Membrane-Based Environmental Remediation

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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. The primary organic pollutants are dyes, antibiotics, phenol compounds, herbicides, phthalate esters, and polycyclic aromatic hydrocarbons [3][4][5]. Inorganic contaminants include diverse toxic heavy metals as cadmium (Cd), chromium (Cr), arsenic

Industries producing paints, fertilizers, metal plating batteries, and electronic discharge a lot of amount of heavy metals in the environment [6]. They have hazardous effects on both humans because they are not metabolized [7] and fish and aquatic flora [8]. The United States Environmental Protection Agency has established the maximum permissible limit of metals for different heavy metal ions [9]. Table 1 reports the maximum contaminant level (MCL) for various heavy metals in the surface water and the health problem associated with them [10].

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 [11][12]. Today, polymeric membranes are used in different separation processes for their easy manufacturing and high efficiency [13][14][15][16]. 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 [17]. Nanofiltration and reverse osmosis permits higher rejection values than the other membrane processes for the removal of metal ions [18].

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 [12][19]. 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 [20].

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 [21] [22]. Membranes, used in MF and UF, are characterized by large pore size and so cannot remove the ions [23]. 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 [24]. In addition, the regeneration and reuse of the complexing agent are possible in specific operating condition (e.g., pH of the solution).

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.

[25] 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. 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 [26].

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 [27]. The characteristics of the membranes and complexing agents are reported in Table 3.

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

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) 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. The authors restored the membrane performance by chemical cleaning (using the dilute chloric acid solution).

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) [28]. The best results have been found by adding 1200 mol (2 × 10−2 mol L−1) of polymer For this reason, chitosan exhibited better behavior than the other polymer [29]. 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 6 reports other results on heavy metal removal by using the UF coupled with the complexation process.

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 [30]. Considering this last aspect, Gao et al. [31] have studied the strength of the complex in the shear field by introducing a rotating disk in the membrane module (see Figure 2).

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 Ni2+ removal more than 98% has been achieved with a rotating disk speed lower than 848 rpm, In addition, the sodium poly-acrylate has been recovered by fixing the rotation of the rate at values higher than 848 rpm.

NF is more selective with divalent ions (rejection value more than 95%), while with monovalent ones the rejection ranged from 20% to 80% [32]. 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 [33]. 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 [32].

In 1999, Ahn et al. [34] 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. [35] 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.

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 [36]. 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). An increase in the feed flow rate has led to a rise of the rejection due to a concentration polar ionization reduction. [37] 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. [38] investigated the arsenic removal from model wastewater with commercial NF spiral-wound membrane modules and their characteristics are summarized in Table 8.

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. 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. 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. 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 [39]. 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 [40]. 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. Other results about applying NF process in removing heavy metals from wastewater are reported in Table 9.

RO membranes possess dense thin selective layers with small free volume regions and are capable of rejecting almost all ions. However, membrane fouling determines a flux decrease and a reduced membrane life [41][42]; the feed pretreatments reduce the fouling [43]. 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 [44]. They found that operating pressure, EDTA concentration, and temperature significantly influenced the permeate flux.

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. 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 [45]. 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.

(typical behavior of the polymeric membranes) [46]. Therefore, TFC membranes can preserve the desired selectivity only at low water permeance (1–20 $Lm^{-2} h^{-1} bar^{-1}$) [47]. 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 [48][49][50]. Currently, these membranes loaded with different inorganic particles are also applied in metal ion removal (see Figure 3)

Mixed matrix NF membranes have been prepared using the phase inversion method and their performance in toxic metal ion removal was studied [51]. In particular, the authors have chosen polyether sulfone as polymer and $CoFe_2O_4/CuO$ 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.

The MMMs are more hydrophilic than the pristine membrane owing to the hydrophilic character of the $CoFe_2O_4$//CuO nanoparticles. In addition [52]. 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.

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 [53]. 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 [54]. The finding was attributed to the changes in surface roughness and hydrophilicity.

Carbon nanotubes (CNTs) are a good candidate for the fabrication of new membranes for their excellent mechanical strength, good electron affinity, and high flexibility [55][56]. Anyway, their hydrophobic nature can cause agglomeration during the preparation of nanocomposite membranes. In a recent paper, functionalized CNTs (f-CNTs) have been added into polyvinylchloride solution for obtaining membranes with hollow-fiber configuration [57]. 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/ 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 [58]. 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 [59].

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 [60]. 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 [61]. 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) [62].

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 [63]. 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. This polymer presents in its chemical structure amino and hydroxyl groups that are capable of forming complexes with metal ions [64]. 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 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.

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%. 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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