PURIFICATION OF WASTE WATER IN PETROLEUM
REFINING INDUSTRIES BY MEMBRANE METHODS

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Some very important problems of environmental protection in industries are to change over to a closed water circulating cycle, to discontinue the diversion of fresh river and lake waters, and to achieve a level of waste water purification which facilitates use of the treated water as process water. The problem of creating water circulation systems is especially acute in regions in which the water sources are unique natural phenomena. However, a solution of this problem is held up by the absence of technically applicable methods of eliminating mineral salts from the waste water.

The hydroeconomic system of the IA "Kirishinefteorgsintez" is connected through the river Volkhov with a system of major European lakes, the Ladozhsk and Onezhsk. This makes it necessary to develop engineering processes to ensure that water consumption by the industry is cut down, effluent discharge reduced, and quality of effluents improved. The method of reverse osmosis was adopted for desalination of the effluents. Rated as the most promising, this method is being increasingly applied the world over [1]. The investigations were carried out on salt-containing effluents of the drainage system II collected in ponds-reservoirs and discharged once a year (during the spring floods) through the Chernaya river into the Volkhov after mechanical, physico-chemical, and two-stage biological purification. In spite of the sufficiently high degree of purification, these effluents are unsuitable as make-up for the water circulation system of the enterprise.

The biologically purified water is contaminated to a definite extent with suspended particles and colloids which, in the process of reverse osmosis, will clog the pores in the membranes. The presence of residues of the biological material in the effluents (microorganisms, bacteria, and products of their activity) also adversely affects the membranes and reduces their service life. Apart from this, on concentration, calcium salts (particularly calcium sulfate) present in the effluents rapidly precipitate and settle on the membrane surfaces. This unavoidably leads to a reduction in selectivity and productivity of the membranes [2].

Information on water pretreatment methods is available in the relevant literature. More often than not, an acid and sodium hexametaphosphate are added to the initial solution for correcting the pH and preventing calcium salts from settling on the membranes [3-5]. Best results in eliminating finely-dispersed suspensions, residues of biological material, and emulsified petroleum products are obtained in case of using the micro- or ultrafiltration methods [6-8]. The cost of water pretreatment by these methods by taking into account the small working pressure in these processes (0.1-0.3 MPa) differs insignificantly from that for pretreatment by other methods. Several water pretreatment stages are incorporated in the water desalination process to eliminate the effect of the above adverse factors. These include filtration using a filter with a granular charge (quartz sand) to entrap the coarse suspensions and dosing the effluent with sulfuric acid and hexametaphosphate with subsequent ultrafiltration.

Biologically purified waste waters of the drainage system II were subjected to ultrafiltration in a batch-operated laboratory installation equipped with a mixer and flat membranes (of 0.009 m² area). Operating conditions of the process were as follows: 0.1-0.3 MPa pressure; 20-25°C temperature; 60-80 rpm of mixer; 0.11 m/sec average linear feed rate of the flow. The following parameters were determined during the experiment: specific output of the membranes; dependence of the specific output on pressure and time; efficiency of removal

TABLE 1

Membrane	CAO, mg O_2/liter	Content, mg/liter	
		suspended matter c_{sm}	petroleum products c_p

With ultrafiltration of waste water from secondary settling tanks of the II stage of BPP[*] (CAO = 172 mg O_2/liter, c_{sm} = 210 mg/liter, c_p = 1.6 mg/liter)

UAM-300	268/120	494/tank	2,4/0,6
UAM-150	—/104	—/tank	7,6/0,8
UAM-100	—/76	—/tank	5,6/0,8
UPM-P[2*]	376/112	1546/tank	3,0/1,0

from ponds-reservoirs of II drainage system[*] (CAO = 66 mg O_2/liter, c_{sm} = 0, c_p = 0.1 mg/liter)

UPM-P[3*]	256/68	520/tank	—/—

the same[*] (CAO = 120 mg O_2/liter, c_{sm} = 0, c_p = 0.8 mg/liter)

UPM-P[4*]	232/96	—/tank	—/—

*Numerator pertains to the concentrate, denominator, to the permeate, and dashes indicate undetermined.
[2*]Steady-state filtration rates ω for pressures p = 0.1, 0.2, and 0.3 MPa are 30.2, 35.1, and 41.7 liter/(m²·h), respectively.
[3*]For p = 0.1 MPa, ω = 30.3 liter/(m²·h).
[4*]For p = 0.1 MPa, ω = 31.7 liter/(m²·h), for p = 0.2 MPa, ω = 47.6 liter/(m²·h).

of the suspended matter; selectivity for petroleum products and organic substances the content of which was indirectly determined on the basis of the CAO (chemical absorption of oxygen).

The experiments were carried out on waste water specimens from secondary settling tanks of stage II of the BPP (biological purifying plant) and from ponds-reservoirs of the drainage system II. Cellulose acetate membranes UAM-100, UAM-150, and UAM-300, as well as polyamide membranes UPM-P on a substrate, were used. The results were analyzed by the known methods [9] and are given in Table 1 and Fig. 1. They show that ultrafiltration using the investigated membranes makes it possible to completely remove the suspended matter and reduce the content of organic substances by 30-60% and petroleum products by 75-90%.

There is a decrease in the output of the membranes with time (see Fig. 1) probably as a result of clogging of the pores by residues of the biological material and products of bacterial metabolism. Evidently, a compact bed of the precipitates which does not break up under the mixer's action is gradually formed on the membrane surface. The working rate of filtration is established after 1.5-2 h. This rate reduces gradually with time.

The aggregate state of the impurities contained in the concentrate varies during the experiments. This can be judged from the turbidity of the solution and precipitation on the membrane surface. It is probable that, as a result of concentration, the dissolved substances coagulate over the membrane. The stabilized specific output of the membrane UPM-P reaches 65-75 liter/(m²·h) at 0.2 MPa pressure (see Fig. 1). It is assumed that, as compared to cellulose acetate membranes, the polyamide membrane UPM-P possesses increased resistance to biocontamination and higher mechanical strength due to the presence of the substrate [10]. This membrane is capable of efficient functioning with the medium pH varying over a wider range (1-13) than type UAM cellulose acetate membranes (pH 5-8).

Since the concentrate characteristics are almost the same as those of the effluents to be biologically purified, its return into the BPP system does not significantly affect the working mode of the BPP. The permeate obtained in the ultrafiltration process was demineralized in a continuous action reverse osmosis laboratory installation. Three cells of the reverse osmosis apparatus of cylindrical form operated in a parallel arrangement. The working surface diameter of the membrane was 0.052 m and height of the near-membrane channel, 0.001 m. The investigations were conducted with a maximum volumetric initial flow rate of 40 liter/h which was ensured by the dosing pump ND-40. The average linear flow rate in the near-membrane channel was 0.14 m/sec. The working pressure was varied from 3 to 6 MPa and
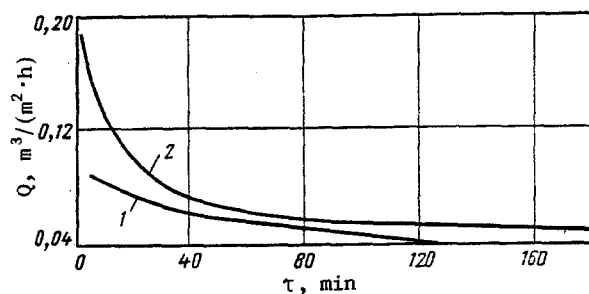
Fig. 1. Dependence of the specific output Q of ultrafil-
tration of the membrane UPM-P on time τ of operation of
the installation of 0.2 MPa pressure: 1) waste water from
secondary settling tanks of stage II of the BPP, 2) waste
water from ponds-reservoirs of the drainage system II.

the process temperature, from 20 to 25°C. Analytical samples were withdrawn at a working
pressure of 4 MPa. The concentrate in the starting solution tank was circulated continuous-
ly.

Membranes used for the reverse osmosis process were grades MGA-70, MGA-80, MGA-95, and
MGA-100 cellulose acetate membranes "Vladipor" and two specimens of the composite polysulfon-
oamide membrane OPM-K with an ultrafine layer on a substrate. These were produced at differ-
ent temperatures and pouring rates. All membrane specimens were manufactured in the SIA
"Polimersintez" (city – Vladimir).

The aim of the experiments was to determine the specific output of the membranes and
its dependences on the working pressure, retentivity of the membranes in relation to the dis-
solved salts (total content of salts was determined from the calcined residue), selectivity
of the membranes for chlorides, sulfates, and nitrates as well as their capacity for blocking
the dissolved organic matter (the quantity of these substances was indirectly determined from
the CAO). The waste water specimens were subjected to reverse osmosis after preliminary ul-
trafiltration. Suspended substances were totally absent in these specimens.

Results of the effluents demineralization are given in Table 2 and Fig. 2. All analy-
ses were made by the methods in [9]. The dependence of the specific output of the membranes
on the working pressure was plotted by using the method of least squares. Analysis of the
experimental data shows that the cellulose acetate membranes MGA-100 are most selective in
relation to the eliminated salts. Their retentivity reaches 98-99%. As was to be expected,
these membranes are rated in the following order of decreasing selectivity in relation to the
total content of salts: MGA-100 > MGA-95 > MGA-80 > MGA-70. This was also true for selectiv-
ity in relation to chlorides. Retention of all types of sulfates by these membranes is al-
most identical, i.e., 97-99%. The degree of retention of nitrate-ions is quite low at 23.1%
for MGA-70 and 46.1% for MGA-80 membranes. Membranes of all the grades exhibited the capac-
ity to retain dissolved organic impurities to a determined extent. This is confirmed by the
significant reduction (70-80%) in the CAO in the permeate.

The dependence of the specific output of cellulose acetate membranes on the working
pressure (see Fig. 2) is linear and can be used for selecting optimum conditions of the pro-
cess. In comparing the selectivity and specific output of MGA type membranes in processing
effluents from ponds-reservoirs, it should be noted that in going over from the MGA-100 to
MGA-70 membrane, there is a 10% decrease in selectivity and more than 3 times increase in
output. The MGA-70 membrane can be recommended for industrial application for demineraliza-
tion of large quantities of waste water since it possesses the maximum output (0.8 m³/m²·h at
4 MPa pressure) among all cellulose acetate membranes.

The polysulfonoamide membrane which has a high selectivity (92%) in relation to salts
can be a comparable membrane. It has adequate retentivity with respect to organic substances
(the CAO is reduced by 85%), sulfates and nitrates (selectivity of 99 and 64%, respectively)
and, in addition, is characterized by a high specific output (0.9 m³/m²·day at 4 MPa pres-
sure).

We know that polysulfonoamide membranes are effective over a wide range of variation in
pH (1-13) [10] and are characterized by increased mechanical strength since they are made on
a substrate. These advantages, in combination with the good separating characteristics and
significant specific output, make it possible to use these membranes for demineralization of
effluents on the condition that the technique for their industrial production is properly
mastered.

TABLE 2

Membrane	CAO, mg O_2/liter	Calcined residue, mg/liter	Content, mg/liter			Selectivity of membrane, %, relative to				
			chloride-ions	sulfate-ions	nitrogenous nitrate	total salt content	CAO	chloride ions	sulfate ions	nitrate ions
For reverse osmosis desalination of waste water from secondary settling tanks of BPP stage II (pH of 7.7, petroleum product content c_p = 1 mg/liter, calcium-ion content c_{Ca} = 100 mg/liter, iron-ion content c_{Fe} = 0)										
MGA-70	392/268	780/190	57,7/39,6	387,8/68,5	—	75,6	31,6	31,4	82,3	—
MGA-80	268/102	890/64	61,0/36,3	448,0/2,0	—	92,8	61,9	40,5	99,6	—
MGA-95	288/80	940/20	—/—	—/—	—	91,9	72,2	—	—	—
MGA-100	264/56	936/9	90,0/16,5	476,0/2,0	—	99,0	78,8	81,7	99,6	—
from ponds-tanks of drainage system II (pH of 5.3, c_p = 0, c_{Ca} = 48 mg/liter, c_{Fe} = 0)										
MGA-70	84/16	500/58	122,0/51,0	254,6/5,6	—	88,4	80,9	58,2	97,8	—
MGA-80	84/16	627/24	141,8/21,4	261,0/1,0	—	96,2	80,9	84,9	99,6	—
MGA-95	96/14	624/8	148,4/19,8	293,8/1,6	—	98,7	85,4	86,7	99,5	—
MGA-100	124/18	920/18	153,0/9,0	337,0/2,0	—	98,0	85,5	94,1	99,4	—
the same (after twofold ultrafiltration, pH of 8.3, c_p = 0, c_{Ca} = 0, c_{Fe} = 0)										
MGA-70	70/20	600/95	135,3/52,6	235/2	—/—	84,2	71,4	61,1	99,1	—
MGA-80	100/12	660/36	147,3/39,0	269/2	10,4/5,6	94,5	88,0	73,5	99,3	46,1
OPM-K № 1	202/36	1050/200	195,0/72	382/1	11,4/4,1	81,0	82,2	63,1	99,7	64,0
the same (pH of 7.5, c_p = 0, c_{Ca} = 40.7 mg/liter, c_{Fe} = 0)										
MGA 70	64/20	627/115	122,2/56,1	229/20,6	5,2/4,0	81,9	68,4	50,0	91,0	23,1
OPM-K № 2	134/20	830/70	133,6/41,2	331/3,4	4,0/1,4	91,6	85,1	69,2	99,0	64,0

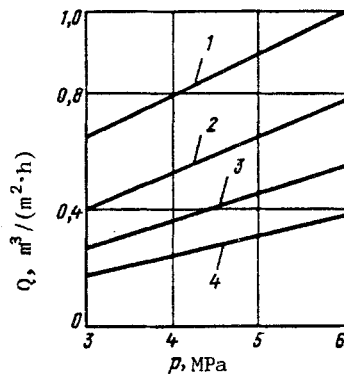Note: Numerator stands for initial solution, denominator for permeate, and dash for not determined.

Fig. 2. Dependence of the specific output Q of cellulose acetate reverse osmosis membranes on working pressure p: 1) MGA-70; 2) MGA-80; 3) MGA-95; 4) MGA-100.

The quality of the purified effluents excels that of waters from the river Volkhov with respect to many parameters (pH of 6.5-8.1, calcined residue of 94.1 mg/liter; suspended substances content of 14.5 mg/liter, petroleum products content of 0.24 mg/liter, nitrogeneous nitrate content of 3 mg/liter, chloride-ions content of 16.7 mg/liter, sulfate-ions content of 16.8 mg/liter, and CAO of 45.9 mg O_2/liter). This gives us the basis to assume the possibility of using these purified effluents, not only as make-up feed of circulating water supply systems, but also as feed water for low-pressure boilers or even for high-pressure boilers after pretreatment. It is suggested that the permeate be drawn off based on actual requirements of the enterprise (50% of the starting quantity of water). The concentrate containing 1500-2000 mg/liter of mineral salts and less than 1 mg/liter of petroleum products should, if necessary, be subjected to repurification by the sorption method and then mixed with the purified domestic-public drainage in order to reduce the concentration of inorganic salts before discharging into the reservoirs.

Thus, investigation of the process of demineralization of salt-containing waste waters of petroleum refining industries pointed to the possibility of producing purified water qualitatively superior to river water. The developed process of effluent desalination, which includes a series of water pretreatment stages including the method of ultrafiltration, makes it possible to utilize the purified water as make-up feed for circulating water supply systems and thereby do away with the need to divert the river waters.

LITERATURE CITED

1. M. V. Kolodin, Khim. Tekh. Vody, 8, No. 6, 35-43 (1986).
2. F. N. Karelin, in: Thesis Reports of IV All-Union Conference on Membrane Methods of Separation, Moscow, May 27-29, 1987 [in Russian], Vol. 4, NIITÉI, Moscow (1987), pp. 1-9.
3. C. D. Moody, J. W. Kaarinen, J. C. Lozier, et al., Desalination, 47, 239-253 (1983).
4. M. Wilf and J. Ricklis, ibid, 47, 209-219 (1983).
5. Motohiro Okazaki and Shoji Kimura, J. Chem. Eng. Jpn., 17, No. 2, 216-218 (1984).
6. N. P. Gnusin, V. I. Zabolotskii, and V. I. Gordeev, Khim. Tekh. Vody, 8, No. 3, 40-43 (1986).
7. "Uf system to pretreat reverse osmosis applications," Ind. Water Eng., 20, No. 6, 19 (1983).
8. S. D. Strauss, Power, 127, No. 2, 19-21 (1983).
9. Methodical Instructions on Analysis of Waste Water of Petroleum Refining Industries [in Russian], Minneftetekhimprom SSSR, Moscow (1977).
10. Yu. I. Dytnerskii, Theory and Calculations of Pressure Membrane Processes [in Russian], Khimiya, Moscow (1986).