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TREATMENT OF WASTE WATER CONTAINING WASTE OIL

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Abstract

The dependence of flow separation membrane emulsion on its stability. The results of the investigation of the stability of emulsified among the various qualitative composition. The experiments on the separation of the most stable emulsion of oil-based mark "I-20A" and surfactant mark "Kosintol-242" of various concentrations followed by a discussion of the experimental data and the identification of the zeta potential and particle size of the dispersed phase of the original emulsion and the filtrate. The substantiation of the need for further purification emulsification media, in particular adsorption methods of alternative sorbents with a brief overview of the results of relevant studies.A principal flowsheet wastewater containing waste oil.

Keywords; Membranes, polysulfone amide, Emulsions

1. Introduction

The current stage of development of petrochemical technology, in general, characterized by the transition of quantitative characteristics - the volume of production, processing and synthesis to quality indicators - expanding the range of the target product, increasing the degree of conversion of raw materials and the selectivity of the process tends to reduce capital expenditures, respectively. In particular, the operation of oil, which is one of the main petrochemical products, an important task is to reduce the wear of the past, helping to reduce operating costs, which is made possible by a one-time improvement of appropriate technologies. However, even under the assumption of perfect process no waste is not possible, because itself, the concept of "non-waste technology" is a utopian according to the law of conservation of energy. During the use of oils for various purposes, including as part of cutting oils, a reduction in their performance, and therefore there is a need for their replacement and disposal, in which it is likely to last enter the environment. Influence of waste oils on the ecosystem is similar in nature to the impact of oil and oil products at which the decrease in the concentration of dissolved oxygen in water bodies due to the formation on the surface of the oil slick, the violation of physiological activity caused by the introduction of hydrocarbons in a living organism, as well as changes in the physicochemical properties of their range. Waste water containing waste oil, produced at the enterprises of chemical, petrochemical, machinery, petrol and car wash, as well as maintenance and repair of road, rail, water and air transport. When present in the formulations of the flow of surface-active agents (surfactants), and various emulsifiers, which include salts, asphaltenes, resins, oil soluble organic acid and the fine impurities such as silt and clay, waste water containing waste oil and fuel is formed stable multi-component structure - emulsion. Kinetic stability of the diluted emulsions (containing the dispersed phase of less than 3%) is directly proportional to viscosity and inversely proportional to the difference in densities of the dispersed phase and the globules of water and the square of the radius of the globules and can be represented by the expression:

$$\mathbf{Ку} = \frac{\mathbf{1}}{\boldsymbol{\vartheta}} = \frac{\mathbf{9\eta}}{\mathbf{2(\rho_в-\rho_н)r^2g}}, \qquad (1)$$

Where υ -sedimentation rate o rfloating particles of the dispersed phase with a radius r, m/s; ($\rho_в$, -$\rho_н$) -the difference indensities of the dispersed phase and the dispersion medium, kg/m^3;η -viscosity of the dispersion medium in m^2/s;g – acceleration of gravity, m/s^2[1].

In this connection it should be noted that with the increase of stability of the emulsified wastewater is increased operating costs for their cleaning, associated with the necessity of destroying the stable emulsion structure by using external force fields. Given the complexity of the multi-component composition, resistance to microorganisms and the forces of gravity, the traditional methods of wastewater treatment, based on the processes of sedimentation, filtration and biodegradation show themselves ineffective. Actually, promising to clean up oil water emulsions are membrane separation techniques, such as ultra filtration, which are the main advantages of high efficiency, no use of chemicals, as well as a small area occupied by the equipment [2-5]. However, without an understanding of the mechanism of the membrane, the introduction of the latest in the industry to become impossible.

The convective transport of substances through the membrane adequately described by the Hagen-Poiseuille:

$$G\kappa = \frac{\varepsilon R^2}{8\eta\tau} \cdot \frac{\Delta P}{l} \qquad (2)$$

whereε -porosity ofthe membrane surface, i.e. the area ratio ofpores to themembrane area, R - average pore radius, η - viscositypenetrate; τ -pore tortuosityfactorwhich increasesthe path length; l -thickness of the membrane, ΔP -pressure differenceon bothsides of the membrane[6].

If the viscosity of the dispersion medium of the emulsion paint formula1as the dependence on the stability and substituted into the formula2, we get the following formula:

$$G\kappa = \frac{\varepsilon R^2}{8\tau} \cdot \frac{\Delta P}{l} \cdot \frac{9}{K y \cdot 2(\rho_в - \rho_н) r^2 g} \qquad (3)$$

On the basis of the obtained expression it shows that with an increase in the stability of the emulsion is a decrease of flow through the membrane.

Thus, increasing the stability ofthe emulsifiedwastewaterreducedseparationperformanceofthe membrane, which from a technological pointof view,is a negative factor.

2. Methods

In this regard, in order to further destruction of the most stable emulsions conducted studies to determine the qualitative composition of the latter to provide the best stabilization. As the dispersed phase of the emulsion in an amount of 20%, the following oil: engine oil - "MM", turbine oil - "TP-22", industrial oil - "I-20A", gear oil - "TM", used motor oil - "M"; as stabilizer - surfactant marks "Kosintol-242", "247-Kosintol" in an amount of 2%; dispersion medium - distilled water. A typical experiment was to observe stratification study environment at 0.1 dm^3 in the graduated cylinder with the same volume of one-time registration of the volume of the oil phase exfoliated after a certain time interval. The results are shown in Figure 1.

3. Results

The analysis ofthe data presentedin Figure 1revealedthat the most stablein most cases arebased onthe emulsionsurfactantmark "Kosintol-242." Furthermore, it is shown thatprovidesthe greatest stability forthe oilgrade"I-20A 'in conjunction with the designatedsurfactant.

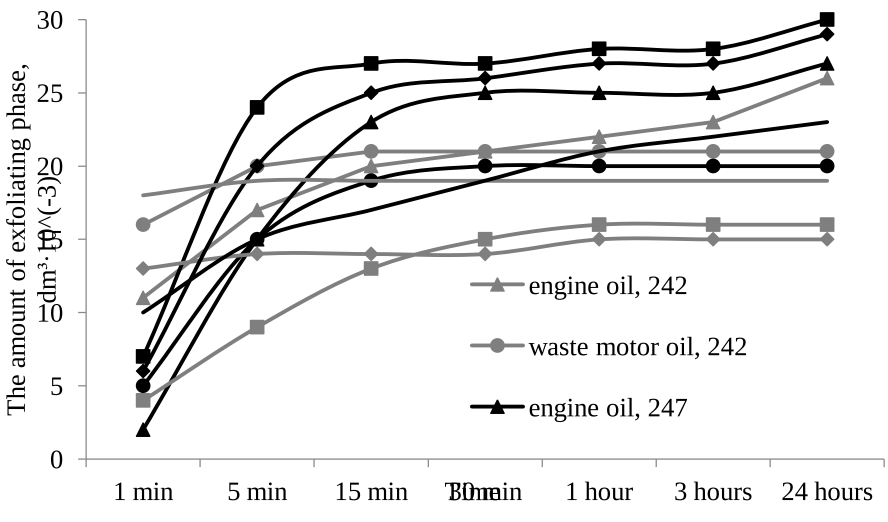

Figure 1. The kinetics of stratification of water-oil emulsions different in the qualitative composition.

In the continuation ofstudydetermined the parametersof membrane separation-the performance and efficiencyin terms ofChemical Oxygen Demandforthe aboveindicatedemulsionsqualitative composition ofan oilwith a concentrationof 1, 3and 5%. Thusappliedultra filtrationpolisulfonamidnye(PSA) membraneswithcut off by theweightof the particles10, 20, 50, 100kDaresults are shownin Figure 2and Table 1.

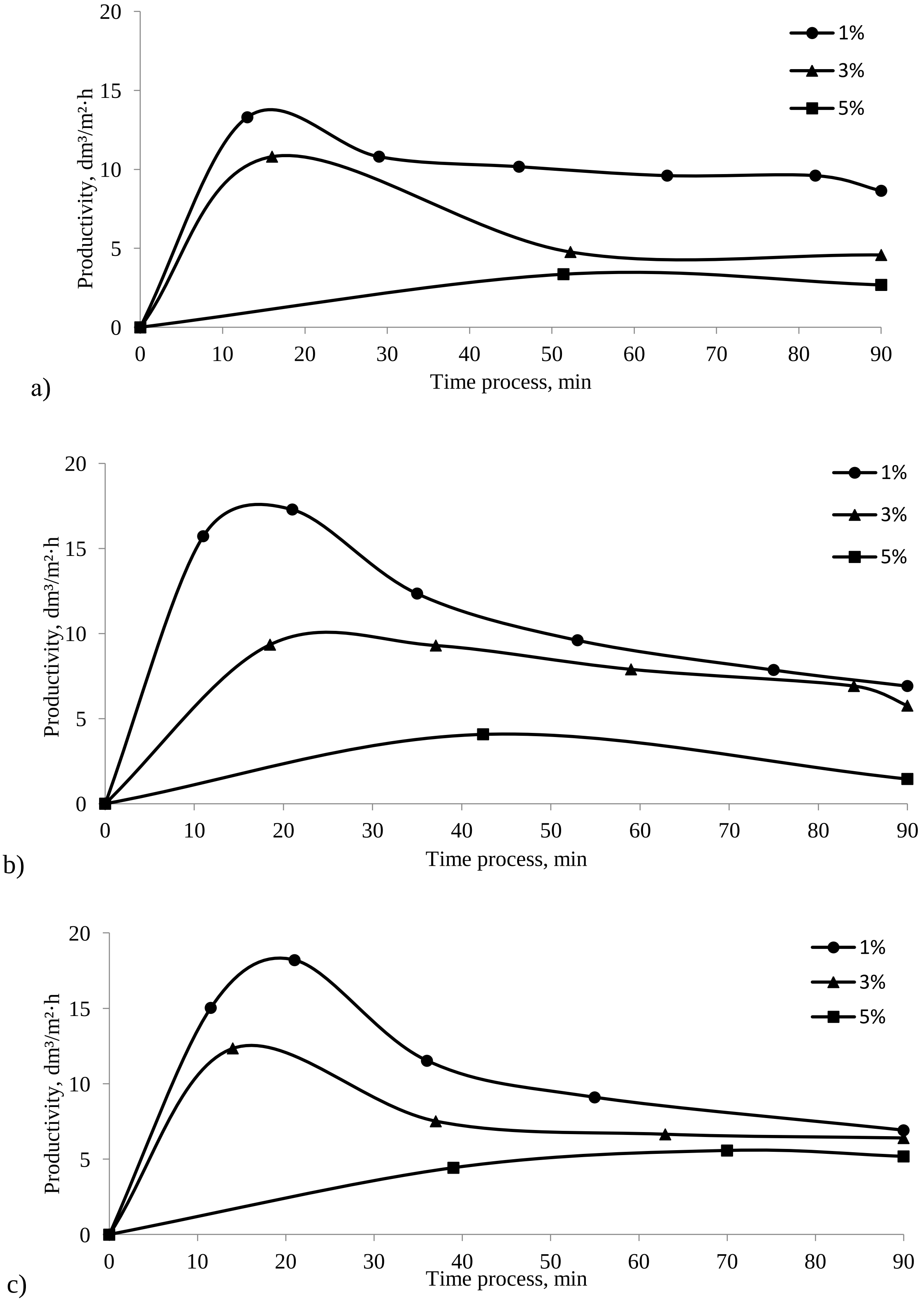

Figure 2. The performance of the separation by polysulfonamide membranes with a molecular weight cut-off: a) 20 kDa, b) 50 kDa, c) 100 kDa.

The immediate step should be noted the absence of separation of oil water emulsions using different concentrations of PSA membranes cut off by the particle with mass of 10 kDa. The analysis of the curves in figure 2, showed improved performance with an increase in the mass of particles cut off by use of membranes and decrease the concentration of the shared environment, which is quite natural.

Table 1 – The COD of the filtrate obtained in the separation of emulsions of different concentrations of PSA membranes with a molecular weight cut-off of20, 50 and 100 kDa.

Molecular weight cut-off, kDa	COD, mg O^2/dm^3		
	The concentration of the original emulsion, %		
	1%	3%	5%
20	3720	7198	8930
50	5220	7880	9800
100	9310	9840	10640
Theoriginalemulsion	9690	22750	39100

Analysis COD values shown in table 1, shows a decrease with increase of the parameter in the initial concentration of the emulsion, and with increasing mass of PSA particles cut off by the membranes. The smallest value of COD = 3720 mg O_2/ l is achieved using PSA filter element with a mass of 20 kDa cut off by the particles in the separation of a 1% emulsion, the efficiency of the process was 61%. One of the main characteristics is the oil water emulsions zeta potential, which is indicative of the stability of colloidal systems, particularly emulsions [7]. In this regard, by electrophoretic light scattering using an instrument «NanoBrook Omni» defined by this indicator, which emulsions with an oil concentration of 1, 3 and 5% was -40.02, -44.97, -8.69 mV, respectively. Thus with the highest value modulo zeta potential most stable it is 3% of the emulsion, and therefore in Figure 3 is the particle size of its dispersed phase, and the particle size of the dispersed phase of the filtrate obtained by separation of the considered emulsions PSA membrane with mass removed particles 50 kDa.

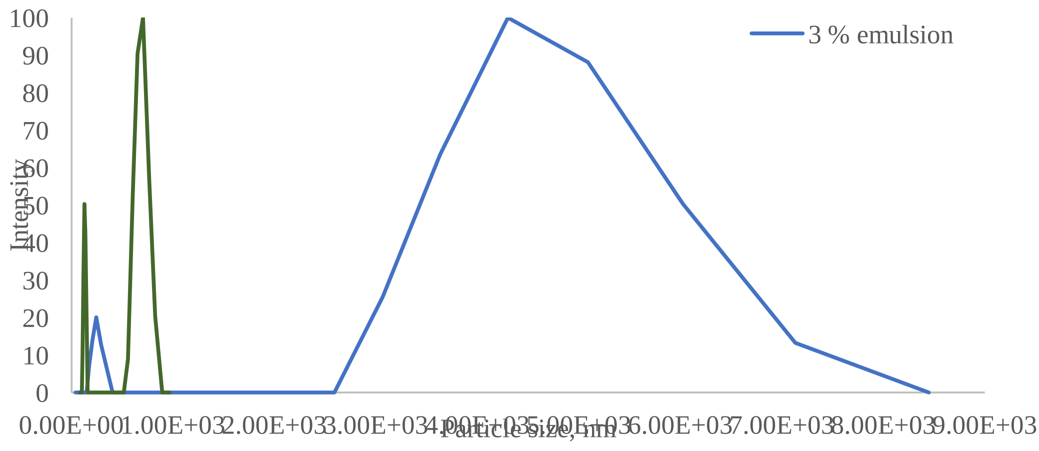

Figure 3. The distribution histogram of the particle size of the dispersed phase of 3 % emulsion, and particles dispersed filtrate resulting from the separation of PSA membrane with a molecular weight cut-off 50 kDa

On the basis of the data presented in figure 3, revealed larger particulate composition of the emulsion, compared with itsfiltrate, which is quite naturalandis due toretention oflarger particlesof the dispersed phasesurface and themembranepores. The largest number of emulsion particles has a size of $2.43 \cdot 10^2$and $4.30 \cdot 10^3$nm, the filtrate $1.25 \cdot 10^2$ and $7.04 \cdot 10^2$nm.

4. Discussion

According to the departmental guidelines for technological design of industrial water supply VUTP-97 waste water containing oil products, after the step of mechanical and physical-chemical treatment must have the COD below 400 mg O_2/dm^3.

Thus, after the ultra filtration step becomes necessary additional cleaning to achieve the designated value.

Achieving any degree of purification becomes possible by using sorption technology and the fundamental question in this case is economic. In this context, it becomes appropriate to use sorbents on the basis of various waste products.

Earlier studies [8] show that the sorption in water-oil emulsion static conditions with a value of COD = 2000 mgO_2/dm^3 clinoptilolite, diatomaceous earth and activated carbon COD end values are 500, 150 and 40 mgO_2/dm^3, respectively. Thus, in the case of diatomaceous earth and activated carbon reaches the value indicated above regulated regulations.

The idea of using cheaper diatomite adapted from previously published studies [9], which reported that oil absorption considered sorbent with respect to various oils range from 0.50 to 0.74 g/g. In [10, 11] that as sorbents to absorb the waste oils used felting production, in particular, fumes and oil absorption value relative button of the oil brand "I-20A" amounted to 20.06 and 18.52 g/g , respectively.

In [12] proposes the use of chemical water treatment sludge Kazan CHP-1, which the sorption capacity of turbine oil is 0.5-0.7 g/g. The thesis [13] presents the results of semi-industrial tests of water sources clean small debit, during which oil concentration after sorption linen fervor decreased from 0.6 to 0.017 mg/dm^3, so efficiency was 97.2%. Of particular interest are vegetable sorbents, particularly in the scientific publication [14] has shown that the sorption capacity with respect to the husks of barley oil is 6.092 g/g.

Based on the foregoing, as well as experimental dataand analysis ofthe literature [6, 15-17] proposeda schematicflow diagram ofpurificationof wasteoil wateremulsionsshown inFigure 4.

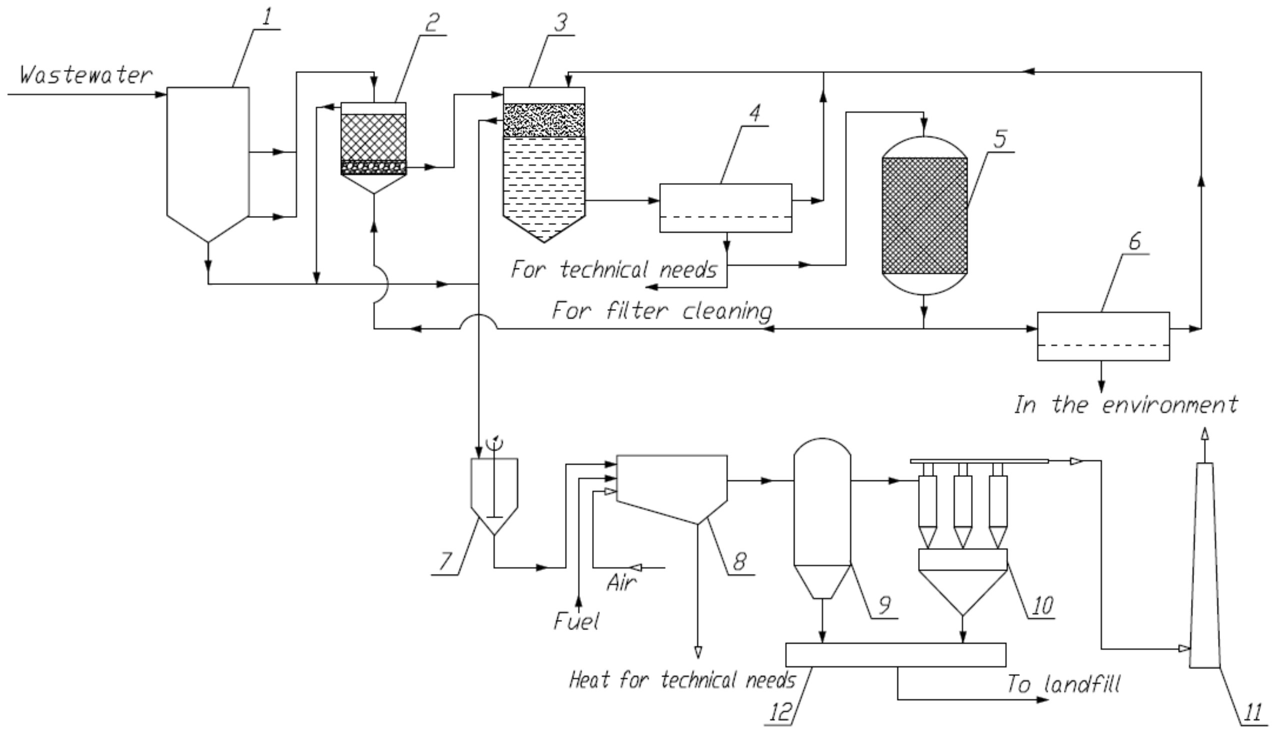

Figure 4. The technological scheme of purification of waste emulsions and subsequent disposal of water-oil phase and the recovery of waste heat: 1 – sump, 2 – filter, 3 – sump-separator, 4 – ultrafilter, 5 – adsorber; 6 – nanofilter; 7 – averager, 8 – chamber furnace, 9 – scrubber, 10 – cyclone, 11 – chimney, 12 – hopper for ash.

Receives raw water to the sump 1, which removes coarse solids in the form of metal shavings or sand followed by a filtration step strainer 2, wherein the fine particles are retained suspended and colloidal solid contaminants. The filtrate flows into the collection separator 3, where the flow separation in an oil and water-oil phase.

The oil phase formed in step 3, together with the solid waste from steps settling and filtration 1 and 2, respectively, through the step of averaging 7 is directed to the combustion furnace 8 to which also supplied with air and additional fuel for maintaining the combustion process, in which formed gases and the energy in the form of waste heat, which is suitable to recover. Gas emissions are further purified in scrubber 9 and hydrocyclone 10 and then through a smoke tube 11 are dispersed in the atmosphere. Ash formed in step 9 and 10, enters into the hopper 12, and then sent to landfill.

Oil-water phase of step 3 is directed to an ultrafiltration step 4, and then supplied to the adsorption stage 5. In order to the final purification step serves nanofiltration 6, after which the purified water is sent to drain natural objects.

5. Conclusions

Thus, the results of the empirical and theoretical research provides a method for solving one of the most important technological challenges, the petrochemical industry, in particular, effective cleaning of aqueous media from waste oils and subsequent disposal of secondary waste in the form of heat, oil and gas, which is made possible through an integrated approach a one-time use of modern analytical equipment, the availability of basic knowledge about the issue being addressed, the proper organization of experimental work, multidisciplinary review of the decision of tasks, as well as the application of basic scientific principle - the pursuit of truth.

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