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IMPROVING THE EFFICIENCY OF WASTEWATER TREATMENT CONTAINING PETROLEUM PRODUCTS

Research article

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Abstract

In order to increase the efficiency of the process of ultrafiltration of wastewater from motor transport enterprises containing petroleum products, their preliminary treatment with ozonation is proposed. Ozonation was carried out to enlarge impurities of petroleum origin. The required ozone concentration was provided by varying the power of the ozonator from 20 to 50 watts. Based on the analysis of literature sources, the most effective ratio of the concentration of ozone and the concentration of petroleum products contained in the test solution was selected, equal to 2.5 to 5% by weight. As a result of the analysis of literary sources and conducted experiments, it was found that the optimal time for ozonation is within 5-10 minutes before the formation of flakes. The resulting heterogeneous medium was then separated by ultrafiltration. Tubular single-channel polymer membranes based on fluoroplast and polysulfonamide with an average pore size of 0.05 microns were used as a separating element. The ultrafiltration process was carried out at a temperature of 323 K of the separated medium and an operating pressure of 0.4 MPa. As a result of the study, satisfactory indicators were obtained for the quality of wastewater treatment, which corresponded to the norms of the maximum permissible concentration of harmful impurities.

Keywords: wastewater, ozonation, ultrafiltration, polymer membranes.

ПОВЫШЕНИЕ ЭФФЕКТИВНОСТИ ОЧИСТКИ СТОЧНЫХ ВОД, СОДЕРЖАЩИХ НЕФТЕПРОДУКТЫ

Научная статья

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Аннотация

С целью повышения эффективности процесса ультрафильтрации сточных вод автотранспортных предприятий, содержащих нефтепродукты предлагается предварительная их обработка озонированием. Озонирование производилось для укрупнения примесей нефтяного происхождения. Нужная концентрация озона обеспечивалась варьированием мощности озонатора от 20 до 50 Вт. На основании анализа литературных источников было выбрано наиболее эффективное соотношение концентрации озона и концентрации нефтепродуктов, содержащихся в исследуемом растворе, равное от 2,5 до 5 мас.%. В результате анализа литературных источников и проведенных экспериментов установлено, что оптимальное время проведения озонирования находится в пределах 5-10 мин. до образования хлопьев. Затем полученная гетерогенная среда подвергалась разделению ультрафильтрацией. В качестве разделяющего элемента использовались трубчатые одноканальные полимерные мембраны на основе фторопласта и полисульфонамида со средним размером пор 0,05 мкм. Процесс ультрафильтрации проводился при температуре разделяемой среды 323 К, и рабочем давлении $\Delta P = 0,4$ МПа. В результате исследования получены удовлетворительные показатели по качеству очистки сточных вод, которые соответствовали нормам предельно допустимой концентрации вредных примесей.

Ключевые слова: сточные воды, озонирование, ультрафильтрация, полимерные мембраны.**Introduction**

Many industrial enterprises generate large volumes of wastewater containing petroleum products (WWPP) that do not comply with environmental regulations. The relevance of such wastewater treatment is due to several factors:

- reduction of pollution and prevention of negative impact on the environment;
- compliance with regulatory requirements for the maximum permissible concentration of petroleum products in wastewater for discharge into central sewers and reservoirs;
- reduction of water supply costs due to the use of recycled water and a closed consumption cycle;
- social responsibility of organizations involved in the treatment of WWPP;
- stimulating research and development of new technologies that can be further applied to other types of industrial and household wastewater.

Thus, treatment of wastewater from petroleum products and other impurities of man-made impact is important for environmental conservation, compliance with legal requirements, economic efficiency and social responsibility of organizations.

This type of waste is a direct emulsion in which the dispersed phase is oil (non-polar liquid) and the dispersed medium is water (polar liquid).

For the separation of petroleum products (PP) and water, there is a wide variety of technological methods based on chemical, biochemical, aerobic and anaerobic, thermal, electrochemical processes, flame neutralization, evaporation, distillation, oxidative processes, decomposition of reagents, as well as coalescence, flotation and sorption [1], [3], [5], [8]. Most of these methods consume a large amount of energy, require the use of reagents, the use of oil traps, and with a large volume of wastewater, an entire system of settling ponds that affect the ecological system around them.

Despite the large number of studies by domestic and foreign scientists in the field of biosphere protection, the problem of deep wastewater treatment from organic and inorganic compounds remains unresolved.

One of the main directions for the development of technology for wastewater treatment is the development of low-energy, non-reactive, low-waste processes [2], [9]. The analysis of scientific papers in a ten-year retrospective shows great interest in membrane technologies and wastewater treatment by ozonation [10], [12], [14], [15], [16].

In one of the works [17], a good result was obtained for the purification of a water-oil emulsion after two stages of ultrafiltration and nanofiltration. The retention of almost all impurities was in the range of 97-99%, the water after nanofiltration was transparent and met the requirements of permissible concentrations of pollutants in wastewater allowed to discharge into wastewater disposal systems.

The disadvantage of the proposed method was the complication of the technological process, a significant increase in energy consumption and a drop in the productivity of the installation as a whole. In addition, there remains the problem of reducing the influence of concentration and gel polarization on the membrane surface, which is the limiting factor of separation [18], [19].

In the study [20], spent coolant was neutralized at an installation with a capacity of 3.5 g/h of ozone at a concentration of an air-ozone mixture up to 33 mg/l. It turned out that ozonation is most effective in an alkaline environment at pH = 12. At pH = 10, 100% ozone absorption was observed for 30-45 minutes. During 1-1.5 hours, the surfactant was almost completely destroyed. Chemical Oxygen Demand (COD) decreased from 7.5 to 2-2.4 g/l, which is 70-72% of the potential. The ozone absorption was 90-96%.

After the destruction of surfactants, the loss of ozone increased sharply, which indicated the presence of difficult-to-oxidize substances. The minimum COD value (0.3-0.4 g/l) was observed after 2.5-3 hours, with a large loss of ozone. Complete oxidation of organic substances could not be achieved. Intermediate products of hydrocarbon decomposition remained in the ozonated water, which could not be further destroyed.

The advantage of ozonation is that ozone is effective against most organic compounds that are difficult to oxidize, which decompose to form safe substances. At the same time, unpleasant odors are eliminated and disinfection occurs due to the bactericidal properties of ozone [21].

Petroleum products in wastewater are in an emulsified state in the form of very fine particles. As shown in [22], the reaction of ozone with emulsified petroleum products has its own characteristics. As a result of the reaction contact of ozone and particles of petroleum products, the upper layer is rapidly oxidized. Then the oxidation process slows down sharply, as the rate of ozone diffusion deep into the emulsified particles of petroleum products decreases. The subsequent process of oxidation of petroleum products with ozone takes a long time, which reduces the effectiveness of this method of purification of oily water. However, numerous experiments on the use of ozone for the purification of oily wastewater have shown that partially oxidized particles of petroleum products intensively coagulate and pass into a floccular phase.

The phenomenon of coagulation of partially oxidized petroleum products has led to a hypothesis about the possibility of intensifying the process of ultrafiltration of wastewater containing petroleum products using ozone, due to a decrease in the formation of a gel polarization layer on the membrane surface.

Thus, the purpose of this work is to study the hybrid separation process of heterogeneous media containing petroleum products and water, based on the consistent application of ozonation and ultrafiltration.

Research methods and principles

Samples taken from stormwater wastewater from the truck maintenance station of the Yarkamp Group of companies in Yaroslavl, presented in Table 1, were used as WWPP.

The efficiency of oil-containing wastewater treatment depends on the ratio of the initial concentrations of ozone C_{oz} and petroleum products C_{pp} .

Complete oxidation of petroleum products occurs under the condition $C_{oz} \geq C_{pp}$, under the condition when $C_{oz} > C_{pp}$ the highest oxidation rate is observed. However, the higher the ozone concentration, the higher the cost of the process. On the other hand, if there is a slight excess of ozone or if the concentrations of $C_{oz} = C_{pp}$ are equal, the ozonation time increases and the loss of expensive gas due to its natural decay is inevitable.

It is advisable not to bring oil products to complete decomposition during ozone oxidation, but to remove partially oxidized and coagulated particles by ultrafiltration.

Based on the analysis of theoretical and experimental studies presented in the literature [22], [23], [24], [25], [26], the optimal concentration ratio was determined to be equal $C_{oz}/C_{pp} = 2.5-5\%$ by weight.

The process of ozonation of WWPP samples was carried out at a temperature of 293 K and atmospheric pressure in a bubbling reactor. Oxygen was used as an ozone source at a gas flow rate of 120-150 ml/min. The required ozone concentration was obtained by changing an ozonator power in the range from 20 to 50 watts. The duration of ozone oxidation was carried out for 5-10 minutes, which led to abundant flocculation of oil-containing impurities in the samples.

The prepared heterogeneous system was then separated in a laboratory ultrafiltration unit [19]. In experimental studies, we used tubular polymer ultrafiltration membranes based on fluoroplast and polysulfonamide with an average pore size of 0.05 microns produced by LLC «Vladipor» in Vladimir city.

Main results

Figure 1 shows the results of the observed permeability parameters of the process of separation of WWPP from time during ultrafiltration and ultrafiltration with ozonation.

Analysis of the curves in Figure 1 shows the effectiveness of applying ozonation before ultrafiltration. The separation process reaches a plateau with a higher specific productivity. This effect can be explained by the coarsening of dirt particles and the formation of a floccular phase, and a smaller gel layer due to the action of tangential forces on it during the flow in the tubular channel.

Table 1 shows the results of chemical analysis of treated real effluents after ozonation followed by ultrafiltration and their comparison with standard indicators of the content of harmful impurities.

Table 1 - Comparison of the concentration of pollutants in the filtrate with permissible values

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Indicator	The standard MPC	Spent WWPP	Ultrafiltration (fluoroplast)		Ozonation and ultrafiltration (fluoroplast)	
			Permeate pollutant concentration value	Degree clearances	Permeate pollutant concentration value	Degree clearances
			C±Δ mg/dm ³ P=0.95, n=2	C±Δ mg/dm ³ P=0.95, n=2	%	C±Δ mg/dm ³ P=0.95, n=2
	6.0-9.0	8.9±0.1	8.9±0.1	-	7.8±0.1	-
Suspended solids, mg/dm ³	300	1554±233	< 0.5	99.9	< 0.5	99.9
Dry residue, mg/dm ³	3000	19900±3980	4700±470	23.2	850±85	81.4
*BOD ₅ , mg/dm ³	300	6305±1261	315±63	80.2	8.8±1.8	97.0
COD, mg/dm ³	500	18215±3643	1052±210	76.2	23.4±4.7	97.6
Nitrate ion, mg/dm ³	-	54.6±11	47±7	13.9	3.15±0.63	92.1
Nitrite ion, mg/dm ³	-	2.91±0.58	2.1±0.42	27.8	<0.02	98.9
Sulfate ion, mg/dm ³	300	121±24	108±16	10.7	9.21±1.84	90.9
Phosphate ion, mg/dm ³	12	54.6±11	20±4	17.7	1.84±0.37	90.4
Chloride ion, mg/dm ³	1000	280±56	277±27.7	1.1	30.8±6.2	88.8
Petroleum products, mg/dm ³	10	14400±2880	109±10.9	93.2	<0.05	99.9
Anionic surfactants, mg/dm ³	10	3.15±0.79	2.6±0.5	10.3	<0.02	99.3
Non-ionic surfactant, mg/dm ³	-	4711±942	2974±446	31.2	1.12±0.22	99.9
Fat content, mg/dm ³	50	10100±2525	149±29.8	94.9	<0.01	99.9

Note: * BOD₅ - Biochemical oxygen demand during 5 days of incubation at 20 °C

According to the results of chemical analysis (Table. 1) it can be seen that the addition of the ozonation stage to the wastewater treatment process makes it possible to almost completely filter out fats and petroleum products, as well as increase the efficiency of neutralization of multivalent metal ions and surfactants.

Possible chemical reactions of wastewater components with ozone and mechanisms for improving filtration quality may include:

- reactions with hydrocarbons contained in petroleum products, which leads to the formation of lighter and less toxic compounds;
- decomposition of petroleum products into less toxic compounds such as acids, aldehydes and ketones;
- the formation of flake-like, larger particles, which simplifies their removal by ultrafiltration.

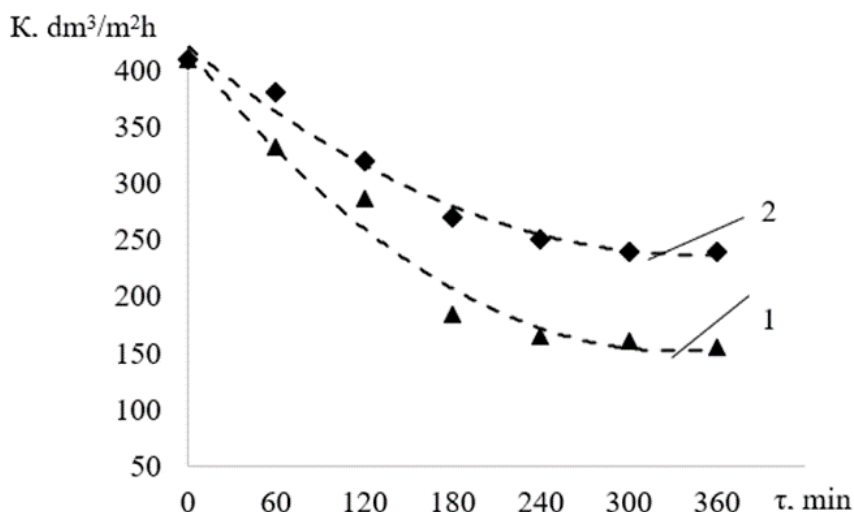


Figure 1 - Dependence of membrane permeability on time at $t=323$ K, $\Delta P = 0.4$ MPa, membrane material - fluoroplast:

1 - ultrafiltration; 2 - ozonation with ultrafiltration

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Conclusion

Based on the presented research results, the hypothesis of increasing the efficiency of the wastewater separation process containing petroleum products through the consistent application of ozonation and ultrafiltration was confirmed.

Further development of the proposed method of separation of WWPP should be carried out in the following directions:

- to obtain the most effective technological modes of ozone treatment, wastewater and stormwater in order to recommend them for practical use as a stage of preparation of solutions before ultrafiltration;
- synthesis of hardware design and its implementation.

Конфликт интересов

Не указан.

Рецензия

Все статьи проходят рецензирование. Но рецензент или автор статьи предпочли не публиковать рецензию к этой статье в открытом доступе. Рецензия может быть предоставлена компетентным органам по запросу.

Conflict of Interest

None declared.

Review

All articles are peer-reviewed. But the reviewer or the author of the article chose not to publish a review of this article in the public domain. The review can be provided to the competent authorities upon request.

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