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Comparison of the bromate ions removal by nanofiltration membranes under different operating conditions

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ABSTRACT

Bromate is toxic compound which represent the carcinogenic effect for human health, a serial research's has been developed by the scientists for the efficient bromate removal methods from the water with low cost in order to obtain water to Bromate a maximum concentration level (10ppb). Bromate ions are formed as a result of the reaction between bromide ions and ozone used as a water disinfectant in membrane demineralization plants Different technologies have been used for Bromate elimination from water such as ion exchange, adsorption, biofiltration, electrolysis and membrane technology. The aim of this work is to study the rejection of bromate ions by nanofiltration membranes (N30F from Nadir and DL from Osmonics) made from different polymers using bromate solution at different conditions (feed bromate concentration, transmembrane pressure, pH and ionic strength).The bromate rejection is related to the feed solution, pH and ionic strength and the nature of the membrane. At pH=8, bromate ions were removed by the DL membrane made from polyamide around with higher than those by the N30F made from polyethersulfone .

1. Introduction

The presence of bromate in drinking water is considered as a potential carcinogen for humans. Several research has been tested for the development of effective methods with low cost in order to reduce the concentration of bromate ions below acceptable standards of the World Health Organization (WHO). (10 ug/l)[1],[2],[3]. Bromate (BrO_3^-) is formed after the ozonation of ground and source water and results from oxidation of bromide (Br^-), which naturally exists in ground water [4],[5]. It is also a contaminant in hypochlorite solutions produced by electrolysis of salts and seawater containing bromide [6], Following the ozonation process, it has been proved that the Bromate ions concentration formed can exceed 50 μg/L for a bromide ions concentration greater than 100 μg/L. Different methods can be used for promoting removal Using various technologies including filtration, photocatalysis, arc discharge, chemical reduction, activated carbon techniques, and biological remediation [7]. Membrane processes can be considered a promising technology for removing Bromate from water. The application of membrane technology in the depollution of water with a relatively low energy cost, no requirement of chemical substances to be added. Reverse osmosis (RO) can remove BrO_3^- [8], [9], but it is an expensive process, as membrane fluxes are low and high operating pressures are needed. The variation of the membrane surface charge is mainly due to anion adsorption of water rather than to fixed charged groups, the Bromate removal from water by nanofiltration membranes. Most research has shown that the surface properties of nanofiltration membranes affect the separation of solutes and this following strict exclusion effect of pore size, but also the phenomena of repulsion and attraction of the charges found on the surface (Donnan exclusion phenomenon) [10]. It has been reported that the nanofiltration membranes with a molecular weight cut off of 150 to 300 a reject up to

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50% of ions from low-turbidity water source and it was found also that BrO_3^-can be effectively rejected in the range between 90% to 95% by nanofiltration membranes due to the charge repulsion mechanism[11],[12]. Sarper and coworkers reported that polyamide nanofiltration (NF) NE90 membrane are very effective at BrO_3^- removal. The removal of BrO_3^- ions by the NE90 membranes was in the range between 75 % to 90% [13]. The efficiency of Bromate control at lower pH values depends on the water quality, particularly the alkalinity. The aim of this research work is to study the effect of the operating conditions on the rejection of bromate ions by nanofiltration membranes (DL and N30F) made from different polymers (polyamide and polyethersulfone). The performance of each nanofiltration membrane was evaluated with relation to both permeate flux and bromate rejection as a function of pressure, Bromate ions concentration in feed solution , pH. and ionic strength.

2.Materials and methods

2.1. Standards and reagents

A standard stock solution of 1000 ppm of BrO_3^- was prepared by dissolving required mass of the reagent grade NaBrO3 (Reagent grade; Fisher Scientific) in dionised water. synthetic solution of BrO_3^- with different concentrations from 100 to 1000 ppb by appropriate dilutions of a 1000 ppm stock solution.

2.2. Membrane properties

The membranes selected for the experiments has different properties such as the chemical composition of the thin layer, the molecular weight cutoff, the permeability, the contact angles and the pores size (table 1)

Table 1 Physical and chemical membranes characteristics [15], [16], [17]

Membranes	DL	N30F
Manufacturers	Osmonics	Nadir
MWCO (Dalton)	150-300	400
Permeability (L/m^2h bar)	8.2	4.11
Roughness (nm)	10.9	3
Max Temperature	90	95
Contact angles	44	88
Radius of pores (nm)	0.52	0.74
pH ranges	1-11	1-11
Composition of skin layer	Polyamide	Polyethersulfone
Zeta potential (mv) pH between 4 to 10	Negative	Negative

3. Description of the pilot unit

The experiments of the nanofiltration membranes were carried on a small dead end filtration unit.The cell was pressurized and supplied by nitrogen gas and the pressure will be controlled by a gas pressure regulator. The solution was stirred by a digital magnetic plate. After each filtration test, The permeate solutions were harvested using a graduated cylinder and the permeate weights were measured with a digital balance.

In order to study the influence of the operating conditions on the retention of bromate ions, it was decided to make the tests under different operating conditions taking into account the variation of the pressure between 2 to 10 bars and the pH 4,7 and 10; the variation of the bromate ion concentrations from 100 to 1000 ppb and the ionic strength: 0.005 M NaCl, 0.01 M NaCl, 0.1 M NaCl.

4.Bromate analysis method

The Bromate ions will be analyzed using an ionic chromatography instrument equipped with Dionex ICS-3000 with conductivity detection.

5.Mathematical calculation of permeate flux

The permeate fluxes (J_v) was determined by measuring the volume of the permeate in a given time interval by the following equation:

$$J_v = \frac{V}{t \times S} \qquad \textbf{Eq1}$$

J_v: Flux ($L.h^{-1}.m^{-2}$)
t:time (min)
V: volume of the permeate
S: The membrane surface (m^2)

6.Mathematical calculation of bromate rejection

The rejection efficiency of Bromate species was determined using the following equation:

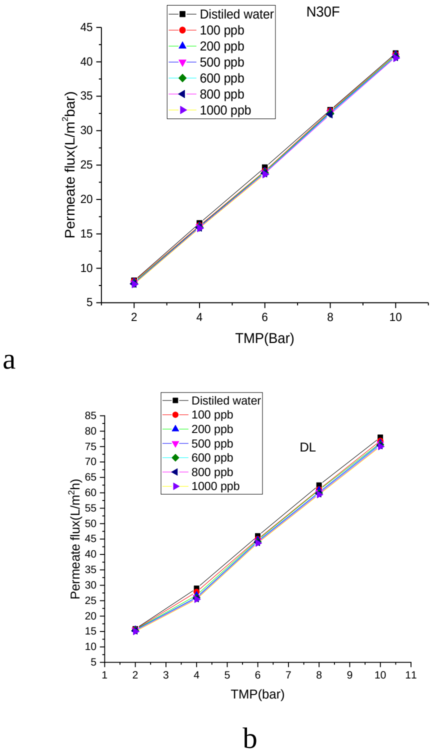
$$R(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \qquad \textbf{Eq2}$$

Where R is the rejection and C_0 (mole/L), C_p (mole/L) are the solute concentrations in feed and permeate, respectively. The relation between the feed and permeate concentration was converted into the rejection efficiency. pH was measured by an Orion Expandable ion analyzer EA 920 pH meter (Allometrics, Inc. LA, USA) with automatic temperature compensation.

7.Results and discussion

7.1. Monitoring of permeate fluxes and bromate removal at different pressure

The results represented in the figure 1 gives the same paces with a linear increase of the permeate fluxes according to the pressures for all the BrO_3^- concentrations It was observed across the membrane N30F that the permeate flux was not influenced by the variation of the concentration of bromate in the feed solution, while the permeate flux for the DL membrane **(Fig.1)**. These results suggested that the water flux through the DL membrane should be affected by the solute permeate flux at different bromate feed concentration. It was observed that the bromate concentration in the permeate of the DL membrane was lower than to the maximum concentration level (10 ppb) **fig2**. Referring to the calculation of the rejection by Eq2, It was shown the rejection of Bromate as a function of TMP for the nanofiltration membranes at a feed Bromate concentration of 100 ppb, a pH of 7 and temperature of 25°C that The removal of Bronte by DL membrane is higher than the value observed with the N30F membrane; For the DL membrane, the rejection is higher than 90%, while for the N30F membrane the rejection towards Bronte was higher than 30%. This phenomenon can be explained assuming to the difference of MWCO between two nanofiltration membranes.



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b

Fig.1: Permeate fluxes versus the pressure at different bromate concentrations Temperature=25 C, pH=8.

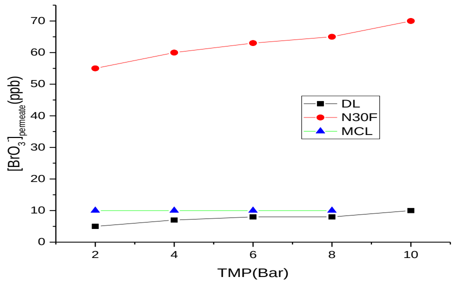

Fig.2: $[BrO_3^-]_{permeate}$ versus hydraulic pressure ($[BrO_3^-]_{feed}$=100 ppb,pH=8).

7.2. Effect of bromate concentration on permeate flux and bromate removal

Figure 3 shows the effect of the Bromate concentration in the feed solution on the permeate flux for the nanofiltration membranes at a transmembtane pressure of 4 bar and a temperature of 25^0C. Basically, there is no effect of promoting concentration on the permeate flux.

The Fig4 shown high bromate rejection efficiency for DL membrane in all Bromate concentration ranges, however, it should be observed that the Bromate rejection by the N30F membrane decrease with increases of promoting feed concentration. The DL membrane showed higher Bromate rejection compared to the N30F membrane, at all ranges of the bromate feed concentration

The nanofiltration test with DL membrane show that the bromate ions concentration detected in the permeate was lower than the maximum concentration level in the concentration ranges comprised between 100 to 500 ppb and slightly higher or equivalent to the maximum concentration level at promoting concentration up to 500 ppb.

However, The concentration of Bromate in the permeate with using of the N30F membrane was higher to the Maximum concentration level of 10 ppb at all feed bromate concentration range.

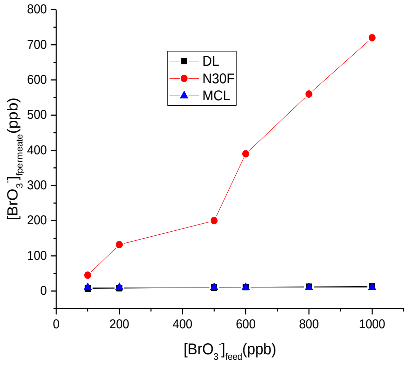

Fig.3: Effect of variation of bromate concentration on the bromate rejection by the nanofiltration membranes (T=25°C ;P=6 bar,pH=8).

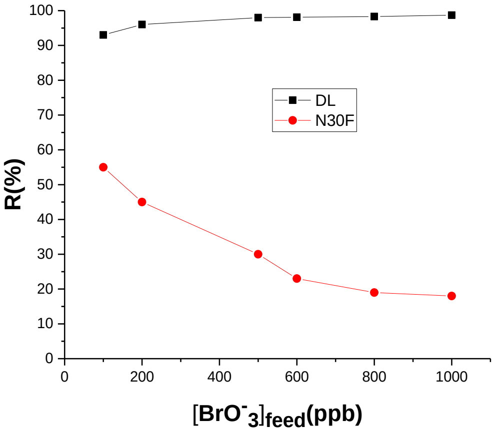

Fig.4: Effect of bromate concentration in bromate rejection (T=25°C, P=6 bar,pH=8).

7.3. Influence of pH on permeate flux and bromate rejection

The effect of pH on the permeate flux for the nanofiltration membranes, at a feed Bromate concentration of 500 ppb, a temperature of 25 0C and a

TMP of 6 bars, is represented in the Fig 5. The curves of each membranes has steady pace with a slight increase up pH=8 for the membrane DL.

The rejection of bromate ions by DL membrane is higher to 94% with a slight increase up to pH=8 with rejection high values between 96% to 96.88% at pH=10.The results obtained by N30F membranes shown increase of bromate rejection between 25% at pH=4 to 55% at pH=8 with slight increase to 57% at pH=10.

These results can be interpreted as follows:

For pH comprised between 4 to 7, the neutral form of However is dominant while the $BrO_3^-$is dominant above pH of 8. Bromate anion can be rejected by the effect of repulsion because the DL membrane was charged negatively (Table 1) with MWCO of 300 DA. For pH above 8, the less dominance of BrO- specifically with a competition effect between BrO^- and BrO_3^-, which cause electrostatic repulsion between these species. For the DL membrane, the Bromote rejection increased from 94% to 98.4% in the range of pH investigated (4–10). This membrane is negatively charged in the neutral pH region and, similar to the N30F membrane, it becomes more negative as the pH value increases: therefore charge exclusion strongly effects the rejection. The minimum values bromate concentration in the permeate is found to pH = 8 with a lower bromate concentration relative to the maximum concentration level

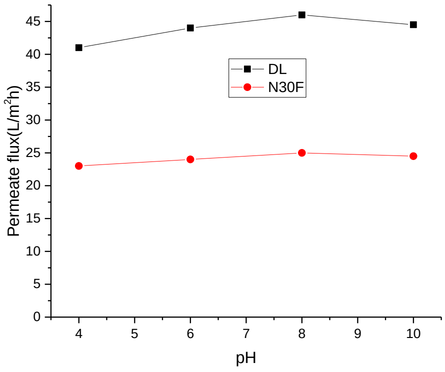

Fig. 5 Effect of pH on the permeate flux for DL and N30F membranes (feed concentration [500 ppb, temperature=25 8C, TMP=6 bar).

7.4. Effect of ionic strength on the rejection of bromate by nanofiltration membranes

Figure 6 shows the permeate fluxes with 0.005 M, 0.01M, 0.1M sodium chloride solutions at a TMP range between 2 to 10 bars. The permeate fluxes for sodium chloride runs decreased with increasing of transmembrane pressure. this is due to the higher concentration polarization effect at high concentration which enhanced the osmotic pressure at the membrane boundary layer and subsequently reduced the permeate flux. Under the effect of variation of the ionic strength, the Bromate rejection by both membrane has been founded with values of 95 % for DL and 80% for the N30F at ionic strength. The increase in transmembrane pressure causes rating decrease the rejection of bromate ions by DL and N30F nanofiltration membranes. The results obtained show that the DL membrane retains bromate ions at a rate with lower values compared to the maximum concentration level. The retention rate of the bromate ions by the DL membrane is very high, which makes it possible to achieve bromate ion concentrations in the permeate lower than the maximum permissible of 10 ppb

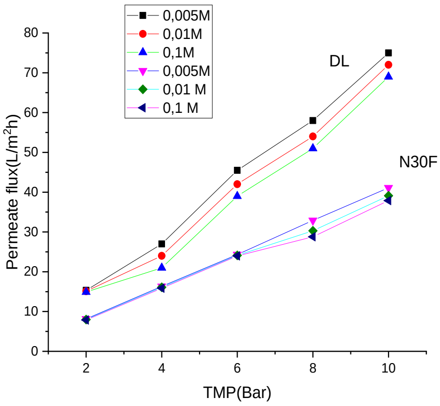

Fig.6: Effect of the ionic strengh on the permeate fluxes ($[BrO_3^-]_{feed}$=100ppb, T=25 °C, TMP=6 bar).

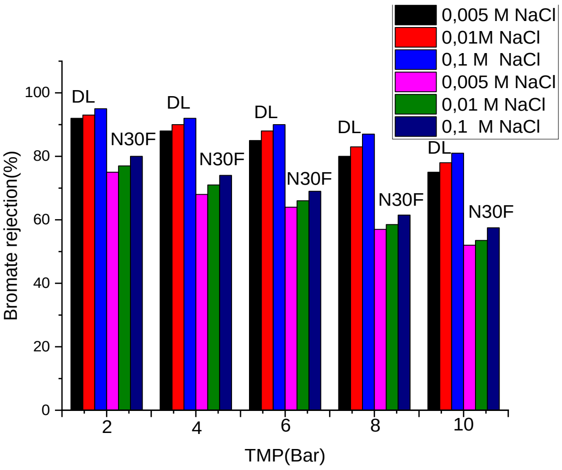

Fig.7: Effect of the ionic strengh on the bromate rejection ($[BrO_3^-]_{feed}$=100ppb, T=25°C).

8. Conclusion

Bromate removal from synthetic water was studied by using two nanofiltration membranes (DL and N30F) made from different polymers (polyamide and polyethersulfone). For both membranes the removal efficiency for BrO_3^- was influenced by the operating conditions such as transmembrane pressure, pH , feed water concentration and ionic strengh.

Particularly, the bromate rejection of the DL membrane was higher compared with the N30F membrane (above 90 %) for all the operating conditions investigated. The bromate ions are very rejected by the polyamide nanofiltration membrane, this is confirmed by the concentration values below the maximum contamination level (10 µg /l) and for a bromate concentration in the feed solution between 100 and 500 ppb. As a common trend, it was observed that an increase of the concentration of bromate ions in the fees solution , pH and ionic strength determined a higher rejection efficiency of bromate ions removal by the two nanofiltration membranes, whereas the pressure slightly affected the bromate rejection by the N30F membrane at higher pressure .It has been found an Increasing permeate flow with pressure up to a limit value at a pH of about 8. The performance of bromate ions by the membrane made from polyamide is higher compared to the nanofiltration test by the polyethersulfone membrane, which highlights the mechanisms of diffusion of bromate ions within the polymeric matrices

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