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Application of membranes to treat wastewater for its recycling and reuse: new considerations to reduce fouling and increase recovery up to 99 percent

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ABSTRACT

The RO process is very attractive for providing high product quality through the removal of a number of contaminants like oil, detergents, organics, nitrates, ammonia, phosphates etc. However the main disadvantages of the modern RO techniques are connected with membrane fouling, concentrate flow and pretreatment that increase operational costs, complicate design and create problems of brine utilization. Often pretreatment costs even exceed reverse osmosis facilities costs. Now a number of successful attempts were undertaken to modify spiral wound membrane channels to limit fouling and scaling potential. As presented in a number of publications, elimination of the spacer mesh from the feed channels eliminates dead regions that provide scaling and fouling conditions whilst also reducing the risk of particle "trapping" and associated dramatic pressure increase. Introduction of a new "open channel" configuration offers a new perspectives to escape fouling and development of novel techniques to treat water with high fouling potential (high suspended matter, organics and supersaturated solutions). This novel concept of spiral wound module with an "open channel" design 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 providing sufficient cross flow velocities, flushings and cleanings. The main principles of high recoveries, low maintenance and zero discharge are ensured by concentration of brine through re-circulation by 50–100 times by volume. Several examples of water treatment flow diagrams are presented to demonstrate of zero concentrate flow discharge. Coagulated suspended matter after membrane flushes is collected, sedimented and finally dewatered. The concentrated solution containing salts and impurities together with the wet sludge constitutes no more than 1 percent of initial water in part due to high supersaturation values due to the strong stability of calcium carbonate solutions.

Keywords: Nanofiltration; Open-channel module; Scaling; Spiral wound module

1. Introduction

Protection of water resources from pollution is considered to be an important ecological problem that becomes more and more complicated with urban growth and development of industrial and agricultural water consumption. The use of different chemicals for industrial, agricultural and domestic purposes tend to constant degradation of water quality, accumulation of detergents, oil products as well as biological nutrients. Rational use of water resources to reduce their contamination should be introduced into practice as

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well as measures should be undertaken to transform sewage into a new source of raw water that could be used by communities for agricultural and technical purposes. To improve quality of wastewater new techniques that should be developed as conventional water treatment methods (coagulation, filtration, sorption, bioreactor etc.) do little to efficiently remove dissolved contaminants and maintain operational costs within reasonable limits.

Modern membrane techniques (UF, NF, RO) have demonstrated high efficiency in removal of suspended matter, bacterial, as well as organic and mineral ingredients. Meanwhile, certain problems of membrane fouling arise, resulting in shortening of membrane life and reduction in product flow. To prevent formation of fouling layers on membrane surface and cake resistance increases, a number of measures are applied, such as backflushes, chemical cleanings, feed pretreatment. Despite these measures, fouling remains a major factor that determines operational costs.

Long operational experience of membrane units to treat natural water as well as theoretical and experimental investigation results enable us to draw to a conclusion that hydraulic, hydrodynamic and chemical processes that occur during membrane separation are closely connected. Many researchers approve of this concept in a number of reports but nevertheless many state-of-the art reviews demonstrate conventional limited description of these processes without relationship [1]. Meanwhile, critical and detailed assessment of different processes separately shows the importance and significance of each process in formation of the whole overview of membrane fouling and deterioration of membrane performance characteristics.

Natural surface water contains high concentrations of suspended and colloidal matter with different particle size distribution, as well as dissolved organics (mainly humus substances) with various molecular weights. Membrane fouling mechanisms caused by different foulants (sparingly soluble compounds, bacterial, organic and colloidal matter) are different. Suspended and colloidal particles deposit and adhere on membrane surface thus building fouling layer that create hydraulic resistance and reduce product flow. Organic compounds adsorb on membrane surface and on deposits of particles.

For a long time formation of colloidal fouling layers was attributed to hydrodynamic flow characteristics (such as cross-flow velocities, concentration polarization level, product flow etc.) and membrane sorption and adhesive properties were totally ignored. Meanwhile, research has revealed that membrane surface characteristics (surface charge, hydrophilic properties that are depended on polymer composition) could have become decisive factors when biofouling, colloidal and organic fouling occurs. This conclusion prompted a new direction of membrane research – development of low-fouling membranes and modification of membrane surface to reduce fouling.

It was also reported that configuration of membrane channel and module also should be considered as decisive factor that influence fouling [1,2]. Spiral wound configuration is widely applied at more than 90% of all water installations but nevertheless is considered as useless to treat surface water that contain suspended and organic matter due to fouling hazard. 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. Besides, tubular and capillary membrane channels, as well as plate and frame and flat sheet elements channels are still very expensive that makes RO pretreatment costs higher than RO itself.

At the early stages of UF applications to treat surface water cross-flow operational mode was applied with tubular membrane channel whereby high velocity values provide efficient shear force to reduce particulate and organic fouling [3]. High cross-flow values require high energy costs that combined with costly membrane equipment exceeds reasonable price level for water treatment. Today the dead-end filtration mode combined with timely backflushing has replaced cross-flow operation at surface water treatment UF techniques due to more economical and operational costs and more membrane surface in capillary modules. Backflushing may not be considered as the most efficient measure to control fouling due to plugging factors and the use of product water. Cross-flow operation of ultrafiltration and nanofiltration is recognized as efficient fouling-free process that could be implemented in tubular modules that is not widely applied in water supply practice due to high membrane costs and power consumption [4].

2. RO and nanofiltration water treatment techniques. Spiral wound membranes

During last years a new membrane process is being introduced into water supply practice that directly treat surface water with nanofiltration membranes without pretreatment [5–7]. As reported, the process efficiency and reliability is attributed mainly to hydraulic flow conditions in the membrane channels that provide enough shear-force for the particles not to foul the membrane [8]. These conditions are provided by channel configuration (using tubular or capillary membranes), by high cross-flow velocities as well as through application of hydraulic flushes and chemical cleanings.

This paper presents results of research that was conducted to improve conventional spiral wound configuration to treat directly wastewater. 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 and this led to a re-evaluation of the layout of the spiral wound module [2,9].

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 used for RO, NF and UF applications is very susceptible to fouling that makes it useless to treat wastewater containing high organics, bacteria and suspended matter. The main disadvantages of spiral wound modules are attributed to presence of the separation spacer mesh in the feed channel as it traps fouling particles and increases flow resistance (Fig. 1). The mechanism of mesh performance and its influence on scaling/fouling process initiation has been proposed in [2,10]. 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 deadlock area providing further conditions for particle coagulation and adhesion to the formed layer promoting expansion of the foulant layer around these areas [2].

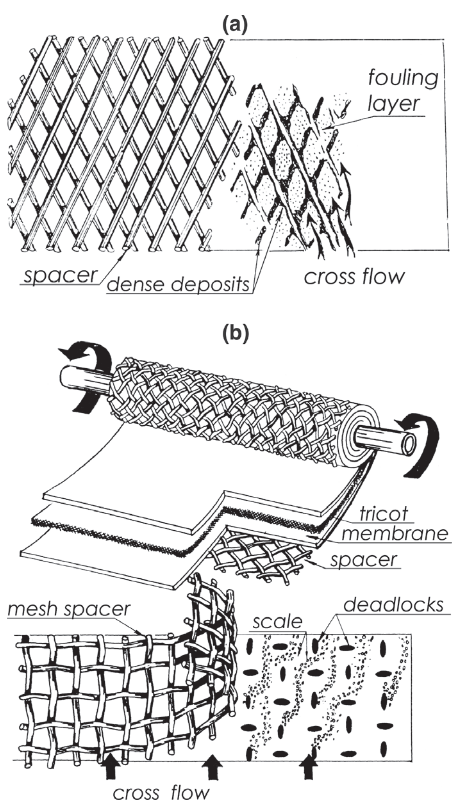

Fig. 1. Fouling/scaling control: formation of fouling layers: a) formation of scale crystals; b) membrane surface with fouling layer.

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 a report devoted to the development of an open-channel spiral wound module [1]. Modification of spiral wound module is shown on Fig. 2 where the mesh is withdrawn from the channel by dividing it into ledges and so providing higher cross-flow velocities.

Nanofiltration process has some advantages over ultrafiltration, such as small pore size that exclude plugging and inhibits cake resistance increase. NF membranes efficiently remove colour (by 70–95%), oxidability (by 50–80%) and hardness (by 50–80%). Nanofiltration units are used at number of large municipal water treatment facilities (up to 10,000 cubic meters per hour capacity) in Paris, Amsterdam, USA, Australia etc. to remove trihalomethans and other low-molecular organics to meet WHO standards (Ventresque C. et al., 2000). Despite high efficiency in drinking water production strong skepticism exists towards perspectives of using NF method

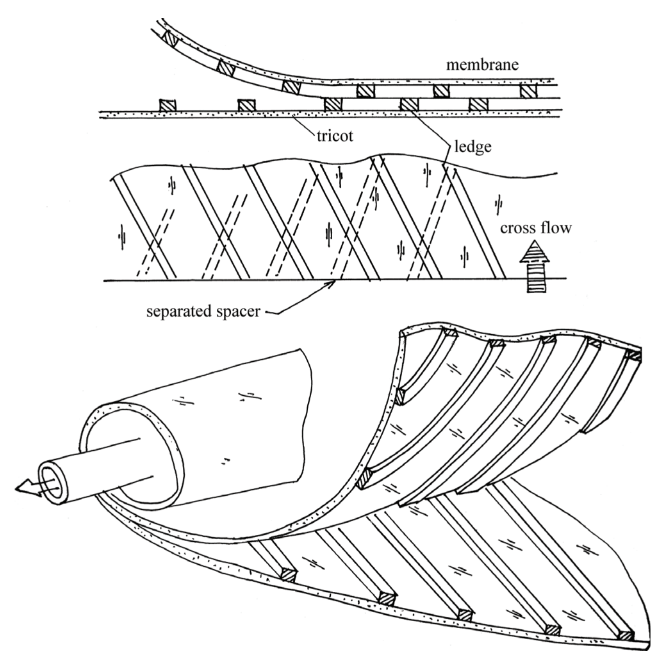

Fig. 2. Spiral wound module with open-channel configuration.

in municipal water treatment. Such an attitude is attributed to existing NF spiral wound modules operation that requires significant pretreatment, high chemical consumption and thus high operational costs.

Meanwhile, during the last few years a number of surface water treatment applications use nanofiltration techniques whereby surface water is directly fed to membrane modules without pretreatment [5,11]. The efficiency of such fouling-free operation is attributed to hydrodynamic conditions in tubular and capillary membrane channels that prevent deposition of suspended particles. Fouling control is also reached through application of flushing (including air scouring), timely chemical cleanings and high cross-flow velocities. But these systems are still not widely used due to high capital and operational costs.

The present work is aimed at development of a new modified spiral wound configuration and optimum operational characteristics (recoveries, cross-flow velocities, flushing cycle durations, cleaning schedules) to ensure long and reliable operation of membrane systems with minimum of operational costs.

The research devoted to introduction of a new membrane technique is not limited only by development and manufacturing of new spiral wound membrane module with decreased fouling propensities, but also includes:

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

3. 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 membrane surface. One of the best solutions was the idea of "separate" spacer where mesh fibers are glued to membrane surface. RO module spacer is a platted mesh where parallel groups of fibers are crossed and welded forming a rhombic structure (Fig. 2). In our construction parallel groups of fibers (ledges) are glued to 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 to each other but ledges separate membrane surfaces providing enough space for flow with very low resistance. The idea of a channel configuration was already patented and some innovations are being continuously introduced. Several modules of standard sise (12 inch long, 1.8 inch in diameter) 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).

4. Experimental procedure and test program

The test program included determination of fouling rates, flushing efficiencies and TMP pressure values in the modules according to a test procedure described i [9].

The research program was aimed at:

- investigation of fouling rate dependencies on hydrodynamic flow characteristics;
- determination of TMP pressure 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 on Fig. 3. Feedwater is pumped from the tank (1) to a spiral module (3) by the pump (2). The working pressure value is controlled by a valve (5) and measured by a pressure gauge (6). Cross-flow velocity is controlled using the by-pass valve (4). The test procedure is conducted in circulation mode whereby reject flow (concentrate) is returned to the tank (1) and product is collected in separate tank (7). Determination of concentration values in the brine

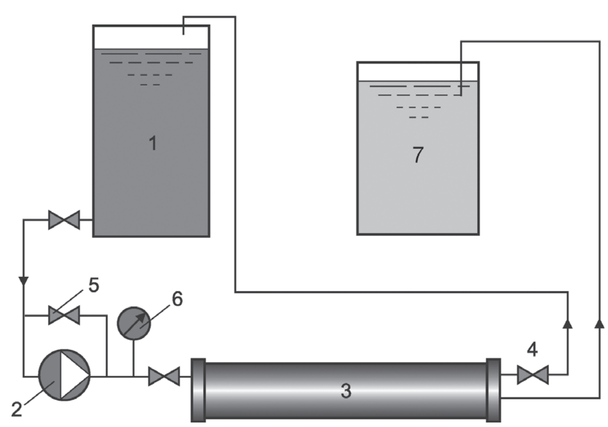

Fig. 3. Schematic diagram for NF test unit.

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.

Figs. 4 and 5 show results of scaling rates determination and membrane rejection characteristics versus cross-flow rate values.

The experimentally obtained relationships are shown on Figs. 6 and 7. Figures show the results of particulate (Fig. 6) and organic (Fig. 7) fouling rate determination depending on cross-flow velocities in membrane module. The higher velocity is the less particulate matter is accumulated on membrane surface. Vice versa, organic material is adsorbed on membrane surface more intensively when cross-flow is higher.

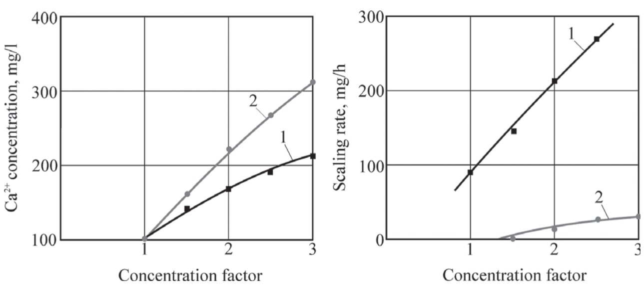

Fig. 4. The results of scaling rate determination for conventional and open channel module configuration: 1 – conventional module (1812, BLN, "CSM"); 2 – open channel module (1812, BLN).

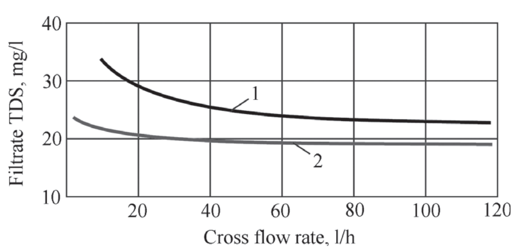

Fig. 5. The influence of cross-flow rate on filtrate TDS: 1 – conventional module; 2 – open channel module.

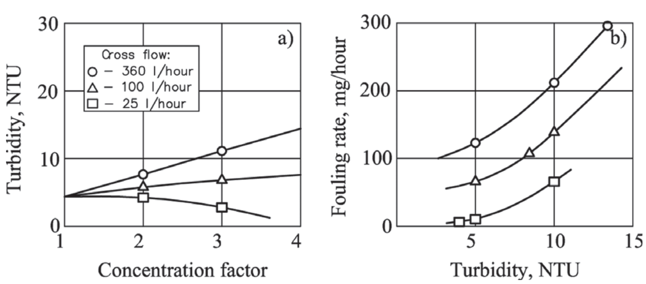

Fig. 6. Determination of particulate fouling rates: a) turbidity versus concentration ratio, b) fouling rate versus turbidity.

Comparison of flow hydraulic resistance values versus flow rates for conventional spiral wound and an open-channel module is shown on Fig. 8. During accumulation of foulant, axial flow resistance increase and product flow decrease. The amount of accumulated foulant could be detected throughout circulation experiments. Fig. 9 shows the delta pressure values versus flow graphs for different amounts of particulate foulants

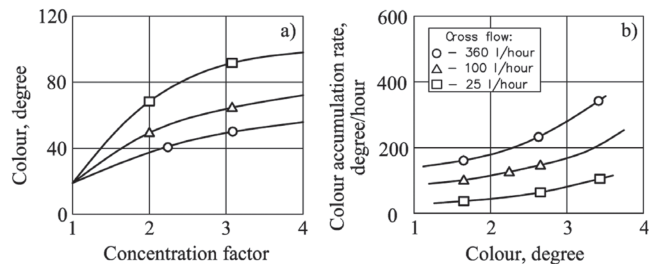

Fig. 7. Dependencies of circulated water colour on concentration ratio (a) and organic fouling rate on feedwater colour (b).

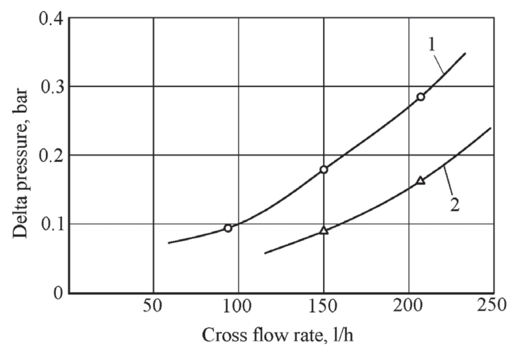

Fig. 8. Delta pressure increase versus cross-flow values: 1 – conventional module (1812, BLN, "CSM"); 2 – open channel module (1812, BLN).

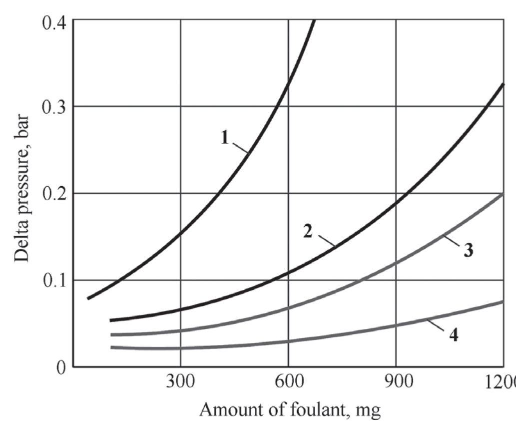

Fig. 9. Determination of delta pressure increase during foulant accumulation. 1, 2 – conventional module (1812, BLN, "CSM"); 3, 4 – open channel module (1812, BLN); cross-flow: 1, 3–100 l/h; 2, 4–50 l/h.

in the module. The growth of axial flow resistance with foulant accumulation is shown on Fig. 10, where calculations are presented by curves each corresponding to certain values of cross-flow.

Application of hydraulic flushings destroys fouling layers and withdraw foulants from membrane surface due to cross-flow velocity increase and water hammer initiation through rapid pressure drop. Fig. 11 shows the product flow values versus time and flow resistance versus time relationships where flushings are constantly applied after certain time periods. Flushing 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 membrane type and module design are factors that influence operational and flushing modes.

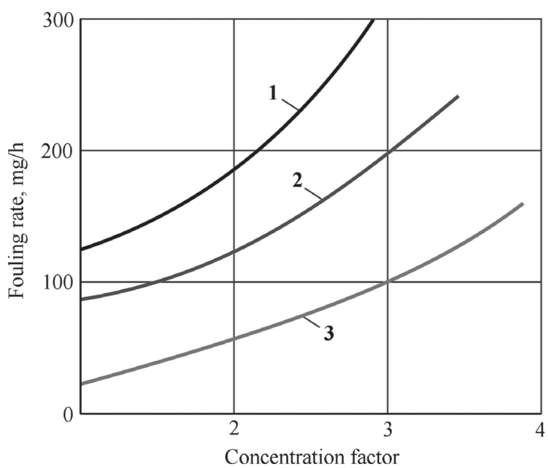

Fig. 10. Dependencies of delta pressure increase versus cross-flow and amount of accumulated foulant amount. Cross-flow: 1–360 l/h; 2–100 l/h; 3–25 l/h.

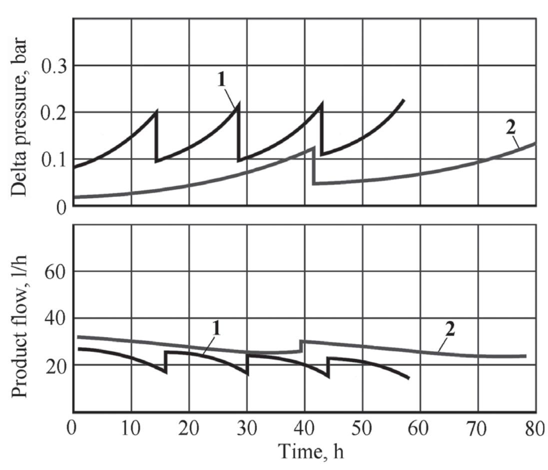

Fig. 11. Comparison of “standard” (1) and “open-channel” (2) modules performance.

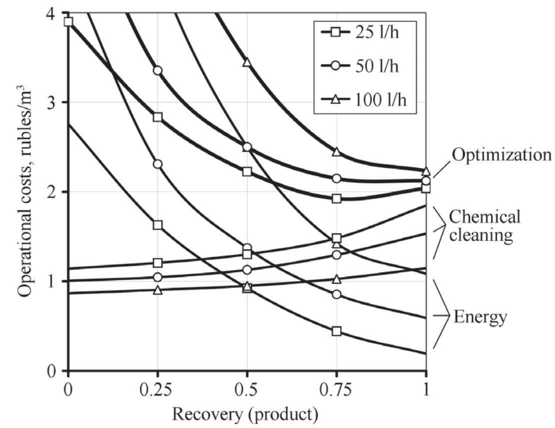

Fig. 12. Determination of optimum recoveries and flow modes for NF unit.

Operational costs depend on the pump characteristics and energy consumption, reject effluent flow, chemical cleaning schedules (to reduce fouling) and could be minimized by selection of optimum operation conditions. Fig. 12 shows an example of determination of optimum recoveries and flow modes. Typical NF units to treat surface water are shown on Fig. 13.

5. Discussion of the results

Suspended and colloidal fouling rates were successfully determined in the circulation mode. Deposition rates depended on the cross-flow velocities that provided shear-forces on the particles. Depending on membrane surface properties (hydrophility, surface charge) rates of colloidal and organic matter deposition could vary. Research is being conducted to modify membrane surface with a purpose to protect it from bacteria and particulate adhesion [11,12]. Acetate membranes are less susceptible to organic and colloidal fouling. The mechanism of organic fouling has been widely investigated. It is based on adsorption of organic molecules from water solution.

Suspended and colloidal particulate fouling is dependent on cross-flow velocities and is rising with flow decrease. Organic sorption provides opposite relationship: the higher the velocity the more is the adsorption rate. This fact could have two explanations. First: colloidal fouling layer blocks the active surface and reduce sorption rate. Secondly: the sorption process occurs according to diffusion mechanism and is going on more intensively with higher flow velocities.

Hydraulic flushings provides efficient measure to control fouling. Large amount of colloidal and organic material accumulated during hours of operation is efficiently flushed-off membrane surface in a few seconds. Meanwhile, analysis of flush water shows that the colour

(a)

(b)

Fig. 13. Nanofiltration units for surface water treatment: production of 10–15 cubic meter per day of quality drinking water; production of 50 cubic meter per day.

of it is different and depends on operation conditions. Colloidal foulant (mainly surface water humic acids) sorbs organics (fulvic acids) due to amide and peptic groups. The more foulant is deposited on the membrane surface, the higher was the colour of the flushing water and vice versa. It was concluded that organics adsorbed by the foulant were successfully flushed off 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 on 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.

6. Conclusions

1. Main disadvantages of spiral wound modules are attributed to 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 scaling and fouling problems. Experimental data confirm that new modules have lower scaling propensities than conventional spiral wounds.
2. Investigation of particulate fouling influence on RO membrane performance indicates that product flow reduction is attributed to flow resistance growth due to particle trapping by the mesh separator. Elimination of mesh provides a benefit to control fouling and facilitate flushings.
3. Application of new modules with an "open-channel" ensures safe operation of membrane facilities even when feedwater has high fouling and scaling potential. This also enables us to simplify pretreatment and decrease operational costs.

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