



## PROBLEMS AND MF SOLUTIONS OF THERMAL WATER

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### **Abstract:**

*The membrane separation was used to minimise or rather to remove the phenol contain of thermal water. PCI tubular UF/RO pilot-plan equipment with AFC99 and ES 209 membrane was used for separation at pressure of 0,6; 1,0 and 6,0 MPa. Its active filter area is 1,2 m<sup>2</sup>.*

*HPLC method was used to determine the phenol contain of retentate and permeate and we used the standard water-analytical, methods (MSZ-1484-1:1992) as well. Ultrafiltration was applied to reduce the phenol contain of the samples below the admmissive value, and the reverse osmosis was used to eliminate of total phenol.*

### **Keywords:**

*Thermal water, phenol contamination, membrane separation.*

## 1. INTRODUCTION

Water reserves of our Earth can be considered to be satisfactory in their totality, but the amount of water being suitable for human consumption is not meeting the demands presenting themselves. It can be well understood that the protection, defence of our potable waters should be an important task of our everyday life.

The purification by membrane separation techniques of the water being not for human consumption, coming from the thermal wells in the environs of Szeged, and thus making it applicable to be used for the heating of glass houses, have been the target of our study.

The wide exploitation of the heating energy content of the thermal water gained from the wells Im34, Im35 and Im36 in the neighbourhood of Szentmihálytelek is highly impeded compromised by its high phenolic and ionic contents. The company operating the wells is paying

considerable sums for wastewater penalties due to the higher than admissible phenolic content of the outlet water.

The aim of our experiments has been the reduction of the phenolic content being higher than admissible to below the limit value by help of membrane separation process.

## 2. LITERATURE SURVEY

The presence of organic compounds is a frequent and undesirable phenomenon in the surfacial and thermal waters and naturally in wastewaters, as well. It is a general problem in the whole world to purify the waters being contaminated with toxic components. The phenolic compounds are severe cell poisons that exert their effect by absorption through the skin or by their steams being inhaled.

In the professional literature studied by us, five basic methods were found for the decomposition i.e. the removal of phenol and of other contaminants [9,8,3,7,6,5,2]

- *photocatalytic decomposition,*
- *enzyme decomposition*
- *fermentation*
- *membrane separation*
- *adsorption*

According to the data published by the WHO, the maximal values of phenolic compounds in potable waters are the followings: from 2,4,6-trichlorophenol 200 µg/l, from pentachlorophenol 9 µg/l, from 2-chlorophenol 10 µg/l, 2,4-dichlorophenol 40 µg/l.

## 3. EXPERIMENTAL MATERIALS AND METHODS

The company FLORATOM LTD. out of its wells Im34 and Im36 provided the thermal water used for our experiments.

The membrane separation measurements were carried out on a semi-industrial membrane filter PC1 provided with tubular modul with a filtering surface area of 0,9 m<sup>2</sup>. The membranes applied: ES209 and AFC99, the pressure values used: 0,6, 1,0, 6,0 MPa.

The amount of the permeate was determined every minute with help of an on-line computer-balance system.

During the investigations, the temperature was measured with an alcoholic rod-thermometer, the conductivity with an equipment type OK 102/1 made by RADELKIS, the absorbed energy by the help of a mobile equipment for capacity measurement.

From the values of flux, the equivalent permeability (NWP, i.e. Normalised Water Permeability; the flux ( $q_m$ ) values referring to a surface (A) unit, a pressure difference ( $\Delta p$ ) unit, a time unit and a temperature ( $f_t$ ) of 20 C°) were determined with the following formula:

$$NWP = \frac{q_m \cdot f_t}{A \cdot \Delta p} \left[ \frac{\text{kg}}{\text{m}^2 \text{h bar}} \right] \quad (1)$$

The phenol concentration was measured after a calibration with samples of known concentration by liquid chromatography (Merck-Hitachi pump type L-7100, and detector type L-4250 UV-Vis). In the testing laboratory accredited by the NAT under number 501/0714 of the Directory for Water Affairs the phenol index was measured according to the specifications fixed in the norm MSz 1484-1:1992 (Water testing, determination of phenol index) with the help of photometry determination based on 4-aminoantipyrine colour reaction, in mg/l.

#### 4. RESULTS AND EVALUATION

With consideration of the fact, that our primary target has been the reduction of the phenol content of thermal water below the limiting values of the regulations i.e. below a value of 3 mg/l, an ultrafiltration technique, having a higher permeability and applicable with lower pressure values, with two different pressure values was used for our investigations

On **Figure 1.**, the equivalent mass-current values belonging to two different pressure values were drawn up, on **Figure 2.**, the changes of phenolic content measured for different samples were illustrated.

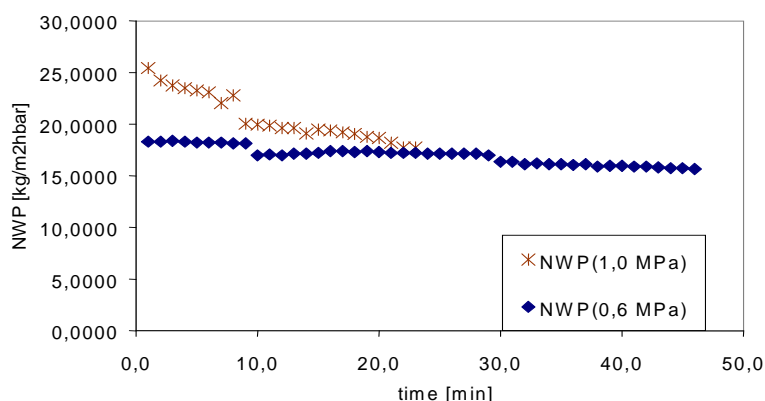


Fig. 1.: UF Flux values

of equivalent flux of the two experiments made with two different pressures got similar and the  $16 \text{ kgm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  value that could be considered as the mean, set in.

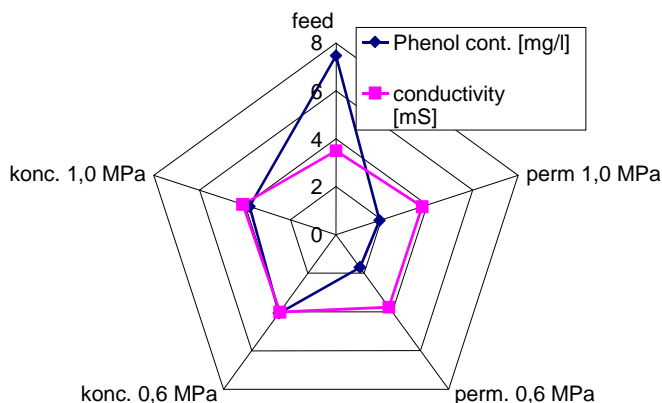
At an ultrafiltration with 6 and with 10 bar pressures, high flux values were measured being very favourable in case of an industrial realisation. After the first 20 minutes of the measuring, the values of equivalent flux of the two experiments made with two different pressures got similar and the  $16 \text{ kgm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  value that could be considered as the mean, set in.

On the figure (**Figure 2.**) presenting the phenol content of the samples, it can be well seen that the water showing originally high (7,48 mg/l) phenol content could be reduced below the limiting value (3 mg/l)

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with 0,6 MPa (1,69 mg/l) and with 1,0 MPa pressures (1,91 mg/l) by ultrafilter membranes.

It can be observed on the figure, that there is no significant difference neither in the conductivity nor in the ionic content determining mostly the conductivity in consideration of the permeate and the concentrate samples.

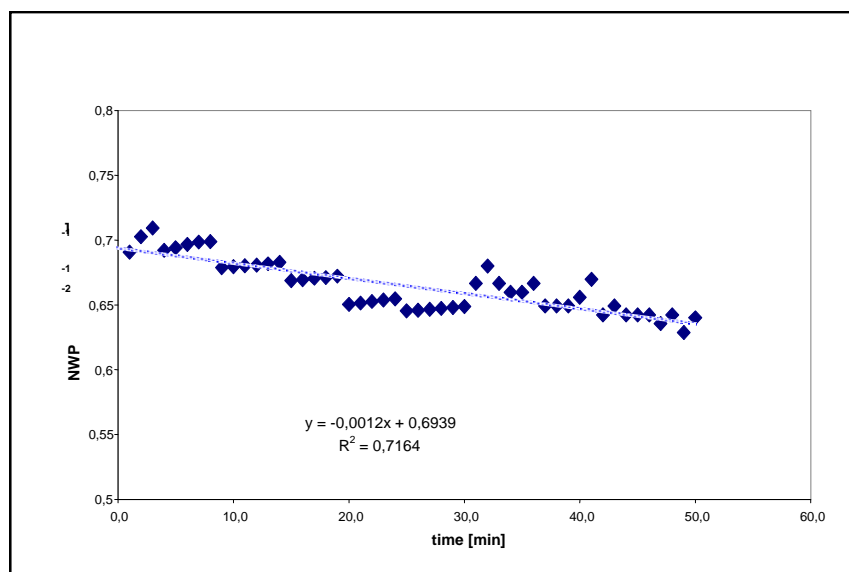


Our experiments have proved, that the reduction of phenolic content can be successfully achieved by help of ultra-filtration, but this separation technic does not cause any significant change in the equally high ionic content of the samples.

Fig.2.: Phenol content and conductivity of samples

In order to reduce the ionic components of the samples, the reverse osmose (RO) with an AFC 99 membrane, with 0,9 m<sup>2</sup> filtering area and a pressure of 6,0 MPa was applied. See Figure.3.

The equivalent mass-current values (NWP) measured at reverse osmosis are lower compared to the values measured at ultra-filtration due to the close pore structure of the membrane. The change of the mass-current in function of time is also significant. In the permeate obtained with reverse osmosis, the phenolic content i.e. the presence of phenolic compounds could not be detected.



The ionic content of the thermal water decreased in a considerable degree in the permeate samples obtained with reverse osmosis, as this has been presented in Figure 4.

Fig.3.: Normalised Water Permeability during RO

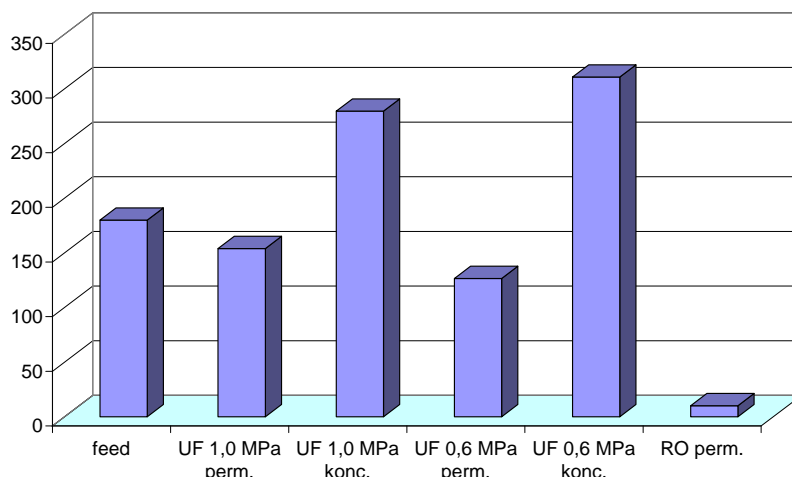


Fig.4.: Ions contain of samples

With the used HPLC method, the separation and exact determination of the ions were impossible, as they were eluted together with the solvent front. Nevertheless, from the size of their sign, the total ion content of the samples could be deduced. The amount of ions is given in the figure in arbitrary relative units being proportionate with the area of the relative chromatographic peak

### 6. SUMMARY

The most important results of our experiments have been summarized in **Figure 5**. On base of this figure it can be found, that for the reduction of the phenolic content of the thermal water to below the limiting value of 3 mg/l, ultra-filtration (ES209 membrane, 0,5 and 1,0 MPa pressures) and also reverse osmose (AFC99 membrane) can be applied as suitable separation technics.

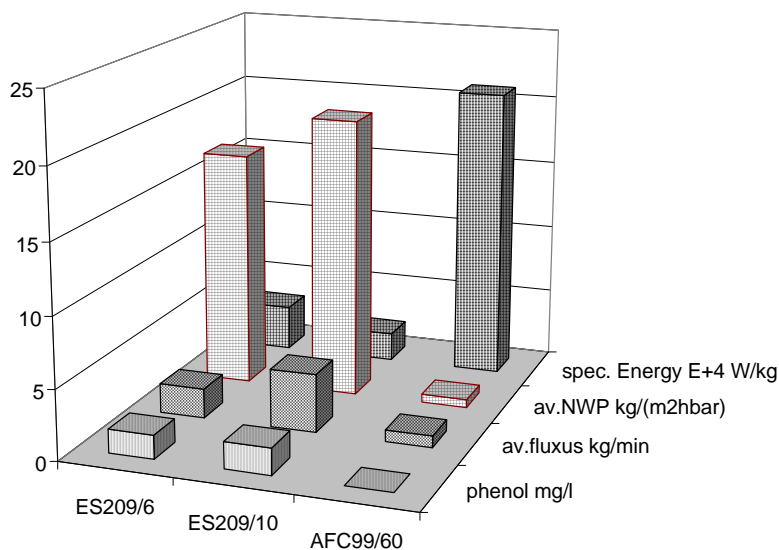


Fig.5.: Summary of results

However, for the removal of total phenolic content, only the reverse osmosis can render possibility, further this technic of membrane separation is capable to reduce the high ionic content of the thermal water, while this effect could not be naturally demonstrated with ultra-filtration. In case of the values of mass-current and the equivalent mass-current, the ultra-filtration technic produces the most favourable higher values and thus, the specific energy consumption i.e. the amount of energy required for the removal of 1 kg permeate show highly more favourable values.

For the removal, decomposition of the phenol cumulated in the concentrate in case of the thermal wells of Szentmihálytelek, the highly effective oxidation and fermentation process seems to be hopeful.

## 7. REFERENCES

1. BARNI B. CAVICCHIOLI A. RIVA E. ZANONI L. BIGNOLI F. AND BELLOBONO R. I. (1995) Pilot-plant-scale photodegradation of phenol. Vol.30. No.10. pp.1861-1874.
2. BÉLAFI-B K. GUBICZA L. (2000) Biocatalysts and Membranes, in Integration of Membrane Processes into Bioconversions. Kluwer Academic, London, pp.131-140
3. DAVI L. M. GNUDI F. (1999) Phenolic compounds in surface water. Wat. Res. Vol.33. No.14. pp.3213-3219.
4. GARCÍA G. I. PENA J. P. R. VENCESLADA BONILLA J. L. MARTÍN M. A. SANTOS MARTÍN M. A. GÓMEZ R. E. (2000) Removal of phenol compounds from olive. Process Biochemistry. Vol.35. pp.751-758.
5. LEE SA. CHOO KH. LEE CH. LEE HI. HYEON T. CHOI W. KWON HH. (2001) Use of ultrafiltration membranes for the separation of  $TiO_2$ . Vol.40. (7). pp.1712-1719.
6. MASQUÉ N. MARCÉ R. M. BORRULL F. (1998) Comparison of different sorbents for on-line solid-phase extraction of pesticides and phenolic compounds. Vol.793. pp.257-263.
7. SIMONIC M. OZIM V. (1998) Thermal water treatment with granular activated carbon. Journal of Hazardous Materials. Vol. 60. pp.205-210.
8. VASSILEV N. FENICE M. FEDERICI F. AND AZCON R. (1997) Olive mill waste water treatment by immobilized cells of *Asp. Niger* and its enrichment with soluble phosphate. Process Biochemistry. Volume 32. Issue 7. pp. 617-620.
9. YAMAGISHI T. LEITE J. UEDA S. YAMAGUCHI F. SAWA Y. (2001) Simultaneous removal of phenol and ammonia by an activated sludge process with crossflow filtration. Water Research. Vol.35. Issue 13. pp.3089-3096. 2001

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