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Review

A Way to Membrane-Based Environmental Remediation for Heavy Metal Removal

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Abstract: During the last century, industrialization has grown very fast and as a result heavy metals have contaminated many water sources. Due to their high toxicity, these pollutants are hazardous for humans, fish, and aquatic flora. Traditional techniques for their removal are adsorption, electro-dialysis, precipitation, and ion exchange, but they all present various drawbacks. Membrane technology represents an exciting alternative to the traditional ones characterized by high efficiency, low energy consumption and waste production, mild operating conditions, and easy scale-up. In this review, the attention has been focused on applying driven-pressure membrane processes for heavy metal removal, highlighting each of the positive and negative aspects. Advantages and disadvantages, and recent progress on the production of nanocomposite membranes and electrospun nanofiber membranes for the adsorption of heavy metal ions have also been reported and critically discussed. Finally, future prospective research activities and the key steps required to make their use effective on an industrial scale have been presented

Keywords: heavy metals; wastewater purification; membrane technology; ultrafiltration; nanofiltration; reverse osmosis; nanocomposite membranes; electrospun nanofiber membranes

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1. Introduction

The continuous growth of worldwide population and industrialization has determined an increase in environmental pollution [1,2]. The discharge of industrial waste effluents into the environment without adequate pretreatment is the main cause of pollution. Two types of pollutants exist: organic and inorganic. The primary organic pollutants are dyes, antibiotics, phenol compounds, herbicides, phthalate esters, and polycyclic aromatic hydrocarbons [3–5]. Inorganic contaminants include diverse toxic heavy metals as cadmium (Cd), chromium (Cr), arsenic (As), lead (Pb), and mercury (Hg) [6]. Their presence in the environment is extremely toxic and therefore dangerous for persons and the environment.

Industries producing paints, fertilizers, metal plating batteries, and electronic discharge a lot of amount of heavy metals in the environment [7]. They have hazardous effects on both humans because they are not metabolized [8] and fish and aquatic flora [9]. The United States Environmental Protection Agency has established the maximum permissible limit of metals for different heavy metal ions [10]. Table 1 reports the maximum contaminant level (MCL) for various heavy metals in the surface water and the health problem associated with them [11].

Table 1. Maximum contaminant level (MCL) for some heavy metals in surface waters and their Health Effects. Adapted with permission from ref. [11]. Copyright 2021 Elsevier.

Heavy Metal	MCL (mg/L)	Potential Health Effects from Long-Term Exposure above the MCL	Source of Contaminant
Cadmium	0.005	Kidney damage	Discharge from metal refineries; runoff from waste batteries and paints
Chromium	0.1	Headache, nausea, diarrhea, vomiting, carcinogenic to human	Discharge from steel mills; erosion of natural deposits
Lead	0.015	Babies and children: Delays in physical or mental development;Adults: Kidney problems; high pressure of blood	Corrosion of household plumbing systems; erosion of natural deposits
Mercury	0.002	Kidney disease	Discharge from refineries and factories; runoff from landfills and croplands
Nickel	0.20	Dermatitis, nausea, cough, Cancer	-
Arsenic	0.010	Risk of developing cancer	Erosion of the rocks; industries for manufacturing ceramic, pesticides, semiconductors

Conventional techniques for their removal are adsorption, electro-dialysis, precipitation, and ion exchange but most of these present different limitations as high operational and maintenance costs, high energy demand, and the production of sludge and harmful by products [12]. Therefore, in these last decades, intense research activity has been devoted to finding alternative processes for the treatment of wastewater. Membrane technology represents an exciting way to solve these environmental problems due to its reduced energy consumption and waste production, high efficiency and easy integration with traditional processes, and no chemical addition in the feed to treat [13,14]. Today, polymeric membranes are used in different separation processes for their easy manufacturing and high efficiency [15–18]. They suffer from different problems such as fouling, low chemical stability, and short lifetime [19]. Fouling is produced by the deposition of organic (colloids, polysaccharides, proteins, etc.) and inorganic constituents (e.g., salts) in the pores and on the surface of the membrane by determining both flux and the permeate quality reduction [20]. Inorganic membranes can be used when the polymeric ones cannot operate for their high chemical stability and so the possibility to operate in aggressive chemical environments and interesting permselective properties. They exhibit reduced fouling due to the low chemical interaction with the organic foulant particles. Nanofiltration and reverse osmosis permits higher rejection values than the other membrane processes for the removal of metal ions [21]. Other membrane processes as membrane contactors [22], membrane distillation [23], and membrane bioreactors [24] are also used for this aim.

In this review, the attention has been focused on using pressure-driven membrane processes for heavy metal removal from wastewater. Finally, the challenges and future perspective for improving their performance has been dealt with.

2. Polymeric Membranes for Heavy Metal Removal

Membrane technology represents an exciting alternative to the traditional separation processes for its low energy consumption, high efficiency, mild operating conditions, and easy scale-up [14,25]. For water and wastewater treatment are used membranes processes where the driving force is a pressure difference applied to the two membrane sides. These processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) and their differences are outlined in Table 2 [26].

Table 2. Pressure-driven membrane processes. Adapted from [26].

Membrane Process	Applied Pressure (bar)	Molecula Weight Cut-Off * (kDa)	Membrane Characteristics	Permeability (Lm^{-2} h^{-1} bar^{-1})	Species Removed
MF	1–3	>500	Porous; Asymmetric or symmetric	500	Suspended particles (bacteria, fat, oil, colloids, organics, microparticles)
UF	2–5	5–500	Microporous; Asymmetric	150	Macro and micromolecules (proteins, pigments, oils, sugar, organics, microplastics)
NF	5–15	0.1–5	Finely porous Asymmetric and thin-film composite	10–20	Divalent cations and anions, lactose, sucrose
RO	15–75	<100 Da	Non-porous Asymmetric and thin-film composite	5–10	Monovalent ions and all contaminants

* Molecular Weigh Cut Off (MWCO) = lowest molecular weight (in Daltons) at which greater than 90% of a solute is retained by the membrane.

2.1. Ultrafiltration Process

Polymeric membranes, prepared with natural and synthetic materials, are currently used for water desalination and wastewater treatment at a large scale owing to their easy manufacture, low cost, and stunning separation performance [27,28]. Generally, MF, UF, and NF serve as pretreatment steps before the reverse osmosis process. Membranes, used in MF and UF, are characterized by large pore size and so cannot remove the ions [29]. More promising seems to be the complexation-UF hybrid process, where a chelating agent (soluble in water) is added to the feed for complexing the metal ion [30]. The complex formation determines an increase of the ion molecular weight and so allows its removal (see Figure 1) [30]. When the complexing agents (CAs) (called to macroligands) are polymeric polyelectrolyte compounds, the process is called PEUF, if the CAs are micelles is called MEUF [31]. The molecular weight of the CAs is higher than the MWCO of the membrane. In this way, the metal ions are retained due to the formation of stable metallic ion-macroligand complexes [30]. However, the performance of the process depends on the operating conditions used as pH, the concentration of the CA, temperature, and CA-metal molar ratio [32,33]. In addition, the regeneration and reuse of the complexing agent are possible in specific operating condition (e.g., pH of the solution).

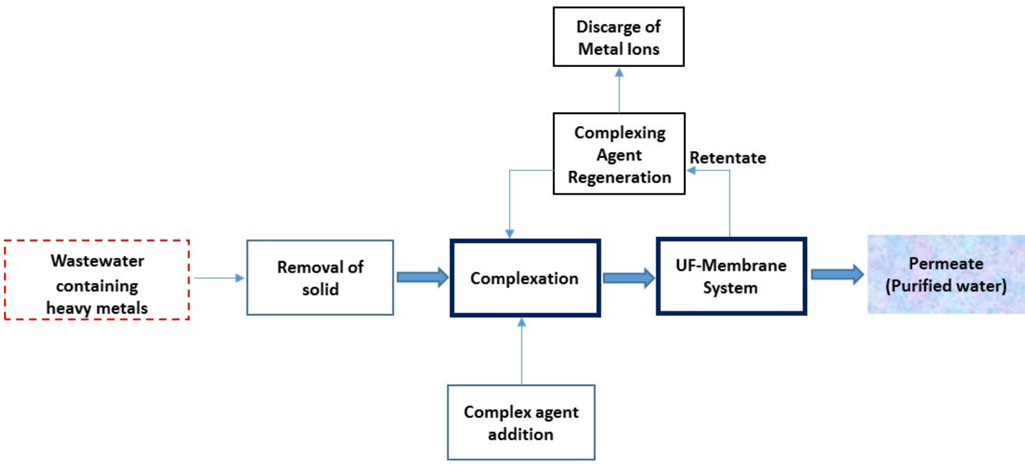

Figure 1. Scheme of the complexation-UF hybrid process, adapted from [33].

The performance of the complexation-UF hybrid process is due to various operating conditions as the concentration of the ligand, temperature, and pH have an essential role in the ion complex stability.

In 1999, Bodzek et al. [34] had used a commercial membrane (polycaprolactam (PA-6) produced by Tarnow, Poland) and polyacrylic acid as complexing agent for the removal of copper, nickel, and zinc in ionic form from synthetic wastewater. The removal of the ions ranged from 86–96% as the polymer/metal ratio was varied from 10 to 25. In addition, an increase in the pH determined an increase of both permeate flux and removal efficiency. This behavior is explained by considering that the pH causes a decrease of the hydrogen ions, so the polymer easily forms the complex with the metal species. Subsequently, other researchers have also found an increase of the removal efficiency for the cadmium and lead ions with the pH, by using the poly(acrylic acid) as metal-ligand and carrying out the PEUF experiments at 50 °C for minimizing the concentration polarization [35].

Borbély and Nagy utilized different membranes and complexing agents for studying the influence of various parameters as membrane and complexing agent properties and pH of the metal solution [36]. The characteristics of the membranes and complexing agents are reported in Table 3.

Table 3. Characteristics of the membrane and complexing agents adapted with permission from ref. [35]. Copyright 2021 Elsevier.

Membrane Characteristics			
Type	**Material of Membrane**	**MWCO (KDa)**	**Manufacturer**
PES-10	Polyether sulphone	10	Alfa-Laval
PES-20	Polyether sulphone	20	AlfA-Laval
CAc-40	Cellulose acetate	40	Celgard
PES-100	Polyether sulphone	100	Celgard
Complexing Agent Characteristics			
Sign	**Material**	**Molecular Weight (g/mol)**	**Manufacturer**
PEI-25	Poly(ethylenimine)	25,000	Aldrich
PEI-70	Poly(ethylenimine)	70,000	
PAA	Poly(acrylic acid)	-	

The retention for the nickel ions obtained with the membranes and complexing agents described before has been summarized in Table 4.

Table 4. Ni retention (%) measure for different CA-membrane systems.

Membrane Characteristics			
Type	**PEI-25**	**PEI-70**	**PAA**
PES-10	92.9 97.8 *	98.2	31.5 78.1 *
PES-20	98.1	97.0	64.1
CAc-40	84.1 88.8 *	90.2 90.3 *	79.8
PES-100	72.6	89.3	62.1

* Membrane used in other tests.

The metal ion removal slightly decreased by increasing the cut-off. The ion removal is good utilizing PEI-25 or PEI-70 as bounding agents.

The removal of mercury has been studied by using a polyethersulfone membrane (MWCO of 10 kDa, supplied by Sepro Membranes Inc., Oceanside, CA, USA) and polyvinylamine as complexing age (polyvinylamine = PVAm with a molecular weight of 340,000 (provided by BASF Corporation, Ludwigshafen, Germany) [37]. A mercury removal as high as 99% has been obtained (high mercury concentration in the feed equal to (20 ppm) and with the 0.1 wt% of PVAm). The PVAm concentration did not affect the mercury rejection, while water flux has been reduced significantly at a higher PVAm amount. These results are due to the concentration polarization on the surface of the membranes [38]. The molecules of solute are adsorbed on the membrane surface. This causes an increase of the solute concentration higher on the membrane surface than the feed stream. Increasing the solute concentration on the membrane surface, a gel layer may be formed. The authors restored the membrane performance by chemical cleaning (using the dilute chloric acid solution). Usually, the fouling of the membrane is reduced using a physical or chemical cleaning or a combination of them [39]. In the first one, the foulant is removed by applying hydraulic (e.g., backflushing) or mechanical (e.g., (sponge ball and fluidized particle cleaning)) force. In the second one, chemical agents are used.

Most of the commercial water-soluble polymers are produced from petroleum-based raw materials and are not environmentally friendly. Today, the research activity is devoted to developing natural and low-cost polymers for reducing waste production and preventing environmental pollution. Considering these aspects, recently, Lam et al. studied the possibility of removing nickel from wastewater by using as CA two eco-friendly polymers: chitosan (molecular weight of 1.8×105 g mol^{-1}, Sigma-Aldrich, St. Louis, MO, USA) and carboxymethyl cellulose (CMC molecular weight of 9×105 g mol^{-1}, Sigma-Aldrich) and a polyamide membrane (Desal GK MWCO = 3.5 kDa, supplied by GE Water & Process Technologies (Trevose, PA, USA) [40]. Metal removal is enhanced by increasing the complexing agent content. The best results have been found by adding 1200 mol (2×10^{-2} mol L^{-1}) of polymer (CA = chitosan and carboxymethyl cellulose) per mol of nichel, and the ion removal obtained for both polymers was higher than 90%. The two polymers display awe-inspiring performance at neutral pH. In addition, at pHs lower than 3 carboxymethyl cellulose shows a weak ability to complex the metal, probably due to the protonation of the carboxyl groups present in its chemical structure. For this reason, chitosan exhibited better behavior than the other polymer [41]. The ultrafiltration process carried out on industrial discharge water revealed better performance by using chitosan, however, the competing effect of other ions caused a decrease of performance. Table 5 summarises the concentrations of some ions present in the industrial wastewater before and after the application of UF and CEUF [40].

Table 5. Concentration of some elements before and after the UF process (with and without the chitosan). Adapted with permission from ref. [40]. Copyright 2021 Elsevier.

	Ions					
	Ni	**Sr**	**Zn**	**Fe**	**Co**	**Mg**
Concentrations in effluent (mg/L)	0.20	0.26	0.72	0.59	1.52	3.46
Concentrations after UF (mg/L)	0.10	0.23	0.42	0.14	1.08	3.19
Concentrations after PEUF (mg/L)	0.06	0.22	0.28	0.09	0.76	9.27
Rejections after UF(%)	50	12	41	76	29	9
Rejections after PEUF (%)	60	24	64	87	45	29

Table 6 reports other results on heavy metal removal by using the UF coupled with the complexation process.

Table 6. Removal of heavy metal by using CEUF and MEUF processes.

Process	Membrane	MWCO * kDa	Complexing Agent	Metal Ion	Rejection (%)	References
PEUF **	Polysulfone	50	Polyethyleneimine	Cr	100	[40]
PEUF	Polyether sulfone	10	Carboxyl methylcellulose	Ni	99	[42]
PEUF	Polyether sulfone	10	Polyvinylamine	Pb	99	[43]
PEUF	Polyether sulfone	10	Poly (ammonium acrylate)	Cd	99	[44]

Table 6. *Cont.*

Process	Membrane	MWCO * kDa	Complexing Agent	Metal Ion	Rejection (%)	References
PEUF	Polyether sulfone	10	Polyvinylamine	Hg	>90	[45]
PEUF	Polyether sulfone	60	Polyethylenimine	Cu	94	[46]
MEUF °	-	10	Rhamnolipid	Ni	99.9	[47]
MEUF	Alumina	200	Sodium dodecyl sulfate	Ni	87	[48]
MEUF	Alumina	200	Sodium dodecyl sulfate	Co	88	[48]
MEUF	Cellulosa	10	Cetylpyridinium chloride	Cd	92	[49]
MEUF	Cellulosa	10	Cetylpyridinium chloride	Pb	92	[49]
MEUF	Cellulosa	3	Humic acid	Co	95	[50]
MEUF	Cellulosa	10	Humic acid	Co	90	[50]

* MWCO = Molecular Weigh Cut Off; ** PEUF = Polyelectrolyte-Enhanced Ultrafiltration; ° Micellar-Enhanced Ultrafiltration.

The results about the toxic metal removal show the potentialities of the complexation–ultrafiltration technology, but it is not used at an industrial scale. The disadvantages are different as the cost of the CAs, the membrane fouling, the chemical cleanings, and the possibility of loss of the complex stability when the shear rate exceeds the critical shear rate [51]. Considering this last aspect, Gao et al. [52] have studied the strength of the complex in the shear field by introducing a rotating disk in the membrane module (see Figure 2).

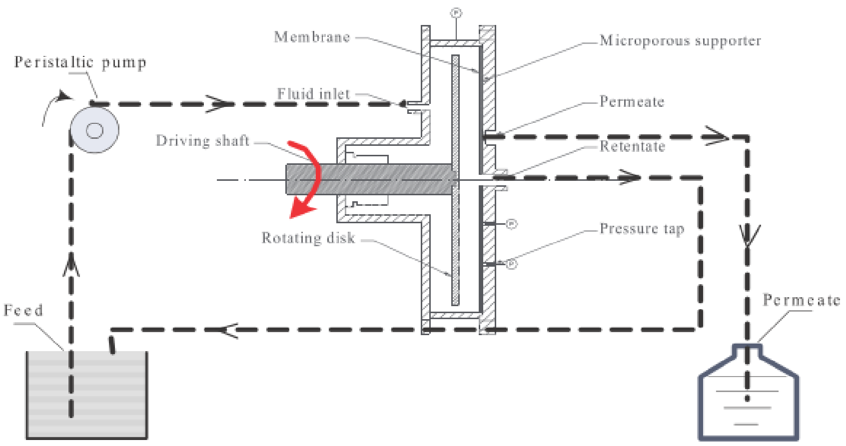

Figure 2. Scheme of the rotating disk enhancing Complex-ultrafiltration process. Adapted with permission from ref. [52]. Copyright 2021 Elsevier.

The disk turned at adjustable velocity, ranging from 0 to 3000 rpm, inducing the shear rate on the membrane. The authors had studied the nickel removal from wastewater by using the sodium poly-acrylate as CA and a PES membrane (MWCO = 10 kDa, SEPRO, La Roche-sur-Yon, France). A Ni^{2+} removal more than 98% has been achieved with a rotating disk speed lower than 848 rpm, pH = 7 and a CA/Ni = 13. In addition, the sodium poly-acrylate has been recovered by fixing the rotation of the rate at values higher than 848 rpm.

2.2. *Nanofiltration Process*

NF and RO processes are also used for removing heavy metals from wastewater. The main difference between NF and RO is the selectivity. NF is more selective with divalent ions (rejection value more than 95%), while with monovalent ones the rejection ranged from 20% to 80% [53]. The RO membranes remove all the ions, including the monovalent ones with very high removal efficiency; for example, the commercial RO membranes used for seawater desalination exhibit rejection values of 99.5–99.8% for the sodium chloride [54]. Recently, NF and RO thin film composite (TFC) membranes have gained much interest for the excellent salt rejection, high water flux, and interesting mechanical resistance [53]. In the TFC for RO, the active layer is made in aromatic polyamide (thick of around 50–200 nm) supported on a macroporous film in polysulfone (thickness 40 μm) and all supported by a non-woven layer (thickness 120 μm) [54]. NF membranes are charged for the dissociation of ionizable chemical groups. The charge is related to the pH of the solution [55]. The metal removal depends on a combination of a steric effect and electrostatic forces [56]. The first effect depends on the shape and size of the solute and pores of the membrane [57], and the electrostatic (repulsion or attraction) forces occur between the ion valance and the fixed charge of the membrane [56].

In 1999, Ahn et al. [58] used a commercial NF membrane (NTR-7250) for performing nickel removal from salt solutions containing $NiCl_2$ or $NiSO_4$. A Ni^{2+} removal of about 94% was found with the $NiSO_4$, while the removal decreased with the other salt (R = 85%). This behavior has been assigned to the higher negative valence of the nickel sulfate that has generated a higher electrostatic repulsion with the membrane negatively charged in certain operating conditions.

Wang et al. [59] have studied the removal of chromium and copper by using three different commercial NF membranes; their properties and ion removal efficiency are reported in Table 7.

Table 7. Characteristics of the NF commercial membranes, adapted with permission from ref. [59]. Copyright 2021 Elsevier.

NF Membranes	MWCO	Max Operating Temperature (°C)	pH Tolerance	Manufacturer	Cr Rejection (%)	Cu Rejection (%)
DL *	150–300	50	2–11	Osmonics	96.6	90
DK *					94.7	82
NTR-7450 °	200	40	2–14	Hydranautics	<70	<70

* DL and DK = NF commercial membranes are polymeric flat thin-film composite membranes in which a polyamide selective layer is supported on a polysulfone layer. ° NTR-7450 = NF commercial membrane in modified polyethersulfone.

The DL and DK membranes exhibited better performance than the NTR-7450 one. The different behavior exerted by the membranes is due to the the pH value of the feed (of about 3) and the isoelectric point of the DL and DK membranes (around 4.0). In these operating conditions, the membrane exhibited negative charges on the surface, and so the pair of ions Cr^{3+}/Cr^{6+} have been vigorously repulsed, showing higher positive charge than Cu^{2+}. Stability investigation results showed that DK membrane had better stability in the raw electroplating wastewater with pH 2.32 than DL membrane.

Murthy and coworkers had studied the effect of feed concentration (5–250 ppm), feed flowrate (5–15 L/min) and pH (2–8) on nickel ion removal [60]. The maximum rejection of nickel ions is 98% and 92% for 5 and 250 ppm feed concentration and using a TFC-NF-300 membrane (300 Da cut-off; the separation layer is in polyamide with a thickness of 5–20 μm; Permionics, Vadodara, India). This result is explained by the increase of the metal concentration in the feed solution that determined a screen formation by the cations close to the membrane surface [61]. This screen can neutralize the negative charge of the membrane. The total charge of the membrane decreases and so the repulsion between the membrane and the anions is reduced. As a result, the ions easily pass through the membrane. An increase in the feed flow rate has led to a rise of the rejection due to a concentration polar ionization reduction. In addition, no significant change of the rejection has been detected with the pH. On the contrary, the water permeability decreased with the increase of the pH. This last aspect was deeply explained by Freger et al. [62] by considering the shrinkage of the skin layer caused by the differences in the hydration of the ionized chemical groups of the membrane and counter-ions at the different pHs.

Figoli et al. [63] investigated the arsenic removal from model wastewater with commercial NF spiral-wound membrane modules and their characteristics are summarized in Table 8.

Table 8. Characteristics of the membrane modules. Adapted with permission from ref. [63]. Copyright 2021 Elsevier.

	Membrane Module	
	NF90–2540	**NF30F-2440**
MWCO (Da)	200	400
Membrane Material	Polyamide thin film composite membranes	Hydrophilized polyethersulfone
Maximum operating temperature (°C)	40	50
pH range	2–11	2–11
Maximun feed flow rate (m^3/h)	1.4	-
$MgSO_4$ rejction (%)	>97	-
NaCl rejction (%)	85–95	25–35
Manufacturer	Dow Chemical	Microdyn-Nadir
Operating conditions used during the experiments		
Trans-membrane pressure (bar)		2–12
pH		3.5–10
Temperature (°C)		15–40
As feed concentration (ppb)		100–1000

The performance of the process was strongly affected by the operating conditions (such as temperature, trans-membrane pressure, pH, and concentration of the feed) for both membranes. The authors found that As removal decreased with the temperature due to an increase of the diffusive transport of the ions through the membrane. The ion removal for the NF-90 membrane was higher than 97% and it was influenced by the As feed concentration, while it was in the range 74–79% for the N30F one. The As concentration in the permeate increased by releasing the As concentration and in the concentration range considered (100–1000 ppb).

The removal of arsenic decreased with the temperature for an increase of the diffusive transport of arsenic through the membrane. The ion removal for the NF-90 membrane was higher than 97%, and it was in the range of 74–79% for the N30F one. For the NF-90 membrane, the As(V) rejection increased from 94% to 98.4% in the pH range investigated (3.4–10). This membrane became more negatively charged with the increase of the pH, and so the charge exclusion effect has strongly affected the ion removal. The As concentration in the permeate of the NF-90 membrane has been found lower than the Bangladesh MCL in all the range of the investigated pH and lower than the EPA MCL at pH value equal 10.

In 2013, thin-film composite NF membranes with hollow-fiber configuration used to remove different heavy metals from electroplating wastewater [64]. Both permeate flux and rejection improved with an increase in operating pressure; the rejection values for Cr, Cu, and Ni ions were 95.76%, 95.33%, and 94.99% respectively. An increase of the temperature did not influence the rejection. Recently, Qi et al. have fabricated NF membranes by using 2-chloro-1-methyliodopyridine as an active agent to graft polyimide polymeric membrane surface via covalent bonding [65]. In this way, it is possible to reduce the number of carboxylic acid groups present on the membrane surface by introducing amine groups (formation of stable amide) and changing the charge ability. This last as aspect was evaluated by the zeta potential measurements [66]. In this work, the pristine and modified membranes exhibited an isoelectric point of 5.8 and 8.6, respectively. Therefore, the modified one exerted a greater repulsion of toxic cations for a better charge repulsion force. Other results about applying NF process in removing heavy metals from wastewater are reported in Table 9.

Table 9. NF membranes used for the removal of metal ions.

Membrane Material	MWCO (Da)	Ion Rejection (%)	References
CA/PMVEMA *	-	Cd^{2+} (72) Pb^{2+} (85)	[67]
PHMA **	300	Cd^{2+} (96) Pb^{2+} (98)	[68]
PA °/PEI •	-	Cu^{2+} (>90)	[69]
SPSf/PES °°	157	Ni^{2+} (>90) Zn^{2+} (>90) Cu^{2+} (>90)	[70]
PA °	-	Cd^{2+} (99)	[71]
CS ••	-	Cd^{2+} (96.3) Pb^{2+} (93)	[72]
CS/PVA/MMT •°	-	Cr^{6+} (88)	[73]

* CA = Cellulose acetate; PMVEMA = Poly (methyl vinyl ether-alt-maleic acid). ** PHMA = Poly(homopiperazine-amide). ° PA = polyamide; • PEI= Polyethylenimine; °° SPSf = sulfonated polysulfone; °° PES = polyethersulfone; •• CS = Chitosan; /•° PVA = polyvinyl alcohol; MMT = montmorillonite.

2.3. Reverse Osmosis Process

RO membranes possess dense thin selective layers with small free volume regions and are capable of rejecting almost all ions. For this reason, the RO process is one of the main technologies used in water treatment. However, membrane fouling determines a flux decrease and a reduced membrane life [74,75]; the feed pretreatments reduce the fouling [76]. The first works date back to the seventies. For example, Kremen and coworkers had demonstrated the possibility to purify wastewater from various metal ions with an integrated process containing RO and precipitation units [77]. Ujang and Anderson showed the possibility of removing Zn^{2+} and Cu^{2+} using a low-pressure RO process in the presence of a chelating agent (EDTA) [78]. They found that operating pressure, EDTA concentration, and temperature significantly influenced the permeate flux. Some years later, the NF and RO performance for copper (Cu^{2+}), and cadmium (Cd^{2+}) removal has been considered [79]. The experiments were performed with polyamide membranes characterized by a spiral wound configuration. The RO process reached a removal efficiency of almost 99% for both ions. On the other hand, in NF process, for cadmium ions the removal ranged from 82% to 97% for an initial feed concentration of 25 and 200 ppm. The Cd ion has been removed with slightly higher efficiency than the copper, probably due to its size larger than the other metal ion [79].

RO membranes are susceptible to fouling, and a possible way of reducing it is to perform the pretreatment of the fed utilizing MF and/or UF processes. The potentiality of UF-RO process for industrial wastewater treatment has been investigated by Petrinic et al. [80]. The UF process permitted to remove of almost 90% of suspended solids. The RO process, subsequently performed, removed the metal ions and organic/inorganic compounds with efficiency range of 91.3–99.8%.

The removal of hexavalent chromium was investigated using two commercial membranes (NF-HL (MWCO = 314 Da) and RO-SG (MWCO = 172 Da) supplied by Osmonics [81]. The NF membrane permitted to reach the highest removal efficiency (R 99.7%). RO-SG membrane exhibited the removal efficiency in the range 85–99.9% depending on the feed concentration and the operating conditions used. In the following Table 10, the rejections of various toxic ions obtained with the RO process are reported.

Table 10. RO membranes used for the removal of metal ions.

Process	Membrane Material	Configuration	Ion Rejection (%)	References
RO	Polyamide (TFC)	Spiral Wound	Cu^{2+} (99.5) Ni^{2+} (99.5)	[82]
RO	AG4021FF (Osmonics)	-	Ni^{2+} (99.3) Zn^{2+} (98.9)	[83]
RO	-	-	As(V) (91–99%) As(III) (20–55%)	[84]
RO	-			
RO	Polyamide	-	Ni^{2+} (99.3)	[85]
RO	Polyamide	-	As(III) (90)	[86]
RO	Polyamide	-	$As(V)^{+}$ (99.8)	[87]

2.4. Nanocomposite Membranes for Heavy Metal Removal

The NF and RO membranes suffer from a trade-off between permeability and selectivity (typical behavior of the polymeric membranes) [88]. Therefore, TFC membranes can preserve the desired selectivity only at low water permeance (1–20 Lm^{-2} h^{-1} bar^{-1}) [89]. Nanocomposite membranes, also known as mixed matrix membranes or hybrid membranes, combine the benefits of both organic membranes and inorganic materials and so permit to successfully increase the water permeability and reduced fouling [90–92]. Currently, these membranes loaded with different inorganic particles are also applied in metal ion removal (see Figure 3) [93].

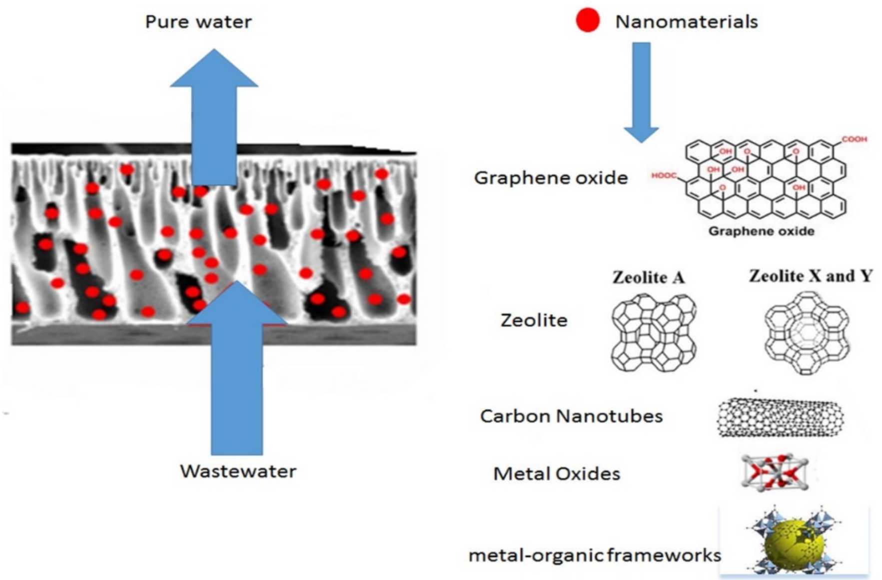

Figure 3. Nanomaterial used for nanocomposite membrane preparation. Adapted with permission from ref. [94]. Copyright 2021 Elsevier.

Mixed matrix NF membranes have been prepared using the phase inversion method and their performance in toxic metal ion removal was studied [95]. In particular, the authors have chosen polyether sulfone as polymer and $CoFe_2O4/CuO$ nanoparticles as fillers; the composition of the prepared membranes and their property in terms of contact angle and pure water flux are shown in Table 11.

Table 11. Composition and water contact angle and flux of MMMs.

Membrane	Filler (%)	Water Contact Angle (°)	Pure Water Flux (Lm^{-2} h^{-1})
M1	0.00	70	12.0
M2	0.05	62	15.0
M3	0.10	56	24.8
M4	0.50	35	34.2
M5	1.00	48	28.0

The MMMs are more hydrophilic than the pristine membrane owing to the hydrophilic character of the $CoFe_2O_{4/}$/CuO nanoparticles. In addition [96]. The better hydrophilicity of the MMMs determined an increase of the pure water flux. The removal of various toxic metal ions is illustrated in Figure 4.

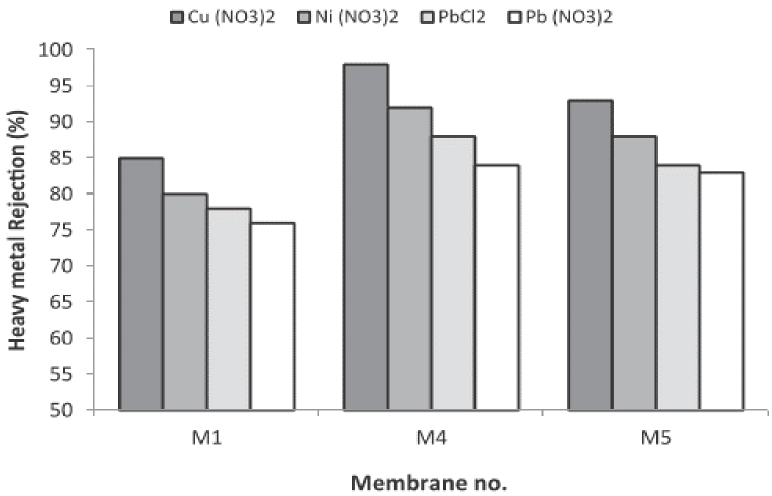

Figure 4. Heavy metal removal by using pristine membrane (M1) and MMMs (M4 and M5) Adapted with permission from ref. [95]. Copyright 2021 Elsevier.

The membrane M4 permitted to obtain the highest ion removal for the improved hydrophilicity that reduced the formation of a polarized layer (see Table 9). The sample M5 did not show exciting performance for the formation of clusters for the high filler concentration.

Zhang et al. prepared PVDF/ZnO membranes by a phase inversion method; these membranes are used for Cu^{2+} adsorption [97]. The hybrid membranes exhibited an adsorption capacity nine times higher than the pure PVDF membrane. In 2018, hybrid membranes-PES-based, and loaded with magnetic graphene particles (MMGO) were synthesized. The magnetic particles were prepared by grafting the surface of graphene oxide sheets with magnetic nanoparticles [98]. The hybrid membranes exhibited higher water flux than the pristine membrane. The finding was attributed to the changes in surface roughness and hydrophilicity. Significant removal of copper ion (92%) was also observed and ascribed to the preferential adsorption of heavy metal on the MMGO [99].

Carbon nanotubes (CNTs) are a good candidate for the fabrication of new membranes for their excellent mechanical strength, good electron affinity, and high flexibility [100,101]. Anyway, their hydrophobic nature can cause agglomeration during the preparation of nanocomposite membranes. A route for improving their dispersion into the polymeric solution is chemical functionalization. In a recent paper, functionalized CNTs (f-CNTs) have been added into polyvinylchloride solution for obtaining membranes with hollow-fiber configuration [102]. The f-CNTs-membranes exhibited a zinc removal that is almost 98 5% by using synthetic water and higher than 70% with real wastewater. The removal mechanism is due to the chemical interaction between the oxygen present in the functionalized CNTs and the positive charge of Zn^{2+}.

Electrospun carbon nanofibers/TiO_2-PAN hybrid membranes have been synthesized by Kumar and coworkers [103]. The contact angle decreased from 38° to 20° by increasing the CNFs/TiO_2 concentration. The hybrid nanofiber membranes show very narrow pore size distribution (270–240 nm). These membranes exhibited a higher flux (650 Lm^{-2} h^{-1}) than the pristine one (180 Lm^{-2} h^{-1}), and the removal efficiency for lead, cupper and cadmium are around 87%, 73%, and 66%, respectively.

The effect of the NaX zeolite crystals incorporated in polysulfone membranes has been evaluated for the removal of lead and nickel ions from synthetic wastewater [104]. The mixed matrix membranes showed the best sorption capacity (Pb^{2+} = 682 mg/g and Ni^{2+} = 122 mg/g). Yuan et al. have developed a composite membrane where the ZIF-300 layer was grown on the alumina substrate by the secondary growth method. An excellent rejection and water flux in wastewater treatment was observed, as shown in Figure 5 [105].

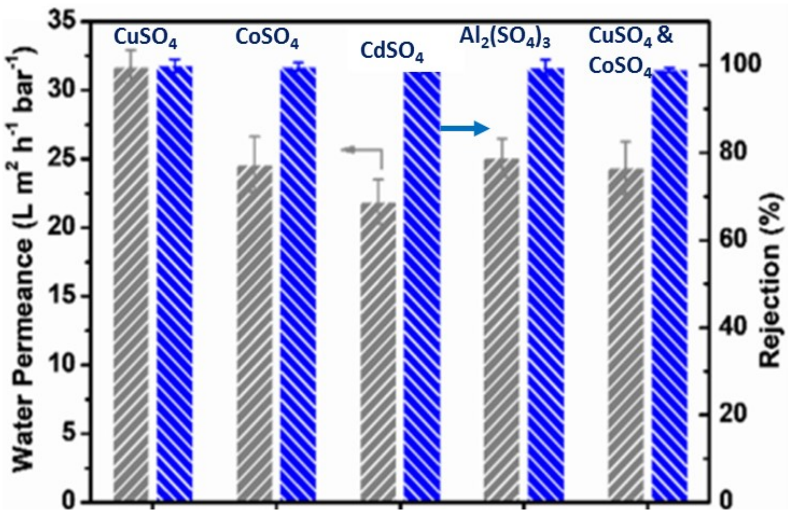

Figure 5. Rejections of different heavy metal ions (All ion solution concentration: 10 mM; Pressure = 1 bar; T = 25 °C). Adapted with permission from ref. [105]. Copyright 2021 Elsevier.

Recently, vacuum filtered membranes (VFMs) and polymer mixed e-spinning membranes (ESPMs) have been produced by using Fe-based ceramic nanomaterials and used for cadmium removal [106]. The Cd^{2+} adsorption has been more efficient in VFMs than in the e-spinning ones. Finally, ESPMs have exhibited better mechanical strength. A novel NF nanocomposite membrane has been prepared by adding Fe_3O_4-MXene nanosheets on commercial cellulose acetate membrane (used as a support) by vacuum filtration [107]. The M-Xenes, a new type of 2D transition metal-carbon/nitride, possess an interesting metallic conductivity (typical of transition metal carbides) with high hydrophilicity (feature of hydroxyl groups or oxygen present on their surface) [108]. An increase of the water flux has been achieved and the results are described in Table 12.

Table 12. Fe_3O_4-MXene-CA membrane performance in heavy metal removal.

Membrane	Fe_3O_4 (mg)	MXene (mg)	Water Flux (Lm^{-2} h^{-1})	Cu^{2+} Removal (%)	Cd^{2+} Removal (%)	Cr^{6+} Removal (%)
M1 *	0	8	80	29.7	30.7	32.8
M4 *	4	8	125	63.2	64.1	70.2
M4 *	4	8	105 *	48.0 *	-	-

After three cycles of washing with HCl solution (pH = 3). * M1 and M4 = NF membrane prepared by adding Fe_3O_4-MXene nanosheets on commercial cellulose acetate membrane.

2.5. Electrospun Nanofiber Membranes for Heavy Metal Adsorption

Electrospun nanofiber membranes (ENMs) characterized by large specific surface area, high porosity and easy separation for the reuse can potentially be used as heavy metal adsorbents [109]. Both natural (as chitosan, keratin and silk fibroin, etc.) and synthetic polymers (as (polyacrylic acid and polyethyleneimine) that possess functional groups capable of interacting with heavy metals are used for the preparation of ENMs. For example, chitosan (CS), a biopolymer with elevated biodegradability and biocompatibility, is very promising for different applications in the biomedical and pharmaceutical field [110]. This polymer presents in its chemical structure amino and hydroxyl groups that are capable of forming complexes with metal ions [111]. In any case, the heavy metal adsorption capacity of pure chitosan is low and also exhibits poor spinnability so different routes are followed for overcoming these drawbacks [112]. Many stabilizers like polyethylene oxide, polyethylene glycol, or polyvinyl alcohol (PVA) can be added to the chitosan solution to overcome these problems [113]. Batch adsorption experiments were performed to evaluate the arsenate adsorption performance of the CS-PVA-nanofibers [114]. The nanofibers have been capable to remove 200.0 $\pm$ 10.0 mg g^{-1} of As(V) and 142.9 $\pm$ 7.2 mg g^{-1} of As(III) from aqueous solution of pH 7.0 at room temperature [114]. Rich amino-functionalized CS-ENMs have been prepared by sequentially grafting the surface of the nanofibers with poly(glycidyl methacrylate) and polyethylenimine [115]. The ability of remove heavy metal ions (Cr(VI), Cu(II) and Co(II)) of the as-prepared membrane (CS-PGMA-PEI) has been investigated. The influence of the pH solution on the metal adsorption is illustrated in Figure 6a. At lower pH, the protonation degree of the amino group (-NH_3^+) increased, allowing a rise of the $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions (electrostatic attraction between anions and amino groups) adsorbed on the nanofibers. As the pH increased, the degree of the protonation decreased, resulting in a decrease in the adsorption amount of Cr(VI). For Cu(II), the higher degree of protonation of the amino group at lower pH determined a strong electrostatic repulsion between NH_3^+ and Cu^{2+}. For Co (II), as the pH increased, the degree of deprotonation of the amino group also increased and so a large amount of ion has been adsorbed on the nanofiber surface [115,116].

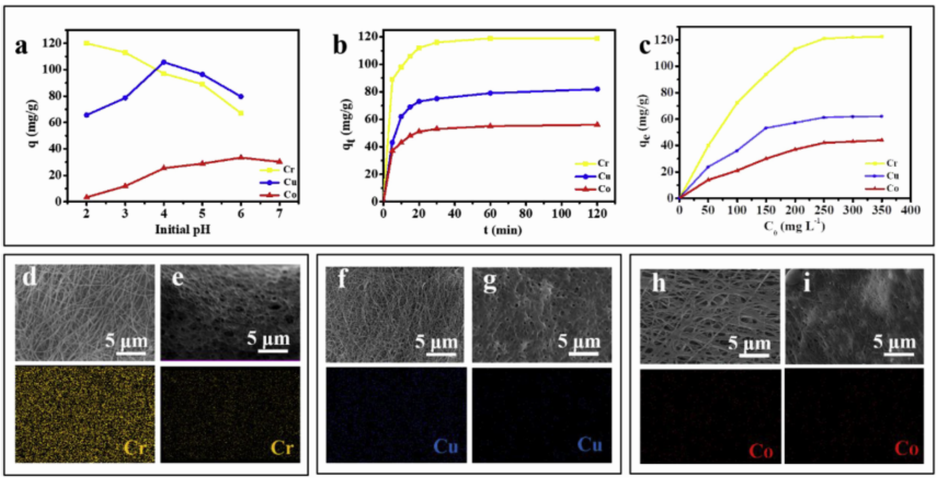

Figure 6. Effect of different factors on heavy metal adsorption, (**a**) pH of solution; (**b**) contact time and (**c**) initial concentrations. SEM pictures and element mapping of CS of CS-PGMA-PEI-ENMs for adsorption and desorption of Cr(VI) (**d**,**e**). Cu(II) (**f**,**g**). Co(II) (**h**,**i**). (**a**: 300 mg/L, t = 5 h, m = 100 mg, V = 100 mL, T = 25 °C; **b**: C = 300 mg L, initial pH = 2.0 (Cr 0 0 (VI)), 4.0 (Cu(II)), 6.0 (Co(II)), m = 100 mg, V = 100 mL, T = 25 °C; c: initial pH = 2.0 (Cr(VI)), 4.0 (Cu(II)), 6.0 (Co(II)), t = 1 h, m = 100 mg, V = 100 mL, T = 25 °C) Adapted with permission from ref. [115]. Copyright 2021 Elsevier.

The ion adsorption is very fast within 30 min due to the presence of a large number of active sites (see Figure 6b). In addition, the adsorption equilibrium has been reached at

60 min. The initial amount of heavy metal also influenced the adsorption capacity, and it raised in the range 50–250 mg/L and remained constant after 250 mg/L (see Figure 6c).

In Table 13 are reported the results obtained in heavy metal adsorption with new and modified polymer electrospun nanofiber membranes.

Table 13. Heavy metal adsorption by using polymer electrospun nanofiber membranes.

Material	Chemical Modifier	Concentration * (mg/L)	T (°C)	Metal Ion	q_{max} (mg/g)	Ref.
Polyacrylonitrile	Amodoxime	100	30	Cu(II) Pb(II)	143.47 178.57	[117]
Polyurethane	Phytic acid	400	-	Pb(II)	136.52	[118]
Chitosa/Poly(ethy-lene oxide	Phosphorylated Nanocellulos	-	25	Cd(II)	232.5	[119]
Polyacrylonitrile/Chitosan	ZnO TiO_2	-	-	Pb(II) Cd(II)	390 461	[120]
Polyacrylonitrile	Tannic Acid	200		Cr(III)	79.48	[121]

* Intitial metal concentration.

3. Conclusions

Membrane technology which is characterized by low energy consumption, high efficiency, and straightforward scale-up, represents an interesting technique for removing heavy metal ions from wastewater. Today, polymeric membranes are used for water desalination and wastewater treatment at an industrial scale owing to their easy fabrication and interesting separation performance. Depending on the polymeric materials of the membrane, the membrane process, and the operating conditions considered, the rejection values for the heavy metal ions ranging from 65% to 99%. Many efforts have been done in this area and different problems have been solved over the years. However, fouling and the trade-off between permeability and selectivity represent the main drawbacks of pressure-driven membrane processes. Therefore, researchers have explored alternative routes for overcoming them.

An improvement of the NF and RO performance in the removal of heavy metals could be achieved by incorporating nanomaterials with peculiar characteristics into the polymeric matrix. Nanocomposite membranes permit one to enhance water flux and heavy metal rejection, as reported in this review. However, further intense research activity needs to be performed for improving membranes' metal ion removal, antifouling properties, permeability, nanoparticle leaching, stability, and reusability. These goals' achievements will permit the nanocomposite membranes to play an important role in heavy metal removal with the possibility of using them at industrial scale.

Electrospinning is a versatile technology that allows the facile production of nanofibers. Nanofiber membranes (ENMs) have attracted a lot of attention for their high specific surface area, high pore interconnectivity, and so seem to be very promising in treating wastewater. Anyway, some challenges should be considered and overcome by improving the pore size, porosity, and mechanical strength of ENMs.

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