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Application of reverse osmosis techniques to treat and reuse biologically treated wastewater

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Abstract. Biological treatment together with sorption and clarification techniques are often applied to treat municipal and industrial (petrochemical, food and pharmaceutical) wastewater. Often treated wastewater does not meet technological standards to be reused for industrial purposes such as: cooling, heating, boiler feed or steam generation. Production of quality water for technical needs is implemented through application of reverse osmosis techniques to post-treat water after biological treatment. Reverse Osmosis (RO) provides perfect rejection of all impurities, but also produces concentrate (retentate) streams that often cannot be discharged into surface water.
A novel technique is developed and field tested to "hide" concentrate in dewatered sludge (digested sludge after biological treatment and dewatering) that is withdrawn from the system as a sludge moisture. The main goal of presented research was to demonstrate treatment of oil refinery wastewater with reverse osmosis membranes and its separation into product quality water and sludge withdrawn from the system. Industrial application experience to treat storm wastewater, municipal wastewater and petrochemical industrial wastewater is described. Flow diagrams of developed double-stage membrane facilities that ensure high RO recovery are presented, and previously developed tools to withdraw calcium carbonate and magnesium hydroxide from concentrate using "seeding" techniques are disclosed.

1. Introduction

RO membranes demonstrate high rejection characteristics for different contaminants. As it was already discussed [1, 2], these rejection characteristics of RO membranes seem very promising to directly treat sewage directly and obtain high-quality water without application of chemical, biological and sorption processes. This approach to using membrane tools substantially reduces costs. However, the main disadvantages of commercially available RO facilities are attributed to their high fouling propensities, high cost pretreatment requirements, and concentrate disposal problems.

To overcome these problems, a series of experimental investigations was performed to develop newly modified "open channel" modules that possess a limited scaling and fouling potential and can be used to treat directly wastewater to remove suspended, colloidal and organic impurities [3, 4].

The main disadvantages of spiral wound module are attributed to presence of separation spacer mesh in the feed channel as it traps fouling particles and increases flow resistance (Figure 1). 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".

Elimination of the mesh could help to develop new types of modules with decreased fouling potential. This idea was discussed by Richard Riddle [4] in a report devoted to the development of an open-channel spiral wound module. Modification of spiral wound module [3] is shown on Figure 2, where the mesh is withdrawn from the channel by dividing it into ledges and so providing higher cross-flow velocities.

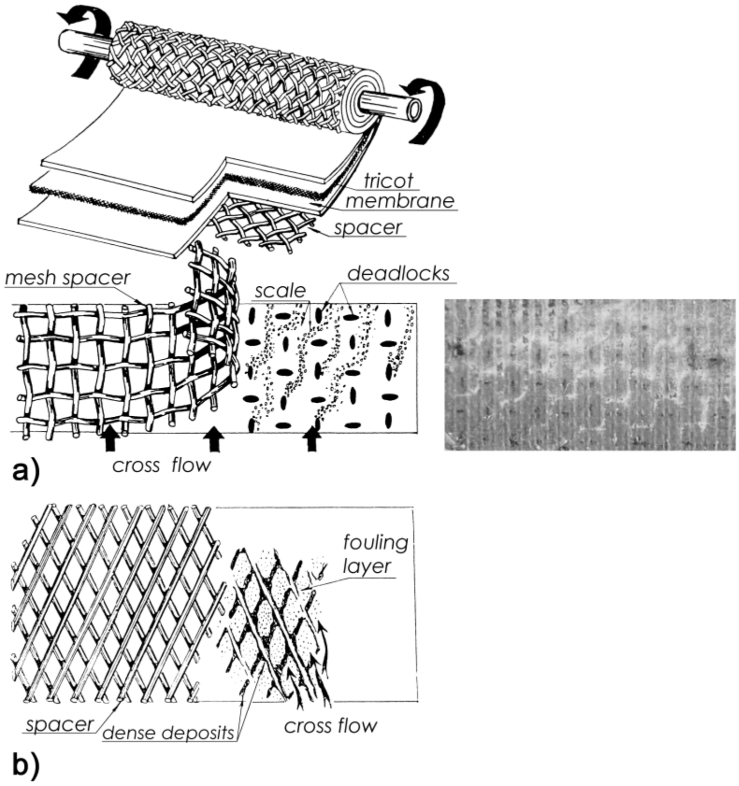


Figure 1. Fouling and scaling: influence of spacer. Formation of crystals in dead areas: a) – formation of scale crystals; b) – particle trapping and fouling layer formation

Elimination of the spacer mesh from the feed channels of a spiral wound membrane configuration eliminates "dead regions" that provide scaling (crystal formation) and fouling conditions while also reducing the risk of particle "trapping" and the increase of associated dramatic flow resistance. Fouling control is achieved by providing sufficient cross-flow velocities, flushing, and cleanings.

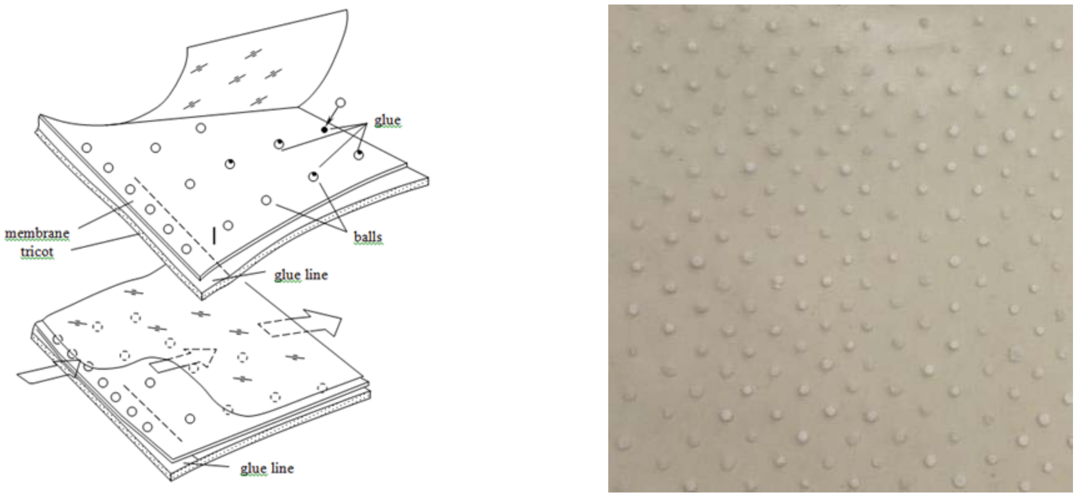


Figure 2. Spiral wound module with open-channel configuration

A new concept of direct wastewater treatment by RO is based on the following principles [5, 6]:
– using of membrane modules with an "open channel" enables us to avoid membrane fouling throughout their operation even with high suspended matter content in the feed water;
– membrane units are operated in the circulation mode with high cross flow velocities that provide the "shear effect" of adhered foulants;
– fouling control is achieved by providing sufficient cross flow velocities, flushes and cleanings; – accumulated on membrane surface are withdrawn from membrane module during membrane flushes. Suspended matter after membrane flushes is collected, sedimented and finally dewatered;
– the main principles of high recovery maintenance are ensured by concentration of feed water in circulation mode by 50-100 times by volume. Concentrate volume constitutes no more than 0,5 – 1%of the initial feed water volume and is withdrawn from the system together with a wet sludge as a sludge humidity.


a)


b)

Figure 3. Double stage RO membrane unit for wastewater treatment, 6 cubic meter per hour capacity: (a) photo of the unit, general view; (b): operation of the membrane units at local storm water treatment facility

To purify a storm waste water (to remove oil, detergents and other dissolved organics) a double stage RO membrane units are developed. Figure 3 (a, b) shows the 6 cubic meter per hour membrane RO unit that treats stormwater at Moscow industrial enterprise. The double stage RO is designed to utilize RO retentate.

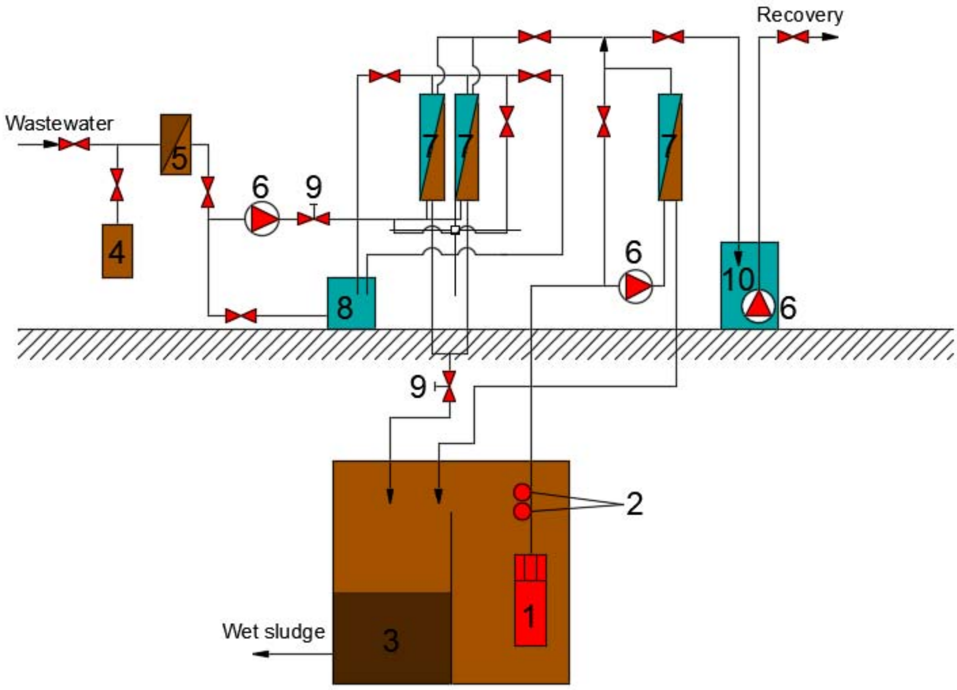


Figure 4. Flow diagram of storm water treatment:1 -wastewater well pump; 2 - float switch; 3 - sedimentation tank; 4 -accumulation tank; 5 - pretreatment screen ;6 -pressure pump;7 - membrane modules; 8- cleaning tank; solenoid valve; 9 - product water tank.

A flow diagram of membrane units to treat storm water is shown on Figure 4. Concentrate flow is decreased by 50-100 times and is withdrawn from the system together with wet sludge as a sludge moisture. To determine required membrane characteristics and optimum operational parameters, a test program was undertaken to investigate membrane fouling process, flushing efficiencies and flushing water sedimentation process.

The main goal of experimental program undertaken by the authors was to experimentally evaluate all technical and operational parameters of the outlined membrane process flow diagram:
- to evaluate membrane rejection characteristics to remove oil, detergents, BODorganics and other wastewater species;
- to evaluate process recovery;
- to determine membrane types, their rejection characteristics, product flow and required membrane areas on both stages of treatment;
- to evaluate optimum flow velocity values in membrane channel, optimum cleaning schedules and flushing programs dependind on wastewater suspended matter characteristics;
- to evaluate the volume of tanks for flushing water collection and sludge sedimentation, basing on suspended matter characteristics.

2. Materials and methods

Three experimental programs were undertaken to evaluate technical characteristics of RO units to directly treat wastewater.

The first series was devoted to evaluation of membrane rejection characteristics to remove oil, detergents, BOD and other impurities.

The second series studied the influence of feed water salinity on membrane rejection characteristics.

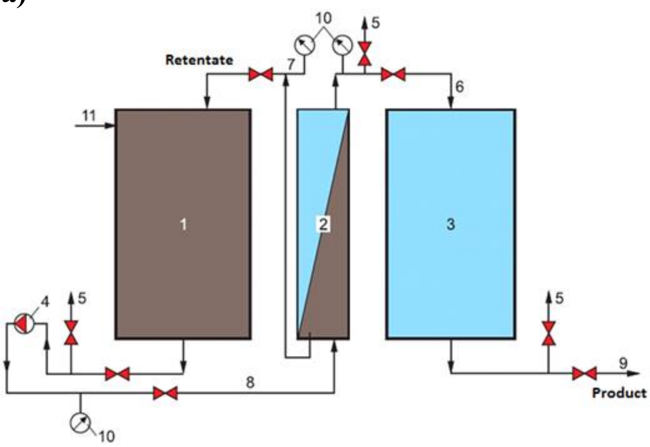
The third series of experimental research was devoted to membrane fouling rates evaluation and to control of membrane particulate fouling by flushings.

During RO system operation, calcium and bicarbonate concentration values in RO concentrate constantly increase, providing a driving force for calcium carbonate crystal growth. The present article shows the experimental results of precipitation kinetics study that are influenced by various factors (such as seed concentration, supersaturation, crystal age, etc.).

A flow diagram of the experimental procedure is presented, showing the circulation loop (Figure 4). Spiral wound modules of 1812 standart (12” length and 1,8” in diameter) tailored with low pressure RO membranes (BLN-type) manufactured by CSM (Korea) wewe used in experimental studies for comparison with newly developed modules. New “open channel” spiral wound modules were manufactured using the same flat sheet membranes, having the same dimensions and fitting the same size pressure vessel. Modules were manufactured in accordance with configuration shown on Figure 2 using rolling machine “Model № RS 4040A” supplied by “Hydrocomponents and Technologies”, CA.

The test unit is shown on figure 5.

a)



b)

Figure 5. Laboratory test unit: a) - flow diagram; b) - photo; 1- feed water tank; 2 - RO membrane element; 3 - product water tank;4 - pump; 5 - water sample valve; 6- product water; 7 - retentate; 8 - feed water pumping line to RO module; 9 - product water discharge; 10 - manometer

Feed water is pumped from feed water tank 1 into membrane module 3 using centrifugal pump 2. The working pressure value was 8 Bars. In RO module feed water stream is separated into two streams: product and concentrate. Product is forwarded to product tank 4 while concentrate is returned back to feed water tank 1. Feed water was concentrated by 6 times throughout the test run. Feed water tank volume was 60 liters. By the end of each test run concentrate volume equaled 10 liters. Membrane surface in test modules was 0,5 sq. meter. Cross flow value in the test unit was 100 liter per hour. Natural water (surface and groundwater) was used as test solutions in experiments. To increase fouling and scaling potential of the test solution (to increase hardness, color or turbidity), natural water was preconcentrated using RO modules. Table 1 shows characteristics of test solutions used in experiments. Natural well water was used, tap water from municipal water supply pipeline, tap water preconcentrated by 2 times and tap water preconcentrated by 4 times.

Membrane treatment efficiencies to remove oil products, detergents, to reduce BOD and TDS under described RO operation conditions (with concentrate volume decreased by 99%) were investigated. Table1 shows membrane efficiencies in separating oil- containing storm wastewater depending on product recovery values. A test program was undertaken to investigate rejection of membranes versus recovery values.

Results of tests are illustrated in Figures 6-10. Figures 8 and 9 shows the drop of membrane flux with recovery increase throughout test run.

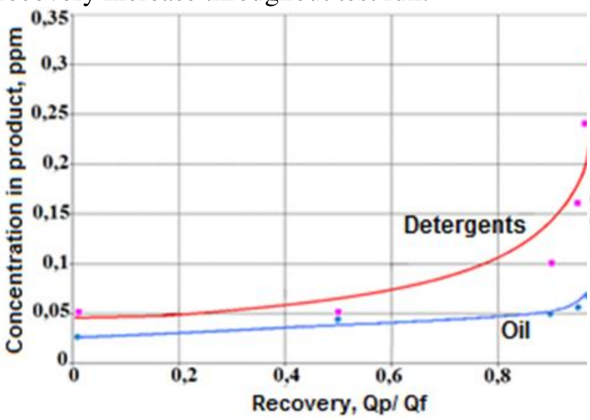


Figure 6. Dependencies of oil and detergent concentrations in RO product water on recovery

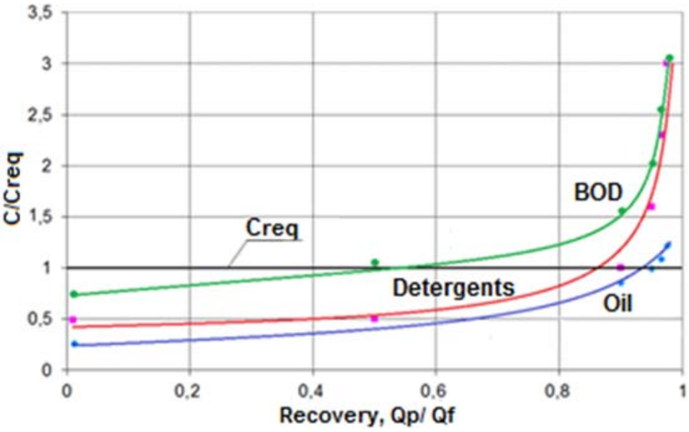


Figure 7. The C/Creq value versus recovery (C - concentration of species, ppm; Creq - the required by discharge regulations concentration value)

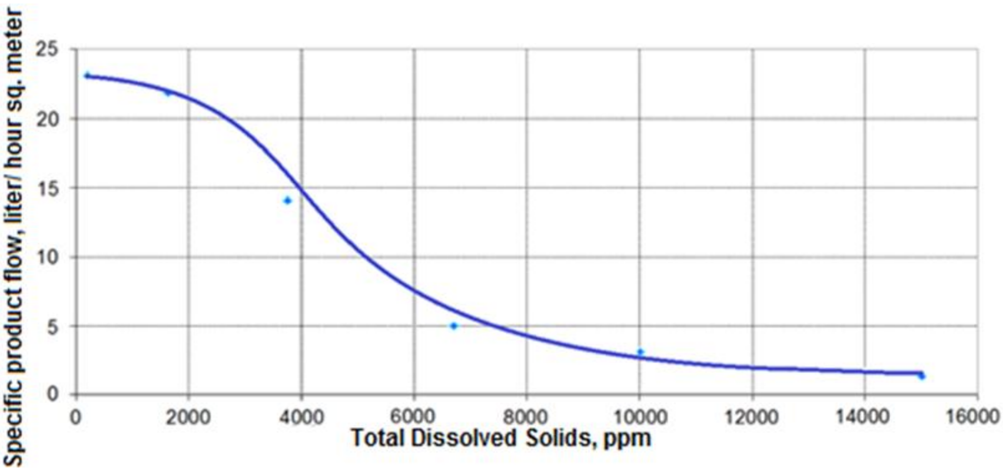


Figure 8. Dependence of specific product flow rate versus feed water TDS

When recovery reaches 0,9-0,95 value, product flow decreases by 2,5 - 3 times. Further recovery increase requires application of second stage membranes operated under higher pressure value. Figure 6 demonstrates relationships of BOD, detergents and oil concentration values in product water on recovery. Reverse osmosis efficiencies can be represented by C/Creq ratio value as a function of recovery, where C is concentration value of the certain impurity in product water and Creq is its required concentration value in product water discharged into surface water source according to existing regulations. Figure 7 shows dependencies of C/Creq ratios on recovery. The growth of feed water salinity (TDS) decreases membrane rejection characteristics.

The second series of experiments were devoted to investigation of feedwater TDS influence on membrane rejection of oil and other wastewater impurities. Figure 10 shows results of experiments aimed at investigation of feed water TDS influence on oil concentration behavior in the product water after treatment of car wash wastewater with different salinities. With TDS growth concentrations of oil in the product water also increase.

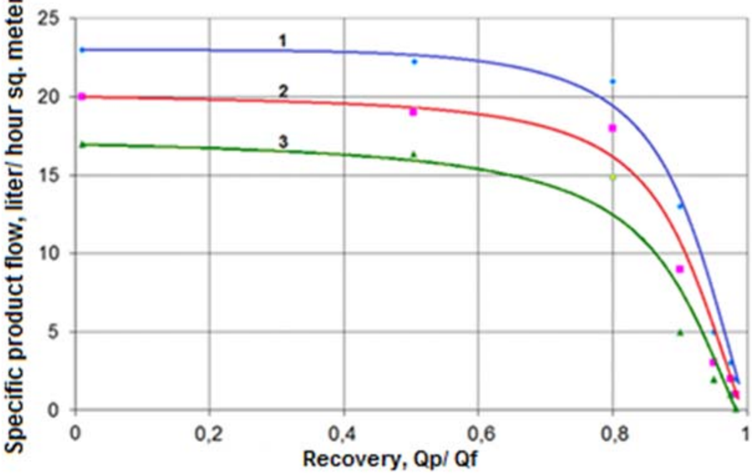


Figure 9. Dependencies of specific product water flow rates on recoveries for different feed water TDS values (1 - 300 ppm; 2 - 600 ppm; 3 - 1000 ppm)

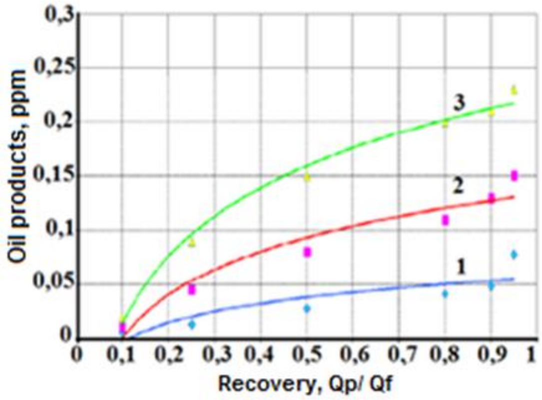


Figure 10. The influence of feed water TDS on rejection of oil products by membranes: dependencies of oil concentrations in product water on recovery for different feed water TDS values: 1 - 770 ppm (feed wastewater TDS); 2 - after addition of 3000 ppm of NaCl; 3 - after addition of 6000 ppm of NaCl

To predict rate of particulate membrane fouling we should know how does fouling rate depend on size and weight of the particles. Belfort and co-authors [7, 8] developed filtration theory that accounted for particle trajectories in membrane channel depending on their weight and velocity. As it was claimed in Belfort's articles [7, 8], filtration theory often predicts higher product flow drop due to fouling than it is observed in reality. Therefore, filtration mechanism that assumes all particles that are contained in water are deposited on membrane surface, was modified basing on all forces that influence the particle in the flow. Al calculations were made for laminar flow conditions with parabolic distribution of velocities in the channel. Above convective flow force that presses the particle to membrane surface and diffusion back force, a lifting force exists that is result of difference between different liquid layers velocities. Accounting for calculated lifting forces, particle trajectories in membrane channels were calculated with a conclusion that not all particles that are contained in water can deposit on membrane surface. The total amount of foulant accumulated on membrane surface is calculated with this account. Belfort [7, 8] has developed the first theory that provided quantitative description of ultrafiltration membrane fouling. According to this theory, fouling begins when convective velocity towards membrane exceeds lifting velocity.

Authors of the present study conducted research to determine rates of particle deposition on RO membranes based on calculation of mass balance of foulant between feed water, product and retentate of the test unit operated in circulation mode [5,6].The influence of hydrodynamics on fouling and shear rate was also described in [9].

To evaluate particulate weight distribution in the feed water and retentate, a method of particle weight determination was used that is based on calculation of sedimentation velocities of the particles.

Figure 11. Experimental investigation of sedimentation characteristics of water samples

Wastewater (11) is added to sedimentation tank (1). Wastewater is delivered by the pump (4) to membrane module (2). Product water (6) is collected to the product water tank (3) and retentate (7) is returned back to the tank (1). Working pressure value is maintained an the level of 7 Bars. Retentate recirculation flow was 25 liters per hour. During operation of the test unit in circulation mode samples of the feed water were withdrawn using the valve (5). Suspended solids concentrations were determined in the samples.

Particulate foulants are removed from membrane surface during flushings. It seems interesting to evaluate the weight ranges of the particles that are primarily deposited on membrane surface as well as to predict sedimentation rates of particles in the flushing tank after flushing. Fouling rates were determined in a laboratory test unit operated in circulation mode shown in figure 5.

Comparative particulate weight study was implemented using 1 liter laboratory glass cylinders (Figure 11). To evaluate weights of particles, their sedimentation rates were determined. Initial wastewater, retentate samples withdrawn throughout test run corresponded to different recovery values, and samples of flush water were investigated. The test procedure consisted of determination of suspended particles in the samples in the cylinders in the beginning of experiment, after 15 minutes, after 5 hours and after 15 hours of sedimentation. Cylinder volume was 500 milliliters and sedimentation volume was 150 milliliters.

If concentration values of suspended matter are determined in water samples in the beginning of the process and after 15 minutes, amount of heavy particle fraction that sediment within 15 minutes will be calculated. Similarly we can determine amounts of particles that sediment within 5 hours and after 15 hours of sedimentation. We can divide all particles containing in wastewater into 4 hypothetical portions:

I - heavy particles (that sediment within 15 minutes)

II - middleweight particles (that sediment within 5 hours)

III - light particles (that sediment within 15 hours)

IV - super light particles that need more than 15 hours for sedimentation.

The volume of water in the sludge does not exceed 1 % of the initial wastewater volume. Thus, membrane plant should not only purify wastewater and remove oil, TDS, BOD, etc., but also to reduce concentrate flow by 100 times (as compared to initial feed water flow). The second stage is used to reduce energy costs while concentrating dissolved salts and organics that increase osmotic pressure. Concentrate of the first stage (constituting about 5- 10% of the initial flow) enters the second stage "tailored" with nanofiltration membranes. Product flow of the second stage is mixed with feed water. The pilot unit contains sedimentation tanks, concentration tanks and membrane flushing systems.

Concentrate flow for the certain conditions depends on wastewater TDS. When low pressure RO and NF membranes are applied, it is reasonable to operate the test unit when concentrate TDS does not exceed 25000 - 30000 ppm. Membrane flux becomes very low under these conditions. To reach higher recoveries, higher pressure is required that needs different membrane and pumping equipment as well as higher power consumption. The lower the initial TDS value, the higher the recovery value that can be reached. For the use of developed "open channel" membrane modules, main principles of RO concentrate utilization are described in previous publications [4].

3. Evaluation of results: determination of operational parameters: guidelines to develop ro process to treat wastewater

To facilitate RO process design relationships and equations were developed to determine the required oil rejection for selected recovery values and feed water TDS (Figure 12). The graphs shown on Figure 11 are developed using the least square method. The developed equation to determine the required rejection is exponential relationship:

Y = cXb,

where Y - membrane rejection, %

X - feed flow decrease ratio: X= 1/ (1- Qp/Qf) , where Qp is product flow rate, Qf - feed flow rate, and Qp/Qf is recovery.

b is an exponent which is determined according to equations:

b = -0.000284 (S-430) - for water with TDS values between 600 -1500 ppm, where S - TDS value, ppm;

b = -0.000115 (S =220) - for water with TDS varying from 50 to 600 ppm;

c - coefficient, determined according to equations:

c = 0.00485 (2337 -S), for water TDS ranging from 600 -1500 ppm;

c = 0.008 (3000 - S) for water TDS ranging from 50 to 600 ppm.

Equations to predict rejection of detergents and other organic species are developed similarly. For the certain feed water composition (concentrations of oil, detergents and TDS) we can determine oil rejection depending on recovery (Figure 16). Using the above shown equations, we can also calculate maximum recovery value, that corresponds to maximum permitted by discharge regulations value of oil in product water (Figure 17). Figure 16 shows the dependence of rejection not on recovery, but on concentration factor defined as: (1/(1- Qp/Qf) which is explained by simplicity of calculation, as this relationship yields an exponential curve.

Figure 12 shows results of experiments presented as particle weigh distribution curves for the feed wastewater (curve 1) and for flush water in the end of experiment (curve 2). Heavy and middleweight particles are primarily sedimented on membrane surface. Therefore, their portion in the overall particle amount in the flush water increases.

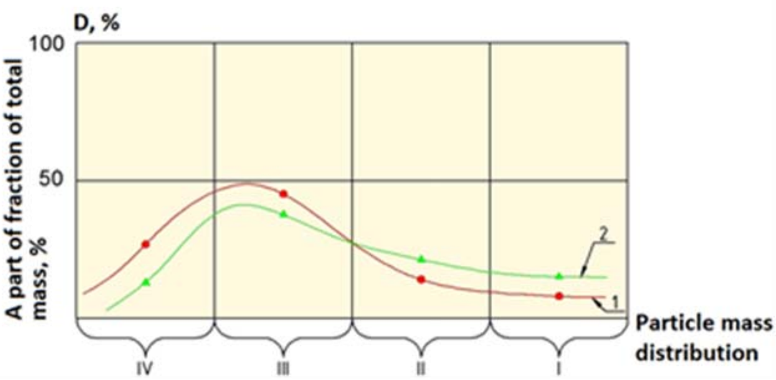


Figure 12. Particle weight distribution. Part of each fraction in the overall amount of particles

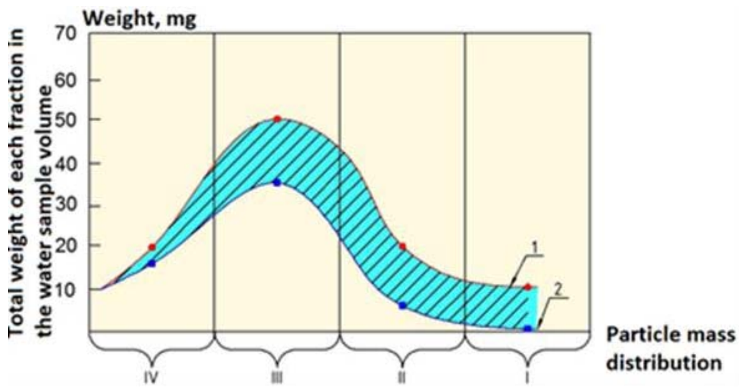


Figure 13. Determination of sedimentation parameters of particles: dependencies of overall weight of each fraction on the weight ranges: I - heavy particles (that sediment within 15 minutes); II - middleweight particles (sediment within 5 hours); III - light particles (sediment within 15 hours); IV - super light particles (need more than 15 hours for sedimentation).
1- feedwater (storm wastewater); 2 - feed water concentrated by 3 times during experiment

Figure 14 shows the results of fouling rates determination. Fouling rates were determined throughout circulation experiments in the test unit (Figure 5) in accordance with the test procedure described in [3]. Figure 14 (a) shows concentration of foulant as a function of concentration factor of feed water. The amount of foulant accumulated on membrane surface versus time is presented on the Figure 14, (b).

Fouling rates are determined as values of slope tangents of curves shown on Figure 14, (b).Fouling rates values versus concentration factor are shown on Figure 14, (c). Fouling rates were evaluated for the particles with different weighs. If we know fouling rate values, we can predict amount of accumulated foulant after certain operation time.

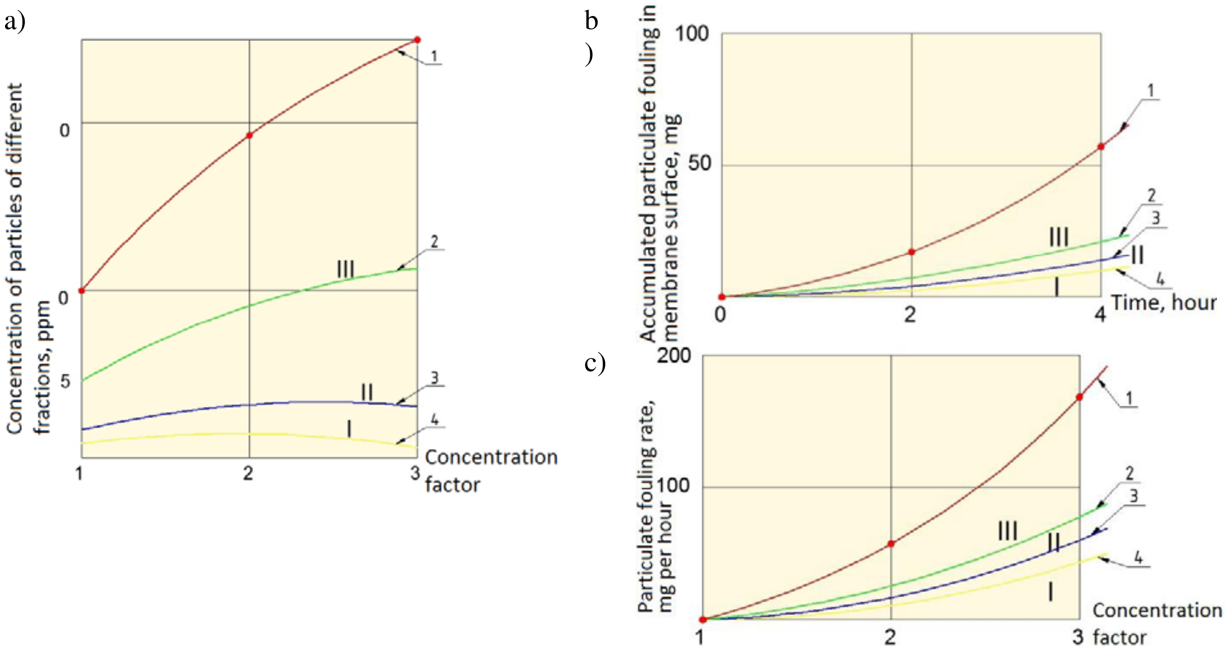


Figure 14. Determination of fouling rates by particles with different weights: a) Concentrations of suspended particles (for different weight fractions) versus concentration factor; b) Amounts of accumulated foulant (for different weight fractions) versus time of experiment; c) Fouling rate values (for different weight fractions) versus concentration factor.
1- feed water; 2 - light particles (fraction III); 3 - middleweight fraction (fraction II); 4 - heavy particles (fraction I).

The obtained results enable us to calculate required characteristics of sedimentation tanks where RO concentrate and flush water are collected (Figure 4). Sedimentation volume and sedimentation time can be determined basing on results of sedimentation studiesand are presented below.

As a result, exponential relationships are obtained that enable us to calculate concentration values of impurities in product water and to determine maximum recovery of the first RO stage of membrane unit. Calculations are efficient for concentration values of oil and detergents in the feed water ranging from 0,5 to 50 ppm, and for TDS ranging from 50 to 1500 ppm.

4. Conclusions

1. To treat wastewater, specially designed membrane "open channel" modules are used that do not possess "dead areas" that cause fouling.
2. The main principles of high recovery maintenance are ensured by concentration of the feed water in circulation mode by 50-100 times by volume. Concentrate volume constitutes no more than 0,5-1% of the initial feed water volume and is withdrawn from the system together with a wet sludge as a sludge moisture.

3. The maximum recovery value is determined that corresponds to the maximum permitted by water regulations concentration value of oil and other impurities in RO product water
4. Experimental research is conducted to evaluate rates of particulate membrane fouling during stormwater RO desalination.
5. Sedimentation of particles containing in wastewater is investigated in respect to their weight range. Prognosis of weight distribution of particles inlant accumulated on membrane surface is developed.
6. Membrane fouling rates are very dependent on the cross flow rates in membrane channels: the higher cross flow velocity is, the lower is fouling rate.
7.Optimum values of main operational parameters, such as: cross flow rates and flushing modes (time interval between flushings) are determined basing on experimentally obtained fouling rate values and understanding of fouling influence on membrane performance.

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References
[1] Duin O, Wessels P etc. 2000 Direct nanofiltration or ultrafiltration at WWTP effluent. Proc. of the conf. on Membranes, Paris, October 2000, Desalination publications, L'Aquila, Italy. Vol. 2, 105-112.
[2] Abdel-Javad M and Ebrahimet S 1999 *Desalination* **124** 251-261.
[3] Pervov A and Andrianov A 2011 *Desalination and water treatment* **35** 2-9.
[4] Riddle R A 1991 Open channel ultrafiltration for reverse osmosis pretreatment. IDA World Conference on Desalination and Water Reuse. August 25-29, 1991, Washington DC. Pretreatment and Fouling.
[5] Pervov A and Matveev N 2013 Use of reverse osmosis to treat domestic wastewater for local utilities and in small industries. Tianjin ida world congress 2013 on desalination and water reuse. IDAWC REF: TIAN13-217. 20-25 october, China, 2013.
[6] Pervov A and Matveev N 2014 *J. of Membrane and Separation Tech.* **3 (1)** 11-28
[7] Pervov A and Matveev N 2014 *Water supply and Sanitary equipment* **1** 23-32.