

EFFECT OF MONOCHLORAMINES ON POLYAMIDE MEMBRANES IN REVERSE OSMOSIS

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Abstract. The membrane separation technology, especially reverse osmosis, is used as an alternative to water production with higher quality and also to wastewater treatment in industrial process for its reuse. However, the use of the membranes is limited by its lifetime which varies according to the species and amount of impurities present in the effluent and the frequency of cleaning. Some impurities also can propitiate the development of microorganisms in the flow channels and on the surface of the membranes that, in some extend, will contribute for the membrane degradation, this phenomenon is known as biofouling. To prevent biofouling is necessary an efficient disinfection process in the feed stream of the reverse osmosis unit, to promote the death of the microorganisms and the oxidation of the organic matter. Chlorination is the practice adopted in many industries, but chlorine can cause environmental damage, health hazards in the industry and damages the polyamide membranes. It is necessary to find a less aggressive agent to the environment and to the polyamide membranes. The objective of this work is to study the effect of the monochloramines on the polyamide membranes in the reverse osmosis process. The inorganic chloramine is less effective as a chlorinating agent than free chlorine but is capable to reduce the total population of bacteria to an acceptable level. The experiments had been carried out in a laboratory scale reverse osmosis unit using solutions of monochloramines (~ 500ppm) and polyamide membranes. It was verified that the permeate flux increases linearly with the exposition time of the membranes to the monochloramine solutions. The saline retention also presented modifications, however monochloramines seems to be less aggressive than chlorine under similarly conditions.

Keywords: Water Disinfection, Reverse Osmosis, Polyamide Membranes, Chloramines

1. Introduction

The application of membrane filtration in water treatment enables the production of biologically safe and stable drinking water by removing microorganisms and inorganic and organic compounds. However the quality of the feed water supply is the single important factor to be considered to ensure the technical and economical viability of a membrane plant.

The presence of impurities can propitiate the development of microorganisms in the flow channels and on the surface of the membranes causing decrease of the permeate flux and the degradation of the membrane. This phenomenon is known as biofouling. To prevent biofouling is necessary an efficient disinfection process in the feed stream of the membrane unit, to promote the death of the microorganisms and the oxidation of the organic matter.

The methods commonly used for the disinfection are ultraviolet radiation, ozonization or addition of oxidant agents such as chlorine, chlorine dioxide, peroxide of hydrogen, chloramine, among others.

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Tanaka et al. (1994) detaches that one of the most important considerations in assessing disinfectants is balancing biocidal effectiveness with by-product formation. They have found that chlorine has the greater potential for generating harmful by-products.

The chlorination is the alternative normally used in the conventional water treatment processes, however aqueous chlorine can cause damage on polyamide membranes, which is a common reverse osmosis (RO) membrane barrier layer material. The manufacturers normally recommend that the concentration of chlorine should be lower than 0.1ppm.

Butterfield (1948), Brodtmann and Russo (1979), cited in the document of USEPA (1994), affirm that inorganic chloramines have been considered poorer disinfectants than hypochlorous acid, but capable to reduced the total population of bacteria to an acceptable level.

Another factor that must be considered is the biocide activity after the disinfection to assure the quality in the water distribution system, mainly when the water is used for human consumption. Chlorine, chloramine and chlorine dioxide present a good residual disinfection effect but ozone and ultraviolet radiation do not. Moreover, chlorine, chloramine and chlorine dioxide easily permeate through the membrane because they have low molecular weight and affinity with water.

The mechanism of chlorine attack on polyamide membrane is investigated in several researches. Glater, Hong and Elimelech (1994) suggest that ring chlorination is considered to take place by two possible reaction pathways. In the first, direct aromatic substitution is suggested. A second mechanism, known as the Orton Rearrangement, involves initial chlorination of amide nitrogen that after rearrangement involves attack to the aromatic ring.

According to Soice et al. (2000), cited for Gabelich et al. (2002), no cleavage of the amide bond takes place, but either N-H chlorination or aromatic ring chlorination could be occurring, resulting in morphological changes in the membrane surface.

Avlonitis, Hanbury and Hodgkiess (1992) have suggested that a two-step chlorine degradation mechanism is occurring on polyamide membranes. In the first step the chlorine transforms the crystalline regions of polymer in amorphous. In this stage the performance separation membrane is apparently not influenced. In the second step chlorine attacks the amorphous regions resulting in an increase of salt permeation through the membrane.

Chloramines are weaker oxidants than aqueous chlorine and have been found that they could be compatible with polyamide membranes in some applications, Soice et al (2000).

Besides, oxidation of membranes is a complex phenomenon due to the large diversity of substances present in the feed water which may interfere in some extent. Gabelich et al. (2002) studied the effects of aluminum sulfate and ferric chloride coagulant residuals on polyamide membrane performance using chloramine as disinfecting agent. The initial results have demonstrated that chloramine can cause membrane degradation. However this result revealed uncertain in complementary tests in the absence of chloramines where membrane degradation also was observed.

The aim of this work is to study the effect of monochloramine (MCh) solution on polyamide membranes in the RO process, since this disinfection agent could represent a good alternative to the substitution of chlorine in the water disinfection resulting in higher water quality and minor environmental impact.

Also it was carried out some experiments to evaluate the catalytic effect of membrane oxidation caused by the presence of iron and aluminum in the MCh solution. These metals could be incorporated in the water during the clarification step as coagulating agents, and remain in small amounts until the end of the process.

1.1. Physical and Chemical Properties of Chloramines

According to Vikesland, Ozekin and Valentine (2001) inorganic chloramines include MCh, dichloramine and trichloramine, however, MCh is the predominant specie under the conditions typically found in drinking water treatment.

Gash (2002) affirm that the disinfection performance of the MChs is superior that of dichloramines, trichloramines and organic chloramines, but they present a lower disinfecting potential than ozone, chlorine dioxide and free chlorine.

Johnson et al. (2002) suggest the preparation of MCh solutions adding sodium hypochlorite (NaOCl) in a solution with ammonium chloride (NH₄Cl) under vigorous stirring. MChs are produced according to Equation (1).



The document of USEPA (1994) relates that the distribution of mono-, di- and trichloramines depends on pH, temperature and the relative ammonium and hypochlorite concentration.

2. Materials and Methods

2.1 Membranes

Commercial thin film composite polyamide membranes had been used in the experiments. A thin film composite membrane consists of a thin active layer of polyamide cast on a thicker supporting layer of polysulfone. The RO membranes tested are the ACM1-TSA (called ACM) manufactured by TRISEP and CPA3 (called CPA) manufactured by Hydranautics.

Before the experiments, the saline rejection of each piece of membrane has been measured and compared with the data supplied by the manufacturer. When the value of saline rejection was different from the specified, the pieces of membranes were rejected. This procedure was adopted to make the comparison of the results easier.

2.2 Reagents

The chloramine solutions were prepared with analytical ammonium chloride (Nuclear, Brazil) and commercial sodium hypochlorite 10 to 12% v/v, supplied for Laborpeq.

The chloramine solutions were prepared with an excess of ammonium chloride in order to assure the MCh formation with total consumption of chlorine. Sodium hydroxide solution was used to adjust pH of the chloramine to maintain its value higher than 8.

In one second stage of this study, iron and aluminum were added to the chloramine solution to test if these substances can behavior as catalysts of the degradation reaction in the membrane. Hex-hydrated ferric chloride, grade for analyses by Nuclear, and commercial aluminum sulfate, supplied for the Laborpeq, were used in the preparation of the MCh solutions.

Analytical sodium chloride (Synth, Brazil) was used to prepare the 2000ppm concentrated solutions for evaluation of the membrane performance.

2.2 Analytical Methodology

Quartz cells with a 1.00cm path length and Varian Cary 300 spectrophotometer UV were used for the absorbance measurements. This equipment is connected to a computer provided with Cary WINUV software.

Sodium hypochlorite concentration in the commercial reagent was evaluated, prior to the start of the preparation of the chloramine solutions, by measuring the absorbance at 293nm, that presents a molar absorptivity at $350 \text{ mol}^{-1} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$ in water.

MCh concentration was evaluated by measuring the absorbance at 245 and 231nm. These wavelengths present respectively a molar absorptivity of 320 and $445 \text{ mol}^{-1} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$ for MCh and of 208 and $591 \text{ mol}^{-1} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$ for dichloramine, according to Valentine, Brandt and Jafvert (1986).

The aluminum and iron concentrations were determined by spectrophotometry, the samples were prepared with reagent kits of MERCK, codes 14761 for aluminum and 14825 for iron and the measurements were accomplished in the spectrophotometer Spectroquant NOVA 60.

The membrane salt rejections were evaluated by measurements of electrical conductivity of samples collected during the retention experiments. The equipment used for these analyses was the condutivimeter Digimed DM-3, with electrode model DMC-010M.

2.3 Experimental Methodology

To evaluate the effect of MCh solutions on polyamide membranes several experiments were carried out in a laboratory scale RO system. Thus the membranes were put in contact with MCh solutions during the operating period of the membrane unit.

The modifications of membrane performance were evaluated by comparison of the values obtained for permeate flux and saline rejection before and after the experiments with MCh solutions. The tests used for this analysis are called retention experiments.

The retention experiment consists of the measurement of permeate flux and saline rejection of the membranes under the following operating conditions: pressure of $8 \text{ kgf} \cdot \text{cm}^{-2}$, feed flow rate of $4 \text{ L} \cdot \text{min}^{-1}$, temperature of 25°C and sodium chloride solution 2000ppm concentrated.

The observed retention (R_e) consists of the ratio between the concentrations that passes through the membrane (C_p) and the concentration of the outlet stream (C_c), according to Equation 2.

$$Re = \left(1 - \frac{C_p}{C_c} \right) \cdot 100 \quad (2)$$

However all the data were normalized to make the comparison more realistic. Saline rejection values and permeate flux values equal to 1 represent the initial condition of a new membrane. Values greater than 1 represent an increase on the permeate flux or saline rejection, and values lower than 1 represent a decrease on the permeate flux or saline retention.

3. Results and Discussion

The membrane manufacturers inform that when polyamide membranes are exposed to free chlorine, under operational conditions in a RO unit, they are severely attacked by this oxidant.

However Vargas (2003) observed that polyamide membranes were not attacked when they are only immersed in free chlorine solutions without any disturbance, but they were attacked when they are submitted to the operational conditions in a RO unit. For this reason, in the present work, the effect of the MChs on polyamide membranes was evaluated studied only under typical operational conditions of a RO system.

Another important concern is that the chloramine solutions are very unstable, i.e., concentration decreases with time, even without the presence of reactive inorganic or organic substances, when exposed to the room conditions. Thus, it was necessary add fresh concentrated solution after a period of 6 hours to keep MCh concentration almost constant during the experiments.

The chloramine concentrations normally used in drinking water treatment vary in the range of 2 to 5ppm. However a very long time (some years) would be necessary to evaluate the effect of the chloramine on the membranes with these very low concentrations. With a higher concentration of the oxidant it was simulated, in much less time, the long exposition of the membrane in typical conditions of operation, even knowing that procedure could not represent the right degradation mechanism.

Thus initially a MCh solution in the concentration of 70ppm was used to perform the experiments during periods of 6 hours. After each exposition period was done tests to evaluate the membrane performance. The results of these experiments are presented in Figure 1.

The saline retention, Figure 1 (a), remained constant during all the experiments. However the permeate flux, Figure (b), had an increase of 30% already in the first 6 hours of experiment. This result suggests a physical damage on the polyamide membranes caused by the chloramine solution under the operating conditions used. The membrane used in this experiment was the ACM.

This phenomenon can be explained by the theory suggests for Avlonitis, Hanbury, and Hodgkiess (1992), cited previously, where the membrane suffer a morphological changes caused by the oxidant which transforms the crystalline regions of polymer into amorphous regions. The separation performance is not influenced in this step according to the authors and also evidenced by the data observed in Figure 1 (a). In a second step the oxidant attacks the amorphous regions resulting in an increase of salt passage through the membrane. The authors

do not make any comments related to the changes of permeate flux, however is expected some increase in its value caused by the modifications of the membrane structure.

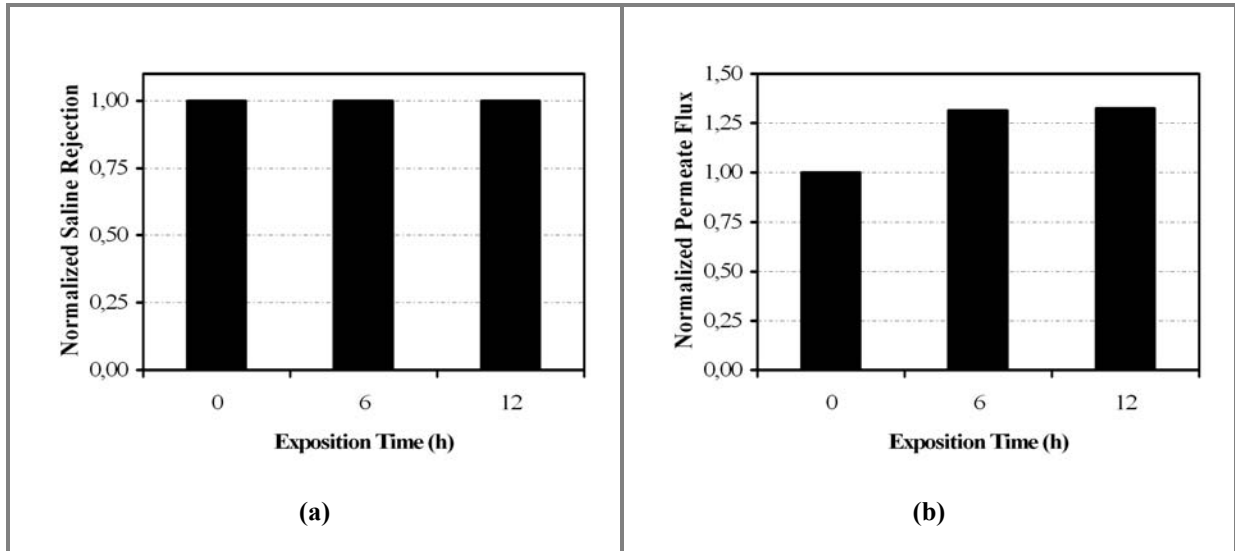


Fig. 1. Data of normalized saline retention (a) and normalized permeate flux (b) after exposition to 70ppm MCh solution, membrane ACM.

Although the modifications of membrane performance were significant using MChs in the concentration of 70ppm it was carried out some experiments with a concentration of 500ppm. In these experiments, the membranes used were ACM and CPA. The results of these experiments are present in Figure 2.

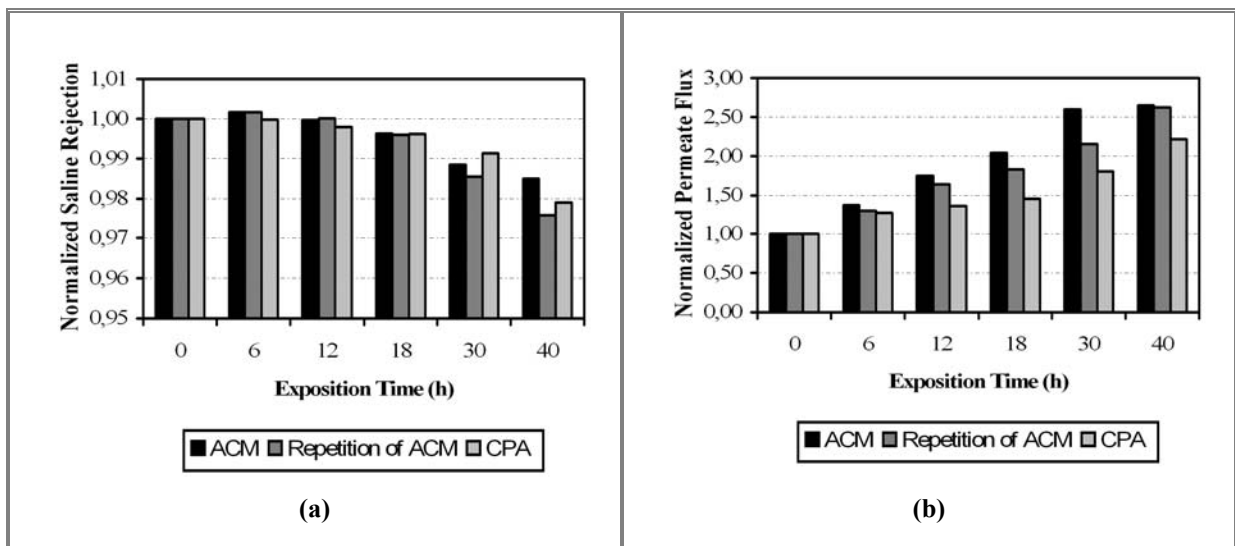


Fig. 2. Data of normalized saline retention (a) and normalized permeate flux (b) after exposition to 500ppm MCh solution.

The permeate flux, in these experiments, increased with exposition time as observed in the experiments with low MCh concentration. Already in the first 6 hours an average increase of 33% for ACM and 27% for CPA was observed and in the end of 40 hours of experiment an increase of 163% for ACM and 121% for CPA.

However for saline rejection a dual behavior was observed. In the first 6 hours of experiment, an increase on the saline rejection occurred and later a reduction with the increase of exposition time.

Adams (1990) who studied the effect of the chlorine dioxide on polyamide membranes also observed this behavior. In his experiments of long duration (between 150 and 200days) with low oxidant concentrations (between 1 and 10ppm), he observed initially an increase in the saline rejection until reaching a maximum value. After that, he observed a decrease of the saline rejection, indicating gradual degradation of the polyamide membrane. Bettiol (2004) also studied the effect of the chlorine dioxide on polyamide membranes but using high concentrations, and his results were similar to those observed by Adams (1990).

Regarding the comments made for Avlonitis, Hanbury, and Hodgkiess (1992), Adams (1990), Bettiol (2004) and the experimental results obtained in this work, it can be concluded that the effect of the MCh on polyamide membranes respects the same degradation mechanism observed for chlorine and chlorine dioxide. However the aggressiveness level observed for the MCh is much lower to that observed for aqueous chlorine and chlorine dioxide.

In this research it was also investigated the existence of some catalytic effect of membrane oxidation caused for aluminum and iron, present in the MCh solutions.

The formal concept of catalyst considered it as any substance that, with small amount, provides notable increase the rate of a reaction and remains unchanged when the reaction is complete.

Silva (2001) studied the catalytic effect of iron and aluminum on polyamide membrane oxidation. The oxidant used in his study was aqueous chlorine in the concentration of 500ppm. The increase of permeate flux and decrease of saline rejection demonstrated aggressive membrane degradation. Also it can be concluded that an increase of metal concentration in solution causes an increase of membrane degradation by chlorine. The maximum metal concentration used was 0.26ppm, which is a higher value than that typically encountered in water treatment streams.

Gabelich et al. (2002) studied osmosis membranes exposed to chloramine solutions in low concentration containing ferric chloride. The initial results had demonstrated an increase in permeate flux and a decrease in saline rejection with time that suggests membrane degradation and a possible catalytic effect by iron. However this result revealed uncertain in complementary tests in the absence of chloramines, where increases of permeate flux and decreases of saline rejection were also observed.

In preliminary studies with MCh solutions containing ferric chloride, was observed that the high MCh concentration oxidate of metallic parts of the RO system. This oxidation caused an increase of the iron concentration in the solution. The final iron concentration measured in the experimental solution had presented an average value of 0.3ppm, which represent an increment of about 300% higher than the initial concentration.

Different experiments should be carried out to study the iron influence as catalyst in the membrane oxidation, however this was not possible to be evaluated because even the experiments previously done already had some amount of iron in the MCh solution.

Even with the unwanted presence of iron in the solution, some experiments were performed to verify the aluminum influence as catalyst in the membrane oxidation by MCh solutions. Aluminum was added to the

500ppm concentrated MCh solution in the following concentrations: 0.05, 0.10 and 0.26ppm. In these experiments, the membrane used was CPA, and the results are present in Figure 3.

The membranes exposed to MCh solutions with different aluminum concentrations presented the same behavior for permeate flux and saline rejection, being the result similar to the observed in solutions without aluminum. Analyses of the iron concentration in the solution were not performed, but it knows that it is about 0.3ppm.

Due the presence of iron in solution together with aluminum it is difficult to conclude if these compounds really act as a catalyst. By taking into account the results obtained it was not observed a significant change in the permeate flux and saline retention when iron and aluminum were present. Can be concluded that: or the aluminum does not behave as catalyst in the membrane degradation or the amount of iron present already supplies the amount necessary for to provide the catalyze.

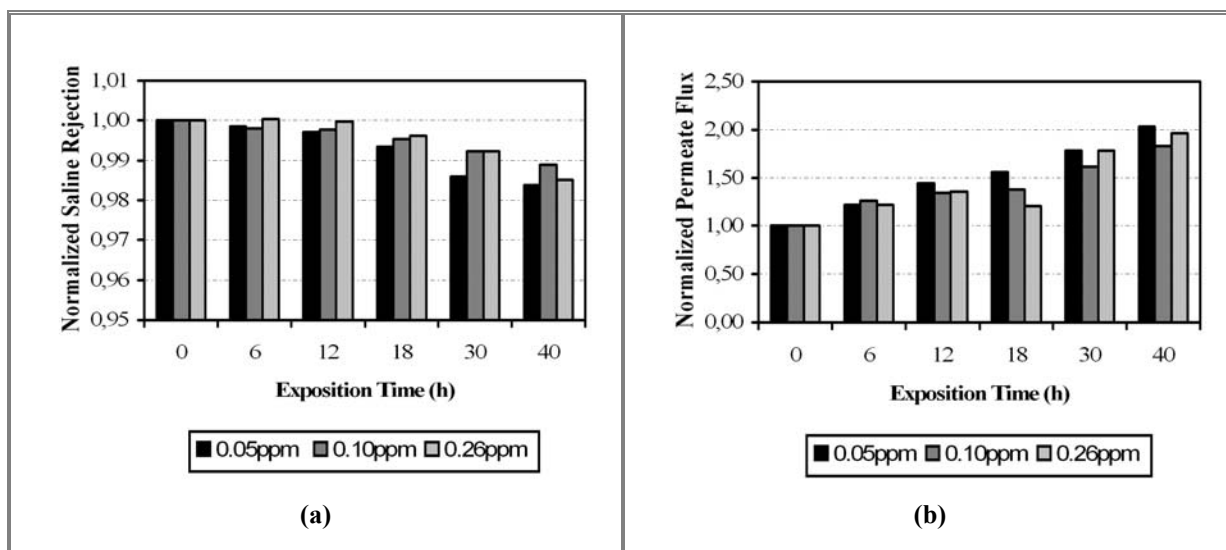


Fig. 3. Data of normalized saline retention (a) and normalized permeate flux after exposition to 500ppm MCh solution with aluminum on CPA membranes.

4. Conclusions

This work demonstrated that high MCh concentrations are capable to degrade polyamide membranes with increasing the permeate flux and decreasing the saline rejection.

Analyzing the data of exposition time and oxidant concentration used for Silva (2001), Bettiol (2004) and the results of the present work, it can be observed the oxidant aggressiveness to reach the same damage in the saline rejection. Thus it can be concluded that chlorine is more aggressive than chlorine dioxide and the last more aggressive than MCh.

Relating the comments made for Avlonitis, Hanbury, and Hodgkiess (1992), Adams (1990), Bettiol (2004) and the experimental results obtained of the present work, it can be concluded that the effect of the MCh on polyamide membranes respects the same degradation mechanism observed for chlorine and chlorine dioxide.

High MCh concentrations caused oxidation of metallic parts of the membrane unit having incorporated iron in the solution. For this reason the study of the effect of metals catalysts on the membrane degradation in MCh solutions was not yet concluded.

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