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# PURIFICATION OF WASTE WATERS FROM OILS, LUBRICATING AND COOLING LIQUIDS

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**Introduction**

Recently for disinfection and purification of waste water from oils, lubricating and cooling waste liquids, and petroleum, a method of electrocoagulation have been proposed. It is very efficient and simple for local purification of small amounts of waste waters which are produced at auto service centers.

Electrocoagulators are compact, occupy small areas, and can be automated. The purification of oil-containing waste waters is based on the separation of phases, which is usually carried out by means of flotation and coagulation.

At large concentration of oils (C > 5 – 7 g/l) its removal is carried out by means of flotation, which allows to decrease concentration up to 60 – 68% [1]. For removal of residual oils up to the safe concentration or for purification of waste water with smaller concentration of oils, it is necessary to add coagulants for destabilization of emulsion, as in the diluted solutions oil droplets form very stable emulsions with water, additionally stabilized by superficial-active substances.

As soon as oil-in-water emulsions are charged negatively, electrogenerated hydroxide compounds of aluminum, received in electrocoagulators with soluble aluminum anodes [2], can be used for their destabilization. It is known [3], that the formed sedimentary of aluminum hydroxide with sorbed oil particles can be processed by thermal methods at temperatures 270 – 350$^{o}$C yielding organic-mineral sorbents, which are used for the further purification of waste water of dyes or others organic substances, which can't be decomposed by biological methods.

We investigated and developed a technology of waste water purification of emulsified oils with the application of electrogenerated aluminum coagulant, followed by the electroflotation.

**Results of research**

Waste water containing emulsified oils is characterized by pH = 5 – 10 and the contents of oils from 2 up to 3 g/l. Investigations were carried out in an electrochemical cell with soluble aluminum plane-parallel electrodes, mounted vertically, with the distance about 3 – 5 mm between them. Cell capacity was 1 l. The electrodes were connected through the rectifier to a source of the electric power. Under the action of the direct current the aluminum anode dissolves ($Al^{o} - 3e \rightarrow Al^{3+}$) and the quantity of dissolved aluminum can be determined according to the formula

$$m(\mathrm{Al}^{3+}) = \frac{\eta j t A}{96500 n}$$

where $m(\mathrm{Al}^{3+})$ is the mass of aluminum ions, g; $j$ – the direct current intensity, A; $t$ – the time of processing, s; $A$ – the atomic mass of aluminum; $n$ is the number of electrons in reaction of aluminum electrooxidation; $\eta$ is the current efficiency of aluminum ions.

Initial waste waters were acidified with HCl up to pH = 3.0 – 3.5, then processed in the electrochemical cell for some time, depending on the initial concentration of aluminum ions and current density. Afterwards, the processed water was transferred to the chamber of flocs formation, where destabilized particles form flocculas and flocs, which partially are being precipitated and removed. Further, water with the residual fine particles of aluminum hydroxide and absorbed petroleum was transferred into electroflotation cell with the insoluble electrodes, where under the influence of electrolytic gases, fine particles rise on a surface and being removed. The residual concentrations of aluminum ions and oils were determined in purified and filtered water according to technique [4].

**Results and discussion**

The obtained experimental results are shown in the tables 1 – 3.

*Table 1. Dependence of efficiency of waste water purification of emulsified oils on different dozes of the electrogenerated ions of aluminum. $pH_{init}$ = 3.5; C, $Al^{3+}$ = 80 mg/l; $C_{init}$ = 3 g/l*

| N | $m(Al^{3+})$, mg/l | residual concentration of oils, mg/l | separation efficiency, % |
|---|---|---|---|
| 1 | 40 | 97 | 96,8 |
| 2 | 60 | 43 | 98,6 |
| 3 | 70 | 31 | 99,0 |
| 4 | 80 | 24 | 99,2 |
| 5 | 90 | 20 | 99,3 |
| 6 | 100 | 15 | 99,5 |

From the obtained experimental results it is evident, that the most effective removal of emulsified oils takes place at the current density of 0.6 – 0.7 A/$dm^2$ and doze of aluminum ions up to 80 mg/l and low values of pH.

Preliminary researches [2, 5] have shown that for destabilization of colloid particles of oils an important meaning has the value of pH, which should be decreased up to 3.0 – 3.5, as the destabilization occurs due to suppression of dissociation of ionogen emulgators, included in the protective shells of oil particles, and on account of increase of quantity and charge of hydroxide compounds of aluminum, formed at lower meaning of pH [6].

*Table 2. Dependence of efficiency of waste water purification of emulsified oils on the current density. $pH_{init}$ = 3.5; $C_{init}$ = 3 g/l*

| N | *j*, A/$dm^2$ | Residual concentration of oils, mg/l | separation efficiency, % |
|---|---|---|---|
| 1 | 0.3 | 72 | 97.6 |
| 2 | 0.5 | 45 | 98.5 |
| 3 | 0.6 | 31 | 99.0 |
| 4 | 0.7 | 24 | 99.2 |
| 5 | 1.0 | 60 | 98.0 |
| 6 | 1.25 | 72 | 97.6 |
| 7 | 1.50 | 70 | 97.0 |

At the increase of solution pH and accumulation ions of OH- the hydrolysis of aluminum ions takes place that results in formation of hydroxide compounds like $\left[Al(OH)\right]^{2+}$, which are being polymerized and reduce its relative charge. The increase of pH of processable water results in increasing of aluminum and electric power consumption [5]. Hence, it is necessary to acidify waste waters before the electrocoagulation treatment. The process of acidification has some advantages. They are as follows.

1. Electrophoretic sedimentation of pollution on electrodes, due to the decrease of the charge of oil particles, is excluded;

2. The aggregate stability of emulsions due to the suppression of ionogen emulgators dissociation, is decreased.

3. Electric conductivity of emulsions is increased that results in decreasing of electric field intensity at electrolysis and power consumption decreased.

4. The ions of $Cl^-$ play the role of the activator for anode dissolution of aluminum, thus increasing an current efficiency up to 100 – 110%.

Anode current density is an important parameter at electrocoagulation waste waters purification of emulsified oils also. It is known [7], that the increasing of current density leads to the increase of the size of received particles of hydroxide compounds of aluminum, which neutralize negative particles of emulsified oils. At increase of the particles size a redistribution of their superficial charge takes place and at their mutual coagulation with the particles of emulsified oils, the equality of opposite charges is broken, that results in incomplete coagulation, irrespective of whether the quantity of added coagulant colloid is too big or too little. It may be accounted for that mutual coagulation of colloids can take place only in a narrow zone of ratios of their concentrations [8]. Besides, the increase of anode current density leads to the increase of the anode potential, that results in simultaneous aluminum anode dissolution and oxygen formation. In this conditions the current efficiency of aluminum decreases and, accordingly, separation efficiency decreases also. Therefore the optimum value of current density is about 0.6 – 0.7 A/dm$^2$.

The major stage in technology of the specified waste waters purification is the process of the deposit separation. In the electrocoagulator the dissolution of the aluminum anode and the formation of gaseous hydrogen at the cathode takes place. Gaseous hydrogen mixes a liquid intensively and promotes coagulation process, simultaneously, the flotation of disperse phase on the surface of liquid occurs. Though these processes take place partially and in one and the same device, they differ from each other both on the mechanism, and on conditions of their realization. It is established [9], that at realization of electrochemical dissolution of anodes in the range of pH = 3.0 – 4.0, when the metal of electrodes and electric power consumption on coagulation is minimal, the flotation proceeds more slowly, than coagulation. The equalizing of velocities of coagulation and flotation takes place only at pH = 6.0 – 6.5, however, because of sharp decrease of the coagulation velocity (for pH = 3.0 coagulation velocity is 3 times higher than at pH = 6.0) and growth of the voltage on the electrodes, the consumption of aluminum on purification is increased in 1.5 – 2 times, and electric power in 5 – 7 times.

Hence, it is not favorable and not effectively to combine these two processes in one device. Therefore we further investigated the process of deposit separation in the electroflotation device with insoluble electrodes. However, at first destabilized and coagulated particles moves to the chamber of flocs formation, where they form flocculas and flocs at the stage of slow hashing. After hashing (during 7 – 10 minutes) formed flocs partially are precipitated, catching fine colloid particles. The deposit is removed, however, after the sedimentation of large flocculas, the fine particles still present in water and must be removed also. To purify water of fine particles the water is processed with the help of a solution $Na_2CO_3$ up to meaning pH = 6.0 – 6.1 and then flows in electroflotation device, where at constant value of direct current occurs electrolysis of water with the formation of electrolytic gases ($H_2$ and $O_2$).

The bubbles rise on the surface the residual fine particles with adsorbed petroleum. The results of processing are shown in the table 3.

*Table 3. The dependence of efficiency of waste water purification of emulsified oils on current density and time of electroflotation*

| N | *j*, A/dm$^2$ | *t*, s | residual concentration of oils, mg/l | Separation efficiency, % |
|---|---|---|---|---|
| 1 | 0.5 | 300 | 35 | 91.2 |
| 2 | 0.6 | 300 | 32 | 92.0 |
| 3 | 0.7 | 300 | 28 | 93.0 |
| 4 | 0.5 | 360 | 29 | 92.7 |
| 5 | 0.6 | 360 | 25 | 93.7 |
| 6 | 0.7 | 360 | 23 | 94.2 |

Hence, for waste waters purification of emulsified oils it is necessary, to process them in the electrocoagulator device with soluble aluminum anodes at pH = 3.0 – 4.0, then in the chamber of flocs formation at slow hashing to remove large flocculas. The residual fine particles are removed by means of electrolytic gases in the electroflotation device at pH = 6.0 – 6.1 and current density of 0.6 – 0.7 A/dm$^2$ within 6 minutes. The purified water contains up to 23 – 25 mg/l of oils and can be directed on urban station of biological purification.

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**Summary**

The process of waste waters purification of emulsified oils by means of electrogenerated hydroxide of aluminum, received in the electrocoagulator at anode current density of 0,6 – 0,7 A/dm$^2$, after a stand in the chamber of flocs formation at slow hashing, was investigated. It is possible to achieve the purification up to 98 – 99% by using the electrochemical method, combining electroprocessing with the soluble aluminum anodes, and subsequent electrochemical processing with insoluble electrodes.

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# ТЕРМОДИНАМИЧЕСКИЕ УСЛОВИЯ ВОЗБУЖДЕНИЯ СТАБИЛЬНЫХ И ВОСПРОИЗВОДИМЫХ АВТОКОЛЕБАНИЙ С ЗАДАННЫМИ ПАРАМЕТРАМИ В КОМПЕНСИРОВАННОМ КРЕМНИИ

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## Введение

Автоколебательные процессы исследовались в различных полупроводниковых материалах [1 – 12]. Авторами [1, 2] обнаружены автоколебания тока в образцах Si, легированного Au и Cu с удельным сопротивлением $\rho \sim 10^4$ Ом·см при достаточно высоких электрических полях $E > 2\cdot10^3$ В/см и $T = 300$ К, в то время как в [3] показано, что в кремнии, легированном Zn, с $\rho \sim 10^4$ Ом·см наблюдаются колебания тока при $T = 240 - 300$ К. В работах [4, 5] такое явление подробно изучалось в Ge, легированном Ni, Au и Mn. Результаты этих исследований показали, что для возбуждения автоколебаний образцы должны иметь удельное сопротивление $\rho > 10^4$ Ом·см, при этом они наблюдаются в интервале температур $T = 250 - 300$ К. Авторами [7 – 10] исследовались автоколебания тока в различных полупроводниковых соединениях. Установлено, что это интересное физическое явление наблюдается при $E > 10^3$ В/см в интервале температур $T = 77 - 200$ К при освещении монохроматическим светом $\lambda = 0{,}5 - 2{,}5$ мкм, когда образцы имеют достаточно высокое удельное сопротивление, а также при наличии внешних воздействий (магнитного поля, интегрального освещения и т.д.).

## Теоретический анализ

Анализ результатов указанных работ позволяет сделать следующие выводы:

1. Наблюдаемые автоколебания нестабильны по параметрам, трудно воспроизводимы, не установлены термодинамические условия возбуждения и закономерности изменения параметров автоколебаний в зависимости от физических параметров материала.

2. Колебания тока в исследуемых материалах наблюдаются при достаточно высоких электрических полях, в узком интервале температур и при освещении светом с определенной длиной волны.

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