

Review

Pressure-Driven Membrane Process: A Review of Advanced Technique for Heavy Metals Remediation

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Abstract: Pressure-driven processes have come a long way since they were introduced. These processes, namely Ultra-Filtration (UF), Nano-Filtration (NF), and Reverse-Osmosis (RO), aim to enhance the efficiency of wastewater treatment, thereby aiming at a cleaner production. Membranes may be polymeric, ceramic, metallic, or organo-mineral, and the filtration techniques differ in pore size from dense to porous membrane. The applied pressure varies according to the method used. These are being utilized in many exciting applications in, for example, the food industry, the pharmaceutical industry, and wastewater treatment. This paper attempts to comprehensively review the principle behind the different pressure-driven membrane technologies and their use in the removal of heavy metals from wastewater. The transport mechanism has been elaborated, which helps in the predictive modeling of the membrane system. Fouling of the membrane is perhaps the only barrier to the emergence of membrane technology and its full acceptance. However, with the use of innovative techniques of fabrication, this can be overcome. This review is concluded with perspective recommendations that can be incorporated by researchers worldwide as a new problem statement for their work.

Keywords: water treatment; heavy metal removal; polymer membranes; nano-filtration; ultra-filtration



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1. Introduction

The rapid industrial revolution has led to the release of heavy metals into the water streams. Even the slightest of exposure to these elements is believed to cause catastrophic consequences [1]. These elements have atomic weights of between 63.5 and 200.6 and have a specific gravity higher than 5 [2]. The life span of these elements in the ecosystem, owing to their property of bio-magnification, makes the situation worse. Therefore, heavy metal removal from industrial wastewater has become an immediate matter of concern worldwide. The most toxic heavy metals are Zinc, Chromium, Nickel, Lead, Cadmium, and Mercury. There are conventional methods to treat wastewater, such as adsorption [3], flotation [4], bio-sorption [5], coagulation [6], ion exchange [7], bioremediation [8], and electro-dialysis [9]. Although these have been well-established, restrictive environmental legislation, more extensive space requirements, labour-intensive operations, lower selectivity, lower separation efficiency, and the high cost of these conventional methods have resulted in the search for more promising and unconventional techniques. Membrane technology in industrial pollution abatement has attracted research interest worldwide due to its high efficiency, smooth operation, and less space requirements.

Membrane technology may help industrial effluents to stay within permissible standards. Treatment through membranes is highly effective and, therefore, a review of the research carried out up to now is quite imperative. There is no detailed paper that covers the application of all the pressure-driven processes in environmental applications and the implications of various parameters on the performance of the membrane process. This

manuscript aims to provide a comprehensive perspective and review of the available literature. This will help researchers to identify the gaps and proceed accordingly. Figure 1 presents the comparison of various kinds of pressure-driven membrane technologies.

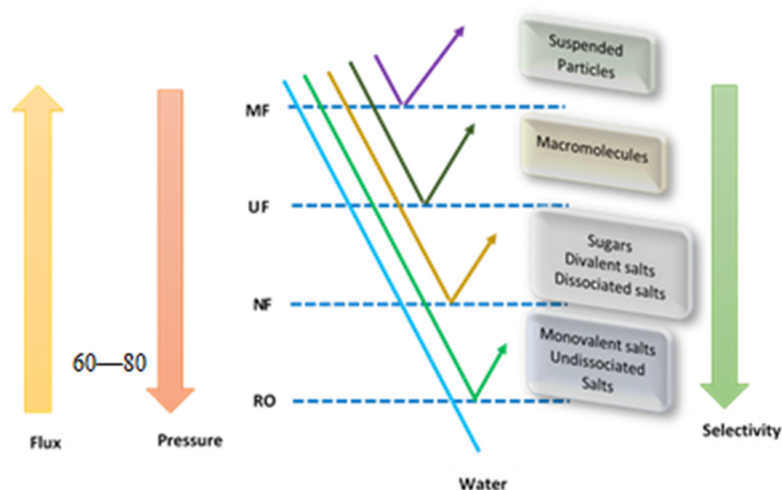


Figure 1. Various pressure-driven membrane processes.

2. Results and Discussion

2.1. Ultrafiltration in Heavy Metal Removal

Ultrafiltration (UF) is the technique under membrane separation where the transmembrane pressure required is relatively low. This method aims to eliminate dissolved as well as colloidal particles. The major limitation of this type of pressure-driven process is the larger size of the pore. The pore size for UF lies between 2 nm and 50 nm [10]. The pore sizes are more significant than the metal ions in their hydrated forms.

Permeate fluxes are determined by varying applied pressure at a fixed temperature. The flux can be predicted by the following equation known as the Hagen- Poiseuille equation [11]:

$$J = \frac{P_T}{R_M + R_F + R_G} \quad (1)$$

where J is the flux through the membrane ($\text{m}^3/\text{m}^2.\text{s}$), P_T is the transmembrane pressure (N/m^2), R_M is the intrinsic membrane resistance ($\text{N.s}/\text{m}^3$), R_F is the fouling resistance, and R_G is the resistance related to concentration polarization. R_M can also be written as:

$$R_M = \frac{32 \times \Delta X \times \mu}{\varepsilon \times d_p^2} \quad (2)$$

where d_p is the mean diameter of the pore (m), μ is the viscosity of the fluid ($\text{N.s}/\text{m}^2$), ΔX is the thickness of the membrane skin (m), and ε is the porosity of the surface of the membrane.

The performance of UF can be increased by adding micelles or polymers, which can aggregate the heavy metal particle. These are referred to as Micellar Enhanced UF (MEUF), and Polymer Enhanced UF (PEUF) (Table 1). Scaemhorn first discovered MEUF for water remediation [12]. Figure 2 shows the process of micellar enhanced filtration. In the process of MEUF, the addition of surfactants either at levels equal to or higher than Critical Micelle Concentration (CMC), lead to the formation of aggregates called micelles. The solubility of metal ions in these micelles is higher and is dependent on electrostatic or Van der Waals forces. These micelles containing metal ions are then subjected to UF membrane, and thus pure water is achieved. The retention of these heavy metal bound micelles is subsequently obtained by using a UF membrane with a pore size smaller than the size of the micelle. To achieve maximum efficiency, surfactants having electrical charges are used worldwide.

As an example, Sodium Dodecyl Sulphate (SDS), having a negative charge, is used to treat wastewater containing metal ions. The removal efficiency is dependent on various parameters, including the pressure which is applied, the concentration of the surfactant, the temperature of feed, the flow rate, and the concentration of the feed. Since the driving force itself is the pressure difference, it is evident that permeate flux will vary with applied pressure at a particular surfactant concentration. However, the applied pressure should be less than the maximum pressure the membrane can withstand [13]. pH also plays a vital role in the removal of heavy metals by MEUF. It was observed that the removal of Cr(VI) by MEUF using Cetyl Trimethyl Ammonium Bromide (CTAB) was maximum (90%) at a pH of 2 [14]. The surfactant to metal molar ratio is an essential variable in MEUF as the formation of micelles depends on the Critical Micelle Concentration (CMC). It has been reported that a rejection coefficient as high as 99% can be obtained by keeping the surfactant to metal molar ratio above 5 [15]. In some unusual cases, it has been observed that metal rejection coefficients as high as 90% could be achieved for Cd(II), Cu(II), Pb(II), and Zn(II) by using the concentration of surfactants less than the Critical Micelle Concentration [16]. This may be attributed to the breakage of aggregates into smaller aggregates at a much higher concentration than CMC. The removal of chromium has also been investigated by using Cetyl Pyridinium Chloride (CPC), and it was reported that the permeate concentration increased with feed concentration. The concentration was observed to increase beyond the Critical Micelle Concentration (CMC) of 43 mM [17]. The removal of Cr(VI) by using CTAB, aggregation was observed at a CTAB concentration of 0.72 mM [18]. Feed temperature is also an important parameter as the thermal expansion of the membrane as well as the viscosity of the solution is directly dependent on the temperature of the solution. Besides, Critical Micelle Concentration (CMC) is dependent on the temperature. A hybrid system containing MEUF and an Activated Carbon Filter (ACF) was employed to obtain 96.2% removal efficiency of Ni(II) [19].

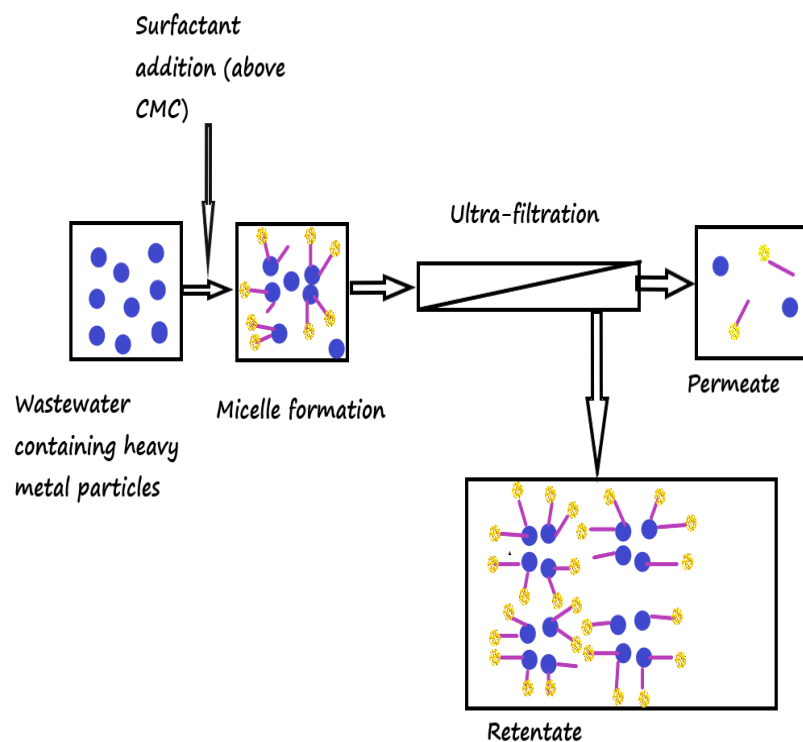


Figure 2. Process of Micellar Enhanced Filtration.

Table 1. Various membranes in wastewater remediation.

Membrane Material	Characteristic of Membrane	Heavy Metal Targeted	Surfactant/Complexing Agent Used	Optimum Pressure (Bar)	Surfactant Concentration (mM)	Initial Concentration (mg/L)	pH	% Removal	Reference
Ceramic	MWCO = 210 kDa	Ni(II) Co(II)	Sodium dodecyl sulphate	2.8	0.025	10	7	53 51	[20]
PAN Membrane	Area = 0.00124 m ²	As(V)	Cetyl Pyridinium Chloride (CPC)	1	5	1	7–8	96.9	[21]
Polyether sulphone	MWCO = 6000 g mol ^{−1} Area = 0.3 m ² TMP <= 0.15 MPa	Cd(II) Zn(II)	Sodium dodecyl sulphate	0.7	2.15	50		92–98	[22]
Amicon regenerated cellulose	MWCO = 10 kDa	Cd(II) Zn(II)	Sodium dodecyl sulphate	3	13.9 14.2	23		99	[23]
Polycarbonate	TMP = 250 kPa	Ni(II)	Sodium lauryl ether sulphate		2	9.2		98.6	[24]
Polyether sulphone	MWCO = 10 kDa Area = 9.6 cm ² Permeate flux = 150 L.m ² /h at 0.35 MPa	Cu(II) Cd(II) Zn(II) Pb(II)	Sodium dodecyl sulphate		8	(50–300)	>3 >3 3–10 3–10	99	[25]
Polyether sulphone	MCO = 10 kDa Area = 32.15 × 10 ^{−4} m ²	Cd(II)	Rhamnolipid	2.76	8.04	60	7.8	92	[26]
Ceramic	MWCO = 1 kDa	Zn(II)	Sodium dodecyl sulphate	0.8	10	2		99	[27]
Polyacrylonitrile (PAN)	MWCO = 300,000 Area = 4.8 m ²	Zn(II)	Sodium dodecyl sulphate	2	0.21	19.32	7	84.67	[28]
Polyether sulphone	MWCO = 10 kDa Area = 1.6 m ²	Cd(II) Cu(II)	Sodium dodecyl sulphate	3	60	0.37 0.41		85 81	[29]
Polysulphone	MWCO = 10 kDa Area = 0.014 m ²	Cr(VI) Cr(III)	Rhamnolipid	0.7	0.02	10	6	98.7 96.2	[30]
Regenerated Cellulose	MWCO = 10 kDa Area = 0.0013 m ²	Cu(II) Cd(II) Zn(II) Ni(II) Mg(II)	nonaoxyethylene oleyl ether carboxylic acid (RO90)	3	30.43	920	6.5	>95%	[31]
Polysulphone	MWCO = 1 kDa Area = 0.004 m ²	Ni(II)	Sodium dodecyl sulphate	2.5	16	10	7	97%	[32]
Polyacrylonitrile (PAN)	MWCO = 100 kDa Area = 0.07 m ²	Ni(II) Zn(II)	Sodium dodecyl sulphate	1	12.75	23	7	96.3 96.7	[33]
Polysulphone	MWCO = 10 kDa Area = 0.004 m ²	Ni(II)	Sodium dodecyl sulphate	1	8	10	11	99	[34]
Polysulphone	MWCO = 10 kDa Area = 0.3 m ²	Cd(II)	Sodium dodecyl sulphate	0.3	8	0.45		97	[35]
Polyether sulphone	MWCO = 5 kDa, 10 kDa, 30 kDa Area = 0.00096 m ²	Cd(II)	Sodium dodecyl sulphate	1	4	10		90	[36]
Polyether sulphone	MWCO = 8 kDa Area = −0.005 m ²	Cd(II)	Sodium dodecyl sulphate		7.33	50		98.4	[37]
Hydrophilic	MWCO = 10 kDa	Cu(II)	polyoxyethylene Octyl phenyl ether (Triton-X) plus Sodium dodecyl sulphate	2.096	1.29 5.67	9.2	5	92	[38]
Polyether sulfone	MWCO = 10 kDa Area = 0.003019 m ²	Cd(II) Cu(II) Pb(II) Zn(II)	Sodium dodecyl sulphate	1	9	10		>90	[16]

Polymer Enhanced UF (PEUF) is also a plausible solution to wastewater treatment. (Table 2). In this method, a water-soluble polymer is added as a complexing agent with metal ions and forms a macromolecule. The molecular weight of the macromolecule is higher than the molecular weight cut off of the membrane. Therefore, the metallic ions, along with the complexing agent, are retained over the UF membrane. The most commonly used complexing agents are Polyacrylic acid (PAA) [39], Polyvinylamine (PVA) [40], Polyethyleneimine (PEI) [41], a copolymer of maleic acid and acrylic acid (PMA) [42], and humic acid [43]. The performance of this method is dependent on the type of metal to be

removed and the type of polymer used. Besides, solution pH and the existence of other ions in the solution also affect the performance. The efficiency of this method is dependent mainly on the type of metal and polymer, the feed concentration, the pH of the solution, and the presence of other salts. It was reported that the rejection coefficient reduced from 90% to 32% when the Cr(VI) concentration in the feed was increased from 25 PPM to 400 PPM [44]. The optimum polymer/metal weight ratio for the selective removal of Ni(II) and Cu(II) by using complexing agent PEI were 6 and 3, respectively [45]. The polymer/metal weight ratio of 25 was observed to be the most suitable for the removal of Ni(II) and Cr(III) with removal efficiencies of 99.5% and 99.8%, respectively [46]. The solution pH also affects the performance of the system. The complete removal of Cr(VI) by PEUF using Poly(*N,N*-dimethylaminoethyl methacrylate) was reported when the pH was kept at 4 [47].

Table 2. Effect of environmental chemistry on the removal of heavy metals by membranes.

Membrane	Characteristic of Membrane (MWCO)	Heavy Metal	Surfactant/Complexing Agent Used	Optimum Pressure (bar)	Surfactant Concentration	Initial Concentration (mg/L)	pH	% Removal	Ref
Ceramic	15 kDa	Cu(II)	Poly (acrylic acid) sodium	3	1 wt%	160	4–5	99.5	[48]
Ceramic	15,000 g/mol	Cr(III)	Polyvinyl alcohol (PVA)		1 wt%	92	5	>90%	[49]
Polyether sulphone	10 kDa	Pb(II) Cu(II) Fe(III)	Polyvinylamine	2	0.1 wt%	25	7	99 97 99	[40]
Ceramic	10 kDa	Cu(II)	Poly (acrylic acid)		0.4 wt%	160	5.5	99.5	[50]
Ceramic	10 kDa	Cu(II) Zn(II)	Partially ethoxylated polyethyleneimine (PEPEI)	3	0.06 wt%	90.62	6	Selectivity ratio Cu(II)/Zn(II) = 12.31	[51]
Polyether sulphone	10 kDa	Cd(II)	Poly (ammonium acrylate)	2	3.71×10^{-4} mol/L	46	6.32	99	[52]
Cellulose	10 kDa	Cu(II) Zn(II)	Poly (acrylic acid)	3	2×10^{-3} mol/L	46	5	97 75	[53]
Thin Film Composite	3.5 kDa	Ni(II)	Chitosan	28	2×10^{-2} mol/L	0.072	5.4	90	[54]
Polyether sulphone	10 kDa	Hg(II)	Polyvinylamine	2	0.05 wt%	10		>90	[55]
Polyether sulphone	60 kDa	Cu(II)	Polyethylenimine (PEI)	1.7	25 mM	230	3	94	[56]
Polysulphone	8 kDa, 15 kDa	Cd(II)	Poly(ammonium) acrylate	2		46	4	98	[57]
Ceramic	10 kDa	Cr(VI)	poly(diallyldimethylammonium chloride) (PDADMAC)	4	0.1 wt%	50	9	99	[58]
Polyethersulphone	10 kDa	Cu(II) Ni(II) Cr(III)	Carboxy methyl cellulose	1	1 g/L	10	7	97.6 99.1 99.5	[59]
Polyether sulphone	10 kDa	Hg(II)	Polyvinylamine	2	0.1 wt%	10	6–7	99	[60]
Ceramic	10 kDa	Cu(II)	Partially ethoxylated polyethylenimine (PEPEI)	4	0.06 wt%	208 mg Cu/g PEPEI	6	97	[61]
Ceramic	10 kDa	Pb(II)	Poly(acrylic) acid (PAA)	4	0.036%	100	6	100	[62]

2.2. Nanofiltration for the Removal of Heavy Metals from Wastewater

Nanofiltration (NF) possesses properties between those of UF and Reverse osmosis (RO), and therefore the pore size is usually less than 2 nm, corresponding to an MWCO of 100–1000 Da [63]. The presence of surface functional groups and their dissociation provides charge to these membranes. NF membranes' charge is highly dependent on solution pH. For example, typical polyamide NF membranes have an isoelectric point

(IEP) between 3.5–5. At pH lower than IEP, amine groups and carboxylic groups are protonated ($\text{R-NH}_2^+/\text{RCOOH}$), which confer to the membrane a positive charge. Contrarily, at $\text{pH} > \text{IEP}$, NF membranes exhibit a negative charge because of the deprotonation of the above-mentioned functional groups ($\text{R-NH}/\text{R-COO}^-$). In view of the fact that most of the heavy metals are cations, NF is of prime importance due to the separation achieved by the combination of steric effect and electrostatic forces [64]. Higher rejection of divalent ions, lower rejection of monovalent ions, and higher flux compared to RO membranes are some of the critical attributes of NF membranes. To reduce energy costs, NF is extensively used in the wastewater treatment processes and is currently trying to replace RO to make the processes more economically viable. The NF membranes separate the solute from the solution via two mechanisms. The first is known as ionic separation and corresponds to the separation based on the charge of solute in water. The second is known as sieving, which corresponds to the molecular weight of uncharged solutes. The non-sieving rejection mechanisms of NF are Donnan exclusion [65] and dielectric exclusion [66]. This is being explored to remove heavy metals from wastewater (Table 2) due to its ease of operation, reliability, and lower energy consumptions. The NF technique has been applied for removal of heavy metals such as Copper [67], Cobalt [68], Nickel [69], Zinc [70], Lead [71], Cadmium [72], Chromium [73], Arsenic [74] and mercury [75].

It was reported that As(V) removal increased with increased pH. The rejection increased from 74% to 88% when the pH was increased from 3.4 to 10. This could be explained by the fact that the monovalent ion H_2AsO_4^- is dominant in the range of pH 4–6 while the divalent ion HAsO_4^{2-} is dominant above pH 7. Owing to the large, hydrated radii of divalent ions, they are rejected by the membrane at a much higher rate. The As(V) removal increased with lower temperature. It was observed that at 15 °C, the arsenic removal was 95.4% which decreased to 93.1% on increasing the temperature to 40 °C. This is because of the increased diffusivity of arsenic with temperature [76]. In another study, it was observed that natural organic matter, humic acid, increased the rejection coefficient of As(V) by using NF membranes. The rejection coefficient for all four types of membranes was recorded to be higher than 94% [74]. Another study reported that the removal of Ni(II) ions increased with feed pressure and feed concentration. The maximum observed rejection coefficient of Ni(II) was 98.94% for an initial feed concentration of 5 PPM [77]. The efficiency of silver recovery was found to be 29%–59% for hybrid cyanidation and membrane separation [78]. Modification of NF membranes at the laboratory scale has also been done to increase their selectivity. A study reported removal efficiencies of 47.9, 44.2, 52.3 for Cu(II), Cd(II) and Cr(VI), respectively by the NF membrane modified by halloysite nanotubes (HNTs) functionalized with 3-aminopropyltriethoxysilane (APTES) [79]. Polyether sulphone (PES) NF membranes were grafted with poly- (amidoamine) dendrimer and showed outstanding performance with almost 99% removal efficiency for Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), and As(V) [80]. Chelating polymers like poly- (acrylic acid-co-maleic acid) (PAM) and poly- (acrylic acid) (PAA) were adsorbed on the NF filtration membranes to treat Cd(II), Zn(II), Pb(II), Ni(II), Cu(II), As(V), and Cr(VI), and rejection coefficients of more than 98% were obtained for all the heavy metals [81]. Hollow fibre NF membranes have been fabricated using polybenzimidazole (PBI) and were investigated for their Cr(VI) removal capacity. The fabricated PBI membranes with Molecular Weight Cut Off (MWCO) of 525 Da showed 95.7% Cr(VI) removal [82]. The removal of Cr(VI) was also attempted by fabricating asymmetric NF membrane with poly- (m-phenylene isophthalamide) (PMIA). It was observed that 98% of Cr(VI) was removed at a pH of 8 with the fabricated membrane [83]. The presence of metal complexing polymer also played a crucial role in the application of membranes in the treatment of heavy metal. It was seen that with the addition of Bovine Serum Albumin (BSA), rejection coefficients of 93%, 99%, 93%, and 99% were obtained by employing a ceramic membrane with MWCO of 450 Da for Zn(II), Cd(II), Pb(II) and Cu(II), respectively [84]. The capillary UF properties were merged with capillary NF to achieve the desired separation of heavy metal from wastewater. This combined technique, called Direct Capillary NF (CNF), was employed to remove Pb(II), and 83% removal ef-

efficiency was obtained with the flux of $20 \text{ L/m}^2 \cdot \text{h}$ [85]. NF was also combined with MF, and the hybrid system was able to obtain 99% removal efficiency of Cr(VI) from aqueous solutions [86]. A dual-layer NF membrane was fabricated with an outer layer of polybenzimidazole (PBI) and a blend of polyethersulfone (PES) and polyvinylpyrrolidone (PVP). This membrane with an active area of 0.0037 m^2 was employed to remove Cr(VI), Pb(II), and Cd(II). It was observed that 98% of Cr(VI) and 93% of Pb(II) were removed at pH of 12 and 2.2, respectively [87]. One study showed the laboratory scale development of an amphoteric hollow fiber NF membrane which was capable of removing 97% of As(V) at a pH of 10 [88]. A positively charged membrane was fabricated by modifying NF membrane with hyperbranched polyethyleneimine (PEI) and removed 91.05% of Pb(II) at a pH of less than 8 [89]. A positively charged NF membrane was developed with the use of 2-chloro-1-methylidopyridine and removed 96% and 95.8% of Cu(II) and Ni(II), respectively [90]. Nanotechnology has also come a long way since its development. Some researchers blended 0.5 weight% of cobalt ferrite nanoparticles in a polyethersulphone NF membrane and achieved rejection of 98%, 92%, and 88% for Cu(II), Ni(II) and Pb(II), respectively [91]. Beside, 1 wt% of cellulose nanocrystals functionalized by amine groups were also embedded in the PES membrane and the fabricated membrane removed 90% of Cu(II) ions [92]. A NF membrane Desal 5 DK was investigated for separating Cr(III) ions from acid solutions. It was evaluated that the Cr(III) concentration profile across the membrane is sensitive to the initial concentration of chromium as well as to the pore dielectric constant [93]. The performance of a semi-aromatic poly(piperazineamide) membrane was assessed for the removal of metals from copper metallurgical process streams. The membrane showed high metal rejections of more than 80%, and the high rejection values were associated with dielectric exclusion [94]. A research group studied the performance of extreme-acid-resistant duracid membrane for the valorisation of copper acidic effluent. The permeate flux and the feed water composition were varied, and it was observed that the metal rejection was more than 90% [95]. A novel nanocomposite membrane was developed for the removal of heavy metals, and its performance was compared to the polymeric membranes. It was concluded that while the polymeric membranes can exhibit a rejection from 77 up to 99%, the nanocomposite membranes can completely reject heavy metals (up to 100%) [96]. Table 3 summarizes the recent literature of various NF membranes used for heavy metal removal and their performance.

2.3. Reverse Osmosis in Heavy Metal Removal from Wastewater

The technique of reverse osmosis (RO) is the most efficient in terms of the contaminants it can separate from water. The semi-permeable membrane mostly allows water to pass and retains most of the pollutants. This technique accounts for more than 20% of the world's desalination capacity [97]. The application of RO in the removal of heavy metals from wastewater is being investigated (Table 4). Low-pressure RO has been applied with a complexing agent to remove Ni(II) and Cu(II), and the removal efficiencies for both single and a mixture of ions achieved over 99% [98]. The complete removal of Ni(II) was obtained by employing the UF/RO hybrid system in the metal finishing industry [99]. A rejection coefficient as high as 99.9% was achieved for removal of Cr(VI) by employing a RO membrane at a pH of 8 [100]. The pH of the solution plays a crucial role in the removal of heavy metals by RO. Researchers obtained 91% removal of Cr(VI) at a pH of 3 [101]. For an initial feed concentration of 200 mg/L , 99% of Cd(II) was rejected by using RO from contaminated wastewater [102]. Commercially available polyamide ultra-low pressure reverse osmosis (ULPRO) and a NF membrane were employed to separate heavy metals. The rejection of heavy metals was achieved to be greater than 97% [103]. A study of the implementation of sequential stages of MF, NF and RO to separate noble metals from a gold mining effluent was carried out. It was observed that the retention of metals in the concentrates of MF and RO was above 95% [104]. Recovery of heavy metals such as Mn, Fe, Cu, Zn, As, Cd, and Pb was assessed using a volume retarded osmosis low-pressure membrane (VRO-LPM), and 95% rejection was obtained for all the heavy metals [105].

Table 3. Review of literature concerning application of NF in heavy metal removal.

Characteristics of Membrane	Heavy Metal Targeted	Initial Metal Concentration (mg/L)	pH	Pressure (bar)	Removal Efficiency (%)	Ref
Flat organic membranes MWCO = 1000 Da Permeability = $1.6 \times 10^{-3} \text{ L m}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$	Ni(II) Cu(II)	69	1.2	14	76.1 72.6	[106]
Polyamide membrane supported by diaminobenzenesulfonic acid (DABSA) MWCO = 500 Da Permeability = $11.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ Negative charged	Cr(VI)	460	9	4	>99	[107]
Chitosan/polyvinyl alcohol/montmorillonite clay membrane Active area = 0.00385 m^2	Cr(VI)	50	7	1	(84–88.34)	[108]
PAN/Sulfonated Polyarylene ether benzonitrile MWCO = 300 Da Permeability = $7.62 \text{ LMH.bar}^{-1}$	Pb(II) Cd(II)	1000	(2–5)	6	94.6 95.1	[109]
Spiral wound Polymeric membrane (NF270–2540) Active area = 2.6 m^2 Negatively charged MWCO = (200–400) Da	Co(II) Ni(II)	20	(3.4–5.6) 3.4	6 10	100 91.94	[110]
Polyamide membrane (NF270) Active area = 0.00076 m^2 . The surface of the membrane is positively charged for pH less than 4 and negatively charged for a higher value.	Cd(II) Mn(II) Pb(II)	1000	1.5	4	99 89 74	[111]
Polyamide membrane Active area = 0.47 m^2 Isoelectric point is at pH 3.3–4	Pb(II) Ni(II)	1	5.5	6–8	86 93	[112]
Polyethersulfone Membrane Area = 0.00001256 m^2 Membrane fabricated with 0.5 wt% magnetic graphene based nanocomposites	Cu(II)	20	5	4	92	[113]
Thin-film composite. Area = 0.024 m^2 The isoelectric point is 3.6. Membrane surface is negatively charged	Pb(II)	150	5.8	25	99	[114]
Polyamide thin film composite membrane MWCO = 400 Zeta potential = -36.8 mV	Cr(VI) As(V)	0.1	8	8.18	(25–95)	[115]
NF 300 Active area = 2.5 m^2	As(V)	0.015 to 0.02	5	50	99.8	[116]
Aromatic polyamide membrane MWCO = (200–300) Water permeability = $2.4 \times 10^{-8} \text{ m}^3 / (\text{s.m}^2.\text{kPa})$	As(V)	0.2	7.5	10	>94	[74]
Thin film composite membrane (NF 2) Active area = 0.01 m^2	As(V)	0.150–0.252	7	11.76	(97–100)	[117]
NF Hollow fibre membrane MWCO = 520 Da Isoelectric point = 6.6 Pure water flux = $47.5 \text{ L}/(\text{m}^2.\text{h})$	Ni(II) Cr(VI) Cu(II)	142.23 121.23 56.55	2.31	4	94.99 95.76 95.33	[118]
Polyamide composite membrane MWCO ranges between 150 and 300 Effective area = 0.00572 m^2	Cu(II)	230	4.5	6.89	98.1	[119]
Thin-film Composite membrane Area = 0.0036 m^2	Pb(II)	400	3	30	97.5	[120]
Thin-film composite membrane (AFC 40) Effective area = 0.024 m^2	Co(II)	100	3	25	97	[64]
NF 300 membrane Effective area = 0.015 m^2	Cd(II) Ni(II)	5	5	20	97.26 98.90	[121]
Polyamide membrane (NF270) Membrane surface area = 0.0012 m^2 Isoelectric point = 3.3	Cu(II)	25,000	(3–10)	30	99.5	[122]
Negatively charged microporous NF, Nanomax50	Cu(II)	200	< 4.5	3	66	[123]
NF spiral-wound membrane	Cu(II)	50	5	3.8	>95	[124]
Polyamide membrane (NTR 729HF) MWCO = 700 pH 6.5 Effective membrane area = 0.006 m^2	As(V) As(III)	0.5	(5–9)	0.1–5	81 57	[125]

Table 3. Cont.

Characteristics of Membrane	Heavy Metal Targeted	Initial Metal Concentration (mg/L)	pH	Pressure (bar)	Removal Efficiency (%)	Ref
Polyamide thin film composite (NF90- 2540) Active surface area = 2.6 m ² MWCO = 200 Da	As(V)	0.1	8	6	>90	[76]
Composite polyamide spiral wound membrane(NFI) Membrane area = 0.75 m ² Pure water permeability = 3.20 L/hm ² bar	Cr(VI)	1000		5–8	99	[73]

Table 4. Review of literature concerning application of RO in heavy metal removal.

Characteristics of Membrane	Heavy Metal Targeted	Initial Metal Concentration (mg/L)	Operating Conditions	Pressure (bar)	Removal Efficiency	Ref
TFC spiral wound membrane Active area = 1.95 m ² Allowable operating pH range = 4–11 Max operating temperature = 45 °C Max feed turbidity, NTU = 1 Max feed SDI = 5	Cu(II) Ni(II)	500	Na ₂ EDTA was added as a chelating agent at pH 5	5.06	99.5	[126]
Disk membranes Polyamide selective layer is supported on the polysulfone layer	Cu(II)	20–100	Addition of Sodium dodecyl sulphate increased the removal efficiency	Low pressure	70–95	[127]
Polyamide thin film composite membrane MWCO = N.A Pure water permeability = 0.75 L m ⁻² d ⁻¹ kPa ⁻¹ pH range = 3–10 Zeta potential = −4.5 mV	Cr(VI) As(V)	0.1	8	5.13	>90	[106]
Polyamide membrane Active area = 0.014 m ²	As(V)	0.1		10–40	99.75	[128]
Brackish water membrane Active surface area = 0.014 m ²	As(III)		pH 9.6	40	99	[129]
SWHR membrane (Filmtec)	As(V) As(III)	0.2	pH 4 pH 9.1	10–35	96.8 92.5	[130]
Polyamide spiral wound membrane Membrane surface area = 2.5 m ² pH range = (4–11)	Cu(II) Cd(II)	500		13	98 99	[131]
SE and MPF44 NF membranes Active membrane surface area = 0.0028 m ²	Cu(II)	2 M		35	>95	[67]

2.4. Fouling of Membranes

Despite its potential in the treatment of wastewater, there are certain limitations that prohibit the application of membranes in large-scale operations. The most challenging of all limitations arise from membrane fouling caused by different inorganic salts, which decreases permeate flux and increases feed pressure. The quality of the product is bad, and the life of the membrane is shortened [132]. The impacts of various model foulants on the performance of RO and NF membranes has also been studied. It was observed that organic foulants such as humic acid and sodium alginate caused the most severe drop in permeate flux [133]. The research was conducted to evaluate the cost of fouling in full-scale RO and NF installations, and it was found that the cost of fouling in RO plants was around 24% of operational expenses. The cost for early membrane replacement accounted for the significant portion of the total cost. It was concluded that cleaning-in-place automation could save up to 3% of operational expenses [134]. A surface-patterned alumina ceramic membrane with a porous gradient structure was fabricated to improve the anti-fouling ability [135]. The effect of gradient profile in ceramic membranes on fouling was also studied by a research group, and it was found that gradient profile reduced membrane resistance and fouling [136]. A hydrogenated TiO₂ membrane with photocatalytically enhanced anti-fouling was developed for the treatment of surface water. It was observed

that upon UV irradiation, the hydrogenated TiO₂ membrane showed 60% higher humic acid removal efficiency as compared to the pristine TiO₂ membrane [137].

3. Conclusions

Membrane processes are the best available techniques for water and wastewater treatment. The capability of separating a wide variety of components from the aqueous stream makes membrane technology one of the most promising methods available. A great deal of research has been done on heavy metal removal by ultra-filtration using surfactants and complexing agents. There is no literature available on separation by using a hybrid system of MEUF and PEUF for heavy metal removal. Although work has been done on the application of nanotechnology in membrane processes, little has been done on their application in the removal of heavy metals from wastewater. The nano-filtration membranes have been modified by using specific materials to enhance their selectivity. The combination of nanoparticles and nanocomposites with membranes seems to be a research gap. Besides, the fouling of the membrane is a significant limitation in the application of membranes in wastewater treatment. New fabrication techniques of membrane development, such that fouling of the membranes can be controlled as well as mitigated, are highly recommended.

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