Nanofiltration: Towards a Breakthrough

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Abstract: Membrane unit operations with a pressure gradient as the driving force have already known a breakthrough in the past decades. Reverse osmosis in the 60s, Ultrafiltration in the 70s, Crossflow Microfiltration in the 90s. The newcomer among those methods, the Nanofiltration strives also to gain a wide application field that would justify the occurrence of a breakthrough! Recent experimental work in our Laboratory of Transport Phenomena and Applied Thermodynamics, at the Technical University of Crete, show that this field of wide application is the brackish water desalination.

Key-words: membrane technology, Nanofiltration, brackish water, softening, desalination

1 Introduction

Pressure driven membrane operations in the crossflow mode of operation (Fig.1) have dominated the second half of the 20th century. Reverse osmosis (RO) has been successfully developed in the sixties. The main reasons of the success was the manufacturing of the first asymmetric membrane by Loeb-Surirajan and the application of the method in sea water desalination. [1] Ultrafiltration (UF) has been successful because of the application in the separation of the pigments in the automobile industry. This happened in the 70s[2]. Crossflow microfitration (CFMF) has obtained its high status because of applications in the biosciences, such as cold sterilization in the dairy industry and downstream processing in Biotechnology[3]. Nanofiltration is a modern technology. Compared to Reverse Osmosis is less energy demanding because the pressure gradients applied are much less than the ones in RO. Also whereas RO rejects nominally all the solutes in an aqueous feed, the Nanofiltration may separate organic solutes from ions and even polyvalent ions from monovalent ones [3].

However, the Nanofiltration is still waiting its great moment. Considering all the above, one method obtains its breakthrough when a major field of application exists. This major field of application was the sea water desalination of RO, the pigment separation of UF and the downstream processing of CFMF.

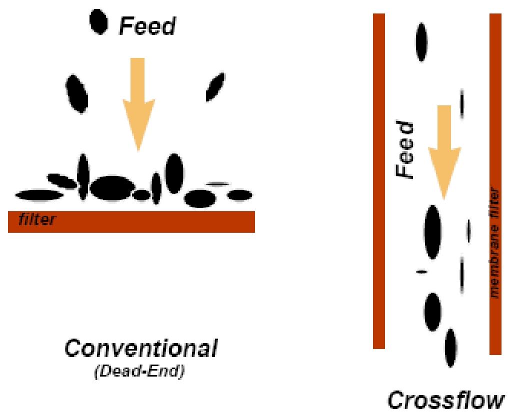

Figure 1 The crossflow mode of operation

Based on preliminary research, we are in the pleasant position to predict that NF it might very much likely to obtain the breakthrough because of brackish water desalination and/or softening applications.

2 The Problem

In many touristic areas in the South (such as the Crete and the Cyprus islands) the scarse of water is notable , especially during the high season and the water available is brackish water, or it has been used to exist of a fair quality subground water but intrusion of sea water has deteriorated this fair quality. The result was , anyway, that brackish water with a more or less high salt concentration is the source of water available. In other areas, within land, needs for tremendous quantities of water are faced by the Power Companies and again the potential source of water is the brackish water. Desalination of brackish water by Reverse osmosis shows some serious disadvantages. Reverse Osmosis membranes are not suitable because there are “too” good for that purpose. Since, we do not wish a total removal of ions but the removal of certain problematic ions. Secondly, RO functions at high pressure gradients, this meaning that the operation cost of the method will be unneccessarily high! The attractive method to consider is the Nanofiltration. To examine this potential we carried out experiments on brackish water representative samples, coming from a touristic area in Milatos, of Crete. The following are just a representative specimen of the work on Nanofiltration done in our laboratory whetre a whole team , the “Nanoteam” deals with this very important unit operation. To these efforts belong the diploma Thesis’ of Dina Giaggou, Dimitris Karakostis, Natassa Wahab, and the Master Thesis’ of Marilena Clonizaki and Georges Foudoulis.

3 Materials and Methods

3.1. Water quality

Three different samples were studied. One of them was a sample of tape water in the Chania of Crete area. Then there were two samples from the tourist area of Milatos, called the B1 and B2 samples. B1 and B2 were the codes of the two wells where from the water samples were taken. Parameters of importance monitored were the hardness, in DH (German degrees) and the total salinity (in micro Siemens). The measured values of hardness and total salinity are shown in the Table below:

	Hardness	Total Salinity
Tap water	6.5	245
Sample B1	40	1215
Sample B2	79	6008

The hardness was measured by a suitable hardness kit and the electrical conductivity by a suitable conductivity meter.

The membrane apparatus

The membrane apparatus was of the M20 type from the DSS company (Danish Separation Systems) This apparatus is of the plate and frame configuration and contains the membranes of a round shape and of a surface area of 0.018 m2 each.

Fig.2 The membrane apparatus in the Laboratory of Transport Phenomena & applied Thermodynamics of the Technical University of Crete.

It is also equipped with all necessary instrumentation (hand pump to compact the sandwich of the membranes and their frames in the space provided inside the module, feed pump, heat exchanger, manometers at the inlet and outlet of the solution feed) For a full description of this unit see the PhD thesis of Camille Sagne [4], Fig. 3, below:

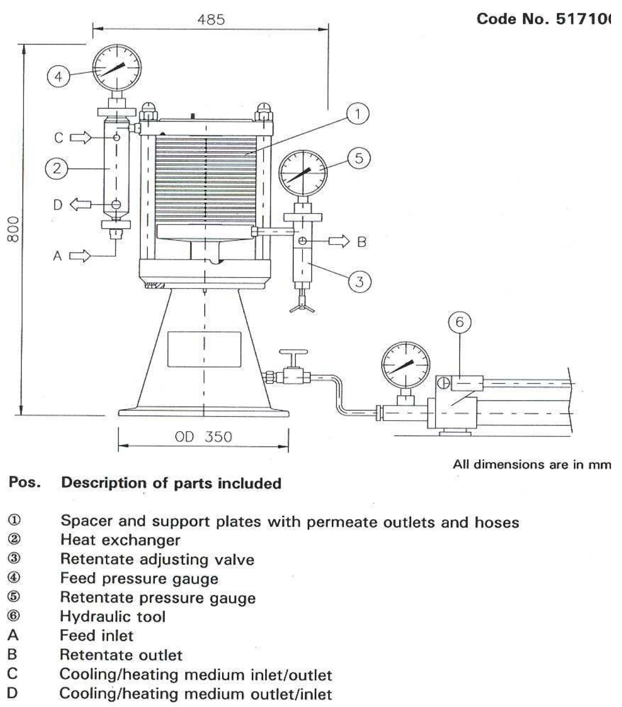

Figure 3. Labstack M20 of DSS company

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In the experiments of the present study two membranes were used with a total surface area of 0.036 m2.

3.3 Types of membranes

The nanofiltration membranes were of the types NFt 50 and NF 99, kindly provided to us as free of charge samples (therefore we are very grateful) by the manufacturer, of the apparatus Labstack M20, the DSS company. Initially the experiments were carried out by using the NFt 50 membrane. Afterwards the membrane NF 99 has been recommended to be used , the manufacturer claiming that a MgSO4 retention of 99% was possible by that membrane. The material of the "improved" composite membrane was polypiperzine amide for the skin and polysulphone for the microporous support layer of the membrane [5]:

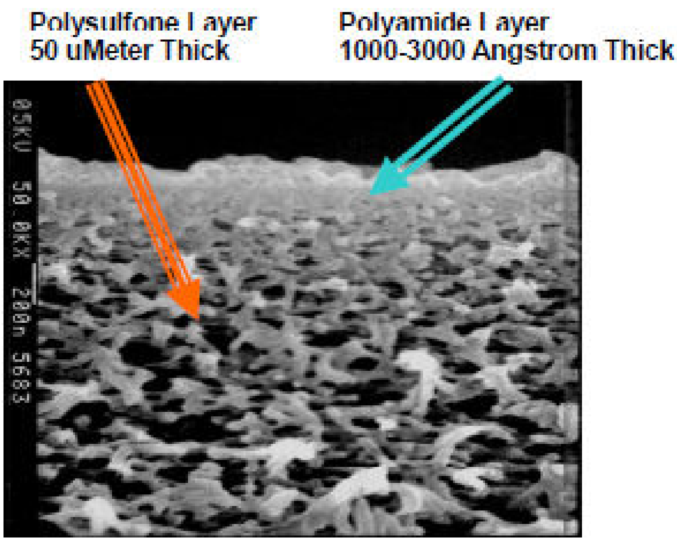

Figure 4. Structure of the NF 99 membrane consisting of a polyamide active skin layer and a polysulphone microporous support layer. (G. Foudoulis, Master Thesis, 2010,[5])

3.4 Calculations

3.4.1 Hardness and Conductivity

German hardness degrees were converted to ppm using the formula DH* 17,86 and conductivity values were converted to ppm by using the formula conductivity/1.4.

3.4.2 *Membrane Performance Parameters*

Two main parameters of membrane performance have been estimated from the experiments. The permeate flux and the retention, or rejection, coefficient. The later is equal to the Initial concentration of the retained species minus its final concentration (remaining in the concentrate) divided by the initial concentration and it is given as a percentage. The flux measurements included flux measurement of deionized water both before and after the treatment of the brackish waters.

4 Experimental results

4.1 Tap water

The initial hardness concentration was 114 ppm and the final one using the NFt 50 membrane was 31.8 ppm, this result giving a rejection coefficient for the hardness of 0,72 or 72%.

The initial total salinity (measured by conductivity) was 245 microSiemens and the final was 74.8 giving a rejection of total salinity coefficient of 0,69 or 69% by the same membrane (NFt 50).

The NF 99 membrane gave even better results with tap water: The rejection of hardness was 80% and the rejection of total salinity 74,4%.

The above performance parameters were average values of three experiments the standard deviation being for the hardness up to 2.1% and for the total salinity up to 0,5% [5,6].

4.2 Brackish water sample B1

The results in terms of the rejection coefficient are shown in the following Table:

	Nft 50	NF 99
Hardness	0,70	0,77
Total Salinity	0,40	0,66

4.3 Brackish water sample B2

The results in terms of the rejection coefficient are shown in the following Table:

	Nft 50	NF 99
Hardness	0,64	0,73
Total Salinity	0,47	0,45

The comparison of the performance of the two types of membranes as far as the rejection is concerned is seen also in the two Figures 5 and 6. From this comparison it is easy to draw the conclusion that the NF 99 membrane had a superior performance, especially in the rejection of hardness. Only in one case, in the rejection of total salinity of sample B2 the NFt 50 membrane was slightly better than the NF 99. :

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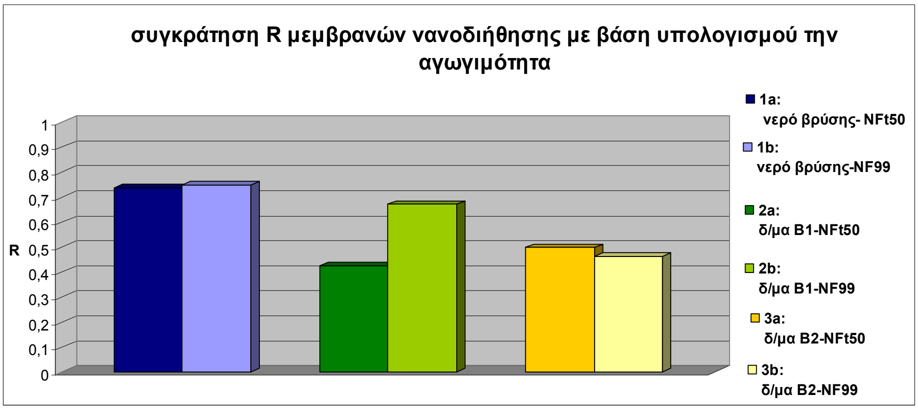

Figure 5 Rejection of total salinity by the membranes NFt 50 and NF 99

First (blue column): NFt 50, tap water, second (light blue) column: NF 99 tap water,

third (green) column: NFt 50, sample B1, fourth (light green) NF99, sample B1,

fifth (yellow) column: NFt 50, sample B2 and sixth column:NF 99, sample B2

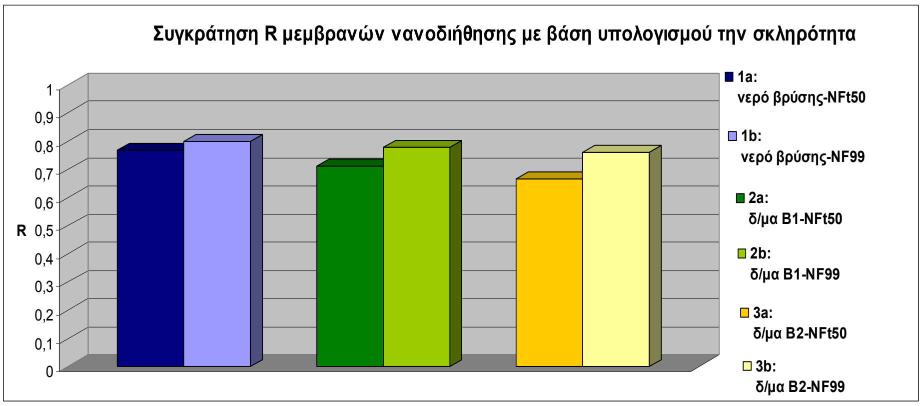

Figure 6 Rejection of hardness by the membranes NFt 50 and NF 99

First (blue column): NFt 50, tap water, second (light blue) column: NF 99 tap water,

third (green) column: NFt 50, sample B1, fourth (light green) NF99, sample B1,

fifth (yellow) column: NFt 50, sample B2 and sixth column:NF 99, sample B2

4.4 Flux performance of the membranes

As far as the flux performance is concerned the NF99 membrane had demonstrated remarkably higher values than the NFt 50 in all cases. This is observed in the diagrams below (Figs 7, 8,9,10) The order of magnitude of the flux was for the membrane NF99 1000 L/m2.day whereas for the NFt membrane was of the order of magnitude of 400 L/m2.day, at a transmembrane pressure of 12 bar.

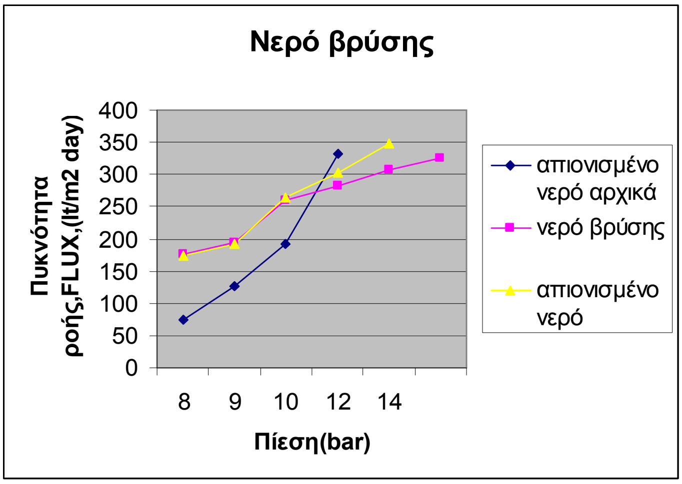

Figure 7. Flux of tap water with the NFt 50 Membrane

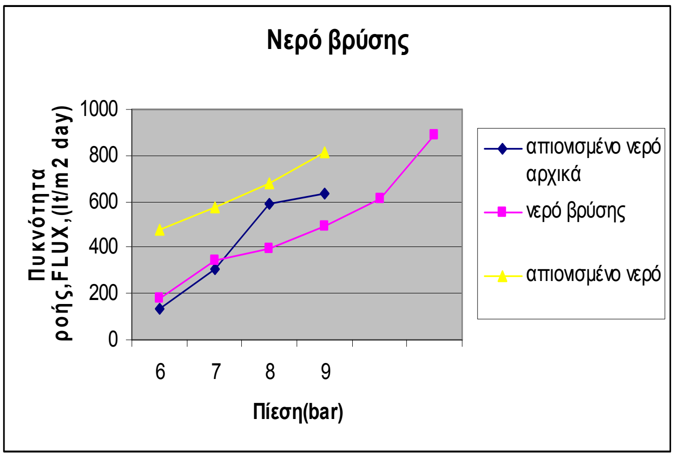

Figure 8. Flux of tap water with the NF 99 Membrane

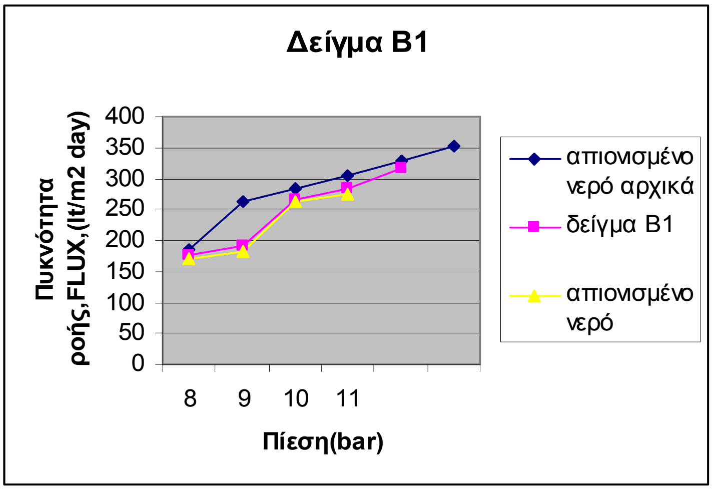

Figure 9. Flux of the sample B1 with the NFt 50 Membrane

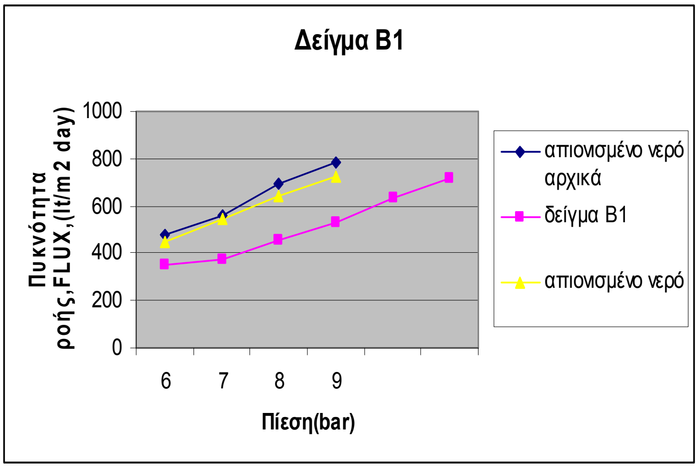

Figure 10. Flux of the sample B1 with the NF 99 Membrane

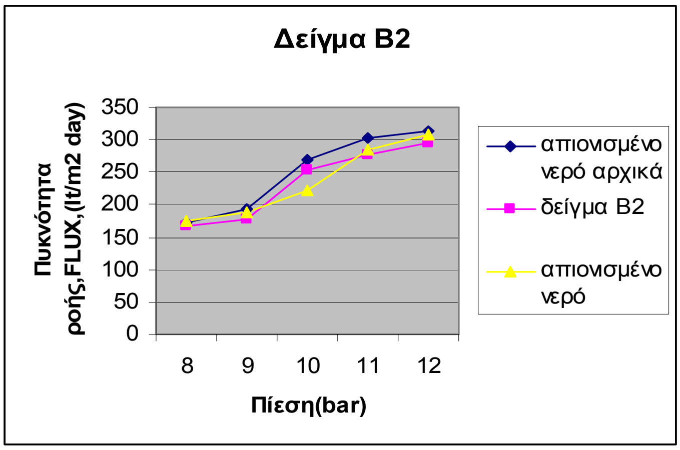

Figure 11. Flux of the sample B2 with the NFt 50 Membrane

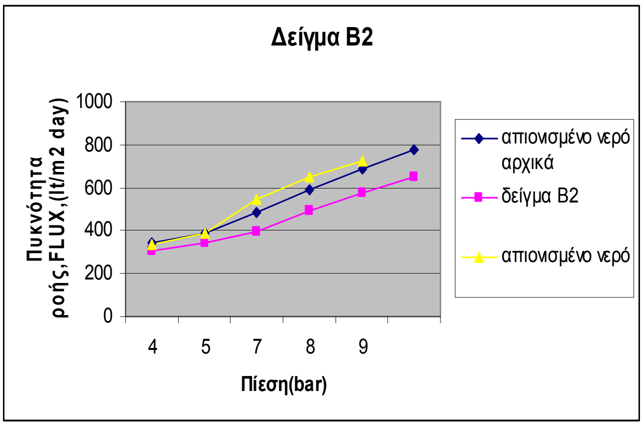

Figure 12. Flux of the sample B2 with the NF 99 Membrane

5 Discussion & Concluding Remarks

Nanofiltration of brackish waters is a promising method of their softening and partial desalination. The NF 99 membrane had a better performance both in the removal of hardness and much better in the flux obtained of the brackish solutions examined. Since, a total desalination is rarely desired the Nanofiltration constitutes a more appealing technology than Reverse Osmosis with its high pressures. Nanofiltration does the job in low pressures therefore is an energy saving and environmentally friendly for the purpose of treatment of brackish waters.

6. Acknowledgements

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