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Cleaning ultrafiltration membranes by different chemical solutions with air bubbles

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ABSTRACT

In many developing countries, the access to safe drinking water is not available to all the population. As a response to these problems, AQUAPOT project developed a water treatment facility based on ultrafiltration (UF) technology able to be used in developing countries that are working in Ecuador and Mozambique. Up to now, the major problem detected in the field application of UF in drinking water production from surface water has been membrane fouling and its cleaning. To study the consequences that lack of cleaning and maintenance of the installation can have over the membranes, AQUAPOT has simulated fouling over UF membrane that suffered from an irreversible fouling after long term filtration of surface water. The experimental study included characterization of the foulant layer and chemicals test (under static and dynamic conditions) to remove membrane fouling, with moderate results for chemicals solutions tested. In this study, air bubbles are used as an alternative, cost effective and environmentally friendly membrane cleaning technique to remove severe fouling. This work describes the experimental procedure performed in the physico-chemical test with chemical solutions bubbled with air, and the main results obtained when comparing the permeability values before and after cleaning the membrane.

Keywords: AQUAPOT; Potabilisation; Ultrafiltration; Surface water; Membrane cleaning; Air bubbles

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1. Introduction

In many developing countries, the access to safe drinking water is not available to all the population. In fact, more than 1.1 billion people live nowadays without access to safe water in these countries. This situation causes high rates of illnesses and high rates of morbidity and mortality, especially in children under five years old.

As a response to these problems, in 1996 the Chemical and Nuclear Engineering Department of the Polytechnic University of Valencia began the international project named AQUAPOT. This project is focused on the development of water treatment technologies based on ultrafiltration (UF) technology able to be used in developing countries [1], and it is being satisfactorily applied in some rural areas of Ecuador [2,3] and Mozambique. Up to now, the major problem detected in the field application of UF in drinking water production from surface water has been membrane fouling and its cleaning [4]. Lack of chemicals, their unaffordable costs or unavailability and application of not optimized cleaning protocols are the main reasons that explain not accurate cleaning and maintenance of the installations. As a consequence, a progressive decrease of flux during UF of surface water is observed over following months of production in spite of periodical cleanings and potential microbial readings could also be detected [5].

To study the consequences that lack of cleaning and maintenance of the installation can have over the UF membranes, AQUAPOT has initiated a research at the

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Naquera Research Center (CIN) to simulate this situation and to investigate most suitable cleaning agents and procedures that allow to recover permeate flow of a UF membrane that suffered from an irreversible fouling after long term filtration of surface water.

The experimental study included on a first stage characterization of the foulant layer directly on the membrane with SEM-EDX and FTIR. Membrane autopsy revealed natural organic matter (NOM), polysaccharides and polysaccharides-like substances as main organic foulants and Si, Ca, Fe and Al as main inorganic foulants, all caused by constituents in surface water. After that, cleaning protocols were planned to evaluate effectiveness of chemical (static [6] and dynamic test [7]) techniques to remove membrane fouling. Chemical tests were performed with affordable and world-wide extended chemicals and optimized to analyze the influence of temperature, chemical concentration, pH, pressure, flow and time over membrane cleaning.

However, in practice, chemical cleaning alone is not sufficient to control fouling, especially in the case of biofouling, because foulants are insufficiently removed by chemical cleaning [8]. In these cases, to remove fouling from membranes, both hydraulic and chemical actions can be used, and the application of air should be a feasible option to be considered. Among the cleaning membrane strategies, the application of air is a relatively new, cost effective and environmentally friendly alternative [9]. In most of the cases, the air is injected during filtration to prevent fouling [10,11], only in a few studies the air is used for membrane cleaning between modes of filtration [12,13].

Air injection has shown to be efficient in flux improvement in numerous applications of ultrafiltration and different kinds of membranes (organic or inorganic). This positive effect is due to the presence of air bubbles which increase turbulence in the liquid phase, so solute separation efficiency is increased as well as permeate flux [14,15].

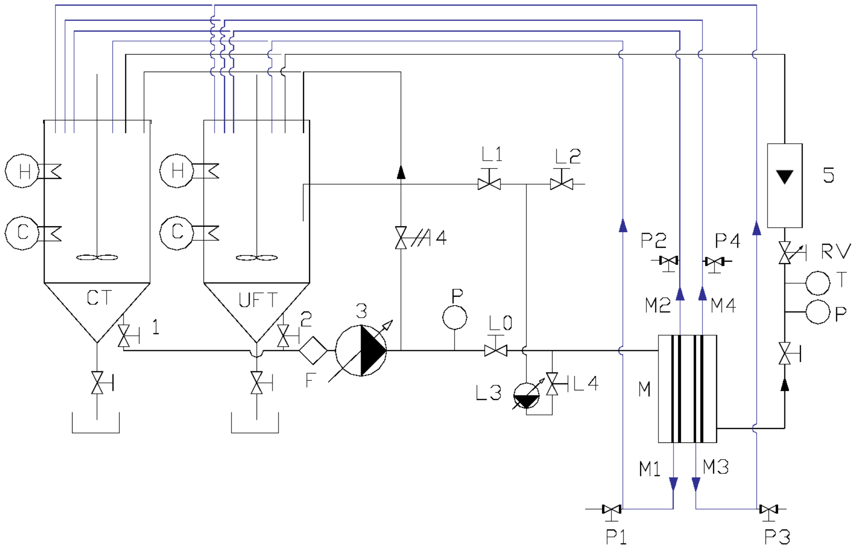
In this study, air is used for membrane cleaning of ultrafiltration membranes after long-term surface water filtration. The innovation presented in this research is that the air is applied in combination with different chemical solutions with the aim of testing both hydraulic and chemical actions simultaneously. The results of cleaning efficiency are compared with the ones obtained with chemicals and to assess the efficiency of introduction of air bubbles as a new cleaning strategy.

2. Materials and methods

2.1. Pilot plant description

Fig. 1 shows the flow diagram of the UF pilot plant used in the cleaning tests with air bubbles in chemical solutions.

Cleaning solutions are prepared in the ultrafiltrate tank (UFT) and taken from it through the inlet valve (L1). Air bubbles are immersed in the cleaning solution through valve L2, due to creation of Venturi effect. Air/cleaning solution flow is pumped with a peristaltic pump



H: Heating system
CT: Cleaning tank
M: Membrane module
T: Thermometer

C: Cooling system
UFT: Ultrafiltrate tank
M1-M4: Permeate collector
3: Centrifugal pump

RV: Pressure regulation valve
F: Pump filter
P: Manometer
L3: Peristaltic pump

Fig. 1. Flow diagram of the UF pilot plant used in the tests with air bubbles.

(L3) into the cleaning circuit and to the membrane module (M). The membrane module (M) comprises four flat membranes with an effective area of 30 cm^2 each. Flat membranes were obtained from the CIN's fouled spiral wound module of polysulfone UF membrane with a cut-off of 100 kD.

Permeate flow during cleaning is measured through P1, P2, P3 and P4 valves by using a graduated cylinder. Permeate and concentrate flows are recirculated till UFT from where they are injected in the cleaning circuit again. The temperature remains constant during all the experiments by using heat exchangers (C and H) located in the ultrafiltrate tank (UFT). Pressure is measured with manometer (P) and remains constant by using a regulation valve (RV).

2.2. Experimental procedure

The experimental procedure consisted in the following three stages:

1. *Water permeability before cleaning*. Membranes were tested for determining the initial water flux with deionised water at a transmembrane pressure (TMP) of 0.25 MPa. Four membrane samples were tested at the same time. The permeate flow of each sample was measured every 15 min during 1 h. The average permeate flux (J_0) was then calculated from the results of each membrane.
2. *Membrane cleaning with air and chemical solutions*. Different chemical solutions (Table 1) containing air bubbles were recirculated during 6 h, with an air pressure of 0.02–0.03 MPa and with a feed flow of 150 L/h. Gas to liquid flow rate performed for the experiments was 0.5. The permeate flow was measured every hour for 6 h, and it was later used for calculating the evolution of the permeate flux with time in order to study the optimal cleaning time. Deionized water was also included as cleaning solution to analyze the effect of air in fouling removal without a chemical agent. The chemicals selected were the ones that showed better results in flux recovery in the previous studies without air [7].
3. *Water permeability after cleaning*. After the chemical cleaning, water flux with deionised water was again determined (J_1) in order to compare it with the initial value (J_0) and to calculate the degree of flux restoration (J_1/J_0). The operation conditions were the same as in first stage.

Table 1
Chemical compounds used in the cleaning experiments with air bubbles

Chemicals	Concentration
Hydrogen peroxide (H_2O_2)	0.5 % (v/v)
Sodium hydroxide (NaOH)	0.001 M
Sodium hypochlorite (NaClO)	100 ppm
Deionised water (H_2O)	—

This experimental procedure was carried out twice for each solution at two different temperatures: 25°C and 40°C. After each experiment, cleaned membranes were replaced for new fouled samples.

3. Results and discussion

3.1. Air/chemical cleaning test at 25°C

Figs. 2 and 3 show the experimental results obtained when cleaning membrane samples at 25°C. Fig. 2 displays the evolution of membrane flux with time (at a transmembrane pressure of 0.02–0.03 MPa) during the tests. It can be observed that the values of the permeate flux during the cleaning stage were quite similar for all the tested solutions, but it seems that sodium hypochlorite got better final values of flux, while the values obtained with deionised water were the lower ones. With regard to the evolution of the cleaning action with time, it can be said that just in the case of sodium hypochlorite the flux increased progressively during the period of cleaning (6 h), while for the rest of the chemicals the flux kept quite steady during the cleaning time. Considering the kinetic study of cleaning at 25°C, it seems that the contact time should be longer than 6 h to improve the effectiveness of the process.

Fig. 3 compares the rate of flux after cleaning (J_1) to the flux before cleaning (J_0) for each tested chemical, with the aim of evaluating the degree of flux restoration due to cleaning reagent. It is clearly shown that flux restoration is higher when NaClO is used, reaching the values of 2.8 for the degree of flux restoration. Hydrogen peroxide and sodium hydroxide display also good values of permeability recovery, in terms of flux restoration, with values

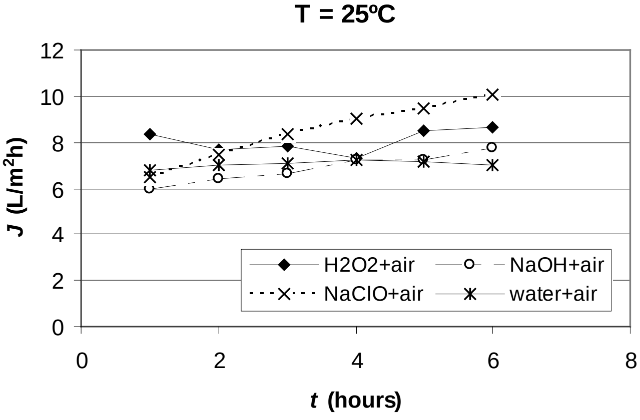


Fig. 2. Membrane flux evolution with time of cleaning in the air/chemical cleaning at 25°C.

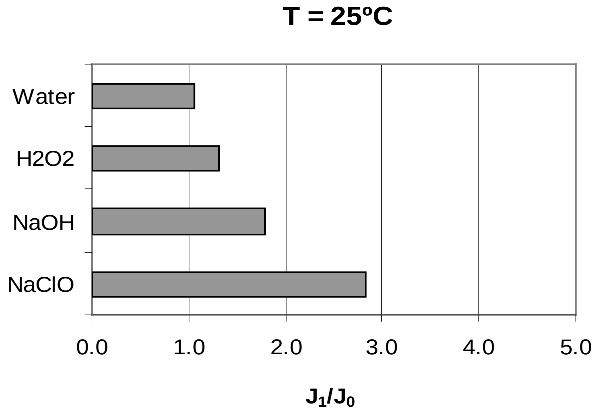


Fig. 3. Effect of air/chemical cleaning at 25°C for different solutions.

of 1.3 and 1.8, respectively. However, deionised water has a poor effect on membrane restoration since the value of flux after cleaning was almost the same as the value before cleaning (degree of flux restoration of 1.1).

3.2. *Air/chemical cleaning test at 40°C*

Experimental results at 40°C can be observed in Figs. 4 and 5, and they are clearly better than those obtained at 25°C, as it was expected. Membrane flux evolution during the stage of cleaning is shown in Fig. 4. In this case, there is a significant difference between the four solutions. Both H_2O_2 and NaOH display the higher values of flux at the end of the cleaning period. In the case of hydrogen peroxide it can be seen that the cleaning effect is significant after approximately 4 h. With regard to sodium hydroxide, the effect of chemical action in cleaning is evident just after 1 h and remains constant during all the cleaning. Deionised water and sodium hypochlorite seem to have a more steady cleaning effect in flux recovery. In this case, it is even clearer (especially in the case of hydrogen peroxide) that the contact time in the cleaning stage should be longer than 6 h in order to get better efficiencies of the process.

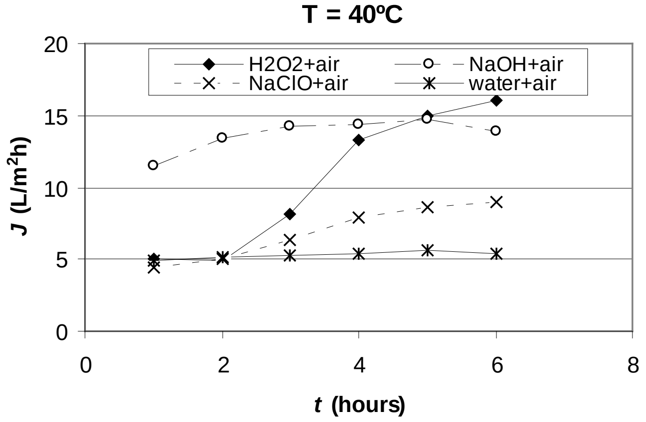


Fig. 4. Membrane flux evolution with time of cleaning in the air/chemical cleaning at 40°C.

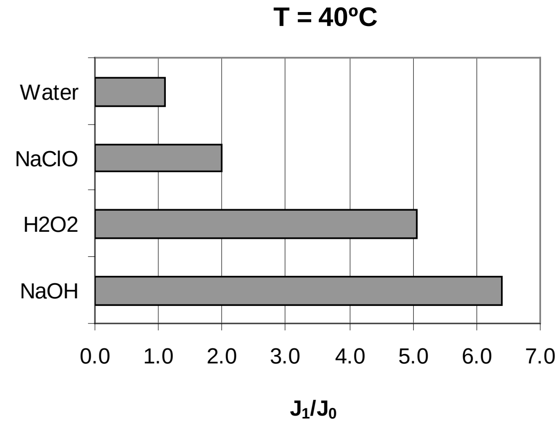


Fig. 5. Effect of air/chemical cleaning at 40°C for different solutions.

Fig. 5 shows the comparison of the rate of flux after cleaning (J_1) to the flux before cleaning (J_0) for each tested chemical. It can be seen that NaOH and H_2O_2 perform high membrane permeability recoveries, with values for degree of flux restoration of 6.4 and 5.1, respectively. As well as it occurred at 25°C, NaClO shows good membrane restoration values, with a degree of flux restoration of 2.0, but deionised water has a very poor effect on membrane recovery (degree of flux restoration of 1.1). So it seems clear that the presence of chemicals improves the efficiency of membrane cleaning.

3.3. *Effect of the air bubbles in membrane chemical cleaning*

In order to study the effect of air bubbles in cleaning efficiency, results of air/chemical cleaning are compared with the ones obtained in chemical cleaning tests performed previously. The experimental conditions for chemical cleaning without air consisted in testing different chemical solutions that were recirculated during 2 h, at a transmembrane pressure of 0.2 MPa and with a feed flow of 160 L/h. The permeate flow was measured every 15 min for 2 h, and it was later used for calculating permeate flux of each sample [7]. The experimental conditions of air/chemical cleaning tests are shown in section 2.2. Experimental procedure.

In this section, Figs. 6 and 7 show the comparison of the degree of flux restoration for the experiments performed with cleaning solutions in previous works and in the experiments carried out with the same cleaning solutions but including air bubbles. For both tested temperatures (25 and 40°C), it is clear that the hydraulic action due to air bubbles significantly improves the cleaning efficiency. This enhancement of flux due to cleaning

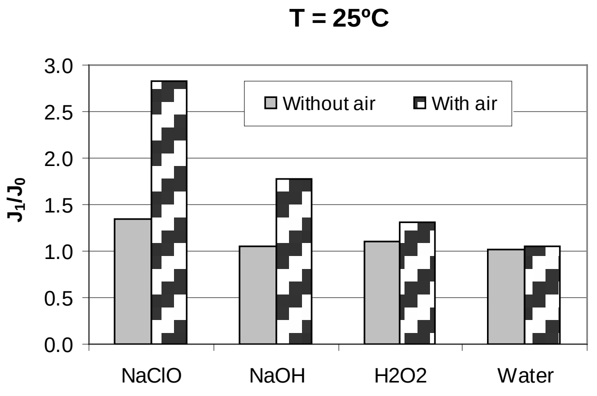


Fig. 6. Effect of air bubbles in membrane cleaning at 25°C.

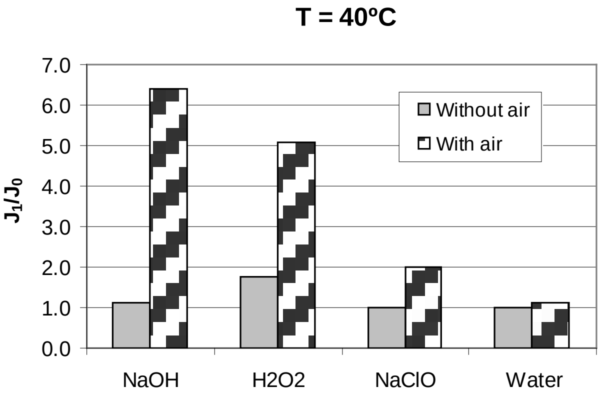


Fig. 7. Effect of air bubbles in membrane cleaning at 40°C.

is higher at 40°C in the cases of hydrogen peroxide and sodium hydroxide. With regard to sodium hypochlorite, cleaning efficiency is lower at higher temperatures, as it occurred when the cleaning was performed without air [7]. Due to cleaning effect observed in the absence of chemicals (the case of deionised water with air bubbles), it is clear that the presence of air bubbles enhances a synergic effect with chemical cleaning solution and improves recovery results (J_1/J_0) as it is shown in Figs. 6 and 7.

According to the results presented, it can be stated that at a temperature of 25°C, the most satisfactory values of flux restoration have been achieved when using NaClO and NaOH in combination with air. At a temperature of 40°C, the best values of flux restoration are the ones achieved when cleaning with H_2O_2 and NaOH, in combination of air. It has been clearly proved that the injection of air bubbles in the stream of chemicals tested improves the cleaning action of all the cleaning solutions studied in this work.

Future research should be done in the optimization of ratio air/chemicals as well as, the characterization of membrane surface to determine the effect of cleaning action on the membrane structure.

4. Conclusions

According to the results analyzed previously, the following conclusions can be stated:

- Hydrogen peroxide, sodium hydroxide and sodium hypochlorite perform very satisfactory results at both tested temperatures (much better at 40°C) when used with air bubbles in cleaning solution. Therefore, all the tested chemicals are suitable for being used in the cleaning process of UF.
- Air bubbles improve the cleaning effect of the chemical solutions. However, the isolated effect of air bubbles is not enough for fouling removing as it has been shown with the poor results of cleaning with air/deionised water.

Further investigation should be developed using mixtures of air bubbles and chemical solutions in order to define a proper cleaning protocol to be applied to spiral wound UF modules, and to analyze the effect of the geometry of the module and the spacer on the distribution of air, and in the mixing of chemicals in circulation. Finally, it is also necessary to study the stability and solubility of the polymeric material of the membrane, in order to state that the tested chemicals, in the operating conditions applied, do not deteriorate the membrane from the point of view of permeability and selectivity.

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