New technology to treat leachate by low pressure reverse osmosis

Alexei Pervov[a,*], Tatiana Shirkova[b], Val Frenkel[c]

[a]Department of Water Supply and Sewerage, Moscow State University of Civil Engineering, 26, Yaroslavskoye Shosse, Moscow, Russian Federation, 129337, Tel. +7985 766-7644; email: ale-pervov@yandex.ru
[b]JSC "MosvodokanalNIIproekt", 22, Pleteshkovsky Pereulok, Moscow, Russian Federation, 105005, Tel. +7985 789-7704; email: mabell@bk.ru
[c]Pacific Coast Operating Group, Greeley and Hansen, 50, California Street, Suite 1500, San Francisco, California, 94111, Tel. +1-4154121380; email: vfrenkel@greely-hansen.com

ABSTRACT

This manuscript presents results of research developing efficient techniques to treat landfill leachate of the largest landfill in Europe located 30 km east of the City of Moscow. The leachate constitutes the complicated chemical solute that contains over 4,500 ppm of organics expressed by chemical oxygen demand (COD), over 5,000 ppm of salts expressed as total dissolved solids (TDS), over 2,500 ppm of ammonia expressed as NH_3. Treatment of this leachate requires complex solution unique to the constituents. Reverse osmosis treatment can address reduction of TDS, COD and ammonia to meet discharge criteria; the target was to reach maximum recovery and utilize RO concentrate; to ensure adequate pretreatment of wastewater that enters RO concentrate; to provide adequate post-treatment of product water prior to discharge. Conventional approach for this challenge involves application of three stages of RO to reduce ammonia concentration to the value of 0.2–1.0 ppm. The first stage of RO requires "direct" treatment of high TDS wastewater with "seawater" membranes under high pressure value of 50–60 Bars followed by two stages of RO at low pressure to reduce ammonia concentration. The newly proposed approach is consists from low pressure RO and nanofiltration (NF) membranes to dramatically decrease operational costs and increase system recovery up to 90% and higher using the same total membrane area. The proposed technique is based on results of experimental investigation that evaluated organic fouling and scaling rates in membrane channels and membrane flow and rejection values as functions of recoveries at each stage of membrane treatment.

Keywords: Landfill leachate; Reverse osmosis; Nanofiltration; Increase of recovery; Concentrate utilization; Organic fouling of RO membranes; Membrane replacement costs; Membrane cleaning; Wastewater sludge handling

1. Introduction

Construction of landfills is a conventional and well adopted worldwide approach for municipal solid wastes disposal and storage [1,2]. Generation of leachate by municipal solid waste landfills causes a significant threat to surface and ground water [3–5]. The landfill leachate contains significant concentrations of organic and inorganic contaminants generated within landfill body [6,7]. To minimize leachate impact on environment different techniques are applied to remove these contaminants, such as chemical and biological treatments [6–8]. To remove dissolved salts and biogenic pollutants (like ammonia and phosphate ions) reverse osmosis (RO) membranes are utilized widely [8,9]. Often leachate that contains total organic carbon (TOC) value (from 1,000 to 5,000 ppm) is subject

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* Corresponding author.

to chemical treatment to remove suspended matter and dissolved organics [10]. High organic content increases osmotic pressure and decreases membrane permeability [11]. The goal of the presented project is to demonstrate experimental results to develop process with minimal volume of the concentrate and to get beneficial use of it.

Beside dissolved solids, such as ammonia and calcium salts, RO removes dissolved organic substances measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD) and TOC [12]. Modern low pressure reverse osmosis membranes reject 95%–97% of dissolved salts thus reducing monovalent ammonia concentration by 20–30 times [13–15]. However, at least 3 RO membrane stages are required [14] to reduce ammonia concentration 2,000–5000 times to meet discharge regulation standards. The increased concentrations of COD and total dissolved solids (TDS) in RO concentrate causes membrane flux reduction [16,17] due to the increase of the osmotic pressure. Practically the low pressure RO membranes cannot

be applied when landfill leachate with high TOC and TDS values is treated, due to the low flux to operate system. Due to this reason in most cases the high pressure rated RO, seawater membranes are utilized and operated under 50–70 bar pressure, and with concentrate flow no less than 30% of feed water flow. Concentrate handling and utilization becomes thus a serious problem [12,18–20]. Increase of system recovery and reduction of concentrate flow causes increase of organics and salts concentration and osmotic pressure resulting in dramatic loss of the flux. The low pressure Nanofiltration (NF) membranes allow reduce concentrate flow substantially [13,21,22]. The "cascade" approach using nanofiltration membranes is often applied when seawater is desalinated [23–25] and when highly saline solutions are concentrated [26]. For the case when landfill leachate is treated, recovery can reach 95%–98% and TDS value of concentrate can reach 80,000–100,000 ppm [16,27].

Concept of the reduction of nanofiltration concentrate flow presented in Fig. 1a. Increase of system recovery and
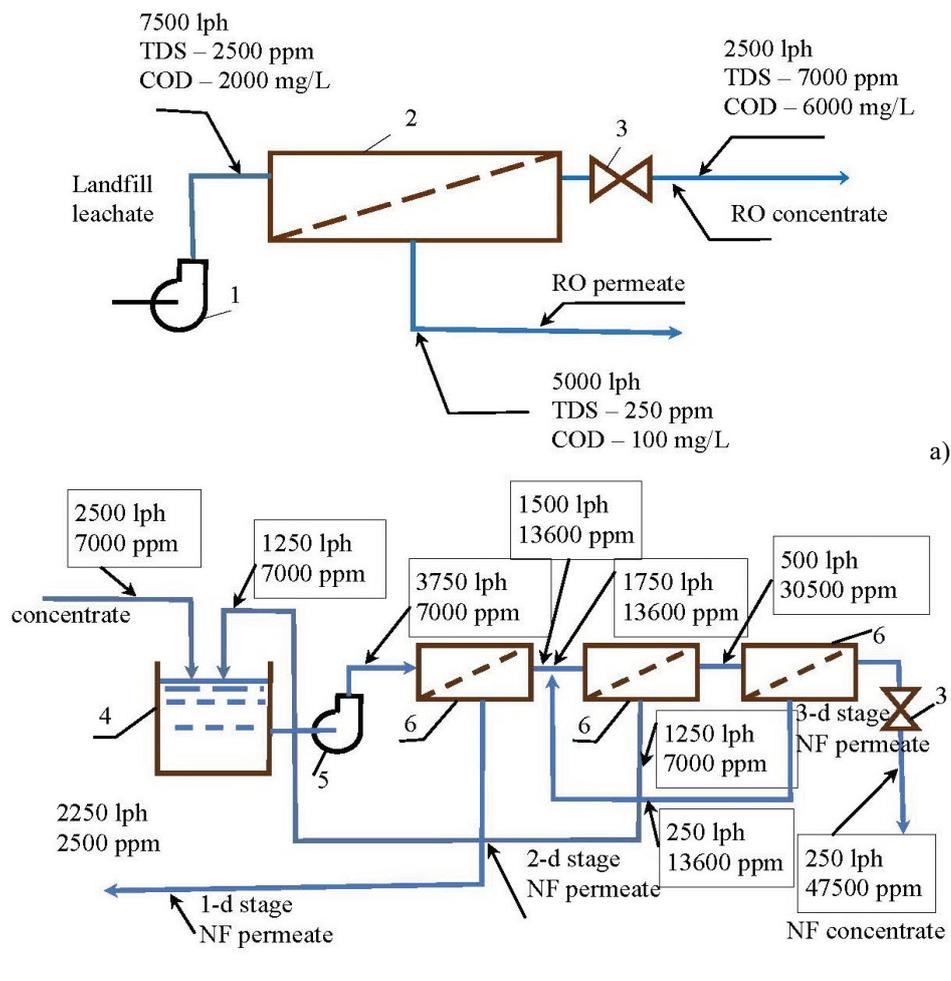
Fig. 1. Flow and salt balance diagrams of landfill leachate treatment using reverse osmosis and nanofiltration membranes: (a) a flow diagram of landfill leachate treatment with reverse osmosis membranes and separation in permeate and concentrate streams and (b) concept to reduce reverse osmosis concentrate flow by treatment with "cascade" concept of nanofiltration modules. 1 – working pump; 2 – reverse osmosis module; 3 – pressure regulation module; 4 – concentrate collection tank; 5 – working pump of nanofiltration unit to reduce concentrate flow; 6 – nanofiltration modules for concentrate flow reduction.

concentrate flow reduction enables us to reach the value that does not exceed 2%–3% of the feed water that enters the membrane system. This effect is achieved due to the removal of dissolved organics of landfill leachate. The diagram on the same concept is presented in Fig. 1b. The RO concentrate passes through membrane modules – "concentrators" consisted from nanofiltration membranes with low rejection. Nanofiltration membranes reject from 60% to 70% of organics and salts contained in the feed water. Therefore, the NF permeate after each stage (Fig. 1b) is forwarded to the head of the modules on the previous membrane stage as permeate of this stage by its quality matches the feed water quality that enters the previous stage. Thus, permeate of the first stage "concentrators" is added to the feed water (leachate) that enters reverse osmosis system as its salinity value similar to salt content in feed water. Permeate of the second stage "concentrators" combines with the feed water that enters the first stage "concentrators" as its salinity is similar to the reverse osmosis concentrate. Permeate of the third stage "concentrators" enters the second stage modules. As a result of this concept the required reduction of the concentrate flow is reached without working pressure increase. For example, as it is shown in Fig. 1b, salt concentration in concentrate reaches 47,500 ppm values with pressure that does not exceed 16–17 bar [27].

The goal of the presented experimental work to treat solid wastes leachate listed below:
- For the treatment process to determine the suitable types of membranes, number of membrane stages and amounts of membrane modules in each stage to ensure the required treated water quality and minimal concentrate flow;
- To evaluate parameters of membrane process and to determine highest possible system recovery and concentrate utilization;

- To develop technique to separate concentrate into two streams of highly concentrated organic solution and ammonia and sodium salts solution.

2. Materials and methods

All membrane characteristics and operational parameters were evaluated in laboratory conditions using membrane test unit. The experimental program consisted of two parts. In the first part the four stages of landfill leachate treatment were investigated. Leachate was treated with nanofiltration and low pressure RO membrane on the first stage of treatment to evaluate product flux and rejection characteristics as a function of initial volume reduction coefficient K value (K is defined as ratio of the feed water volume to the concentrate volume obtained throughout of test run). RO membrane characteristics were investigated on the second, third and fourth stages as a function of coefficient K value.

In the second part of the experimental program possibilities to separate concentrate into two (organic and inorganic) concentrated solutions were investigated.

The second part of experimental program consisted of experiments to separate organics and mineral salts in concentrate. Concentrate of landfill leachate was used (Table 1) that is usually obtained using "Kaiser scheme". Concentrate TDS was 5,000 ppm and TOC was 2,000 ppm. Experiments were conducted in 4 stages:

- *first stage*: reduction of feed water volume (15 L) in tank 1 by 5 times using nanofiltration membranes;
- *second stage*: dilution of concentrate with deionized water in a ratio of 1:4. For concentrate dilution we used permeate after treatment of the groundwater with RO membranes;
- *third stage*: reduction of the newly produced feed water with nanofiltration membrane by 5 times and further

Table 1
Results of chemical analyses of leachate treatment

No.	Characteristics	Feed water (leachate)	Permeate (IV stage) (RO)	Concentrate		Concentrate after separation	
				Stage I	Stage II	Stage I	Stage II
				NF	RO	NF	RO
1	Leachate flow, m³/h	5.2–5.3	5	0.1	0.15	0.06	0.1
2	TOC, ppm	4,387	2.9	85,000	6,500	122,800	2,100
3	pH	7.7	5.6	7.7	7.8	7.7	7.8
4	Calcium, ppm	190	0.8	1,660	460	720	600
5	Sodium, ppm	1,144	4.8	5,100	23,500	1,800	28,100
6	Alkalinity, ppm	76.0	1.4	900	3,600	720	1,440
7	Ammonia, ppm	380	0.2	4,000	8,500	600	12,800
8	Nitrates, ppm	1.2	–	10	26	3.1	39
9	Chlorides, ppm	980	3.5	17,000	42,000	8,000	90,000
10	Sulphates, ppm	627	1.0	9,100	1,400	22,000	200
11	Iron, ppm	36	0.05	–	–	–	–
12	Suspended solids, ppm	329	–	–	–	–	–
13	TDS	3,580	–	39,000	90,000	9,000	165,000

treatment obtaining permeate (15 L) and concentrate (3 L);

- *fourth stage*: treatment of nanofiltration membrane permeate with RO membrane to provide coefficient K value of 20. The test unit flow diagram is shown in Fig. 2. The feed water (landfill leachate) after passing through the cartridge filter 1 was collected in the feed water tank 2. The feed water volume in tank 2 was 15 L. Pump 3 delivered feed water to the module 4 loaded with nanofiltration or low pressure RO membranes. Concentrate after module 4 was returned back to tank 2 and product flow was forwarded to product tank 6. The first stage permeate was pumped by the second stage pump 7 to the second stage membrane module 8. Concentrate after module 8 was returned back to the tank 6 and permeate was collected in the second stage permeate tank 9. Pressure value on each stage was regulated using the pressure valve 5 and controlled by pressure gauge 10. Reverse osmosis of 1812 BLN model and nanofiltration membrane elements of 1812 70 NE model were manufactured and supplied by CSM Company, Korea. For the first stage of leachate concentrate treatment, 70 NE membranes were used (model 1812 70 NE). In the second stage, RO elements (model 1812 BLN and RE 2012-100) were used. The gear pumps 3 and 7 (model "RO 900-220") were used to provide working pressure. Pressure value was 6–7 bar. The pumps were supplied by "Raifil" Company (Moscow, Russia). The membrane area of the 1812 module was 0.5 m^2.

During the test run as the product water accumulated in the tank 5 the feed water (leachate) volume in tank 2 was decreasing, concentration values of salts and organics increased and membrane product flux was decreasing. In the first part (series) of our experimental program the feed water volume in tank 2 reduced from 20 to 2 L. The ratio of initial feed water volume V_f in tank 2 to the volume of water in the tank 2 at the time when the sample was taken, V_c, is called by us as "concentration coefficient", or "initial volume reduction coefficient" whose value is determined by:

$K = V_f/V_c$. In the second test run which simulated the second membrane stage 16 L of the first stage permeate were used (collected in the tank 5) after the leachate volume in the feed tank 2 was decreased by 5 times that corresponds to the recovery value 0.8. At higher recoveries and higher coefficient K values the quality of nanofiltration membrane permeate by the salt content is approaching the quality of feed water. Fig. 5 shows the results of determining the concentrations of different species values in permeates at each membrane stage presented in the form of concentration dependencies on the K value.

COD values were determined by the titrimetric method. To evaluate organics concentrations also method of spectrophotometry was used. An atomic adsorption spectrophotometer of the "AN-2" (produced by "Neftechimavtomatika", Saint Petersburg, Russia) model was used. Concentrations of calcium and magnesium were determined trilometrically. Determination of sulphate concentrations were carried out using the turbidimetric method. Ammonia concentrations were determined using the photometric method. A photoelectric photometer of the "KFK-3" (produced by "Zagorski optical and mechanical plant") model was used. Sodium concentrations were determined using the atomic adsorption method and the "dry residue" was determined by the weight method. Electronic laboratory scale of the "Pioneer PA 64" model (supplied by "Ohaus Corporation", USA) were used. TDS and conductivity values were determined using liquid condumetric analyzer of the "INOLAB COND model level 1" (supplied by "Wissenschaftlich-tecnische werkstatten GMBH").

Chemical compositions of landfill leachate, as well as of concentrate and of permeate produced throughout membrane treatment are presented in Table 1.

3. Results

Monovalent ions (ammonia, bicarbonates and chlorides) passing the nanofiltration membranes and are rejected by RO membranes in the second stage. Thus the second stage concentrate contains ammonia and sodium chlorides
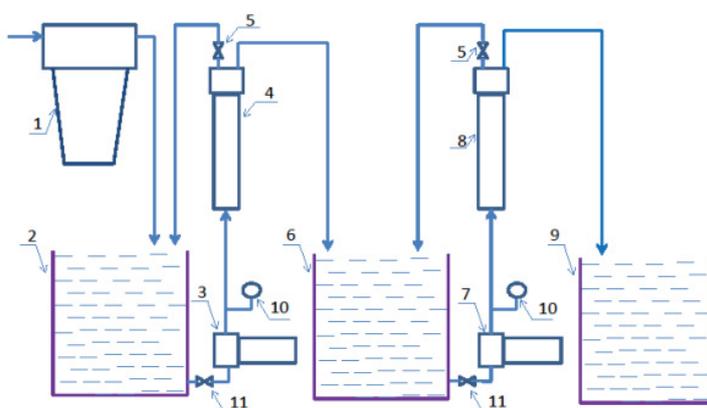
Fig. 2. A flow diagram of experimental membrane unit: 1 – cartridge filter for leachate pretreatment; 2 – feed water tank; 3 – first stage pump; 4 – nanofiltration membrane element; 5 – pressure regulation valve; 6 – first stage permeate collection tank; 7 – second stage pump; 8 – second stage low pressure reverse osmosis membrane module; 9 – second stage permeate collection tank; 10 – pressure gauge; 11 – ball valve.
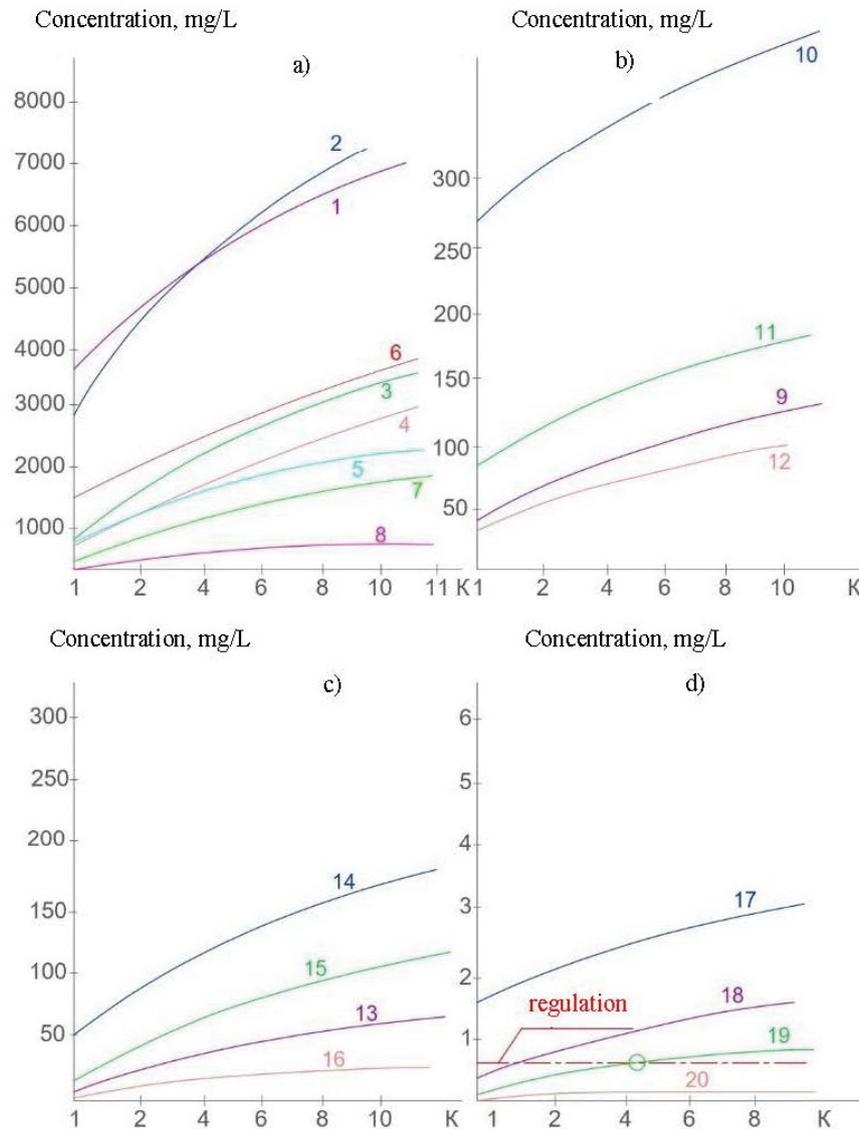
Fig. 3. Dependencies of total oxygen demand (TOC) and ammonia concentration values on coefficient *K* values for the cases when low pressure BLN membranes are used at all stages: (a) in concentrate in the first RO stage and in product water in the first RO stage product water, (b) in the second RO stage concentrate, (c) in the second stage concentrate and (d) in the fourth stage concentrate; 1 – COD; 2 – chlorides; 3 – ammonia; 4 – calcium; 5 – COD in the first stage concentrate; 6 – chlorides in the first stage concentrate; 7 – ammonia in the first stage permeate; 8 – calcium in the first stage permeate; 9 – COD in the second stage concentrate; 10 – chlorides in the second stage concentrate; 11 – ammonia in the second stage concentrate; 12 – calcium in the second stage concentrate; 13 – COD in the third stage concentrate; 14 – chlorides in the third stage concentrate; 15 – ammonia in the third stage concentrate; 16 – calcium in the third stage concentrate; 17 – COD in the fourth stage concentrate; 18 – chlorides in the fourth stage concentrate; 19 – ammonia in the fourth stage concentrate; 20 – calcium in the fourth stage concentrate.

(Table 1). To further reduce concentration of monovalent ions in the first stage concentrate a special concept was developed that consists from dilution of the first stage concentrate by the product water of the second stage. And the concentration cycle repeated. This approach enables us to efficiently separate organics from inorganic monovalent salts.

As the theory of membrane separation states [24], when reverse osmosis membrane unit is operated, salt concentration in permeate and concentrate are the function of salt rejection *R* and recovery and it can be described by the following formulas:

$$C_c = C_f \cdot (1-\alpha)^{-R} \qquad \text{(for concentrate):} \qquad (1)$$

$$C_p = C_f \cdot (1-R) \cdot (1-\alpha)^{-R} \quad \text{(for permeate):} \qquad (2)$$

where C_f – concentration of the certain component in the feed water; C_p – concentration in permeate, C_c – concentration in

Membrane rejection, R, %
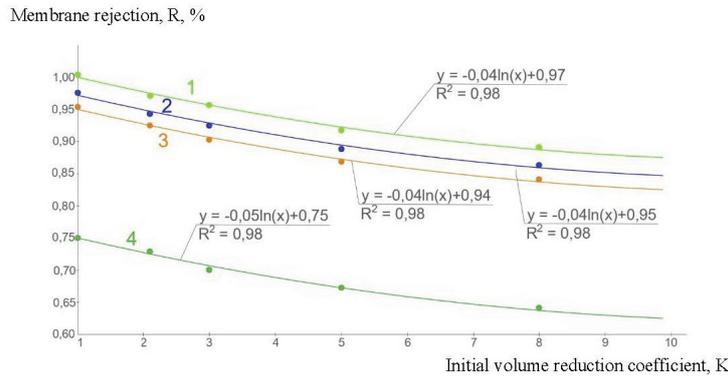
Fig. 4. Dependencies of membrane rejection values of different species on *K* value during treatment of: (a) feed water and first stage product water and (b) second stand third stage product water. 1 – BE membrane (feed water TDS 2,000–2,500 ppm); 2 – BLN membrane (feed water TDS 2,000–2,500 ppm); 3 – BLN membrane (feed water TDS 1,000–5,000 ppm, feed water COD 500–1,000 ppm); 4 – nanofiltration membrane 70 NE (feed water TDS 1,000–10,000 ppm, feed water COD 1,000–4,500 ppm).

Specific membrane flux, Q, liter/sq.meter·hour
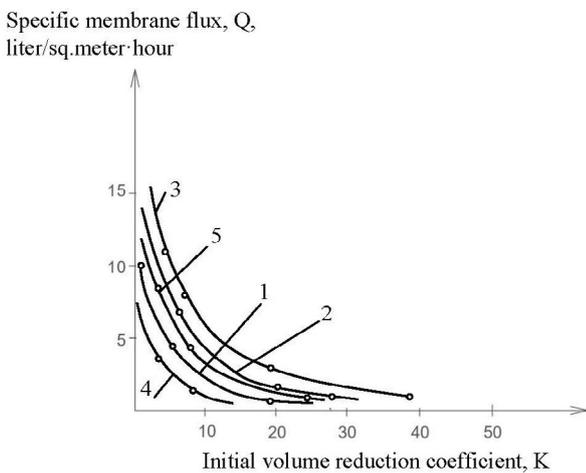
Fig. 5. Reduction of product flow with *K* increase for different membranes used in the first stage during "Aleksandrov" landfill leachate treatment: 1 – nanofiltration 70 NE membrane; 2 – nanofiltration 90 NE membrane; 3 – low pressure reverse osmosis membrane BLN; 4 – high rejection brackish water membrane BE; 5 – high pressure seawater desalination membrane SW; 6 – high rejection membrane RE.

concentrate for the given recovery value α; *R* – membrane rejection value of the required component defined as a ratio: $R = (C_f – C_p)/C_{f'}$ where C_f и C_p – concentration values in the feed water and permeate respectively. Let's evaluate how ratio of the ammonia concentration to organic concentration is changing in permeate and concentrate of RO for the case when ammonia ion rejection and organics (COD) rejection values are different. The ratio of ammonia to organics concentration will have the following value:

$$\frac{C^c_{NH_4}}{C^c_{COD}} = \frac{C^f_{NH_4}}{C^f_{COD}} \cdot (1-\alpha) R_{COD} - R_{NH_4} \tag{3}$$

For the case when nanofiltration membranes model 70 NE is applied (manufacturer of CSM, Korea), the rejection value of monovalent ammonia ions are 0.65 and

BOD – 0.85 [2]. Then, with a recovery value of 0.9 (α = 0.9) the ratio of ammonia to COD concentrations will be:

$$\frac{C^c_{NH_4}}{C^c_{COD}} = (1-0.9)^{0.2} = 0.63 \tag{4}$$

Respectively, the ratio of ammonia ion and COD concentrations at a recovery value of 0.9 (α = 0.9) will have the following value:

$$\frac{C^p_{NH_4}}{C^p_{COD}} = \frac{(1-0.65)}{(1-0.85)} \cdot 0.1^{0,2} = 2.33 \cdot 0.63 = 1.47 \tag{5}$$

The higher the rejection values difference of the removed impurities, the higher is the ratio of their concentration values in concentrate.

To further change the ratios of concentration values of separated components in permeate and concentrate, after we reached recovery value of 0.9 (α = 0.9), we can dilute the solution again with deionized water in the ratio of 9:1. Then after re-concentrating and reaching the recovery value of 0.9 (α = 0.9) we will get a new ratio value of ammonia and COD concentrations in concentrate as shown below:

$$\frac{C^{c2}_{NH_4}}{C^{c2}_{COD}} = (1-0.9)^{0.2} \cdot 0.63 = 0.63^2 = 0.4 \tag{6}$$

And in permeate:

$$\frac{C^{p2}_{NH_4}}{C^{p2}_{COD}} = \frac{(1-0.65)}{(1-0.85)} \cdot (1-0.9)^{0.2} \cdot 2.33 \cdot 0.63 = 2.33^2 \cdot 0.63^2 = 2.17 \tag{7}$$

We can also change the ratio of ammonia and TOC concentrations further by diluting concentrate with deionized water in a ratio of 9:1 and then after operation of the test unit until the recovery reaches value of 0.9 (α = 0.9). Then we will get the following ratio value in concentrate:

$$\frac{C_{NH_4}^{c3}}{C_{COD}^{c3}} = (1-0.9)^{0.2} \cdot 0.63 \cdot 0.63 = 0.63^3 = 0.25 \qquad (8)$$

And the following value in permeate:

$$\frac{C_{NH_4}^{p3}}{C_{COD}^{p3}} = \frac{(1-0.65)}{(1-0.85)} \cdot (1-0.9)^{0.2} \cdot 2.33^2 \cdot 0.63^2 = 2.33^3 \cdot 0.63^3 = 3.15 \qquad (9)$$

Thus, diluting concentrate with deionized water and concentrating it again, we will get different ratios of ammonia and TOC concentrations in permeate and concentrate. To obtain a highly concentrated solution, the resulting permeate can be concentrated using RO membranes to a value of 20,000 ppm and then to a value of 80,000 ppm using nanofiltration membranes as demonstrated in Fig. 13b.

Experimental data was consistently processed with the goal to obtain values of the main technical parameters of membrane unit. Fig. 3 shows the obtained dependencies of ionic concentrations of sulphates, chlorides, calcium, ammonia ions and COD values on concentration coefficient _K_ values for first, second and third stages.

To determine the amount of membrane elements required to reach the desired recoveries, decrease of membrane product flow throughout the experiment was evaluated. Dependencies of specific membrane flux on _K_ values for different membranes are presented in Fig. 4. Method of the required membrane area determination for membrane facilities with recovery increase is developed and described in [28,29]. Fig. 4 shows reduction of product flow with _K_ value increase for different membranes used in the first stage of landfill leachate treatment. Figs. 5–8 present example of required membrane surface area determination for three stages of leachate membrane Fig. 5 shows reduction of membrane flux in the first, second and third stages. Using the obtained values of membrane specific product flux, for each range of changes of _K_ value, volumes of permeate produced within each range and membrane

surface areas required to produce these amounts of permeate are calculated. The values of specific membrane fluxes were determined based on the membrane area in spiral wound element of 1812 model with area 0.5 m². The calculations are made for membrane system producing 1 m³/h.

Figs. 6–8 show the steps to determine membrane area values at each stage of membrane treatment. Results of calculation enable us to determine the required membrane area and amount of commercial membrane elements as well as their replacement costs. Maximum reached _K_ value is determined based on minimal product flux in the first
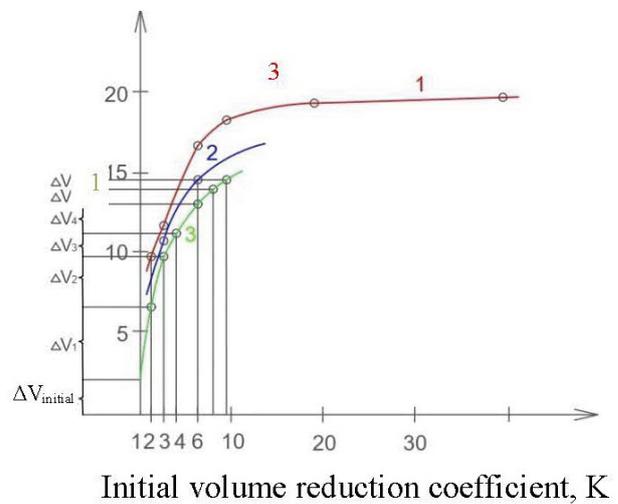
Fig. 7. Dependencies of the produced permeate volume on the feed volume reduction coefficient _K_ value, obtained in different experiments: 1 – first stage, 70 NE membranes; 2 – second stage, BLN membranes; 3 – third stage, BLN membranes.

Fig. 6. Reduction of specific product flow with _K_ value increase: 1 – first stage, 70 NE membranes; 2 – second stage, BLN membrane; 3 – third stage, BLN membrane.
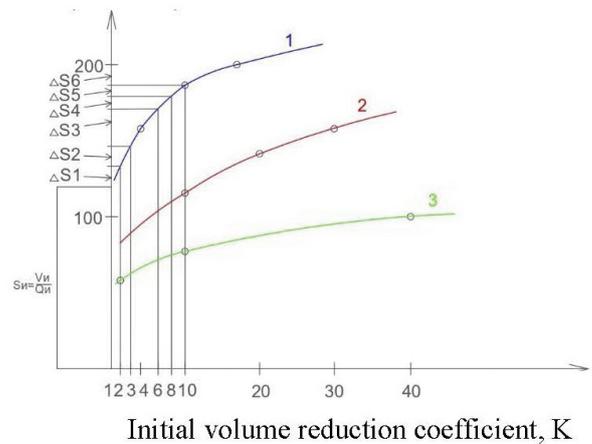
Fig. 8. Dependencies of the required membrane surface values on the feed volume reduction coefficient _K_ value: 1 – first stage, 70 NE membranes; 2 – second stage, BLN membranes; 3 – third stage, BLN membranes.

and the second membrane stages. For 70NE membranes maximum K value corresponds to 70–80 g/L. According to leachate composition (Table 1) concentrate flow is 5%–6% of the total amount of feed water that enters membrane facility.

In the second part of experimental program separation of concentrate was investigated. Fig. 9 shows results of COD, ammonia and chloride concentrations determination as a function of K value during treatment of leachate concentrate. Concentrate from the first stage was used, which was leachate treated with nanofiltration membrane with recovery value of 0.8 ($K = 5$). COD. Ammonia and chloride concentrations are presented in two stages of concentration and dilution.

As it can be seen in Fig. 9, concentration efficiency increases as dilution increases, and the ability of leachate to concentrate increases as well as the possibility to decrease the concentrate volume and increase K value. After dilution process of organics concentration is efficient that enables us to increase COD value from 5,000 to 40,000 ppm and reduce concentrate flow by 20 times. Fig. 12 shows reduction of nanofiltration membrane flux during leachate concentrate treatment without and after dilution.

Permeate after dilution and subsequent concentration can also be treated to produce highly concentrated solutions of ammonia and sodium salts with concentration of 80,000 ppm and higher (according to Fig. 1a schematic) and demineralized water that can be used for dilution. Fig. 14 shows dependencies of concentrations of calcium, ammonia, chloride ions and COD values on K values during nanofiltration permeate treatment. Nanofiltration permeate was collected after the third cycle of concentrate dilution. Low TDS nanofiltration permeate was treated with reverse osmosis BLN membranes and coefficient K reached value of 100. Thus, nanofiltration concentrate with initial volume of 15 L was separated in organic solution with volume 0.7 L and concentrated ammonia salts solution volume of 1.0 L. The produced volume of deionized water was 13.3 L.

Fig. 12 demonstrates results of the spectral analysis of nanofiltration concentrate samples obtained after conducting concentration cycles, after dilution and after further concentration. The plots show dependencies of light absorption on wavelength of light transmitted through the water sample. Changes in optical density in different ranges of the spectrum enable us to evaluate molecular weight values of organic substances that are contained in leachate.

4. Discussion and conclusions

To treat landfill leachate and to reach required value of ammonia and other pollutant that are discharged to
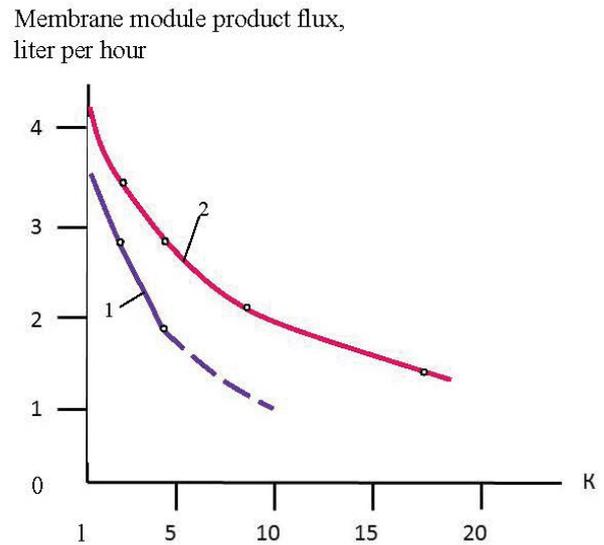
Fig. 10. Reduction of nanofiltration NE 70-1812-100 membrane flux with K value increase: 1 – treatment of landfill leachate concentrate; 2 – treatment of concentrate after dilution by 10 times.

Fig. 9. Dependencies of COD, chloride and ammonia concentration values on K values during treatment of leachate concentration: 1 – COD; 2 – ammonia; 3 – chlorides.
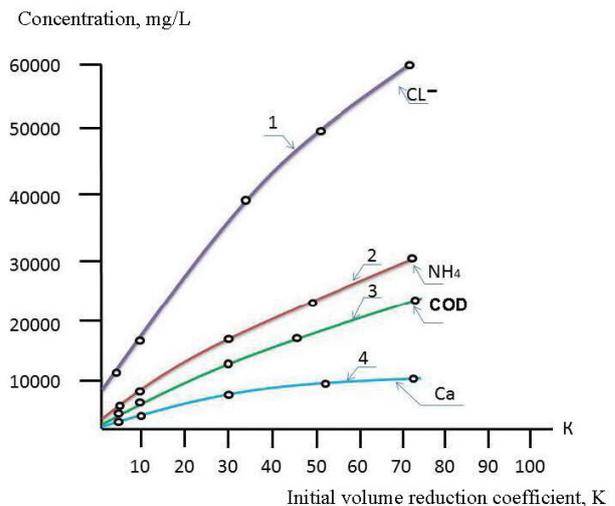
Fig. 11. Dependencies of chloride, ammonia, COD and calcium concentration values in RO membrane concentrate during treatment in the first stage nanofiltration membrane concentrate: 1 – chlorides; 2 – ammonia; 3 – COD; 4 – calcium.
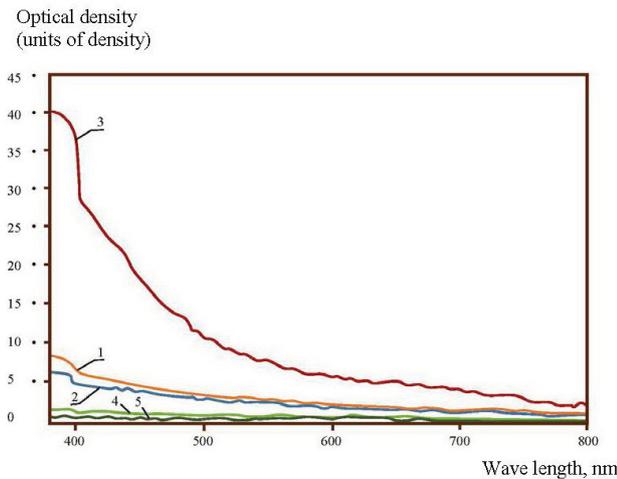
Fig. 12. Changes in optical density as a function of wavelength of light transmitted through water samples of: 1 – feed water (leachate); 2 – concentrate after being diluted 10 times before the beginning of the second concentration cycle; 3 – concentrate after second cycle of concentration by 20 times; 4 – nanofiltration permeate after the first cycle; 5 – nanofiltration permeate after the second cycle.

natural water reservoirs, the three- and four-staged flow diagrams were developed [28,29] that are shown in Fig. 13. Fig. 13a shows the conventionally applied technique that uses seawater membranes in the first stage and low pressure RO membranes in the second and the third stages. This "conventional" approach is common for the majority of landfills serving Moscow region. Prior to the entering RO landfill leachate undergoes pretreatment using flocculation and sand filtration to remove suspended matter. Reverse osmosis contains from three stages. High pressure RO utilized in the first stage and is operated under pressure 60–70 bar. This is explained by the fact that landfill leachates does not only have high TDS value (from 2,000 to 90,000 ppm) but also contains organics with TOC value varying from 1,700 to 3,000 ppm and even higher. The second and the third stages are equipped with low pressure RO membranes which are reducing ammonia and other pollutants to meet wastewater discharge regulated limits. In Russian Federation the described above "conventional" flow diagram is called "Kaiser scheme". It was named after Oliver Kaiser, President of Austrian company "Ecocon" which was the first company to start landfill leachate business in Russian Federation. Fig. 13b presents the four-stage schematic using nanofiltration in the first stage to reduce organics and then to reduce the concentrate flow. Application of nanofiltration membranes on the first stage with further three stages of low pressure RO provides substantial reduction of capital and operational costs as compared to "conventional" "Kaiser scheme" as the total membrane surface area in this case is lower [28]. Low rejection (70%) nanofiltration membranes are applied in the first stage that enables to reach the required recovery value in the first stage. When the first stage recovery is increased, the TDS value of first stage permeate increases and permeate composition approaches the composition

of the feed water value. Therefore, a part of the first stage permeate produced at the recovery value of 75%–80% enters the second RO stage and the last part of the first stage permeate of nanofiltration membranes produced at high recovery values is mixed with the feed water that enters membrane plant. This RO performance increases the feed water flow that enters membrane system and it requires increase of number of membrane modules used in the first stage. The second, third and fourth stages use the RO membranes. Ammonia rejection efficiency as well as the efficiency of the entire process depends on the second stage recovery value as the second stage permeate is further treated in the third and the fourth stages.

To calculate a multi-stage membrane system we need to know the K values (ratio of the feed water flow to concentrate flow) in each stage, working pressure values, membrane types and required amount of membrane modules in each stage. The calculation is carried out based on specified flow values of the last stage permeate and first stage concentrate (Fig. 13b). Recovery value in the last (fourth) stage is accepted 0.9. The last stage concentrate is forwarded to front of the previous stage. The permeate flow of the third stage (penultimate stage) is calculated as the sum of permeate and concentrate flows in the last stage.

The reduced concentrate volume can be utilized beneficially by mixing with dewatered sludge or used as a raw material (such as ammonia salts) in the production of fertilizers. To avoid the sludge poisoning with toxic pollutants contained in the leachate, authors developed a novel approach to separate concentrate into different flows and utilize them separately.

In the case when the wastewater dewatered sludge is stored in the landfill, the formation of high concentration of ammonia in the sludge can be prevented. For this case authors have developed a new approach to separate the concentrate flow into two streams: the stream containing organics in high concentrations and the stream with a high content of ammonia salts and high TDS value [18,19]. The flow diagram of this concept is shown in Fig. 15. Concentrate from the first nanofiltration stage (Fig. 13b) that poorly rejects monovalent ions contains high concentration of organics and multivalent ions (calcium and magnesium ions, sulphates, iron and heavy metal ions).

The obtained data processed in such a way as to obtain the calculated equations of dependencies of membrane rejection on recoveries for different membrane types and water compositions (Fig. 4). Using the obtained equations (Fig. 4), ammonia concentrations in each stage and recoveries (or K values) can be determined. By setting a normative (regulation) value for ammonia (0.5 ppm) and setting maximum possible K value ($K = 10$), we can determine ammonia rejection value and calculate ammonia concentration in the feed water that enters the fourth membrane stage. This value corresponds to quality of the third stage permeate.

The concentration value of ammonia contained in feed water that enters 4th stage can be calculated from equation: $R = 100 \times (C_f - C_p)/C_f$, where R is membrane ammonia rejection, %; C_f – concentration of ammonia in feed water; C_p – concentration of ammonia in permeate.

Similarly, given the maximum value of K in the third stage ($K = 10$) and given the calculated value of ammonia
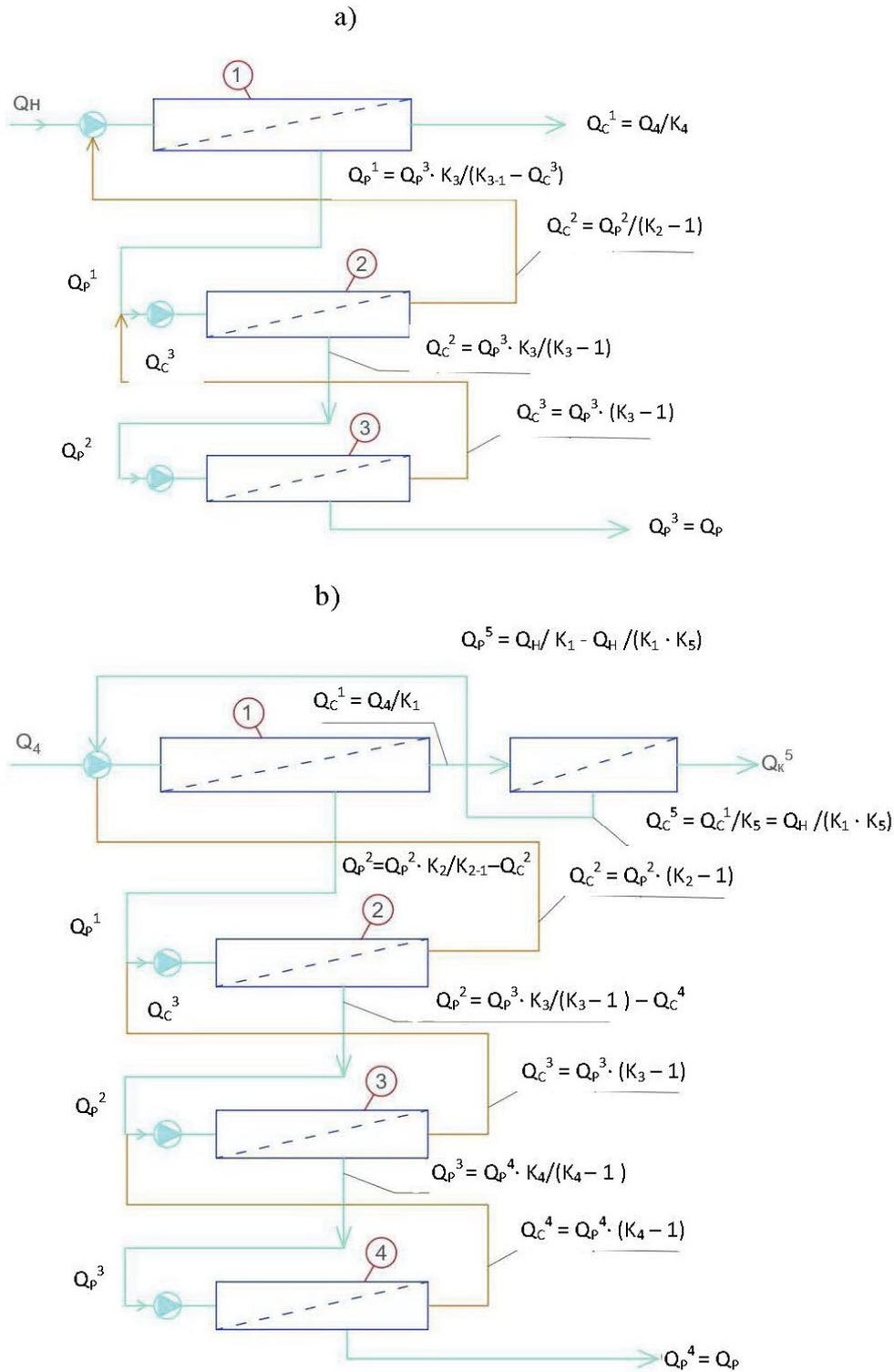
Fig. 13. Flow diagrams of landfill leachate treatment utilizing reverse osmosis membranes in the first stage (a) and nanofiltration membranes to reduce concentrate flow (b). 1 – first stage membrane; 2 – second stage membrane; 3 – third stage membrane; 4 – fourth stage.
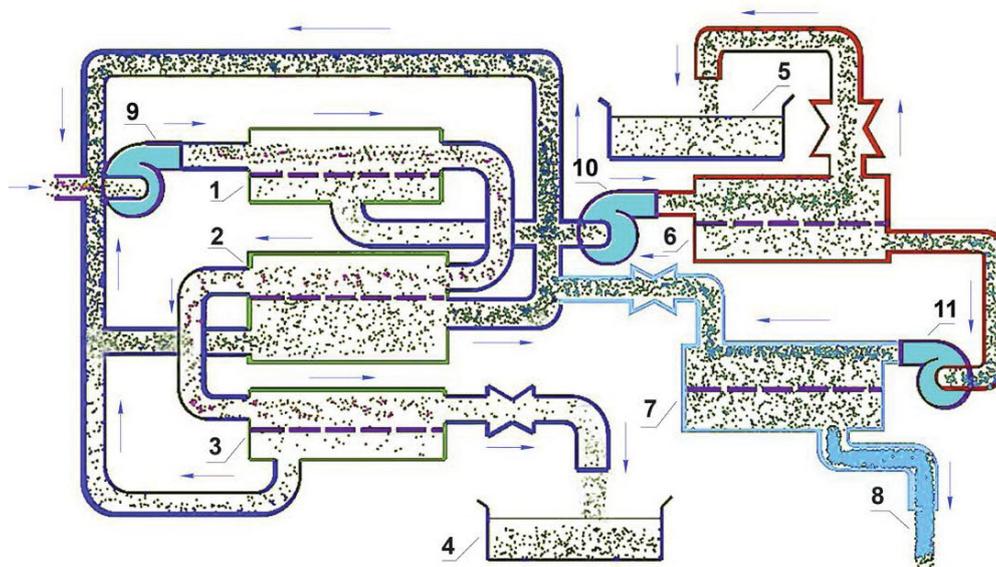
Fig. 14. Concepts to separate concentrate into different streams: different first and second stage concentrates: 1 – first stage membrane treatment; 2 – second stage membrane to reduce concentrate; 3 – third stage membrane to reduce concentrate; 4 – concentrated organics tank; 5 – ammonia salts concentrated solution tank; 6 – second stage membrane to reduce first stage permeate; 7 – third stage membrane to reduce membrane 6 permeate; 8 – product water tank; 9 – first stage pump; 10 – second stage pump; 11 – third stage pump.

concentration in the third stage permeate, we can determine ammonia concentration in the feed water that enters the third stage, which corresponds to the concentration in the second stage permeate (Fig. 13b).

Based on experimentally obtained results of landfill leachate membrane treatment a new technique was developed that consists from 4 stages of membrane treatment that provides reduction of feed water flow by 20 times. This result was achieved by rejection of organics from leachate in the first stage of membrane treatment using nanofiltration membranes. This also facilitates treatment of the nanofiltration first stage permeate in the second stage using RO BLN membranes. As TDS value of feed water (landfill leachate) has relatively high value of 3,600 ppm (Table 1), it was not a simple task to reach high recovery value in the second stage with BLN membranes. Therefore, the coefficient K value in the second stage was selected 3 (Fig. 11). With the increase of K the membrane flux decreases. The reduction of concentrate flow and increase of recovery as a result was achieved by applying the cascade concept in membranes arrangement (Fig. 1b). The balanced schematic of landfill leachate treatment is presented in Fig. 15.

As a result, treatment of leachate with COD value of 1,700 ppm, TDS value of 3,600 ppm, ammonia concentration of 425 ppm produced product water (4-th stage permeate) with ammonia concentration value of 0.5 ppm and TDS value of 4.5 ppm. The total amount of concentrate flow was 0.25 m³/h, which is only 5% of the feed water flow. Concentrate is divided into two separate streams: the first stage concentrate with 0.1 m³/h flow having COD value of 85,000 and 90,000 ppm TDS. Compositions of permeates from the second, third and fourth stages presented in Fig. 15. Fig. 16 shows results of operational cost calculations

to compare "Kaiser scheme" and new proposed technique. To evaluate operational costs, calculations were made to determine: energy costs assuming working pressure, permeate and concentrate flows; membrane replacement costs; chemicals cost that includes antiscalants, membrane chemical cleaning, pretreatment chemicals. Calculations were made for membrane facility that produces 5 m³/h of permeate. Application of nanofiltration low pressure and low rejection membranes in the first stage enable us to reduce membrane area and membrane costs accordingly. The total membrane area and number of membrane modules of the developed scheme is lower than in the "Kaiser scheme". Also, the use of nanofiltration membranes eliminated needs in antiscalants in the first and second stages of membrane system. Also efficient removal of organics in on the first membrane stage enables to reduce consumption of cleaning agents.

It is obvious that the use of nanofiltration membranes in landfill leachate treatment techniques substantially simplifies water treatment process and reduces operational costs [22,23,25,30,31]. It is also obvious that the proposed new approach to increase recovery by the use of additional cycles of concentrate dilution and concentration does not substantially increase total operational costs as nanofiltration membrane flux increases after the dilution cycle. Fig. 17 demonstrates a simplified flow diagram of membrane facility used to reduce concentrate flow that provides separation of concentrate into concentrated organic and mineral salt solutions and to produce additional amount of mineralized water. The flow values are specified in parentheses expressed in cubic meters per hour. Application of these additional measures can enable us to reduce concentrate flows by 2–3 times, obtained according to balance the diagram shown in Fig. 16.

Feed water (landfill leachate)
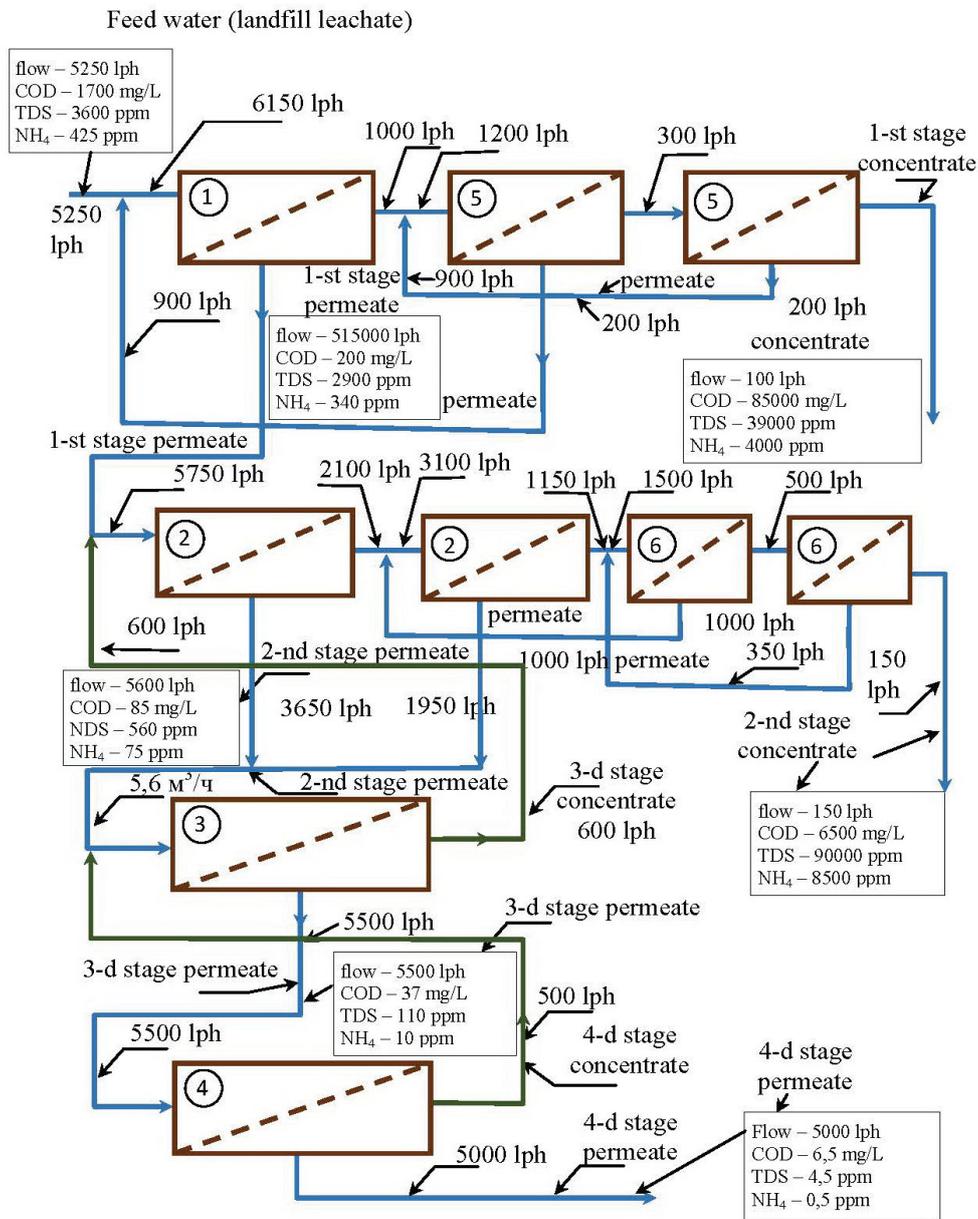
Fig. 15. A balanced flow diagram of landfill leachate treatment by reverse osmosis system producing 5,000 L of permeate per hour and and concentrate flow reduced to 250 L/h: 1 – first stage nanofiltration membrane; 2 – second stage reverse osmosis membrane; 3 – third stage reverse osmosis membrane; 4 – fourth stage reverse osmosis membrane; 5 – first stage nanofiltration membrane for the first stage concentrate flow reduction; 6 – second stage nanofiltration membrane for the second stage concentrate flow reduction
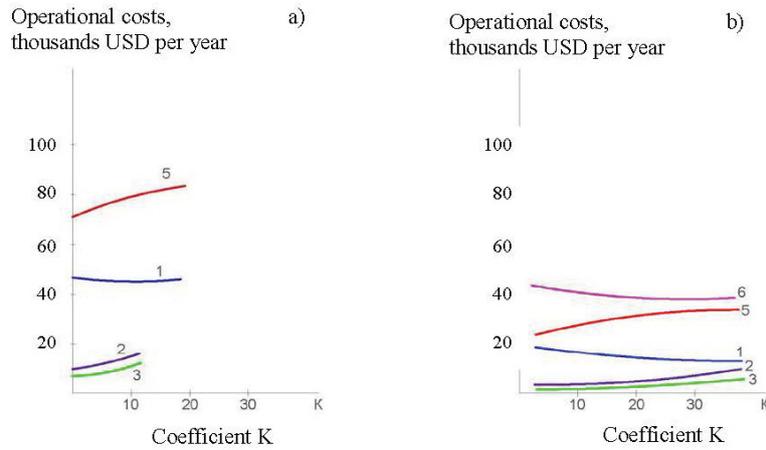
Fig. 16. Dependencies of operational costs on *K* values reached throughout leachate treatment (for the facility with 5,000 m³/d to treat "Aleksandrov" landfill using different techniques): (a) "Kaiser" technique using seawater membranes in the first stage and (b) new developed approach using low rejection nanofiltration membranes in the first stage: 1 – electricity; 2 – membrane costs; 3 – membrane cleaning; 5 – total operational costs; 6 – total operational costs with an account to utilize organic concentrate with dewatered wastewater sludge.
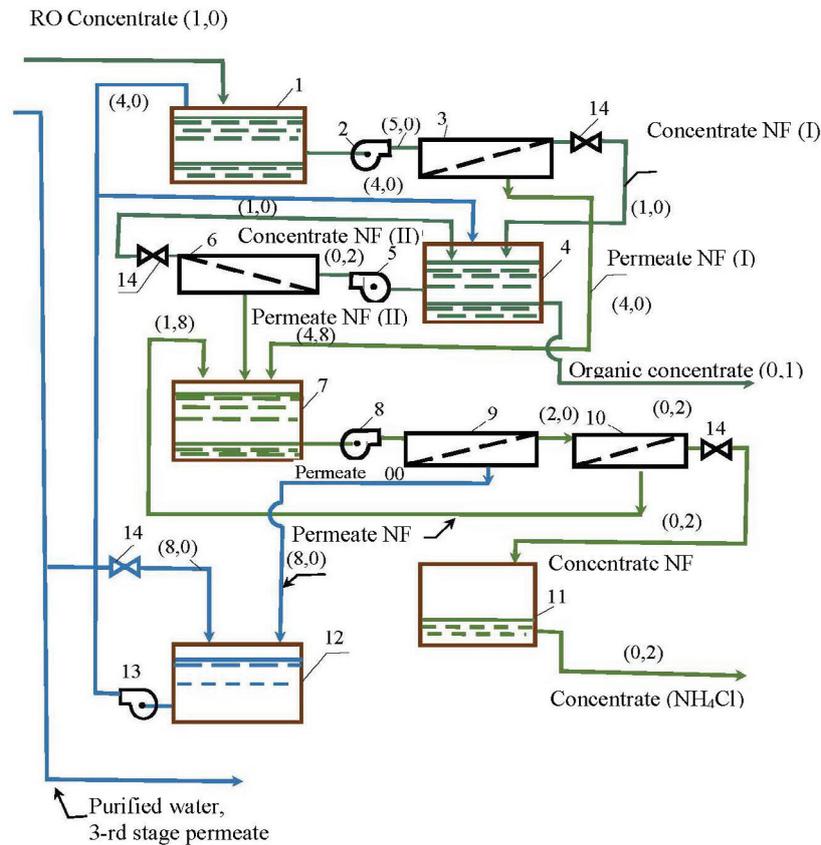
Fig. 17. Reverse osmosis concentrate separation balance schematic using nanofiltration and reverse osmosis membranes: 1 – concentrate accumulation tank used to dilute concentrate for the first cycle; 2 – working pressure pump for the first stage; 3 – first cycle membrane module with nanofiltration membranes; 4 – first stage concentrate accumulation tank used to dilute concentrate for the second cycle; 5 – working pressure pump for the second concentration cycle; 6 – second cycle nanofiltration module; 7 – tank for permeate accumulation after membrane modules 3 and 6; 8 – working pressure pump for permeate concentration; 9 – reverse osmosis module to reduce nanofiltration permeate flow; 10 – nanofiltration module to reduce RO concentrate flow; 11 – permeate collection tank; 13 – pumping station to deliver deionized water for dilution; 14 – regulation valve.

5. Conclusions

- To purify landfill leachate with high TOC and TDS values it is reasonable to use nanofiltration membranes in the first stage of membrane facility. Application of nanofiltration membranes enables us to reduce concentrate flow and decrease operational costs. High recovery values are reached through the additional treatment of concentrate with nanofiltration membranes.

- Influence of dissolved organics defined as COD on membrane performance studied. Leachate COD decreases membrane flux and should be accounted when membrane area is calculated.

- Application of reverse osmosis and nanofiltration membranes combined with chemical leachate pretreatment enables to produce quality water that meets discharge regulation standards and concentrate flow not to exceed 0.3%–0.5% of the total feed water that enters water treatment system.

- To facilitate concentrate utilization, a new technique was developed to split concentrate into two flows: the flow with high organic content and the flow with high TDS containing ammonia and sodium chlorides.

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