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Purification of Oil-Containing Sewage with Synergetic Mixture

Key words: *oil wastewater, oil products, hydrated lime, ferric chloride, hydrolysis, hydrodynamic conditions, hlope-visible deposit model*

Annotation: *the possibilities of use of synergetic mixture (hydrated lime and ferric chloride) for purification of oil sewage are considered. The pilot studies showed the effectiveness of the use of such mixture for sewage disposal from oil products and particles of a solid phase. Models for calculation of the amount of the absorbed mixture are offered. The received results of the made experiments show that with a body height of concentration of reagents. Wastewater is very efficiently purified from impurity and becomes almost transparent. The advantage of the synergetic mixture in comparison with the use of hydrated lime and ferric chloride separately is shown.*

Introduction. Separation processes of oil emulsions are an important stage for preparation and purification of petroleum crude of water, the inorganic salts and various accompanying impurity of a solid phase (clay, sand, etc.) which are contained in naphtha. Separation processes of oil emulsions which purpose is the complete decrease of their aggregate, and kinetic stability are carried out in various paths: in gravitational (settling systems and other modifications), in centrifugal, electric and magnetic fields , and also with use of filtering through solid and fluid layers, with use of microwave and membranous technology. As a result of the division of oil emulsions sewage in which also to contain various oil products, including asphaltic connections, a solid phase and various by-products which are exposed to padding cleaning for rather pure receiving for practical use are formed. Purification of oil sewage from oil products is carried out by liquid-phase extraction (5) after which there is water with finely divided solids, giving it particular turbidity. In work (6) these purifications of waste oil waters of oil refineries are given in different stages. The oil content in the wastewater is 4000-16000 milligram/liter before the oil traps, after the oil traps 160-500, after the pond of additional sedimentation 70-300 milligram/liter, after filtering (sandy) 50-125 milligram/liter, after the biological post-treatment 15 -20 milligram/liter and after the second stage of biological purification 6-18 milligram/liter. The processes of sewage treatment from various refined and oil-producing products are currently carried out by adsorption, membrane, extraction and combined methods (3-5). After such treatment in wastewater, the content of petroleum products decreases to 25-35 milligram/liter, including 55-60% in the dissolved state a, 5-10 milligram/liter in emulsified form. Sewage of oil refineries after mechanical treatment is an aggregate-stable system. Therefore, for their purification, coagulation methods are used, as a result of which aggregate and kinetic stability is violated, larger aggregates of particles are formed which are removed from the sewage by precipitation.

The purpose of this work is to investigate the possibility of cleaning sewage oil water after preliminary purification from petroleum products using a synergistic mixture of hydrated lime and ferric chloride.

Experimental part. Taking into account the abovementioned, oil wastewater contaminated with various products was chosen as the research objects. Iron chlorides ($FeCl_3$, $FeCl_2$) were obtained from the waste of a tube plant (from scale) and PO Khimprom in place of $Al_2(SO_4)_3 5H_2O$, (7) for drinking water purification. The content of oil and oil products in waste water was determined by the weight method (8).

Figure 1 shows the scheme of a laboratory plant for treating sewage from impurities using a synergetic mixture. To purify wastewater from oil products and the solid phase as a coagulant, we used chlorine iron and hydrated lime (a synergistic mixture).

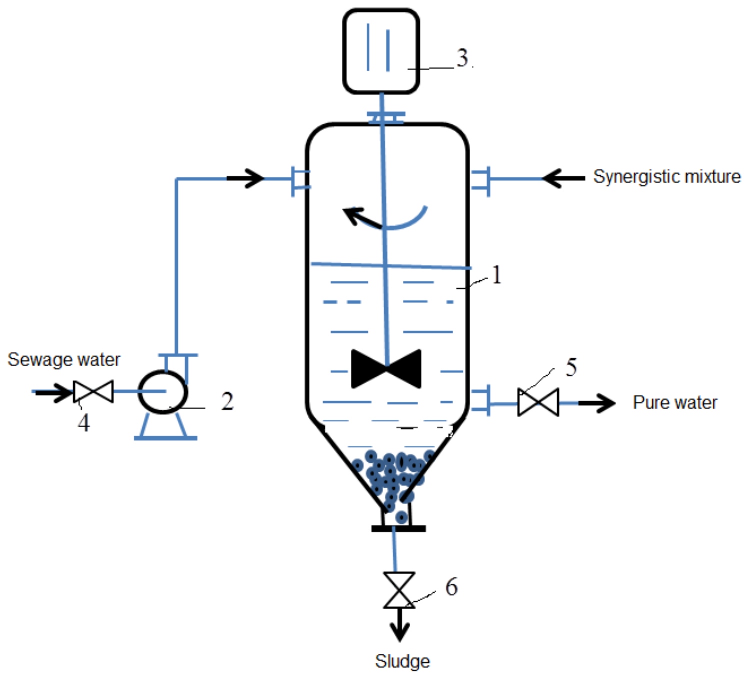

Fig. 1. Scheme of a laboratory sewage treatment plant: 1 stirrer; 2-pump; 3-electric motor with a stirring device; 4,5,6-valves.

With closed valves 5 and 6, 250 ml of sewage is pumped into a 1-l stirring device with pump 2, which also receives a synergistic mixture. At the first stage of the experimental study, only the scavenger in the form of hydrated lime is fed into the mixer as a synergetic mixture $Ca(OH)_2$.

Table 1. Treatment of sewage from impurities, depending on the amount introduced absorber-Ca (OH)$_2$. pH-7.46; d = 1071 kg/m^3; V = 250ml.

№	Slaked lime, g	pH	Color	Turbidity	Smell H_2S	C., mg / ml	
						Before cleaning	Before cleaning
1.	-	7,46	yellow	muddy	jarring	320	320
2.	0,1	7,60	"	"	"	"	315
3.	0,2	8,00	"	"	"	"	305
4.	0,4	8,50	"	"	"	"	300
5.	0,6	9,00	"	"	"	"	290
6.	0,8	9,50	"	"	"	"	280
7.	1,0	9,90	"	"	weak	"	264
8.	1,2	10,25	"	weak	"	"	255
9.	1,4	10,80	"	"	"	"	240
10.	1,6	11,30	yellowish	"	"	"	223
11.	2,0	11,60	"	"	"	"	200
12.	3,0	12,50	"	"	"	"	175

As follows from the data obtained, with the addition of an absorber, the amount of impurities in the system pH increases and the amount of impurity decreases. At a concentration of the absorber up to 3 g and in water remains 175 mg /l of sediment with a characteristic smell, color and turbidity. Using the data in the table, the amount of sediment can be determined from formula

$$C = C_0 \exp\left(-0.2C_1\right) \quad (1)$$

where C – the amount of impurity in wastewater, mg/l; C_1 – the amount of extinguished lime. At the second stage, in the mixer synergetic mixture of extinguished lime moves $Ca(OH)_2$ and $FeCl_3$

During the experiments it was observed that when ferric chloride is added to the sewage water as a result of hydrolysis, the iron hydroxide soluble in water is formed which is sorbed on the developed flocculent surface in the form of suspended, finely dispersed and colloidal particles which, under favorable hydrodynamic conditions, settle on the bottom of the sedimentation tank, forming a precipitate by the equation:

$FeCl_3$,+ $3H_2O$ = ↓$Fe(OH)_3$+3HCl ; $2FeCl_3$+$3Ca(HCO_3)_2$ =↓$2Fe(OH)_3$+$3CaCl_2$ +$6CO_2$

Acid, formed in the course of hydrolysis, is neutralized by extinguished lime. From the literature, it is known that the maximum value of sorption is observed by a hydroxide of iron in the environment closer to alkalescent. The isoelectric point of a hydroxide lies in this area; there is a falling of electrokinetic potential of all colloidal particles. Therefore, kinetic factors begin to prevail; there is a heteroagulation and oil products are besieged together with an iron hydroxide. The results of wastewater treatment from oil products, depending on the amount of coagulant, in the presence of hydrated lime are shown in Table 2.

Table 2. Wastewater treatment of impurities, depending on the amount of introduced $Ca(OH)_2$ и $FeCl_3$. pH =7,48; d=1072 $кг/м^3$; V=250ml.

№	$Ca(OH)_2$ g	$FeCl_3$ ml	pH	Color	Turbidity	Smell H_2S	C., mg / ml	
							Before cleaning	After cleaning
1.	-	-	7,46	yellow	muddy	jarring	320	320
2.	0,1	0,01	7,50	"	"	"	"	300
3.	0,2	0,02	7,60	yellowish	"	"	"	260
4.	0,4	0,03	8,00	"	weak	"	"	200
5.	0,6	0,04	8,50	"	"	weak	"	120
6.	0,8	0,05	8,90	"	"	"	"	80,0
7.	1,0	0,06	9,30	transparent	-	-	"	50,0

8.	1,2	0,08	9,80	"	-	-	"	50,0
9.	1,4	0,10	10,20	"	-	-	"	50,0
10.	1,6	0,20	10,70	"	-	-	"	50,0
11.	2,0	0,30	11,10	yellowish	-	-	"	50,0
12.	3,0	0,40	11,60	-	-	-	"	48,0

From the data of the table, it follows that in the presence of the absorber and coagulant in the system the pH of the medium gradually increases, and the color, turbidity, and odor remain. With increasing concentration of reagents (synergistic mixture), the content of these impurities also changes at a concentration of 1g Ca(OH)2 and 0.06 ml of ferric chloride solution, the water is completely cleared of impurities and becomes transparent. In our opinion, this depends on the acidity of FeCl3. Also, at this concentration, the turbidity and the smell completely disappeared. Such a picture, apparently, is due to the influence of the synergetic effect on the purification process.

It should be noted that water is simultaneously completely purified from the hydrogen sulphide present in the system (9, 10).

The change in the impurity concentration in water depends on the rate of change in the concentration of the synergistic mixture $C_S = C_1 C_2$ and is written in the form

$$\frac{dC}{dt} = k\left(C - C_\infty\right)\frac{dC_S}{dt} \qquad (2)$$

where C_1, C_2 - the concentration of hydrated lime (g) and ferric chloride (ml), C_∞ the concentration of impurity in the water after its purification, $k-$ is the rate constant. The solution of this equation is represented in the form

$$Ln\left(C - C_\infty\right) = -kC_1C_2 + A \qquad (3)$$

Here is A –the integration constant, which is determined from the condition: $C_S = 0,\ C = C_0 -$ initial impurity concentration in water in the absence of a synergistic mixture or $A = Ln\left(C_0 - C_\infty\right)$

Using the experimental data of Table 2 and expressions (2) and (3), the kinetics of the wastewater treatment process in the presence of a synergistic mixture can be described by the following equation

$$Ln\left(\frac{C-C_{\infty}}{C_0-C_{\infty}}\right)=-kC_1C_2$$
$$k=54.5 \tag{4}$$

The kinetic curve corresponding to the experimental data of Table 2 and model (4) is shown in Fig 2.

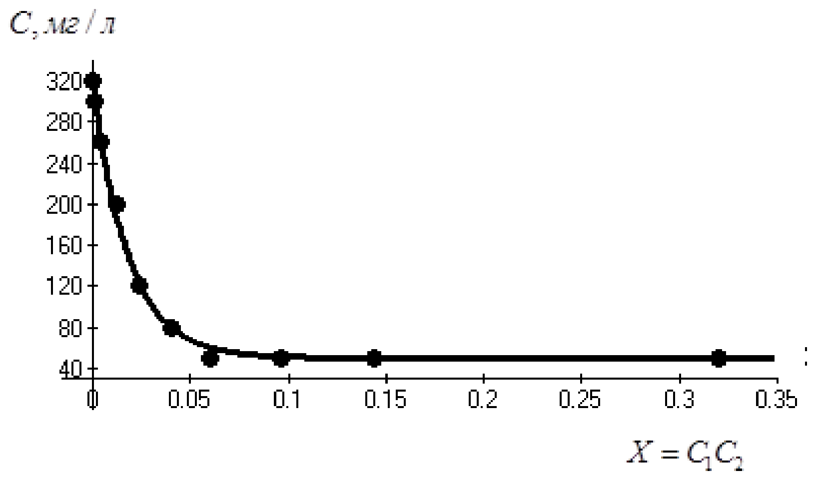

Fig.2. Correspondence of experimental data and calculations on the model (3).

Analysis and discussion of the results. An experimental study of the processes of cleaning oil wastewater from various petroleum products and solid particles using a synergistic mixture of hydrated lime $Ca(OH)_2$ and ferric chloride $FeCl_3$ showed satisfactory results.

Experimental studies show that the most acceptable concentrations are $C_1 = 1.0 г$ and $C_2 = 0.06 мл$. Further increase in the concentration of hydrated lime and ferric chloride does not affect the purification of water. The proposed models (1) and (4) describe quite satisfactorily the kinetics of wastewater treatment processes in the presence of a synergistic mixture. It should be noted that the wastewater treatment proposed by the method refers to the diffusion processes, which results in the formation of coagulation structures as a result of the coagulation of the impurity particles with the participation of the synergistic mixture with their further free precipitation in water, i.e. In general, the aggregate and kinetic instability of the system is observed.

A clearer picture of the spatial interpretation of the proposed methods for wastewater treatment from impurities is shown in Fig. 3

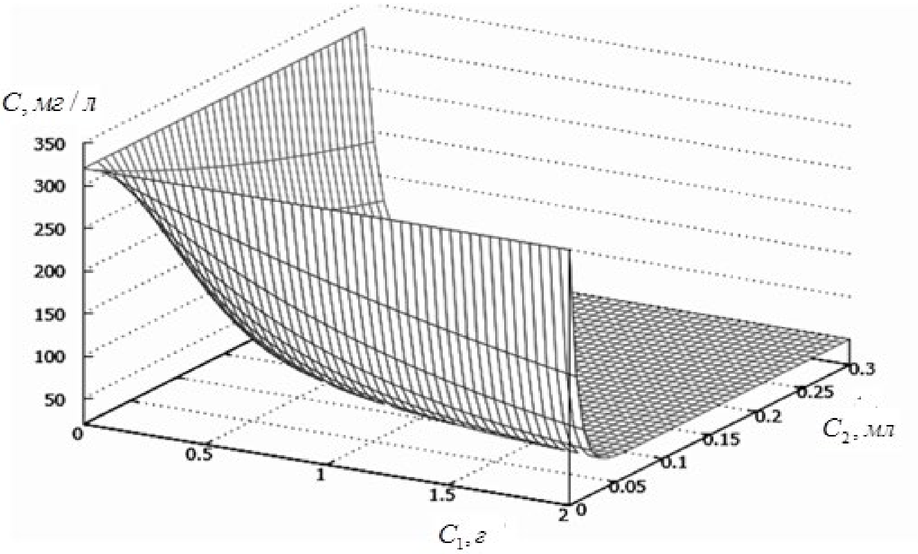

Fig.3. Three-dimensional interpretation of wastewater treatment processes.

As follows from Fig. 3, the degree of wastewater treatment with an increasing amount of synergetic mixture decreases and tends to a small constant value.

Thus, the results of laboratory tests on wastewater treatment from impurities using hydrated lime and chlorine gland obtained by production wastes confirm that these reagents can be successfully applied for the purification of oil effluents on an industrial scale while maintaining the corresponding proportions in the synergistic mixture.

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