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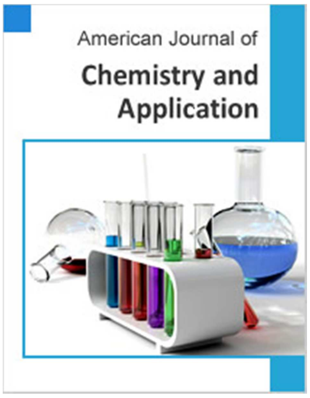

Membranes Selection for Effluent Treatment with Cadmium Sulfate

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Abstract
The membrane process that is unitary process has grown for effluent treatment due to reduce energy consumption and to be easy operation. Polymeric materials featuring high mechanical and thermal resistance have been widely employed in membranes preparation. The present work aims to investigate the performance of commercial membranes (polyamides and cellulose acetate) on the removal of cadmium sulfate, a highly toxic contaminant, largely found in industrial wastewater generated by steel industry, galvanization and other sources. Synthetic solutions of cadmium sulfate, at concentrations 150 and 500 mg L^{-1}, were used for membrane treatment (reverse osmosis and nanofiltration) at lab scale, concentrations, simulating processes from metal mechanics industrial wastewater. Experimental results indicated that the rejection degree for all reverse osmosis membranes were over 96%. It is important to point out that the Low Energy Reverse Osmosis polyamide membrane presented the best performance: water permeate flux (48.44 L h^{-1} m^{-2}) and heavy metal removal (98%). Besides it is biodegradable and features low chemical resistance to acid solutions, due to it has special morphology to treat brackish water at a low pressure.

1. Introduction

Industrial processes from metal mechanics usually demand a large amount of water and, consequently, generate a great amount of liquid effluents. These effluents are contaminated with heavy metals that are extremely pollutant and require treatment before being discharged into the environment [1-2]. Therefore, the environmental impact caused by industries will be greatly reduced by the heavy metal removal using membrane processes [3-8].

Stringent regulations have increased the demand for new technologies for metal removal from wastewater to attain today's toxicity-driven limits [3, 5]. Cadmium (Cd) has attracted wide attention of environmentalists as one of the most toxic metals. The major sources of cadmium into the environment have been generated by waste streams of electroplating, smelting, alloy manufacturing, pigments, plastic, battery and, mining processes [2, 6, 9]. It has been recognized for its negative action on the environment where it readily accumulates in living systems. Its accumulation on human beings systems causes illnesses such as bone lesions, a varied number of cancer and hypertension [10].

Considerable research has been carried out in developing cost-effective heavy metal removal techniques. Physical-chemical methods, such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, solvent extraction and ion-exchange processes, have been traditionally employed for heavy metal removal from industrial wastewater [3, 5]. However, these processes are not satisfactory technological solution where the concentration of heavy metals is above 100 mg L^{-1} [1, 11]. In this case, the separation process using membranes is highly efficient in removing salts and heavy metals, in addition to being cost-effective. Effluent treatment systems like these have been the object of keen interest from many environmental field researchers [8, 12-14]. Then, reverse osmosis and nanofiltration processes have been increasingly used by scientists and industries in global wastewater treatment for removal of salt, heavy metals, colorants and other dissolved substances due to high removal efficiency, easy operation, and lacks of chemical products during the process [2, 4, 6, 12].

The aim of this work is evaluate commercial membranes performance used for the separation process (reverse osmosis and nanofiltration) using synthetic solution of cadmium sulfate at low concentrations, simulating processes from metal mechanics industrial wastewater. Heavy metals removal, water permeate flux and hydraulic permeability were the main parameters investigated by membrane process.

2. Materials and Methods

2.1. Forward Osmosis System and Module

The experiments were run on a bench-scale laboratory system. The system was operated in batches, by dead-end flow and required the use of nitrogen as driven force. A schematic diagram is presented in Figure 1.

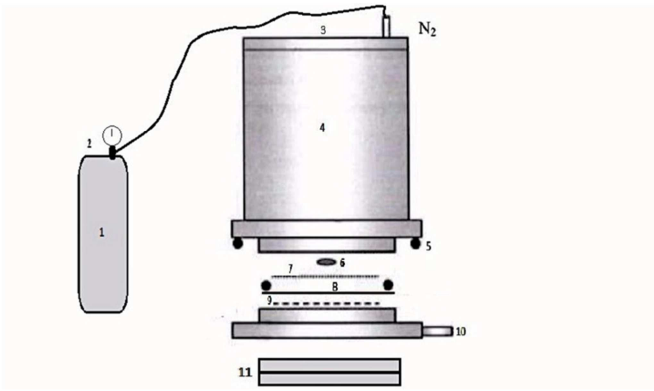

Figure 1. *Experimental set-up: 1–nitrogen, 2–manometer, 3–membrane module, 4–feed/concentrated, 5 -oring, 6–magnetic shaker, 7–screen protection, 8–membrane, 9–porous middle, 10–permeate, 11– magnetic plate.*

The experimental set-up a flat sheet membrane is placed in a stainless steel cell (78.5 cm^2), which allows frontal flow of the feed stream, constant flow feed, temperature and pressure.

2.2. Membranes

Four commercial membranes were selected for effluent treatment, as specified on Table 1. All membranes were measured three times in different parts on the same temperature (25°C) and pressure conditions (1 bar), with Mitutoyo micrometer external (model 103-178).

Table 1. *Commercial membranes used to heavy metal treatment.*

Membrane Code	Polymeric Matrix	Membrane Process	Thickness (μm)	Manufacturer
HRP98PP	Cellulose Acetate	Reverse Osmosis	40	Alfa Laval
SW30	Polyamide	Reverse Osmosis	20	Filmtec Dow
BW30LE	Polyamide	Low Energy Reverse Osmosis	20	Filmtec Dow
NF-90	Polyamide	Nanofiltration	20	Filmtec Dow

2.3. Feed and Draw Solutions

The solutions of $CdSO_4$ were prepared from $CdSO_4.8H_2O$ (VETEC, PA) with pH around 5.5, adjusted with the addition of HCl or NaOH at 0.1M. The system was operated at room temperature (25±2°C).

The synthetic effluents containing cadmium sulfate at two concentrations (150 and 500 mg L^{-1}) were used in the feed system, and the system pressure was continuously monitored at 10 bar for reverse osmosis membranes and 2 bar nanofiltration membrane, the same procedure was done to collect the permeate, but in these tests the ionic conductivity of the solutions also was measured, with the objective of calculating the cadmium rejection degree.

2.4. Experimental Procedure

The system was initially operated with one liter of pure solvent (deionized water), using mechanical stirring and maintaining a constant pressure of 20 bar for all membranes to compress them. After this, it was applied operation pressure of 20, 15, 10 and 5 bar, respectively, for all membranes. Permeated were collected all along the process, in test tubes of 50 ml, in order to calculate the hydraulic permeability. The experimental procedures, which can take 1 or 2 hours, were always replicated.

The permeated concentrations were achieved in an indirect way, by producing a calibration curve with different cadmium sulfate concentrations. The heavy metal concentrations referred in this paper were previously determined by atomic absorbance spectrometry and were correlated with the corresponding conductivities. The tools utilized to achieve the calibration curve were the Atomic Absorption Spectrophotometer - FAAS, Perkin Elmer Analyst 300 and the Thermo Orion Conductivimeter.

The water permeates flux (J, $L.h^{-1}$ m^{-2}) and the hydraulic permeability (L_p, L h^{-1} m^{-2} bar^{-1}) were determined by Eq. (1)

and (2), at different operation conditions. The salt or ion rejection degree (R,%), Eq. (3), was usually applied to characterize the efficiency of the separation membrane process.

$$J = \frac{V}{A.\Delta t} \quad (1)$$

$$L_p = \frac{J}{\Delta p - \Delta \pi} \quad (2)$$

$$R = \left[1 - \frac{C_p}{C_f}\right].100 \quad (3)$$

Where, V is the permeate volume (L), Δt is the time interval (h), A is the membrane superficial area (m^2), Δp and Δπ are the pressure and osmotic pressure differences (bar), C_f and C_p are the ion concentration in the feed and permeate solution, respectively.

The permeate flux is directly proportional to the pressure gradient; however, the global permeability coefficient may present a strong dependence on the system operating conditions (Pressure and Temperature) as well as on the physical-chemical properties of the membrane and the solution to be processed [3, 12].

3. Results and Discussion

The separation membrane process was carried out with deionized water under pressures of 20, 15, 10 and 5 bar, respectively; in order to meet the NF-90, SW30, HRP98PP and BW30LE membranes (Figure 2) hydraulic permeability.

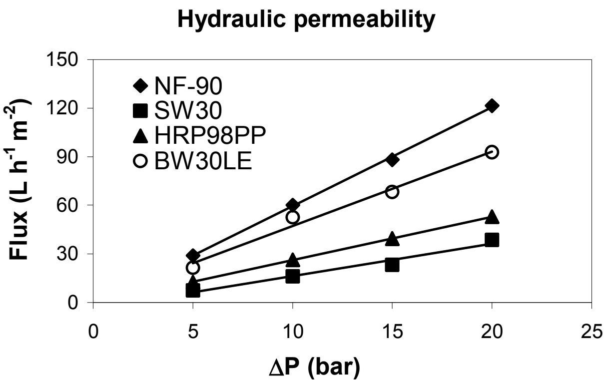

Figure 2. Hydraulic permeability of NF-90, SW30, HRP98PP and BW30LE membranes obtained varying operation pressure and therefore their water fluxes.

The hydraulic permeability considers in its calculus the effects of the membranes' thickness and water affinity Hence, through Figure 2, it was possible to know the membranes' hydrophilic feature. However, the supports weren't pondered during the discussion, due to the most important fact in this work, which is to select one membrane that has the highest water flux and ion rejection, in order to remove Cd of industrial wastewater avoiding the contamination of the environment. How it showed in the results (Figures 3 and 4) that allow seeing the behaviors of different membranes during the process of cadmium sulfate removal.

Hydraulic permeability (Lp) is an inherent constant to each membrane and can be obtained by the coefficient angle of the straight flux in function of the pressure variation applied to membrane, as already described by

Eq. 2. Thus, the Lp's of the NF-90, SW30, HRP98PP and BW30LE membranes were equal to 6.10, 2.00, 2.68 and 4.58 L h^{-1} m^{-2} bar^{-1}, respectively.

The nanofiltration membrane (NF-90) obtained the higher hydraulic permeability. It is known that a membrane with nanofiltration characteristic (NF) presents a higher flux on higher operation pressure, due to its predominant transport engine is convection instead of diffusion [15]. So, as all reverse osmosis membranes have the diffusion with the transport mechanism, it was possible to check that the BW30LE has the second higher hydraulic permeability, followed of HRP98PP and SW30.

The Figure 3 illustrates the ion retention and membranes permeate fluxes, in the feed solution of cadmium sulfate at 150 mg L^{-1} at pH 5.5 was used on reverse osmosis membrane with pressure of 10 and on nanofiltration membrane at P = 2 bar.

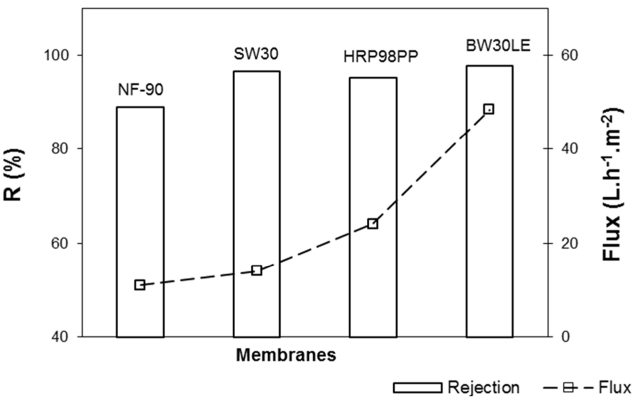

Figure 3. Rejection degree and water fluxes of NF-90, BW30LE, SW30 and HRP98PP membranes at 150 mg.L^{-1} of cadmium in the feed solution.

Experimental results presented follow ascending order of ion retention by the membranes: NF-90 < HRP98PP < SW30 < BW30LE. The membrane BW30LE had ion retention above 97% and a greater water flux. This result is likely attributed to the membrane's morphological characteristics [15, 16], which were not investigated in this work. As expected, the nanofiltration membrane (NF-90) obtained the lowest ion retention, below 90%, because its nanopores facilitate the passage of heavy metals. On the other hand, the reverse osmosis membranes (SW30 and HRP98PP) have exhibited high ion retention (over 95%), but their fluxes were different.

The water fluxes for the reverse osmosis membranes occur in the following ascending order: SW30 < HRP98PP < BW30LE. The BW30LE membrane obtained high removal of cadmium sulfate and greater flux (48.44 L h^{-1} m^{-2}) than other commercial membranes. Its membrane performance is specific to treat brackish water, which has less salt concentration. Then, its active layer is lower than those of other reverse osmosis membranes (Redondo, 2001). Moreover, fixed functional groups in the polymeric matrix can also provide higher affinity for water induces a higher water flux [16]. The SW30 and HRP98PP obtained water flux of 14.08 and 32.68 L h^{-1} m^{-2}, respectively. This value is directly corresponding their hydraulic permeability, as well as it is represented in Eq. 2, for the similar operation pressure (10 bar). The nanofiltration membı (a) '-90) obtained water flux equal 11.00 L h^{-1} m^{-2} on ı pressure of 2 bar, this flux is less than the others membranes due to the less pressure operation applied on membrane. Because the nanofiltration membranes decrease its ion retention with the increase of the pressure, and the most important in this work is remove the cadmium, which is very toxic.

The Figure 4 shows the ion retention and membranes' water fluxes. In this case, a feed solution of cadmium sulfate at 500 mg L^{-1} at pH 5.5 was used on reverse osmosis membrane with pressure of 10 and on nanofiltration membrane at P = 2 bar.

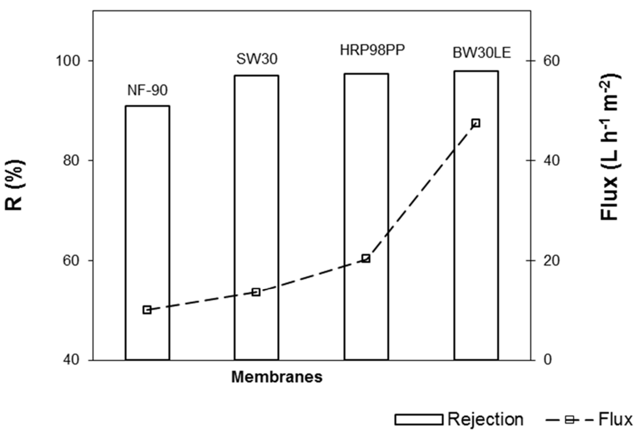

Figure 4. *Rejection degree and water fluxes of NF-90, BW30LE, SW30 and HRP98PP membranes at 500 mg L^{-1} of cadmium in the feed solution.*

With the cadmium sulfate concentration in the feed solution was equal at 500 mg L^{-1}, the solute retentions of three membranes remained constant; however, their respective permeate fluxes were modified. The reverse osmosis membranes showed ion retention above 97% and water flux in the range of 10-47.56 L h^{-1} m^{-2}. The NF-90 membrane obtained ion retention lower than 92%. This is high ion retention for the nanofiltration membrane and though the water flux was approximately 10 L.h^{-1} m^{-2} at 2 bar with driving force. The membrane SW30 achieved a water flux of 13.61 L h^{-1} m^{-2}, mainly when compared to the acetate cellulose membranes (HRP98PP) and the low-pressure polyamides (BW30LE) with water fluxes of 20.33 and 47.56 L h^{-1} m^{-2}, respectively.

The HRP98PP membrane has a flux lower than the BW30LE. However, its thickness is twice bigger. How the flux is reversely proportional the membrane thickness, the acetate cellulose membrane might has great water flux if it was less thick.

When the concentration of cadmium sulfate solution increased about 150 to 500 mg L^{-1}, It was observed that occurred an increase in ion rejection, however the water flux decreased in all membranes. Since ion rejection and water flux are antagonists. This fact may be correlated with polarization of concentration that is an interfacial phenomenon caused when the feed concentration increase the resistance into the system hindering the solvent transport.

4. Conclusion

All membranes evaluated showed suitable to remove heavy metal in industrial wastewater contents cadmium sulfate. Although the nanofiltration membrane (NF-90) shows a higher hydraulic permeability, due to its nanopores and the contribution of the convective transport, its average ion rejection degree at Cd^{2+} was not higher than reverse osmosis membranes. Therefore, the most competitive membranes for cadmium sulfate removal were the cellulose acetate reverse osmosis membrane (HRP98PP) and the low energy reverse osmosis membrane (BW30LE). They presented excellent ion rejections degree and water fluxes at the investigated operating conditions. However, the BW30LE offers more advantages than the cellulose acetate membranes, since the latter is biodegradable, features low chemical resistance to acid solutions and use few pressure to operate, expending less cost.

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