ZERO CONCENTRATE FLOW DISCHARGE MEMBRANE TECHNIQUES FOR NATURAL WATER TREATMENT

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Abstract

The main problem of modern RO and NF membrane techniques is the existence of concentrate flow that creates a problem of its utilization. Large amounts of RO/NF effluents are mainly attributed to fouling and scaling protection. Research of scaling and fouling mechanisms showed that these processes depend not only on hydraulic and hydrodynamic factors, but on membrane channel configuration as well.

The novel concept of spiral wound module with the modified membrane channel (called "open channel") is developed, field-tested and introduced into practice. Fouling control is achieved due to the elimination of spacer and the implementation of an optimum hydraulic mode.

Modification of channel provides the possibility to reach high recoveries and high supersaturation values due to strong stability of calcium carbonate solutions. The main principles of high recoveries and zero discharge are ensured by concentration of brine through re-circulation by 50-100 times by volume. Coagulated suspended matter after membrane flushes is collected, sedimented and finally dewatered. In case of hard water treatment the excessive calcium carbonate could be concentrated in membrane modules and subsequently precipitated, sedimented and dewatered. Several examples of water treatment flow diagrams are presented to demonstrate the principles of zero concentrate flow discharge.

Streszczenie

Podstawowym problemem współczesnych instalacji odwróconej osmozy i nanofiltracji jest powstawanie dużych ilości trudnego do zagospodarowania koncentratu. Problem ten nasila się w przypadku wystąpienia zjawisk fouling'u i scaling'u. Badania mechanizmu procesów fouling'u i scaling'u wykazały, że obok warunków hydraulicznych i hydrodynamicznych ma na nie wpływ konfiguracja kanałów ukierunkowujących przepływ przez membranę.

Opracowano nową koncepcję modułu spiralnego z ukierunkowanym przepływem (nazywaną "open channel") dzięki zastosowaniu odpowiednich przekładek w konstrukcji modułu membrany. Dobranie optymalnych parametrów hydraulicznych i eliminacja stref martwych pomogło w kontroli zjawiska foulingu i scalingu.

Zastosowane rozwiązanie budowy modułów membranowych zapewnia możliwość uzyskania recurkulatu o dużym stężeniu dzięki silnej stabilności roztworu węglanu wapnia. Wysoki odzysk zapewnia 50-100-krotna recyrkulacja stężonej solanki. Zawiesina wypłukiwana z membran po koagulacji jest poddawana sedymentacji i odwadnianiu. Zaprezentowano kilka przykładowych schematów uzdatniania wody wykorzystujących przyjęte rozwiązania.

Keywords: **Reverse osmosis; Spiral wound module; Water softening; water treatment; Zero-discharge.**

1. INTRODUCTION

Nowadays reverse osmosis and nanofiltration are wide spread in all water treatment application. This technology became cheaper and can successfully compete with conventional water purification technologies. The main disadvantage of modern membrane techniques is the existence of concentrate flow that creates a problem of its utilization and in some cases makes economically and ecologically unprofitable use RO and NF in public water supply. Large amounts of RO/NF effluents are mainly attributed to fouling and scaling protection.

It is known that the configuration of membrane channel and module should be considered as a decisive factor which influences fouling [1-5]. Spiral wound configuration is widely applied at more than 90% of all water installations but nevertheless is considered useless to treat surface water that contains suspended and organic matter due to fouling hazards. At the present time ultrafiltration is considered as the best pretreatment tool for RO facilities where tubular and capillary UF membranes are utilized. These membrane configurations are supposed to demonstrate better reliability than spiral wound flat sheet channel due to lower hydraulic resistance values, better conditions for hydraulic flushing and backwashing performance. Nevertheless, this technology is still expensive that makes RO pretreatment costs comparable with RO itself.

Continuing the success of hollow fiber ultrafiltration technology direct capillary nanofiltration started to be used for surface waters treatment [6, 7]. The process efficiency and reliability is attributed mainly to hydraulic and air flow conditions in the membrane channels that provide enough shear-force for the particles not to foul the membrane. But these systems are still not widely used in water practice.

This paper presents results from research that was conducted to improve conventional spiral wound configuration to directly treat natural water. The conclusion that membrane fouling is dependent not only on hydraulic factors but on channel configuration as well was claimed in publications as early as 1991 [2, 8] and this led to a reevaluation of the layout of the spiral wound module.

Spiral wound configuration is recognized as optimum both economically and technically, as it uses flat sheet membranes and provides high membrane area/module volume ratio at significantly low costs. However, the existing spiral wound module configuration is very susceptible to fouling and scaling that makes it useless to treat water containing high organics and suspended matter. The main disadvantages of spiral wound modules are attributed to the presence of a separation spacer mesh in the feed channel as it traps fouling particles and increases flow resistance. The mechanism of mesh performance and its influence on scaling/fouling process initiation has been proposed in [2, 8]. The places (spots) where mesh contacts membrane surface provide dead areas without cross-flow, thus resulting in high concentration increase at the membrane surface within this area. Concentration polarization increases and initiates formation of crystals and coagulation of colloids inside these dead areas. Membrane autopsies performed at different stages of fouling formation enabled us to trace crystals trajectories withdrawn from the dead areas and subsequently sedimented on the membrane surface. Organics and colloidal matter coagulate and sediment within the deadlock area providing further conditions for particle coagulation and adhesion to the formed layer promoting expansion of the foulant layer around these areas.

Elimination of the mesh could help to develop new types of modules with decreased fouling potential and provide new reliable and efficient techniques for surface water treatment. This idea was discussed by Richard Riddles in the report [1] devoted to the development of an open-channel spiral wound module. Many authors proposed various spacer types [4, 5, 9-12].

Most researches are made to improve the hydraulic conditions in order to decrease head pressure losses and to treat more contaminated streams [9-12]. Some researchers focus on the dependence of concentration polarization from spacer configuration [4, 5]. Less often, the effect of the spacer configuration on the scaling propensities of membrane module is examined.

The present research is devoted to the introduction of a new membrane technique based on new spiral wound membrane module with decreased fouling propensities and includes:

- selection of an optimum operational mode characterized by minimal values of cross-flow velocities corresponding to a minimum of chemical cleaning;
- development of an economical operation mode that corresponds to the minimum of concentrate and flush water disposal that could be reached due to an efficient selection of flushing frequency and duration;
- selection of membrane material with the best surface adhesive characteristics that provide lowest

fouling rates with the maximum shear-off effect during flushings.

2. DEVELOPMENT OF AN "OPEN-CHANNEL" MODULE DESIGN

Different innovations were implemented and tested throughout the research program performed. Various types of spacers, as well of double spacers were tried and tested. To eliminate dead areas and provide low flow resistance, a spacer should not touch the membrane surface. One of the best solutions was the idea of a "separate" spacer where mesh fibers are glued to the membrane surface. RO module spacer is a platted mesh where parallel groups of fibers are crossed and welded forming a rhombic structure (Fig. 1a). In our construction parallel groups of fibers (ledges) are glued to the membrane surface whereby ledges on opposite sides are oriented in different directions. The glued fibers form a rhombus having 1.2 mm width and 0.35 mm thickness. When a module is rolled, opposite membrane sides are pressed together but ledges separate the membrane surfaces providing enough space for flow with a very low resistance. The idea of a channel configuration was already patented and some innovations are being continuously introduced [2, 13-15]. Our second construction spacer is made using small plastic spots glued to the membrane. Several modules of the standard 1218 size were rolled using various types of NF and low pressure RO membranes (cellulose acetate, TFC based on polyvinyl alcohol and polyamide). Cellulose acetate asymmetric NF membranes were provided by Vladipore Co (Vladimir, Russia) and TFC RO membranes were ESPA samples (Hydranautics).

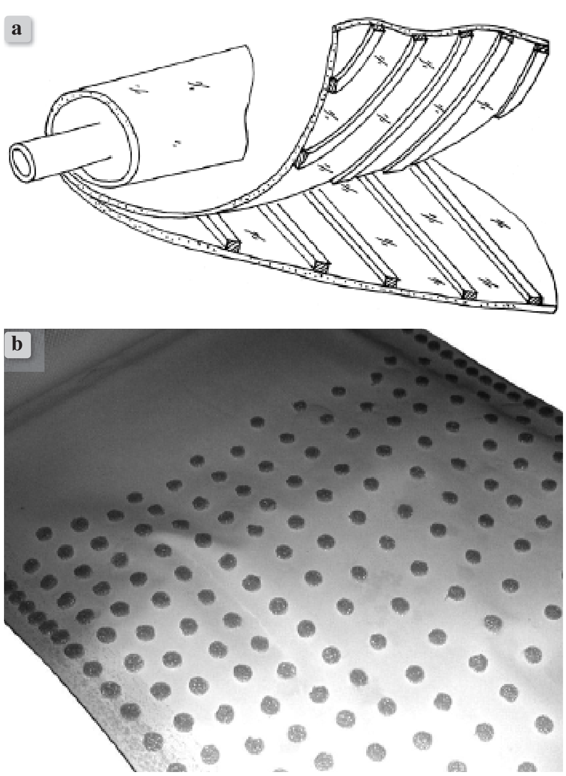

Figure 1.
Spiral wound modules with open-channel configuration

3. EXPERIMENTAL PROCEDURE AND TEST PROGRAM

The test program included:

- investigation of fouling rate dependencies on hydrodynamic flow characteristics;
- determination of TMP increases;
- investigation of chemical cleaning efficiencies;
- membrane performance (flow decrease);
- determination of fouling rates depending on membrane material.

The experimental program was performed using the membrane laboratory test unit shown in Figure 2.

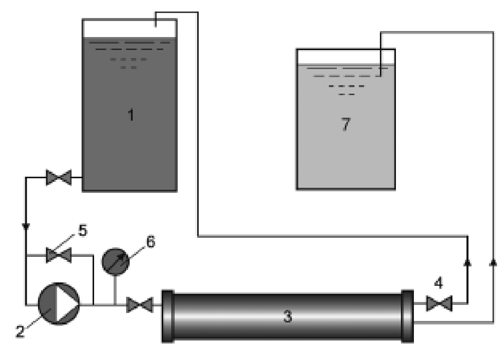

Figure 2.
Schematic diagram for NF test unit: 1 – feedwater tank, 2 – high pressure pump, 3 – RO/NF module, 4 – concentrate line valve; 5 – by-pass valve for adjusting operational pressure; 6 – pressure gauge; 7 – product tank

The test procedure is conducted in a circulation mode whereby rejected flow (concentrate) is returned to the feed water tank and product is collected in a separate tank. Determination of concentration values in the brine tank and in the product tank enables us to calculate the amount of foulant accumulated in the membrane module and fouling rates.

Natural river water was tested that had turbidity of 40 NTU, colour of 40-45 degrees, oxidability of 20-24 ppm.

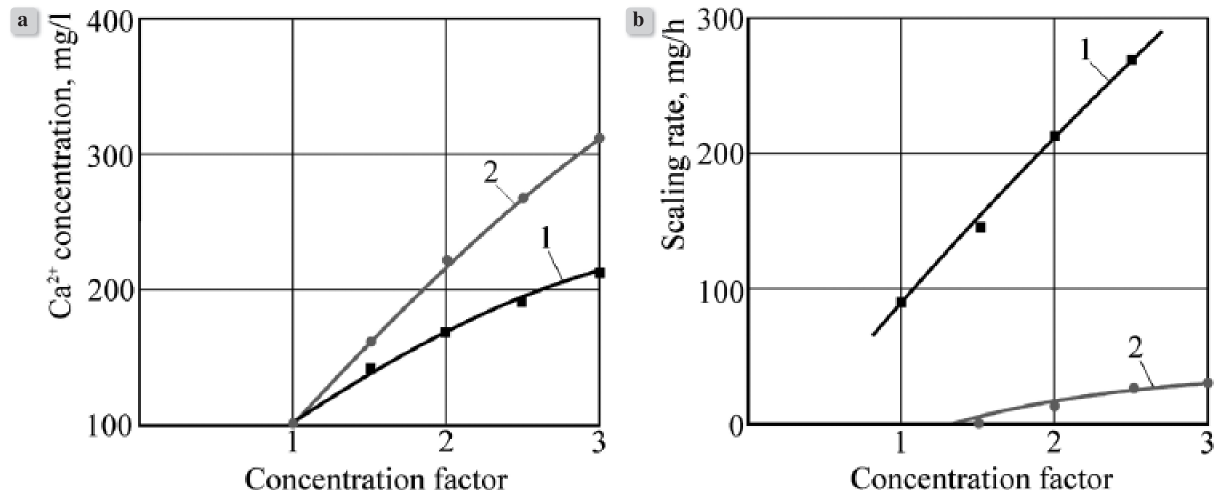

Figure 3.
The results of the scaling rate determination for conventional and open channel module configuration: 1 – conventional module (1812, BLN, "CSM"); 2 – open channel module (1812, BLN, "CSM")

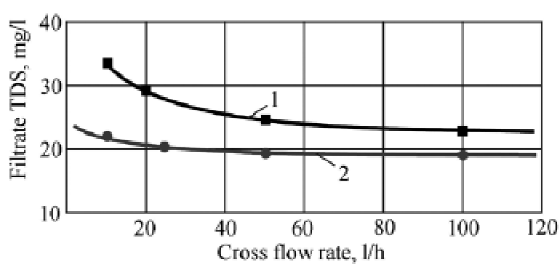

Figure 4.
The influence of the cross-flow rate on filtrate TDS: 1 – conventional module; 2 – open channel module

Figures 3 and 4 show the results of the scaling rates determination and membrane rejection characteristics versus cross-flow rate values.

The experimentally obtained relationships are shown in Figures 5 and 6. Figures show the results of particulate (Fig. 5) and organic (Fig. 6) fouling rate determination depending on cross-flow velocities in membrane module. The higher velocity the less particulate matter is accumulated on membrane surface. Vice versa, organic material is adsorbed on membrane surface more intensively when the cross-flow is higher.

Comparison of flow hydraulic resistance values versus flow rates for conventional spiral wound and an open-channel module is shown in Figure 7. During accumulation of foulant, axial flow resistance increase and product flow decrease. The amount of accumulated foulant could be detected throughout

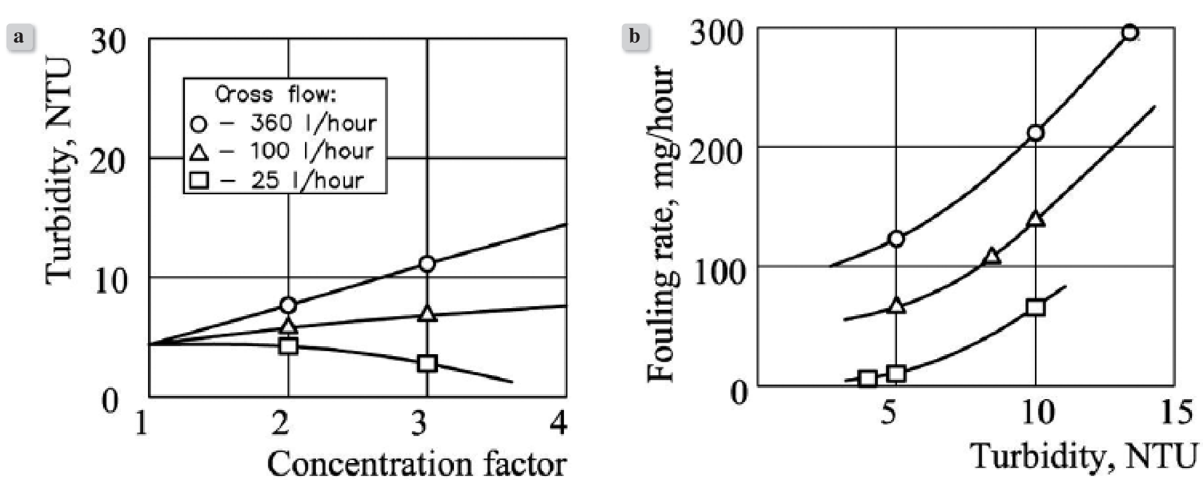

Figure 5.
Determination of the particulate fouling rates: a) turbidity versus the concentration ratio, b) fouling rate versus turbidity

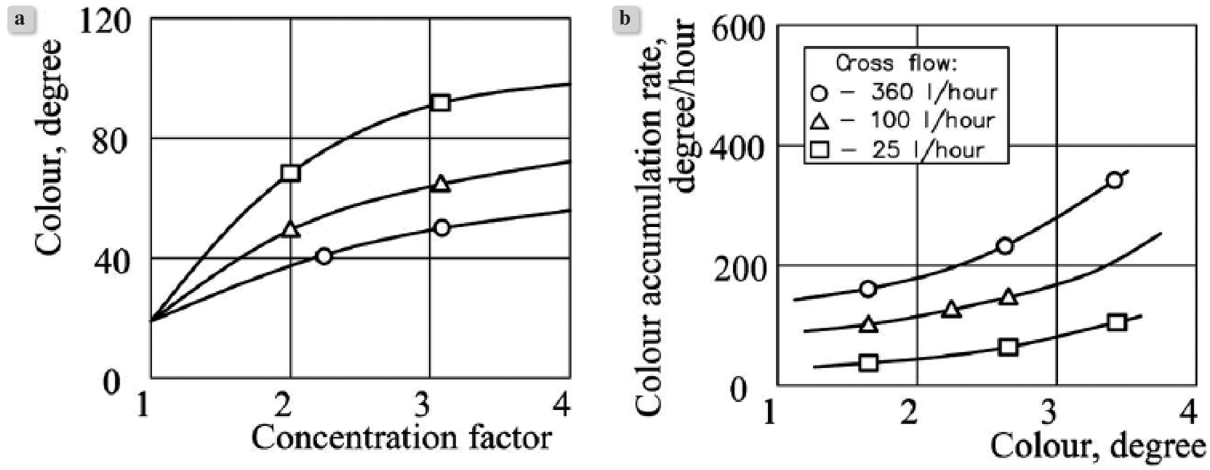

Figure 6.
Dependencies of circulated water colour on concentration ratio (a) and organic fouling rate on feedwater colour (b)

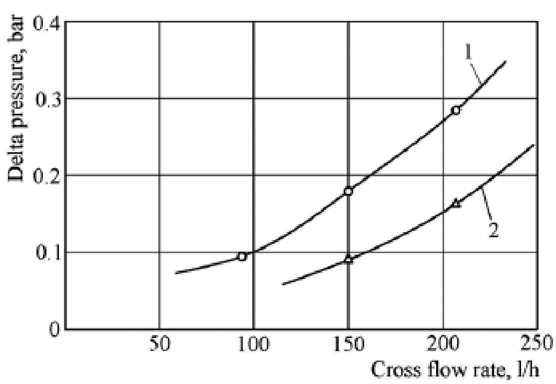

Figure 7.
Delta pressure increase versus cross-flow values: 1 – conventional module (1812, BLN, "CSM"); 2 – open channel module (1812, BLN)

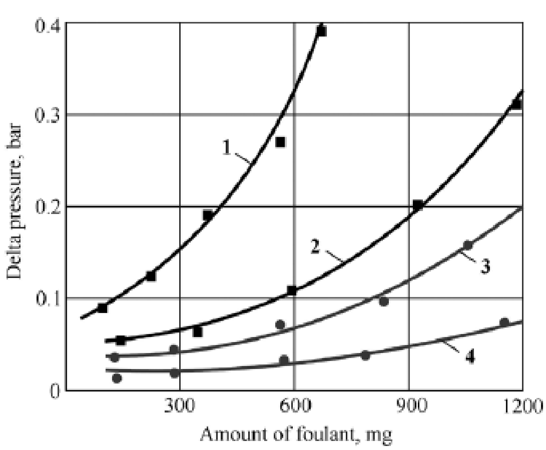

Figure 8.
Determination of delta pressure increase during foulant accumulation. 1, 2 – conventional module (1812, BLN, "CSM"); 3, 4 – open channel module (1812, BLN); cross-flow: 1, 3 – 100 l/h; 2, 4 – 50 l/h

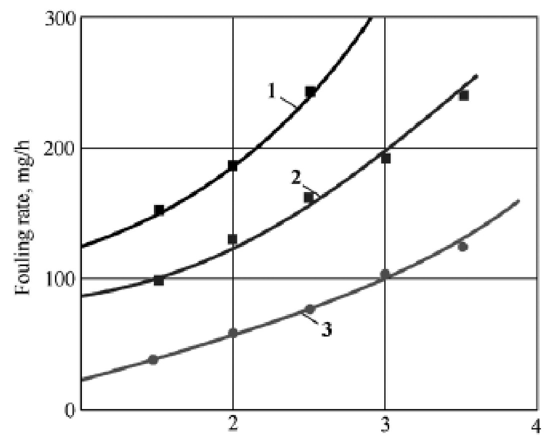

Figure 9.
Dependencies of delta pressure increase versus cross-flow and amount of accumulated foulant amount. Cross-flow: 1 – 360 l/h; 2 – 100 l/h; 3 – 25 l/h

the circulation experiments. Figure 8 shows the delta pressure values versus flow graphs for different amounts of particulate foulants in the module. The growth of axial flow resistance with foulant accumulation is shown in Figure 9, where calculations are presented by curves each corresponding to certain values of cross-flow.

The application of hydraulic forward flushings destroys fouling layers and withdraw foulants from membrane surface due to cross-flow velocity increase and water hammer initiation through rapid pressure drop that is provided by solenoid valve opening on the concentrate line. Figure 10 shows the product flow values versus time and flow resistance versus time relationships where forward flushings are constantly applied after certain time periods. Flushing

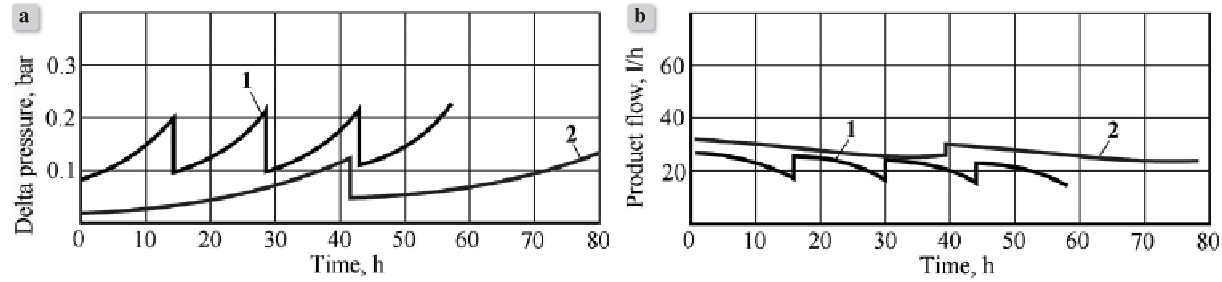

Figure 10.
Comparison of "standard" (1) and "open-channel" (2) modules performance

modes (time between flushes and flush duration) are very important to maintain fouling control and product flow on the desired level. Suspended solids concentration, colour, recovery, pressure, cross-flow velocities as well as the membrane type and the module design are factors that influence operational and flushing modes.

Operational costs depend on energy consumption, reject effluent flow, chemical cleaning schedules (to reduce fouling) and could be minimized by the selection of optimum operation conditions. Figure 11 shows an example of determination of optimum recoveries and flow modes.

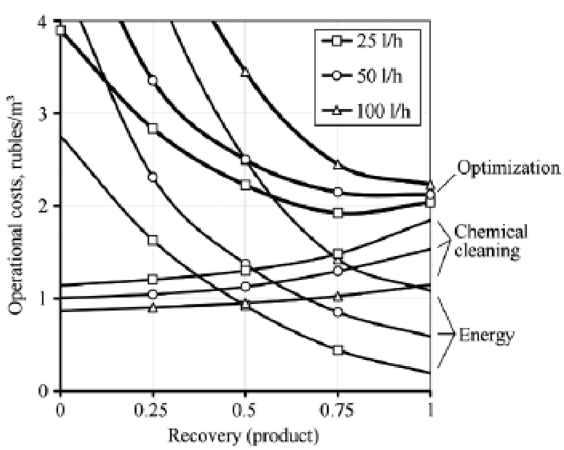

Figure 11.
Determination of optimum recoveries and flow modes for NF unit

4. DISCUSSION OF THE RESULTS

Suspended and colloidal fouling rates were successfully determined in the circulation mode. Deposition rates of suspended and colloidal matter are dependent on cross-flow velocities and are rising when the flow decreases. Organic sorption provides opposite relationship: the higher the velocity the greater the adsorption rate. This fact could have two explanations. First: the colloidal fouling layer blocks the active surface and reduces the sorption rate. Secondly: the sorption process occurs according to the diffusion mechanism and is going on more intensively with higher flow velocities.

Hydraulic flushings provides efficient measures to control the fouling. Large amounts of colloidal and organic material accumulated during hours of operation are efficiently flushed-off the membrane surface in a few seconds. Meanwhile, analysis of flush water shows that the colour of it is different and depends on the operation conditions. Colloidal foulant (mainly surface water humic acids) sorbs organics (fulvic acids) due to amide and peptic groups. The more foulant deposited on the membrane surface, the higher the colour of the flushing water and vice versa. It was concluded that the organics adsorbed by the foulant were successfully flushed off from the membrane surface and that organics were more intensively adsorbed by the membrane surface than by the fouling layer.

Channel geometry is a strong factor that influences the membrane performance if fouling occurs. During foulant accumulation flow resistance through the module is growing. When open-channel modules were tested the observed rates of flow resistance increase and product flow decrease was significantly lower.

5. APPLICATION OF THE RESULTS

Figure 12a shows the flow diagram of surface water treatment system to remove colloidal and suspended particles, colour and organics. Flush water effluents are collected in sedimentation tank. The membrane unit is operated in the circulation mode and the brine is concentrated between 50-100 times by volume. Coagulated suspended matter is collected after the membrane flushes, sedimented and finally dewatered.

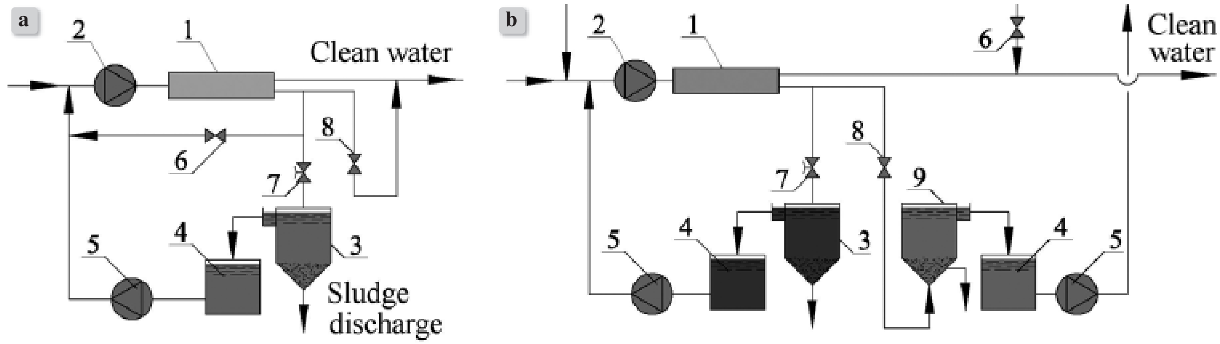

Figure 12.
A flow diagram of the surface (a) and well (b) water treatment with reverse osmosis membranes without concentrate discharge: 1 – membrane module, 2 – high pressure pump; 3 – flush water sedimentation tank; 4 – clean water collection tank; 5 – pump; 6 – pressure valve; 7 – solenoid valve; 8 – pressure regulation gauge; 9 – calcium carbonate precipitation tank

Table 1 presents results of chemical analysis of surface water, RO concentrates and product water (membrane permeate).

Table 1.
Water quality characteristics

№	Parameters	Surface water (Desna river)	Filtrate	Concentrate
1	Calcium, meq/l	3.8	0.5	9.5
2	Magnesium, meq/l	2.3	0.4	6.5
3	Chlorides, mg/l	72.4	53.3	364.0
4	Sulfates, mg/l	39.7	10.2	208.0
5	Alkalinity, meq/l	5.9	2.2	20.5
6	pH	6.75	6.84	7.6
7	Oxygen demand, mg/l	6.48	9.52	108.0
8	Colour, degree	42.0	17.5	368.0
9	Turbidity, mg/l	12.1	1.1	145.0

The described membrane techniques could be applied only in cases when feedwater contains colloidal matter, iron, colour etc. When water contains excessive hardness, fluorides, ammonia etc. other membrane tools are applied. In these cases the product flow is mixed with a part of concentrate (reject) flow, another part of reject flow could be concentrated and withdrawn together with sedimented sludge. Sludge humidity averagely constitutes from 0.8 to 1.0% of initial water volume. The membrane reject stream could be concentrated between 50-100 times by volume.

As it was already mentioned above the use of an "open channel" membrane modules enables us to concentrate calcium carbonate and calcium sulphate solutions that become supersaturated without a risk to scale-up the membrane. The use of such reliable modules could also suggest new chemical-free techniques to remove calcium carbonate from the feedwater.

The flow diagram showing principles of calcium carbonate precipitation from the RO concentrate is shown in Figure 12b. The RO unit is operated in a constant concentration mode; concentrate pumped into the calcium carbonate precipitation tank, the excessive calcium carbonate is crystallized on a seed mass and withdrawn from the tank.

Table 2 offers concentration values of calcium, carbonate, chloride ions and pH. While concentrate passes through the precipititation tank calcium carbonate is precipitated on the seed mass and calcium concentration does not increase, as it is shown in Figure 13. The concentrate solution containing salts and other impurities together with the wet sludge constitutes no more than one per cent of the initial water, in part due to high supersaturation values, due to the strong stability of calcium carbonate solutions. The described calcium carbonate removal procedure offers new and efficient water softening tools that do not require chemicals and do not increase the water TDS value.

Table 2.
Concentrate composition transformation after contact with seed mass

Parameters	Feedwater	Concentrate	Concentrate after contact with seed mass
Calcium, meq/l	3.75	8.2	7.4
Alkalinity, meq/l	3.4	8.4	4.8
Chlorides, mg/l	9.23	17.8	17.8
pH	6.8	7.11	7.0

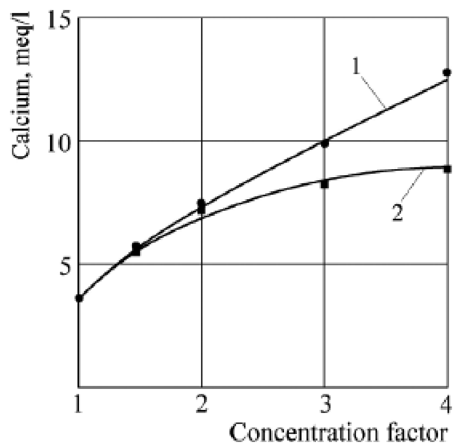

Figure 13.
Dependence of calcium ion concentration value on the feed water concentration ratio: 1 – concentrate of membrane unit; 2 – water at the exit from precipitation tank (after contact with seed mass)

6. CONCLUSIONS

The main disadvantages of spiral wound modules are attributed to the presence of spacer mesh in the channel trap fouling particles and provide dead areas where scaling occurs. Introduction of new open-channel modules enables us to escape the scaling and fouling problems. Experimental data confirms that new modules have lower scaling propensities than conventional spiral wounds. Investigation of particulate fouling influence on RO membrane performance indicates that product flow reduction is attributed to the flow resistance growth due to particle trapping by the mesh separator. Elimination of mesh provides the benefit of control of the fouling and facilitate forward flushings. Application of new modules with an "open-channel" ensures safe operation of the membrane facilities even when feedwater has a high fouling and scaling potential. This also enables us to simplify pretreatment and decrease the operational costs. To reduce the concentrate discharge (in hardness removal) up to zero the calcium carbonate precipitation tank on the concentrate flow can be applied.

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