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WASTE WATER TREATMENT OF PETROCHEMICAL PRODUCTION PLANT BY THE METHODS OF ELECTRODIALYSIS AND REVERSE OSMOSIS

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ABSTRACT

Interpolymer and heterogeneous membranes have been synthesized and pilot tests of the designed electrodialysis and reverse osmosis units for the treatment of waste waters of Pavlodar Petrochemical Plant LLP have been carried out. A hybrid process flowsheet for industrial waste water treatment has been developed and a comparative efficiency analysis of the electrodialysis and reverse osmosis processes by the depth of treatment and demineralization has been performed.

Key words: Membranes, Electrochemical properties, Electrodialysis, Reverse osmosis, Capacity, Pre-treatment block, Ozonizer, Hybrid circuit, Waste water, Mineralization, Treatment.

INTRODUCTION

Membrane methods are modern tools for the implementation of a number of priority directions for the development of science, technologies and technique. Their practical importance is connected primarily with the solution of global problems facing the mankind in the XXI century. These are the creation of high technologies, provision of human habitation safety, production of ecologically clean food products, high quality drinking water, as well as the formation of a proper balance between the solution of social and economic problems and environment conservation.

An intensive development of new technologies and creation of new materials, on the

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one hand, completely transforms all human scope of activity – the state of science, industry, agriculture, household, medicine, healthcare and others, on the other hand, it results in equally intensive accumulation of wastes. The world statistics testifies that only 7-12% of the initial raw materials transforms into the final product, and about 90% transforms into wastes at different stages of production and consumption, which may be, however, valuable raw materials themselves, and their processing may be several-fold more cost efficient than that of the initial raw material. Certainly, this is on condition of implementation of environmentally-friendly technologies and obtaining, herewith, of high quality, competitive products. In this connection, one may even today make an assumption that the XXI century shall be directed, to a significant extent, to the creation of environmentally safe and, most importantly, economically cost effective and technologically-based processes of processing materials and wastes, and obtaining on their basis useful products, needed for the community. That is why membrane and combined processes of processing of substances and materials should be related to one of the most advanced technologies. Modern membrane processes are characterized by high selectivity, low power consumption, simplicity of instrumentation, they are the basis for the creation of waste-free technologies, they are able to "bridge the abyss" between industry and environment purity. They just cannot have any negative consequences, since they are reagentless[1].

Demineralization of mineralized waters with the help of electrodialysis with minimum power consumption is more economically efficient in comparison with the known methods (distillation, freezing, etc.), even with significant salt concentrations. The development of rational and cost efficient designs of high capacity multi-chamber electrodialyzers, both in Kazakhstan and abroad, has created the necessary prerequisites for the wide use of this demineralization method[2].

Electrodialysis has a number of advantages, making it promising for demineralization of diluted solutions, such as a possibility of pure water recycling and extraction of components, low consumption of reagents, reduction of power consumption with a decrease of salt content of the initial solution, etc. Electrodialysis with the use of ion-exchange membranes was initially developed as a method for desalination of brackish sources and sea water[3].

Among the membrane processes, being intensively developed in the recent years, baromembrane processes, reverse osmosis, ultra-, micro- and nanofiltration, play a special part[4]. This is connected with their universality and wide scope of application. They are characterized by such peculiar features as low power consumption, simplicity of instrumentation, possibility to operate at the ambient temperature[5].

Baromembrane processes are used in many branches of industry for demineralization of salt waters and treatment of waste waters, separation of azerotropic water mixtures, concentration of water solutions (reverse osmosis), purification of waste waters from heavy metals and high molecular organic compounds, concentration of water suspensions, latexes, isolation and purification of biologically active compounds, vaccines, viruses, blood purification (nanofiltration), concentration of milk, fruit and vegetable juices, (ultrafiltration), purification of process solutions and waters from finely dispersed substances, separation of emulsions, preliminary treatment and softening of sea and brackish waters before desalination (microfiltration), etc.[6]

EXPERIMENTAL

Synthesis of interpolymer membranes was carried out in a three-necked reactor with a polymer binder-polyvinylchlodide (PVC) in a general solvent. PVC, diglycidyl ether of resorcin (DGER) or hydroquinone (DGEH) and polyamine (polyethyleneimin (PEI), polyethylenepolyamine (PEPA), preliminary diluted in dimethylformaldehyde (DMFA), were placed into the reactor. The reaction temperature was maintained at 70^{o}C during 3 hr mixing. The reaction mixture was then poured on a smooth surface and dried under UF-light[7].

Synthesis of heterogeneous membranes was carried out by mixing of finely ground anionite, based on DGER or DGEH, and polyamines (the grain size of 0.25-0.50 mm) with a high density solution of polyethylene (PEVP) in benzene at 60^{0}C until mass homogenization. The dried mass was then rolled at 110^{o}C during 5-10 min and pressed at 120^{o}C during 7-10 min. To avoid swelling of the membranes upon the release of hot presses, they were cooled under pressure[8].

RESULTS AND DISCUSSION

A study of electrochemical properties of the obtained heterocyclic and interpolymer membranes has been carried out on laboratory electrodialysis cells. An analysis of the main physical and mechanical indices (Table 1), testifies to stability of the membranes in the solutions of mineral acids, alkalis, boiling water (the boiling temperature of 100^{o}C). The differences in their stability are stipulated by density variations of the macromolecular network.

An electrodialysis unit[9,10], comprising an electrodialysis device, DC electric power source, pumps, capacities for the purified water and concentrate and shut-off valves (Fig. 1), and a reverse osmosis unit (Fig. 2), representing a construction on whose frame membrane devices, control box, high pressure pump are placed[11,12], have been created. The device body has nipples for the initial water inlet and purified water (filtrate) and concentrate outlet.

Table 1: Electrochemical properties of the membranes, synthesized on the basis of DGER, DGEH with PEI and PEPA (A) COE_{HCl}, mg-equ/g; (B) specific electrical resistance, Ohm·cm; (C) transfer numbers, %; (D) specific water permeability, $cm^3 \cdot s/g \cdot 10^{-14}$)

Membrane basis	A	B	C	D	SEC_{const}/stability (%)				
					5 n H_2SO_4	5 n NaOH	1 n HNO_3	10 % H_2O_2	H_2O_2, 100^{o}C 48 hr
Interpolymer membranes									
DGER-PEI	7.2	45.0	98	1.2	7.1/98.6	7.2/100	6.8/94.4	6.5/90.3	7.0/97.2
DGEH-PEI	5.4	53.4	98	1.7	5.2/96.3	5.3/98.2	5.1/94.4	4.9/90.7	5.1/94.4
DGER-PEPA	5.6	49.2	97	1.8	5.5/98.2	5.6/100	5.4/96.4	4.9/87.5	5.5/98.2
DGEH-PEPA	4.2	56.2	97	1.9	4.1/97.6	4.2/100	4.1/7.6	3.9/92.9	4.0/95.2
MA-41*	2.0	240	94	6.2	2.0	2.0	1.7	1.4	1.8
Heterogeneous membranes									
DGER-PEI	5.2	210	95	6.2	5.1	5.0	4.9	4,9	4.9
DGEH-PEI	3.5	230	95	6.4	3.5	3.4	3.2	3,1	3.3
DGEH - PEI	4.2	220	96	5.8	4.1	4.1	4.0	3,9	3.9
DGEH-PEPA	2.9	240	95	6.3	2.9	2.8	2.7	2,6	2.7
MA-40*	3.8	340	96	6.4	3.6	3.6	3.0	3,0	3.4

Note: SEC – static exchange capacity, mg-equ/g; MA-40 and MA-41 – industrial marks of anion-exchange membranes

Fig. 1: A constructed electrodialysis unit

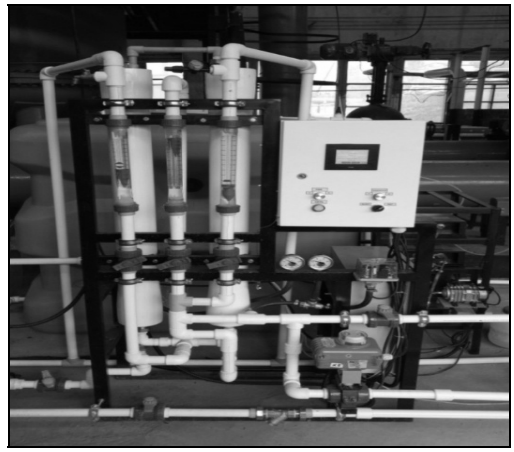


Fig. 2: A constructed reverse osmosis unit

In the period from August 12 through 28, 2015 in the territory of workshop No. 8 of Pavlodar Petrochemical Plant LLP (PPP LLP), we have performed pilot tests (PT) of the constructed demineralization units. A complete chemical analysis of the waste water after biological purification and the norms for the purified water, required by the plant, are presented in Table 2.

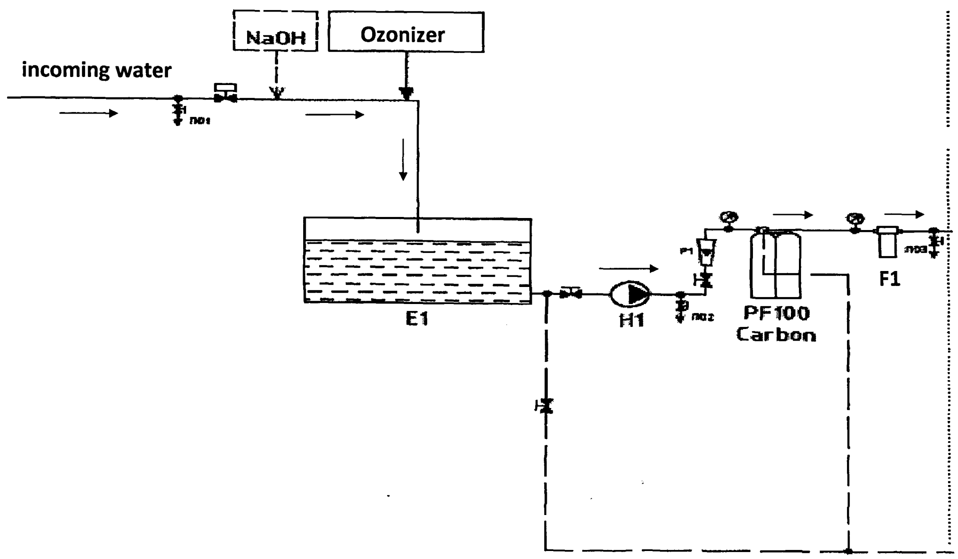
Table 2: The analysis data of waste water of PPP LLP, provided by the plant laboratory, and the requirements to the purified water

Parameters	Initial waste water	Requirements of PPP LPP to the purified water
Oil products (mg/L)	5.5	1.0
Suspended substances (mg/L)	30.5	No more than 25
Chlorides (mg/L)	−	No more than 10
Total hardness (mmol/L)	2.1	No more than 2.0
Total base number (mg-equ/L)	2.5	From 0,6 to 6
Sulfates (mg/L)	−	No more than 150
Ammonia nitrogen (mg/L)	88.5	No more than 50

Cont…

Parameters	Initial waste water	Requirements of PPP LPP to the purified water
Phenols (mg/L)	0.1	No more than 1.0
Density of microorganisms (CFU/mL)	10^3	Less than 10^3
pH	6.2	Less than 8.5
Salt content (mg/L)	750-1600	No more than 350

In dependence of the provided complete chemical analysis of the waste water, the most effective and economically feasible pre-treatment method has been chosen, which includes a cup-and-cone filter with activated coking coal, ozonizer for the oxidation of phenol and oil products, as well as an alkali injection unit for pH adjustment (Fig. 3).



NaOH – Alkali injection for pH adjustment; an ozonizer – injection of generated ozone; E1 – A capacity of 1 м^3; H1 – An injection pump; P1 – A rotameter; PF100 Carbon – A cup-and-cone filter; Ф1 – A cartridge filter BB20

Fig. 3: A preliminary treatment unit

It has been established (Table 3), that the preliminary treatment unit is able to decrease the content of oil products by 84.6%, from 1.56 down to 0.24 mg/L (the sampling of August 12, 2015), and on August 13 and 14, 2015 it has provided a decrease down to 0.64

and 0.22 mg/L. The content of phenol after the pre-treatment on August 13 and 14, 2015 has made up 0.0074 and 0.0164 mg/L, respectively.

Table 3: The data on oxidation and filtration of oil products and phenols in the preliminary treatment unit

Indicators (mg/L)	Initial water	Water after oxidation			Water after the coal filter		
	Sampling date (August 2015)						
	12.08	12.08	13.08	14.08	12.08	13.08	14.08
Oil products (totally)	1.56	1.35	1.13	1.61	0.24	0.64	0.22
Phenolic index (volatile phenols)	0.0466	–	0.209	0.0226	–	0.0074	0.0164

Fig. 4 presents a general view of the developed hybrid process flowsheet, including a pre-treatment unit.

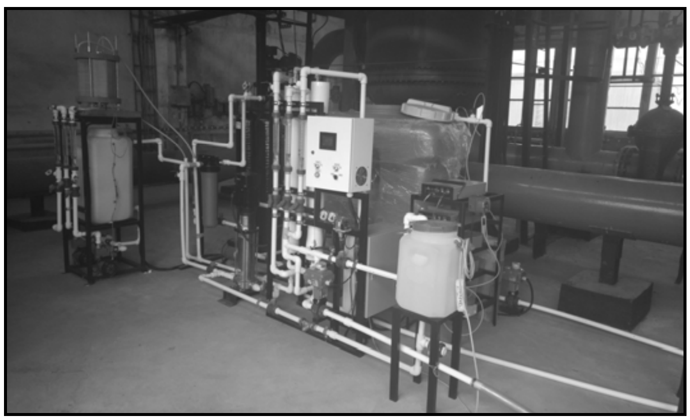


Fig. 4: A hybrid water purification process flowsheet in the territory of PPP LLP

In the course of the pilot tests, a comparative efficiency analysis of the electrodialysis and reverse osmosis units by the depth of purification and demineralization has been carried out (Table 4).

It is seen that both; the electrodialysis and reverse osmosis membranes deeply purify the initial waste water with the high content of salts from high concentrations of ammonia nitrogen and demineralize it to a sufficiently high extent, as well as reduce the content of suspended substances.

Table 4: A comparative efficiency analysis by the depth of purification and mineralization based on the main parameters

Parameters	Reverse osmosis (%)			Electrodialysis (%)	
	25.08.15	27.08.15	28.08.15	25.08.15	27.08.15
Suspended substances	–	> 69.4	–	–	> 69.4
Mineralization	99.2	97.9	99.2	90.9	98.2
Ammonia nitrogen	> 99.8	96.1	96.6	> 99.8	59.0

CONCLUSION

The results of the performed tests of the electrodialysis and reverse osmosis units have shown a high degree of demineralization. The actual indices of the initial water have been effectively adjusted on the electrodialysis and reverse osmosis units to the required norms, established for the purified water, directed to the recycling systems. The conducted studies have also shown that an optimum alternative for PPP LLP is a pre-treatment, using the technology of oxidation and sorption of organic substances, followed by demineralization on the reverse osmosis unit.

REFERENCES

1. Y. P. Ageyev, Cryt. Technol. Membr., **9**, 42-56 (2001).
2. V. D. Grebenyuk, J. D. I. Mendeleyev High Chem. Soc., **32(6)**, 648-652 (1987).
3. F. Xu, Ch. Innocent and G. Pourcelly, Separ. Purific. Technol., **43**, 17-24 (2005).
4. Q. Li, Elimelech Menachem, Environ. Sci. Technol., **38(17)**, 4683-4693 (2004).
5. K. Bechthold, S. Bretz, R. Kabasci and A. Kopitzky, Chem. Engg. Technol., **31(5)**, 647-654 (2008).
6. V. B. Korobov and S. I. Lazarev, Russ. J. Appl. Chem., **74(2)**, 226-230 (2001).
7. E. E. Ergozhin, T. K. Chalov and T. V. Kovrigina, Inter. Conf. PERMEA 2009», Praha, 29 (2009).
8. E. E. Ergozhin, T. K. Chalov, V. I. Zabolozkiy, T. V. Kovrigina and G. T. Alkenova, 5th Inter. Conference-School in Chemistry and Physical Chemistry of Oligomers, Volgograd (2015) p. 140.

9. E. E. Ergozhin, A. A. Tskhai, T. K. Chalov, T. V. Kovrigina and K. T. Serikbaeva, Intern. Meeting Electromembrane Processes and Materials, Cesky Krumlov, 223-227 (2012).

10. E. E. Ergozhin, T. K. Chalov, A. A. Tskhai, T. V. Kovrigina and G. T. Alkenova, J. Water: Chem. Ecol., **2**, 59-64 (2015).

11. G. T. Alkenova, T. V. Kovrigina, T. K. Chalov and E. E. Ergozhin, Remediation, **25(4)**, 111-126 (2015).

12. E. E. Ergozhin, A. A. Tskhai, T. K. Chalov, T. V. Kovrigina and G. T. Alkenova, J. Curr. Issues Human. Natural Sci., **73(2)**, 84-89 (2015).

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