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Combination of Membrane Separation and Ozonation in Waste Water Management

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Abstract

One of the environmentally friendly energy sources is the geothermal energy. There are numerous thermal water sources in Hungary, but their high ion concentration and other harmful component contents (e.g. phenolic compounds) in water is the limit of the applicability of this type of energy. The objective of our work is to reduce the high phenol content of water. In recent work we aimed the comparison of different membrane separation techniques and advanced oxidation processes to eliminate phenol from thermal wastewater, and reducing concentration of other pollutants below the permissible level.
It was found that the ultrafiltration and reverse osmosis is applicable to remove the phenol and sodium-ion content from water. The high phenol content of wastewater and retentatum (causing other environmental problem) was reduced by ozonation. The effect of preozonation of wastewater on efficiency of membrane separation also was investigated.

Keywords: Thermal water, phenol, membrane separation, reverse osmosis, ultrafiltration, ozone treatment

INTRODUCTION

One of the environmentally friendly energy sources is the geothermal energy. There are numerous thermal springs in Hungary, but the waters contain ions in high concentration and other harmful components (e.g. phenolic compounds). The protection, defence of our potable waters should be an important task of our everyday life, thus the water quality limits the applicability of these thermal waters.

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

The other problem is that saliferous waters or waste waters leaded to living waters may damage the life, especially in the stagnant waters, lakes or dead channels.

The most frequently used methods to remove the salinity are the membrane separation processes. This methods (e.g. reverse osmosis) can decrease the dissolved ion concentration in the water, or even the organic pollutants, but these compounds concentrate in the retentate, which thus became dangerous waste.

Therewith are several methods to eliminate the organic pollutants from water (Barni et al., 1995., Bélafi-B K., Gubicza, L., 2000., Davi L.M., Gnudi, F., 1999. Yamashigi, T et al., 2001.) as:
- enzyme decomposition,
- fermentation,
- adsorption,
- or advanced oxidation processes: ozonation, UV radiation, or photocatalitic decomposition.

The wide exploitation of the heat energy content of the thermal water is highly impeded compromised by its high phenolic and ionic contents. The companies operating the wells are paying considerable sums for wastewater penalties due to the higher than admissible phenolic content of the outlet water.

The aim of our work has been purification of the water coming from the thermal wells in the county of Szeged by membrane separation techniques, and thus making it applicable to be used for the heating of greenhouses, and to lead the residual thermal water to a living water or the Tisza-dead channel.

MATERIALS AND METHODS

The thermal water provided the company FLORATOM Ltd. wells marked Im34 and Im36 was used for our experiments. Initial temperature of the water is about 70°C and pH is 8.78.

Crossflow membrane filtration was performed for raw and ozonated water respectively. The ultrafiltration measurements were carried out on a pilot-plan membrane filter PC1 provided with tubular module with a filtering surface area of 0.9 m². The pressure values of the membranes applied ES209 used: 0.6, 1.0 MPa. The amount of permeate was measured in every minutes with help of an on-line computer-balance system.

The reverse osmosis measurements were carried out on a laboratory membrane filter Uwatech 3DTA (Uwatech Gmbh., Germany) provided with a filtering surface area of 0.02 m². The membranes applied: for reverse osmosis made from composite were AK (theoretical NaCl retention 99.0%, ideal for brackish water filtration), AD (NaCl retention 99.5%, ideal for sea water filtration). The pressure values used: 30 and 50 bar. The measurements were carried out in 20°C and 40°C.

The temperature was measured with an alcoholic rod-thermometer, the conductivity with an equipment type OK 102/1 made by RADELKIS during the investigations. From the values of flux (q_m) the equivalent permeability (NWP, i.e. Normalised Water Permeability, values referring to a surface (A) unit, a pressure difference (Δp) unit, a time unit and a temperature (f_t) of 20 C°) were determined with the following formula:

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

Ozone was produced from oxygen by a flow-type ozone-generator, operating silent electric discharge. The ozone containing gas continuously was bubbling throughout a batch reactor, during the treatment. The treating time was 60 min in all cases, the flow rate was 1 dm³ min⁻¹. The ozone concentration of bubbling gas before and after the reactor was followed by an UV spectrophotometer (WPA Lightwave S2000) at 254 nm. The ozone concentration of the feed gas was 1.7 mg dm⁻³.

The phenol concentration was measured by liquid chromatography (Merck-Hitachi pump type L-7100, and detector type L-4250 UV-Vis) using a calibration with samples of known concentration 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.

RESULTS

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.
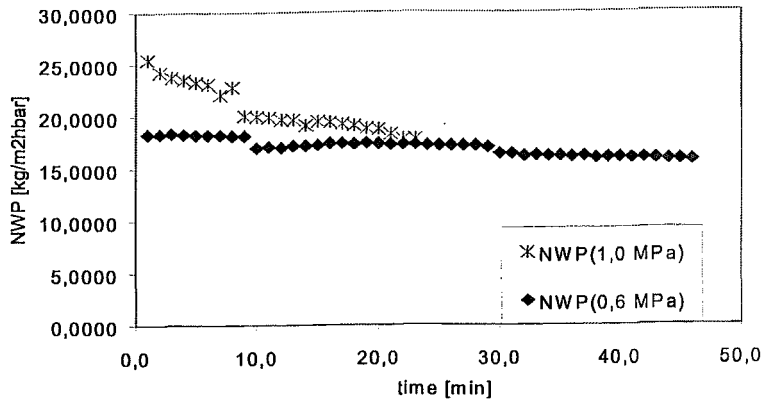
Figure.1.: UF Flux values

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 measurement, the values of equivalent flux of the two experiments made with two different pressures got similar and the 16 kg m^{-2} h^{-1} 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), with 0,6 MPa (1.69 mg/l) and with 10 bar pressures (1.91 mg/l) by ultrafilter membranes. On the other hand it can be seen 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.
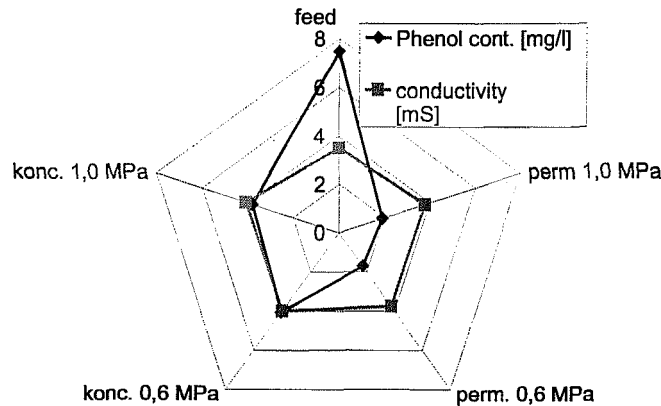

Figure.2.: Phenol content and conductivity of permeates (perm) and the retentate (konc.)

In order to reduce the ion-contents of the samples, the reverse osmosis (RO) was applied with different membranes, temperatures and pressures.

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 exception was only the AD membrane at 50 bar pressure in the early stage of the filtration, then the NWP values reached 140 kg m^{-2}bar h.

Two types of reverse osmosis membrane were compared in Fig. 3. It was found that at 30 bar pressure the NWP of two membranes is similar, and it is decreases with filtration time. At higher pressure, the permeability of the AD membrane decreases very fast, however in the early stage of the filtration it was extremely high value. On he other hand, the permeability of the AK membrane did not changed practically.
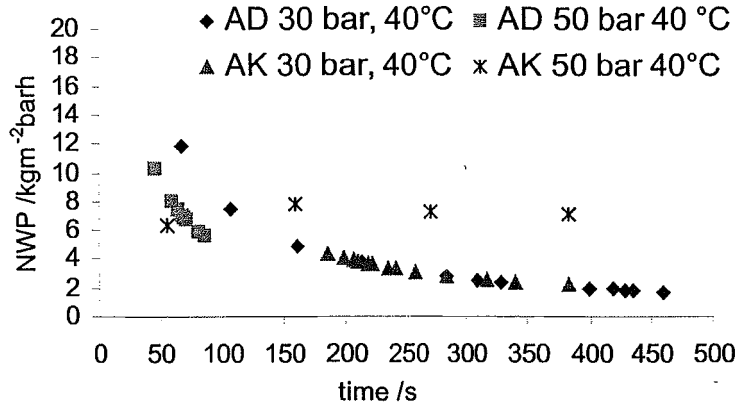
Figure 3. Normalised Water Permeability of different membranes during RO .

Significant difference was observed in phenol retention ability of the two membrane: AD membrane had no retention ability for phenolic components at 30 bar pressure, and only slight effect at 50 bar, while the AK membrane was very effective in decreasing phenol concentration at 30 bar. (Fig. 4)
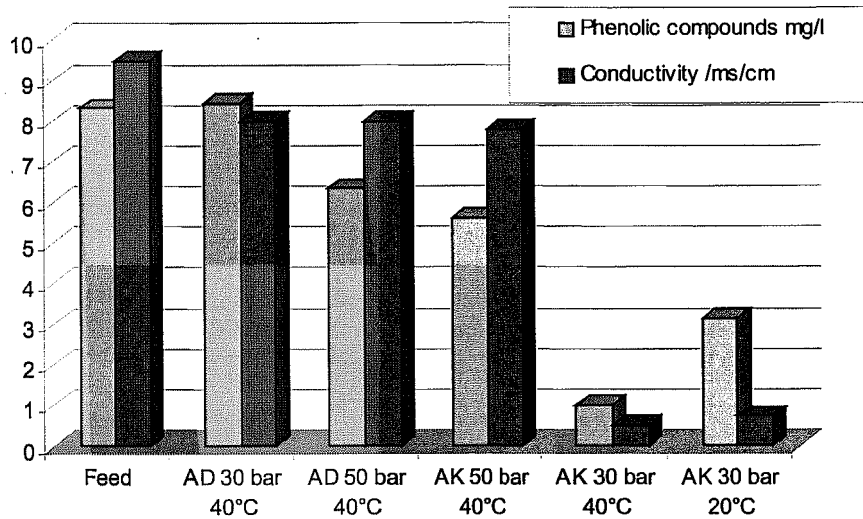

Figure 4.: Phenol content and conductivity of permeates

The results show, that the AK membrane is not useable at higher pressures, but it decreases the phenol concentration and the produced ion content is below the permissible value, thus it is suitable for treating the thermal water. The experiments also show, that the membrane filtration in higher temperature (at 40°C) more effective than in 20°C.

Nevertheless the problem remains that the phenol content of the thermal water concentrated in the retentate may cause environmental problems, the rather because the volume of the retentate is about fifth of the feed, thus the phenol concentration is more higher than in the feed.

In an other series of experiments ozone was used to eliminate the toxic phenolic components from the water and retentate. The change of phenol conversion rates in feed thermal water and the concentrate are shown in Fig.5. The results show that the phenolic index of both solutions decreases, the phenolic compounds decompose. The volume of the feed water was 1.8 dm^3, the volume of the retentate obtained from 1.8 dm^3 thermal water after membrane filtration (with AK membrane, at 30 bar, and 40°C) was 0.2 dm^3. The total amount of phenolic compounds was nearly equal and the ozone doses in the feed gas were equivalent in both cases. It was found that the degradation time of the phenolic compounds is shorter in retentate. This means that the ozone demand for degradation of phenolic compounds less in the retentate, than in original thermal water, according to the

experiences that the reaction of ozone with phenolic compounds is first-order reaction represents by the following relationship (Langlais et al.1991):

$$\ln \frac{[Ph]}{[Ph]_0} = -k \times [O_3] \times t \qquad (2)$$

where [Ph] the phenolic index (mg dm^{-3}), k (min^{-1}) is the rate constant, [O$_3$] the ozone concentration in the solution (mg dm^{-3}) and t (min) is the reaction time. According to the relationship, higher ozone concentration in less reaction volume (in retentate) results shorter degradation time, while the amount of conversed phenolic compounds are equal. Significant effect of higher ion concentration in the retentate on the degradation rate of phenolic compounds was not observed.
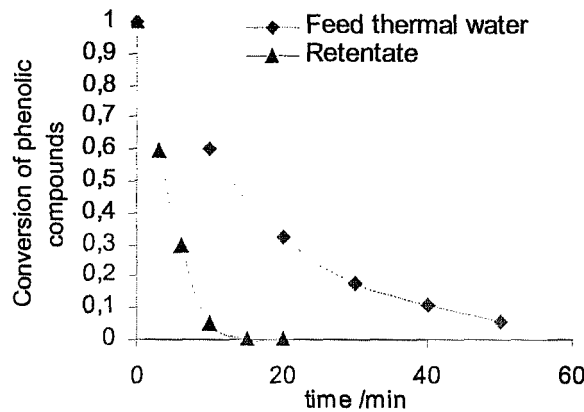

Figure 5. Conversion of phenolic compounds in thermal water (1.8 dm^3) and in retentate (0,3 dm^3) after membrane separation, absorbing 1.7 mg ozone/min.

In the next series of experiments it was investigated that the elimination of phenolic compounds affects on the permeability of the reverse osmosis. It was found that the normalised water permeability values did not changed significantly after ozonation. (Fig. 6.)
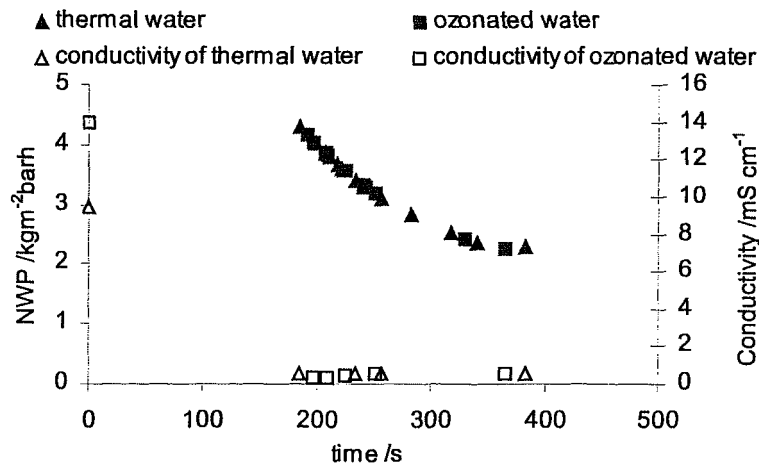

Figure 6. Normalised Water Permeability and changes of conductivity during RO with AK membrane, at 30 bar and 40°C.

The conductivity of the ozonated solutions was also measured. It was observed that the conductivity increased during ozonation, probably aliphatic organic acids formed from the phenol. The reverse osmosis is suitable to filter these compounds also, the conductivity of the ozonated solution also decrease during RO treatment. (Fig.6.)

CONCLUSIONS

The aim of our work was to find a method to reduce the phenol content and decrease the high ion concentration of thermal water used to heat greenhouses. Membrane separation techniques and ozone treatment was investigated. It was found that the phenol concentration can be decreased below the limiting value by ultrafiltration and reverse osmosis with AK type composite membrane, and it can be removed perfectly by ozone treatment. It was found that the higher ion concentration has not affected on the efficiency of degradation of phenolic compounds, while the higher ozone concentration increased the degradation rate.

The ozonation of retentate seems more suitable method for degradation of phenolic components, taking into consideration that the preozonation has no significant effect on filtration permeability. The reverse osmosis was only the suitable method for removal of ion content of thermal water. It is capable to reduce the high ionic content of the thermal water, while this effect could not be naturally demonstrated with ultra-filtration. , the ultra-filtration techniques produces the most favourable higher values for mass-current and the equivalent mass-current

It was also found that the reverse osmosis treatment for removing ion content and phenolic compounds more efficient at higher temperature.
On the basis of above results the following appropriation was proposed to achieve the desired wastewater quality (Fig. 7.)
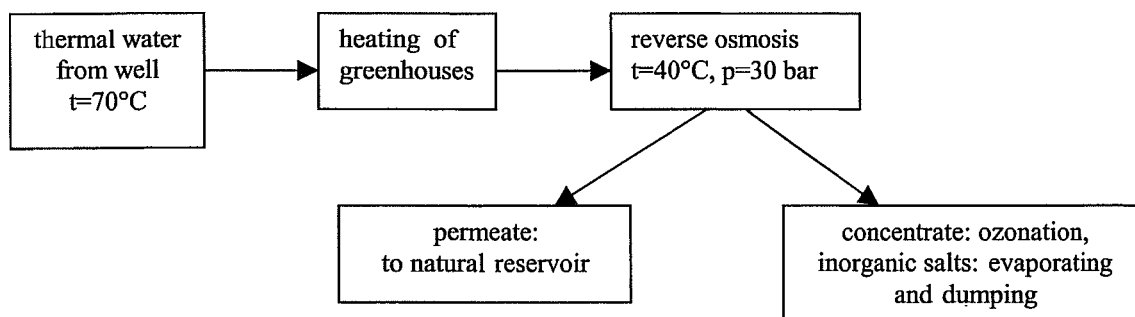

Figure 7. Scheme of the thermal water treatment

ACKNOWLEDGEMENTS

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. Bellamy, W.D., Damez, F., Langlais, B., Montiel, A., Rakness, K.L., Reckhow, D.A., Robson, C.M.. 1991. Engineering Aspects, in Ozone in Water Treatment, Langlais, B., Reckhow, D.A., Brink, D.R, Lewis Publishers Inc. 121 South Main Street, Chelsea, Michigan 48118
5. Yamagishi T. Leite J. Ueda S. Yamaguchi F. Sawa Y. 2001. Simoltaneous removal of phenol and ammonia by an activated sluged process with crossflow filtration. Water Research. Vol.35. Issue 13. pp.3089-3096. 2001