca. 92%)  
417 (Abdi et al., 2018). The authors also stated that these GO-filled NF membranes can also be good  
418 candidates in other types of water treatment applications, such as water softening, decolorization,  
419 natural organic matter removal (Wei et al., 2018).

420 A more recent approach to improving GO-based nanocomposite PVDF membranes was done by  
421 Ren et al. (2019), who fabricated PVDF-GO membrane via electrospinning with immobilization  
422 of nano-zero valent iron (nZVI) particles. Such particles were deposited on the surface by *in-situ*  
423 synthesis. This membrane was designed and tested to remove Cd (II) and trichloroethylene (TCE)  
424 contaminants from groundwater, following a mechanism of gravity-driven membrane filtration. In  
425 principle, the hydrophilicity and improved membrane flux was obtained by the functionalization  
426 of GO into PVDF. Results showed that the hydrophilicity of the membranes increased by raising  
427 the GO concentration, leading to an improved permeability property. This resulted in the  
428 achievement of high and stable fluxes of  $255\text{ L m}^{-2}\text{ h}^{-1}$  for Cd and  $265\text{ L m}^{-2}\text{ h}^{-1}$  for TCE.  
429 Moreover, using 1 wt.% GO loaded PVDF-GO-nZVI membrane, removal performances of 100%  
430 and 82% were successfully achieved towards Cd (II) and TCE, respectively. The authors attributed  
431 such relevant Cd removal to a chemisorption phenomenon, while the TCE removal mechanism  
432 consisted of a multi-step dechlorination process involving several reactions. To sum up, the study  
433 has demonstrated that the functionalized PVDF-GO membrane can be a promising barrier for  
434 water remediation due to its high reactivity towards the evaluated pollutants.



435 An interesting future approach on GO-based nanofillers for nanocomposite filtration membranes  
436 has been the one synthesized by Ma et al. (2020). They embedded GO-polyethylene glycol (P-GO)  
437 into a PVDF ultrafiltration membrane and thus proposed such a composite membrane for removing  
438 heavy metals within a wastewater treatment strategy. The membranes prepared via phase inversion  
439 method revealed outstanding results in terms of improved hydrophilicity, permeability and  
440 antifouling properties, while crosslinking between polyethylene glycol and GO contributed to an  
441 increase in thermal stability, pore size as well as surface porosity. The membrane containing 0.5  
442 wt.% P-GO obtained the highest water flux of  $94 \text{ L m}^{-2} \text{ h}^{-1}$ . This was due to the hydrophilicity  
443 provided by the embedded hydrophilic functional groups into the membrane matrix. The same  
444 membrane formulation showed a 94% bovine serum albumin rejection rate, indicating good  
445 separation properties. Furthermore, excellent antifouling properties were acquired by the obtention  
446 of the lowest surface roughness, the lowest total and irreversible resistance values, as well as by a  
447 78% flux recovery obtained after 3 performance cycles. Antifouling property of the membrane  
448 was assigned to hydrophilic groups forming a hydration layer that repulses pollutant contact and  
449 contaminant deposition. The authors highlighted that further studies must be conducted on the  
450 application of this nanocomposite membrane towards the removal of heavy metals due to its  
451 excellent anti-fouling, permeability and hydrophilicity properties.

452 **Table 3** enlists some of the latest studies in nanocomposite membrane synthesis for heavy metal  
453 removal reported by the research community. It is obvious that the separation performance of a  
454 membrane depends on multiple factors, but the membrane preparation procedure is crucial.  
455 Regardless of these important factors, most of the nanocomposite membranes generally display  
456 removal rates ranged from 27 to 100%.

457

458 **Table 3.** Latest development works on tailoring novel nanocomposite membranes for heavy

459 metal ions removal.

460

461 For instance, Ali et al. (2019) reported a 98% zinc ions ( $Zn^{2+}$ ) removal from synthetic water  
462 through filling functionalized MWCNTs into PVC, in which the retention rate was stable over 60  
463 min process time. Interestingly, these membranes also allowed to remove more than 70% zinc ions  
464 ( $Zn^{2+}$ ), when treating real wastewater effluent. The core of success in these membranes was the  
465 chemical functionalization of the MWCNTs. The authors stated that the resulting removal  
466 efficiency of CNT membrane could be associated with the high absolute zeta potential together  
467 with the hydrophilicity of the fillers embedded on the inside surface of the hollow fiber membrane,  
468 and of course the plenty number of oxygen functional groups on CNT surfaces. Theoretically, the  
469 removal capacity can be a function of electrostatic interactions among the positive charge of  $Zn^{2+}$   
470 ions and the negative charge surface of CNTs at specific conditions (e.g. higher pH values) (Lu  
471 and Chiu, 2006), which foster the strong surface complexation reaction. This enabled the  
472 membranes to demonstrate high adsorption ability, as represented in **Figure 1**. The use of  
473 sulfonated MWCNTs also represents a promising pathway in membranes with efficient removal  
474 of heavy metals, these membranes had shown an adsorption removal over 59% for Cu (II) ions  
475 (Ge et al., 2014). Such MWCNTs membranes were also enabled to remove about 99.2% of other  
476 types of toxic components, e.g. rhodamine B (Peydayesh et al., 2018).

477

478 **Figure 1.** Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et  
479 al., 2019).

480 Another example of surface functionalization of materials in nanocomposite membranes showing  
481 promising results on ion removal regards the polyether imide (PEI) nanofiltration membrane using  
482 a nanofiller additive, which consisted of L-cysteine modified glycidyl-polyhedral oligomeric

483 silsesquioxane (POSS) (Bandehali et al., 2020). The PEI membrane filled with 1 wt.% of L-  
484 cysteine modified-POSS provided an outstanding separation efficiency towards  $\text{Cr}^{+2}$  and  $\text{Na}^{+}$  ions  
485 with a rejection percentage of 79% and 80%, respectively, which was attributed to the porous  
486 membrane morphology and the presence of negatively charged hydrophilic functional groups on  
487 the membrane surface, both features promoted the absorption of positively charged ions, as well  
488 as an increase of ion adsorption active spots (Bandehali et al., 2019). Moreover, L-cysteine  
489 functionalized POSS NPs incorporated into the PEI nanofiltration membrane led to a cross-linking  
490 reaction between the amino groups ( $\text{NH}_2$ ) in L-cysteine modified-POSS filler and imide rings in  
491 PEI. This increased the membrane surface hydrophilicity due to the hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ) and amine ( $-\text{NH}_2$ ) functional groups present in these materials, resulting in high water  
492 permeation fluxes of  $95 \text{ L m}^{-2} \text{ h}^{-1}$  (in 1 wt.% of L-cysteine modified-POSS-PEI composite), from  
493  $17.63 \text{ L m}^{-2} \text{ h}^{-1}$  in neat PEI membrane. In addition to the exceptional performance, the modified  
494 filler also offered other benefits to the nanocomposite membranes, such as improved the  
495 antifouling properties to the resulting nanocomposite membranes by decreasing the roughness, a  
496 flux recovery ratio of 95%, increased degree of wetting, as well as an increment in the membrane  
497 surface smoothness, which all added up to the obtention of a better membrane structure for  
498 avoiding salt accumulation.  
499

500 To date, the blending of inorganic phases into polymers has been also a smart alternative for the  
501 simultaneous removal of different types of heavy metal ions. At this point, the filling of multiple  
502 fillers is likely a feasible option for such a task. For instance, Suresh et al. (2018) tailored a hybrid  
503 nanocomposite membrane embedding carbon nanofibers and  $\text{TiO}_2$  into PAN polymer, the  
504 generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards  $\text{Pb}^{2+}$ ,  
505  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  metal ions, respectively. Towards the efficient separation of  $\text{Pb}^{2+}$ , Suresh et al. (2018)  
506 explored and demonstrated that amino-functionalized metal-organic frameworks (MOFs)



507 combined with a ceramic ultrafiltration membrane represent to be an effective material for the  $\text{Pb}^{2+}$   
508 removal, which revealed at least 61.4% removal, whereas the best efficiency depended on the  
509 operating conditions, but it reached up to 100% (Yin et al., 2016). It is worth mentioning that the  
510 UF process also exhibited high flux ca.  $1,300 \text{ L m}^{-2} \text{ h}^{-1}$  (at 0.23 Mpa), which was stable during  
511 120 min operating time.

512  
513 Very recently, another kind of MOF-based nanocomposite has proven an unprecedented removal,  
514 ca. 100%, of multiple heavy metal ions from wastewaters. Yuan et al. (2019) developed a  
515 composite asymmetric membrane by coating  $\text{Al}_2\text{O}_3$  with ZIF-300, as illustrated in **Figure 2**.

516  
517 **Figure 2.** Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic  
518 dye from water (Yuan et al., 2019).

519  
520 The success of Yuan's membranes was based on the impressive size-exclusion mechanism of ZIF-  
521 300. As reported by the authors, this water-stable MOF may possess an aperture size of pores  
522 around  $7.9 \text{ \AA}$ , which represents a larger kinetic diameter than the one of water ( $\text{H}_2\text{O}$ ,  $\sim 2.8 \text{ \AA}$ ), but  
523 still smaller than the hydrated diameter of heavy metal ions (e.g.  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{2+}$ ). The  
524 membranes remarkably reached to remove completely such compounds (Yuan et al., 2019).  
525 Furthermore, the ZIF-300 membrane demonstrated a high permeation (water permeance of  $39.2 \text{ L}$   
526  $\text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) and rejection rate of 99.2% towards  $\text{CuSO}_4$ , together with stable performance.  
527 Towards the coating of different materials on organic or inorganic supports, Ibrahim et al. (2018)  
528 combined PSF and poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated  
529 (PAH) to remove over 91% for  $\text{Pb}^{2+}$  and 72% for  $\text{Cd}^{2+}$  ions. In fact, the authors concluded an



530 impressive adsorption ability of such composite, which led to the UF process to be enough for the  
531 efficient removal of these heavy metal ions.

532 Among novel materials for UF, MF and NF filtration processes, ceramic materials are also  
533 promising tools for wastewater treatment due to their large specific surface area and convenient  
534 interior pore structure for filtration, catalysis and adsorption (Wu et al., 2019). Fe-based ceramic  
535 nanomaterials were used by Wu et al. (2019) for the fabrication of vacuum filtered membranes  
536 (VFMs) and polymer mixed e-spinning membranes (ESPMs), which were later assayed for Cd<sup>2+</sup>  
537 ions removal from aqueous solutions. During the ceramic synthesis, a hydrothermal method was  
538 implemented for tailoring the Fe-based nanomaterials using FeOOH and  $\mu$ -Fe<sub>2</sub>O<sub>3</sub> nanowires as  
539 well as Fe<sub>3</sub>O<sub>4</sub> NPs. Experimentally, VFMs showed a higher removal capacity than ESPMs; in  
540 contrast, ESPMs demonstrated to have better mechanical strength and stability. Particularly, VFM  
541 exhibited the highest Cd<sup>2+</sup> adsorption capacity, ca. 29.3 mg g<sup>-1</sup>, owed to a larger surface area  
542 provided by NPs in the membrane and a plenty internal pore structure, however, this resulted in  
543 drawbacks in terms of structural reliability shown by looseness and micro-cracks after the third  
544 filtration process, therefore, further studies aimed to improve mechanical strength properties  
545 should be conducted. On the other hand, nanoparticles doped ESPM after the fourth filtration  
546 maintained the original structure without fractures thanks to the better ductility properties and  
547 magnetic cores inside the nanofiber. According to the authors, chemical sorption, consisting of  
548 electron exchange between membranes and ions, was suggested to be the rate-controlling  
549 mechanism for Cd<sup>2+</sup> adsorption, but the Cd adsorption mechanism was also indicated to be a multi-  
550 step process involving an external membrane surface adsorption and intraparticle diffusion. As  
551 concluding remarks from this study, it was observed that the ESPMs adsorption capacity was  
552 definitely enhanced with the Fe<sub>3</sub>O<sub>4</sub> NPs as membrane precursors, but Cd<sup>2+</sup> removal capacity should  
553 be improved in further studies by possibly modifying the polymers on the membrane surface.



554 Within the last years of research on novel materials for improving nanocomposite fillers, particular  
555 attention has been given to mostly synthetic-based fillers, leaving aside green material-based ones,  
556 which are categorized in such a way due to their plant, animal, or natural origin. In this framework,  
557 Kamari and Shahbazi (2020) initiated and innovated the preparation of green nanofillers made  
558 from Fe<sub>3</sub>O<sub>4</sub> magnetic NPs coated with rice husk extracted silica (SiO<sub>2</sub>) functionalized with 3-  
559 Aminopropyl trimethoxy silane. The obtained Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanofiller was then embedded  
560 into the matrix of a PES NF membrane, and subsequently tested the removal of Cd (II) and methyl  
561 red dye coming from industrial effluents. Results showed that the membrane presented an  
562 asymmetrical morphology and highly dense layer, assigned to the fact Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanofiller  
563 acted as a pore causing agent, promoting porosity. It was also seen that greater concentration  
564 amounts (ca. 0.5 wt.%) of the nanofiller into the membrane demonstrated to increase the water  
565 diffusion due to its hydrophilic functional groups (such as amine) present on the surface. The  
566 membrane filled with 0.5wt.% Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> yielded the best salt rejection performance, as  
567 well as the highest removal efficiencies of 93% and 97% for Cd (II) and methyl red dye,  
568 respectively. Cd (II) adsorption was also found to be enhanced by the presence of polar primary  
569 amine NH<sub>2</sub> functional groups on the surface, acting as active binding sites. While methyl red dye  
570 adsorption was associated with the electrostatic interactions and non-covalent bonds given by the  
571 hydrophilicity nature of the green nanofiller. In addition to this, an excellent antifouling capacity  
572 was revealed by the novel membrane together with good reusability property for Cd removal, e.g.  
573 it demonstrated a 7% decrease in removal efficiency after the fifth Cd (II) filtration cycle. Long-  
574 term stability and anti-contamination properties for methyl red dye removal were also confirmed  
575 by the maintenance of a constant 97% filtration efficiency and a slight decrease in solution flux  
576 after a 40h filtration process. Hence, this pioneering study should be considered as a starting point





577 within the implementation of green material-based nanofillers for filtration membranes since it has  
578 proven to be an innovative promising alternative for the removal of pollutants.

579 Up to now, it is evident that nanocomposite membranes implemented in UF, MF and NF processes  
580 for the removal of heavy metals is a research field with a promising future ahead, coring the  
581 development of sustainable wastewater treatment strategies. At this point, research efforts must  
582 continue to be done on discovering innovative mixtures of nanocomposite materials and their  
583 interactions, that may result in membrane enhancements in terms of mechanical strength,  
584 adsorption mechanisms, metal removal efficiency rates, antifouling, reusability, permeability, and  
585 selectivity properties. All these properties will foster **the implementation of** efficient and reliable  
586 processes. Based on current findings, the research community is extensively working on the  
587 development of novel types of composites. For instance, **Table 4** presents a variety of novel  
588 nanocomposites that have not been implemented yet in the fabrication of filtration membranes,  
589 however, they represent a promising future since they count with effective adsorption mechanisms,  
590 innovative material combinations and also synthesized following novel methodologies for the  
591 removal of heavy metals, offering new clues on what is next on improving nanocomposite  
592 membrane technology. It is quite possible that such new composites will be assayed in membrane-  
593 based separations expecting acceptable performance based on their relevant findings in separating  
594 metal ions from water systems.

595  
596 **Table 4.** Novel nanocomposite materials with outstanding heavy metal removal efficiency that  
597 have not been implemented in membranes.

598  
599 Recently, Dinh et al. (2020) tailored a chitosan-MnO<sub>2</sub> nanocomposite which was tested as an  
600 adsorbent to remove Cr(VI) from an aqueous solution. Thanks to its high Langmuir monolayer



601 adsorption capacity of about  $61.5 \text{ mg g}^{-1}$ , this new material displayed high Cr removal (of about  
602 94%) in the effluent from industrial zones. The authors claimed that electrostatic attraction was  
603 fundamental to the uptake of Cr onto the composite. Importantly, such composite was also  
604 evaluated during 5 cycles, showing a removal efficiency decrease up to 80%. Unlike Dinh's study,  
605 a core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C) exhibited a  
606 tremendous adsorption capacity (over  $800 \text{ mg g}^{-1}$  for Cr) and thus revealing an acceptable Cr (VI)  
607 removal efficiency of 80% (Zhou et al., 2020).

608 The adsorption capacity depends on the characteristics of elements forming the nanocomposite,  
609 their synergistic effect and their resulting properties, for example, Mahmoud et al. (2019) notified  
610 a higher adsorption capacity in  $\text{SiO}_2@\text{VB9}$  nanocomposite for Pb (over  $900 \text{ mg g}^{-1}$ ) than Cd (ca.  
611  $562 \text{ mg g}^{-1}$ ) and Cu (ca.  $152 \text{ mg g}^{-1}$ ), such metal uptake capacities allowed to the resulting  
612 composite to show high removal efficiency ranged from 81 to 100% for all tested heavy metal  
613 ions. Dai et al. (2020) have very recently proved that the strategic selection of the elements  
614 proposed for the nanocomposite fabrication may result in a high-performance material, for  
615 instance, Dai et al. introduced  $\text{Fe}_3\text{O}_4/\text{GO}$  composite into graphitic carbon nitride  $\text{g-C}_3\text{N}_4$ , which  
616 provided an impressive U (VI) extraction capacity (up to  $2880 \text{ mg g}^{-1}$ ) together with high removal  
617 efficiency (ca. 96 %). Due to its chemisorption properties, an EDTA modified magnetic iron oxide  
618 loaded with sawdust carbon ( $\text{EDTA}@\text{Fe}_3\text{O}_4/\text{SC}$ ) composite has demonstrated a 98% Cd (II)  
619 removal capacity; according to the study, the Cd (II) removal efficiency increased as pH value and  
620 adsorbent dose increase. Moreover, this nanocomposite also presented good multi-metal ion  
621 uptake (over 80%) for Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI), and high  
622 adsorption efficiency (ca. 83%) after three cycles, proving an input of its reusability. At this point,  
623 most of the newly nanocomposite materials (presented in **Table 4**) release a satisfactorily good  
624 metal ion uptake ability being potential candidates for the fabrication of membranes towards water



625 purification and disinfection (Castro-Muñoz, 2020b). However, the synthesis and preparation  
626 methodologies, as well as the resulting cost, implied in the fabrication protocols may represent a  
627 drawback during the further implementation of such materials in membranes. Even if the ongoing  
628 progress and innovation of new composite materials have been pointed out over this review, the  
629 economic feasibility related to the fabrication cost is a critical driver for their establishment and  
630 implementation. Unfortunately, economic feasibility, which may represent a profitable and  
631 competitive business, is a fundamental factor for the investment of companies and suppliers  
632 (Urbancová, 2013; Skapa, 2012). Herein, scientists must also be focused on developing new  
633 materials and fabrication protocols considering fewer sources and less costly aimed at producing  
634 economically sustainable materials. In this context, there is today a new trend in utilizing green  
635 and bio-based materials for the development of economically viable feedstocks and products.  
636 Since different carbonaceous materials, such as GO, activated carbon and CNTs, have shown their  
637 potentiality as adsorbents for copper decontamination (Ren et al. 2013), it is likely that other  
638 potential materials, like biochar, may also be a promising candidate in the preparation of  
639 composites. It is worth mentioning that biochar is commonly manufactured by pyrolysis of  
640 biomass and plant-based derivatives. Therefore, the synthesis and usage of biochar represent an  
641 environmentally friendly way to produce low-cost adsorbents (Marousek et al., 2020ab), which  
642 have been recently involved in the fabrication of membranes for the selective separation of  
643 phosphate from phosphate-rich wastewaters (Mohammadi et al., 2020).

644 Most of the nanocomposite materials and membranes tend to display impressive metal ion uptake,  
645 and more importantly, some composites can concurrently remove more than one type of ion.  
646 However, to core the complete resource recovery (i.e. water), it is important to consider the  
647 synthesis of nanocomposite membranes which may offer the simultaneous removal of heavy metal  
648 ions and organic contaminants, e.g. Zhang et al. (2020) developed composite membranes filling

649 polydopamine-coated ferric oxide ( $\text{Fe}_3\text{O}_4@\text{PDA}$ ) in PES. In addition to the higher permeabilities  
650 of the composite membranes (e.g. over  $2600 \text{ L/m}^2 \text{ h bar}$  corresponding to 20wt.%  $\text{Fe}_3\text{O}_4@\text{PDA}$   
651 PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive  
652 removal of  $\text{Pb}^{2+}$  and catalytic degradation of methylene blue, e.g. acceptable  $\text{Pb}^{2+}$  removal  
653 efficiency (above 80%) together with high methylene blue degradation (above 90%). In this case  
654 of study, the authors strategically designed the composite to display a synergistic effect. For  
655 example, the phenolic hydroxy and amino groups on the surface of PDA were able to chelate the  
656 cations to promote the adsorption of heavy metal ions, while the electron transfer in the Fenton-  
657 like reaction was promoted due to the phenoquinone structure of the surface of the PDA, boosting  
658 the catalytic reaction. With a similar scope, Fan et al. (2019) documented the simultaneous and  
659 rapid removal of organic micropollutants (bisphenol) and metal ions ( $\text{Pb}^{2+}$ ) using an electrospun  
660  $\beta$ -cyclodextrin/chitosan/polyvinyl alcohol nanofibers. These novel nanocomposites exhibited a  
661 large number of adsorption sites, e.g. the cyclodextrin owed a featured molecule structure with a  
662 hydrophilic outer surface and hydrophobic inner cavity for binding organic contaminants while  
663 chitosan has plenty of hydroxyl and amino groups to form complex with metal ions and thus  
664 remove them. Both authors concluded that their nanocomposites represent a new pathway to deal  
665 with hard-to-be-treated wastewaters (e.g. paper making, leather, textile, etc.)

## 666 667 **5. Concluding remarks, future perspectives, and strategies for new researchers in the field**

668 Throughout this review paper, it has been recognized the potential ability of polymeric membranes  
669 in separating various heavy metal ions, including  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  
670  $\text{Cr}^{4+}$ , among others. These membranes can exhibit a removal efficiency between 77-99%.  
671 However, by smartly introducing inorganic nanomaterials into polymer membranes,  
672 nanocomposite membranes have overcome the main drawbacks of polymeric membranes together  
673 with improved removal efficiencies up to 100%. This review has released a clear outlook on the

674 benefits of implementing composite membranes for the separation and removal of a wide range of  
675 toxic and heavy metal ions, in which their elimination from water has been proposed attending the  
676 current worldwide necessity for clean water scarcity.

677 **To date**, a huge number of studies have provided promising proofs and insights that the MF  
678 composite membranes have been able to remove **macropollutants**, but the separation of  
679 **micropollutants** may need the usage of UF and NF membranes. Interestingly, nanocomposite  
680 membranes have shown their impressive adsorption ability for the removal of heavy metal ions,  
681 being strongly dependent on the smart selection of the inorganic materials according to their  
682 **physicochemical** features. This means that the adsorption efficiency of nanoparticles and their  
683 sieving mechanism must be considered during the tailored manufacturing of nanocomposite  
684 membranes towards the removal of specific heavy metal ions. In the light of process feasibility,  
685 nanocomposite membranes have also shown enough features to be implemented in efficient  
686 separation processes with good permeation rates, which is also a relevant parameter in terms of  
687 productivity. Based on the current findings of this review, and the current developments works and  
688 efforts in developing new composite materials, it is likely that **the** research community will  
689 continue looking for new inorganic and hybrid materials **that** could not only overcome the  
690 drawbacks (such as permeation and retention rates) of polymeric membranes but also  
691 **physicochemical** properties (e.g. chemical, mechanical and thermal stability) as well. To finalize,  
692 it is presented below some recommendations for planning the research of new researchers aiming  
693 to improve the efficiency of nanocomposite membranes:

- 694 • Initially, researchers must identify the potential polymers that display high enough removal  
695 efficiency. Based on this, further investigation can be planned and directed based on the  
696 main bottleneck and weakness of the pristine polymers.

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- When dealing with filling nanomaterials into polymers, it is essential to mention that such inorganic phases must be smartly embedded considering two important factors: 1) the physicochemical features of the nanomaterials (porosity, stability, morphology, among others), and ii) their metal uptake mechanisms related to the removal of heavy metals (sieving, adsorption, size-exclusion, etc.). Such basic analysis will bring big benefits in a shorter time and fewer sources, i.e. low filler loading may synergistically improve the properties of polymer membranes. For example, 1wt.% GO loaded PVDF-GO-nZVI membrane cannot only reach high 100% Cd (II) removal but also impressive permeation fluxes (ca.  $255 \text{ L m}^{-2} \text{ h}^{-1}$ ) (Ren et al., 2019), which is also an important factor during the feasibility of large scale processes. Finally, the usage of a low quantity of fillers will result in a reduced membrane cost.
  - The membrane preparation protocols also play an important role in the resulting separation efficiency in membranes. Even if most of the advances in the field have been assigned to the properties of the nanomaterials, it is also important to point out that the exploration of new membrane fabrication procedures, together with the improvement of the existing ones, will allow tailoring of substantially enhanced membranes. This also applies when embedding simultaneously more than one inorganic phase.
  - Most of the research has satisfactorily demonstrated excellent performance towards metal ion separations, however, there are few reports demonstrating the feasibility of the membranes in a long-term operation, which is a current lack in research. By extending the testing of membranes, the chemical engineers will have a better outlook about the potentiality of membranes for possible implementation in industrial processes.
  - To finalize, based on the relevant insights and ability of the novel nanocomposite materials enlisted in **Table 4**, it is recommended to the new scientists to explore the ability of such



721 new materials into membrane processes for the removal of metal ions. Importantly, the  
722 separation efficiency of membrane processes not only depends on membrane features but  
723 also on the operating conditions.

724

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## 734 **References**

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**Table 1.** Polymeric membranes used for the removal of metal ions.

Separation process:	Material/membrane	Heavy metals	Removal efficiency (%)	Reference
NF	PBI/PES	Mg <sup>2+</sup> , Cd <sup>2+</sup>	98%, 95%	(Zhu et al., 2014)
NF	PA	Cu <sup>2+</sup> , Cd <sup>2+</sup>	98%, 99%	(Qdais and Moussa, 2004)
RO	PA	Cu <sup>2+</sup> , Cd <sup>2+</sup>	>90%	(Qdais and Moussa, 2004)
ED	sulfonated PVDF	Co <sup>2+</sup> , Ni <sup>2+</sup>	90 % , 69 %,	(Tzanetakis et al., 2003)
NF	CA/ PMVEMA	Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>+6</sup>	85%, 72%	(Lavanya et al., 2019)
NF	PES-PE	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup>	>90%	(Mokhter et al., 2017)
NF	PAN-PEI/PSS	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup>	98%, 96%, 96%, 95%	(Qin et al., 2013)
UF	PVDF/2-Aminobenzothiazole	Cr <sup>6+</sup>	92%	(Wang et al., 2017)
UF	PVDF/PANI	Pb <sup>2+</sup> , Cd <sup>2+</sup>	98.5%, 97.3%	(Pereira et al., 2014)

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**Table 2.** Different filling materials embedded into nanocomposite membranes for different water treatment applications.

Filling material:	Membrane-based process:	Application:	Polymer phase:	Reference:	
ZnO	MF	Synthetic wastewater treatment		(Liang et al., 2012)	
		Removal of copper ions	PVDF	(Xia Zhang et al., 2014)	
		Wastewater treatment		(Hong and He, 2012)	
		Humic acid removal	PES	(Ahmad et al., 2016)	
		Humic acid removal	PSF	(Chung et al., 2016)	
		Water treatment		(Dipheko et al., 2017)	
			Pollutants removal	PES	(Li et al., 2015)
		UF	Water treatment	PES-PVA	(Zhao et al., 2015)
			Wastewater treatment		(Pintilie et al., 2017)
			Bacterial removal from aqueous solutions	PSF	(Ronen et al., 2013)
			Water treatment	PVC	(Rabiee et al., 2015)
			Humic acid removal	PES	(Balta et al., 2012)
			Water purification	PVP	(Bai et al., 2012)
			Removal of metal ions ( $Zn^{2+}$ , $Cd^{2+}$ , $Pb^{2+}$ , $Mn^{2+}$ , $Ni^{2+}$ , $Fe^{2+}$ , $Al^{3+}$ , $Sb^{3+}$ , $Sr^{3+}$ )	CA	(Bahadar et al., 2015)
			Humic acid removal	PSF	(Tao et al., 2017)
	NF				

GO	RO	Humic acid removal		(Ekambaram and Doraisamy, 2017)
		Humic acid removal	PVDF	(Li et al., 2017)
	MF	Removal of bivalent ions ( $\text{Ca}^{2+}$ , $\text{SO}_4^{2-}$ and $\text{Mg}^{2+}$ ), monovalent ions ( $\text{Cl}^-$ and $\text{Na}^+$ ), and bacterias.	PA	(Isawi et al., 2016)
		Dyes removal from effluents	PSF	(Badrinezhad and Ghasemi, 2017)
	UF	Wastewater treatment	PVDF	(Zhao et al., 2014)
		Water treatment	PSF	(Zhao et al., 2013)
		Water treatment	PVP-PVDF	(Chang et al., 2014)
		Water treatment		(Wu et al., 2014)
		Natural organic matter removal		(Xia and Ni, 2015)
		Water treatment		(Zhao et al., 2013)
		Natural organic matter removal	PVDF	
		Natural organic matter removal	PA	(Xia et al., 2015)
		Wastewater treatment	PSF	(Lee et al., 2013)
		Organic pollutants removal	Cellulose ester	(Morales-Torres et al., 2015)
Distillery effluent treatment	PES	(Kiran et al., 2016)		
Water softening production	PAI-PEI	(Goh et al., 2015)		
Dyes removal from effluents	PMIA	(Yang et al., 2017)		
Dyes removal from effluents	PAN	(Zhang et al., 2017)		
Dyes removal from effluents	PES	(Zinadini et al., 2014)		
Water purification	PPA	(Jin Wang et al., 2016)		





Graphene	UF	Wastewater treatment	PSF	(Crock et al., 2013)
	NF	Water purification	PVDF	(Han et al., 2013)
		Wastewater treatment		(Zhang et al. , 2012)
MF /UF	Wastewater treatment		(Alpatova et al., 2013)	
Ag-nanoparticles		Water purification	PSF	
		Wastewater treatment	PES	(Rehan et al., 2016)
		Wastewater treatment	PES, PSF, CA	(Sile-Yuksel et al., 2014)
		Wastewater treatment		(Koseoglu-Imer et al., 2013)
		Wastewater treatment	PSF	(Hoek et al., 2011)
	UF	Wastewater treatment		(Escobar et al., 2015.)
		Wastewater treatment	CA	(Andrade et al., 2015)
Ag-NO <sub>3</sub>		Wastewater treatment	PA-PVA	(Yang Zhang et al., 2016)
	NF			
	RO	Wastewater treatment	PA	(Ben-Sasson et al., 2014)
		Wastewater treatment	PA/PSF/	(Yang et al., 2016)
		Bacterial removal from water	PET	
		CA	(Ahmad et al., 2016)	
		Water treatment		(Zhang et al., 2013)
	RO		PES	

Ag-nanoparticles	RO	Water treatment	PAN	(Liu et al., 2016)
	UF	Water treatment	PES	(Zhang et al., 2014)
	NF	Water treatment and removal of salt (Na <sub>2</sub> SO <sub>4</sub> )	PA	(Liu et al., 2015)
bio-Ag0		Water treatment		(Liu et al., 2016)
Cu-nanoparticles		Water treatment		(Hoek et al., 2011)
			PSF	
CuAc <sub>2</sub>		Humic acid removal	PAN/PEI	(Xu et al., 2012)
Cu-nanoparticles		Wastewater treatment	PES	(Akar et al., 2013)
	UF			
Ag-nanoparticles		Wastewater treatment	PSF	(Kar et al., 2011)
Cu-nanoparticles				
	NF	Seawater softening: removal of salts (SO <sub>4</sub> <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , Cl <sup>-</sup> ).	PAN/PEI	(Xu et al., 2015)
CuSO <sub>4</sub>				
CuCl <sub>2</sub>	RO	Wastewater treatment		(Zhang et al., 2017)
Cu nanoparticles		Water treatment	PA	(Ben-Sasson et al., 2014)
		Humic acid removal		(Teow et al, 2012)
		Water treatment		(Rajaeian et al., 2015)
		Wastewater treatment	PVDF	(Shi et al., 2012)
		Water treatment		(Méricq et al., 2015)
	UF	Water treatment	PP	(Pi et al., 2016)



		Water treatment	PSF	(Mollahosseini and Rahimpour, 2014)
		Water treatment	CA	(Abedini et al., 2011)
		Water treatment		(Ngo et al., 2016)
			PA	
TiO <sub>2</sub> nanoparticles	NF	Wastewater treatment	PES	(Sotto et al., 2011)
CNTs	NF	Drinking-water purification	NC	(Ahmeh et al., 2013)
	UF	Water treatment and biofouling control application	PES	(Celik et al., 2011)
	NF	Wastewater treatment	PES	(Daraei et al., 2013)
	NF	Water treatment	PA	(Kim et al., 2013)
	NF	Metal removal (Cr (VI), Cd (II))	PSF	(Shah and Murthy, 2013)
	NF	Water treatment for salt removal (NaCl, Na <sub>2</sub> SO <sub>4</sub> ).	PMMA	(Shen et al., 2013)
	NF	Water treatment	Polyimide 84	(Grosso et al., 2014)
	UF	Water treatment	PSF	(Sianipar et al., 2016)
	UF	Wastewater treatment by membrane bioreactor	PSF	(Khalid et al., 2018)
	MF	Bleach effluent treatment by membrane bioreactor	PSF	(Mulopo, 2017)

**Acronyms:** polyethersulfone (PES), polysulfone (PSF), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinylidene fluoride (PVDF), poly(methyl methacrylate) (PMMA), nitrocellulose (NC), cellulose acetate (CA), polyamide (PA), polyphthalamide (PPA), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polyvinylpyrrolidone (PVP), polyamide-imides (PAI), polyethylenimine (PEI).



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**Table 3.** Latest development works on tailoring novel nanocomposite membranes for heavy metal ions removal.

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Nanocomposite membrane type:	Membrane process:	Metal ion removal :	Reference:
MMGO filled PES	NF	Copper ions removal (92%)	(Abdi et al., 2018)
f-MWCNTs filled PVC	NF	Zinc ( $Zn^{2+}$ ) ions removal (98%)	(Ali et al., 2019)
s-MWCNTs	-	Copper (II) ions removal (59%)	(Ge et al., 2014)
CNFs/ $TiO_2$ filled PAN	-	Lead ( $Pb^{2+}$ ) ions removal (87%)	(Suresh et al., 2018)
		Copper ( $Cu^{2+}$ ) ions removal (73%)	
		Cadmium ( $Cd^{2+}$ ) ions removal (66%)	
(MEUF)PES	UF	Cadmium ( $Cd^{2+}$ ) ions removal (90%)	(Huang et al., 2019)
(MEUF) cellulose	UF	Arsenic (V) ions removal (89%)	(Chen et al., 2018)
PAH-PSF	UF	Lead ( $Pb^{2+}$ ) ions removal (91.5%)	(Ibrahim et al., 2018)
		Cadmium ( $Cd^{2+}$ ) ions removal (72.3%)	
s-PES	UF	Ferric ( $Fe^{3+}$ ) ions removal (>90%)	(López et al., 2019)
MMT-GO-EDA	UF	Ag (I) ions removal (100%)	( Ma, 2019)
		Cu (III) ions removal (100%)	
		Cr (IV) ions removal (27.0%)	
CF- $TiO_2$ - $C_3N_4$	MR	Cr (VI) ions removal (88.0%)	(Shen et al., 2018)
Composite -CA	RO	Pb ( $Pb^{2+}$ ) ions removal (100%)	(Thaçi and Gashi, 2019)
		Cd ( $Cd^{2+}$ ) ions removal (100%)	
		Ni ( $Ni^{2+}$ ) ions removal (100%)	
		Zn ( $Zn^{2+}$ ) ions removal (100%)	



		Mn (Mn <sup>2+</sup> ) ions removal (100%)	
		Co (Co <sup>2+</sup> ) ions removal (100%)	
Composite GPC	UF	Pb (Pb <sup>2+</sup> ) ions removal (>95%)	(Jing Wang et al., 2018)
PECN	NF	Zn (Zn <sup>2+</sup> ) ions removal (100%)	(Ye et al., 2019)
f- MOFs-CUF	UF	Pb (Pb <sup>2+</sup> ) ions removal (61.4%)	(Yin et al., 2016)
ZIF-300-Al <sub>2</sub> O <sub>3</sub>	NF	Cu (Cu <sup>2+</sup> ) ions removal (100 %)	(Yuan et al., 2019)
		Co (Co <sup>2+</sup> ) ions removal (100 %)	
		Cd (Cd <sup>2+</sup> ) ions removal (100 %)	
		Al (Al <sup>2+</sup> ) ions removal (100 %)	
Goethite filled PAN	UF	Cu (Cu <sup>2+</sup> ) ions removal (49 %)	(Soghra et al., 2019)
Composite PEI- zein	FO	Pb (Pb <sup>2+</sup> ) ions removal (>99.5%)	(X. Zhao & Liu, 2019)
		Cd (Cd <sup>2+</sup> ) ions removal (>99.5%)	
		Ni (Ni <sup>2+</sup> ) ions removal (>99.5%)	
GMA-PAN	UF	Cu (Cu <sup>2+</sup> ) ions removal (98 %)	(Yanhong Zhang et al., 2019)

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467 **Acronyms:** functionalized multi-walled carbon nanotubes (f-MWCNTs), modified magnetic graphene oxide(MMGO), sulfonated multi-walled carbon nanotubes (s-  
468 MWCNTs), carbon nanofibers (CNFs), micellar enhanced ultrafiltration (MEUF), poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH),  
9 sulfonated polyethersulfone(s-PES),GO-based membranes via the intercalation of montmorillonite and ethylenediamine ( MMT-GO-EDA), C<sub>3</sub>N<sub>4</sub>-decorated carbon-  
0 fiber (CF-TiO<sub>2</sub>-C<sub>3</sub>N<sub>4</sub>), membrane reactor (MR), graphene oxide-polydopamine-(β-cyclodextrin) (GPC), polyelectrolyte complex nanofiltration (PECN), functionalized  
1 MOFs-CUF (f- MOFs-CUF), grafting glycidyl methacrylate (GMA).  
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1474 **Table 4.** Novel nanocomposite materials with outstanding heavy metal removal efficiency that have not been implemented in membranes.

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Nanocomposite materials	Heavy metals removal efficiency	Adsorption mechanism	Parameters affecting adsorption mechanism	Fabrication method	Synthesis conditions	Reusability	Reference
MnO <sub>2</sub> coated by chitosan nanocomposite	Cr (VI) adsorption (61.56 mg g <sup>-1</sup> )  Cr (VI) removal efficiency (94.21%)	Physisorption and electrostatic attraction	<b>pH effect</b>  Adsorption efficiency decreases with ascending pH values (optimal pH=2)  <b>Ion strength</b>  Ionic strength, with an increase in the KCL concentration decreases Cr (VI) removal efficiency  <b>Adsorbent dosage</b>  The material concentration affects Cr (VI) adsorption capacity	MnO <sub>2</sub> /CS was fabricated by mixing, filtering and drying a suspension made up by C <sub>2</sub> H <sub>5</sub> OH, deionized (DI) water, CS and saturated KMnO <sub>4</sub> solution	<b>Mixing</b> 8 h at room temperature  Different shaking speeds were tested  <b>Oven drying</b> 60°C for 12 h	5 cycles. Removal efficiency decreased (from 94% to 80%)	(Dinh et al., 2020)
Core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C)	Cr (VI) adsorption capacity (814.9 mg g <sup>-1</sup> )  Cr (VI) removal efficiency (80%)	Chemical reduction reaction of Cr (VI) into Cr (III)	<b>Cr (VI) Initial concentration effect</b>  High initial Cr (VI) concentration values increased the reduction capacity  <b>pH effect</b>	Hydrothermal-calcination method	<b>Drying</b>  Vacuum conditions at 80°C for 24h.  <b>Carbonization</b>  Pipe oven under N <sub>2</sub> atmosphere, at 800 C° for 30 min	No tests were performed	(Zhou et al., 2020)



			pH affects the electron utilization process (Optimal pH below 3)				
			<b>C/Fe molar ratio</b>				
			20 C/Fe optimal ratio				
Nanocomposite of 20% hickory biochar and 80% expanded vermiculite (20%-BC/VE)	As (V) adsorption capacity (20.1 mg g <sup>-1</sup> )	Heterogeneous adsorption processes, both physisorption and chemisorption, ion exchange and electrostatic attraction	<b>Nanocomposite ratio effect</b>  Optimal ratio: 20%-BC/VE  <b>pH effect</b>  pH affects the BC/VE surface charge, as well as the electrostatic interactions (optimal pH= 6)  <b>Coexisting anions effect</b>  <i>PO<sub>4</sub><sup>3-</sup></i> reduced considerably adsorption rate of As (V)	Ball milling method	<b>Ball milling</b>  At 300 rpm for 12 h	No tests were performed	(Li et al., 2020)
Fe <sub>3</sub> O <sub>4</sub> /GO (mGO) composite introduced into graphitic carbon nitride g-C <sub>3</sub> N <sub>4</sub> .	U (VI) extraction capacity (2880.6 mg g <sup>-1</sup> )  U (VI) extraction efficiency (96.02%)	Chemical reaction of photocatalytic reduction of U (VI) under LED light irradiation	<b>pH effect on photocatalytic activity</b>  Optimal pH=6  <b>U (VI) concentration effect on photoreduction in mGCN-1</b>	Ultrasonication was applied to the individual suspensions and then to the mixture of mGO and g-C <sub>3</sub> N <sub>4</sub>  The solids of the mGO and g-C <sub>3</sub> N <sub>4</sub> mixture were centrifuged and dried	<b>Ultrasonication</b>  Individually for 1 h and as mixture for 2h.  <b>Drying</b>  In a vacuum at 60°C	5 cycles  There were not significant changes in removal and stability rates	(Dai et al., 2020)

			Optimal U(VI) concentration range: 1 – 100 mg L <sup>-1</sup>				
Silicon dioxide composite with tea waste (SiO <sub>2</sub> @TW)	<p>Adsorption capacities:</p> <p>Pb<sup>2+</sup> (153 mg g<sup>-1</sup>) and Cd<sup>2+</sup> (222 mg g<sup>-1</sup>)</p> <p>Removal rates:</p> <p>Pb<sup>2+</sup> (89.22%) and Cd<sup>2+</sup> (94.28%)</p>	Electrostatic attraction and physical adsorption	<p><b>pH effect</b></p> <p>Optimal pH values:</p> <p>Pb<sup>2+</sup> (pH= 6) and Cd<sup>2+</sup> (pH=7)</p> <p><b>SiO<sub>2</sub>@TW dosage effect</b></p> <p>High dose of SiO<sub>2</sub>@TW enhanced adsorption sites, increasing removal capacity</p> <p><b>Temperature effect</b></p> <p>Elevated temperature was a catalyst for adsorption, due to chemical bond rupture that enhanced contact between metal ions and surface-active sites</p>	<p>Modified Stober method for SiO<sub>2</sub> NPs fabrication</p> <p>SiO<sub>2</sub>@TW synthesis consisted of sonication, centrifugation and drying of SiO<sub>2</sub> - tea waste powder suspension</p>	<p><b>Stirring</b></p> <p>For 30 min at 25°C</p> <p><b>Sonication</b></p> <p>For 1h</p> <p><b>Drying</b></p> <p>For 3h at 80°C</p>	5 cycles	(Joshi et al., 2020)
Hybrid bio-nanocomposite of nano-hydroxy ferric phosphate (n-HFP) and hydroxy ferric sulfate (n-HFS) particles coated on fungal hyphae of <i>Aspergillus Niger</i> ( <i>An</i> ) ((n-HFP + n-HFS) @An).	<p>Simultaneous adsorption rates:</p> <p>As (III) (76.84%), Cd (II) (73.62 %) and Pb (II) (94.31%)</p> <p>Adsorption capacities:</p> <p>As (III) (162 mg g<sup>-1</sup>), Cd (II) (205.83</p>	Chemical adsorption for the three metals	No tests were performed	<p>Co-precipitation method was used to fabricate n-HFP and n-HFS NPs</p> <p>Potato dextrose broth (PDB) medium containing dissolved n-HFP and n-HFS NPs as well as magnetically stirred <i>An</i> mycelium inoculate was cultured</p>	<p><b>Magnetic stirring</b></p> <p>At 1000 rpm for 6 h</p> <p><b>Culturing</b></p> <p>In PDB medium at 30°C, 170 rpm for 1-2 days</p>	Reduced risk for contamination: 10-day stability of loaded NPs in solution	(Liao et al., 2019)



	mg g <sup>-1</sup> ), and Pb (II) (730.79 mg g <sup>-1</sup> )						
Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) entrapped in calcium-alginate matrix (nZVI/BC/CA)	Cr (VI) adsorption capacity (86.4 mg g <sup>-1</sup> )	Ion exchange, intraparticle diffusion, chemical adsorption and redox reaction	<b>pH effect</b>  Optimal pH= 4	Modified liquid-phase method	<b>Pyrolysis</b>  At 500°C for 3 h in a muffle furnace (15°C / min) under N <sub>2</sub> atmosphere  <b>Stirring</b> 500 rpm at 25°C for 30 min.	Removal capacity decreased at the 1 <sup>st</sup> cycle but remained stable in further regenerations	(Wan et al., 2019)
Nanocomposite made from wastewater hyacinth derived biochar (BC) and ZnO NPs	Cr (VI) removal efficiency (95%)  Cr (VI) adsorption capacity (43.48 mg g <sup>-1</sup> )	Chemisorption and photocatalytic reduction	<b>Carbonization temperature effect</b> Optimal carbonization temperature: 700°C  <b>ZnO content effect</b> 30 wt.% optimal ZnO concentration	BC powder was impregnated into Zn(NO <sub>3</sub> ) <sub>2</sub> aqueous solution, by drying and calcination steps	<b>Drying</b> At 105°C for 12h. <b>Calcination</b> At 380°C for 3h under N <sub>2</sub> atmosphere	Removal efficiency (87.1% at 1 <sup>st</sup> run) and (67.1% at 5 <sup>th</sup> run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe <sub>3</sub> O <sub>4</sub> ), loaded with SC (sawdust carbon) (EDTA@Fe <sub>3</sub> O <sub>4</sub> /SC)	Cd (II) adsorption capacity (63.3 mg g <sup>-1</sup> )  Cd (II) removal capacity (98%)  Multi-metal ion removal (>80%), for the following ions: Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI)	Chemisorption	<b>pH effect</b>  Cd (II) removal efficiency increases as pH value rises  (Optimal pH= 6.5)  <b>Adsorbent dose effect</b>  Cd (II) removal increased as adsorbent dose increased  <b>Contact time effect</b>	Biogenic green synthesis approach for fabrication	<b>Stirring</b> At 90°C for 1h  <b>Carbonization</b> In muffle furnace at 180°C for 12h	<b>Desorption</b>  Maximum Cd (II) desorption was achieved with HCl (99%), HNO <sub>3</sub> (100%) and H <sub>2</sub> SO <sub>4</sub> (100%)  <b>Reusability</b>  After three cycles, adsorption efficiency (83%) and at the	(Kataria and Garg, 2018)

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Optimum contact time for Cr (II) removal: 120 min

fifth cycle (57%)

**Coexisting ions effect**

Divalent ions ( $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$ ) caused a decrease in Cr (II) removal efficiency

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Silica ( $\text{SiO}_2$ ) functionalized folic acid (VB9) ( $\text{SiO}_2@VB9$ ) nanocomposite

Adsorption capacities: Cd (II) ( $562.1 \text{ mg g}^{-1}$ ), Pb (II) ( $973.8 \text{ mg g}^{-1}$ ) and Cu (II) ( $152.1 \text{ mg g}^{-1}$ )

Physio-chemical process and stable complex formation

**pH effect**

Optimal pH values: Cd (II) (pH = 7), Cu (II) (pH = 6) and Pb (II) (pH = 5)

Methodology consisting of microwave assistance for covalent immobilization of VB9 with chlorinated silica

**Stirring**  
1 hour  
**Oven drying**  
At  $60^\circ\text{C}$   
**Microwaving**  
For 2min

No tests were performed

(Mahmoud et al., 2019)

Extraction rates:

Cu (II) (94-100%), Pb (II) (100%) and Cd (II) (57- 81%)

**Nanocomposite dosage effect**

Removal efficiency increased with ascending dosage values (Optimum dosage: 10 mg)

**Contact time effect**

Optimum contact time for metal removal: 25 min

**Initial metal ion concentration effect**

Optimal metal ion concentration: 0.25 mg/L

**Coexisting ions effect**

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Ni (II) and Co (II)  
decreased metal ion  
removal capacity

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1477 **Acronyms:** *Aspergillus niger* (*An*), biochar (BC), calcium - alginate (CA), ethylenediaminetetraacetic (EDTA), nanoparticles (NPs), nano hydroxy ferric phosphate (n-  
1478 HFP), nano hydroxy ferric sulfate (n-HFS), nanoscale Zero Valent Iron (nZVI), Protein Dextrose Broth (PDB), sawdust carbon (SC), tea waste (TW), vitamin B9 folic  
1479 acid (VB9), vermiculite (VE).

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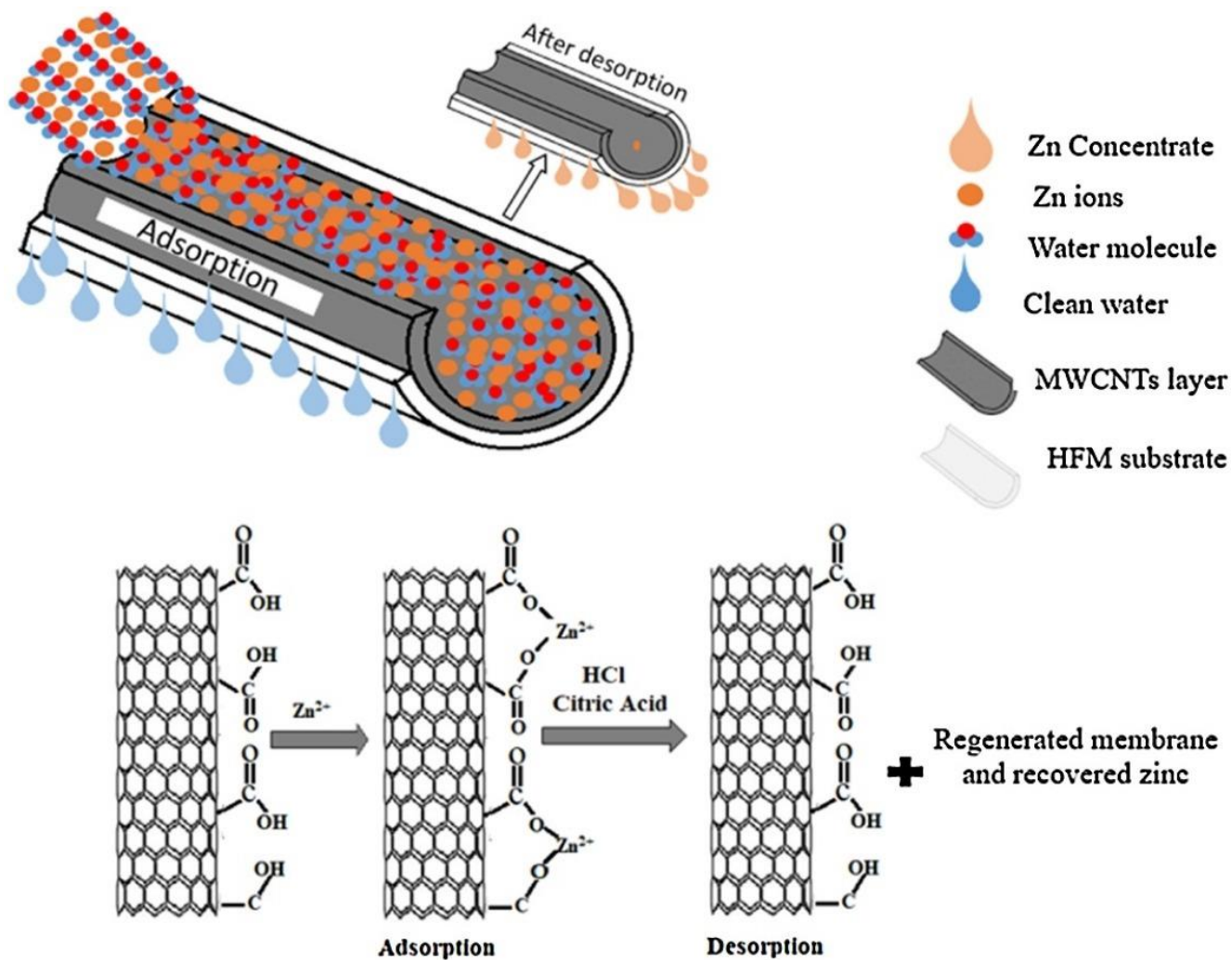
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**Figure 1.** Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et al., 2019).



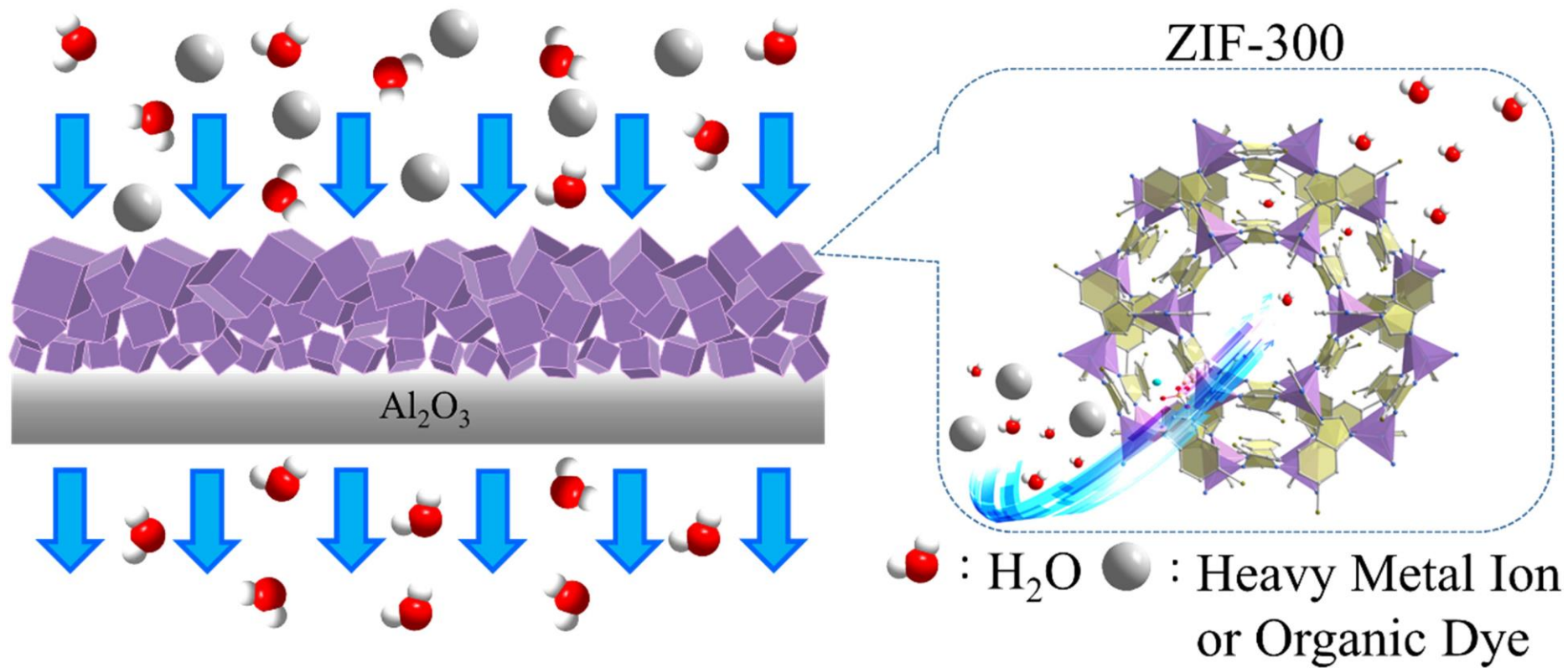
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**Figure 2.** Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).

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1 **Ongoing progress on novel nanocomposite membranes for the separation of heavy metals**  
2 **from contaminated water**

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## 26 **Abstract**

27 Membranes, as the primary separation element of membrane-based processes, have greatly  
28 attracted the attention of researchers in several water treatment applications, including wastewater  
29 treatment, water purification, water disinfection, toxic and non-toxic chemical molecules, heavy  
30 metals, among others. Today, the removal of heavy metals from water has become challenging, in  
31 which chemical engineers are approaching new materials in membrane technologies. Therefore,  
32 the current review elucidates the progress of using different concepts of membranes and potential  
33 novel materials for such separations, identifying that polymeric membranes can exhibit a removal  
34 efficiency from 77 up to 99%; while novel nanocomposite membranes are able to offer complete  
35 removal of heavy metals (up to 100%), together with unprecedented permeation rates (from 80 up  
36 to 1, 300 L m<sup>-2</sup> h<sup>-1</sup>). Thereby, the review also addresses the highlighted literature survey of using  
37 polymeric and nanocomposite membranes for heavy metal removal, highlighting the relevant  
38 insights and denoted metal uptake mechanisms. Moreover, it gives up-to-date information related  
39 to those novel nanocomposite materials and their contribution to heavy metals separation. Finally,  
40 the concluding remarks, future perspectives, and strategies for new researchers in the field are  
41 given according to the recent findings of this comprehensive review.

## 43 **Keywords**

44 *Heavy metals; water treatment; membrane-based technologies, water purification, novel composite*  
45 *materials.*

## 47 **Abbreviations:**

48 Ag: silver

49 As: Arsenic

50 APTS: 3-Aminopropyltriethoxysilane

- 51 CA: Cellulose acetate
- 52 Cd: Cadmium
- 53 CNT: Carbon Nanotubes
- 54 Co: Cobalt
- 55 Cr: Chromium
- 56 Cu: copper
- 57 DCMD: Direct contact membrane distillation
- 58 ESPM: Polymer Mixed e-spinning Membranes
- 59 Fe: Iron
- 60 f-GO: functionalized Graphene Oxide
- 61 GO: Graphene Oxide
- 62 IPDI: Isophorone diisocyanate
- 63 MD: Membrane distillation
- 64 MF: Microfiltration
- 65 MMGO: Modified magnetic Graphene Oxide
- 66 MMM: Mixed Matrix Membranes
- 67 MOF: Metal-Organic Frameworks
- 68 MWCNT: Multi-walled carbon nanotubes
- 69 NF: Nanofiltration
- 70 Ni: Nickel
- 71 NPs: Nanoparticles
- 72 nZVI: nano– Zero Valent Iron
- 73 PAH: Poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated
- 74 PAN: Polyacrylonitrile



- 75 PBI: Polybenzimidazole
- 76 PES: Polyethersulfone
- 77 PMVEMA: Poly(methyl vinyl ether-alt-maleic acid)
- 78 POSS: Polyhedral Oligomeric Silsesquioxane
- 79 PSF: Polysulfone
- 80 PSS: Poly(sodium 4-styrenesulfonate)
- 81 PV: Pervaporation
- 82 PVA: Polyvinyl alcohol
- 83 PVP: Polyvinylpyrrolidone
- 84 PVDF: Polyvinylidene fluoride
- 85 RO: Reverse Osmosis
- 86 TCE: Trichloroethylene
- 87 UF: Ultrafiltration
- 88 VFM: Vacuum filtered membranes
- 89 ZIF: Zeolite imidazolate framework

90  
91  
92

### 93 **1. Introduction**

94 The removal of pollutants (including metal ions) from water has been approached using several  
95 traditional treatments and protocols, such as chemical precipitation (Chabot et al., 2014), microbial  
96 decomposition (Yang et al., 2016), and physical adsorption (Kumar et al., 2013). Inherently, these  
97 pollutants represent strong issues to the environment (i.e. plants, animals, ecology climate) and  
98 humans. However, the removal of heavy metals through conventional protocols (such as flotation,  
99 chemical precipitation, ion exchange, adsorption, and electrochemical deposition) is still

100 challenging, requiring further efforts to circumvent the production of a high amount of toxic sludge  
101 and liquid waste, long time consumption, and extreme use of supplies (e.g. solvents, resins, among  
102 others), together with poor separation efficiency.

103 Currently, according to the scarcity of drinking water and the increasingly serious water pollution  
104 (Marousek et al., 2019), water treatment with membrane-based processes has potentially attracted  
105 the attention of the research community. Membranes are involved in various prominent large-scale  
106 advanced treatment approaches applied worldwide for artificial groundwater recharge, indirect  
107 potable reuse, and industrial process-water production. Particularly, ultrafiltration, nanofiltration  
108 and reverse osmosis are among the emerging membrane technologies used at a large-scale for  
109 resource recovery (i.e. water) from wastewater treatment plants (Kehrein et al., 2020). To date,  
110 polymeric membranes are likely the most used membranes for water treatment applications  
111 (Castro-Muñoz et al., 2018a), including treatment of agro-food wastes (Castro-Muñoz et al., 2016),  
112 textile (Chao et al., 2016), petroleum industry streams (Alzahrani and Wahab, 2014), acid mine  
113 waters (Lopez et al., 2019), and seawater desalination (Castro-Muñoz, 2020a). Membranes are  
114 capable to separate the compounds from aqueous streams and thus reduce the contaminants  
115 contained in wastewater (Castro-Muñoz et al., 2018b). Extensive sources and a large number of  
116 molecules, as well as ions contained in polluted water, challenge the effective purification and  
117 separation of water by membranes. The membranes, based on their intrinsic properties, can be  
118 implemented among different types of membrane-based technologies including pressure-driven  
119 membrane processes, such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and  
120 Reverse osmosis (RO). These are potentially recognized as excellent candidates for the removal  
121 of large amounts of organic macropollutants; in which NF and RO membranes are among the  
122 barriers with the highest efficiency in withdrawing micropollutants (Castro-Muñoz et al., 2017).  
123 Other membrane technologies, e.g. membrane distillation (MD) (Criscuoli and Carnevale, 2015),

124 membrane bioreactors (Santos and Judd, 2010), membrane contactors (Bey et al., 2010), have also  
125 been proven to remove specific heavy metal ions, such as arsenic (As), fluoride (F) and uranium  
126 (U). In particular, As is a natural tasteless and odorless element that may be highly toxic to humans  
127 exposed to it from air, food and water. It is known that this element exists in the earth's crust at  
128 average levels between 2000–5000 µg per kg (Figoli et al., 2010).

129 In this way, membranes have shown to be efficient in removing different metal ions (e.g. Cd<sup>2+</sup>,  
130 Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Al<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>4+</sup>) from water streams. A large number of studies has  
131 been now devoted to the manufacture of synthetic membranes for these particular separations,  
132 demonstrating compelling benefits, such as permeability, selectivity, enhanced chemical and  
133 physical properties within the removal of metal ions. When dealing with the removal efficiency of  
134 such membranes, the material properties, including chemical, physical, mechanical, play an  
135 important role in their efficiency, but also the membrane preparation protocols are crucial. In this  
136 context, several techniques have been used in membrane manufacture, such as stretching, track-  
137 etching, sintering, electrospinning, phase inversion (Lalia et al., 2013), and interfacial  
138 polymerization (Peydayesh et al., 2018), in which plenty of organic and inorganic materials have  
139 been proposed and used in tailoring membranes (Castro-Muñoz et al. 2020). Polymers have been  
140 the most used organic materials in membrane preparation, followed by the inorganic ones (e.g.  
141 ceramics, metals and glass) (Ulbricht, 2006). Polymer membranes tend to present great design  
142 flexibility, while the advantages of inorganic membranes, e.g. ceramic membranes, compared with  
143 polymeric ones comprise their higher thermal, mechanical and chemical stability (Castro-Muñoz  
144 et al. 2018c). Also, the hydrophilicity and the surface charge in ceramic membranes are higher.  
145 Ceramic membranes can also be operated under extreme conditions of pH, temperature and high  
146 oxidizing environment (Yong et al., 2013). As a current trend in the field of development of new  
147 membrane materials, the merging of both materials to produce nanocomposite membranes is also



148 a promising tool for the efficient removal of heavy metals. However, there is a lack of reviewing  
149 the progress and latest nanocomposite membrane concepts and their role in water treatment and  
150 separation of heavy metals. Very recently, novel breakthroughs in tailoring nanocomposite  
151 materials have been released, such as nanoscale zerovalent iron impregnated biochar entrapped in  
152 calcium-alginate matrix (Wan et al., 2019), MnO<sub>2</sub>/chitosan (Dinh et al., 2020), core-shell  
153 structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe<sub>3</sub>O<sub>4</sub>/GO composite  
154 introduced into graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> (Dai et al., 2020), to mention just a few of them.  
155 Thereby, this review paper aims at providing the ongoing progress of using different concepts of  
156 membranes (polymeric, composite and nanocomposite) and potential novel materials for removing  
157 heavy metals. Herein, a highlighted literature survey of using polymeric and nanocomposite  
158 membranes for heavy metal removal from water is provided. Ultimately, the current advances and  
159 future trends of nanocomposite membranes in the field are also given.

160

## 161 **2. Metal ions removal using pristine polymeric and chemically modified polymeric** 162 **membranes**

163 Polymers are probably the most widely applied membrane material for wastewater treatment. Due  
164 to their advantages including facile pore-forming mechanism, low cost and high flexibility (Yong  
165 et al., 2013), polymers are leading as the main material for membrane manufacture for different  
166 membrane-based technologies, such as electrodialysis, UF, NF and RO. Experimentally,  
167 polymeric membranes can remove different types of contaminants, such as organic matter, organic  
168 and inorganic compounds (e.g. heavy metal ions), and suspended pollutants (Wieszczycka and  
169 Staszak, 2017).

170 Polymeric membranes are typically manufactured from natural or chemically-synthesized  
171 polymers. The membranes are creating a selective interface barrier between two adjacent phases

172 (feed and permeate) which governates the transport behavior of species between them. In general,  
173 the separation performance of the membrane depends on the properties of transported species (e.g.  
174 molecule size, shape and chemical nature), as well as physicochemical properties  
175 (hydrophilicity/hydrophobicity, surface charge, roughness) of the polymer membrane, especially  
176 porous structure. For instance, **Table 1** enlists some of the reported studies in which the removal  
177 of heavy metal ions has been performed by means of different polymeric membranes and  
178 processes. It can be seen that the removal efficiency towards metal ions using polymer membranes  
179 has been reported between 77 to 99%.

180

181 **Table 1.** Polymeric membranes used for the removal of metal ions.

182

183 For instance, Qdais and Moussa (2004) evaluated the separation performance of the RO and NF  
184 technologies using polyamide spiral wound membranes for the removal of copper (Cu) and  
185 cadmium (Cd) metals from industrial wastewater. While the RO process showed Cu and Cd  
186 removal efficiencies of about 98 and 99%, respectively, the NF process exhibited more than 90%  
187 of Cu ions. Interestingly, the membranes were able to concurrently treat wastewater containing  
188 more than one heavy metal ion. As an example, these membranes reduced the ion concentration  
189 from 500 ppm to 3 ppm, meaning a removal efficiency of over 99%. Another typical polymeric  
190 membrane material is polyethersulfone (PES), which has been successfully consolidated in  
191 membrane preparation owing to its high thermal and mechanical stability, physiological and  
192 chemical neutrality and wide range pH resistance. PES, however, tends to present a hydrophobic  
193 nature which results in high membrane fouling when applied for organic aqueous filtration. Thus,  
194 with the aim of improving its separation performance and properties, efforts have been proposed  
195 to shift the surface properties of this hydrophobic polymer. It is known that hydrophobic polymers



196 are more prone to membrane fouling due to the particles contained in the feed bulk tend to  
197 accumulate on hydrophobic and rough surfaces, minimizing the interfacial tension between water  
198 and membrane (Pichardo-Romero et al., 2020). Therefore, the on-going strategies are aimed at  
199 mitigating the interaction between the foulants and the barrier layer. For example, an easy approach  
200 is to chemically modify the surface properties of the membrane by immersing it in a polyelectrolyte  
201 solution. It has been found that the polyelectrolyte adsorbed onto the membranes may significantly  
202 improve the membrane performance in terms of metal ions removal due to the presence of  
203 chelating functions in their structure. In this way, Mokhter et al. (2017) performed the chemical  
204 modification of PES membranes by polyelectrolyte multilayers, made of poly(allylamine  
205 hydrochloride) with poly(styrene sulfonate). The resulting membranes were employed to treat  
206 aqueous solutions containing single or mixed heavy metals,  $\text{Cu}^{2+}$ , zinc ( $\text{Zn}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ), at  
207 various concentrations (50–1200 ppm). The tested membrane was efficient in separating all the  
208 tested metals either alone or mixed with high long-term stability and removal efficiencies over  
209 90%. Similarly, polyacrylonitrile (PAN) membranes were modified by Qin et al. (2013), who  
210 synthesized positively charged membranes by depositing polyelectrolytes. Researchers used PAN  
211 membranes modified by the layer-by-layer assembly of polyethyleneimine (PEI) and poly(sodium  
212 4-styrenesulfonate) (PSS), to successfully separate  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  aqueous solutions,  
213 achieving removal efficiencies in the range of 95–98%. Particularly, the NF tests showed that the  
214 removal efficiency of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions increased with the number of bilayers, but a decrease in  
215 permeate fluxes was observed. The usage of additional polymeric layers could also be applicable  
216 in the case of hollow fiber membranes. The great benefit of multi-layer materials lies in the fact  
217 that a relatively cheap material could be used as a support while a high-performance material  
218 (commonly a more expensive material) can be used as the selective layer. For instance, Zhu et al.  
219 (2014) tailored a high-performance dual-layer NF hollow fiber membrane and tested for the



220 removal of  $\text{Cd}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pb}^{2+}$  salts from model wastewater, attaining removal efficiencies  
221 above 95%. Herein, researchers applied polybenzimidazole (PBI) as the outer selective layer while  
222 the blend of PES and polyvinylpyrrolidone (PVP) was implemented as the support layer. Thanks  
223 to the unique charge characteristics and high chemical resistance of PBI, the novel developed dual-  
224 layer NF membrane demonstrated a great salt rejection value due to the Donnan exclusion effect  
225 enhancement and low adsorption of heavy metal ions on the PBI surface.

226 Polyvinylidene fluoride (PVDF) is definitely another hydrophobic polymer that remains popular  
227 in a wide number of water treatment applications (Gontarek et al., 2019; Xia & Ni, 2015). PVDF  
228 membranes are well recognized for their multiple advantages including high chemical tolerance,  
229 good mechanical and thermal properties. Tzanetakis et al. (2003) have proved that the performance  
230 of chemically sulfonated PVDF membrane in the electro dialysis process can be comparable with  
231 the one given by a perfluorosulfonic Nafion 117 commercial membrane. The sulfonated PVDF  
232 membrane has displayed removal efficiencies towards Co and Ni ions of about 90% and 69%,  
233 respectively. In addition to this, a meaningful enhancement of the amounts of transported metal  
234 ions was seen while using corrugated membranes, which resulted in an increase in membrane area  
235 of 60% compared with those using flat membranes. Wang et al. (2017) have developed the  
236 modification of PVDF membrane for post UF testing. In general, the results revealed that the  
237 interaction by blending of PVDF with 2-aminobenzothiazole conducted to the efficient removal of  
238 chromium (Cr) from the wastewater. As a disadvantage of such membrane preparation, the  
239 membranes showed a low permeate flux when compared with the typical UF membranes. Since a  
240 long time ago, it is documented that one of the simplest approaches to improve the water flux in  
241 hydrophobic polymeric membranes, like PVDF, is to mitigate the membrane fouling, which can  
242 be reached through hydrophilicity enhancement. For instance, Pereira et al. (2014) combined  
243 PVDF polymer matrix with polyaniline nanofibers, which was, in this case, proposed as a

244 hydrophilic agent to fabricate enhanced hydrophilic membranes. The authors described that the  
245 resulting membranes exhibited better hydrophilicity and better membrane properties, as well as a  
246 relatively high rejection toward heavy metal ions, such as  $Pb^{2+}$  and  $Cd^{2+}$ , e.g. around 98.5% and  
247 97.3%, respectively.

248 Cellulose acetate (CA), originated from natural sources and feedstocks, is a polymer material  
249 widely used in UF membrane manufacture. Such a polymer combines the advantages to have low  
250 cost and high biocompatibility with other materials. Unfortunately, this polymer does not reveal  
251 high enough fluxes, and it can allow preparing low porous sub-layers, as well as easy fouling issues  
252 (Combe et al., 1999). However, the blending of CA with hydrophilic agents may result in  
253 membranes with a superior antifouling property. This has been indeed demonstrated by Lavanya  
254 et al. (2019), who carried out the blending of CA with poly(methyl vinyl ether-alt-maleic acid)  
255 (PMVEMA). The generated membranes displayed enhanced antifouling capacity in the blend  
256 membranes in comparison with the pristine CA membrane. When dealing with their separation  
257 performance, the flux recovery ratio was reached up to 95%. Importantly, the pure water fluxes  
258 of such blend membranes were raised with the content of PMVEMA, since PMVEMA conducted  
259 to higher porosity and hydrophilicity. Concurrently, the blend membranes were also more efficient  
260 for the removal of heavy metal ions compared to pure CA membrane.

261 Taking into account the advantages and disadvantages of polymeric membranes, the popularity of  
262 their use and implementation for removing heavy metal ions is also attributed to their low  
263 manufacture costs and ease of modification. However, such polymeric membranes still lack  
264 different desired properties for membrane separation processes, including the ones that required  
265 high selectivity towards low solutes and species. To date, many works have been done at aiming  
266 the enhancement of the separation performance of the polymeric membranes (as listed in **Table**  
267 **1**). Nevertheless, the membrane fouling and low mechanical strength in polymeric membranes are





268 recognized as the most relevant issue in limiting their application. The development and  
269 manufacture of membranes with high selectivity, permeability, rejection, and superior antifouling  
270 properties are the biggest challenges among scientists who work on membrane development and  
271 separation processes. Despite these drawbacks, the membranes have shown interesting results  
272 during the removal of heavy metal ions. For example, Uddin et al. (2007) analyzed the removal  
273 capacity of two commercial NF polyamide membranes (NF90 and NF200) towards As (III) and  
274 As (V). The effect of the operating conditions on the rejection performance was investigated in the  
275 study. As set by authors, the feed stream contained mainly in tap water together with arsenate and  
276 arsenite. In all tests, As (V) was generally rejected better than As (III), and the membranes offered  
277 the high removals over 98% and 65% for As (V) and As (III), respectively.

278 Amy et al. (1998) previously designed a bench-scale RO process implementing a commercial  
279 membrane (DK2540F manufactured by DESAL) for As removal. The experiments comprised the  
280 single element testing in flat sheet membrane for lake water and deionized water filtration. The  
281 findings demonstrated high removal efficiency towards arsenate (up to 96%), and acceptable  
282 removal efficiency for arsenite (60–85%).

283 More recently, using a different membrane process, i.e. membrane distillation (MD), it has been  
284 demonstrated its ability to effectively separate specific heavy metal ions. For example, direct  
285 contact MD (DCMD) technology can be feasible in removing up to 99.95% arsenic molecules,  
286 like As (III) and As (V), from a contaminated water model solution. Interestingly, this process was  
287 operated for 250 h containing  $500 \mu\text{g L}^{-1}$ , the process did not evidence any change in the permeate  
288 fluxes and As content (Pal and Manna, 2010). Similarly, Manna and Pal (2016) used a similar  
289 DCMD unit, but in this case possessing a hydrophobic flat sheet membrane (nominal pore size  
290  $0.13 \mu\text{m}$ , thickness  $150 \mu\text{m}$ , porosity 70–75%). As a result, the systems proved an As removal of



291 about 100% from contaminated groundwater, and no flux decline was recorded during 4 days of  
292 operation.

293 Today, the most important approach in obtaining membranes with exceptional separation  
294 performance and properties relies on the synthesis and preparation of nanocomposites. This  
295 concept of membranes is well defined together with their features in the following section, and  
296 finally, the progress and latest development works in manufacturing such membranes for heavy  
297 metals removal.

298

### 299 **3. Beginnings of nanocomposite membranes for the removal of heavy metal ions**

300 Polyethersulfone (PES), polysulfone (PSF), PAN, polytetrafluoroethylene, polypropylene, and  
301 PVDF are among the main polymer materials used in the manufacture and production of  
302 membranes for pressure-driven membrane processes. It is known that most of these materials have  
303 excellent permeability, selectivity, and acceptable chemical, mechanical and thermal stability  
304 when used in water treatment applications. Particularly, PSF and PES membranes are the most  
305 used materials for manufacturing UF membranes. Such standard chemically synthesized polymers  
306 are also involved within the fabrication of NF and RO membranes, while polypropylene and PVDF  
307 are more exploited in MF membranes production (Pendergast, & Hoek, 2011). However, it is still  
308 challenging the optimization and enhancement of the separation performance of these pristine  
309 polymeric membranes (Alzahrani& Wahab, 2014), as well as the improvement of some other  
310 physicochemical properties, such as stability, hydrophilicity/hydrophobicity, fouling resistance,  
311 among others (Hana et al., 2016).

312 The enhancement of such properties has been recently breakthrough by using nanotechnology,  
313 which has been extended in a wide range of applications into membrane-based technologies, e.g.  
314 to enhance the membranes' efficiency for the removal of heavy metals, which is a relevant matter

315 within water treatment (Ursino et al., 2018). Nanocomposite membranes are recognized as “*the*  
316 *next generation of membranes*”. In theory, a typical nanocomposite membrane includes the  
317 dispersion or deposition of nanosized filling materials into polymer matrices (Castro-Muñoz et al.,  
318 2018d; Castro-Muñoz et al., 2018e; Song et al., 2012). This concept of membranes can be  
319 implemented in different membrane-based separations, including gas–gas, liquid–liquid, and  
320 liquid–solid separation. In the early 1990s, nanocomposite membranes were initially developed  
321 for membrane gas separation processes (Ahmadizadegan et al., 2018; Robeson, 1991), where  
322 selective zeolites were embedded into polymers to improve both permeability and selectivity (Li  
323 et al., 2017). Due to such success on gas separation approaches, nanocomposite membranes were  
324 then initiated to be explored in other fields of applications and processes, such as sensor  
325 applications (Jiang et al., 2004; Pandey et al., 2018), direct methanol fuel cells (Chen et al., 2006),  
326 lithium-ion battery (Li et al., 2008), proton exchange membrane fuel cells (Boaretti et al., 2017;  
327 Jalani et al., 2005), pervaporation (PV) (Castro-Muñoz et al., 2018e; Yang et al., 2009), organic  
328 solvent nanofiltration (Sorribas et al., 2013), water treatment, to mention just a few.

329 Nanocomposite membranes, also known as mixed matrix membranes (MMM), are not only  
330 tailored by embedding nanosized materials into a continuous matrix phase, nanoparticles or fillers  
331 can also be coated onto the membrane surface, which is actually well denoted as a nanocomposite  
332 membrane. Currently, the preparation and implementation of these membranes are a current trend  
333 in the nanotechnological field for water treatment, especially in the separation of metal ions  
334 (Marino et al., 2017). Importantly, such nanosized filling materials not only possess exceptional  
335 features that may be provided to the primary element (e.g. polymer) but also good compatibility  
336 when embedded. Nanocomposite membranes have concurrently revealed low-fouling issues when  
337 embedding the inorganic materials (Kim and Bruggen, 2010), together with improved permeability  
338 and selectivity, compared with polymeric membranes (Madaeni et al., 2015). To date, plenty of

339 nanosized fillers have been utilized in the preparation of nanocomposite membranes, such as  
340 titanium dioxide (TiO<sub>2</sub>) (Zhang et al., 2013), silver (Ag) (Prince et al., 2014), carbon nanotubes  
341 (CNTs) (Celik et al., 2011), zinc oxide (ZnO) (Balta et al., 2012), copper oxide (CuO) (García et  
342 al., 2017), graphene-based materials (e.g. graphene, graphene oxide or reduced graphene oxide)  
343 (Gontarek et al., 2019; Kashyap, Pratihari and Behera, 2016; Xia and Ni, 2015), alumina (Al<sub>2</sub>O<sub>3</sub>)  
344 (Arsuaga et al., 2013), silica (SiO<sub>2</sub>) (Yu et al., 2009), magnetite (Fe<sub>3</sub>O<sub>4</sub>) (Alam et al., 2016), cobalt  
345 (Co) (Gzara et al., 2016), zirconium dioxide (ZrO<sub>2</sub>) (Maximous et al., 2010), clay (Mierzwa et al.,  
346 2013) and zeolites (e.g. NaX) (Fathizadeh et al., 2011), among others. For instance, **Table 2**  
347 summarizes recent studies in which such inorganic fillers have been filled among several polymers  
348 and then applied in different applications of water treatment, wastewater treatment, toxic and metal  
349 ions removal from water.

350

351 **Table 2.** Different filling materials embedded into nanocomposite membranes for different water  
352 treatment applications.

353

354 Specially, these nanocomposite membranes have shown valid insights during the removal of  
355 metal ions. For example, Bahadar et al. (2015) developed and tested ZnO-filled CA nanocomposite  
356 membranes for the separation of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup>, Sb<sup>3+</sup>, and Sr<sup>3+</sup>,  
357 concluding that these membranes were highly selective towards Fe<sup>2+</sup>. Furthermore, the developed  
358 membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>. Some  
359 authors have tailored nanocomposite membranes based on functionalized multi-walled carbon  
360 nanotube (MWCNT)/polysulfone (Shah and Murthy, 2013), which also has demonstrated ability  
361 for heavy metal removal (up to 98%). In this study, the percent of rejection towards heavy metal  
362 was noted to increase by increasing the MWCNTs amount due to MWCNTs reduced the



363 membranes' pore size, the best nanocomposite performances were about 94.2% and 78.2%  
364 removal for Cr(VI) and Cd(II), respectively. It is important to mention that pristine polymer offered  
365 only 10.2% and 9.9% removal, respectively. Here, the use of inorganic materials is showing  
366 remarkable enhancement of polymeric membranes towards heavy metal ions retention. Therefore,  
367 the research community is today putting big efforts into the development of novel nanocomposite  
368 membranes that may efficiently separate heavy metal ions from several aqueous streams. Herein,  
369 the following section provides the progress, latest developments and breakthroughs in the field.

370

371

#### 372 **4. Progress in nanocomposite membranes for heavy metal ions separation**

373 To date, different categories of fillers and additives have been involved in the manufacture of  
374 nanocomposite membranes. Graphene oxide (GO) is likely one of the main materials that has been  
375 fully explored. GO has attracted the attention of the research community, especially for the  
376 separation of toxic ions and organic molecules in polluted water (An et al., 2016). GO has proven  
377 its excellent separation ability towards different molecules (e.g. water molecules) and ions. GO  
378 possesses interlayer nano-capillary networks that are formed thanks to their connected interlayer  
379 spaces, together with the gaps between edges of non-interlocked neighbouring GO sheets (An et  
380 al., 2016; He et al., 2015), facilitating the transport of molecules or ions through the GO membrane.  
381 At this point, multiple factors, including molecules' size or ions, the charge of ions, and numerous  
382 interactions (such as electrostatic interaction, metal coordination, and cation- $\pi$  interaction between  
383 ions and GO sheets) strictly influence the separation performance of the GO. These properties  
384 make to consider GO as a promising candidate material within the removal of pharmaceutical  
385 traces from water and wastewater (Sophia et al., 2016). More interestingly, the embedding of GO  
386 can also bring some benefits to the properties of the polymeric membranes, e.g. thanks to the high



387 hydrophilicity of GO, the change of the hydrophobic to hydrophilic nature of polymeric  
388 membranes has been done, resulting in enhanced permeation fluxes (Xia et al., 2015). As an  
389 example, Chang et al. (2014) analyzed the synergistic effect of GO and PVP on the performance  
390 of PVDF UF membranes. The study found out that the membrane's hydrophilicity and anti-fouling  
391 properties were enhanced by the addition of both GO and PVP. The authors concluded that this  
392 enhancement could be associated with the possible formation of hydrogen bonds between PVP  
393 and GO. Recognizing the multiple benefits that GO has given to polymeric membranes,  
394 researchers have initiated the improvement of the structural features of GO, e.g. the chemical  
395 modification has been an alternative in the field. According to researchers' insights, the chemical  
396 modification (to a positive charge) of GO is suggested for better metal ions removal efficiency (Yu  
397 Zhang et al., 2015). In this sense, Xu et al. (2014) performed the chemical functionalization of  
398 graphene oxide (f-GO) through a simple covalent functionalization with 3-  
399 aminopropyltriethoxysilane (APTS). The resulting organosilane-GO was then filled in PVDF UF  
400 membranes (Xu et al., 2014), the PVDF/ f-GO membranes had higher hydrophilicity, water flux,  
401 and protein rejection than pristine PVDF membranes and conventional PVDF/GO membranes. For  
402 instance, the membranes, containing 1wt.% f-GO, released a high permeate flux of about 401.3 L  
403  $\text{m}^{-2} \text{h}^{-1}$ , a higher value compared to the one provided by the pristine PVDF (ca. 240  $\text{L m}^{-2} \text{h}^{-1}$ )  
404 and PVDF/GO membranes, pointing out that these composite membranes also had better anti-  
405 fouling properties due to their higher hydrophilicity (Xu et al., 2014).

406 More recently, Zhang et al. (2017) carried out the cross-linking procedure in GO composite with  
407 isophorone diisocyanate (IPDI), later coated on PVDF membrane. Basically, the cross-linking  
408 methodology helped to improve the removal of dyes (over 96%) and heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  
409  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ) (between 40-70 %) in the MF membrane compared to the pattern GO-PVDF  
410 membrane. It is worth mentioning that these composite membranes also showed high permeation

411 rates between  $80\text{-}100\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$  under low external pressure (i.e. 1.0 bar). By embedding  
412 modified magnetic GO (MMGO), it was also eventuated a significant increase in the pure water  
413 flux due to changes in surface roughness and hydrophilicity of PES NF membranes. Regarding the  
414 copper and dye removal ability of the membranes remarkably increased thanks to the presence of  
415 hydrophilic functional groups on the surface of MMGO hybrid. The prepared NF membrane,  
416 containing 0.5 wt.% MMGO hybrid, demonstrated the highest copper ions removal (ca. 92%)  
417 (Abdi et al., 2018). The authors also stated that these GO-filled NF membranes can also be good  
418 candidates in other types of water treatment applications, such as water softening, decolorization,  
419 natural organic matter removal (Wei et al., 2018).

420 A more recent approach to improving GO-based nanocomposite PVDF membranes was done by  
421 Ren et al. (2019), who fabricated PVDF-GO membrane via electrospinning with immobilization  
422 of nano-zero valent iron (nZVI) particles. Such particles were deposited on the surface by *in-situ*  
423 synthesis. This membrane was designed and tested to remove Cd (II) and trichloroethylene (TCE)  
424 contaminants from groundwater, following a mechanism of gravity-driven membrane filtration. In  
425 principle, the hydrophilicity and improved membrane flux was obtained by the functionalization  
426 of GO into PVDF. Results showed that the hydrophilicity of the membranes increased by raising  
427 the GO concentration, leading to an improved permeability property. This resulted in the  
428 achievement of high and stable fluxes of  $255\text{ L m}^{-2}\text{ h}^{-1}$  for Cd and  $265\text{ L m}^{-2}\text{ h}^{-1}$  for TCE.  
429 Moreover, using 1 wt.% GO loaded PVDF-GO-nZVI membrane, removal performances of 100%  
430 and 82% were successfully achieved towards Cd (II) and TCE, respectively. The authors attributed  
431 such relevant Cd removal to a chemisorption phenomenon, while the TCE removal mechanism  
432 consisted of a multi-step dechlorination process involving several reactions. To sum up, the study  
433 has demonstrated that the functionalized PVDF-GO membrane can be a promising barrier for  
434 water remediation due to its high reactivity towards the evaluated pollutants.



435 An interesting future approach on GO-based nanofillers for nanocomposite filtration membranes  
436 has been the one synthesized by Ma et al. (2020). They embedded GO-polyethylene glycol (P-GO)  
437 into a PVDF ultrafiltration membrane and thus proposed such a composite membrane for removing  
438 heavy metals within a wastewater treatment strategy. The membranes prepared via phase inversion  
439 method revealed outstanding results in terms of improved hydrophilicity, permeability and  
440 antifouling properties, while crosslinking between polyethylene glycol and GO contributed to an  
441 increase in thermal stability, pore size as well as surface porosity. The membrane containing 0.5  
442 wt.% P-GO obtained the highest water flux of  $94 \text{ L m}^{-2} \text{ h}^{-1}$ . This was due to the hydrophilicity  
443 provided by the embedded hydrophilic functional groups into the membrane matrix. The same  
444 membrane formulation showed a 94% bovine serum albumin rejection rate, indicating good  
445 separation properties. Furthermore, excellent antifouling properties were acquired by the obtention  
446 of the lowest surface roughness, the lowest total and irreversible resistance values, as well as by a  
447 78% flux recovery obtained after 3 performance cycles. Antifouling property of the membrane  
448 was assigned to hydrophilic groups forming a hydration layer that repulses pollutant contact and  
449 contaminant deposition. The authors highlighted that further studies must be conducted on the  
450 application of this nanocomposite membrane towards the removal of heavy metals due to its  
451 excellent anti-fouling, permeability and hydrophilicity properties.

452 **Table 3** enlists some of the latest studies in nanocomposite membrane synthesis for heavy metal  
453 removal reported by the research community. It is obvious that the separation performance of a  
454 membrane depends on multiple factors, but the membrane preparation procedure is crucial.  
455 Regardless of these important factors, most of the nanocomposite membranes generally display  
456 removal rates ranged from 27 to 100%.

457

458 **Table 3.** Latest development works on tailoring novel nanocomposite membranes for heavy



459 metal ions removal.

460

461 For instance, Ali et al. (2019) reported a 98% zinc ions ( $Zn^{2+}$ ) removal from synthetic water  
462 through filling functionalized MWCNTs into PVC, in which the retention rate was stable over 60  
463 min process time. Interestingly, these membranes also allowed to remove more than 70% zinc ions  
464 ( $Zn^{2+}$ ), when treating real wastewater effluent. The core of success in these membranes was the  
465 chemical functionalization of the MWCNTs. The authors stated that the resulting removal  
466 efficiency of CNT membrane could be associated with the high absolute zeta potential together  
467 with the hydrophilicity of the fillers embedded on the inside surface of the hollow fiber membrane,  
468 and of course the plenty number of oxygen functional groups on CNT surfaces. Theoretically, the  
469 removal capacity can be a function of electrostatic interactions among the positive charge of  $Zn^{2+}$   
470 ions and the negative charge surface of CNTs at specific conditions (e.g. higher pH values) (Lu  
471 and Chiu, 2006), which foster the strong surface complexation reaction. This enabled the  
472 membranes to demonstrate high adsorption ability, as represented in **Figure 1**. The use of  
473 sulfonated MWCNTs also represents a promising pathway in membranes with efficient removal  
474 of heavy metals, these membranes had shown an adsorption removal over 59% for Cu (II) ions  
475 (Ge et al., 2014). Such MWCNTs membranes were also enabled to remove about 99.2% of other  
476 types of toxic components, e.g. rhodamine B (Peydayesh et al., 2018).

477

478 **Figure 1.** Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et  
479 al., 2019).

480 Another example of surface functionalization of materials in nanocomposite membranes showing  
481 promising results on ion removal regards the polyether imide (PEI) nanofiltration membrane using  
482 a nanofiller additive, which consisted of L-cysteine modified glycidyl-polyhedral oligomeric

483 silsesquioxane (POSS) (Bandehali et al., 2020). The PEI membrane filled with 1 wt.% of L-  
484 cysteine modified-POSS provided an outstanding separation efficiency towards  $\text{Cr}^{+2}$  and  $\text{Na}^{+}$  ions  
485 with a rejection percentage of 79% and 80%, respectively, which was attributed to the porous  
486 membrane morphology and the presence of negatively charged hydrophilic functional groups on  
487 the membrane surface, both features promoted the absorption of positively charged ions, as well  
488 as an increase of ion adsorption active spots (Bandehali et al., 2019). Moreover, L-cysteine  
489 functionalized POSS NPs incorporated into the PEI nanofiltration membrane led to a cross-linking  
490 reaction between the amino groups ( $\text{NH}_2$ ) in L-cysteine modified-POSS filler and imide rings in  
491 PEI. This increased the membrane surface hydrophilicity due to the hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ) and amine ( $-\text{NH}_2$ ) functional groups present in these materials, resulting in high water  
492 permeation fluxes of  $95 \text{ L m}^{-2} \text{ h}^{-1}$  (in 1 wt.% of L-cysteine modified-POSS-PEI composite), from  
493  $17.63 \text{ L m}^{-2} \text{ h}^{-1}$  in neat PEI membrane. In addition to the exceptional performance, the modified  
494 filler also offered other benefits to the nanocomposite membranes, such as improved the  
495 antifouling properties to the resulting nanocomposite membranes by decreasing the roughness, a  
496 flux recovery ratio of 95%, increased degree of wetting, as well as an increment in the membrane  
497 surface smoothness, which all added up to the obtention of a better membrane structure for  
498 avoiding salt accumulation.  
499

500 To date, the blending of inorganic phases into polymers has been also a smart alternative for the  
501 simultaneous removal of different types of heavy metal ions. At this point, the filling of multiple  
502 fillers is likely a feasible option for such a task. For instance, Suresh et al. (2018) tailored a hybrid  
503 nanocomposite membrane embedding carbon nanofibers and  $\text{TiO}_2$  into PAN polymer, the  
504 generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards  $\text{Pb}^{2+}$ ,  
505  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  metal ions, respectively. Towards the efficient separation of  $\text{Pb}^{2+}$ , Suresh et al. (2018)  
506 explored and demonstrated that amino-functionalized metal-organic frameworks (MOFs)



507 combined with a ceramic ultrafiltration membrane represent to be an effective material for the  $\text{Pb}^{2+}$   
508 removal, which revealed at least 61.4% removal, whereas the best efficiency depended on the  
509 operating conditions, but it reached up to 100% (Yin et al., 2016). It is worth mentioning that the  
510 UF process also exhibited high flux ca.  $1,300 \text{ L m}^{-2} \text{ h}^{-1}$  (at 0.23 Mpa), which was stable during  
511 120 min operating time.

512  
513 Very recently, another kind of MOF-based nanocomposite has proven an unprecedented removal,  
514 ca. 100%, of multiple heavy metal ions from wastewaters. Yuan et al. (2019) developed a  
515 composite asymmetric membrane by coating  $\text{Al}_2\text{O}_3$  with ZIF-300, as illustrated in **Figure 2**.

516  
517 **Figure 2.** Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic  
518 dye from water (Yuan et al., 2019).

519  
520 The success of Yuan's membranes was based on the impressive size-exclusion mechanism of ZIF-  
521 300. As reported by the authors, this water-stable MOF may possess an aperture size of pores  
522 around  $7.9 \text{ \AA}$ , which represents a larger kinetic diameter than the one of water ( $\text{H}_2\text{O}$ ,  $\sim 2.8 \text{ \AA}$ ), but  
523 still smaller than the hydrated diameter of heavy metal ions (e.g.  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{2+}$ ). The  
524 membranes remarkably reached to remove completely such compounds (Yuan et al., 2019).  
525 Furthermore, the ZIF-300 membrane demonstrated a high permeation (water permeance of  $39.2 \text{ L}$   
526  $\text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) and rejection rate of 99.2% towards  $\text{CuSO}_4$ , together with stable performance.  
527 Towards the coating of different materials on organic or inorganic supports, Ibrahim et al. (2018)  
528 combined PSF and poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated  
529 (PAH) to remove over 91% for  $\text{Pb}^{2+}$  and 72% for  $\text{Cd}^{2+}$  ions. In fact, the authors concluded an



530 impressive adsorption ability of such composite, which led to the UF process to be enough for the  
531 efficient removal of these heavy metal ions.

532 Among novel materials for UF, MF and NF filtration processes, ceramic materials are also  
533 promising tools for wastewater treatment due to their large specific surface area and convenient  
534 interior pore structure for filtration, catalysis and adsorption (Wu et al., 2019). Fe-based ceramic  
535 nanomaterials were used by Wu et al. (2019) for the fabrication of vacuum filtered membranes  
536 (VFMs) and polymer mixed e-spinning membranes (ESPMs), which were later assayed for Cd<sup>2+</sup>  
537 ions removal from aqueous solutions. During the ceramic synthesis, a hydrothermal method was  
538 implemented for tailoring the Fe-based nanomaterials using FeOOH and  $\mu$ -Fe<sub>2</sub>O<sub>3</sub> nanowires as  
539 well as Fe<sub>3</sub>O<sub>4</sub> NPs. Experimentally, VFMs showed a higher removal capacity than ESPMs; in  
540 contrast, ESPMs demonstrated to have better mechanical strength and stability. Particularly, VFM  
541 exhibited the highest Cd<sup>2+</sup> adsorption capacity, ca. 29.3 mg g<sup>-1</sup>, owed to a larger surface area  
542 provided by NPs in the membrane and a plenty internal pore structure, however, this resulted in  
543 drawbacks in terms of structural reliability shown by looseness and micro-cracks after the third  
544 filtration process, therefore, further studies aimed to improve mechanical strength properties  
545 should be conducted. On the other hand, nanoparticles doped ESPM after the fourth filtration  
546 maintained the original structure without fractures thanks to the better ductility properties and  
547 magnetic cores inside the nanofiber. According to the authors, chemical sorption, consisting of  
548 electron exchange between membranes and ions, was suggested to be the rate-controlling  
549 mechanism for Cd<sup>2+</sup> adsorption, but the Cd adsorption mechanism was also indicated to be a multi-  
550 step process involving an external membrane surface adsorption and intraparticle diffusion. As  
551 concluding remarks from this study, it was observed that the ESPMs adsorption capacity was  
552 definitely enhanced with the Fe<sub>3</sub>O<sub>4</sub> NPs as membrane precursors, but Cd<sup>2+</sup> removal capacity should  
553 be improved in further studies by possibly modifying the polymers on the membrane surface.



554 Within the last years of research on novel materials for improving nanocomposite fillers, particular  
555 attention has been given to mostly synthetic-based fillers, leaving aside green material-based ones,  
556 which are categorized in such a way due to their plant, animal, or natural origin. In this framework,  
557 Kamari and Shahbazi (2020) initiated and innovated the preparation of green nanofillers made  
558 from  $\text{Fe}_3\text{O}_4$  magnetic NPs coated with rice husk extracted silica ( $\text{SiO}_2$ ) functionalized with 3-  
559 Aminopropyl trimethoxy silane. The obtained  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$  nanofiller was then embedded  
560 into the matrix of a PES NF membrane, and subsequently tested the removal of Cd (II) and methyl  
561 red dye coming from industrial effluents. Results showed that the membrane presented an  
562 asymmetrical morphology and highly dense layer, assigned to the fact  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$  nanofiller  
563 acted as a pore causing agent, promoting porosity. It was also seen that greater concentration  
564 amounts (ca. 0.5 wt.%) of the nanofiller into the membrane demonstrated to increase the water  
565 diffusion due to its hydrophilic functional groups (such as amine) present on the surface. The  
566 membrane filled with 0.5wt.%  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$  yielded the best salt rejection performance, as  
567 well as the highest removal efficiencies of 93% and 97% for Cd (II) and methyl red dye,  
568 respectively. Cd (II) adsorption was also found to be enhanced by the presence of polar primary  
569 amine  $\text{NH}_2$  functional groups on the surface, acting as active binding sites. While methyl red dye  
570 adsorption was associated with the electrostatic interactions and non-covalent bonds given by the  
571 hydrophilicity nature of the green nanofiller. In addition to this, an excellent antifouling capacity  
572 was revealed by the novel membrane together with good reusability property for Cd removal, e.g.  
573 it demonstrated a 7% decrease in removal efficiency after the fifth Cd (II) filtration cycle. Long-  
574 term stability and anti-contamination properties for methyl red dye removal were also confirmed  
575 by the maintenance of a constant 97% filtration efficiency and a slight decrease in solution flux  
576 after a 40h filtration process. Hence, this pioneering study should be considered as a starting point



577 within the implementation of green material-based nanofillers for filtration membranes since it has  
578 proven to be an innovative promising alternative for the removal of pollutants.

579 Up to now, it is evident that nanocomposite membranes implemented in UF, MF and NF processes  
580 for the removal of heavy metals is a research field with a promising future ahead, coring the  
581 development of sustainable wastewater treatment strategies. At this point, research efforts must  
582 continue to be done on discovering innovative mixtures of nanocomposite materials and their  
583 interactions, that may result in membrane enhancements in terms of mechanical strength,  
584 adsorption mechanisms, metal removal efficiency rates, antifouling, reusability, permeability, and  
585 selectivity properties. All these properties will foster the implementation of efficient and reliable  
586 processes. Based on current findings, the research community is extensively working on the  
587 development of novel types of composites. For instance, **Table 4** presents a variety of novel  
588 nanocomposites that have not been implemented yet in the fabrication of filtration membranes,  
589 however, they represent a promising future since they count with effective adsorption mechanisms,  
590 innovative material combinations and also synthesized following novel methodologies for the  
591 removal of heavy metals, offering new clues on what is next on improving nanocomposite  
592 membrane technology. It is quite possible that such new composites will be assayed in membrane-  
593 based separations expecting acceptable performance based on their relevant findings in separating  
594 metal ions from water systems.

595

596 **Table 4.** Novel nanocomposite materials with outstanding heavy metal removal efficiency that  
597 have not been implemented in membranes.

598

599 Recently, Dinh et al. (2020) tailored a chitosan-MnO<sub>2</sub> nanocomposite which was tested as an  
600 adsorbent to remove Cr(VI) from an aqueous solution. Thanks to its high Langmuir monolayer



601 adsorption capacity of about  $61.5 \text{ mg g}^{-1}$ , this new material displayed high Cr removal (of about  
602 94%) in the effluent from industrial zones. The authors claimed that electrostatic attraction was  
603 fundamental to the uptake of Cr onto the composite. Importantly, such composite was also  
604 evaluated during 5 cycles, showing a removal efficiency decrease up to 80%. Unlike Dinh's study,  
605 a core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C) exhibited a  
606 tremendous adsorption capacity (over  $800 \text{ mg g}^{-1}$  for Cr) and thus revealing an acceptable Cr (VI)  
607 removal efficiency of 80% (Zhou et al., 2020).

608 The adsorption capacity depends on the characteristics of elements forming the nanocomposite,  
609 their synergistic effect and their resulting properties, for example, Mahmoud et al. (2019) notified  
610 a higher adsorption capacity in  $\text{SiO}_2@\text{VB9}$  nanocomposite for Pb (over  $900 \text{ mg g}^{-1}$ ) than Cd (ca.  
611  $562 \text{ mg g}^{-1}$ ) and Cu (ca.  $152 \text{ mg g}^{-1}$ ), such metal uptake capacities allowed to the resulting  
612 composite to show high removal efficiency ranged from 81 to 100% for all tested heavy metal  
613 ions. Dai et al. (2020) have very recently proved that the strategic selection of the elements  
614 proposed for the nanocomposite fabrication may result in a high-performance material, for  
615 instance, Dai et al. introduced  $\text{Fe}_3\text{O}_4/\text{GO}$  composite into graphitic carbon nitride  $\text{g-C}_3\text{N}_4$ , which  
616 provided an impressive U (VI) extraction capacity (up to  $2880 \text{ mg g}^{-1}$ ) together with high removal  
617 efficiency (ca. 96 %). Due to its chemisorption properties, an EDTA modified magnetic iron oxide  
618 loaded with sawdust carbon ( $\text{EDTA}@\text{Fe}_3\text{O}_4/\text{SC}$ ) composite has demonstrated a 98% Cd (II)  
619 removal capacity; according to the study, the Cd (II) removal efficiency increased as pH value and  
620 adsorbent dose increase. Moreover, this nanocomposite also presented good multi-metal ion  
621 uptake (over 80%) for Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI), and high  
622 adsorption efficiency (ca. 83%) after three cycles, proving an input of its reusability. At this point,  
623 most of the newly nanocomposite materials (presented in **Table 4**) release a satisfactorily good  
624 metal ion uptake ability being potential candidates for the fabrication of membranes towards water



625 purification and disinfection (Castro-Muñoz, 2020b). However, the synthesis and preparation  
626 methodologies, as well as the resulting cost, implied in the fabrication protocols may represent a  
627 drawback during the further implementation of such materials in membranes. Even if the ongoing  
628 progress and innovation of new composite materials have been pointed out over this review, the  
629 economic feasibility related to the fabrication cost is a critical driver for their establishment and  
630 implementation. Unfortunately, economic feasibility, which may represent a profitable and  
631 competitive business, is a fundamental factor for the investment of companies and suppliers  
632 (Urbancová, 2013; Skapa, 2012). Herein, scientists must also be focused on developing new  
633 materials and fabrication protocols considering fewer sources and less costly aimed at producing  
634 economically sustainable materials. In this context, there is today a new trend in utilizing green  
635 and bio-based materials for the development of economically viable feedstocks and products.  
636 Since different carbonaceous materials, such as GO, activated carbon and CNTs, have shown their  
637 potentiality as adsorbents for copper decontamination (Ren et al. 2013), it is likely that other  
638 potential materials, like biochar, may also be a promising candidate in the preparation of  
639 composites. It is worth mentioning that biochar is commonly manufactured by pyrolysis of  
640 biomass and plant-based derivatives. Therefore, the synthesis and usage of biochar represent an  
641 environmentally friendly way to produce low-cost adsorbents (Marousek et al., 2020ab), which  
642 have been recently involved in the fabrication of membranes for the selective separation of  
643 phosphate from phosphate-rich wastewaters (Mohammadi et al., 2020).

644 Most of the nanocomposite materials and membranes tend to display impressive metal ion uptake,  
645 and more importantly, some composites can concurrently remove more than one type of ion.  
646 However, to core the complete resource recovery (i.e. water), it is important to consider the  
647 synthesis of nanocomposite membranes which may offer the simultaneous removal of heavy metal  
648 ions and organic contaminants, e.g. Zhang et al. (2020) developed composite membranes filling





649 polydopamine-coated ferric oxide ( $\text{Fe}_3\text{O}_4@\text{PDA}$ ) in PES. In addition to the higher permeabilities  
650 of the composite membranes (e.g. over  $2600 \text{ L/m}^2 \text{ h bar}$  corresponding to 20wt.%  $\text{Fe}_3\text{O}_4@\text{PDA}$   
651 PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive  
652 removal of  $\text{Pb}^{2+}$  and catalytic degradation of methylene blue, e.g. acceptable  $\text{Pb}^{2+}$  removal  
653 efficiency (above 80%) together with high methylene blue degradation (above 90%). In this case  
654 of study, the authors strategically designed the composite to display a synergistic effect. For  
655 example, the phenolic hydroxy and amino groups on the surface of PDA were able to chelate the  
656 cations to promote the adsorption of heavy metal ions, while the electron transfer in the Fenton-  
657 like reaction was promoted due to the phenoquinone structure of the surface of the PDA, boosting  
658 the catalytic reaction. With a similar scope, Fan et al. (2019) documented the simultaneous and  
659 rapid removal of organic micropollutants (bisphenol) and metal ions ( $\text{Pb}^{2+}$ ) using an electrospun  
660  $\beta$ -cyclodextrin/chitosan/polyvinyl alcohol nanofibers. These novel nanocomposites exhibited a  
661 large number of adsorption sites, e.g. the cyclodextrin owed a featured molecule structure with a  
662 hydrophilic outer surface and hydrophobic inner cavity for binding organic contaminants while  
663 chitosan has plenty of hydroxyl and amino groups to form complex with metal ions and thus  
664 remove them. Both authors concluded that their nanocomposites represent a new pathway to deal  
665 with hard-to-be-treated wastewaters (e.g. paper making, leather, textile, etc.)

## 666 **5. Concluding remarks, future perspectives, and strategies for new researchers in the field**

668 Throughout this review paper, it has been recognized the potential ability of polymeric membranes  
669 in separating various heavy metal ions, including  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  
670  $\text{Cr}^{4+}$ , among others. These membranes can exhibit a removal efficiency between 77-99%.  
671 However, by smartly introducing inorganic nanomaterials into polymer membranes,  
672 nanocomposite membranes have overcome the main drawbacks of polymeric membranes together  
673 with improved removal efficiencies up to 100%. This review has released a clear outlook on the

674 benefits of implementing composite membranes for the separation and removal of a wide range of  
675 toxic and heavy metal ions, in which their elimination from water has been proposed attending the  
676 current worldwide necessity for clean water scarcity.

677 To date, a huge number of studies have provided promising proofs and insights that the MF  
678 composite membranes have been able to remove macropollutants, but the separation of  
679 micropollutants may need the usage of UF and NF membranes. Interestingly, nanocomposite  
680 membranes have shown their impressive adsorption ability for the removal of heavy metal ions,  
681 being strongly dependent on the smart selection of the inorganic materials according to their  
682 physicochemical features. This means that the adsorption efficiency of nanoparticles and their  
683 sieving mechanism must be considered during the tailored manufacturing of nanocomposite  
684 membranes towards the removal of specific heavy metal ions. In the light of process feasibility,  
685 nanocomposite membranes have also shown enough features to be implemented in efficient  
686 separation processes with good permeation rates, which is also a relevant parameter in terms of  
687 productivity. Based on the current findings of this review, and the current developments works and  
688 efforts in developing new composite materials, it is likely that the research community will  
689 continue looking for new inorganic and hybrid materials that could not only overcome the  
690 drawbacks (such as permeation and retention rates) of polymeric membranes but also  
691 physicochemical properties (e.g. chemical, mechanical and thermal stability) as well. To finalize,  
692 it is presented below some recommendations for planning the research of new researchers aiming  
693 to improve the efficiency of nanocomposite membranes:

- 694 • Initially, researchers must identify the potential polymers that display high enough removal  
695 efficiency. Based on this, further investigation can be planned and directed based on the  
696 main bottleneck and weakness of the pristine polymers.



- 697
- When dealing with filling nanomaterials into polymers, it is essential to mention that such  
698 inorganic phases must be smartly embedded considering two important factors: 1) the  
699 physicochemical features of the nanomaterials (porosity, stability, morphology, among  
700 others), and ii) their metal uptake mechanisms related to the removal of heavy metals  
701 (sieving, adsorption, size-exclusion, etc.). Such basic analysis will bring big benefits in a  
702 shorter time and fewer sources, i.e. low filler loading may synergistically improve the  
703 properties of polymer membranes. For example, 1wt.% GO loaded PVDF-GO-nZVI  
704 membrane cannot only reach high 100% Cd (II) removal but also impressive permeation  
705 fluxes (ca.  $255 \text{ L m}^{-2} \text{ h}^{-1}$ ) (Ren et al., 2019), which is also an important factor during the  
706 feasibility of large scale processes. Finally, the usage of a low quantity of fillers will result  
707 in a reduced membrane cost.
  - The membrane preparation protocols also play an important role in the resulting separation  
708 efficiency in membranes. Even if most of the advances in the field have been assigned to  
709 the properties of the nanomaterials, it is also important to point out that the exploration of  
710 new membrane fabrication procedures, together with the improvement of the existing ones,  
711 will allow tailoring of substantially enhanced membranes. This also applies when  
712 embedding simultaneously more than one inorganic phase.
  - Most of the research has satisfactorily demonstrated excellent performance towards metal  
713 ion separations, however, there are few reports demonstrating the feasibility of the  
714 membranes in a long-term operation, which is a current lack in research. By extending the  
715 testing of membranes, the chemical engineers will have a better outlook about the  
716 potentiality of membranes for possible implementation in industrial processes.
  - To finalize, based on the relevant insights and ability of the novel nanocomposite materials  
717 enlisted in **Table 4**, it is recommended to the new scientists to explore the ability of such  
718  
719  
720



721 new materials into membrane processes for the removal of metal ions. Importantly, the  
722 separation efficiency of membrane processes not only depends on membrane features but  
723 also on the operating conditions.

724

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732

733

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**Table 1.** Polymeric membranes used for the removal of metal ions.

Separation process:	Material/membrane	Heavy metals	Removal efficiency (%)	Reference
NF	PBI/PES	Mg <sup>2+</sup> , Cd <sup>2+</sup>	98%, 95%	(Zhu et al., 2014)
NF	PA	Cu <sup>2+</sup> , Cd <sup>2+</sup>	98%, 99%	(Qdais and Moussa, 2004)
RO	PA	Cu <sup>2+</sup> , Cd <sup>2+</sup>	>90%	(Qdais and Moussa, 2004)
ED	sulfonated PVDF	Co <sup>2+</sup> , Ni <sup>2+</sup>	90 % , 69 %,	(Tzanetakis et al., 2003)
NF	CA/ PMVEMA	Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>+6</sup>	85%, 72%	(Lavanya et al., 2019)
NF	PES-PE	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup>	>90%	(Mokhter et al., 2017)
NF	PAN-PEI/PSS	Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup>	98%, 96%, 96%, 95%	(Qin et al., 2013)
UF	PVDF/2-Aminobenzothiazole	Cr <sup>6+</sup>	92%	(Wang et al., 2017)
UF	PVDF/PANI	Pb <sup>2+</sup> , Cd <sup>2+</sup>	98.5%, 97.3%	(Pereira et al., 2014)

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**Table 2.** Different filling materials embedded into nanocomposite membranes for different water treatment applications.

Filling material:	Membrane-based process:	Application:	Polymer phase:	Reference:	
ZnO	MF	Synthetic wastewater treatment		(Liang et al., 2012)	
		Removal of copper ions	PVDF	(Xia Zhang et al., 2014)	
		Wastewater treatment		(Hong and He, 2012)	
		Humic acid removal	PES	(Ahmad et al., 2016)	
		Humic acid removal	PSF	(Chung et al., 2016)	
		Water treatment		(Dipheko et al., 2017)	
		UF	Pollutants removal	PES	(Li et al., 2015)
			Water treatment	PES-PVA	(Zhao et al., 2015)
			Wastewater treatment		(Pintilie et al., 2017)
			Bacterial removal from aqueous solutions	PSF	(Ronen et al., 2013)
			Water treatment	PVC	(Rabiee et al., 2015)
			Humic acid removal	PES	(Balta et al., 2012)
			Water purification	PVP	(Bai et al., 2012)
			Removal of metal ions ( $Zn^{2+}$ , $Cd^{2+}$ , $Pb^{2+}$ , $Mn^{2+}$ , $Ni^{2+}$ , $Fe^{2+}$ , $Al^{3+}$ , $Sb^{3+}$ , $Sr^{3+}$ )	CA	(Bahadar et al., 2015)
	NF	Humic acid removal	PSF	(Tao et al., 2017)	

GO	RO	Humic acid removal		(Ekambaram and Doraisamy, 2017)
		Humic acid removal	PVDF	(Li et al., 2017)
		Removal of bivalent ions ( $\text{Ca}^{2+}$ , $\text{SO}_4^{2-}$ and $\text{Mg}^{2+}$ ), monovalent ions ( $\text{Cl}^-$ and $\text{Na}^+$ ), and bacterias.	PA	(Isawi et al., 2016)
	MF	Dyes removal from effluents	PSF	(Badrinezhad and Ghasemi, 2017)
		Wastewater treatment	PVDF	(Zhao et al., 2014)
		Water treatment	PSF	(Zhao et al., 2013)
		Water treatment	PVP-PVDF	(Chang et al., 2014)
	UF	Water treatment		(Wu et al., 2014)
		Natural organic matter removal		(Xia and Ni, 2015)
		Water treatment		(Zhao et al., 2013)
			PVDF	
		Natural organic matter removal	PA	(Xia et al., 2015)
		Wastewater treatment	PSF	(Lee et al., 2013)
		Organic pollutants removal	Cellulose ester	(Morales-Torres et al., 2015)
		Distillery effluent treatment	PES	(Kiran et al., 2016)
Water softening production		PAI-PEI	(Goh et al., 2015)	
Dyes removal from effluents	PMIA	(Yang et al., 2017)		
Dyes removal from effluents	PAN	(Zhang et al., 2017)		
Dyes removal from effluents	PES	(Zinadini et al., 2014)		
Water purification	PPA	(Jin Wang et al., 2016)		



Graphene	UF	Wastewater treatment	PSF	(Crock et al., 2013)
	NF	Water purification	PVDF	(Han et al., 2013)
		Wastewater treatment		(Zhang et al., 2012)
MF /UF	Wastewater treatment		(Alpatova et al., 2013)	
Ag-nanoparticles		Water purification	PSF	
		Wastewater treatment	PES	(Rehan et al., 2016)
		Wastewater treatment	PES, PSF, CA	(Sile-Yuksel et al., 2014)
		Wastewater treatment		(Koseoglu-Imer et al., 2013)
		Wastewater treatment	PSF	(Hoek et al., 2011)
	UF	Wastewater treatment		(Escobar et al., 2015.)
		Wastewater treatment	CA	(Andrade et al., 2015)
Ag-NO <sub>3</sub>		Wastewater treatment	PA-PVA	(Yang Zhang et al., 2016)
	NF			
	RO	Wastewater treatment	PA	(Ben-Sasson et al., 2014)
		Wastewater treatment	PA/PSF/	(Yang et al., 2016)
		Bacterial removal from water	PET	
		CA	(Ahmad et al., 2016)	
		Water treatment		(Zhang et al., 2013)
	RO		PES	

Ag-nanoparticles	RO	Water treatment	PAN	(Liu et al., 2016)
	UF	Water treatment	PES	(Zhang et al., 2014)
	NF	Water treatment and removal of salt (Na <sub>2</sub> SO <sub>4</sub> )	PA	(Liu et al., 2015)
bio-Ag0		Water treatment		(Liu et al., 2016)
Cu-nanoparticles		Water treatment		(Hoek et al., 2011)
			PSF	
CuAc <sub>2</sub>		Humic acid removal	PAN/PEI	(Xu et al., 2012)
Cu-nanoparticles		Wastewater treatment	PES	(Akar et al., 2013)
	UF			
Ag-nanoparticles		Wastewater treatment	PSF	(Kar et al., 2011)
Cu-nanoparticles				
	NF	Seawater softening: removal of salts (SO <sub>4</sub> <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , Cl <sup>-</sup> ).	PAN/PEI	(Xu et al., 2015)
CuSO <sub>4</sub>				
CuCl <sub>2</sub>	RO	Wastewater treatment		(Zhang et al., 2017)
Cu nanoparticles		Water treatment	PA	(Ben-Sasson et al., 2014)
		Humic acid removal		(Teow et al, 2012)
		Water treatment		(Rajaeian et al., 2015)
		Wastewater treatment	PVDF	(Shi et al., 2012)
		Water treatment		(Méricq et al., 2015)
	UF	Water treatment	PP	(Pi et al., 2016)



		Water treatment	PSF	(Mollahosseini and Rahimpour, 2014)
		Water treatment	CA	(Abedini et al., 2011)
		Water treatment		(Ngo et al., 2016)
			PA	
TiO <sub>2</sub> nanoparticles	NF	Wastewater treatment	PES	(Sotto et al., 2011)
CNTs	NF	Drinking-water purification	NC	(Ahmeh et al., 2013)
	UF	Water treatment and biofouling control application	PES	(Celik et al., 2011)
	NF	Wastewater treatment	PES	(Daraei et al., 2013)
	NF	Water treatment	PA	(Kim et al., 2013)
	NF	Metal removal (Cr (VI), Cd (II))	PSF	(Shah and Murthy, 2013)
	NF	Water treatment for salt removal (NaCl, Na <sub>2</sub> SO <sub>4</sub> ).	PMMA	(Shen et al., 2013)
	NF	Water treatment	Polyimide 84	(Grosso et al., 2014)
	UF	Water treatment	PSF	(Sianipar et al., 2016)
	UF	Wastewater treatment by membrane bioreactor	PSF	(Khalid et al., 2018)
	MF	Bleach effluent treatment by membrane bioreactor	PSF	(Mulopo, 2017)

**Acronyms:** polyethersulfone (PES), polysulfone (PSF), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinylidene fluoride (PVDF), poly(methyl methacrylate) (PMMA), nitrocellulose (NC), cellulose acetate (CA), polyamide (PA), polyphthalamide (PPA), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polyvinylpyrrolidone (PVP), polyamide-imides (PAI), polyethylenimine (PEI).





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**Table 3.** Latest development works on tailoring novel nanocomposite membranes for heavy metal ions removal.

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Nanocomposite membrane type:	Membrane process:	Metal ion removal :	Reference:
MMGO filled PES	NF	Copper ions removal (92%)	(Abdi et al., 2018)
f-MWCNTs filled PVC	NF	Zinc ( $Zn^{2+}$ ) ions removal (98%)	(Ali et al., 2019)
s-MWCNTs	-	Copper (II) ions removal (59%)	(Ge et al., 2014)
CNFs/ $TiO_2$ filled PAN	-	Lead ( $Pb^{2+}$ ) ions removal (87%)	(Suresh et al., 2018)
		Copper ( $Cu^{2+}$ ) ions removal (73%)	
		Cadmium ( $Cd^{2+}$ ) ions removal (66%)	
(MEUF)PES	UF	Cadmium ( $Cd^{2+}$ ) ions removal (90%)	(Huang et al., 2019)
(MEUF) cellulose	UF	Arsenic (V) ions removal (89%)	(Chen et al., 2018)
PAH-PSF	UF	Lead ( $Pb^{2+}$ ) ions removal (91.5%)	(Ibrahim et al., 2018)
		Cadmium ( $Cd^{2+}$ ) ions removal (72.3%)	
s-PES	UF	Ferric ( $Fe^{3+}$ ) ions removal (>90%)	(López et al., 2019)
MMT-GO-EDA	UF	Ag (I) ions removal (100%)	( Ma, 2019)
		Cu (III) ions removal (100%)	
		Cr (IV) ions removal (27.0%)	
CF- $TiO_2$ - $C_3N_4$	MR	Cr (VI) ions removal (88.0%)	(Shen et al., 2018)
Composite -CA	RO	Pb ( $Pb^{2+}$ ) ions removal (100%)	(Thaçi and Gashi, 2019)
		Cd ( $Cd^{2+}$ ) ions removal (100%)	
		Ni ( $Ni^{2+}$ ) ions removal (100%)	
		Zn ( $Zn^{2+}$ ) ions removal (100%)	



		Mn (Mn <sup>2+</sup> ) ions removal (100%)	
		Co (Co <sup>2+</sup> ) ions removal (100%)	
Composite GPC	UF	Pb (Pb <sup>2+</sup> ) ions removal (>95%)	(Jing Wang et al., 2018)
PECN	NF	Zn (Zn <sup>2+</sup> ) ions removal (100%)	(Ye et al., 2019)
f- MOFs-CUF	UF	Pb (Pb <sup>2+</sup> ) ions removal (61.4%)	(Yin et al., 2016)
ZIF-300-Al <sub>2</sub> O <sub>3</sub>	NF	Cu (Cu <sup>2+</sup> ) ions removal (100 %)	(Yuan et al., 2019)
		Co (Co <sup>2+</sup> ) ions removal (100 %)	
		Cd (Cd <sup>2+</sup> ) ions removal (100 %)	
		Al (Al <sup>2+</sup> ) ions removal (100 %)	
Goethite filled PAN	UF	Cu (Cu <sup>2+</sup> ) ions removal (49 %)	(Soghra et al., 2019)
Composite PEI- zein	FO	Pb (Pb <sup>2+</sup> ) ions removal (>99.5%)	(X. Zhao & Liu, 2019)
		Cd (Cd <sup>2+</sup> ) ions removal (>99.5%)	
		Ni (Ni <sup>2+</sup> ) ions removal (>99.5%)	
GMA-PAN	UF	Cu (Cu <sup>2+</sup> ) ions removal (98 %)	(Yanhong Zhang et al., 2019)

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467 **Acronyms:** functionalized multi-walled carbon nanotubes (f-MWCNTs), modified magnetic graphene oxide(MMGO), sulfonated multi-walled carbon nanotubes (s-  
468 MWCNTs), carbon nanofibers (CNFs), micellar enhanced ultrafiltration (MEUF), poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH),  
9 sulfonated polyethersulfone(s-PES),GO-based membranes via the intercalation of montmorillonite and ethylenediamine ( MMT-GO-EDA), C<sub>3</sub>N<sub>4</sub>-decorated carbon-  
0 fiber (CF-TiO<sub>2</sub>-C<sub>3</sub>N<sub>4</sub>), membrane reactor (MR), graphene oxide-polydopamine-(β-cyclodextrin) (GPC), polyelectrolyte complex nanofiltration (PECN), functionalized  
1 MOFs-CUF (f- MOFs-CUF), grafting glycidyl methacrylate (GMA).  
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1474 **Table 4.** Novel nanocomposite materials with outstanding heavy metal removal efficiency that have not been implemented in membranes.

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Nanocomposite materials	Heavy metals removal efficiency	Adsorption mechanism	Parameters affecting adsorption mechanism	Fabrication method	Synthesis conditions	Reusability	Reference
MnO <sub>2</sub> coated by chitosan nanocomposite	Cr (VI) adsorption (61.56 mg g <sup>-1</sup> )  Cr (VI) removal efficiency (94.21%)	Physisorption and electrostatic attraction	<b>pH effect</b>  Adsorption efficiency decreases with ascending pH values (optimal pH=2)  <b>Ion strength</b>  Ionic strength, with an increase in the KCL concentration decreases Cr (VI) removal efficiency  <b>Adsorbent dosage</b>  The material concentration affects Cr (VI) adsorption capacity	MnO <sub>2</sub> /CS was fabricated by mixing, filtering and drying a suspension made up by C <sub>2</sub> H <sub>5</sub> OH, deionized (DI) water, CS and saturated KMnO <sub>4</sub> solution	<b>Mixing</b> 8 h at room temperature  Different shaking speeds were tested  <b>Oven drying</b> 60°C for 12 h	5 cycles. Removal efficiency decreased (from 94% to 80%)	(Dinh et al., 2020)
Core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C)	Cr (VI) adsorption capacity (814.9 mg g <sup>-1</sup> )  Cr (VI) removal efficiency (80%)	Chemical reduction reaction of Cr (VI) into Cr (III)	<b>Cr (VI) Initial concentration effect</b>  High initial Cr (VI) concentration values increased the reduction capacity  <b>pH effect</b>	Hydrothermal-calcination method	<b>Drying</b>  Vacuum conditions at 80°C for 24h.  <b>Carbonization</b>  Pipe oven under N <sub>2</sub> atmosphere, at 800 C° for 30 min	No tests were performed	(Zhou et al., 2020)

			pH affects the electron utilization process (Optimal pH below 3)				
			<b>C/Fe molar ratio</b>				
			20 C/Fe optimal ratio				
Nanocomposite of 20% hickory biochar and 80% expanded vermiculite (20%-BC/VE)	As (V) adsorption capacity (20.1 mg g <sup>-1</sup> )	Heterogeneous adsorption processes, both physisorption and chemisorption, ion exchange and electrostatic attraction	<b>Nanocomposite ratio effect</b>  Optimal ratio: 20%-BC/VE  <b>pH effect</b>  pH affects the BC/VE surface charge, as well as the electrostatic interactions (optimal pH= 6)  <b>Coexisting anions effect</b>  <i>PO<sub>4</sub><sup>3-</sup></i> reduced considerably adsorption rate of As (V)	Ball milling method	<b>Ball milling</b>  At 300 rpm for 12 h	No tests were performed	(Li et al., 2020)
Fe <sub>3</sub> O <sub>4</sub> /GO (mGO) composite introduced into graphitic carbon nitride g-C <sub>3</sub> N <sub>4</sub> .	U (VI) extraction capacity (2880.6 mg g <sup>-1</sup> )  U (VI) extraction efficiency (96.02%)	Chemical reaction of photocatalytic reduction of U (VI) under LED light irradiation	<b>pH effect on photocatalytic activity</b>  Optimal pH=6  <b>U (VI) concentration effect on photoreduction in mGCN-1</b>	Ultrasonication was applied to the individual suspensions and then to the mixture of mGO and g-C <sub>3</sub> N <sub>4</sub>  The solids of the mGO and g-C <sub>3</sub> N <sub>4</sub> mixture were centrifuged and dried	<b>Ultrasonication</b>  Individually for 1 h and as mixture for 2h.  <b>Drying</b>  In a vacuum at 60°C	5 cycles  There were not significant changes in removal and stability rates	(Dai et al., 2020)

			Optimal U(VI) concentration range: 1 – 100 mg L <sup>-1</sup>				
Silicon dioxide composite with tea waste (SiO <sub>2</sub> @TW)	<p>Adsorption capacities:</p> <p>Pb<sup>2+</sup> (153 mg g<sup>-1</sup>) and Cd<sup>2+</sup> (222 mg g<sup>-1</sup>)</p> <p>Removal rates:</p> <p>Pb<sup>2+</sup> (89.22%) and Cd<sup>2+</sup> (94.28%)</p>	Electrostatic attraction and physical adsorption	<p><b>pH effect</b></p> <p>Optimal pH values:</p> <p>Pb<sup>2+</sup> (pH= 6) and Cd<sup>2+</sup> (pH=7)</p> <p><b>SiO<sub>2</sub>@TW dosage effect</b></p> <p>High dose of SiO<sub>2</sub>@TW enhanced adsorption sites, increasing removal capacity</p> <p><b>Temperature effect</b></p> <p>Elevated temperature was a catalyst for adsorption, due to chemical bond rupture that enhanced contact between metal ions and surface-active sites</p>	<p>Modified Stober method for SiO<sub>2</sub> NPs fabrication</p> <p>SiO<sub>2</sub>@TW synthesis consisted of sonication, centrifugation and drying of SiO<sub>2</sub> - tea waste powder suspension</p>	<p><b>Stirring</b></p> <p>For 30 min at 25°C</p> <p><b>Sonication</b></p> <p>For 1h</p> <p><b>Drying</b></p> <p>For 3h at 80°C</p>	5 cycles	(Joshi et al., 2020)
Hybrid bio-nanocomposite of nano-hydroxy ferric phosphate (n-HFP) and hydroxy ferric sulfate (n-HFS) particles coated on fungal hyphae of <i>Aspergillus Niger</i> ( <i>An</i> ) ((n-HFP + n-HFS) @An).	<p>Simultaneous adsorption rates:</p> <p>As (III) (76.84%), Cd (II) (73.62 %) and Pb (II) (94.31%)</p> <p>Adsorption capacities:</p> <p>As (III) (162 mg g<sup>-1</sup>), Cd (II) (205.83</p>	Chemical adsorption for the three metals	No tests were performed	<p>Co-precipitation method was used to fabricate n-HFP and n-HFS NPs</p> <p>Potato dextrose broth (PDB) medium containing dissolved n-HFP and n-HFS NPs as well as magnetically stirred <i>An</i> mycelium inoculate was cultured</p>	<p><b>Magnetic stirring</b></p> <p>At 1000 rpm for 6 h</p> <p><b>Culturing</b></p> <p>In PDB medium at 30°C, 170 rpm for 1-2 days</p>	Reduced risk for contamination: 10-day stability of loaded NPs in solution	(Liao et al., 2019)

	mg g <sup>-1</sup> ), and Pb (II) (730.79 mg g <sup>-1</sup> )						
Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) entrapped in calcium-alginate matrix (nZVI/BC/CA)	Cr (VI) adsorption capacity (86.4 mg g <sup>-1</sup> )	Ion exchange, intraparticle diffusion, chemical adsorption and redox reaction	<b>pH effect</b> Optimal pH= 4	Modified liquid-phase method	<b>Pyrolysis</b> At 500°C for 3 h in a muffle furnace (15°C / min) under N <sub>2</sub> atmosphere  <b>Stirring</b> 500 rpm at 25°C for 30 min.	Removal capacity decreased at the 1 <sup>st</sup> cycle but remained stable in further regenerations	(Wan et al., 2019)
Nanocomposite made from wastewater hyacinth derived biochar (BC) and ZnO NPs	Cr (VI) removal efficiency (95%)  Cr (VI) adsorption capacity (43.48 mg g <sup>-1</sup> )	Chemisorption and photocatalytic reduction	<b>Carbonization temperature effect</b> Optimal carbonization temperature: 700°C  <b>ZnO content effect</b> 30 wt.% optimal ZnO concentration	BC powder was impregnated into Zn(NO <sub>3</sub> ) <sub>2</sub> aqueous solution, by drying and calcination steps	<b>Drying</b> At 105°C for 12h. <b>Calcination</b> At 380°C for 3h under N <sub>2</sub> atmosphere	Removal efficiency (87.1% at 1 <sup>st</sup> run) and (67.1% at 5 <sup>th</sup> run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe <sub>3</sub> O <sub>4</sub> ), loaded with SC (sawdust carbon) (EDTA@Fe <sub>3</sub> O <sub>4</sub> /SC)	Cd (II) adsorption capacity (63.3 mg g <sup>-1</sup> )  Cd (II) removal capacity (98%)  Multi-metal ion removal (>80%), for the following ions: Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI)	Chemisorption	<b>pH effect</b>  Cd (II) removal efficiency increases as pH value rises  (Optimal pH= 6.5)  <b>Adsorbent dose effect</b>  Cd (II) removal increased as adsorbent dose increased  <b>Contact time effect</b>	Biogenic green synthesis approach for fabrication	<b>Stirring</b> At 90°C for 1h  <b>Carbonization</b> In muffle furnace at 180°C for 12h	<b>Desorption</b>  Maximum Cd (II) desorption was achieved with HCl (99%), HNO <sub>3</sub> (100%) and H <sub>2</sub> SO <sub>4</sub> (100%)  <b>Reusability</b>  After three cycles, adsorption efficiency (83%) and at the	(Kataria and Garg, 2018)

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Optimum contact time for Cr (II) removal: 120 min

fifth cycle (57%)

**Coexisting ions effect**

Divalent ions ( $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$ ) caused a decrease in Cr (II) removal efficiency

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Silica ( $\text{SiO}_2$ ) functionalized folic acid (VB9) ( $\text{SiO}_2@VB9$ ) nanocomposite

Adsorption capacities: Cd (II) ( $562.1 \text{ mg g}^{-1}$ ), Pb (II) ( $973.8 \text{ mg g}^{-1}$ ) and Cu (II) ( $152.1 \text{ mg g}^{-1}$ )

Physio-chemical process and stable complex formation

**pH effect**

Optimal pH values: Cd (II) (pH = 7), Cu (II) (pH = 6) and Pb (II) (pH = 5)

Methodology consisting of microwave assistance for covalent immobilization of VB9 with chlorinated silica

**Stirring**  
1 hour  
**Oven drying**  
At  $60^\circ\text{C}$   
**Microwaving**  
For 2min

No tests were performed

(Mahmoud et al., 2019)

Extraction rates:

Cu (II) (94-100%), Pb (II) (100%) and Cd (II) (57- 81%)

**Nanocomposite dosage effect**

Removal efficiency increased with ascending dosage values (Optimum dosage: 10 mg)

**Contact time effect**

Optimum contact time for metal removal: 25 min

**Initial metal ion concentration effect**

Optimal metal ion concentration: 0.25 mg/L

**Coexisting ions effect**

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Ni (II) and Co (II)  
decreased metal ion  
removal capacity

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1477 **Acronyms:** *Aspergillus niger* (An), biochar (BC), calcium - alginate (CA), ethylenediaminetetraacetic (EDTA), nanoparticles (NPs), nano hydroxy ferric phosphate (n-  
1478 HFP), nano hydroxy ferric sulfate (n-HFS), nanoscale Zero Valent Iron (nZVI), Protein Dextrose Broth (PDB), sadwust carbon (SC), tea waste (TW), vitamin B9 folic  
1479 acid (VB9), vermiculite (VE).

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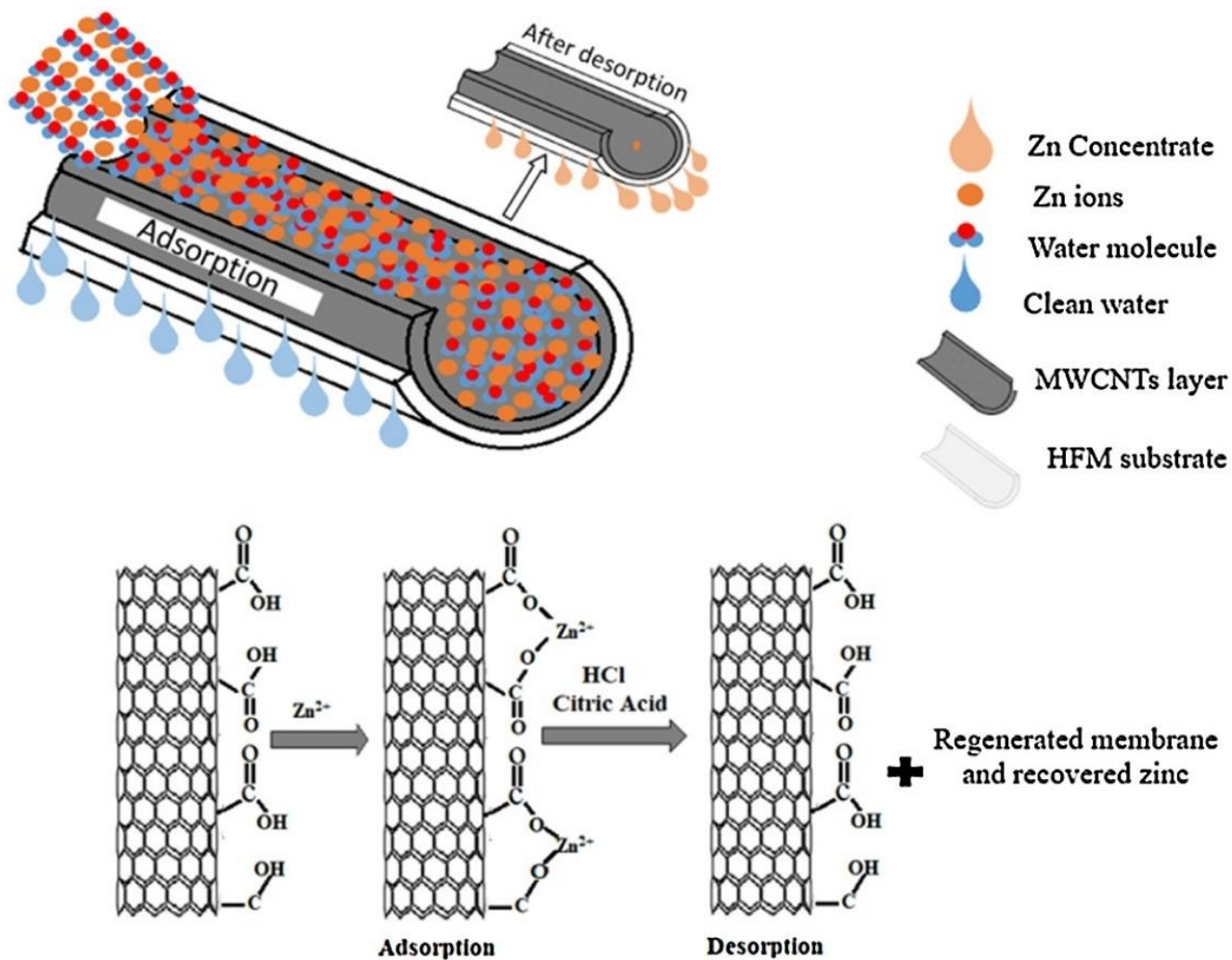
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**Figure 1.** Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et al., 2019).



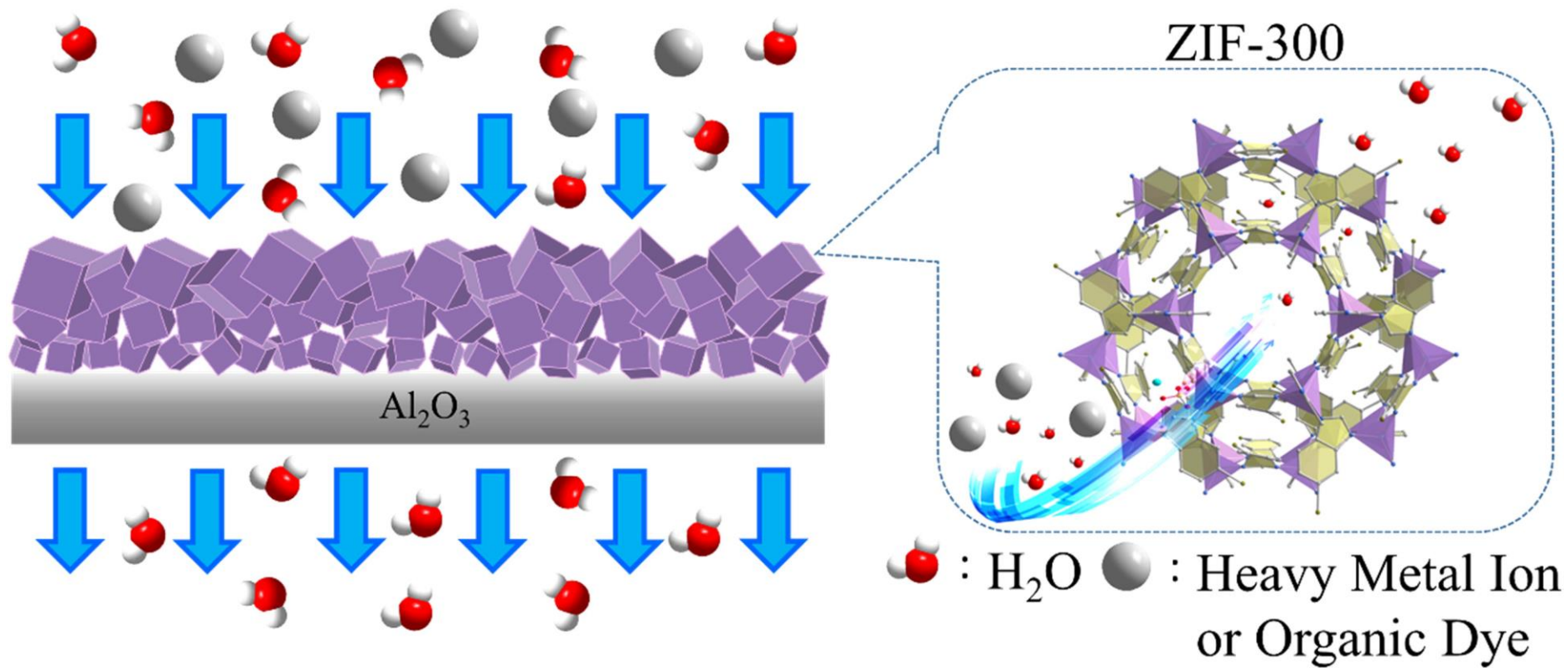
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**Figure 2.** Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).

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1 **CRedit authorship contribution statement**

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3 **Roberto Castro-Muñoz**: Conceptualization, Investigation, Formal analysis, Writing -  
4 original draft, review & editing. **Luisa Loreti González-Melgoza & Octavio García-**

5 **Depraect**: Writing - review & editing.

1 **Conflict of Interest**

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3 The authors declare no conflict of interest.

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