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Use of electrolytic processes applied as an alternative treatment to chlorine in water pretreatment in reverse osmosis system.

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Abstract. Reverse osmosis filtration is one of the water treatments used by industry because it is very effective in removing dissolved salts from water since it uses a specific type of thin, semi-permeable membrane. These membranes have characteristically small pores to allow the passage of pure water and reject larger molecules, such as ions and other tiny impurities like bacteria and viruses[1]. Several precautions need to be considered in water treatment before starting the filtration process in the equipment. These precautions are necessary to avoid premature loss of the membranes in the reverse osmosis system equipment. One of the most common problems that cause this damage is the oxidation reaction of the polyamide layer by the chlorine-based disinfectant, which corrodes this layer, substantially decreasing its filtration properties. The objective of this study, therefore, was to verify the possibility of substituting the use of chlorine in water treatment, for the removal of microorganisms, by the passage of an electric current, reducing the probability of biofilm formation and membrane perforation. The methodology consisted of experimental research, to verify the efficiency of the electric current as a biocide in a sample of raw water with cultivated microorganisms. An electrical load of 24 volts was applied, varying the exposure time, using Copper and Stainless Steel 304 as electrodes. The final results showed that in the treatment with the copper electrode and 30-minute retention of the water the results were satisfactory, and the treatment, therefore, could be used in conjunction with other biocides or in isolation reaching up to 10^3 CFU/ml of Aerobic Bacteria in the feed water.

Keywords. *Microorganisms; Biofilm, Electric Current, Polyamide, Reverse Osmosis*

Introduction. Water is a fundamental substance for the existence of life. Besides being a solvent widely used in chemical laboratories and industrial processes[2]. According to the National Water Agency, 9.5% of water withdrawn in Brazil is used by industry[3]. In the industrial sector, besides the water being used on a large scale, it often needs to undergo some treatments before its application, so that it can go through the processes as pure as possible, since the membrane is very sensitive to certain agents and contaminants that can damage it, such as high hardness, the presence of silica outside the recommended standards, iron, chemical treatments like chlorination and others[4].

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One solution found for this situation is demineralization by reverse osmosis through electrolytic processes. This is the separation of salts and water, reaching a low conductivity of up to 0.2 µS/cm, this is because the current flows through liquids at the atomic or ionic level and the ease with which the current is transmitted over a defined area helps quantify the ionic concentration of a sample[4]. Ions, therefore, are charged particles that float freely in solution, not coupled to other molecules. They are capable of carrying and transmitting a current, and thus their measurement is done using a conductivity meter.

This retention of microorganisms and contaminants is done by the membrane, in a reverse osmosis system, which contains micropores of an average size of 0.001 micrometers, and can, therefore, deionize the treatment without the use of chemicals to do the same, because the filtration is done mechanically through the respective membranes[5].

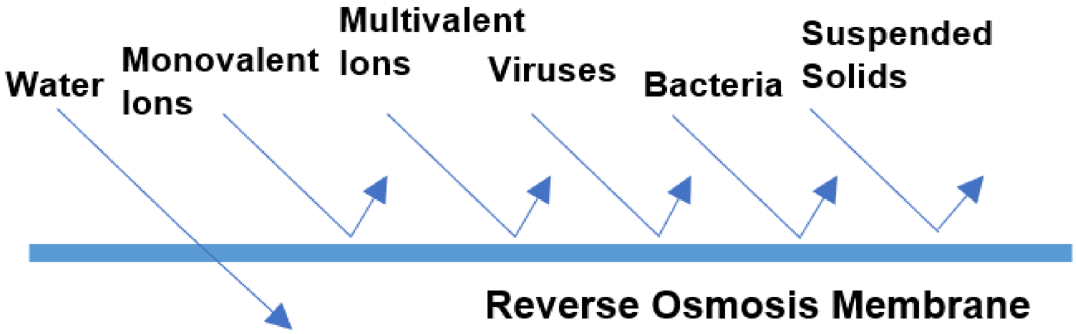


Figure 1. Illustration of the operation of the dam of a reverse osmosis membrane. (Source: Own).

This equipment works inversely to osmosis, that is, between two solutions of distinct concentrations are separated by a semipermeable membrane together with a pressure exerted on the solutes side, allowing only the solvent (pure water) to pass through and retaining the solutes (dissolved salts, microorganisms, and contaminants), as shown in Fig.2 [6].

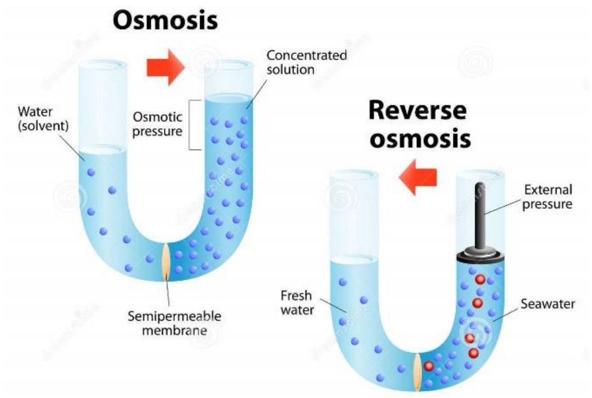


Figure 2. Illustration of the operation of Reverse Osmosis (reverse). (Source: Petrochem, 2021).

However, the Reverse Osmosis Membrane, the industrial equipment used to make these filtrations, can present certain problems if not taken care of properly. One of these problems, which is quite common, is the appearance of fouling on the membranes, called fouling which is caused by the accumulation of inorganic materials on the layers of the membrane. Usually, chemical cleaning is performed to remove the deposits. This aggregation leads to physical and chemical deterioration of the membranes and consequently increased pressures due to the increased resistance of the water to pass through. Accumulations can be avoided by effective water pretreatment [7].

In addition to fouling, the accumulation of biological material can also occur on the surfaces, also from the feed water of the equipment, with the presence of microorganisms such as bacteria, viruses, algae, and fungi called biofouling. The formation of biofilm is the most worrying deposition because it radically reduces the efficiency of the membranes. In this situation, the flow is impaired by reducing the area available for water passage and by increasing roughness[7]. Some biofilms are also difficult to remove by chemical cleaning because the organisms produce extracellular polymers that promote greater attachment to the walls and protection against water friction. For these reasons, pre-treatment, control and monitoring care are indispensable[8].

To avoid biofouling, several different types of disinfection treatments can be used in raw water, such as ozonation, hydrogen peroxide application, filtration, surfactants, and especially chlorination, which although it has one of the lowest costs and highest efficiencies, nevertheless irreversibly damages the physical structure of the membrane[8].

In this context, the need arose to seek alternatives to chlorine for the elimination of microorganisms before passing through the Reverse Osmosis Membrane, so this work will verify the possibility of replacing the application of chlorine by the passage of electric current in water before use in the equipment, in order to eliminate or reduce the microorganisms present in order to avoid or even reduce the formation of biofouling.

To support this objective it was understood that, according to Alayemieka[9], free chlorine is a very common biocide used in desalination processes by reverse osmosis membranes, in the prior disinfection of water, however, because it is incompatible with polyamide, treatment with this halogen ends up causing damage to the equipment, and may even deteriorate them in a way that makes them unusable. For this reason, it is believed that the present study is important to optimize the process of water disinfection, whereby passing through the membranes no chlorine residues remain, making the process safer. To this end, previous research and methods were sought to provide a theoretical basis for the study, mainly seeking solutions for the reduction of microorganisms present in the water through the passage of electric current.

This solution is called the electrolytic process, and basically consists of applying electrical energy to separate electrodes, arranged in parallel and immersed in the solution to be treated. The treatment is a system consisting of an electrolytic cell with the passage of a continuous or alternating electric current through electrodes into the treatment solution, called the electrolytic solution. During the treatment, electrochemical reactions are produced that can chemically transform recalcitrant substances that compose the pollutants. It also allows a reduction in the ionic concentration, causing the death of microorganisms and the production of disinfectant substances, such as chlorine gas.

Due to the bioelectric effect caused in biofilms by electric currents, since it does not have a satisfactory explanation, J. L. Del Pozo[11] therefore conducted a literature review regarding this effect and found some hypotheses. One of these possibilities is that the application of electric current can generate oxidants electrochemically and increase the vulnerability of microorganisms due to an increase in the internal temperature of biofilms, thus causing their elimination. Such hypotheses may explain the experiment of this paper, if not only the biofilms, but also the microorganisms in their planktonic (suspended) form are affected by the internal temperature increase.

Tolentino and Bidóia[12], also developed a study on the action of electric current in biofilms, but focused on the disinfection of conductive or semiconductor surfaces, bringing a proposed alternative to abrasive materials or biocide agents, which usually bring damage to assets, the environment or even the products generated in the treated equipment. With an application of 5 mA/cm^2 for ten minutes, it was observed the reduction in the polymeric matrix of the biofilm, its detachment from the equipment walls and the release of the microorganisms' intracellular material. The total energy consumption in this experiment was 0.008 kWh/m^2. The release of intracellular material indicates that the applied current may have been sufficient to break the cell wall of bacteria and this fact also positively indicates that the electric current may present a biocidal effect.

Pareilleux's study[13] was conducted using E. Coli as the study base, trying to reduce the amount of them from the electric current as well. The maximum exposure time was 10 seconds and the minimum current was 25 mA. After exposure the sample is allowed to stand for a while and then an aliquot is taken for counting. When performed without resting the sample the effect was not satisfactory. This may indicate that the application of electricity is not the direct cause of the reduction, but it is not known what the indirect reason would be. The lethal effect occurred with platinum and stainless steel electrodes, but not with common steel electrodes.

In Matsunaga's experiment[14] it was possible to decrease the survival rate of E. Coli by using a carbon cloth, wrapped in platinum wires in a glass and applying a voltage of 0.6V. It is stated that the death occurred due to oxidation of intracellular Coenzyme A, which led to decreased respiration and consequently cell death. Matsunaga points out that the deaths occurred due to the use of the carbon cloth and not just the platinum electrodes and therefore it cannot be said that the deaths occurred due to disinfectant generation by electrochemical oxidation.

The results found by the cited authors provided a better understanding of the subject that, together with the methodology described below, provided technical and methodological support for the research.

Methods and material. This work resulted from applied experimental research with the objective of verifying the efficiency of electric current as a biocide. Eight tests were performed in the laboratory where a sample of raw water with cultivated microorganisms was submitted to an electrical load of 24 volts, varying the exposure time between 3, 5, 7, 15, and 30 minutes. The electrode materials used were copper and stainless steel 304.

To perform the experiment the materials used were: 2 liters of raw water; 9 beakers; 1 multimeter; wires with "alligator" tips; 25 volts stabilized power supply; 2 copper electrodes, with 1.02 cm^2 of the submerged area; and 2 stainless steel electrodes 304, with 5.625 cm^2 of the submerged area. In Fig. 3 it is possible to visualize the experiment setup. And in Fig. 4 it is possible to understand, through illustration, the electrolytic behavior that is happening with the submerged electrodes.

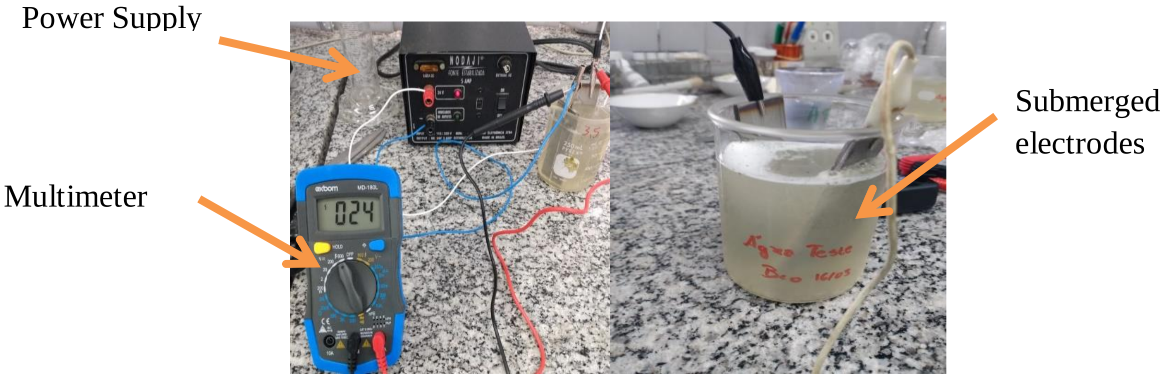


Figure 3. Layout of the experiment. (Source: Own).

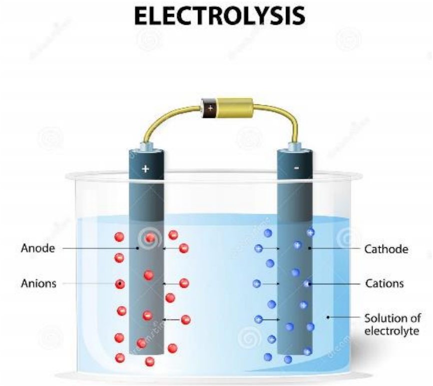


Figure 4. Schematic illustration of the electrolytic behavior. (Source: Brazil, 2021).

The effectiveness of each test was measured from the results in the counts of aerobic heterotrophic bacteria, molds, and yeasts, because the lower the number of total microorganisms after treatment, the greater the biocidal effect of the current passage will have been. The chemical analysis of the samples resulting from the tests is performed to explain the effects generated by them and how they can affect the water treatment for Reverse Osmosis Membrane.

Regarding the analyses used as parameters for discussion, microbiological analyses were performed, based on the Heterotrophic Bacteria Analysis procedure of the Standard Methods for the Examination of Water and Wastewater - 21st Edition. We used 3M Petrifilm Plates for aerobic heterotrophic bacteria and for mold and yeast, 0.1% Peptone Water reagents, 1000µL and 100µL volumetric pipettes; incubator adjusted to 35 ± 2 ºC; test tube shaker and a laminar flow hood.

The pH and conductivity analyses were also performed, based on the procedures established in the Standard Methods for the Examination of Water and Wastewater - 23rd Edition for pH and Conductivity. The equipment used was pH and conductivity electrodes and standards for calibration of the equipment. Conductivity was measured in a Thermo - Orion Star conductivity meter and pH in a Methrom Model 855 Titrator.

The analysis of metals was performed using the ICP OES 5100 equipment from Agilent by optical emission spectrometry with inductively coupled plasma and based on the analysis procedure for metals in the Standard Methods for the Examination of Water and Wastewater - 23rd Edition. Finally, the chloride analysis was performed according to the Chloride Analysis by Spectrophotometry procedure of the Standard Methods for the Examination of Water and Wastewater - 23rd Edition. The equipment used was a Thermo Fischer Gallery Plus Spectrophotometer.

At the end of the experiments, it is expected to obtain a large reduction in the amount of mold, yeast, and aerobic bacteria in the sample, decreasing the total microbiological load and dispense the use of chlorine as a biocide. Furthermore, among the materials used, copper should present a greater biocidal effect, according to the study conducted by the United States Environmental Protection Agency[15], because of its antibacterial properties.

Initially, nine aliquots of 200ml of the raw water sample were separated into beakers, where one was used as "blank", i.e., did not receive any treatment, and the others were separated by electrode material and exposure time to a voltage of 24 volts, according to Tab. 1. The electrodes were immersed in the sample connected to the stabilized source by copper wires and with a multimeter connected to measure the voltage supplied. The current measured in the copper electrode was 400mA and in the stainless steel electrode 520mA.

Table 1. Sample Identification. (Source: Own).

N°	Electrode material	Exposure Time
1	White	0 min
2	Copper	3,5 min
3	Copper	7 min
4	Copper	15 min
5	Copper	30min
6	Stainless Steel	3,5 min
7	Stainless Steel	7 min
8	Stainless Steel	15 min
9	Stainless Steel	30 min

Results and discussions. During the tests, foaming was observed due to the release of gas and color change in the samples due to the release of part of the material from the electrodes. These factors indicate the occurrence of electrolysis[16]. As represented in Fig. 5, after the electrical treatment, aliquots of each sample were separated for the execution of the analyses.

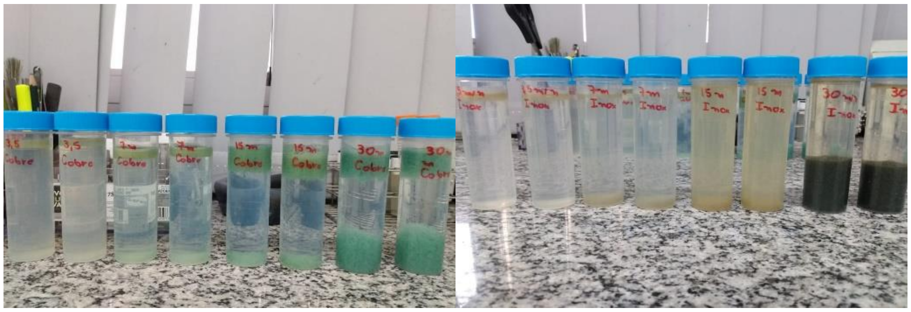


Figure 5. Post-treatment samples. (Source: Own).

The first information to be sought after the treatment was to verify whether or not there was a decrease in the microbiological load of the sample, because the efficiency of the experiment will be measured mainly through these results. Fig. 6 presents the graphs with the relationship between the microorganism count in CFU/ml (Colony Forming Units per milliliter) and the time of the experiment.

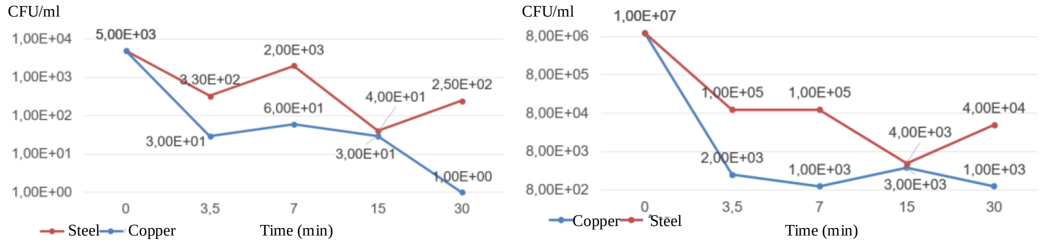


Figure 6. Mold and Yeast ratio on the left and Aerobic Bacteria ratio on the right respectively. (Source: Own).

The results of the microbiological analysis were positive. It was possible to observe that with both electrodes there was a decrease in the amount of both mold and yeast and aerobic bacteria. With both electrodes, copper performed better, both in final quantity and stability, although with a smaller submerged area and current. After 3.5 minutes of exposure, there was a significant decrease, but the best results were after 15 minutes for stainless steel and 30 minutes for copper, the latter reaching 10 CFU/ml for mold and yeast. Although positive, the final results were not totally satisfactory, however, because in the best case the water remained at approximately 1000 CFU/ml.

Fig. 7 shows the results obtained from the pH and conductivity analyses in graphs, with the variation of the measurements in each sample. The conductivity decreases in the tests of the two electrodes but has a more accentuated drop with copper. This also occurs inversely with the pH, because copper causes a significant rise, reaching 9.8 while with the stainless steel electrode the pH also rises, but less sharply.

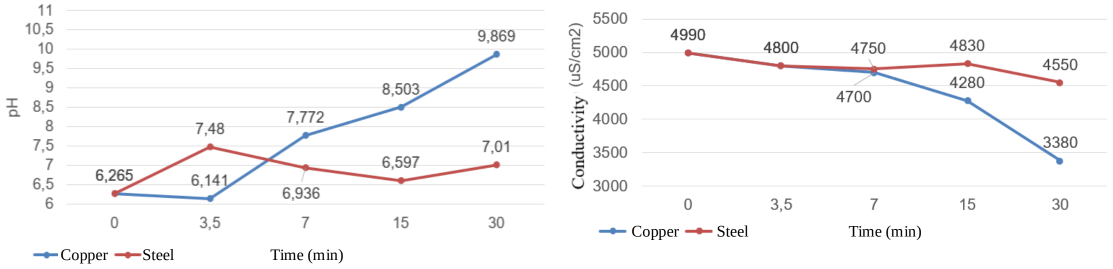


Figure 7. pH Variation on the left and Conductivity Variation on the right. (Source: Own).

In the analysis of metals, with the possible occurrence of electrolysis, the main metals evaluated in the samples were iron and copper, due to the material of the electrodes. In general, the concentration of metals in the samples also decreased more in the treatment with copper than with Stainless Steel, because part of the salts and ions precipitated and were removed in the filtration, however, as there are indications of the occurrence of electrolysis, the variation curve of copper and iron in the sample was checked separately.

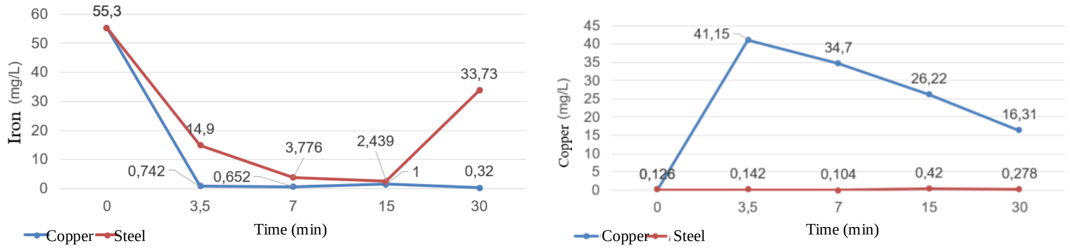


Figure 8. Iron Variation on the left and Copper Variation on the right. (Source: Own).

In the tests with the copper electrode, the total dissolved iron decreases by more than 95%, while with the stainless steel this value has a drop until 15 minutes and then rises again. This irregular behavior was not expected and can be explained by an analytical error. The concentration of dissolved copper in the sample remains stable in the tests with the stainless electrode but has a different behavior with the copper electrode. Without treatment, the sample had only 0.126 mg/L of copper and after 3.5 minutes the final concentration becomes 41 mg/L and subsequently, it decreases with increasing exposure time. The possible explanation for this phenomenon may be the complete occurrence of electrolysis, where 3.5 minutes is not enough for the ions to pass from one pole to the other, but as time passes this transition increases, decreasing the concentrations in the sample.

Finally, in the chloride analyses, the analyzed sample already presented a number of chloride ions, which may be in the form of salts. In the test with the stainless steel electrode, there was a small variation in concentration after 30 minutes, while with the copper electrode the concentration decreased significantly as can be seen in Fig. 9.

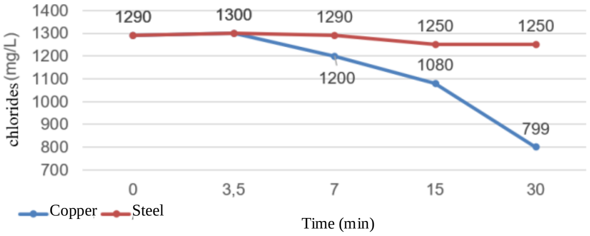


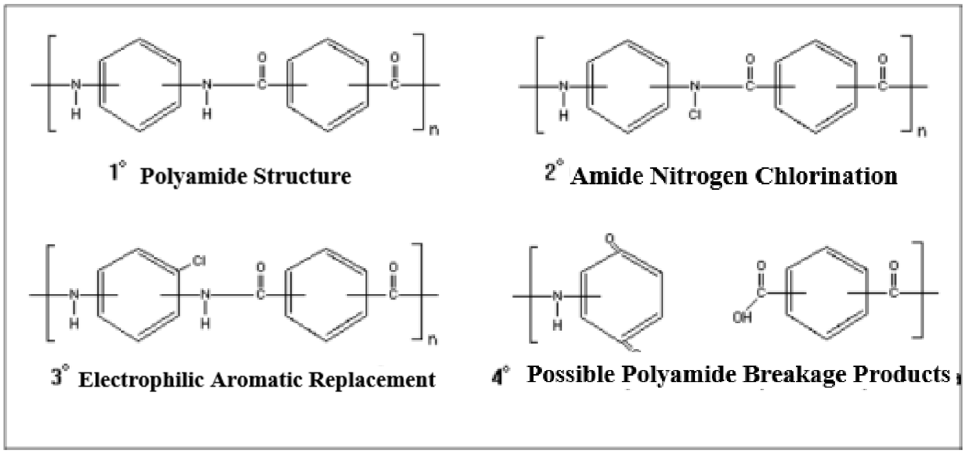
Figure 9. Chloride variation. (Source: Own).

Eliminating or reducing microorganisms and substances that are undissolved or that may precipitate during the process in the feed water minimizes membrane fouling, thus maintaining a good production rate, low salt passage, and extended lifetime. The complexity of the reverse osmosis water pretreatment system varies greatly, depending on the quality of the feed stream and the size of the membrane system involved. This can range from a simple micron cartridge filter to a sophisticated system that may include clarification, media filtration, and cartridge filters. While cost considerations may dictate the final choice of system, cost alone should not be the primary factor[17].

The acquisition cost and operational economics are important issues when considering what type of pretreatment to use. In addition to the equipment itself, there are a number of in-process chemical treatments that can be used. These include sodium hypochlorite or other biocides, polymeric flocculants, mineral acids, antiscaling agents, and sodium metabisulfite to remove chlorine[17].

Although Reverse Osmosis Membranes are very efficient, they are also easily degraded when exposed to oxidizing biocides such as free chlorine or chlorine dioxide, because the halogens present in these substances react with polyamide and polysulfone, the main materials of the mentioned equipment[18].

According to Glater[19], membrane halogenation occurs by Orton Rearrangement, where first there is chlorination of the nitrogen of the amides, then chlorine attack of the aromatic ring.



1° Polyamide Structure

2° Amide Nitrogen Chlorination

3° Electrophilic Aromatic Replacement

4° Possible Polyamide Breakage Products

Figure 10. Orton rearrangement. (Source: Silva, 2013[18]).

Besides the risk that polyamide brings, chlorine is also harmful to the environment, human and marine health. When chlorine reacts with organic substances, Trihalomethanes, or THMs, can be created, which are carcinogenic substances and can harm the endocrine system, cause tumors, among other risks[20].

Conclusion. The results obtained indicated that electrical treatment, under the conditions under which they were studied, can be a promising complementary technology for the microbiological treatment of feed water for reverse osmosis membrane and has the potential to be used as a substitute for chlorine, provided that the microbiological load of 10^3 CFU/ml is safe, or in conjunction with other less aggressive biocides and in smaller quantities.

The drop in conductivity, the concentration of dissolved metals in the water, and the precipitate formation show that the studied treatment can also contribute to the decantation in the clarification process.

The tests performed with the copper electrode showed more satisfactory results compared to the tests with stainless steel in all analyses, but especially in the microbiological ones, the object of study of this article, in which the final values of CFU/ml were lower and more stable, reaching 10^3 CFU/ml for aerobic bacteria and 1 for molds and yeasts after 30 minutes. This can be explained by the already proven bactericidal characteristics of copper[15].

In addition, the copper electrode used comprised of a lower current and area five times smaller than the stainless steel one, consequently if transferred to an industrial scale the energy cost would be lower in the industrial use than in comparison to the laboratory scale. For these reasons, copper was considered the most suitable material to be used as a biocide, and within the variables studied, the time of 30 minutes presented the best results.

A possible application of the electrical treatment studied in this work could be done right at the entrance of the raw water in the first tank, also including a sieving step to remove the larger suspended solids and then follow the clarification process already foreseen.

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