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IMPROVING THE QUALITY OF RECYCLED WATER IN OIL-REFINERES BY SORPTION AND MEMBRANE METHODS

Abstract. In this article is devoted to the synthesis and study of ion exchangers and finding ways of their practical application. In this work, a pilot reverse osmosis unit was manufactured and its laboratory and pilot tests were performed on the territory of Pavlodar Oil Chemistry Refinery (POCR LLP). Its efficiency is shown at water purification from oil products, ammonium nitrogen, suspended solids and other organic and inorganic impurities.

Key words: anion exchanger, cation exchanger, static exchange capacity, technological scheme, pilot reverse osmosis unit, water samples, laboratory and pilot tests.

One of the main problems of industrial water consumption is to reduce water use and wastewater discharge. The most important condition for the functioning of a number of enterprises and industrial complexes is the presence of closed water use cycles, the so-called circulating water consumption systems. These measures are aimed at reducing the load on the citywide sewage treatment plants, minimizing the anthropogenic impact on the environment and, in general, increasing the sustainability of the ecological balance of natural ecosystems of urbanized territories. One of the most dangerous for the environment pollutants are petroleum products and their derivatives. As a rule, this complex of pollutants is an integral part of the flow of industrial facilities for the production of synthetic dyes, herbicides, wastewater from refineries, as well as carwash stations. One of the main problems of the low efficiency of wastewater treatment is the incorrect selection of local cleaning equipment and the treatment scheme in general. When designing or installing a complete wastewater treatment system, it is necessary to take into account not only the plant performance, but also changing qualitative and quantitative indicators of runoff contamination. In this regard, there is a need to develop and introduce into production new, more advanced, thermophysical processes for the treatment of natural and wastewaters [1].

For minimize the negative impact of pollutants on the environment, a variety of wastewater treatment methods are used. Most of them are expensive and complex in execution. Today, it is necessary to search and develop methods that allow the extraction of eco toxicants without additional anthropogenic pressure on the environment [2]. Various structures of settling structures are used to remove the bulk of suspended solids and oil products from surface runoff: thin-layer, horizontal and radial septic tanks, oil traps, filters for physical and chemical cleaning, which are influenced by the service life and corrosion processes [3, 4].

The oil refining and petrochemical industries are among the largest environmental polluters. The enterprises of this industry have a negative impact on the environmental situation in many regions, polluting atmospheric air, water bodies and soil [5]. In terms of wastewater discharges, these enterprises are the largest sources of pollution of water bodies. The share of enterprises of the fuel and energy, petrochemical and chemical complexes accounts for 50% of the total volume of wastewater discharges into surface water bodies. Over 89% of the total mass of pollutants entering the water bodies with wastewater is accounted for by the enterprises of the chemical and petrochemical industries. Efficient and high-quality wastewater treatment is a prerequisite for maintaining the purity of water bodies. However, it is not always possible to achieve the required quality of cleaning at existing treatment facilities.

Modern water purification technologies, including highly efficient sorption and membrane separation processes, allow the creation of closed water circulation cycles.

Taking into account the above, the purpose of this work is to minimize the liquid waste of refineries using sorption and membrane technologies to ensure recycled water supply.

EXPERIMENTAL PART

Polyfunctional anion exchangers were synthesized by polycondensation of alliglycidyl ether (AGE), dioxydiphenylpropane diglycidyl ether (ED-20) and various amines (polyethyleneimine (PEI), polyethylene polyamine (PEPA), hexamethylenediamine (HMDA)) in the presence of hydrogen peroxide initiator. An ether solution in DMF and an initiator (H_2O_2) were loaded into a three-neck reactor equipped with a stirrer and a thermometer. The mixture was stirred at 70 °C for 1 hour. Then, amine was slowly introduced, after which the reaction mass was kept at this temperature for 0.5-2 hours. The resulting gel was transferred to a porcelain dish and cured in a thermostat for 14 hours at 80-110 °C.

Cation exchangers were obtained by sulfonation of resorcinol diglycidyl ether (DGER), hydroquinone diglycidyl ether (DGEH), pyrocatechol monoglycidyl ether (MGEP) with formaldehyde by sulfonation with concentrated sulfuric acid. The amount of the latter varied in the range of 1.5-6.0 moles per 1.0 mol of the glycidic monomer and formaldehyde – 1.5-12.0 moles per mole of DGER, DGEH and MGEP.

In a reactor with a solution of 1 mole of glycidic monomer in cyclohexanone, 2.5-4.0 moles of concentrated H_2SO_4 were added dropwise, under the action of which condensation occurs and simultaneously sulfonation. Reaction temperature 40-60 °C, duration 0.5-3.0 h.

RESULTS AND DISCUSSION

Much attention is paid to industrial water softening, as some industries cannot do without special water treatment. There are various methods of water softening, the most common technology of softening using ion-exchange resins. It is based on a process in which hardness ions dissolved in water are replaced by ions, without the formation of sediment in pipelines and on the surface of heating equipment.

The principle of operation of ion-exchange filter softeners is as follows: in the water passing through the layer of ion-exchange resin, calcium and magnesium ions are replaced by sodium ions associated with the active ionic groups of the cationite. After the cessation of ion exchange, restoration of the exchange capacity of the ion-exchange resin is required-regeneration, which is carried out by supplying the aqueous solution of sodium chloride to the filter and re-replacing calcium and magnesium ions with sodium ions.

The use of the ion exchange method is advisable in water treatment technologies with low water salinity: below 100–200 mg/l of salts, since with moderate water salinity (about 1 g/l of salt), to clean 1 m^3 of water it is necessary to spend 5 l of 30% hydrochloric acid solution and 4 l of 50% alkali solution. Diagram of the installation of ion-exchange filters is shown in figure 1.

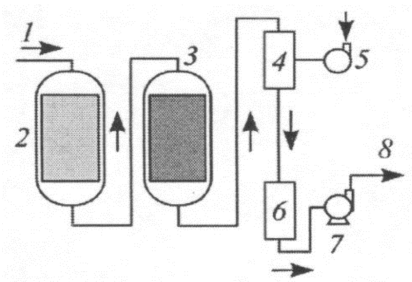


Figure 1 – Installation scheme
of ion exchange filters:
1 - water supply; 2 - hydrogen cation filter;
3 - anion-exchange filter; 4 - calciner;
5 - fan; 6 - decarbonated water tank;
7 - pump; 8 - demineralized water

We have synthesized highly selective anion exchangers based on epoxy and allyl compounds intended for prefilter filters [6]. Studied their basic physico-chemical properties. Some physico-chemical properties of the obtained ion exchangers are presented in table 1.

Table 1 – Capacitive characteristics of the synthesized anion exchange resin

Anion exchanger based	The ratio of the original components, mass	SEC_{HCl}, mg-eq/g	V_{sp}, ml/g
AGE : ED-20 : PEI	1 : 1 : 0.2	1.26	3.2
AGE : ED-20 : PEI	1 : 0.5 : 0.2	dissolves	–
AGE : ED-20 : PEI	1 : 0.5 : 0.4	3.75	2.4
AGE : ED-20 : PEPA	1 : 1 : 0.4	3.5	4.3
AGE : ED-20 : PEPA	1 : 1 : 0.2	dissolves	–
AGE : ED-20 : PEPA	1 : 0.5 : 0.2	dissolves	–
AGE : ED-20 : PEPA	1 : 0.5 : 0.4	2.55	2.1
AGE : ED-20 : HMDA	1 : 1 : 1	dissolves	–
AGE : ED-20 : HMDA	1 : 1 : 2	dissolves	–
AGE : ED-20 : HMDA	1 : 0.5 : 1	dissolves	–

It can be seen that the obtained samples have a high static exchange capacity (SEC), which ranges from 1.26 to 3.75 mg-eq/g, which will allow using them as highly selective ion exchangers in the processes of purification and desalination of water.

Sulfonic cation exchangers, highly selective for hardness ions, have been synthesized. It has been found that the efficiency of the process of sulfonating polymers depends on the size and shape of the granules, the degree of crosslinking, the nature and amount of the sulphating agent, the temperature and duration of the reaction, the preliminary swelling of the product in various solvents or the sulphating agent and the removal of the latter from the interaction zone.

It was established that an increase in the sulfonation temperature from 20 to 80 °C leads to an increase in the exchange capacity and the sulfur content in the samples to 3.4 mg-eq/g and 10.8%, respectively (table 2). The swelling capacity changes with an increase in the exchange capacity and increases even when the exchange capacity at high sulfonation temperatures begins to fall. This indicates polymer degradation. The total sulfur content in samples of sulfonated ionites at temperatures above 90 °C also decreases.

Table 2 – Effect of sulfonation temperature on the physico-chemical properties of cation exchanger (ratio of polymer : H_2SO_4 = 1.0 : 4.0 mass., τ – 3 h)

T, °C	SEC_{NaCl}, mg-eq/g	Vsp, ml/g	Sulfur content, %	
			total	active
20	0,4	0,7	1,5	1,3
30	1,9	1,0	6,4	6,1
50	2,3	1,5	7,9	7,4
60	2,5	2,5	8,2	8,0
70	3,4	2,8	11,2	10,9
80	3,2	3,0	10,8	9,8
90	3,0	3,5	10,2	9,6

It was found that in 0.5 hours of sulfonation SEC is equal to 1.5 mg-eq/g, the content of total sulfur is 4.9%, and in 5 hours it reaches 4.1 mg-eq/g, the content of total sulfur is 13.2% active (calculated by SEC) 13.1%, swelling of 4.0 ml/g. The difference in the values of the sulfur found and calculated indicates that in the process of sulfonation there is an additional crosslinking due to the formation of sulfonic bridges. It was established that the obtained cation exchangers is a monofunctional strongly acidic ion exchanger with an apparent dissociation constant of p*Ka* = 1,8.

The technological scheme of water purification for POCR LLP, which is presented in figure 2, has been developed.

Next, we made a pilot reverse osmosis plant with a capacity of 700 l/h, presented in figure 3 [7].

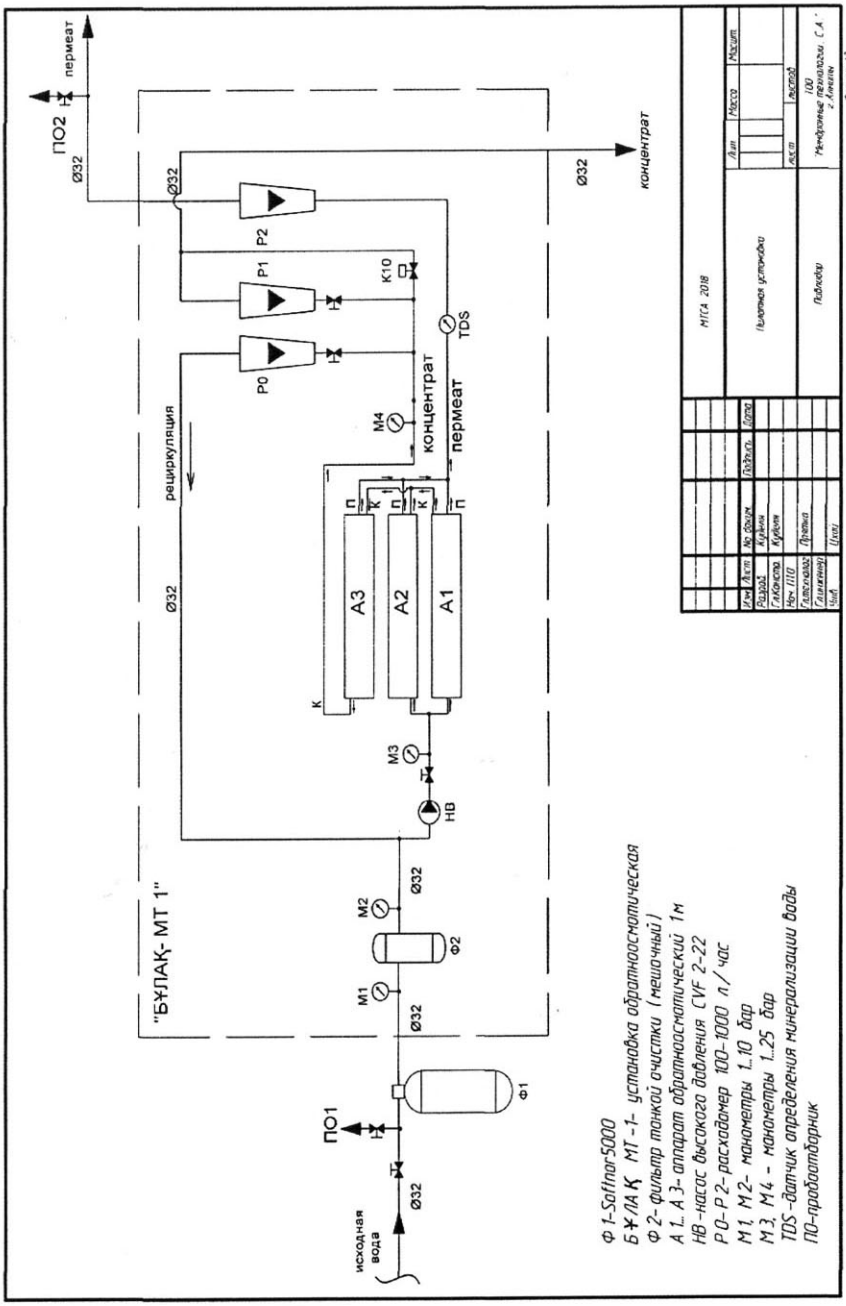


Figure 2 – Technological scheme of the pilot reverse osmosis plant

Figure 3 – General view of a pilot reverse osmosis plant with a capacity of 700 l/h

Tests of the pilot plant in the laboratory were carried out on water samples brought from POCR LLP after the water treatment facilities (WTF) for recharge into the circulating water supply unit (BCWS) in the 1st and 2nd systems, as well as samples of industrial water from Irtysh river (STV), fed to the feed in the BCWS 2A system.

Selection of reverse osmosis elements was carried out in accordance with the task – reducing not only the salt content, but also the removal of residual aluminum and ammonium ions. It is worth noting that the water brought from the sewage treatment plant was completely transparent, according to the data of the laboratory of the RRPIC "KAZECOLOGY", the turbidity – 0, smell – 0, Al – 0.065 mg/l, petroleum products – 0.4 mg/l, ammonium nitrogen less than 0.05 mg/l. The brought water was purified prior to the presented requirements.

The next step was the installation of a pilot plant on the territory of POCR LLP, previously tested in laboratory conditions.

After the installation of the installation at the plant and its connection to the water supply line from the sewage treatment plant to the 1st and 2nd water recycling unit (WTF) system, tests were started.

The water samples taken before cleaning on the pilot installation and after cleaning on the pilot installation were handed over to the Pavlodar branch of the JSC "National Center for Expertise and Certification" (table 3).

The results of analyzes of purified water supplied as feed 1 and 2 of the BCWS systems by reverse osmosis unit show that:

– petroleum products decreased by 7–13 times;
– ammonium nitrogen – 3.5 times;
– suspended substances (mechanical impurities) – 4 times;
– total stiffness – 32 times;
– sulfates – 4.7 times;
– activated sludge concentration – 3–7 times.

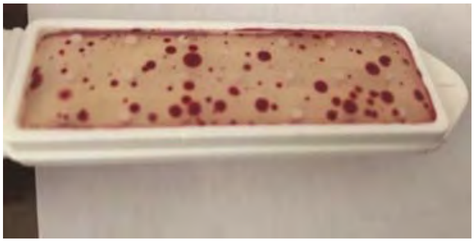
Figure 4 shows samples of rapid tests for bio-growth of microorganisms. It can be seen that the membranes are almost completely cleared from microorganisms.

It has been established that reverse osmosis for the water treatment of POCR LLP has a number of advantages: compactness of the equipment, equipment simplicity and the possibility of increasing capacity due to the modular design of the equipment, low energy consumption, full automation of the treatment processes and water demineralization up to 7%.

Thus, as a result of the research, highly efficient anion exchangers and cation exchangers were obtained, which can be used in the processes of desalination, purification and softening of water. A pilot reverse osmosis plant with a capacity of 700 l/h was manufactured. In laboratory conditions and on the territory of POCR LLP relevant tests were conducted. It has been established that its use allows to sufficiently purify water from oil products, ammonium nitrogen, suspended solids, and also to reduce water hardness.

Table 3 – The results of the tests for water purification and desalination in the territory of POCR LLP

Date	Time	$P_{in.}$, bar	$P_{out.}$, bar	$Q_{perm.}$ l/h	$Q_{conc.}$ l/h	$Q_{rec.}$ l/h	TDS, ppm (mg/l) init.	TDS, ppm (mg/l) perm.	$P_{in.}$ polyprop. fil.	$P_{out.}$ polyprop. fil.	Notes
13.09-14.09	Commissioning installation										
14.09	14-00	12.0	11.5	700	300	300	440	26.5	6.5	6.0	Run the installation. Left the installation to work on the weekend
	15-30	Sampling for delivery to the laboratory before and after testing for the following indicators: ammonium nitrogen, petroleum products									
15.09	8-00	Torn out the water supply hose from the installation due to contaminated filters. Disabled									
17.09	9-00	We washed the filters, the propylene filter was very dirty, we installed a new one. The pre-filter was all polluted, mechanical impurities and microorganisms were visible. Run installation									
	10-00	11.0	10.5	700	300	300	450	26.7	6.0	5.5	
	11-00	Sampling for delivery to the laboratory before and after testing for the following indicators: pH, sulfates, aluminum									
	14-00	Disconnected the installation due to the lack of pressure at the inlet of the outlet of the propylene filter, washed, the pre-filter was also washed, it was very dirty, mechanical impurities were visible									
	15-00	11.0	10.5	700	300	300	440	23.5	5.5	4.5	
	17-00	11.0	10.5	700	300	300	440	25.1	4.5	4.0	Disable installation
18.09	9-00	Sampling before cleaning, washing the filters. Microorganisms and mechanical impurities are visible. Run installation									
	10-00	13.0	12.5	700	300	300	400	24.0	5.5	5.0	
	10-30	Sampling for delivery to the laboratory after testing for the following indicators: hardness, dry residue									
	14-15	11.0	10.5	700	300	300	400	16.7	5.0	4.5	
	15-00	11.5	11.0	700	300	300	430	25.7	5.0	4.5	Took samples for microorganisms (Nalco)
	16-30	11.5	11.0	700	300	300	430	21.6	5.0	4.5	Disable installation
19.09	9-20	Sampling before cleaning, washing the filters. When opening the pre-filter, microorganisms are present. Run installation									
	9-50	12.5	12.0	700	300	300	450	24.0	4.5	4.0	
	10-30	Sampling for delivery to the laboratory after testing for the following indicators: suspended solids, sulfates									
	14-00	11.0	10.5	700	300	300	440	20.8	4.0	3.5	
	14-40	11.5	11.0	700	300	300	440	22.3	4.5	4.0	After hydro-washing, the pressure at the inlet and outlet of the filter increases
	15-00	11.5	11.0	700	300	300	430	22.2	4.0	3.5	
	15-45	11.5	11.0	700	300	300	430	24.3	4.5	4.0	After hydro-washing, the pressure at the inlet and outlet of the filter increases
	16-30	11.5	11.0	700	300	300	430	24.0	4.0	3.5	Disable installation

a b

c d

Figure 4 – Samples of Nalco rapid tests for bioabsorption of microorganisms
(a, b – before treatment; c, d – after treatment)

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Резюме

Е. Е. Ерғожин, Т. К. Чалов, Т. В. Ковригина, Е. А. Мельников

СОРБЦИЯЛЫҚ ЖӘНЕ МЕМБРАНАЛЫҚ ӘДІСТЕРМЕН МҰНАЙ ӨҢДЕУ ЗАУЫТТАРЫНЫҢ АЙНАЛМА СУЫНЫҢ САПАСЫН ЖОҒАРЫЛАТУ

Мақала иониттерді синтездеу мен зерттеуге және олардың практикалық қолданылу жолдарын табуға арналған. Осы жұмыста пилоттық кері осмостық қондырғы дайындалды және оның зертханалық және тәжірибелік-өндірістік сынақтары «Павлодар мұнай-химия зауыты» ЖШС аумағында жүргізілді. Мұнай өнімдерінен, аммоний азотынан, қалқымалы заттардан және басқа да органикалық және бейорганикалық қоспалардан суды тазартуда оның тиімділігі көрсетілді.

Түйін сөздер: анионит, катионит, статикалық алмасу сыйымдылығы, технологиялық сұлба, пилоттық кері осмостық қондырғы, судың сынамалары, зертханалық және тәжірибелік-өндірістік сынақтар

Резюме

Е. Е. Ергожин, Т. К. Чалов, Т. В. Ковригина, Е. А. Мельников

ПОВЫШЕНИЕ КАЧЕСТВА ОБОРОТНОЙ ВОДЫ НЕФТЕПЕРЕРАБАТЫВАЮЩИХ ЗАВОДОВ СОРБЦИОННЫМИ И МЕМБРАННЫМИ МЕТОДАМИ

Статья посвящена синтезу и изучению ионитов и нахождению путей их практического применения. В данной работе изготовлена пилотная обратноосмотическая установка и проведены ее лабораторные и опытно-промышленные испытаний на территории ТОО «Павлодарский нефтехимический завод». Показана ее эффективность при очистке воды от нефтепродуктов, аммонийного азота, взвешенных веществ и других органических и неорганических примесей.

Ключевые слова: анионит, катионит, статическая обменная емкость, технологическая схема, пилотная обратноосмотическая установка, пробы воды, лабораторные и опытно-промышленные испытания.