FLOTATION METHOD FOR WASTEWATER TREATMENT FROM OIL PRODUCTS CONTAMINANTS

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Industrial and natural wastewater is one of factors of the environmental pollution, in particular, its water basin. Among others, fuel and oil pollutants are toxic substances that cause a significant harm to all living things. It is necessary to create technologies using effective methods of wastewater treatment to solve such problems. It is possible to properly select and effectively use methods of treatment taking into account the nature, condition and concentration of contaminants in wastewater. These are the issues addressed in this article. Particular attention is paid to the use of flotation as a method of treatment of stable highly dispersed emulsified wastewater containing oil or fuel contaminants in the technology of this type wastewater treatment. The main objectives of a study were to evaluate the impact of parameters and flotation reagents on an efficiency of the treatment process of stable highly dispersed emulsified wastewater. Flotation of such wastewater was carried out on a laboratory flotation installation of pneumatic type and compared with the process of wastewater settling over time. Studies have shown that for stable emulsified wastewater containing oil or fuel contaminants with a low content of highly dispersed particles of inorganic nature or a stabilizer is present in them, it is advisable to use the flotation method with flotation units of pneumatic type. Analysing the results, it should be noted that the flotation method significantly reduces a purification time of highly dispersed emulsified wastewater from 3-5 hours of their settling in settling tanks-oil traps up to 10-20 minutes by a method of pneumatic flotation, while the degree of wastewater treatment increases in at least 1.5-2 times depending on the presence of fuel or oil contaminants in wastewater. If wastewater contains a stabilizer, such as a surfactant, it can be used as an effective flotation reagent in the purification of this type of wastewater by a flotation, which is not suitable for the settling process.

Key words: emulsified wastewater, flotation, petroleum products, settling, stabilizer, surfactants.

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1. Introduction

The problem of wastewater treatment is one of the important problems of a modern world to preserve the planet's ecosystem. Oil and its products should be mentioned among other wastewater pollutants. Oil and petroleum products are characterized by a significant toxicity, which poses a threat to the environment. In addition, a significant amount of wastewater is formed during extraction, processing, transportation and use of oil and petroleum products. Petrochemical and oil refineries, oil terminals, depots and storage facilities are the main sources of wastewater pollution by oil and oil products. The amount of waste containing oil and fuel contaminants at such facilities is tens and hundreds of thousands of cubic meters. It should be noted that 12 dm^3 of oil make 1 ton of water unusable (Shestopalov et al., 2015).

As practice shows, there is a high probability of getting oil and fuel contaminants into territorial or urban wastewater and into natural waters. The situation is complicated by the fact that wastewater usually contains many other substances like dispersed particles, surfactants that can stabilize oil and fuel contaminants. This causes a formation of stable highly dispersed emulsified wastewater, which is too difficult to treat by a traditional settling, using different types of settling tanks. Therefore, there is an urgent need to create new approaches in the treatment process of such wastewater.

The aim of this work is to use flotation as a method of treatment of stable highly dispersed emulsified wastewater containing oil or fuel contaminants in the technology of such type wastewater treatment.

The main tasks of the work are:

- to select effective flotation reagents and flotation process parameters;

- to compare the efficiency of the flotation method with the settling treatment of wastewater containing oil and fuel contaminants;

- to prove the expediency of use of a flotation method in the technological scheme of wastewater treatment from oil and fuel contaminants on a basis of experimental researches.

2. Materials and Methods

2.1. Model systems of highly dispersed emulsified wastewater

As a rule, highly dispersed emulsified wastewater contains many dispersed pollutants of different nature, for example, dispersed pollutants of inorganic nature, oil and fuel contaminants of organic nature. But in addition, emulsifiers and stabilizers are very often present; in most cases they are surfactants that get into wastewater with domestic or industrial flushing water, which contains a lot of detergents. Present surfactants in the wastewater are absorbed by their nature on the interface (Lanhe, 2004) dispersed contaminant-liquid, hydrophobizing the surface of a dispersed particle, and thus preventing it from settling in time, which leads to too stable emulsified wastewater. An effective purification of such waters requires special purification methods, as well as certain approaches to combine them with other methods in the technological scheme of purification process. Attention should also be paid to the concentration of the above contaminants. Wastewater can contain both high and low concentrations of various contaminants and can be stabilized or not, respectively.

Based on all the above, in this work the research objects were two types of model highly dispersed emulsified wastewater prepared in the laboratory.

The first type is model wastewater, similar in a composition to flushing wastewater, formed after washing an equipment for the transportation or storage of petroleum products, stabilized or not stabilized (in the presence or absence of emulsifier) with a certain content of dispersed contaminants.

The second type is model wastewater, which is similar in a composition to wastewater generated at the oil refinery after additional dehydration of oil received for refining. Such wastewater usually has a low concentration of dispersed contaminants and may contain a stabilizer.

Regarding the composition of wastewater, low-concentration (in terms of both fuel and oil and dispersed contaminants) model wastewater was prepared, containing:

0.15-0.18% of diesel fuel contaminants (type I model wastewater) or the same amount of oil contaminants (type II);

0.25-0.3% of dispersed contaminants, the same amount in both types of model wastewater;

0.003% of a stabilizer maximum.

Oil and fuel contaminants were added into model wastewater as direct oil or fuel emulsion obtained by the dispersion method, where a content of these contaminants was 1.5-1.8 g/dm^3, taking into account the density of corresponding oil or fuel. The oil emulsion was prepared on the basis of high sulphur oil from Kachanivka oil and gas condensate deposit in Ukraine. The fuel emulsion was prepared on the basis of a "summer" diesel fuel.

The size of oil and fuel contaminants (droplets) was estimated by the "turbidity spectrum" method to determine an average size of dispersed particles that are colourless, white or slightly turbid (Ivanov et al., 2009), and this size was 1-2•10^{-7} m. The size of dispersed contaminants (clay and/or carbonate particles) was determined by the sieve method (Chumak et al., 2017) and it was about 1-5•10^{-6} m.

Montmorillonite clay dispersed particles of this size from Cherkasy deposit of Ukraine were used as clay contaminants. We used an ordinary chalk crushed to the specified size as carbonate contaminants.

The anionic surfactant sodium dodecyl sulfate, NaDDS (manufactured in China) was used as a stabilizer. This surfactant was selected on the basis of a performed experiment to determine the stability of highly dispersed model wastewater, stabilized by surfactants of various types: nonionic - oxyethylated 12 mol dodecyl alcohol, OEDS (manufactured in Turkey), anionic - NaDDS, cationic - cetyltrimethylammonium bromide, CTAB (manufactured in Germany).

The experiment was performed by adding a certain dose of a surfactant to equal volumes of prepared model wastewater of each type. Model wastewater was settled for three hours, and then we determined the purification degree of wastewater. During this time emulsified wastewater was clarified by 30-40%, which confirms a stabilizing nature of surfactants.

The best stabilizer of emulsified wastewater was the anionic surfactant NaDDS. Wastewater is rich in anionic surfactants as waste products of various detergents. That is why NaDDS was used as a stabilizer in model systems in this investigation. Doses of this surfactant were determined experimentally.

2.2 Methods of delamination of highly dispersed emulsified wastewater

Settling and flotation methods were used to delaminate highly dispersed emulsified wastewater. The settling took place at room temperature 18-20 °C in the time range from 30 minutes up to 5.5 hours with sampling for analysis every 30 minutes.

The efficiency of mechanical settling methods of highly dispersed emulsified wastewater is insignificant and reaches 50-60% maximum, it is also described in the scientific literature (Dolina, 2005).

Flotation methods are much more effective than settling. The essence of flotation processes is an adhesion of inert gas bubbles to the surface of a contaminant, making its surface hydrophobic, with a formation of "particle-bubble" complexes, which float during a flotation and are removed from a foam layer of the surface of the liquid to be cleaned (Glembotskii, 1980). The flotation method of purification also provides reducing the values of biological and chemical oxygen demand (BOD and COD), removal of volatile components, dissolution of oxygen in water, in addition to the removal of mechanical impurities, dissolved and colloidal contaminants. The efficiency of a flotation process varies widely: from 20 to 90% depending on the use of flotation reagents, the method of gas dispersion, and, accordingly, the type of the flotation installation. In most cases the flotation method of treatment is used in local treatment plants to remove most of contaminants. The flotation process is in 4-6 times faster than the settling process with the same effect of contaminants removal (Stahov, 1983).

In this work, a flotation treatment of highly dispersed emulsified wastewater was carried out on a laboratory flotation installation of the pneumatic type (Fig. 1).

The flotation installation consists of a glass column *3* of a certain diameter and a certain height, which are selected depending on the flotation process. The bottom part of flotation column is a gas dispersant *4*, it is a glass Schott filter with a pore diameter of $1.6 \cdot 10^{-5}$ m for this installation. An air was blown through the Schott filter and bubbles of approximately the same size were obtained to remove contaminants by a flotation.

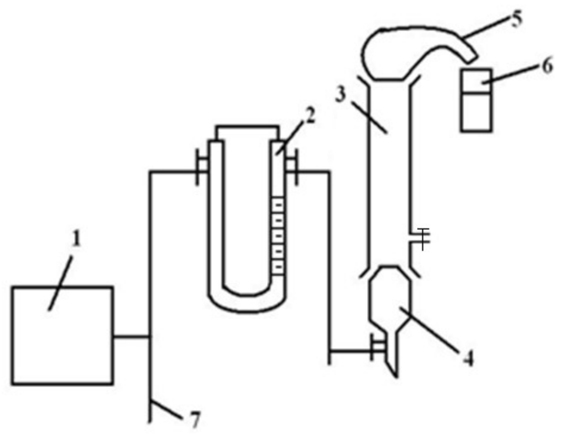

Fig. 1. *Flotation installation of the pneumatic type: 1 — source of compressed air; 2 — rotameter (flow meter); 3 — flotation column; 4 — removable porous baffles; 5 — foam receiver; 6 — a glass for foam collecting; 7 — clamp*

Columns with different volumes of wastewater supply from 0.05 to 0.2 dm^3 were tested for a flotation before the start of the research. Studies have shown that more amounts of treated wastewater require more air. An air cylinder was the source of gas. The flotation time varied.

The air flow rate is another important parameter for flotation, which was determined experimentally in this work. The method of estimating the amount of used air per sample is as follows.

50 cm^3 of water was poured into the flotation column. The air was passed through the column in such a way that the same volume of air was maintained by means of a clamp 7 (Fig. 1) on the flow meter (on one of the labels of the right calibration side of the flow meter). The top of a column is closed with a foam collector, to which a rubber hose was attached. The latter is brought under an inverted measuring cylinder filled with water and lowered into a container with water. The air supplied through a filter displaces a certain amount of water from a cylinder over time.

The speed of air passing through the filter is directly proportional to the volume of air passed through the filter and inversely proportional to the time of its passage $v = V/t$. Air flow U is determined by the formula:

$$U = \frac{v}{S} = \frac{V}{S \cdot t}\left[\frac{m^3}{m^2 \cdot s}\right],$$

where S – the area of the filter, which is calculated by the formula: $S = \pi d^2/4$, respectively, d is the diameter of the filter, measured three times (at different points of the filter), with an average value of the size $d_{av.} = 21.6 \cdot 10^{-3}$ m. Hence, the area of a filter is $S_f = 3{,}6625 \cdot 10^{-4}\ m^2$.

Thus, it was calculated the value of air flow, which was fed through a filter into the flotation column by fixing the clamp 7 (Fig. 1) on each of the labels of the right calibration side of the flow meter. The experimental data and results of calculations of an air flow are shown in the table 1, as an example, for the mark 10 on a calibration side of a flow meter.

Purified water samples were taken after flotation, analyzed by determining an optical density using a photoelectrocolorimeter KFK-2 (Russian Federation), designed to measure coefficients of transmission or optical density of solutions or dispersed systems in some parts of a wavelength range 315-870 nm. KFK-2 allows to determine the coefficients of transmission in the range from 100 to 5% (optical density from 0 to 1.5) with an error of measurement of transmission coefficients not more than 1% and is characterized by simplicity of research methods (Chudnovskij et al., 2019).

Table 1. *Air spending* for flotation of one sample of waste water*

$V_{w.w.}\cdot 10^6$, m^3	t gas passing, s	$U\cdot 10^3$, $m^3/(m^2\cdot s)$	$U_{av.}\cdot 10^3$, $m^3/(m^2\cdot s)$
50	315	0.4334	0.432
	316	0.4320	
	317	0.4306	
150	378	1.083	1.089
	376	1.089	
	374	1.095	
200	328	1.665	1.665
	326	1.675	
	330	1.655	

* mark 10 on the right calibration side of a flow meter

Optical density measurements were performed at a wavelength of incident light of 540 nm, using cuvettes with a working length of $5\cdot 10^{-2}$ m.

We estimate the degree of wastewater treatment α knowing the optical density of wastewater $D_{init.}$, and purified water D by the equation:

$$\alpha = \frac{D_{init.} - D}{D_{init.}} \cdot 100\%,$$

where optical density is the following ratio: $D = lg\ (I_0/I_p)$, and I_0 – the intensity of light falling on a cuvette with a solution; I_p – the intensity of light passed through a cuvette.

A significant role in the flotation process is given to the flotation time, i.e. optimal time is selected, during which the highest degree of purification of a sample is achieved. Flotation is considered impractical if the flotation time is more than 20 minutes, and the most optimal is 10 minutes, especially in laboratory conditions.

Industrial pneumatic flotation installations of a height of 3-5 m are designed for flotation time of 20-30 minutes; wastewater is supplied into the upper part, and air dispersed in bubbles of 1-10 mm is supplied into the lower part. The flow rate of the air supplied by the compressor is 0.25-0.30 $m^3/(m^2\cdot h)$ depending on a volume of wastewater. The speed of water movement in the flotation unit is 2-4 mm/s (Samygin et al., 2005).

3. Results and Discussion

Studies on the purification of highly dispersed emulsified wastewater containing fuel or oil contaminants were performed on model systems of two types, which are described in section 2.1 of this article. These model systems had a low content of dispersed contaminants and were studied without and in the presence of a stabilizer.

Model highly dispersed emulsified wastewater with fuel or oil pollution was settled for 5.5 hours, resulting in 53% purification of wastewater with fuel contaminants, and 60% – for wastewater with oil contaminants, respectively (Fig. 2).

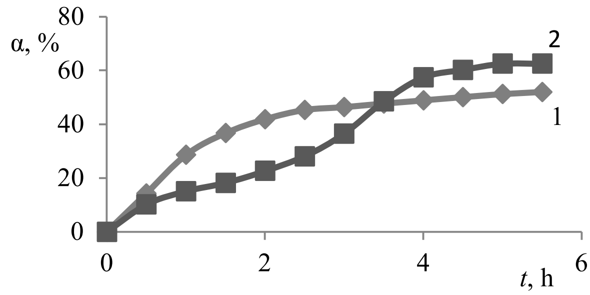

Fig. 2. *Dependence of the degree of purification of highly emulsified wastewater containing fuel (1) and oil (2) contaminants by settling in time*

You can see from the dependences on Fig. 2 that the purification of highly dispersed emulsified wastewater by settling in time is an inefficient process for this type of wastewater in terms of the degree of purification. In addition, this process requires a large amount of equipment (settling tanks-oil catchers) in the case of technological processes with significant volumes of wastewater of this type.

It is considered that the settling process is expedient if the settling time does not exceed three hours (Dolina, 2005).

The flotation method was used for the same model systems to increase a degree of purification of highly emulsified wastewater. Reagent-free flotation was carried out on a pneumatic type installation (Fig. 1). The results obtained in the form of graphical dependences are shown in Fig. 3.

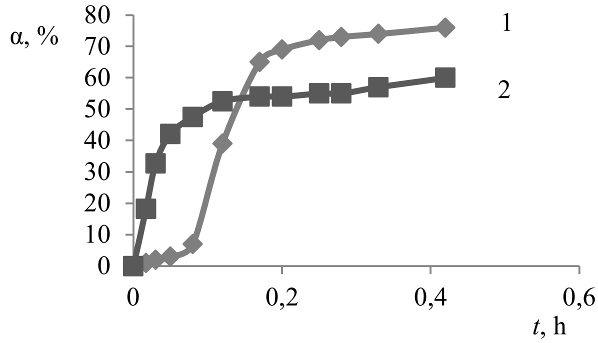

Fig. 3. *Dependence of the degree of purification of highly dispersed emulsified wastewater containing fuel (1) and oil (2) contaminants on the flotation time*

The flotation method of purification makes it possible to reduce significantly the purification time of highly dispersed emulsified wastewater containing fuel or oil contaminants, from 3-5 hours of purification by settling to 0.1-0.4 h (6-24 minutes), using reagent-free flotation. In addition, flotation method slightly increases the degree of purification (from 53-60% to 60-70%) of these waters – Fig. 2, 3.

The time of pneumatic flotation is considered appropriate if it does not exceed 20 minutes, including even industrial flotation installations at purification structures of plants with the formation of highly dispersed emulsified wastewater (Stahov, 1983). Flotation was performed for 10 minutes in further investigations of such wastewater purification in the laboratory conditions.

Reagent flotation is much more effective in the case of correctly selected flotation reagents like coagulants, surfactants and flocculants both individually and in mixtures with each other. Surfactants and flocculants are often used as effective additives to coagulants (Zapolskyi et al., 2000).

The effect of a coagulant – aluminum sulfate on the process of emulsified wastewater treatment was investigated in this work. Coagulant solutions were prepared with $Al_2(SO_4)_3 \cdot 18H_2O$ (manufactured in Turkey), which is often used in the treatment of both natural and wastewater. The effect of an anionic surfactant NaDDS was also investigated as one of the components of many types of wastewater.

Figure 4 shows the dependences of the degree of purification by different methods of highly dispersed emulsified wastewater containing fuel or oil contaminants from the dose of aluminum sulfate.

We see when comparing the dependences 1 and 3 (Fig. 4) that the coagulant aluminum sulfate affects the process of purification of highly emulsified wastewater from fuel contaminants by flotation, while the efficiency of a settling process of these wastewater does not change with the addition of this coagulant. The effect of coagulant on increasing the degree of purification (curve 2, Fig. 4) is insignificant in a flotation method, compared with reagent-free flotation (Fig. 3).

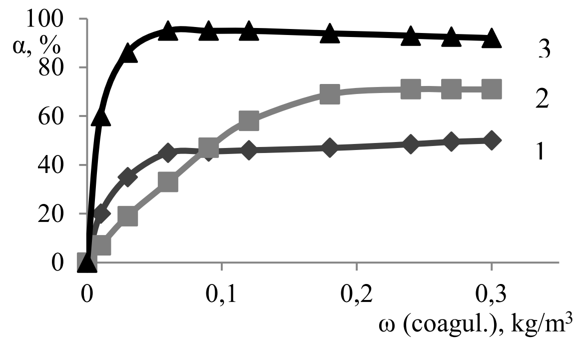

Fig. 4. *Dependence of the degree of purification of highly dispersed emulsified wastewater containing fuel contaminants by settling (1), and oil (2) and fuel (3) contamination — by flotation, on the dose of coagulant — aluminum sulfate*

If surfactants are present in highly dispersed emulsified wastewater, they stabilize wastewater by adsorption on the surface of fuel or oil contaminants and preventing contaminants from settling to the bottom of a settling tank-oil trap or floating to its surface. This behaviour of surfactants leads to the inefficiency of a settling process of highly dispersed emulsified wastewater containing a stabilizer. This is confirmed by the dependence 1 in Fig. 5.

As you can see, the degree of purification of wastewater containing fuel contaminants by settling is about 30%, which confirms the low efficiency of this process. In contrast, curves 2 and 3 show the effectiveness of this stabilizer in a process of wastewater purification by flotation. Here, anionic surfactant sodium dodecylsulfate is an effective flotation reagent. It significantly increases the degree of purification of highly dispersed emulsified wastewater contaminated with both oil (curve 2, Fig. 5) and fuel (curve 3, Fig. 5) by the method of reagent flotation comparing with the settling of these waters (curve 1, Fig. 5) and their purification by the method of reagent-free flotation (Fig. 3).

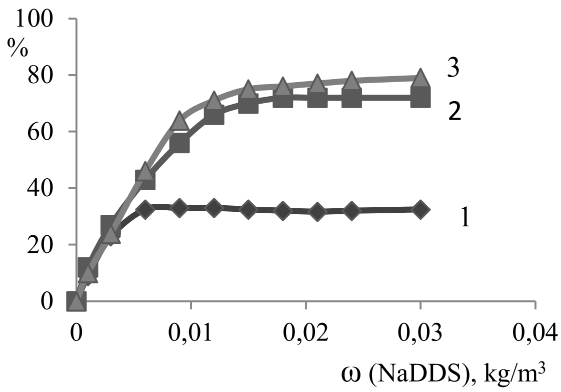

Fig. 5. *Dependence of the degree of purification of highly emulsified wastewater on the dose of anionic surfactant —- sodium dodecylsulfate for wastewater containing fuel*

contaminants, and purified by settling (1); for wastewater containing oil (2) and fuel (3) contaminants, and purified by flotation.

4. Conclusions

It should be noted based on the performed work the importance of choosing a method of wastewater treatment depending on the contaminants present in them. In addition, it is important to know the state of these contaminants (dispersed, highly dispersed, colloidal, suspended, emulsified) and their nature (organic, inorganic, hydrophilic, hydrophobic). All this makes it possible to properly select and effectively use wastewater treatment methods.

The research results showed that it is expedient to use a flotation method of treatment using pneumatic flotation units for emulsified wastewater containing fuel or oil contaminants with a low content of highly dispersed particles of inorganic nature or a stabilizer presence.

Analysing the results of the work, we see that a flotation method significantly reduces the purification time of highly dispersed emulsified wastewater from 3-5 hours of their settling in settling tanks-oil traps to 10-20 minutes by the method of flotation. The degree of purification of wastewater containing fuel contaminants increases in at least 1.5 times, i.e. from 52% when settling for 5.5 h up to 65% when flotation for 10 min and, accordingly, up to 75% when flotation for 20 min without any flotation reagents (Fig. 2 and 3).

There is no such a clear confirmation for wastewater with oil contaminants, although the time of treatment by flotation method is reduced by 16 times compared to settling, while the degree of purification of wastewater is 60%, which is quite good for reagent-free flotation. (Stahov, 1983).

Reagent flotation is much more efficient if the flotation reagents and their doses are selected correctly. In this work, aluminum sulfate was used as a coagulant, which was added to wastewater samples during settling and flotation. As the results showed (Fig. 4), the degree of purification of model wastewater containing fuel contaminants increases from 50% after settling, to – 92% after 20 min of flotation.

The effect of coagulant on the degree of purification of model wastewater containing oil contaminants is slightly smaller compared to model wastewater with fuel contaminants and is 71%, which is better compared to the degree of purification of this wastewater in the settling process ($\alpha = 62\%$).

As for the effect of anionic surfactants – NaDDS, this substance is ineffective ($\alpha = 33\%$) in a settling process for wastewater treatment, it mainly stabilizes contaminants.

The degree of purification of model wastewater of both types increases more than in 2 times – up to 79% and 72% (Fig. 5) – for model wastewater of type I and II, respectively, in a flotation process using this flotation reagent. If such a stabilizer is present in wastewater, it can be used as a flotation reagent in the process of its treatment by a flotation method.

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ВИКОРИСТАННЯ ФЛОТАЦІЙНОГО МЕТОДУ ДЛЯ ОЧИЩЕННЯ СТІЧНИХ ВОД, ЗАБРУДНЕНИХ НАФТОПРОДУКТАМИ

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Промислові та природні стічні води є одним із факторів забруднення навколишнього середовища, зокрема, його водного басейну. На ряду з іншими, паливні та нафтові забруднювачі відносяться до токсичних речовин, що наносять значну шкоду всьому живому. Для вирішування таких проблем, необхідно створювати технології з використанням ефективних методів очищення стічних вод. Враховуючи природу, стан та концентрацію забруднювачів у стічних водах, можна правильно підібрати та ефективно використати методи їх очищення. Це питання, які розглядаються в даній статті. Особлива увага приділена використанню флотації як методу очищення стійких високодисперсних емульгованих стічних вод, що містять нафтові або паливні забруднення, в технології очищення стічних вод такого типу. Основними завданнями були дослідження напрямлені на оцінювання впливу параметрів та флотореагентів на ефективність процесу очищення стійких високодисперсних емульгованих стічних вод. Флотацію цих стічних вод здійснювали на лабораторній флотаційній установці пневматичного типу і порівнювали з процесом їх відстоюванням в часі. Як показали проведені дослідження, для стійких емульгованих стічних вод, що містять нафтові або паливні забруднення з низьким вмістом високодисперсних частинок неорганічної природи або в їх складі присутній стабілізатор, доцільно застосовувати флотаційний метод очищення з використанням флотаційних установок пневматичного типу. Аналізуючи результати роботи, слід відзначити, що флотаційний метод значно скорочує час очищення високодисперсних емульгованих стічних вод з 3-5 год. їх відстоювання у відстійниках-нафтовловлювачах до 10-20 хв. методом пневматичної флотації, при цьому ступінь очищення стічної води зростає як мінімум в 1,5 – 2 рази в залежності від присутності паливних чи нафтових забруднень у стічній воді. Якщо у складі стічної води присутній стабілізатор, наприклад поверхнево-активна речовина, то його можна використовувати як ефективний флотореагент в очищенні такого типу стічних вод методом флотації., що зовсім не підходить для процесу відстоювання.

Ключові слова: *флотація, нафтопродукти, відстійник, стабілізатор, ПАР.*