Environment Protection Engineering

Vol. 31 2005 No. 3–4

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# THE INFLUENCE OF ORGANIC COMPOUNDS ON REJECTION OF INORGANIC COMPOUNDS IN THE NANOFILTRATION PROCESS

The influence of the glucose addition on the rejection of organic and inorganic compounds and on the changes of the permeate flux has been studied. The feed comprised aqueous solutions of mono- and divalent salts (KCl, NaCl, $K_2SO_4$, $Na_2CO_3$ and $NaHCO_3$) in various concentrations. The permeate flux was not changed in any solution of inorganic salts, except the solution of $K_2SO_4$, when glucose was added to these solutions. In this case, the permeate fluxes decreased by about 9–13%. The retention coefficient of total dissolved solids (for various solutions) was not affected by glucose added to the feed containing inorganic compounds. The rejection of total organic carbon in the mixture of $Na_2CO_3$ and glucose was lower by about 6% than that in glucose solution.

Keywords: *nanofiltration, Donnan effect, organic compounds*

## 1. INTRODUCTION

Waters containing low-molecular weight (MW) humic substances can be difficult to treat by coagulation processes, as small molecules and uncharged species are less effectively removed. The charged impurities can be removed from water by ion exchangers or adsorbents. Oxidative degradation, followed by biological treatment, is the option of removing all organic species. There is the scope for a vastly improved approach to achieve a more economical treatment of organics [1]. The nanofiltration membranes have the capabilities to retain the organic compounds of a molecular weight greater than 200 g/mol [2].

Size effects of uncharged molecules may contribute to rejection, especially in the cases where the hydrophilic character of solutes is similar. In the case of swollen polymeric networks, the size exclusion is not the only determining factor, since

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the solubility effects may be important as well. This makes the use of molecular weight cut-off to evaluate the separation characteristic rather arbitrary [3].

Nanofiltration (NF) membranes can also be used to separate monovalent ionsfrom bivalent ions or to adjust their ratio. As is well known, for the above purpose, the membrane not only should be a nano-sized pore structure, but it also should be charged on the surface. The separation mechanism of NF membranes is assumed to be based on a combination of several processes such as size exclusion, charge exclusion, and sometimes is referred to as dielectric exclusion [4].

The multivalent ions are separated by the NF membrane in a high degree, whereas a majority of monovalent ions pass freely through the membrane. This phenomenon is associated with the Donnan effect [5], [6]. The retention coefficient (RC) of divalent cations is approximately three times larger than that of the monovalent cations [7]. The retention coefficient in the NF process may be also affected by a degree of ion hydration.

The objective of these studies was to determine the influence of glucose on the rejection of organic and inorganic compounds in nanofiltration process and on variation of the permeate flux.

## 2. EXPERIMENTAL

The NF process was carried out at a pilot plant equipped with a spiral wound module with the membrane NF 270-2540 (Filmtec) whose working area amounted to 2.6 $m^2$. This is the composite membrane containing a semi-aromatic piperazine-based polyamide layer on top of a polysulfone microporous support reinforced with a non-woven polyester backing layer [8]. The scheme of NF pilot plant is presented in figure 1.

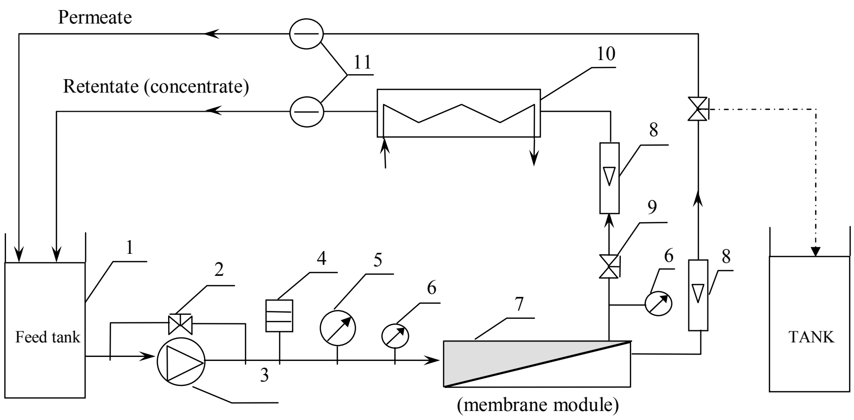


Fig. 1. Scheme of NF/UF pilot plant:
1 – feed tank, 2 – by-pass valve, 3 – pump, 4 – dampener, 5 – pressure gauge, 6 – manometer, 7 – module, 8 – rotameter, 9 – throttling valve, 10 – heat exchanger, 11 – control of temperature and conductivity

The process proceeded in a closed system in which the permeate was recycled directly to the feed tank to ensure a constant feed concentration. The feeding was performed in a cross-flow system. The investigations were carried out at a constant transmembrane pressure equal to 1.0 MPa and at the feed temperature of 25 °C.

In the experiment, two kinds of feed were used: a permeate from the RO pilot plant or one-component solution of glucose and NaCl, KCl, $Na_2CO_3$ and $K_2SO_4$ or two-component solutions containing selected salts and glucose (40 or 80 mg C/dm$^3$). The model solutions were prepared using the RO permeate. The RO permeate was a pure water of the TOC content of 0.3 mg/dm$^3$ and the electrical conductivity of 10 μS/cm. The RO permeate was used as a feed which allowed determining the maximum permeate flux (MPF) under given process conditions.

The samples of permeate and feed were collected at various time intervals (every hour or every 10 minutes) in order to determine the retention coefficient of the organic compounds (total organic carbon (TOC)) and inorganic compounds (total dissolved solids (TDS)). The retention coefficient (RC) was calculated as follows:

$$\text{RC} = \left(1 - \frac{C_P}{C_F}\right) \cdot 100\% , \qquad (1)$$

where: $C_P$ – the concentration of the component in the permeate, $C_F$ – the concentration of the component determined in the feed.

The content of total dissolved solids in the solutions tested was determined using a 6P Ultrameter (Myron L Company). The content of TOC was measured using a Multi N/C Analyzer (Analytic Jena) with a detection limit of 0.02 mg/dm$^3$.

## 3. RESULTS AND DISCUSSION

The investigations were carried out to determine the influence of glucose addition to aqueous solutions of inorganic compounds on the rejection of these compounds. At the beginning of the studies the nanofiltration process was performed in order to determine the permeate flux and the retention coefficient of salts at their various concentration (100–1000 mg of inorganic salts/dm$^3$) in the feed. The results of nanofiltration of $K_2SO_4$ aqueous solution are presented in figure 2.

It can be seen in figure 2 that at an increased concentration of inorganic salt in the feed the permeate flux (PF) decreased gradually. This effect was observed only for the solutions of $K_2SO_4$. The PF was equal to 44 dm$^3$/m$^2$·h (at 100 mg/dm$^3$) and decreased by about 16% when the concentration of $K_2SO_4$ in the feed was increased up to 1000 mg/dm$^3$. The PF decreased by about 9–13% when glucose was added to the feed.

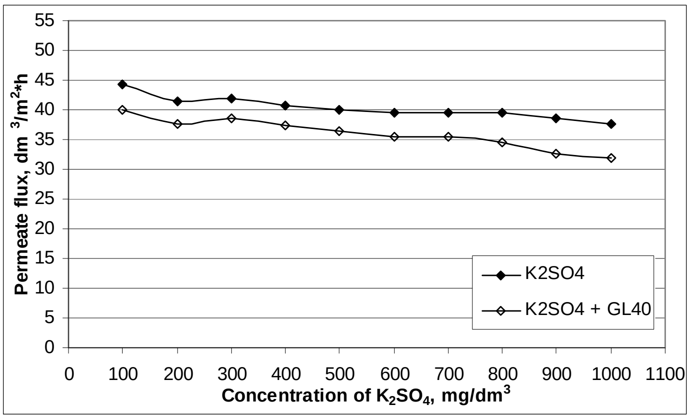


Fig. 2. The dependence of the permeate flux on the concentration of inorganic salt.
The composition of feeds was as follows: aqueous solution of $K_2SO_4$
and aqueous solution of $K_2SO_4$ with glucose addition
(GL40 – solution of glucose whose constant concentration was equal to 40 mg C/$dm^3$)

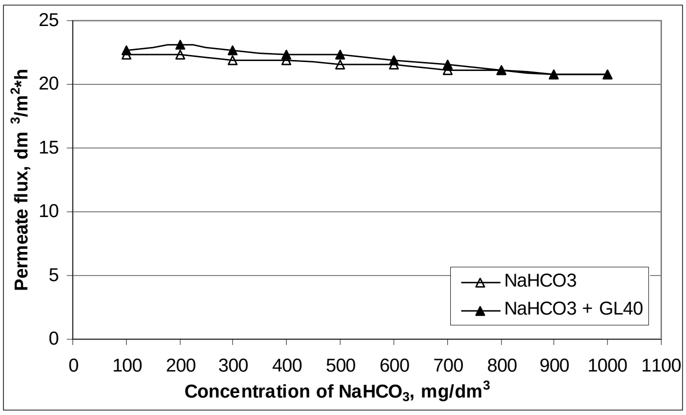


Fig. 3. The dependence of the permeate flux on the concentration of inorganic salt.
The feeds: aqueous solution of $NaHCO_3$ and aqueous solution of $NaHCO_3$ with glucose addition

Figure 3 shows variations in PF when the solution of $NaHCO_3$ was used as a feed. The permeate flux slightly decreased with an increase in the concentration of salts in the feed. Glucose added to the feed did not change the permeate flux. During the NF process of aqueous solution of $K_2SO_4$ and $NaHCO_3$ with the glucose addition the solute concentration near the membrane surface was large which caused a decline of PF. In the case of the other solutions containing NaCl, $Na_2CO_3$ or KCl, the change of the permeate flux with an increase in these feed concentrations was practically negligible. The glucose effect on the permeate flux was negligible, too.

The values of retention coefficient of TOC and TDS were determined and the results are presented in figure 4.

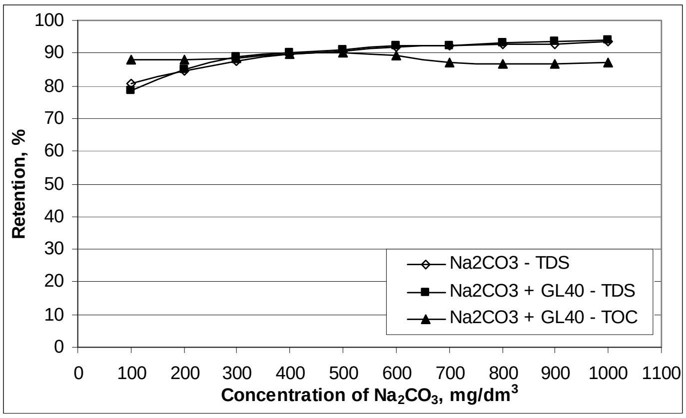


Fig. 4. The influence of the glucose addition on the retention coefficient of TOC and TDS. The feeds: aqueous solution of $Na_2CO_3$ with or without glucose addition

The results showed that the retention coefficient of TDS increased with an increase in the concentration of salt in the feed. However, the rejection of TDS did not change after glucose addition to the feed. On the other hand, the rejection of TOC in the mixture decreased by about 5% when the salt concentration ranged from 100 to 600 mg/dm$^3$ compared to the glucose solution, especially when the feed concentration containing the inorganic compounds was increased from 600 to 1000 mg/dm$^3$. The rejection of TOC reached 93% when the glucose solution of the concentration of 40 mg/dm$^3$ was employed as a feed. For the remaining solutions investigated the retention coefficient of TDS was constant and dependent on the separation characteristic of the membrane. Moreover, the degree of TOC rejection was constant and equal to the rejection of TDS.

Then the experiments were carried out on both NF modules: tubular (with the NF AFC30 membrane) and spiral-wound (with NF 270-2540 membrane). The feed contained such an inorganic salt as KCl whose concentration reached 500 and 1000 mg per 1 dm$^3$. These feed solutions were enriched with glucose (40 mg C/dm$^3$). The results obtained are presented in figures 5–6.

The changes of the permeate flux were not observed in the case the NF 270-2540 membrane when glucose was added to the solutions of KCl. The PF approached 40 dm$^3$/m$^2$·h. However, the PF was greater by about 10% compared to the AFC 30 membrane. When the feed containing glucose was used for both membranes the permeate flux for the NF270-2540 membrane was higher by 28% than that for AFC30 membrane. Different materials of the membrane and formation of linear flow streams in the modules are responsible for the differences in the permeate fluxes for both membranes.

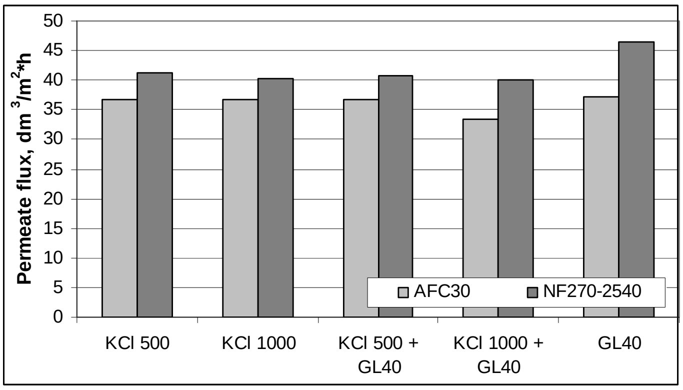


Fig. 5. Determination of permeate flux when the solution of KCl with or without glucose was the feed. The feeds: KCl – solution of KCl in two concentrations, GL40 – solution of glucose in a constant concentration equal to 40 mg C/dm$^3$, and KCl + GL40 – the solution of KCl with glucose

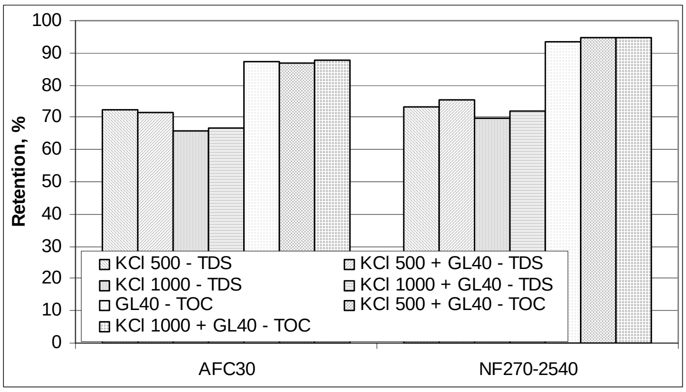


Fig. 6. Determination of the retention coefficient of TDS and TOC for the solutions investigated. Feeds: KCl – solutions in two concentrations of KCl, TDS and TOC – retention coefficient of TDS or TOC, GL40 – solution of glucose in a constant concentration (40 mg C/dm$^3$), KCl + GL40 – solutions of KCl with glucose

The rejections of TOC and TDS are presented in figure 6. When glucose was added to the feed the changes in the retention coefficient of TOC were not observed in the case of any membrane. The rejections were equal to 93% for NF 270-2540 membrane and 87% for AFC30 membrane. Glucose in the feed did not change the retention coefficient of TDS. Subsequently the concentration of glucose was increased up to 80 mg C/dm$^3$ in the feed and the permeate flux was again determined. It was found that the higher concentration of glucose did not affect the permeate flux. The permeate flux was on the same level as in the case of KCl solution.

## 4. CONCLUSIONS

The NF process was carried out using various aqueous solutions ($K_2SO_4$, KCl, $Na_2CO_3$, $NaHCO_3$ with the addition of glucose). It was found that glucose did not affect the changes in retention coefficient of the salts studied with the exception of the solution of $Na_2CO_3$. The retention coefficient of TOC for $Na_2CO_3$ solution with the glucose addition was lower by 5–6% than that for the solution of glucose. The permeate fluxes obtained for all aqueous solutions of inorganic salts with glucose addition did not change (with the exception for $K_2SO_4$), but the permeate fluxes differed from each other. The permeate flux for $K_2SO_4$ was equal to 44 $dm^3/m^2\cdot h$ (at the 100 $mg/dm^3$) and decreased by about 16% when the salt concentration in the feed was increased up to 1000 $mg/dm^3$. The permeate flux decreased by about further 9–13% when glucose was added to the feed.

The permeate flux for the mixture of KCl and glucose solution did not change with an increase in the glucose concentration up to 80 mg $C/dm^3$ with the exception of the permeate flux obtained when the glucose was used as a feed. In this case, the permeate flux was on the same level as for the KCl solution. The values of the retention coefficient of TDS and TOC were not changed when the glucose was added to the feed.

## REFERENCES


[1] BOLTO B., DIXON D., ELDRIDGE R., *Ion exchange for the removal of natural organic matter*, Reactive & Functional Polymers, 2004, 60, pp. 171–182

[2] LOPES C.N., PETRUS J.C.C., RIELLA H.G., *Color and COD retention by nanofiltration membranes*, Desalination, 2005, 172, pp. 77–83.

[3] SCHAFER A.I., FANE A.G., WAITE T.D., *Nanofiltration – Principles and Applications*, Elsevier, 2005, pp. 96–97.

[4] TONGWEN X., YINGQIANG F., XIAOLIN W., *Membrane potential model for an asymmetrical nanofiltration membrane consideration of noncontinuous concentration at the interface*, Desalination, 2004, 171, pp. 155–165.

[5] VEZZANI D., BANDINI S., Desalination, 2002, 149, pp. 477–483.

[6] TANNINEN J., NYSTRÖM M., *Separation of ions in acidic conditions using NF*, Desalination, 2002, 147, pp. 295–299.

[7] CHAUFER B., RAABILLER-BAUDRY M., GUIHARD L., DAUFIN G., Desalination, 1996, 104, pp. 37–46.

[8] MÄNTTÄRI M., PEKURI T., NYSTRÖM M., *NF270, a new membrane having promising characteristics and being suitable for treatment of dilute effluents from the paper industry*, Journal of Membrane Science, 2004, 242, pp. 107–116.