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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 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-contamined 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 (3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

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. Enviromental 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.*

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 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.

Abbreviations:

Ag: silver

As: Arsenic

APTS: 3-Aminopropyltriethoxysilane

CA: Cellulose acetate

Cd: Cadmium

CNT: Carbon Nanotubes

Co: Cobalt

Cr: Chromium

Cu: copper

DCMD: Direct contact membrane distillation

ESPM: Polymer Mixed e-spinning Membranes

Fe: Iron

f-GO: functionalized Graphene Oxide

GO: Graphene Oxide

IPDI: Isophorone diisocyanate

MD: Membrane distillation

MF: Microfiltration

MMGO: Modified magnetic Graphene Oxide

MMM: Mixed Matrix Membranes

MOF: Metal-Organic Frameworks

MWCNT: Multi-walled carbon nanotubes

NF: Nanofiltration

Ni: Nickel

NPs: Nanoparticles

nZVI: nano– Zero Valent Iron

PAH: Poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated

PAN: Polyacrylonitrile

PBI: Polybenzimidazole

PES: Polyethersulfone

PMVEMA: Poly(methyl vinyl ether-alt-maleic acid)

POSS: Polyhedral Oligomeric Silsesquioxane

PSF: Polysulfone

PSS: Poly(sodium 4-styrenesulfonate)

PV: Pervaporation

PVA: Polyvinyl alcohol

PVP: Polyvinylpyrrolidone

PVDF: Polyvinylidine fluoride

RO: Reverse Osmosis

TCE: Trichloroethylene

UF: Ultrafiltration

VFM: Vacuum filtered nembranes

ZIF: Zeolite imidazolate framework

1. Introduction

The removal of pollutants (including metal ions) from water has been approached using several traditional treatments and protocols, such as chemical precipitation (Chabot et al., 2014), microbial decomposition (Yang et al., 2016), and physical adsorption (Kumar et al., 2013). Inherently, these pollutants represent strong issues to the environment (i.e. plants, animals, ecology climate) and humans. However, the removal of heavy metals through conventional protocols (such as flotation, chemical precipitation, ion exchange, adsorption, and electrochemical deposition) is still challenging, requiring further efforts to circumvent the production of a high amount of toxic sludge and liquid waste, long time consumption, and extreme use of supplies (e.g. solvents, resins, among others), together with poor separation efficiency.

Currently, according to the scarcity of drinking water and the increasingly serious water pollution (Marousek et al., 2019), water treatment with membrane-based processes has potentially attracted the attention of the research community. 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). To date, polymeric membranes are likely the most used membranes for water treatment applications (Castro-Muñoz et al., 2018a), including treatment of agro-food wastes (Castro-Muñoz et al., 2016), textile (Chao et al., 2016), petroleum industry streams (Alzahrani and Wahab, 2014), acid mine waters (Lopez et al., 2019), and seawater desalination (Castro-Muñoz, 2020a). Membranes are capable to separate the compounds from aqueous streams and thus reduce the contaminants contained in wastewater (Castro-Muñoz et al., 2018b). Extensive sources and a large number of molecules, as well as ions contained in polluted water, challenge the effective purification and separation of water by membranes. The membranes, based on their intrinsic properties, can be implemented among different types of membrane-based technologies including pressure-driven membrane processes, such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). These are potentially recognized as excellent candidates for the removal of large amounts of organic macropollutants; in which NF and RO membranes are among the barriers with the highest efficiency in withdrawing micropollutants (Castro-Muñoz et al., 2017). Other membrane technologies, e.g. membrane distillation (MD) (Criscuoli and Carnevale, 2015), membrane bioreactors (Santos and Judd, 2010), membrane contactors (Bey et al., 2010), have also been proven to remove specific heavy metal ions, such as arsenic (As), fluoride (F) and uranium (U). In particular, As is a natural tasteless and odorless element that may be highly toxic to humans exposed to it from air, food and water. It is known that this element exists in the earth's crust at average levels between 2000–5000 µg per kg (Figoli et al., 2010).

In this way, membranes have shown to be efficient in removing different metal ions (e.g. Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Al^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cr^{4+}) from water streams. A large number of studies has been now devoted to the manufacture of synthetic membranes for these particular separations, demonstrating compelling benefits, such as permeability, selectivity, enhanced chemical and physical properties within the removal of metal ions. When dealing with the removal efficiency of such membranes, the material properties, including chemical, physical, mechanical, play an important role in their efficiency, but also the membrane preparation protocols are crucial. In this context, several techniques have been used in membrane manufacture, such as stretching, track-etching, sintering, electrospinning, phase inversion (Lalia et al., 2013), and interfacial polymerization (Peydayesh et al., 2018), in which plenty of organic and inorganic materials have been proposed and used in tailoring membranes (Castro-Muñoz et al. 2020). Polymers have been the most used organic materials in membrane preparation, followed by the inorganic ones (e.g. ceramics, metals and glass) (Ulbricht, 2006). Polymer membranes tend to present great design flexibility, while the advantages of inorganic membranes, e.g. ceramic membranes, compared with polymeric ones comprise their higher thermal, mechanical and chemical stability (Castro-Muñoz et al. 2018c). Also, the hydrophilicity and the surface charge in ceramic membranes are higher. Ceramic membranes can also be operated under extreme conditions of pH, temperature and high oxidizing environment (Yong et al., 2013). As a current trend in the field of development of new membrane materials, the merging of both materials to produce nanocomposite membranes is also a promising tool for the efficient removal of heavy metals. However, there is a lack of reviewing the progress and latest nanocomposite membrane concepts and their role in water treatment and separation of heavy metals. Very recently, novel breakthroughs in tailoring nanocomposite materials have been released, such as nanoscale zerovalent iron impregnated biochar entrapped in calcium-alginate matrix (Wan et al., 2019), MnO_2/chitosan (Dinh et al., 2020), core-shell structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe_3O_4/GO composite introduced into graphitic carbon nitride g-C_3N_4 (Dai et al., 2020), to mention just a few of them. Thereby, this review paper aims at providing the ongoing progress of using different concepts of membranes (polymeric, composite and nanocomposite) and potential novel materials for removing heavy metals. Herein, a highlighted literature survey of using polymeric and nanocomposite membranes for heavy metal removal from water is provided. Ultimately, the current advances and future trends of nanocomposite membranes in the field are also given.

2. Metal ions removal using pristine polymeric and chemically modified polymeric membranes

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

Polymeric membranes are typically manufactured from natural or chemically-synthesized polymers. The membranes are creating a selective interface barrier between two adjacent phases (feed and permeate) which governates the transport behavior of species between them. In general, the separation performance of the membrane depends on the properties of transported species (e.g. molecule size, shape and chemical nature), as well as physicochemical properties (hydrophilicity/hydrophobicity, surface charge, roughness) of the polymer membrane, especially porous structure. For instance, **Table 1** enlists some of the reported studies in which the removal of heavy metal ions has been performed by means of different polymeric membranes and processes. It can be seen that the removal efficiency towards metal ions using polymer membranes has been reported between 77 to 99%.

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

For instance, Qdais and Moussa (2004) evaluated the separation performance of the RO and NF technologies using polyamide spiral wound membranes for the removal of copper (Cu) and cadmium (Cd) metals from industrial wastewater. While the RO process showed Cu and Cd removal efficiencies of about 98 and 99%, respectively, the NF process exhibited more than 90% of Cu ions. Interestingly, the membranes were able to concurrently treat wastewater containing more than one heavy metal ion. As an example, these membranes reduced the ion concentration from 500 ppm to 3 ppm, meaning a removal efficiency of over 99%. Another typical polymeric membrane material is polyethersulfone (PES), which has been successfully consolidated in membrane preparation owing to its high thermal and mechanical stability, physiological and chemical neutrality and wide range pH resistance. PES, however, tends to present a hydrophobic nature which results in high membrane fouling when applied for organic aqueous filtration. Thus, with the aim of improving its separation performance and properties, efforts have been proposed to shift the surface properties of this hydrophobic polymer. It is known that hydrophobic polymers are more prone to membrane fouling due to the particles contained in the feed bulk tend to accumulate on hydrophobic and rough surfaces, minimizing the interfacial tension between water and membrane (Pichardo-Romero et al., 2020). Therefore, the on-going strategies are aimed at mitigating the interaction between the foulants and the barrier layer. For example, an easy approach is to chemically modify the surface properties of the membrane by immersing it in a polyelectrolyte solution. It has been found that the polyelectrolyte adsorbed onto the membranes may significantly improve the membrane performance in terms of metal ions removal due to the presence of chelating functions in their structure. In this way, Mokhter et al. (2017) performed the chemical modification of PES membranes by polyelectrolyte multilayers, made of poly(allylamine hydrochloride) with poly(styrene sulfonate). The resulting membranes were employed to treat aqueous solutions containing single or mixed heavy metals, Cu^{2+}, zinc (Zn^{2+}) and nickel (Ni^{2+}), at various concentrations (50–1200 ppm). The tested membrane was efficient in separating all the tested metals either alone or mixed with high long-term stability and removal efficiencies over 90%. Similarly, polyacrylonitrile (PAN) membranes were modified by Qin et al. (2013), who synthesized positively charged membranes by depositing polyelectrolytes. Researchers used PAN membranes modified by the layer-by-layer assembly of polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS), to successfully separate Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} aqueous solutions, achieving removal efficiencies in the range of 95–98%. Particularly, the NF tests showed that the removal efficiency of Ni^{2+} and Cd^{2+} ions increased with the number of bilayers, but a decrease in permeate fluxes was observed. The usage of additional polymeric layers could also be applicable in the case of hollow fiber membranes. The great benefit of multi-layer materials lies in the fact that a relatively cheap material could be used as a support while a high-performance material (commonly a more expensive material) can be used as the selective layer. For instance, Zhu et al. (2014) tailored a high-performance dual-layer NF hollow fiber membrane and tested for the removal of Cd^{2+}, $Cr_2O_7^{2-}$ and Pb^{2+} salts from model wastewater, attaining removal efficiencies above 95%. Herein, researchers applied polybenzimidazole (PBI) as the outer selective layer while the blend of PES and polyvinylpyrrolidone (PVP) was implemented as the support layer. Thanks to the unique charge characteristics and high chemical resistance of PBI, the novel developed dual-layer NF membrane demonstrated a great salt rejection value due to the Donnan exclusion effect enhancement and low adsorption of heavy metal ions on the PBI surface.

Polyvinylidene fluoride (PVDF) is definitely another hydrophobic polymer that remains popular in a wide number of water treatment applications (Gontarek et al., 2019; Xia & Ni, 2015). PVDF membranes are well recognized for their multiple advantages including high chemical tolerance, good mechanical and thermal properties. Tzanetakis et al. (2003) have proved that the performance of chemically sulfonated PVDF membrane in the electrodialysis process can be comparable with the one given by a perfluorosulfonic Nafion 117 commercial membrane. The sulfonated PVDF membrane has displayed removal efficiencies towards Co and Ni ions of about 90% and 69%, respectively. In addition to this, a meaningful enhancement of the amounts of transported metal ions was seen while using corrugated membranes, which resulted in an increase in membrane area of 60% compared with those using flat membranes. Wang et al. (2017) have developed the modification of PVDF membrane for post UF testing. In general, the results revealed that the interaction by blending of PVDF with 2-aminobenzothiazole conducted to the efficient removal of chromium (Cr) from the wastewater. As a disadvantage of such membrane preparation, the membranes showed a low permeate flux when compared with the typical UF membranes. Since a long time ago, it is documented that one of the simplest approaches to improve the water flux in hydrophobic polymeric membranes, like PVDF, is to mitigate the membrane fouling, which can be reached through hydrophilicity enhancement. For instance, Pereira et al. (2014) combined PVDF polymer matrix with polyaniline nanofibers, which was, in this case, proposed as a hydrophilic agent to fabricate enhanced hydrophilic membranes. The authors described that the resulting membranes exhibited better hydrophilicity and better membrane properties, as well as a relatively high rejection toward heavy metal ions, such as Pb^{2+} and Cd^{2+}, e.g. around 98.5% and 97.3%, respectively.

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

Taking into account the advantages and disadvantages of polymeric membranes, the popularity of their use and implementation for removing heavy metal ions is also attributed to their low manufacture costs and ease of modification. However, such polymeric membranes still lack different desired properties for membrane separation processes, including the ones that required high selectivity towards low solutes and species. To date, many works have been done at aiming the enhancement of the separation performance of the polymeric membranes (as listed in **Table 1**). Nevertheless, the membrane fouling and low mechanical strength in polymeric membranes are recognized as the most relevant issue in limiting their application. The development and manufacture of membranes with high selectivity, permeability, rejection, and superior antifouling properties are the biggest challenges among scientists who work on membrane development and separation processes. Despite these drawbacks, the membranes have shown interesting results during the removal of heavy metal ions. For example, Uddin et al. (2007) analyzed the removal capacity of two commercial NF polyamide membranes (NF90 and NF200) towards As (III) and As (V). The effect of the operating conditions on the rejection performance was investigated in the study. As set by authors, the feed stream contained mainly in tap water together with arsenate and arsenite. In all tests, As (V) was generally rejected better than As (III), and the membranes offered the high removals over 98% and 65% for As (V) and As (III), respectively.

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

More recently, using a different membrane process, i.e. membrane distillation (MD), it has been demonstrated its ability to effectively separate specific heavy metal ions. For example, direct contact MD (DCMD) technology can be feasible in removing up to 99.95% arsenic molecules, like As (III) and As (V), from a contaminated water model solution. Interestingly, this process was operated for 250 h containing 500 μg L^{-1}, the process did not evidence any change in the permeate fluxes and As content (Pal and Manna, 2010). Similarly, Manna and Pal (2016) used a similar DCMD unit, but in this case possessing a hydrophobic flat sheet membrane (nominal pore size 0.13 μm, thickness 150 μm, porosity 70–75%). As a result, the systems proved an As removal of about 100% from contaminated groundwater, and no flux decline was recorded during 4 days of operation.

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

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

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

The enhancement of such properties has been recently breakthrough by using nanotechnology, which has been extended in a wide range of applications into membrane-based technologies, e.g. to enhance the membranes' efficiency for the removal of heavy metals, which is a relevant matter within water treatment (Ursino et al., 2018). Nanocomposite membranes are recognized as *"the next generation of membranes"*. In theory, a typical nanocomposite membrane includes the dispersion or deposition of nanosized filling materials into polymer matrices (Castro-Muñoz et al., 2018d; Castro-Muñoz et al., 2018e; Song et al., 2012). This concept of membranes can be implemented in different membrane-based separations, including gas–gas, liquid–liquid, and liquid–solid separation. In the early 1990s, nanocomposite membranes were initially developed for membrane gas separation processes (Ahmadizadegan et al., 2018; Robeson, 1991), where selective zeolites were embedded into polymers to improve both permeability and selectivity (Li et al., 2017). Due to such success on gas separation approaches, nanocomposite membranes were then initiated to be explored in other fields of applications and processes, such as sensor applications (Jiang et al., 2004; Pandey et al., 2018), direct methanol fuel cells (Chen et al., 2006), lithium-ion battery (Li et al., 2008), proton exchange membrane fuel cells (Boaretti et al., 2017; Jalani et al., 2005), pervaporation (PV) (Castro-Muñoz et al., 2018e; Yang et al., 2009), organic solvent nanofiltration (Sorribas et al., 2013), water treatment, to mention just a few.

Nanocomposite membranes, also known as mixed matrix membranes (MMM), are not only tailored by embedding nanosized materials into a continuous matrix phase, nanoparticles or fillers can also be coated onto the membrane surface, which is actually well denoted as a nanocomposite membrane. Currently, the preparation and implementation of these membranes are a current trend in the nanotechnological field for water treatment, especially in the separation of metal ions (Marino et al., 2017). Importantly, such nanosized filling materials not only possess exceptional features that may be provided to the primary element (e.g. polymer) but also good compatibility when embedded. Nanocomposite membranes have concurrently revealed low-fouling issues when embedding the inorganic materials (Kim and Bruggen, 2010), together with improved permeability and selectivity, compared with polymeric membranes (Madaeni et al., 2015). To date, plenty of nanosized fillers have been utilized in the preparation of nanocomposite membranes, such as titanium dioxide (TiO_2) (Zhang et al., 2013), silver (Ag) (Prince et al., 2014), carbon nanotubes (CNTs) (Celik et al., 2011), zinc oxide (ZnO) (Balta et al., 2012), copper oxide (CuO) (García et al., 2017), graphene-based materials (e.g. graphene, grahene oxide or reduced graphene oxide) (Gontarek et al., 2019; Kashyap, Pratihar and Behera, 2016; Xia and Ni, 2015), alumina (Al_2O_3) (Arsuaga et al., 2013), silica (SiO_2) (Yu et al., 2009), magnetite (Fe_3O_4) (Alam et al., 2016), cobalt (Co) (Gzara et al., 2016), zirconium dioxide (ZrO_2) (Maximous et al., 2010), clay (Mierzwa et al., 2013) and zeolites (e.g. NaX) (Fathizadeh et al., 2011), among others. For instance, **Table 2** summarizes recent studies in which such inorganic fillers have been filled among several polymers and then applied in different applications of water treatment, wastewater treatment, toxic and metal ions removal from water.

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

Specially, these nanocomposite membranes have shown valid insights during the removal of metal ions. For example, Bahadar et al. (2015) developed and tested ZnO-filled CA nanocomposite membranes for the separation of Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Al^{3+}, Sb^{3+}, and Sr^{3+}, concluding that these membranes were highly selective towards Fe^{2+}. Furthermore, the developed membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m^{-2} h^{-1} bar^{-1}. Some authors have tailored nanocomposite membranes based on functionalized multi-walled carbon nanotube (MWCNT)/polysulfone (Shah and Murthy, 2013), which also has demonstrated ability for heavy metal removal (up to 98%). In this study, the percent of rejection towards heavy metal was noted to increase by increasing the MWCNTs amount due to MWCNTs reduced the membranes' pore size, the best nanocomposite performances were about 94.2% and 78.2% removal for Cr(VI) and Cd(II), respectively. It is important to mention that pristine polymer offered only 10.2% and 9.9% removal, respectively. Here, the use of inorganic materials is showing remarkable enhancement of polymeric membranes towards heavy metal ions retention. Therefore, the research community is today putting big efforts into the development of novel nanocomposite membranes that may efficiently separate heavy metal ions from several aqueous streams. Herein, the following section provides the progress, latest developments and breakthroughs in the field.

4. Progress in nanocomposite membranes for heavy metal ions separation

To date, different categories of fillers and additives have been involved in the manufacture of nanocomposite membranes. Graphene oxide (GO) is likely one of the main materials that has been fully explored. GO has attracted the attention of the research community, especially for the separation of toxic ions and organic molecules in polluted water (An et al., 2016). GO has proven its excellent separation ability towards different molecules (e.g. water molecules) and ions. GO possesses interlayer nano-capillary networks that are formed thanks to their connected interlayer spaces, together with the gaps between edges of non-interlocked neighbouring GO sheets (An et al., 2016; He et al., 2015), facilitating the transport of molecules or ions through the GO membrane. At this point, multiple factors, including molecules' size or ions, the charge of ions, and numerous interactions (such as electrostatic interaction, metal coordination, and cation−π interaction between ions and GO sheets) strictly influence the separation performance of the GO. These properties make to consider GO as a promising candidate material within the removal of pharmaceutical traces from water and wastewater (Sophia et al., 2016). More interestingly, the embedding of GO can also bring some benefits to the properties of the polymeric membranes, e.g. thanks to the high hydrophilicity of GO, the change of the hydrophobic to hydrophilic nature of polymeric membranes has been done, resulting in enhanced permeation fluxes (Xia et al., 2015). As an example, Chang et al. (2014) analyzed the synergistic effect of GO and PVP on the performance of PVDF UF membranes. The study found out that the membrane's hydrophilicity and anti-fouling properties were enhanced by the addition of both GO and PVP. The authors concluded that this enhancement could be associated with the possible formation of hydrogen bonds between PVP and GO. Recognizing the multiple benefits that GO has given to polymeric membranes, researchers have initiated the improvement of the structural features of GO, e.g. the chemical modification has been an alternative in the field. According to researchers' insights, the chemical modification (to a positive charge) of GO is suggested for better metal ions removal efficiency (Yu Zhang et al., 2015). In this sense, Xu et al. (2014) performed the chemical functionalization of graphene oxide (f-GO) through a simple covalent functionalization with 3-aminopropyltriethoxysilane (APTS). The resulting organosilane-GO was then filled in PVDF UF membranes (Xu et al., 2014), the PVDF/ f-GO membranes had higher hydrophilicity, water flux, and protein rejection than pristine PVDF membranes and conventional PVDF/GO membranes. For instance, the membranes, containing 1wt.% f-GO, released a high permeate flux of about 401.3 L m^{-2} h^{-1}, a higher value compared to the one provided by the pristine PVDF (ca. 240 L m^{-2} h^{-1}) and PVDF/GO membranes, pointing out that these composite membranes also had better anti-fouling properties due to their higher hydrophilicity (Xu et al., 2014).

More recently, Zhang et al. (2017) carried out the cross-linking procedure in GO composite with isophorone diisocyanate (IPDI), later coated on PVDF membrane. Basically, the cross-linking methodology helped to improve the removal of dyes (over 96%) and heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}) (between 40-70 %) in the MF membrane compared to the pattern GO-PVDF membrane. It is worth mentioning that these composite membranes also showed high permeation rates between 80-100 L m^{-2} h^{-1} bar $^{-1}$ under low external pressure (i.e. 1.0 bar). By embedding modified magnetic GO (MMGO), it was also eventuated a significant increase in the pure water flux due to changes in surface roughness and hydrophilicity of PES NF membranes. Regarding the copper and dye removal ability of the membranes remarkably increased thanks to the presence of hydrophilic functional groups on the surface of MMGO hybrid. The prepared NF membrane, containing 0.5 wt.% MMGO hybrid, demonstrated the highest copper ions removal (ca. 92%) (Abdi et al., 2018). The authors also stated that these GO-filled NF membranes can also be good candidates in other types of water treatment applications, such as water softening, decolorization, natural organic matter removal (Wei et al., 2018).

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

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

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

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

metal ions removal.

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

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

Another example of surface functionalization of materials in nanocomposite membranes showing promising results on ion removal regards the polyether imide (PEI) nanofiltration membrane using a nanofiller additive, which consisted of L-cysteine modified glycidyl-polyhedral oligomeric silsesquioxane (POSS) (Bandehali et al., 2020). The PEI membrane filled with 1 wt.% of L-cysteine modified-POSS provided an outstanding separation efficiency towards Cr^{+2} and Na^{+} ions with a rejection percentage of 79% and 80%, respectively, which was attributed to the porous membrane morphology and the presence of negatively charged hydrophilic functional groups on the membrane surface, both features promoted the absorption of positively charged ions, as well as an increase of ion adsorption active spots (Bandehali et al., 2019). Moreover, L-cysteine functionalized POSS NPs incorporated into the PEI nanofiltration membrane led to a cross-linking reaction between the amino groups (NH_2) in L-cysteine modified-POSS filler and imide rings in PEI. This increased the membrane surface hydrophilicity due to the hydroxyl (–OH), carboxyl (–COOH) and amine ($–NH_2$) functional groups present in these materials, resulting in high water permeation fluxes of 95 L m^{-2} h^{-1} (in 1 wt.% of L-cysteine modified-POSS-PEI composite), from 17.63 L m^{-2} h^{-1} in neat PEI membrane. In addition to the exceptional performance, the modified filler also offered other benefits to the nanocomposite membranes, such as improved the antifouling properties to the resulting nanocomposite membranes by decreasing the roughness, a flux recovery ratio of 95%, increased degree of wetting, as well as an increment in the membrane surface smoothness, which all added up to the obtention of a better membrane structure for avoiding salt accumulation.

To date, the blending of inorganic phases into polymers has been also a smart alternative for the simultaneous removal of different types of heavy metal ions. At this point, the filling of multiple fillers is likely a feasible option for such a task. For instance, Suresh et al. (2018) tailored a hybrid nanocomposite membrane embedding carbon nanofibers and TiO_2 into PAN polymer, the generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards Pb^{2+}, Cu^{2+}, Cd^{2+} metal ions, respectively. Towards the efficient separation of Pb^{2+}, Suresh et al. (2018) explored and demonstrated that amino-functionalized metal-organic frameworks (MOFs) combined with a ceramic ultrafiltration membrane represent to be an effective material for the Pb^{2+} removal, which revealed at least 61.4% removal, whereas the best efficiency depended on the operating conditions, but it reached up to 100% (Yin et al., 2016). It is worth mentioning that the UF process also exhibited high flux ca. 1, 300 L m^{-2} h^{-1} (at 0.23 Mpa), which was stable during 120 min operating time.

Very recently, another kind of MOF-based nanocomposite has proven an unprecedented removal, ca. 100%, of multiple heavy metal ions from wastewaters. Yuan et al. (2019) developed a composite asymmetric membrane by coating Al_2O_3 with ZIF-300, as illustrated in **Figure 2**.

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

The success of Yuan's membranes was based on the impressive size-exclusion mechanism of ZIF-300. As reported by the authors, this water-stable MOF may possess an aperture size of pores around 7.9 Å, which represents a larger kinetic diameter than the one of water (H_2O, ~2.8 Å), but still smaller than the hydrated diameter of heavy metal ions (e.g. Cu^{2+}, Co^{2+}, Cd^{2+}, Al^{2+}). The membranes remarkably reached to remove completely such compounds (Yuan et al., 2019). Furthermore, the ZIF-300 membrane demonstrated a high permeation (water permeance of 39.2 L m^{-2} h^{-1} bar^{-1}) and rejection rate of 99.2% towards $CuSO_4$, together with stable performance. Towards the coating of different materials on organic or inorganic supports, Ibrahim et al. (2018) combined PSF and poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH) to remove over 91% for Pb^{2+} and 72% for Cd^{2+} ions. In fact, the authors concluded an impressive adsorption ability of such composite, which led to the UF process to be enough for the efficient removal of these heavy metal ions.

Among novel materials for UF, MF and NF filtration processes, ceramic materials are also promising tools for wastewater treatment due to their large specific surface area and convenient interior pore structure for filtration, catalysis and adsorption (Wu et al., 2019). Fe-based ceramic nanomaterials were used by Wu et al. (2019) for the fabrication of vacuum filtered membranes (VFMs) and polymer mixed e-spinning membranes (ESPMs), which were later assayed for Cd^{2+} ions removal from aqueous solutions. During the ceramic synthesis, a hydrothermal method was implemented for tailoring the Fe-based nanomaterials using FeOOH and μ-Fe_2O_3 nanowires as well as Fe_3O_4 NPs. Experimentally, VFMs showed a higher removal capacity than ESPMs; in contrast, ESPMs demonstrated to have better mechanical strength and stability. Particularly, VFM exhibited the highest Cd^{2+} adsorption capacity, ca. 29.3 mg g^{-1}, owed to a larger surface area provided by NPs in the membrane and a plenty internal pore structure, however, this resulted in drawbacks in terms of structural reliability shown by looseness and micro-cracks after the third filtration process, therefore, further studies aimed to improve mechanical strength properties should be conducted. On the other hand, nanoparticles doped ESPM after the fourth filtration maintained the original structure without fractures thanks to the better ductility properties and magnetic cores inside the nanofiber. According to the authors, chemical sorption, consisting of electron exchange between membranes and ions, was suggested to be the rate-controlling mechanism for Cd^{2+} adsorption, but the Cd adsorption mechanism was also indicated to be a multi-step process involving an external membrane surface adsorption and intraparticle diffusion. As concluding remarks from this study, it was observed that the ESPMs adsorption capacity was definitely enhanced with the Fe_3O_4 NPs as membrane precursors, but Cd^{2+} removal capacity should be improved in further studies by possibly modifying the polymers on the membrane surface.

Within the last years of research on novel materials for improving nanocomposite fillers, particular attention has been given to mostly synthetic-based fillers, leaving aside green material-based ones, which are categorized in such a way due to their plant, animal, or natural origin. In this framework, Kamari and Shahbazi (2020) initiated and innovated the preparation of green nanofillers made from Fe_3O_4 magnetic NPs coated with rice husk extracted silica (SiO_2) functionalized with 3–Aminopropyl trimethoxy silane. The obtained Fe_3O_4@SiO_2-NH_2 nanofiller was then embedded into the matrix of a PES NF membrane, and subsequently tested the removal of Cd (II) and methyl red dye coming from industrial effluents. Results showed that the membrane presented an asymmetrical morphology and highly dense layer, assigned to the fact Fe_3O_4@SiO_2-NH_2 nanofiller acted as a pore causing agent, promoting porosity. It was also seen that greater concentration amounts (ca. 0.5 wt.%) of the nanofiller into the membrane demonstrated to increase the water diffusion due to its hydrophilic functional groups (such as amine) present on the surface. The membrane filled with 0.5wt.% Fe_3O_4@SiO_2-NH_2 yielded the best salt rejection performance, as well as the highest removal efficiencies of 93% and 97% for Cd (II) and methyl red dye, respectively. Cd (II) adsorption was also found to be enhanced by the presence of polar primary amine NH_2 functional groups on the surface, acting as active binding sites. While methyl red dye adsorption was associated with the electrostatic interactions and non–covalent bonds given by the hydrophilicity nature of the green nanofiller. In addition to this, an excellent antifouling capacity was revealed by the novel membrane together with good reusability property for Cd removal, e.g. it demonstrated a 7% decrease in removal efficiency after the fifth Cd (II) filtration cycle. Long-term stability and anti-contamination properties for methyl red dye removal were also confirmed by the maintenance of a constant 97% filtration efficiency and a slight decrease in solution flux after a 40h filtration process. Hence, this pioneering study should be considered as a starting point within the implementation of green material-based nanofillers for filtration membranes since it has proven to be an innovative promising alternative for the removal of pollutants.

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

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

Recently, Dinh et al. (2020) tailored a chitosan-MnO_2 nanocomposite which was tested as an adsorbent to remove Cr(VI) from an aqueous solution. Thanks to its high Langmuir monolayer adsorption capacity of about 61.5 mg g^{-1}, this new material displayed high Cr removal (of about 94%) in the effluent from industrial zones. The authors claimed that electrostatic attraction was fundamental to the uptake of Cr onto the composite. Importantly, such composite was also evaluated during 5 cycles, showing a removal efficiency decrease up to 80%. Unlike Dinh's study, a core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C) exhibited a tremendous adsorption capacity (over 800 mg g^{-1} for Cr) and thus revealing an acceptable Cr (VI) removal efficiency of 80% (Zhou et al., 2020).

The adsorption capacity depends on the characteristics of elements forming the nanocomposite, their synergistic effect and their resulting properties, for example, Mahmoud et al. (2019) notified a higher adsorption capacity in SiO_2@VB9 nanocomposite for Pb (over 900 mg g^{-1}) than Cd (ca. 562 mg g^{-1}) and Cu (ca. 152 mg g^{-1}), such metal uptake capacities allowed to the resulting composite to show high removal efficiency ranged from 81 to 100% for all tested heavy metal ions. Dai et al. (2020) have very recently proved that the strategic selection of the elements proposed for the nanocomposite fabrication may result in a high-performance material, for instance, Dai et al. introduced Fe_3O_4/GO composite into graphitic carbon nitride g-C_3N_4, which provided an impressive U (VI) extraction capacity (up to 2880 mg g^{-1}) together with high removal efficiency (ca. 96 %). Due to its chemisorption properties, an EDTA modified magnetic iron oxide loaded with sawdust carbon (EDTA@Fe_3O_4/SC) composite has demonstrated a 98% Cd (II) removal capacity; according to the study, the Cd (II) removal efficiency increased as pH value and adsorbent dose increase. Moreover, this nanocomposite also presented good multi-metal ion uptake (over 80%) for Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI), and high adsorption efficiency (ca. 83%) after three cycles, proving an input of its reusability. At this point, most of the newly nanocomposite materials (presented in **Table 4**) release a satisfactorily good metal ion uptake ability being potential candidates for the fabrication of membranes towards water purification and disinfection (Castro-Muñoz, 2020b). However, the synthesis and preparation methodologies, as well as the resulting cost, implied in the fabrication protocols may represent a drawback during the further implementation of such materials in membranes. Even if the ongoing progress and innovation of new composite materials have been pointed out over this review, the economic feasibility related to the fabrication cost is a critical driver for their establishment and implementation. Unfortunately, economic feasibility, which may represent a profitable and competitive business, is a fundamental factor for the investment of companies and suppliers (Urbancová, 2013; Skapa, 2012). Herein, scientists must also be focused on developing new materials and fabrication protocols considering fewer sources and less costly aimed at producing economically sustainable materials. In this context, there is today a new trend in utilizing green and bio-based materials for the development of economically viable feedstocks and products. Since different carbonaceous materials, such as GO, activated carbon and CNTs, have shown their potentiality as adsorbents for copper decontamination (Ren et al. 2013), it is likely that other potential materials, like biochar, may also be a promising candidate in the preparation of composites. It is worth mentioning that biochar is commonly manufactured by pyrolysis of biomass and plant-based derivatives. Therefore, the synthesis and usage of biochar represent an environmentally friendly way to produce low-cost adsorbents (Marousek et al., 2020ab), which have been recently involved in the fabrication of membranes for the selective separation of phosphate from phosphate-rich wastewaters (Mohammadi et al., 2020).

Most of the nanocomposite materials and membranes tend to display impressive metal ion uptake, and more importantly, some composites can concurrently remove more than one type of ion. However, to core the complete resource recovery (i.e. water), it is important to consider the synthesis of nanocomposite membranes which may offer the simultaneous removal of heavy metal ions and organic contaminants, e.g. Zhang et al. (2020) developed composite membranes filling polydopamine-coated ferric oxide (Fe_3O_4@PDA) in PES. In addition to the higher permeabilities of the composite membranes (e.g. over 2600 L/m^2 h bar corresponding to 20wt.% Fe_3O_4@PDA PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive removal of Pb^{2+} and catalytic degradation of methylene blue, e.g. acceptable Pb^{2+} removal efficiency (above 80%) together with high methylene blue degradation (above 90%). In this case of study, the authors strategically designed the composite to display a synergistic effect. For example, the phenolic hydroxy and amino groups on the surface of PDA were able to chelate the cations to promote the adsorption of heavy metal ions, while the electron transfer in the Fenton-like reaction was promoted due to the phenoquinone structure of the surface of the PDA, boosting the catalytic reaction. With a similar scope, Fan et al. (2019) documented the simultaneous and rapid removal of organic micropollutants (bisphenol) and metal ions (Pb^{2+}) 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.)

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

Throughout this review paper, it has been recognized the potential ability of polymeric membranes in separating various heavy metal ions, including Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Al^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cr^{4+}, among others. These membranes can exhibit a removal efficiency between 77-99%. However, by smartly introducing inorganic nanomaterials into polymer membranes, nanocomposite membranes have overcome the main drawbacks of polymeric membranes together with improved removal efficiencies up to 100%. This review has released a clear outlook on the benefits of implementing composite membranes for the separation and removal of a wide range of toxic and heavy metal ions, in which their elimination from water has been proposed attending the current worldwide necessity for clean water scarcity.

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

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

- 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 L m^{-2} 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

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

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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)

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	PVDF	(Liang et al.. 2012)
		Removal of copper ions		(Xia Zhang et al., 2014)
		Wastewater treatment		(Hong and He, 2012)
		Humic acid removal	PES	(Ahmad et al., 2016)
		Humic acid removal	PSF	(Chung et al., 2016)
		Water treatment		(Dipheko et al., 2017)
	UF	Pollutants removal	PES	(Li et al., 2015)
		Water treatment	PES-PVA	(Zhao et al., 2015)
		Wastewater treatment	PSF	(Pintilie et al., 2017)
		Bacterial removal from aqueous solutions		(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)
	NF	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)

GO		Humic acid removal	PVDF	(Ekambaram and Doraisamy, 2017)
		Humic acid removal		(Li et al., 2017)
	RO	Removal of bivalent ions (Ca^{2+}, $SO4^{2-}$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)
	UF	Water treatment	PSF	(Zhao et al., 2013)
		Water treatment	PVP-PVDF	(Chang et al., 2014)
		Water treatment	PVDF	(Wu et al., 2014)
		Natural organic matter removal		(Xia and Ni, 2015)
		Water treatment		(Zhao et al., 2013)
		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)
			PSF	
		Water purification	PES	(Rehan et al., 2016)
Ag-nanoparticles		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)
	NF			
	RO	Wastewater treatment	PA	(Ben-Sasson et al., 2014)
		Wastewater treatment	PA/PSF/	(Yang et al., 2016)
Ag-NO_3			PET	
		Bacterial removal from water	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_2SO_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	PA	(Ngo et al., 2016)
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_2SO_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), polyvinylidine 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).

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_2O_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)

Acronyms: functionalized multi-walled carbon nanotubes (f-MWCNTs), modified magnetic graphene oxide(MMGO), sulfonated multi-walled carbon nanotubes (s-MWCNTs), carbon nanofibers (CNFs), micellar enhanced ultrafiltration (MEUF), poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH), sulfonated polyethersulfone(s-PES),GO-based membranes via the intercalation of montmorillonite and ethylenediamine ((MMT-GO-EDA), C_3N_4-decorated carbon-fiber (CF-TiO_2-C_3N_4), membrane reactor (MR), graphene oxide-polydopamine-(β-cyclodextrin) (GPC), polyelectrolyte complex nanofiltration (PECN), functionalized MOFs-CUF (f- MOFs-CUF), grafting glycidyl methacrylate (GMA).

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

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_2H_5OH, 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** PO_4^{3-} 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_3O_4/GO (mGO) composite introduced into graphitic carbon nitride g-C_3N_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_3N_4 The solids of the mGO and g-C_3N_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)	Adsorption capacities: Pb^{2+} (153 mg g^{-1}) and Cd^{2+} (222 mg g^{-1}) Removal rates: Pb^{2+} (89.22%) and Cd^{2+}(94.28%)	Electrostatic attraction and physical adsorption	**pH effect** Optimal pH values: Pb^{2+} (pH= 6) and Cd^{2+} (pH=7) **SiO$_2$@TW dosage effect** High dose of SiO$_2$@TW enhanced adsorption sites, increasing removal capacity **Temperature effect** Elevated temperature was a catalyst for adsorption, due to chemical bond rupture that enhanced contact between metal ions and surface-active sites	Modified Stober method for SiO$_2$ NPs fabrication SiO$_2$@TW synthesis consisted of sonication, centrifugation and drying of SiO$_2$ - tea waste powder suspension	**Stirring** For 30 min at 25°C **Sonication** For 1h **Drying** For 3h at 80°C	5 cycles From the second round there was a considerable decrease in removal efficiency	(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 Aspergillus Niger (*An*) ((n-HFP + n-HFS) @An).	Simultaneous adsorption rates: As (III) (76.84%), Cd (II) (73.62 %) and Pb (II) (94.31%) Adsorption capacities: As (III) (162 mg g^{-1}), Cd (II) (205.83	Chemical adsorption for the three metals	No tests were performed	Co-precipitation method was used to fabricate n-HFP and n-HFS NPs Potato dextrose broth (PDB) medium containing dissolved n-HFP and n-HFS NPs as well as magnetically stirred *An* mycelium inoculate was cultured	**Magnetic stirring** At 1000 rpm for 6 h **Culturing** In PDB medium at 30°C, 170 rpm for 1-2 days	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 1st 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 1st run) and (67.1% at 5th run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe_3O_4), loaded with SC (sawdust carbon) (EDTA@Fe_3O_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_2SO_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 **Coexisting ions effect** Divalent ions (Ca^{2+} & Mg^{2+}) caused a decrease in Cr (II) removal efficiency			fifth cycle (57%)	
Silica (SiO_2) functionalized folic acid (VB9) (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}) Extraction rates: Cu (II) (94-100%), Pb (II) (100%) and Cd (II) (57- 81%)	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) **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**	Methodology consisting of microwave assistance for covalent immobilization of VB9 with chlorinated silica	**Stirring** 1 hour **Oven drying** At 60℃ **Microwaving** For 2min	No tests were performed	(Mahmoud et al., 2019)

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

Acronyms: *Aspergillus niger* (*An*), biochar (BC), calcium - alginate (CA), ethylenediaminetetraacetic (EDTA), nanoparticles (NPs), nano hydroxy ferric phosphate (n-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 acid (VB9), vermiculite (VE).

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

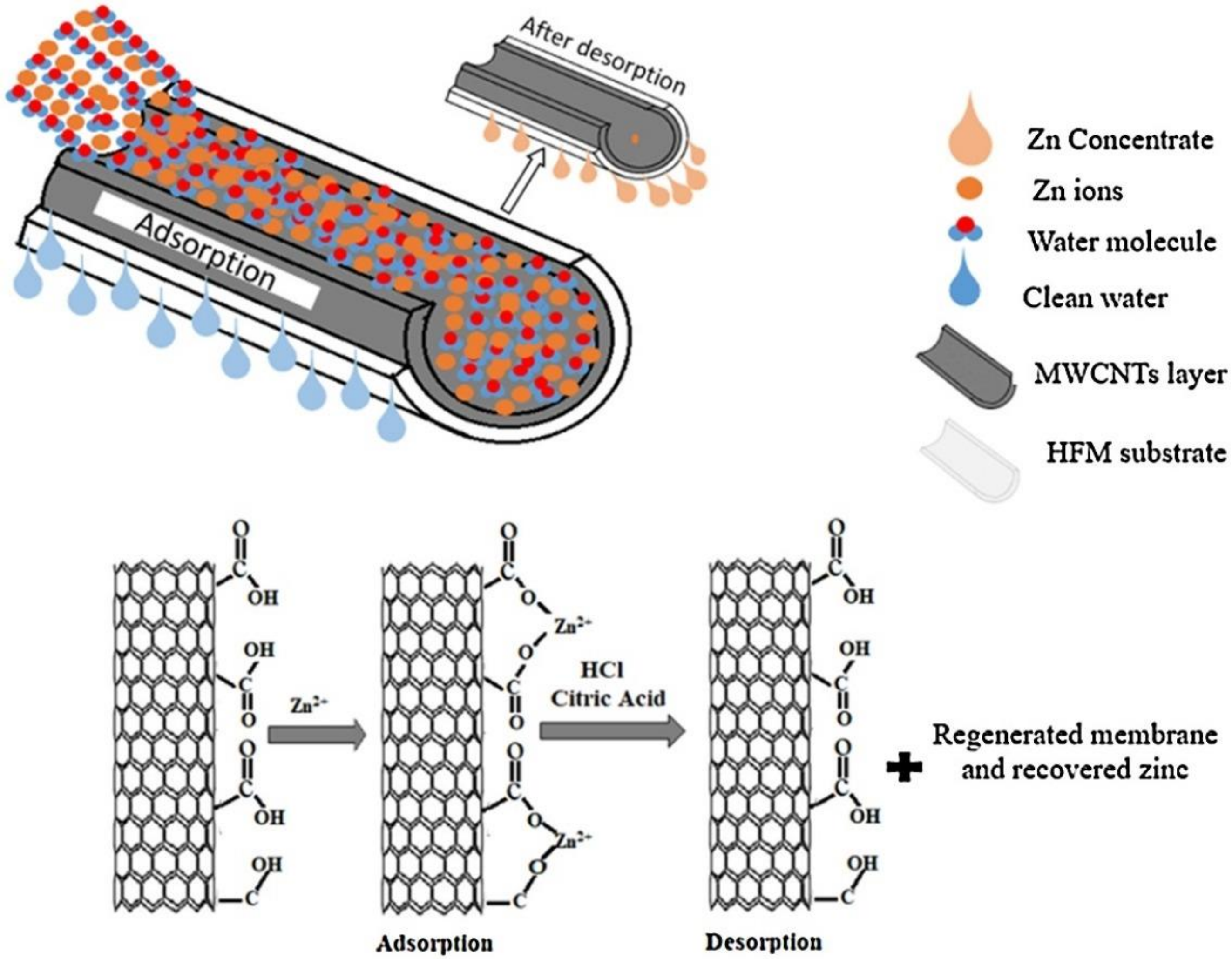
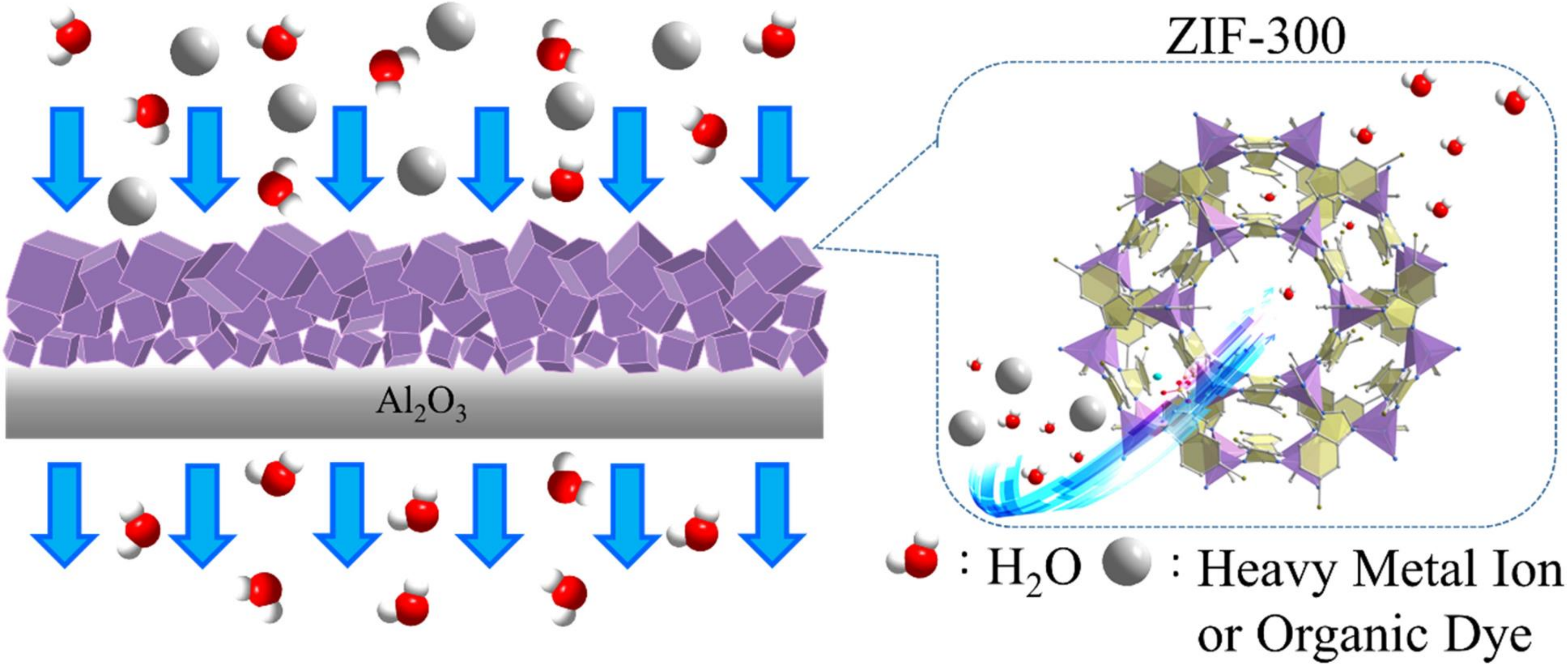


Figure 2. Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).



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 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.

Abbreviations:

Ag: silver

As: Arsenic

APTS: 3-Aminopropyltriethoxysilane

CA: Cellulose acetate
Cd: Cadmium
CNT: Carbon Nanotubes
Co: Cobalt
Cr: Chromium
Cu: copper
DCMD: Direct contact membrane distillation
ESPM: Polymer Mixed e-spinning Membranes
Fe: Iron
f-GO: functionalized Graphene Oxide
GO: Graphene Oxide
IPDI: Isophorone diisocyanate
MD: Membrane distillation
MF: Microfiltration
MMGO: Modified magnetic Graphene Oxide
MMM: Mixed Matrix Membranes
MOF: Metal-Organic Frameworks
MWCNT: Multi-walled carbon nanotubes
NF: Nanofiltration
Ni: Nickel
NPs: Nanoparticles
nZVI: nano– Zero Valent Iron
PAH: Poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated
PAN: Polyacrylonitrile

PBI: Polybenzimidazole

PES: Polyethersulfone

PMVEMA: Poly(methyl vinyl ether-alt-maleic acid)

POSS: Polyhedral Oligomeric Silsesquioxane

PSF: Polysulfone

PSS: Poly(sodium 4-styrenesulfonate)

PV: Pervaporation

PVA: Polyvinyl alcohol

PVP: Polyvinylpyrrolidone

PVDF: Polyvinylidine fluoride

RO: Reverse Osmosis

TCE: Trichloroethylene

UF: Ultrafiltration

VFM: Vacuum filtered nembranes

ZIF: Zeolite imidazolate framework

1. Introduction

The removal of pollutants (including metal ions) from water has been approached using several traditional treatments and protocols, such as chemical precipitation (Chabot et al., 2014), microbial decomposition (Yang et al., 2016), and physical adsorption (Kumar et al., 2013). Inherently, these pollutants represent strong issues to the environment (i.e. plants, animals, ecology climate) and humans. However, the removal of heavy metals through conventional protocols (such as flotation, chemical precipitation, ion exchange, adsorption, and electrochemical deposition) is still challenging, requiring further efforts to circumvent the production of a high amount of toxic sludge and liquid waste, long time consumption, and extreme use of supplies (e.g. solvents, resins, among others), together with poor separation efficiency.

Currently, according to the scarcity of drinking water and the increasingly serious water pollution (Marousek et al., 2019), water treatment with membrane-based processes has potentially attracted the attention of the research community. 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). To date, polymeric membranes are likely the most used membranes for water treatment applications (Castro-Muñoz et al., 2018a), including treatment of agro-food wastes (Castro-Muñoz et al., 2016), textile (Chao et al., 2016), petroleum industry streams (Alzahrani and Wahab, 2014), acid mine waters (Lopez et al., 2019), and seawater desalination (Castro-Muñoz, 2020a). Membranes are capable to separate the compounds from aqueous streams and thus reduce the contaminants contained in wastewater (Castro-Muñoz et al., 2018b). Extensive sources and a large number of molecules, as well as ions contained in polluted water, challenge the effective purification and separation of water by membranes. The membranes, based on their intrinsic properties, can be implemented among different types of membrane-based technologies including pressure-driven membrane processes, such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). These are potentially recognized as excellent candidates for the removal of large amounts of organic macropollutants; in which NF and RO membranes are among the barriers with the highest efficiency in withdrawing micropollutants (Castro-Muñoz et al., 2017). Other membrane technologies, e.g. membrane distillation (MD) (Criscuoli and Carnevale, 2015), membrane bioreactors (Santos and Judd, 2010), membrane contactors (Bey et al., 2010), have also been proven to remove specific heavy metal ions, such as arsenic (As), fluoride (F) and uranium (U). In particular, As is a natural tasteless and odorless element that may be highly toxic to humans exposed to it from air, food and water. It is known that this element exists in the earth's crust at average levels between 2000–5000 µg per kg (Figoli et al., 2010).

In this way, membranes have shown to be efficient in removing different metal ions (e.g. Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Al^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cr^{4+}) from water streams. A large number of studies has been now devoted to the manufacture of synthetic membranes for these particular separations, demonstrating compelling benefits, such as permeability, selectivity, enhanced chemical and physical properties within the removal of metal ions. When dealing with the removal efficiency of such membranes, the material properties, including chemical, physical, mechanical, play an important role in their efficiency, but also the membrane preparation protocols are crucial. In this context, several techniques have been used in membrane manufacture, such as stretching, track-etching, sintering, electrospinning, phase inversion (Lalia et al., 2013), and interfacial polymerization (Peydayesh et al., 2018), in which plenty of organic and inorganic materials have been proposed and used in tailoring membranes (Castro-Muñoz et al. 2020). Polymers have been the most used organic materials in membrane preparation, followed by the inorganic ones (e.g. ceramics, metals and glass) (Ulbricht, 2006). Polymer membranes tend to present great design flexibility, while the advantages of inorganic membranes, e.g. ceramic membranes, compared with polymeric ones comprise their higher thermal, mechanical and chemical stability (Castro-Muñoz et al. 2018c). Also, the hydrophilicity and the surface charge in ceramic membranes are higher. Ceramic membranes can also be operated under extreme conditions of pH, temperature and high oxidizing environment (Yong et al., 2013). As a current trend in the field of development of new membrane materials, the merging of both materials to produce nanocomposite membranes is also a promising tool for the efficient removal of heavy metals. However, there is a lack of reviewing the progress and latest nanocomposite membrane concepts and their role in water treatment and separation of heavy metals. Very recently, novel breakthroughs in tailoring nanocomposite materials have been released, such as nanoscale zerovalent iron impregnated biochar entrapped in calcium-alginate matrix (Wan et al., 2019), MnO_2/chitosan (Dinh et al., 2020), core-shell structured nanocomposite of zero-valent iron with carbon (Zhou et al. 2020), Fe_3O_4/GO composite introduced into graphitic carbon nitride g-C_3N_4 (Dai et al., 2020), to mention just a few of them. Thereby, this review paper aims at providing the ongoing progress of using different concepts of membranes (polymeric, composite and nanocomposite) and potential novel materials for removing heavy metals. Herein, a highlighted literature survey of using polymeric and nanocomposite membranes for heavy metal removal from water is provided. Ultimately, the current advances and future trends of nanocomposite membranes in the field are also given.

2. Metal ions removal using pristine polymeric and chemically modified polymeric membranes

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

Polymeric membranes are typically manufactured from natural or chemically-synthesized polymers. The membranes are creating a selective interface barrier between two adjacent phases (feed and permeate) which governates the transport behavior of species between them. In general, the separation performance of the membrane depends on the properties of transported species (e.g. molecule size, shape and chemical nature), as well as physicochemical properties (hydrophilicity/hydrophobicity, surface charge, roughness) of the polymer membrane, especially porous structure. For instance, **Table 1** enlists some of the reported studies in which the removal of heavy metal ions has been performed by means of different polymeric membranes and processes. It can be seen that the removal efficiency towards metal ions using polymer membranes has been reported between 77 to 99%.

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

For instance, Qdais and Moussa (2004) evaluated the separation performance of the RO and NF technologies using polyamide spiral wound membranes for the removal of copper (Cu) and cadmium (Cd) metals from industrial wastewater. While the RO process showed Cu and Cd removal efficiencies of about 98 and 99%, respectively, the NF process exhibited more than 90% of Cu ions. Interestingly, the membranes were able to concurrently treat wastewater containing more than one heavy metal ion. As an example, these membranes reduced the ion concentration from 500 ppm to 3 ppm, meaning a removal efficiency of over 99%. Another typical polymeric membrane material is polyethersulfone (PES), which has been successfully consolidated in membrane preparation owing to its high thermal and mechanical stability, physiological and chemical neutrality and wide range pH resistance. PES, however, tends to present a hydrophobic nature which results in high membrane fouling when applied for organic aqueous filtration. Thus, with the aim of improving its separation performance and properties, efforts have been proposed to shift the surface properties of this hydrophobic polymer. It is known that hydrophobic polymers are more prone to membrane fouling due to the particles contained in the feed bulk tend to accumulate on hydrophobic and rough surfaces, minimizing the interfacial tension between water and membrane (Pichardo-Romero et al., 2020). Therefore, the on-going strategies are aimed at mitigating the interaction between the foulants and the barrier layer. For example, an easy approach is to chemically modify the surface properties of the membrane by immersing it in a polyelectrolyte solution. It has been found that the polyelectrolyte adsorbed onto the membranes may significantly improve the membrane performance in terms of metal ions removal due to the presence of chelating functions in their structure. In this way, Mokhter et al. (2017) performed the chemical modification of PES membranes by polyelectrolyte multilayers, made of poly(allylamine hydrochloride) with poly(styrene sulfonate). The resulting membranes were employed to treat aqueous solutions containing single or mixed heavy metals, Cu^{2+}, zinc (Zn^{2+}) and nickel (Ni^{2+}), at various concentrations (50–1200 ppm). The tested membrane was efficient in separating all the tested metals either alone or mixed with high long-term stability and removal efficiencies over 90%. Similarly, polyacrylonitrile (PAN) membranes were modified by Qin et al. (2013), who synthesized positively charged membranes by depositing polyelectrolytes. Researchers used PAN membranes modified by the layer-by-layer assembly of polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS), to successfully separate Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} aqueous solutions, achieving removal efficiencies in the range of 95–98%. Particularly, the NF tests showed that the removal efficiency of Ni^{2+} and Cd^{2+} ions increased with the number of bilayers, but a decrease in permeate fluxes was observed. The usage of additional polymeric layers could also be applicable in the case of hollow fiber membranes. The great benefit of multi-layer materials lies in the fact that a relatively cheap material could be used as a support while a high-performance material (commonly a more expensive material) can be used as the selective layer. For instance, Zhu et al. (2014) tailored a high-performance dual-layer NF hollow fiber membrane and tested for the removal of Cd^{2+}, $Cr_2O_7^{2-}$ and Pb^{2+} salts from model wastewater, attaining removal efficiencies above 95%. Herein, researchers applied polybenzimidazole (PBI) as the outer selective layer while the blend of PES and polyvinylpyrrolidone (PVP) was implemented as the support layer. Thanks to the unique charge characteristics and high chemical resistance of PBI, the novel developed dual-layer NF membrane demonstrated a great salt rejection value due to the Donnan exclusion effect enhancement and low adsorption of heavy metal ions on the PBI surface.

Polyvinylidene fluoride (PVDF) is definitely another hydrophobic polymer that remains popular in a wide number of water treatment applications (Gontarek et al., 2019; Xia & Ni, 2015). PVDF membranes are well recognized for their multiple advantages including high chemical tolerance, good mechanical and thermal properties. Tzanetakis et al. (2003) have proved that the performance of chemically sulfonated PVDF membrane in the electrodialysis process can be comparable with the one given by a perfluorosulfonic Nafion 117 commercial membrane. The sulfonated PVDF membrane has displayed removal efficiencies towards Co and Ni ions of about 90% and 69%, respectively. In addition to this, a meaningful enhancement of the amounts of transported metal ions was seen while using corrugated membranes, which resulted in an increase in membrane area of 60% compared with those using flat membranes. Wang et al. (2017) have developed the modification of PVDF membrane for post UF testing. In general, the results revealed that the interaction by blending of PVDF with 2-aminobenzothiazole conducted to the efficient removal of chromium (Cr) from the wastewater. As a disadvantage of such membrane preparation, the membranes showed a low permeate flux when compared with the typical UF membranes. Since a long time ago, it is documented that one of the simplest approaches to improve the water flux in hydrophobic polymeric membranes, like PVDF, is to mitigate the membrane fouling, which can be reached through hydrophilicity enhancement. For instance, Pereira et al. (2014) combined PVDF polymer matrix with polyaniline nanofibers, which was, in this case, proposed as a hydrophilic agent to fabricate enhanced hydrophilic membranes. The authors described that the resulting membranes exhibited better hydrophilicity and better membrane properties, as well as a relatively high rejection toward heavy metal ions, such as Pb^{2+} and Cd^{2+}, e.g. around 98.5% and 97.3%, respectively.

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

Taking into account the advantages and disadvantages of polymeric membranes, the popularity of their use and implementation for removing heavy metal ions is also attributed to their low manufacture costs and ease of modification. However, such polymeric membranes still lack different desired properties for membrane separation processes, including the ones that required high selectivity towards low solutes and species. To date, many works have been done at aiming the enhancement of the separation performance of the polymeric membranes (as listed in **Table 1**). Nevertheless, the membrane fouling and low mechanical strength in polymeric membranes are recognized as the most relevant issue in limiting their application. The development and manufacture of membranes with high selectivity, permeability, rejection, and superior antifouling properties are the biggest challenges among scientists who work on membrane development and separation processes. Despite these drawbacks, the membranes have shown interesting results during the removal of heavy metal ions. For example, Uddin et al. (2007) analyzed the removal capacity of two commercial NF polyamide membranes (NF90 and NF200) towards As (III) and As (V). The effect of the operating conditions on the rejection performance was investigated in the study. As set by authors, the feed stream contained mainly in tap water together with arsenate and arsenite. In all tests, As (V) was generally rejected better than As (III), and the membranes offered the high removals over 98% and 65% for As (V) and As (III), respectively.

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

More recently, using a different membrane process, i.e. membrane distillation (MD), it has been demonstrated its ability to effectively separate specific heavy metal ions. For example, direct contact MD (DCMD) technology can be feasible in removing up to 99.95% arsenic molecules, like As (III) and As (V), from a contaminated water model solution. Interestingly, this process was operated for 250 h containing 500 µg L^{-1}, the process did not evidence any change in the permeate fluxes and As content (Pal and Manna, 2010). Similarly, Manna and Pal (2016) used a similar DCMD unit, but in this case possessing a hydrophobic flat sheet membrane (nominal pore size 0.13 µm, thickness 150 µm, porosity 70–75%). As a result, the systems proved an As removal of about 100% from contaminated groundwater, and no flux decline was recorded during 4 days of operation.

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

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

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

The enhancement of such properties has been recently breakthrough by using nanotechnology, which has been extended in a wide range of applications into membrane-based technologies, e.g. to enhance the membranes’ efficiency for the removal of heavy metals, which is a relevant matter within water treatment (Ursino et al., 2018). Nanocomposite membranes are recognized as *"the next generation of membranes"*. In theory, a typical nanocomposite membrane includes the dispersion or deposition of nanosized filling materials into polymer matrices (Castro-Muñoz et al., 2018d; Castro-Muñoz et al., 2018e; Song et al., 2012). This concept of membranes can be implemented in different membrane-based separations, including gas–gas, liquid–liquid, and liquid–solid separation. In the early 1990s, nanocomposite membranes were initially developed for membrane gas separation processes (Ahmadizadegan et al., 2018; Robeson, 1991), where selective zeolites were embedded into polymers to improve both permeability and selectivity (Li et al., 2017). Due to such success on gas separation approaches, nanocomposite membranes were then initiated to be explored in other fields of applications and processes, such as sensor applications (Jiang et al., 2004; Pandey et al., 2018), direct methanol fuel cells (Chen et al., 2006), lithium-ion battery (Li et al., 2008), proton exchange membrane fuel cells (Boaretti et al., 2017; Jalani et al., 2005), pervaporation (PV) (Castro-Muñoz et al., 2018e; Yang et al., 2009), organic solvent nanofiltration (Sorribas et al., 2013), water treatment, to mention just a few.

Nanocomposite membranes, also known as mixed matrix membranes (MMM), are not only tailored by embedding nanosized materials into a continuous matrix phase, nanoparticles or fillers can also be coated onto the membrane surface, which is actually well denoted as a nanocomposite membrane. Currently, the preparation and implementation of these membranes are a current trend in the nanotechnological field for water treatment, especially in the separation of metal ions (Marino et al., 2017). Importantly, such nanosized filling materials not only possess exceptional features that may be provided to the primary element (e.g. polymer) but also good compatibility when embedded. Nanocomposite membranes have concurrently revealed low-fouling issues when embedding the inorganic materials (Kim and Bruggen, 2010), together with improved permeability and selectivity, compared with polymeric membranes (Madaeni et al., 2015). To date, plenty of nanosized fillers have been utilized in the preparation of nanocomposite membranes, such as titanium dioxide (TiO_2) (Zhang et al., 2013), silver (Ag) (Prince et al., 2014), carbon nanotubes (CNTs) (Celik et al., 2011), zinc oxide (ZnO) (Balta et al., 2012), copper oxide (CuO) (García et al., 2017), graphene-based materials (e.g. graphene, grahene oxide or reduced graphene oxide) (Gontarek et al., 2019; Kashyap, Pratihar and Behera, 2016; Xia and Ni, 2015), alumina (Al_2O_3) (Arsuaga et al., 2013), silica (SiO_2) (Yu et al., 2009), magnetite (Fe_3O_4) (Alam et al., 2016), cobalt (Co) (Gzara et al., 2016), zirconium dioxide (ZrO_2) (Maximous et al., 2010), clay (Mierzwa et al., 2013) and zeolites (e.g. NaX) (Fathizadeh et al., 2011), among others. For instance, **Table 2** summarizes recent studies in which such inorganic fillers have been filled among several polymers and then applied in different applications of water treatment, wastewater treatment, toxic and metal ions removal from water.

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

Specially, these nanocomposite membranes have shown valid insights during the removal of metal ions. For example, Bahadar et al. (2015) developed and tested ZnO-filled CA nanocomposite membranes for the separation of Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Al^{3+}, Sb^{3+}, and Sr^{3+}, concluding that these membranes were highly selective towards Fe^{2+}. Furthermore, the developed membranes displayed acceptable permeability ranged from 0.9 up to 6.6 L m^{-2} h^{-1} bar^{-1}. Some authors have tailored nanocomposite membranes based on functionalized multi-walled carbon nanotube (MWCNT)/polysulfone (Shah and Murthy, 2013), which also has demonstrated ability for heavy metal removal (up to 98%). In this study, the percent of rejection towards heavy metal was noted to increase by increasing the MWCNTs amount due to MWCNTs reduced the membranes' pore size, the best nanocomposite performances were about 94.2% and 78.2% removal for Cr(VI) and Cd(II), respectively. It is important to mention that pristine polymer offered only 10.2% and 9.9% removal, respectively. Here, the use of inorganic materials is showing remarkable enhancement of polymeric membranes towards heavy metal ions retention. Therefore, the research community is today putting big efforts into the development of novel nanocomposite membranes that may efficiently separate heavy metal ions from several aqueous streams. Herein, the following section provides the progress, latest developments and breakthroughs in the field.

4. Progress in nanocomposite membranes for heavy metal ions separation

To date, different categories of fillers and additives have been involved in the manufacture of nanocomposite membranes. Graphene oxide (GO) is likely one of the main materials that has been fully explored. GO has attracted the attention of the research community, especially for the separation of toxic ions and organic molecules in polluted water (An et al., 2016). GO has proven its excellent separation ability towards different molecules (e.g. water molecules) and ions. GO possesses interlayer nano-capillary networks that are formed thanks to their connected interlayer spaces, together with the gaps between edges of non-interlocked neighbouring GO sheets (An et al., 2016; He et al., 2015), facilitating the transport of molecules or ions through the GO membrane. At this point, multiple factors, including molecules' size or ions, the charge of ions, and numerous interactions (such as electrostatic interaction, metal coordination, and cation−π interaction between ions and GO sheets) strictly influence the separation performance of the GO. These properties make to consider GO as a promising candidate material within the removal of pharmaceutical traces from water and wastewater (Sophia et al., 2016). More interestingly, the embedding of GO can also bring some benefits to the properties of the polymeric membranes, e.g. thanks to the high hydrophilicity of GO, the change of the hydrophobic to hydrophilic nature of polymeric membranes has been done, resulting in enhanced permeation fluxes (Xia et al., 2015). As an example, Chang et al. (2014) analyzed the synergistic effect of GO and PVP on the performance of PVDF UF membranes. The study found out that the membrane's hydrophilicity and anti-fouling properties were enhanced by the addition of both GO and PVP. The authors concluded that this enhancement could be associated with the possible formation of hydrogen bonds between PVP and GO. Recognizing the multiple benefits that GO has given to polymeric membranes, researchers have initiated the improvement of the structural features of GO, e.g. the chemical modification has been an alternative in the field. According to researchers' insights, the chemical modification (to a positive charge) of GO is suggested for better metal ions removal efficiency (Yu Zhang et al., 2015). In this sense, Xu et al. (2014) performed the chemical functionalization of graphene oxide (f-GO) through a simple covalent functionalization with 3-aminopropyltriethoxysilane (APTS). The resulting organosilane-GO was then filled in PVDF UF membranes (Xu et al., 2014), the PVDF/ f-GO membranes had higher hydrophilicity, water flux, and protein rejection than pristine PVDF membranes and conventional PVDF/GO membranes. For instance, the membranes, containing 1wt.% f-GO, released a high permeate flux of about 401.3 L m^{-2} h^{-1}, a higher value compared to the one provided by the pristine PVDF (ca. 240 L m^{-2} h^{-1}) and PVDF/GO membranes, pointing out that these composite membranes also had better anti-fouling properties due to their higher hydrophilicity (Xu et al., 2014).

More recently, Zhang et al. (2017) carried out the cross-linking procedure in GO composite with isophorone diisocyanate (IPDI), later coated on PVDF membrane. Basically, the cross-linking methodology helped to improve the removal of dyes (over 96%) and heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}) (between 40-70 %) in the MF membrane compared to the pattern GO-PVDF membrane. It is worth mentioning that these composite membranes also showed high permeation rates between 80-100 L m^{-2} h^{-1} bar $^{-1}$ under low external pressure (i.e. 1.0 bar). By embedding modified magnetic GO (MMGO), it was also eventuated a significant increase in the pure water flux due to changes in surface roughness and hydrophilicity of PES NF membranes. Regarding the copper and dye removal ability of the membranes remarkably increased thanks to the presence of hydrophilic functional groups on the surface of MMGO hybrid. The prepared NF membrane, containing 0.5 wt.% MMGO hybrid, demonstrated the highest copper ions removal (ca. 92%) (Abdi et al., 2018). The authors also stated that these GO-filled NF membranes can also be good candidates in other types of water treatment applications, such as water softening, decolorization, natural organic matter removal (Wei et al., 2018).

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

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

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

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

metal ions removal.

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

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

Another example of surface functionalization of materials in nanocomposite membranes showing promising results on ion removal regards the polyether imide (PEI) nanofiltration membrane using a nanofiller additive, which consisted of L-cysteine modified glycidyl-polyhedral oligomeric silsesquioxane (POSS) (Bandehali et al., 2020). The PEI membrane filled with 1 wt.% of L-cysteine modified-POSS provided an outstanding separation efficiency towards Cr^{+2} and Na^{+} ions with a rejection percentage of 79% and 80%, respectively, which was attributed to the porous membrane morphology and the presence of negatively charged hydrophilic functional groups on the membrane surface, both features promoted the absorption of positively charged ions, as well as an increase of ion adsorption active spots (Bandehali et al., 2019). Moreover, L-cysteine functionalized POSS NPs incorporated into the PEI nanofiltration membrane led to a cross-linking reaction between the amino groups (NH_2) in L-cysteine modified-POSS filler and imide rings in PEI. This increased the membrane surface hydrophilicity due to the hydroxyl (–OH), carboxyl (–COOH) and amine ($–NH_2$) functional groups present in these materials, resulting in high water permeation fluxes of 95 L m^{-2} h^{-1} (in 1 wt.% of L-cysteine modified-POSS-PEI composite), from 17.63 L m^{-2} h^{-1} in neat PEI membrane. In addition to the exceptional performance, the modified filler also offered other benefits to the nanocomposite membranes, such as improved the antifouling properties to the resulting nanocomposite membranes by decreasing the roughness, a flux recovery ratio of 95%, increased degree of wetting, as well as an increment in the membrane surface smoothness, which all added up to the obtention of a better membrane structure for avoiding salt accumulation.

To date, the blending of inorganic phases into polymers has been also a smart alternative for the simultaneous removal of different types of heavy metal ions. At this point, the filling of multiple fillers is likely a feasible option for such a task. For instance, Suresh et al. (2018) tailored a hybrid nanocomposite membrane embedding carbon nanofibers and TiO_2 into PAN polymer, the generated hybrid membranes have proved rejection percentages of 87%, 73%, 66% towards Pb^{2+}, Cu^{2+}, Cd^{2+} metal ions, respectively. Towards the efficient separation of Pb^{2+}, Suresh et al. (2018) explored and demonstrated that amino-functionalized metal-organic frameworks (MOFs) combined with a ceramic ultrafiltration membrane represent to be an effective material for the Pb^{2+} removal, which revealed at least 61.4% removal, whereas the best efficiency depended on the operating conditions, but it reached up to 100% (Yin et al., 2016). It is worth mentioning that the UF process also exhibited high flux ca. 1, 300 L m^{-2} h^{-1} (at 0.23 Mpa), which was stable during 120 min operating time.

Very recently, another kind of MOF-based nanocomposite has proven an unprecedented removal, ca. 100%, of multiple heavy metal ions from wastewaters. Yuan et al. (2019) developed a composite asymmetric membrane by coating Al_2O_3 with ZIF-300, as illustrated in **Figure 2**.

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

The success of Yuan's membranes was based on the impressive size-exclusion mechanism of ZIF-300. As reported by the authors, this water-stable MOF may possess an aperture size of pores around 7.9 Å, which represents a larger kinetic diameter than the one of water (H_2O, ~2.8 Å), but still smaller than the hydrated diameter of heavy metal ions (e.g. Cu^{2+}, Co^{2+}, Cd^{2+}, Al^{2+}). The membranes remarkably reached to remove completely such compounds (Yuan et al., 2019). Furthermore, the ZIF-300 membrane demonstrated a high permeation (water permeance of 39.2 L m^{-2} h^{-1} bar^{-1}) and rejection rate of 99.2% towards $CuSO_4$, together with stable performance. Towards the coating of different materials on organic or inorganic supports, Ibrahim et al. (2018) combined PSF and poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH) to remove over 91% for Pb^{2+} and 72% for Cd^{2+} ions. In fact, the authors concluded an impressive adsorption ability of such composite, which led to the UF process to be enough for the efficient removal of these heavy metal ions.

Among novel materials for UF, MF and NF filtration processes, ceramic materials are also promising tools for wastewater treatment due to their large specific surface area and convenient interior pore structure for filtration, catalysis and adsorption (Wu et al., 2019). Fe-based ceramic nanomaterials were used by Wu et al. (2019) for the fabrication of vacuum filtered membranes (VFMs) and polymer mixed e-spinning membranes (ESPMs), which were later assayed for Cd^{2+} ions removal from aqueous solutions. During the ceramic synthesis, a hydrothermal method was implemented for tailoring the Fe-based nanomaterials using FeOOH and μ-Fe_2O_3 nanowires as well as Fe_3O_4 NPs. Experimentally, VFMs showed a higher removal capacity than ESPMs; in contrast, ESPMs demonstrated to have better mechanical strength and stability. Particularly, VFM exhibited the highest Cd^{2+} adsorption capacity, ca. 29.3 mg g^{-1}, owed to a larger surface area provided by NPs in the membrane and a plenty internal pore structure, however, this resulted in drawbacks in terms of structural reliability shown by looseness and micro-cracks after the third filtration process, therefore, further studies aimed to improve mechanical strength properties should be conducted. On the other hand, nanoparticles doped ESPM after the fourth filtration maintained the original structure without fractures thanks to the better ductility properties and magnetic cores inside the nanofiber. According to the authors, chemical sorption, consisting of electron exchange between membranes and ions, was suggested to be the rate-controlling mechanism for Cd^{2+} adsorption, but the Cd adsorption mechanism was also indicated to be a multi-step process involving an external membrane surface adsorption and intraparticle diffusion. As concluding remarks from this study, it was observed that the ESPMs adsorption capacity was definitely enhanced with the Fe_3O_4 NPs as membrane precursors, but Cd^{2+} removal capacity should be improved in further studies by possibly modifying the polymers on the membrane surface.

Within the last years of research on novel materials for improving nanocomposite fillers, particular attention has been given to mostly synthetic-based fillers, leaving aside green material-based ones, which are categorized in such a way due to their plant, animal, or natural origin. In this framework, Kamari and Shahbazi (2020) initiated and innovated the preparation of green nanofillers made from Fe_3O_4 magnetic NPs coated with rice husk extracted silica (SiO_2) functionalized with 3–Aminopropyl trimethoxy silane. The obtained $Fe_3O_4@SiO_2\text{-}NH_2$ nanofiller was then embedded into the matrix of a PES NF membrane, and subsequently tested the removal of Cd (II) and methyl red dye coming from industrial effluents. Results showed that the membrane presented an asymmetrical morphology and highly dense layer, assigned to the fact $Fe_3O_4@SiO_2\text{-}NH_2$ nanofiller acted as a pore causing agent, promoting porosity. It was also seen that greater concentration amounts (ca. 0.5 wt.%) of the nanofiller into the membrane demonstrated to increase the water diffusion due to its hydrophilic functional groups (such as amine) present on the surface. The membrane filled with 0.5wt.% $Fe_3O_4@SiO_2\text{-}NH_2$ yielded the best salt rejection performance, as well as the highest removal efficiencies of 93% and 97% for Cd (II) and methyl red dye, respectively. Cd (II) adsorption was also found to be enhanced by the presence of polar primary amine NH_2 functional groups on the surface, acting as active binding sites. While methyl red dye adsorption was associated with the electrostatic interactions and non–covalent bonds given by the hydrophilicity nature of the green nanofiller. In addition to this, an excellent antifouling capacity was revealed by the novel membrane together with good reusability property for Cd removal, e.g. it demonstrated a 7% decrease in removal efficiency after the fifth Cd (II) filtration cycle. Long-term stability and anti-contamination properties for methyl red dye removal were also confirmed by the maintenance of a constant 97% filtration efficiency and a slight decrease in solution flux after a 40h filtration process. Hence, this pioneering study should be considered as a starting point within the implementation of green material-based nanofillers for filtration membranes since it has proven to be an innovative promising alternative for the removal of pollutants.

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

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

Recently, Dinh et al. (2020) tailored a chitosan-MnO_2 nanocomposite which was tested as an adsorbent to remove Cr(VI) from an aqueous solution. Thanks to its high Langmuir monolayer adsorption capacity of about 61.5 mg g^{-1}, this new material displayed high Cr removal (of about 94%) in the effluent from industrial zones. The authors claimed that electrostatic attraction was fundamental to the uptake of Cr onto the composite. Importantly, such composite was also evaluated during 5 cycles, showing a removal efficiency decrease up to 80%. Unlike Dinh's study, a core-shell structured nanocomposite of zero-valent iron with carbon (ZVI@C) exhibited a tremendous adsorption capacity (over 800 mg g^{-1} for Cr) and thus revealing an acceptable Cr (VI) removal efficiency of 80% (Zhou et al., 2020).

The adsorption capacity depends on the characteristics of elements forming the nanocomposite, their synergistic effect and their resulting properties, for example, Mahmoud et al. (2019) notified a higher adsorption capacity in SiO_2@VB9 nanocomposite for Pb (over 900 mg g^{-1}) than Cd (ca. 562 mg g^{-1}) and Cu (ca. 152 mg g^{-1}), such metal uptake capacities allowed to the resulting composite to show high removal efficiency ranged from 81 to 100% for all tested heavy metal ions. Dai et al. (2020) have very recently proved that the strategic selection of the elements proposed for the nanocomposite fabrication may result in a high-performance material, for instance, Dai et al. introduced Fe_3O_4/GO composite into graphitic carbon nitride g-C_3N_4, which provided an impressive U (VI) extraction capacity (up to 2880 mg g^{-1}) together with high removal efficiency (ca. 96 %). Due to its chemisorption properties, an EDTA modified magnetic iron oxide loaded with sawdust carbon (EDTA@Fe_3O_4/SC) composite has demonstrated a 98% Cd (II) removal capacity; according to the study, the Cd (II) removal efficiency increased as pH value and adsorbent dose increase. Moreover, this nanocomposite also presented good multi-metal ion uptake (over 80%) for Zn (II), Cd (II), Cu (II), Pb (II), Ni (II), Co (II), As (III), U (VI), and high adsorption efficiency (ca. 83%) after three cycles, proving an input of its reusability. At this point, most of the newly nanocomposite materials (presented in **Table 4**) release a satisfactorily good metal ion uptake ability being potential candidates for the fabrication of membranes towards water purification and disinfection (Castro-Muñoz, 2020b). However, the synthesis and preparation methodologies, as well as the resulting cost, implied in the fabrication protocols may represent a drawback during the further implementation of such materials in membranes. Even if the ongoing progress and innovation of new composite materials have been pointed out over this review, the economic feasibility related to the fabrication cost is a critical driver for their establishment and implementation. Unfortunately, economic feasibility, which may represent a profitable and competitive business, is a fundamental factor for the investment of companies and suppliers (Urbancová, 2013; Skapa, 2012). Herein, scientists must also be focused on developing new materials and fabrication protocols considering fewer sources and less costly aimed at producing economically sustainable materials. In this context, there is today a new trend in utilizing green and bio-based materials for the development of economically viable feedstocks and products. Since different carbonaceous materials, such as GO, activated carbon and CNTs, have shown their potentiality as adsorbents for copper decontamination (Ren et al. 2013), it is likely that other potential materials, like biochar, may also be a promising candidate in the preparation of composites. It is worth mentioning that biochar is commonly manufactured by pyrolysis of biomass and plant-based derivatives. Therefore, the synthesis and usage of biochar represent an environmentally friendly way to produce low-cost adsorbents (Marousek et al., 2020ab), which have been recently involved in the fabrication of membranes for the selective separation of phosphate from phosphate-rich wastewaters (Mohammadi et al., 2020).

Most of the nanocomposite materials and membranes tend to display impressive metal ion uptake, and more importantly, some composites can concurrently remove more than one type of ion. However, to core the complete resource recovery (i.e. water), it is important to consider the synthesis of nanocomposite membranes which may offer the simultaneous removal of heavy metal ions and organic contaminants, e.g. Zhang et al. (2020) developed composite membranes filling polydopamine-coated ferric oxide (Fe_3O_4@PDA) in PES. In addition to the higher permeabilities of the composite membranes (e.g. over 2600 L/m^2 h bar corresponding to 20wt.% Fe_3O_4@PDA PES membrane) compared to the pristine PES, the composites achieved competitive adsorptive removal of Pb^{2+} and catalytic degradation of methylene blue, e.g. acceptable Pb^{2+} removal efficiency (above 80%) together with high methylene blue degradation (above 90%). In this case of study, the authors strategically designed the composite to display a synergistic effect. For example, the phenolic hydroxy and amino groups on the surface of PDA were able to chelate the cations to promote the adsorption of heavy metal ions, while the electron transfer in the Fenton-like reaction was promoted due to the phenoquinone structure of the surface of the PDA, boosting the catalytic reaction. With a similar scope, Fan et al. (2019) documented the simultaneous and rapid removal of organic micropollutants (bisphenol) and metal ions (Pb^{2+}) 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.)

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

Throughout this review paper, it has been recognized the potential ability of polymeric membranes in separating various heavy metal ions, including Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Al^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cr^{4+}, among others. These membranes can exhibit a removal efficiency between 77-99%. However, by smartly introducing inorganic nanomaterials into polymer membranes, nanocomposite membranes have overcome the main drawbacks of polymeric membranes together with improved removal efficiencies up to 100%. This review has released a clear outlook on the benefits of implementing composite membranes for the separation and removal of a wide range of toxic and heavy metal ions, in which their elimination from water has been proposed attending the current worldwide necessity for clean water scarcity.

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

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

- 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 L m^{-2} 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

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

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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)

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	PVDF	(Liang et al.. 2012)
		Removal of copper ions		(Xia Zhang et al., 2014)
		Wastewater treatment		(Hong and He, 2012)
		Humic acid removal	PES	(Ahmad et al., 2016)
		Humic acid removal	PSF	(Chung et al., 2016)
		Water treatment		(Dipheko et al., 2017)
	UF	Pollutants removal	PES	(Li et al., 2015)
		Water treatment	PES-PVA	(Zhao et al., 2015)
		Wastewater treatment	PSF	(Pintilie et al., 2017)
		Bacterial removal from aqueous solutions		(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)
	NF	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)

GO		Humic acid removal	PVDF	(Ekambaram and Doraisamy, 2017)
		Humic acid removal		(Li et al., 2017)
	RO	Removal of bivalent ions (Ca^{2+}, $SO4^{2-}$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)
	UF	Water treatment	PSF	(Zhao et al., 2013)
		Water treatment	PVP-PVDF	(Chang et al., 2014)
		Water treatment		(Wu et al., 2014)
		Natural organic matter removal		(Xia and Ni, 2015)
		Water treatment		(Zhao et al., 2013)
			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)
			PSF	
		Water purification	PES	(Rehan et al., 2016)
Ag-nanoparticles		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)
	NF			
	RO	Wastewater treatment	PA	(Ben-Sasson et al., 2014)
		Wastewater treatment	PA/PSF/	(Yang et al., 2016)
Ag-NO_3			PET	
		Bacterial removal from water	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_2SO_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	UF	Wastewater treatment	PES	(Akar et al., 2013)
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_2SO_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), polyvinylidine 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).

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_3N_4	MR	Cr (VI) ions removal (88.0%)	(Shen et al., 2018)
Composite -CA	RO	Pb (Pb^{2+}) ions removal (100%)	(Thaçi and Gashi, 2019)
		Cd (Cd^{2+}) ions removal (100%)	
		Ni (Ni^{2+}) ions removal (100%)	
		Zn (Zn^{2+}) ions removal (100%)	

		Mn (Mn^{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_2O_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)

Acronyms: functionalized multi-walled carbon nanotubes (f-MWCNTs), modified magnetic graphene oxide(MMGO), sulfonated multi-walled carbon nanotubes (s-MWCNTs), carbon nanofibers (CNFs), micellar enhanced ultrafiltration (MEUF), poly[styrene-alt-(N-4-benzoylglycine-maleamic acid)] cumene terminated (PAH), sulfonated polyethersulfone(s-PES),GO-based membranes via the intercalation of montmorillonite and ethylenediamine ((MMT-GO-EDA), C_3N_4-decorated carbon-fiber (CF-TiO_2-C_3N_4), membrane reactor (MR), graphene oxide-polydopamine-(β-cyclodextrin) (GPC), polyelectrolyte complex nanofiltration (PECN), functionalized MOFs-CUF (f- MOFs-CUF), grafting glycidyl methacrylate (GMA).

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

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_2H_5OH, 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** PO_4^{3-} 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_3O_4/GO (mGO) composite introduced into graphitic carbon nitride g-C_3N_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_3N_4 The solids of the mGO and g-C_3N_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)	Adsorption capacities: Pb^{2+} (153 mg g^{-1}) and Cd^{2+} (222 mg g^{-1}) Removal rates: Pb^{2+} (89.22%) and Cd^{2+} (94.28%)	Electrostatic attraction and physical adsorption	**pH effect** Optimal pH values: Pb^{2+} (pH= 6) and Cd^{2+} (pH=7) **SiO_2@TW dosage effect** High dose of SiO_2@TW enhanced adsorption sites, increasing removal capacity **Temperature effect** Elevated temperature was a catalyst for adsorption, due to chemical bond rupture that enhanced contact between metal ions and surface-active sites	Modified Stober method for SiO_2 NPs fabrication SiO_2@TW synthesis consisted of sonication, centrifugation and drying of SiO_2 - tea waste powder suspension	**Stirring** For 30 min at 25°C **Sonication** For 1h **Drying** For 3h at 80°C	5 cycles From the second round there was a considerable decrease in removal efficiency	(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 Aspergillus Niger (*An*) ((n-HFP + n-HFS) @An).	Simultaneous adsorption rates: As (III) (76.84%), Cd (II) (73.62 %) and Pb (II) (94.31%) Adsorption capacities: As (III) (162 mg g^{-1}), Cd (II) (205.83	Chemical adsorption for the three metals	No tests were performed	Co-precipitation method was used to fabricate n-HFP and n-HFS NPs Potato dextrose broth (PDB) medium containing dissolved n-HFP and n-HFS NPs as well as magnetically stirred *An* mycelium inoculate was cultured	**Magnetic stirring** At 1000 rpm for 6 h **Culturing** In PDB medium at 30°C, 170 rpm for 1-2 days	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 1st 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 1st run) and (67.1% at 5th run)	(Yu et al., 2018)
EDTA modified magnetic iron oxide NPs (Fe_3O_4), loaded with SC (sawdust carbon) (EDTA@Fe_3O_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_2SO_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 **Coexisting ions effect** Divalent ions (Ca^{2+} & Mg^{2+}) caused a decrease in Cr (II) removal efficiency			fifth cycle (57%)	
Silica (SiO_2) functionalized folic acid (VB9) (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}) Extraction rates: Cu (II) (94-100%), Pb (II) (100%) and Cd (II) (57- 81%)	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) **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**	Methodology consisting of microwave assistance for covalent immobilization of VB9 with chlorinated silica	**Stirring** 1 hour **Oven drying** At 60℃ **Microwaving** For 2min	No tests were performed	(Mahmoud et al., 2019)

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

Acronyms: *Aspergillus niger* (*An*), biochar (BC), calcium - alginate (CA), ethylenediaminetetraacetic (EDTA), nanoparticles (NPs), nano hydroxy ferric phosphate (n-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 acid (VB9), vermiculite (VE).

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

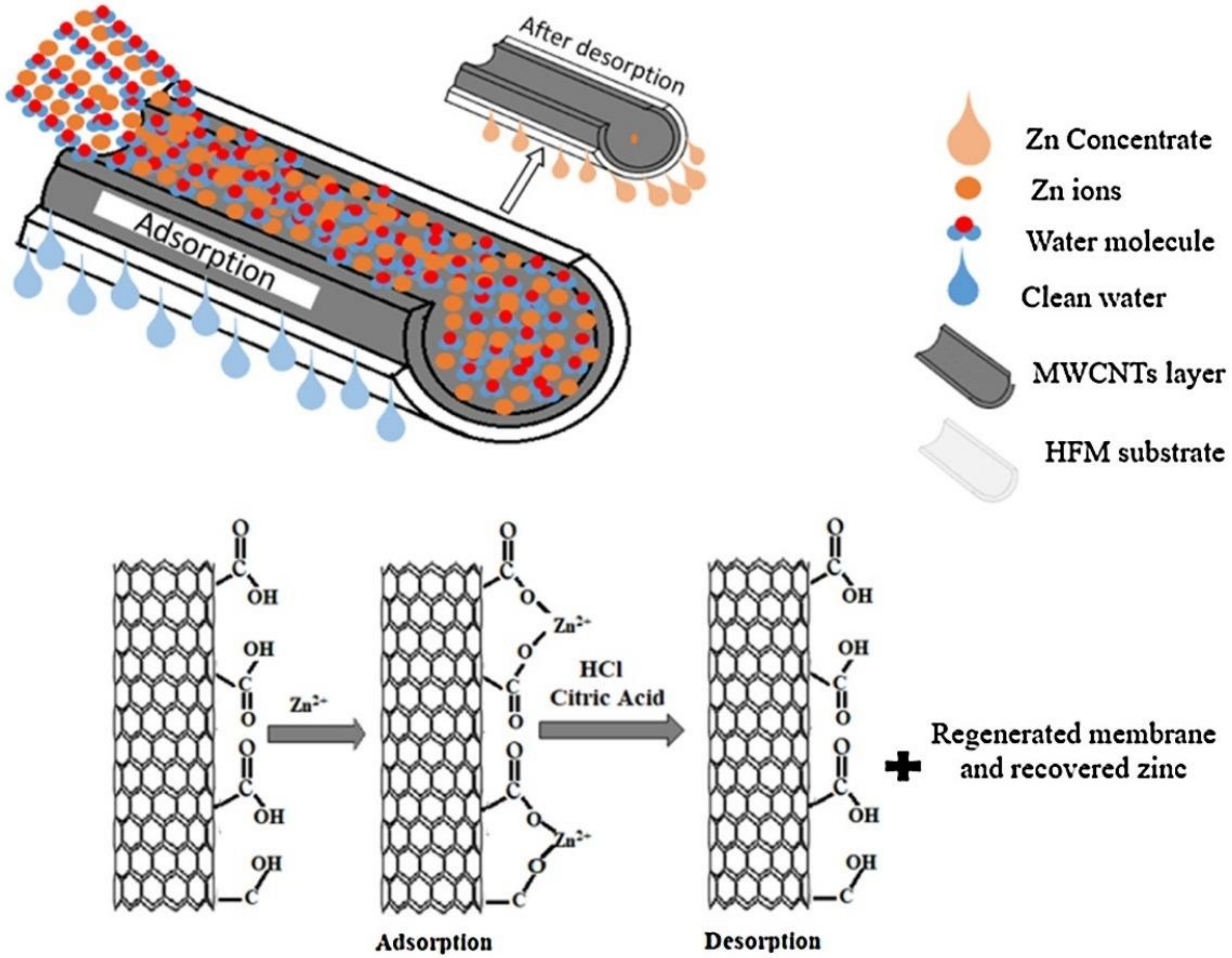
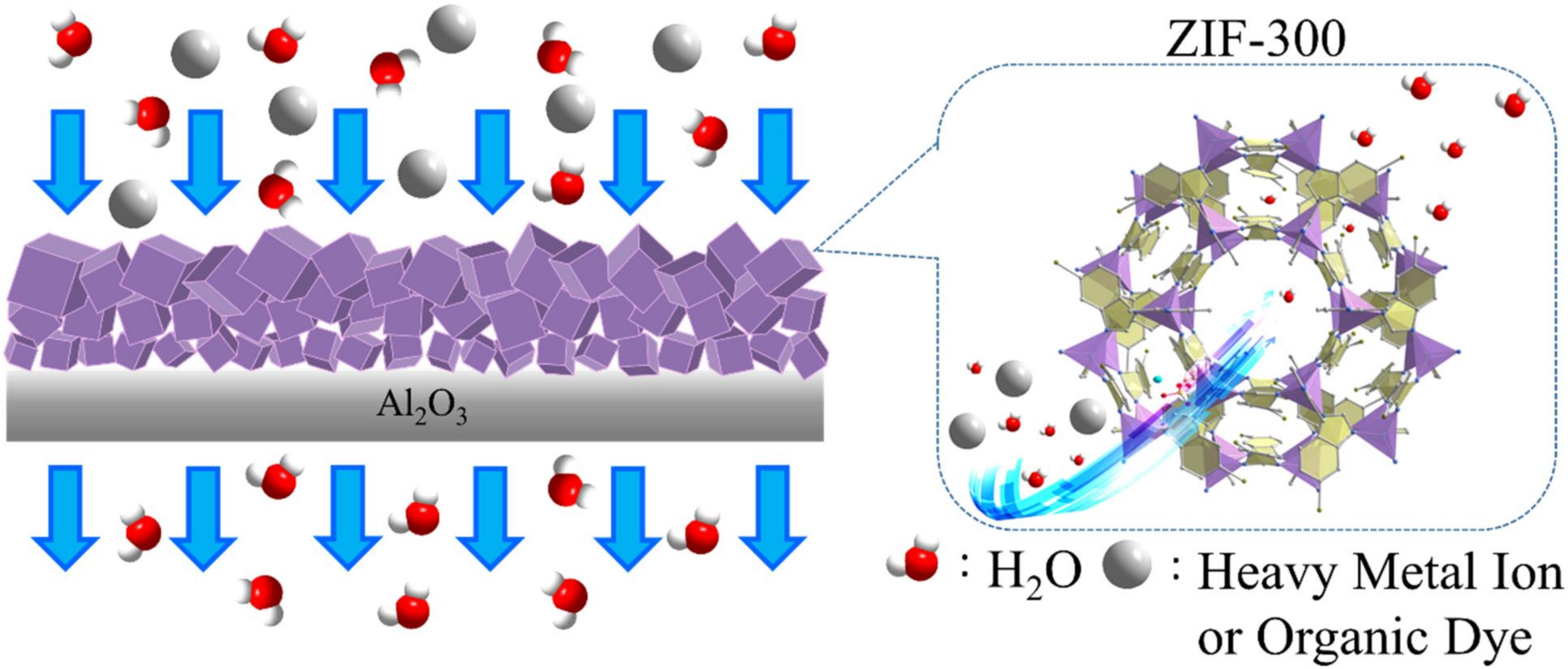


Figure 2. Graphical drawing of ZIF-300 deposited on alumina for metal ion removal and organic dye from water (Yuan et al., 2019).



CRediT authorship contribution statement

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

Conflict of Interest

The authors declare no conflict of interest.