Application of high molecular weight flocculants for the purification of oily waters

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Abstract. In flotation separators, to intensify the purification process, the method of preliminary reagent treatment is used with a combination of solutions of mineral coagulants and organic flocculants. This method causes the corrosive activity of water, a significant amount of sediment, and secondary water pollution with products of hydrolysis of mineral salts. The above disadvantages are not typical of the method of preliminary treatment of oily waters with ionogenic high-molecular flocculants, which is used in the practice of coastal treatment of oily waters. The paper presents the results of the experimental studies on the use of high-molecular flocculants for the preliminary reagent treatment of bilge water sent to the flotation unit. The following high-molecular flocculants were investigated: Praestol 852, Praestol 853, Praestol 2540. It was found that Praestol 853 provides the highest degree of oil pollution recovery from the bilge water solution. The fractional composition of oil products in bilge water was analyzed before and after cleaning. It was determined that in the flotation cleaning, coarse and medium-dispersed particles of oil pollution are completely extracted.

1. Introduction
To intensify the flotation process in ship bilge water separators, the method of preliminary reagent treatment is used. It involves the destabilization and coalescence of particles of fine oil-water emulsions achieved by preliminary treatment of bilge water entering the skimmer with reagent solutions. When treating ship bilge waters, mineral coagulants and organic flocculants are used together; inorganic electrolyte coagulants (aluminum and iron salts) neutralize charges of fine particles and polymer flocculants enlarge neutralized particles [1].

A cardinal way of improving the technology of preliminary reagent treatment of wastewater is the use of cationic and anionic organic flocculants, which both neutralize and enlarge particles.

High-molecular flocculants - Praestol 852, Praestol 853, Praestol 2540 - have been successfully used for the reagent treatment of oily water at onshore treatment facilities. The organic flocculants reduce the corrosiveness of water, the consumption of reagent dozens, the amount of sediment, and increase the purification efficiency [2].

2. Problem statement
Numerous studies on regularities of flocculation of dispersed systems established that the efficiency of the process is determined by a number of independent and interrelated factors [2, 3].

When choosing a flocculant for preliminary reagent treatment of bilge water, priority factors should include characteristics of the dispersed phase (nature, dispersion and sign of the pollution charge) and...
the dispersed medium (content of suspended solids, surfactants, content of mineral salts). In addition to oil particles, the composition of ship bilge waters includes detergents, chemicals, and solid particles that have a stabilizing effect on oil particles [4].

In addition, the priority factors are characteristics of the flocculant - charge, kinematic viscosity of the solution, molecular weight, charge density of flocculant solutions.

When choosing an optimal flocculant for the reagent treatment, one should take into account the flotation method of extracting large neutralized oil particles from the bilge water solution and the accumulated experience in the treatment of similar types of polluted water.

3. Materials and methods

Research on the selection of a flocculant for the reagent treatment of bilge water entering the flotation unit was conducted on real bilge water delivered from collecting vessels (Novorossiysk).

At the initial stage, the following indicators of the initial bilge water were analyzed: concentration of oil products and their fractional composition.

To determine the fractional composition of oil particles in bilge water, the Goryaev counting chamber (a device designed to count the number of drops in a given volume of liquid) and the microscope were used. The concentration of oil products was determined by the fluorimetric method on the "Fluorat-02-3M" fluid analyzer.

The following high-molecular flocculants were analyzed: Praestol 852, Praestol 853, Praestol 2540. Praestol granulated powder flocculants are produced by Solenis LLC (Perm).

![Figure 1](image_url)

**Figure 1.** The scheme of the laboratory setup: 1 - reservoir of initial solution, 2 - reservoir of flocculant solution, 3 - flotation device, 4 - air disperser, 5 - foam mass outlet, 6 - purified water reservoir, 7 - compressor.

Experimental studies were carried out on a specially designed and manufactured pilot plant (Figure 1). The experimental installation for the flotation treatment included the following units: an aeration chamber (3), tanks (1, 2, 6), a compressor for air supply (7). Flocculant Praestol was added to the feed water as a 0.3% solution. The air disperser (4) was made of cermet; based on the particle size of impurities (Table 1), it formed air bubbles with a diameter of 0.5-1 mm. Branch (5) is intended for the periodic removal of oil concentrate.
4. Results

At the first stage, the fractional composition of oil particles in the initial bilge water was determined. The results are presented in Table 1 and in Figure 2.

Table 1. Disperse composition of oil products in bilge water

| Concentration of petroleum products, PPM | Particle size of petroleum products (average data) | % |
|-----------------------------------------|-----------------------------------------------|----|
|                                         | micron                                       |   |
|                                         | < 0.1                                        | 19.6 |
|                                         | 0.1 – 10                                      | 28.6 |
|                                         | 10 – 40                                       | 24 |
|                                         | 40 – 100                                      | 13.4 |
|                                         | > 100                                        | 14.4 |
| 420 - 570                               |                                              |    |

As follows from the analysis of the material, the content of coarse impurities (> 100 μm) in the oilwater emulsion of bilge waters is ~ 14.4%; the size of medium-dispersed particles ranged from 10 to 100 microns ~ 37.4%; the share of fine particles, incl. colloidal impurities with a particle size of less than 10 microns was ~ 48.2%. Thus, bilge waters are polydisperse multiple emulsions, while half of the pollution is microheterogeneous systems. An analysis of the fractional composition of bilge water under the microscope showed that all the water samples had a heterogeneous structure, contained oil particles in the form of lenticular round or oval droplets with clear edges [5].

A variety of the phase-dispersed state of oil pollution in bilge waters predetermines the need for experimental studies when choosing the most effective reagent.

Experimental studies on the most effective flocculant were carried out on bilge water with an initial concentration of oil products equal to 350 PPM. The results are shown in Figure 3 (averaged data).
Figure 3. Dependence of the cleaning efficiency on the flocculant dose: E1 - Praestol 853, E2 - Praestol 852, E3 - Praestol 2540

An analysis of the experimental material indicates that the highest degree of oil pollution recovery from the bilge water solution is provided by high-molecular cationic flocculants; Praestol 853 turned out to be the most effective one. At the same time, the content of oil products in the purified water is 28 - 30 PPM.

The degree of oil pollution recovery from the bilge water solution using Praestol 2540 does not exceed 38%.

The high efficiency of cationic flocculants is due to the negative charge of emulsified particles of petroleum products, as well as the presence of other anionic groups in the bilge water solution.

With an increase in the dose of cationic flocculants over 3 mg/l, the efficiency of the purification process decreases. A similar result may be due to the formation mechanism of destabilized emulsion systems. The cationic flocculant absorbs macromolecules on the surface of dirt particles. With an excess of flocculant in the solution, when the particles are completely covered with polymer macromolecules, their stabilization occurs and the cleaning efficiency deteriorates [2, 3].

At the final stage, the fractional composition of particles of petroleum products in purified water was analyzed. Table 2 and Figure 4 show the dispersed composition of oil products in bilge water after the flotation treatment with Praestol 853.

Table 2. The disperse composition of oil products in purified bilge water

| Concentration of oil products, PPM | Particle size of oil products (average data) |
|------------------------------------|---------------------------------------------|
|                                    | micron | %    |
| < 0.1                             |        | 59.4 |
| 0.1 – 10                           |        | 40.6 |
| 10 – 40                            |        | –    |
| 40 – 100                           |        | –    |
| > 100                              |        | –    |
| 30 – 35                            |        | –    |
Figure 4. Fractional composition of oil products in bilge water after flotation treatment

In the flotation treatment, coarse (> 100 µm) and medium-dispersed (10 - 100 µm) particles of oil products are completely removed from the bilge water. Fine particles of oil pollution remain in the purified water; these pollutants can be extracted using adsorption filters.

5. Conclusion
The study proved the expediency of using Praestol 853 for the preliminary reagent treatment of bilge water sent to the flotation unit. The cationic flocculant used instead of a combination of reagents (mineral coagulant – flocculant) allows us not to increase the corrosive activity of water, to reduce the consumption of the reagent, to reduce the amount of sediment, and to purify water.

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