

Chemosphere

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

--Manuscript Draft--

Manuscript Number:	CHEM78274R2
Article Type:	VSI:WWT-Resources
Section/Category:	Treatment and Remediation
Keywords:	heavy metals; Water treatment; membrane-based technologies, water purification, novel composite materials
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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 complete removal of heavy metals (up to 100%), together with unprecedented permeation rates (from 80 up to 1, 300 L m ⁻² h ⁻¹). 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.
Opposed Reviewers:	

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⁻² h⁻¹). 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), MnO₂/chitosan (Dinh et al., 2020), core-shell structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe₃O₄/GO composite introduced into graphitic carbon nitride g-C₃N₄ (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-MnO₂ 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-C₃N₄ 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 (Fe₃O₄@PDA) in PES. In addition to the higher permeabilities of the composite membranes (e.g. over 2600 L/m² h bar corresponding to 20wt.% Fe₃O₄@PDA PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive removal of Pb²⁺ and catalytic degradation of methylene blue, e.g. acceptable Pb²⁺ 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 (Pb²⁺) 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⁻² h⁻¹). 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

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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. Cd²⁺,
130 Pb²⁺, Ni²⁺, Cu²⁺, Al²⁺, Co²⁺, Zn²⁺, Mn²⁺, Cr⁴⁺) 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), MnO₂/chitosan (Dinh et al., 2020), core-shell
153 structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe₃O₄/GO composite
154 introduced into graphitic carbon nitride g-C₃N₄ (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, Cu^{2+} , zinc (Zn^{2+}) and nickel (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 Ni^{2+} , Cu^{2+} , Zn^{2+} and 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 Ni^{2+} and 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 Cd^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ and 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 (TiO₂) (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, Pratihara and Behera, 2016; Xia and Ni, 2015), alumina (Al₂O₃)
344 (Arsuaga et al., 2013), silica (SiO₂) (Yu et al., 2009), magnetite (Fe₃O₄) (Alam et al., 2016), cobalt
345 (Co) (Gzara et al., 2016), zirconium dioxide (ZrO₂) (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 Zn²⁺, Cd²⁺, Pb²⁺, Mn²⁺, Ni²⁺, Fe²⁺, Al³⁺, Sb³⁺, and Sr³⁺,
357 concluding that these membranes were highly selective towards Fe²⁺. Furthermore, the developed
358 membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m⁻² h⁻¹ bar⁻¹. 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- π 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⁻² h⁻¹, a higher value compared to the one provided by the pristine PVDF (ca. 240 L m⁻² 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 (Pb²⁺, Cu²⁺,
409 Cd²⁺, Cr³⁺) (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 Cr^{+2} and 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 (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 TiO_2 into PAN polymer, the
504 generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards Pb^{2+} ,
505 Cu^{2+} , Cd^{2+} metal ions, respectively. Towards the efficient separation of 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 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 Al_2O_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 \AA , which represents a larger kinetic diameter than the one of water (H_2O , $\sim 2.8 \text{ \AA}$), but
523 still smaller than the hydrated diameter of heavy metal ions (e.g. Cu^{2+} , Co^{2+} , Cd^{2+} , 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 L
526 $\text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and rejection rate of 99.2% towards 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 Pb^{2+} and 72% for 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 Cd²⁺
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 μ -Fe₂O₃ nanowires as
539 well as Fe₃O₄ 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 Cd²⁺ adsorption capacity, ca. 29.3 mg g⁻¹, 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 Cd²⁺ 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 Fe₃O₄ NPs as membrane precursors, but Cd²⁺ 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_3O_4 magnetic NPs coated with rice husk extracted silica (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 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-MnO₂ 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 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 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 mg g^{-1}) than Cd (ca.
611 562 mg g^{-1}) and Cu (ca. 152 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 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 ($\text{EDTA@Fe}_3\text{O}_4/\text{SC}$) 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 Pb^{2+} and catalytic degradation of methylene blue, e.g. acceptable 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 (Pb^{2+}) using an electrospun
660 β -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 Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Al^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} ,
670 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

725 **Acknowledgements**

726 R. Castro-Muñoz acknowledges the School of Science and Engineering and the FEMSA-
727 Biotechnology Center at Tecnológico de Monterrey for their support through the Bioprocess
728 (0020209I13) Focus Group. Financial support from Polish National Agency for Academic
729 Exchange (NAWA) under Ulam Programme (Agreement No. PPN/ULM/2020/1/00005/U/00001)
730 is also gratefully acknowledged. The Regional Government of Castilla y León and the EU-FEDER
731 programme [grant numbers CLU 2017-09 and UIC 071] are also gratefully acknowledged.

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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 ²⁺ , Cd ²⁺	98%, 95%	(Zhu et al., 2014)
NF	PA	Cu ²⁺ , Cd ²⁺	98%, 99%	(Qdais and Moussa, 2004)
RO	PA	Cu ²⁺ , Cd ²⁺	>90%	(Qdais and Moussa, 2004)
ED	sulfonated PVDF	Co ²⁺ , Ni ²⁺	90 % , 69 %,	(Tzanetakis et al., 2003)
NF	CA/ PMVEMA	Pb ²⁺ , Cd ²⁺ , Cr ⁺⁶	85%, 72%	(Lavanya et al., 2019)
NF	PES-PE	Cu ²⁺ , Zn ²⁺ , Ni ²⁺	>90%	(Mokhter et al., 2017)
NF	PAN-PEI/PSS	Cu ²⁺ , Zn ²⁺ , Ni ²⁺ , Cd ²⁺	98%, 96%, 96%, 95%	(Qin et al., 2013)
UF	PVDF/2-Aminobenzothiazole	Cr ⁶⁺	92%	(Wang et al., 2017)
UF	PVDF/PANI	Pb ²⁺ , Cd ²⁺	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)
		Removal of bivalent ions (Ca^{2+} , SO_4^{2-} and Mg^{2+}), monovalent ions (Cl^- and 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)
	Wastewater treatment	PA-PVA	(Yang Zhang et al., 2016)	
Ag-NO ₃	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 ₂ SO ₄)	PA	(Liu et al., 2015)
bio-Ag0		Water treatment		(Liu et al., 2016)
Cu-nanoparticles		Water treatment		(Hoek et al., 2011)
			PSF	
CuAc ₂		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 ₄ ²⁺ , Mg ²⁺ , Na ⁺ , Cl ⁻).	PAN/PEI	(Xu et al., 2015)
CuSO ₄				
CuCl ₂	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 ₂ 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 ₂ SO ₄).	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 ₃ N 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 ²⁺) ions removal (100%)	
		Co (Co ²⁺) ions removal (100%)	
Composite GPC	UF	Pb (Pb ²⁺) ions removal (>95%)	(Jing Wang et al., 2018)
PECN	NF	Zn (Zn ²⁺) ions removal (100%)	(Ye et al., 2019)
f- MOFs-CUF	UF	Pb (Pb ²⁺) ions removal (61.4%)	(Yin et al., 2016)
ZIF-300-Al ₂ O ₃	NF	Cu (Cu ²⁺) ions removal (100 %)	(Yuan et al., 2019)
		Co (Co ²⁺) ions removal (100 %)	
		Cd (Cd ²⁺) ions removal (100 %)	
		Al (Al ²⁺) ions removal (100 %)	
Goethite filled PAN	UF	Cu (Cu ²⁺) ions removal (49 %)	(Soghra et al., 2019)
Composite PEI- zein	FO	Pb (Pb ²⁺) ions removal (>99.5%)	(X. Zhao & Liu, 2019)
		Cd (Cd ²⁺) ions removal (>99.5%)	
		Ni (Ni ²⁺) ions removal (>99.5%)	
GMA-PAN	UF	Cu (Cu ²⁺) ions removal (98 %)	(Yanhong Zhang et al., 2019)

466
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), C₃N₄-decorated carbon-
0 fiber (CF-TiO₂-C₃N₄), 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 ₂ coated by chitosan nanocomposite	Cr (VI) adsorption (61.56 mg g ⁻¹) Cr (VI) removal efficiency (94.21%)	Physisorption and electrostatic attraction	pH effect Adsorption efficiency decreases with ascending pH values (optimal pH=2) Ion strength Ionic strength, with an increase in the KCL concentration decreases Cr (VI) removal efficiency Adsorbent dosage The material concentration affects Cr (VI) adsorption capacity	MnO ₂ /CS was fabricated by mixing, filtering and drying a suspension made up by C ₂ H ₅ OH, deionized (DI) water, CS and saturated KMnO ₄ solution	Mixing 8 h at room temperature Different shaking speeds were tested Oven drying 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 ⁻¹) Cr (VI) removal efficiency (80%)	Chemical reduction reaction of Cr (VI) into Cr (III)	Cr (VI) Initial concentration effect High initial Cr (VI) concentration values increased the reduction capacity pH effect	Hydrothermal-calcination method	Drying Vacuum conditions at 80°C for 24h. Carbonization Pipe oven under N ₂ 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)				
			C/Fe molar ratio				
			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 ⁻¹)	Heterogeneous adsorption processes, both physisorption and chemisorption, ion exchange and electrostatic attraction	Nanocomposite ratio effect Optimal ratio: 20%-BC/VE pH effect pH affects the BC/VE surface charge, as well as the electrostatic interactions (optimal pH= 6) Coexisting anions effect <i>PO₄³⁻</i> reduced considerably adsorption rate of As (V)	Ball milling method	Ball milling At 300 rpm for 12 h	No tests were performed	(Li et al., 2020)
Fe ₃ O ₄ /GO (mGO) composite introduced into graphitic carbon nitride g-C ₃ N ₄ .	U (VI) extraction capacity (2880.6 mg g ⁻¹) U (VI) extraction efficiency (96.02%)	Chemical reaction of photocatalytic reduction of U (VI) under LED light irradiation	pH effect on photocatalytic activity Optimal pH=6 U (VI) concentration effect on photoreduction in mGCN-1	Ultrasonication was applied to the individual suspensions and then to the mixture of mGO and g-C ₃ N ₄ The solids of the mGO and g-C ₃ N ₄ mixture were centrifuged and dried	Ultrasonication Individually for 1 h and as mixture for 2h. Drying 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 ⁻¹				
Silicon dioxide composite with tea waste (SiO ₂ @TW)	<p>Adsorption capacities:</p> <p>Pb²⁺ (153 mg g⁻¹) and Cd²⁺ (222 mg g⁻¹)</p> <p>Removal rates:</p> <p>Pb²⁺ (89.22%) and Cd²⁺ (94.28%)</p>	Electrostatic attraction and physical adsorption	<p>pH effect</p> <p>Optimal pH values:</p> <p>Pb²⁺ (pH= 6) and Cd²⁺ (pH=7)</p> <p>SiO₂@TW dosage effect</p> <p>High dose of SiO₂@TW enhanced adsorption sites, increasing removal capacity</p> <p>Temperature effect</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 SiO₂ NPs fabrication</p> <p>SiO₂@TW synthesis consisted of sonication, centrifugation and drying of SiO₂ - tea waste powder suspension</p>	<p>Stirring</p> <p>For 30 min at 25°C</p> <p>Sonication</p> <p>For 1h</p> <p>Drying</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⁻¹), 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>Magnetic stirring</p> <p>At 1000 rpm for 6 h</p> <p>Culturing</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 ⁻¹), and Pb (II) (730.79 mg g ⁻¹)						
Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) entrapped in calcium-alginate matrix (nZVI/BC/CA)	Cr (VI) adsorption capacity (86.4 mg g ⁻¹)	Ion exchange, intraparticle diffusion, chemical adsorption and redox reaction	pH effect Optimal pH= 4	Modified liquid-phase method	Pyrolysis At 500°C for 3 h in a muffle furnace (15°C / min) under N ₂ atmosphere Stirring 500 rpm at 25°C for 30 min.	Removal capacity decreased at the 1 st 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 ⁻¹)	Chemisorption and photocatalytic reduction	Carbonization temperature effect Optimal carbonization temperature: 700°C ZnO content effect 30 wt.% optimal ZnO concentration	BC powder was impregnated into Zn(NO ₃) ₂ aqueous solution, by drying and calcination steps	Drying At 105°C for 12h. Calcination At 380°C for 3h under N ₂ atmosphere	Removal efficiency (87.1% at 1 st run) and (67.1% at 5 th run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe ₃ O ₄), loaded with SC (sawdust carbon) (EDTA@Fe ₃ O ₄ /SC)	Cd (II) adsorption capacity (63.3 mg g ⁻¹) 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	pH effect Cd (II) removal efficiency increases as pH value rises (Optimal pH= 6.5) Adsorbent dose effect Cd (II) removal increased as adsorbent dose increased Contact time effect	Biogenic green synthesis approach for fabrication	Stirring At 90°C for 1h Carbonization In muffle furnace at 180°C for 12h	Desorption Maximum Cd (II) desorption was achieved with HCl (99%), HNO ₃ (100%) and H ₂ SO ₄ (100%) Reusability After three cycles, adsorption efficiency (83%) and at the	(Kataria and Garg, 2018)

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

fifth cycle (57%)

Coexisting ions effect

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

Silica (SiO_2) functionalized folic acid (VB9) ($\text{SiO}_2@VB9$) nanocomposite

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



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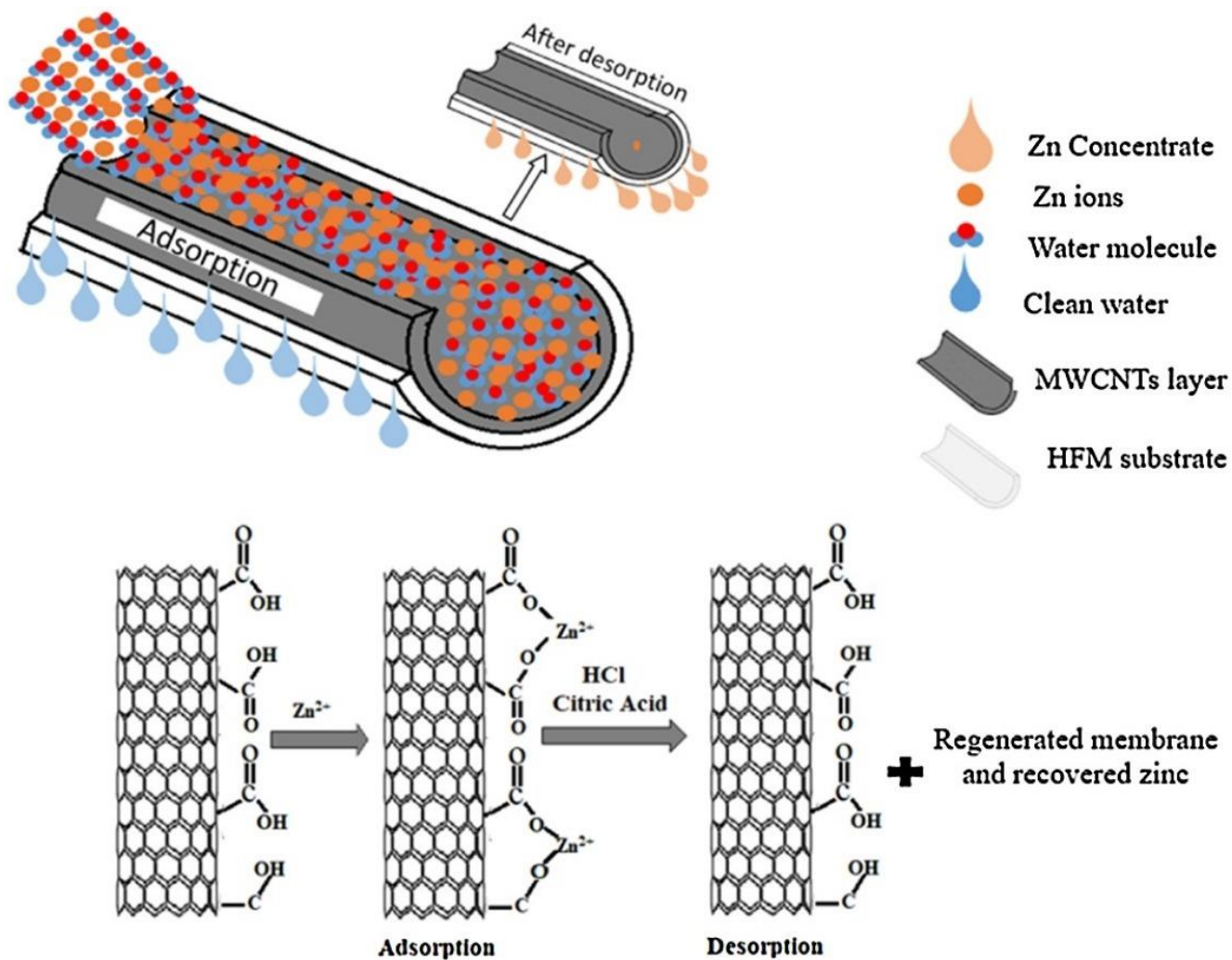
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Figure 1. Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et al., 2019).



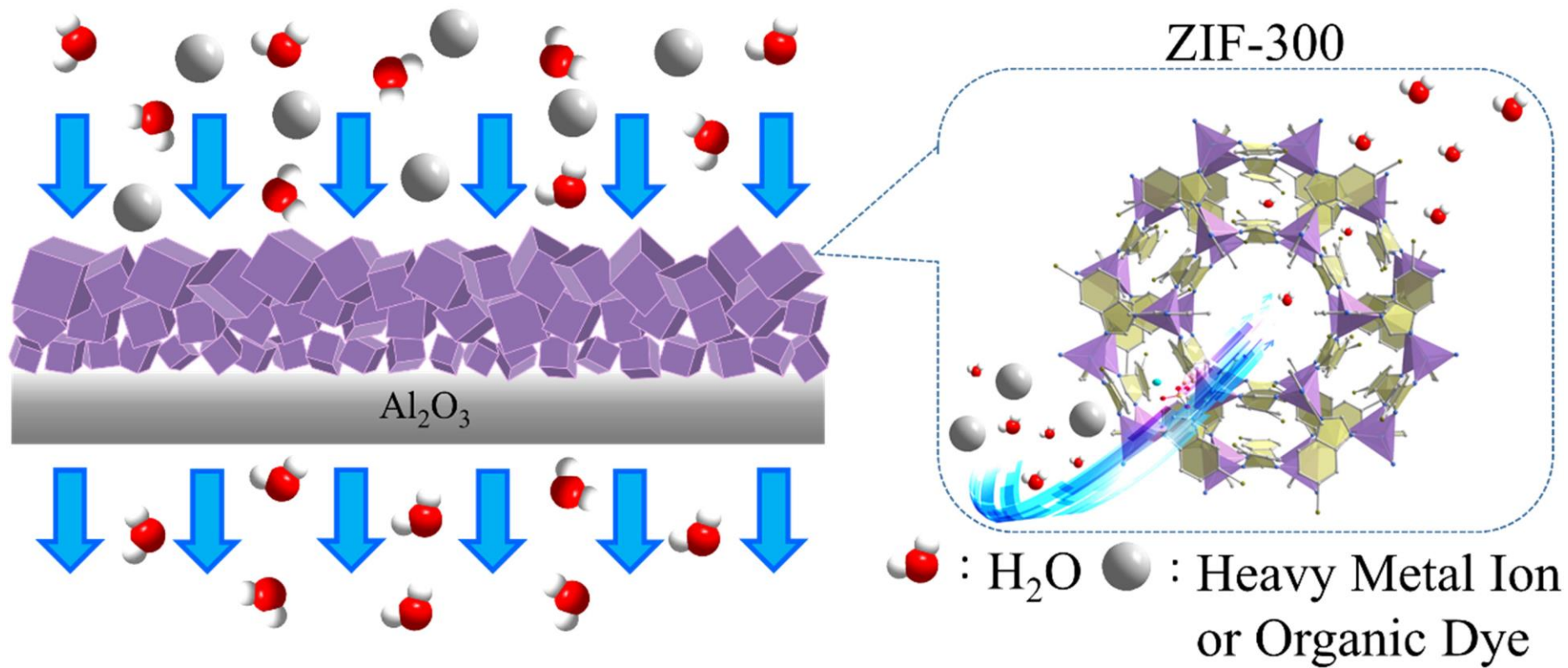
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Figure 2. Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).

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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⁻² h⁻¹). 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

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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. Cd²⁺,
130 Pb²⁺, Ni²⁺, Cu²⁺, Al²⁺, Co²⁺, Zn²⁺, Mn²⁺, Cr⁴⁺) 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), MnO₂/chitosan (Dinh et al., 2020), core-shell
153 structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe₃O₄/GO composite
154 introduced into graphitic carbon nitride g-C₃N₄ (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%.

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

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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, Cu^{2+} , zinc (Zn^{2+}) and nickel (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 Ni^{2+} , Cu^{2+} , Zn^{2+} and 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 Ni^{2+} and 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 Cd^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ and 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 (TiO₂) (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 (Al₂O₃)
344 (Arsuaga et al., 2013), silica (SiO₂) (Yu et al., 2009), magnetite (Fe₃O₄) (Alam et al., 2016), cobalt
345 (Co) (Gzara et al., 2016), zirconium dioxide (ZrO₂) (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 Zn²⁺, Cd²⁺, Pb²⁺, Mn²⁺, Ni²⁺, Fe²⁺, Al³⁺, Sb³⁺, and Sr³⁺,
357 concluding that these membranes were highly selective towards Fe²⁺. Furthermore, the developed
358 membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m⁻² h⁻¹ bar⁻¹. 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- π 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 (Pb^{2+} , Cu^{2+} ,
409 Cd^{2+} , 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 Cr^{+2} and 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 (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 TiO_2 into PAN polymer, the
504 generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards Pb^{2+} ,
505 Cu^{2+} , Cd^{2+} metal ions, respectively. Towards the efficient separation of 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 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 Al_2O_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 \AA , which represents a larger kinetic diameter than the one of water (H_2O , $\sim 2.8 \text{ \AA}$), but
523 still smaller than the hydrated diameter of heavy metal ions (e.g. Cu^{2+} , Co^{2+} , Cd^{2+} , 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 L
526 $\text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and rejection rate of 99.2% towards 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 Pb^{2+} and 72% for 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 Cd²⁺
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 μ -Fe₂O₃ nanowires as
539 well as Fe₃O₄ 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 Cd²⁺ adsorption capacity, ca. 29.3 mg g⁻¹, 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 Cd²⁺ 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 Fe₃O₄ NPs as membrane precursors, but Cd²⁺ 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_3O_4 magnetic NPs coated with rice husk extracted silica (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 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-MnO₂ 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 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 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 mg g^{-1}) than Cd (ca.
611 562 mg g^{-1}) and Cu (ca. 152 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 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 ($\text{EDTA@Fe}_3\text{O}_4/\text{SC}$) 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 Pb^{2+} and catalytic degradation of methylene blue, e.g. acceptable 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 (Pb^{2+}) using an electrospun
660 β -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 Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Al^{3+} , Co^{2+} , Zn^{2+} , Mn^{2+} ,
670 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

725 **Acknowledgements**

726 R. Castro-Muñoz acknowledges the School of Science and Engineering and the FEMSA-
727 Biotechnology Center at Tecnológico de Monterrey for their support through the Bioprocess
728 (0020209I13) Focus Group. Financial support from Polish National Agency for Academic
729 Exchange (NAWA) under Ulam Programme (Agreement No. PPN/ULM/2020/1/00005/U/00001)
730 is also gratefully acknowledged. The Regional Government of Castilla y León and the EU-FEDER
731 programme [grant numbers CLU 2017-09 and UIC 071] are also gratefully acknowledged.

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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 ²⁺ , Cd ²⁺	98%, 95%	(Zhu et al., 2014)
NF	PA	Cu ²⁺ , Cd ²⁺	98%, 99%	(Qdais and Moussa, 2004)
RO	PA	Cu ²⁺ , Cd ²⁺	>90%	(Qdais and Moussa, 2004)
ED	sulfonated PVDF	Co ²⁺ , Ni ²⁺	90 % , 69 %,	(Tzanetakis et al., 2003)
NF	CA/ PMVEMA	Pb ²⁺ , Cd ²⁺ , Cr ⁺⁶	85%, 72%	(Lavanya et al., 2019)
NF	PES-PE	Cu ²⁺ , Zn ²⁺ , Ni ²⁺	>90%	(Mokhter et al., 2017)
NF	PAN-PEI/PSS	Cu ²⁺ , Zn ²⁺ , Ni ²⁺ , Cd ²⁺	98%, 96%, 96%, 95%	(Qin et al., 2013)
UF	PVDF/2-Aminobenzothiazole	Cr ⁶⁺	92%	(Wang et al., 2017)
UF	PVDF/PANI	Pb ²⁺ , Cd ²⁺	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)
		Removal of bivalent ions (Ca^{2+} , SO_4^{2-} and Mg^{2+}), monovalent ions (Cl^- and 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 ₃		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 ₂ SO ₄)	PA	(Liu et al., 2015)
bio-Ag0		Water treatment		(Liu et al., 2016)
Cu-nanoparticles		Water treatment		(Hoek et al., 2011)
			PSF	
CuAc ₂		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 ₄ ²⁺ , Mg ²⁺ , Na ⁺ , Cl ⁻).	PAN/PEI	(Xu et al., 2015)
CuSO ₄				
CuCl ₂	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 ₂ 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 ₂ SO ₄).	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.

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 ₃ N 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 ²⁺) ions removal (100%)	
		Co (Co ²⁺) ions removal (100%)	
Composite GPC	UF	Pb (Pb ²⁺) ions removal (>95%)	(Jing Wang et al., 2018)
PECN	NF	Zn (Zn ²⁺) ions removal (100%)	(Ye et al., 2019)
f- MOFs-CUF	UF	Pb (Pb ²⁺) ions removal (61.4%)	(Yin et al., 2016)
ZIF-300-Al ₂ O ₃	NF	Cu (Cu ²⁺) ions removal (100 %)	(Yuan et al., 2019)
		Co (Co ²⁺) ions removal (100 %)	
		Cd (Cd ²⁺) ions removal (100 %)	
		Al (Al ²⁺) ions removal (100 %)	
Goethite filled PAN	UF	Cu (Cu ²⁺) ions removal (49 %)	(Soghra et al., 2019)
Composite PEI- zein	FO	Pb (Pb ²⁺) ions removal (>99.5%)	(X. Zhao & Liu, 2019)
		Cd (Cd ²⁺) ions removal (>99.5%)	
		Ni (Ni ²⁺) ions removal (>99.5%)	
GMA-PAN	UF	Cu (Cu ²⁺) 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), C₃N₄-decorated carbon-
0 fiber (CF-TiO₂-C₃N₄), 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 ₂ coated by chitosan nanocomposite	Cr (VI) adsorption (61.56 mg g ⁻¹) Cr (VI) removal efficiency (94.21%)	Physisorption and electrostatic attraction	pH effect Adsorption efficiency decreases with ascending pH values (optimal pH=2) Ion strength Ionic strength, with an increase in the KCL concentration decreases Cr (VI) removal efficiency Adsorbent dosage The material concentration affects Cr (VI) adsorption capacity	MnO ₂ /CS was fabricated by mixing, filtering and drying a suspension made up by C ₂ H ₅ OH, deionized (DI) water, CS and saturated KMnO ₄ solution	Mixing 8 h at room temperature Different shaking speeds were tested Oven drying 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 ⁻¹) Cr (VI) removal efficiency (80%)	Chemical reduction reaction of Cr (VI) into Cr (III)	Cr (VI) Initial concentration effect High initial Cr (VI) concentration values increased the reduction capacity pH effect	Hydrothermal-calcination method	Drying Vacuum conditions at 80°C for 24h. Carbonization Pipe oven under N ₂ 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)				
			C/Fe molar ratio				
			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 ⁻¹)	Heterogeneous adsorption processes, both physisorption and chemisorption, ion exchange and electrostatic attraction	Nanocomposite ratio effect Optimal ratio: 20%-BC/VE pH effect pH affects the BC/VE surface charge, as well as the electrostatic interactions (optimal pH= 6) Coexisting anions effect <i>PO₄³⁻</i> reduced considerably adsorption rate of As (V)	Ball milling method	Ball milling At 300 rpm for 12 h	No tests were performed	(Li et al., 2020)
Fe ₃ O ₄ /GO (mGO) composite introduced into graphitic carbon nitride g-C ₃ N ₄ .	U (VI) extraction capacity (2880.6 mg g ⁻¹) U (VI) extraction efficiency (96.02%)	Chemical reaction of photocatalytic reduction of U (VI) under LED light irradiation	pH effect on photocatalytic activity Optimal pH=6 U (VI) concentration effect on photoreduction in mGCN-1	Ultrasonication was applied to the individual suspensions and then to the mixture of mGO and g-C ₃ N ₄ The solids of the mGO and g-C ₃ N ₄ mixture were centrifuged and dried	Ultrasonication Individually for 1 h and as mixture for 2h. Drying 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 ⁻¹				
Silicon dioxide composite with tea waste (SiO ₂ @TW)	<p>Adsorption capacities:</p> <p>Pb²⁺ (153 mg g⁻¹) and Cd²⁺ (222 mg g⁻¹)</p> <p>Removal rates:</p> <p>Pb²⁺ (89.22%) and Cd²⁺ (94.28%)</p>	Electrostatic attraction and physical adsorption	<p>pH effect</p> <p>Optimal pH values:</p> <p>Pb²⁺ (pH= 6) and Cd²⁺ (pH=7)</p> <p>SiO₂@TW dosage effect</p> <p>High dose of SiO₂@TW enhanced adsorption sites, increasing removal capacity</p> <p>Temperature effect</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 SiO₂ NPs fabrication</p> <p>SiO₂@TW synthesis consisted of sonication, centrifugation and drying of SiO₂ - tea waste powder suspension</p>	<p>Stirring</p> <p>For 30 min at 25°C</p> <p>Sonication</p> <p>For 1h</p> <p>Drying</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⁻¹), 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>Magnetic stirring</p> <p>At 1000 rpm for 6 h</p> <p>Culturing</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 ⁻¹), and Pb (II) (730.79 mg g ⁻¹)						
Nanoscale zerovalent iron (nZVI) impregnated biochar (BC) entrapped in calcium-alginate matrix (nZVI/BC/CA)	Cr (VI) adsorption capacity (86.4 mg g ⁻¹)	Ion exchange, intraparticle diffusion, chemical adsorption and redox reaction	pH effect Optimal pH= 4	Modified liquid-phase method	Pyrolysis At 500°C for 3 h in a muffle furnace (15°C / min) under N ₂ atmosphere Stirring 500 rpm at 25°C for 30 min.	Removal capacity decreased at the 1 st 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 ⁻¹)	Chemisorption and photocatalytic reduction	Carbonization temperature effect Optimal carbonization temperature: 700°C ZnO content effect 30 wt.% optimal ZnO concentration	BC powder was impregnated into Zn(NO ₃) ₂ aqueous solution, by drying and calcination steps	Drying At 105°C for 12h. Calcination At 380°C for 3h under N ₂ atmosphere	Removal efficiency (87.1% at 1 st run) and (67.1% at 5 th run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe ₃ O ₄), loaded with SC (sawdust carbon) (EDTA@Fe ₃ O ₄ /SC)	Cd (II) adsorption capacity (63.3 mg g ⁻¹) 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	pH effect Cd (II) removal efficiency increases as pH value rises (Optimal pH= 6.5) Adsorbent dose effect Cd (II) removal increased as adsorbent dose increased Contact time effect	Biogenic green synthesis approach for fabrication	Stirring At 90°C for 1h Carbonization In muffle furnace at 180°C for 12h	Desorption Maximum Cd (II) desorption was achieved with HCl (99%), HNO ₃ (100%) and H ₂ SO ₄ (100%) Reusability After three cycles, adsorption efficiency (83%) and at the	(Kataria and Garg, 2018)

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

fifth cycle (57%)

Coexisting ions effect

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

Silica (SiO_2) functionalized folic acid (VB9) ($\text{SiO}_2@VB9$) nanocomposite

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



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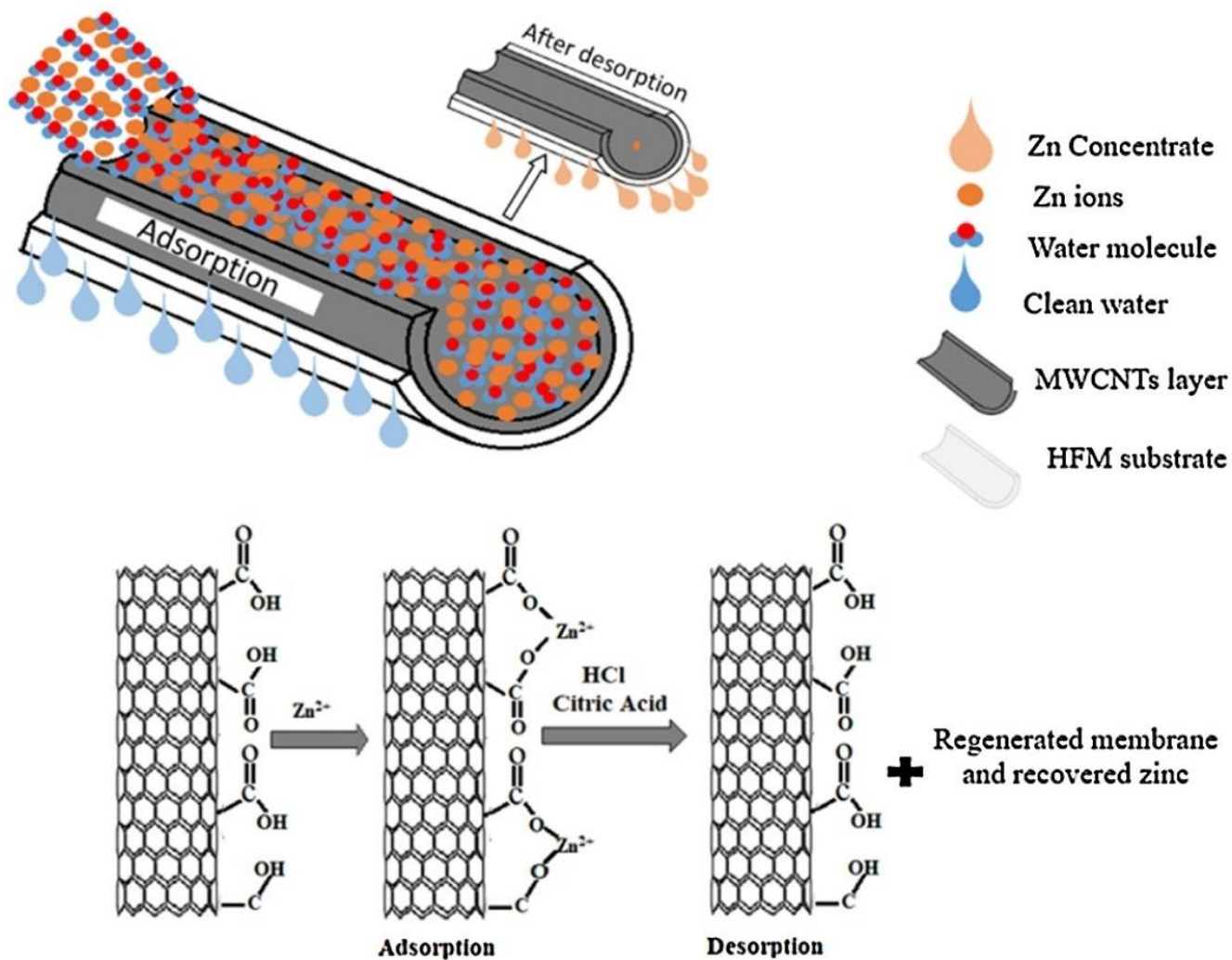
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Figure 1. Adsorption and desorption mechanisms of zinc ions in functionalized MWCNTs (Ali et al., 2019).



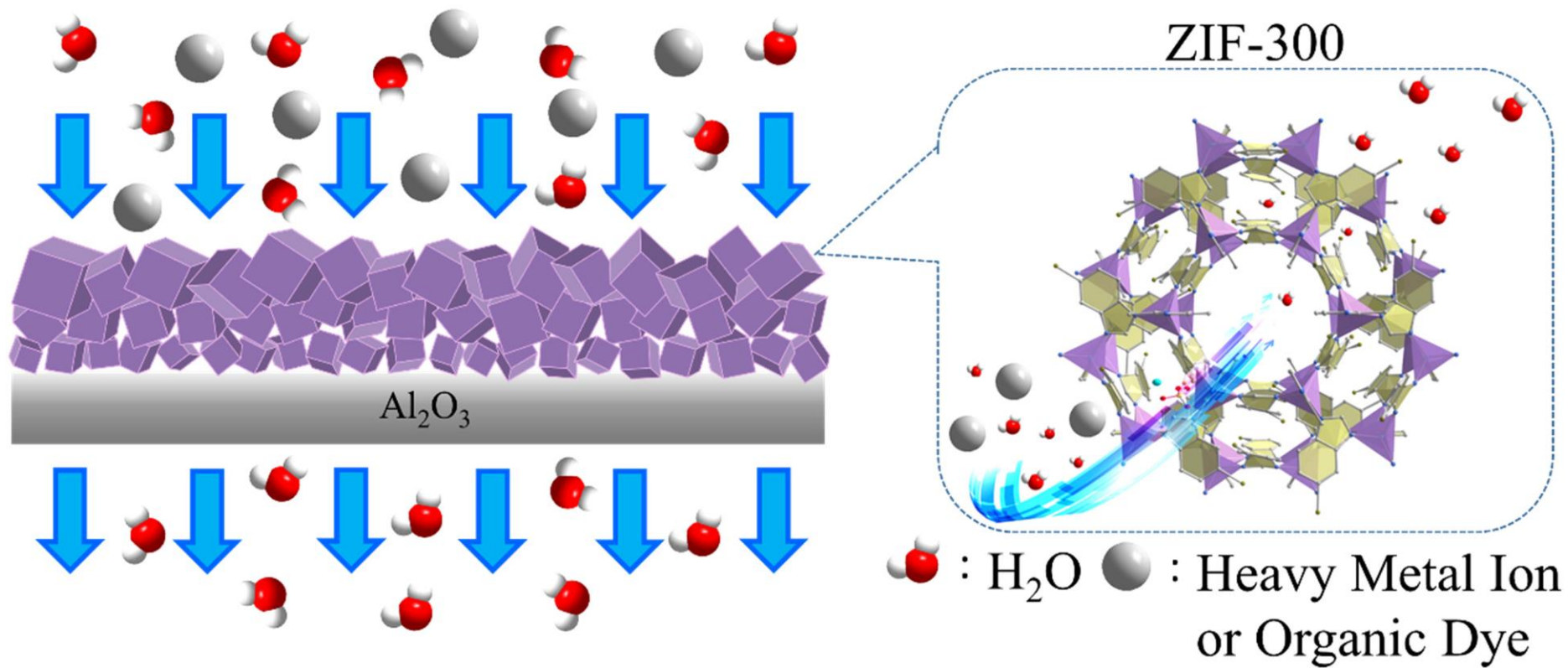
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Figure 2. Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).

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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.

4