
ЕКОЛОГІЯ ТА РЕСУРСОЗБЕРЕЖЕННЯ

УДК 628.349.087.4

Marta VOZNIUK, Tetiana SHABLIY*
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»

EVALUATION OF THE ELECTROFLOTATION EFFICIENCY FOR THE OIL-CONTAINING SHIPPING WATERS TREATMENT

The article describes the problems of formation and purification of ship oil-containing waters. The effectiveness of electroflotation using aluminum and iron anodes for the extraction of oil from water-oil emulsions with different mineralization was assessed.

Electroflotation treatment of water-oil solutions provides 98.6–99.9 % oil removal using aluminum or iron electrodes at an anodic current density of 1.65–7.39 A/dm² for highly mineralized waters and 0.07–0.50 A/dm² for fresh water. Water treatment during the first 15 minutes provides a sharp decrease in oil content from 100 mg/dm³ to 1.31–2.52 mg/dm³, almost regardless of the type of anode metal. The efficiency of oil extraction from water mainly depends on its mineralization. In mineralized (salty) water, the treatment process is more efficient. In fresh waters, aluminum anode provides higher water purification efficiency compared to iron anode. However, in the case of pre-treatment of the iron anode with an alkali solution with the formation of a magnetite layer on it, this anode is characterized by the highest purification efficiency for low-salt waters, providing a degree of water purification at the level of 99.9 %.

Keywords: oil-containing waters, bilge water, electroflotation, ship wastewater, electrolysis, aluminum anode, iron anode.

DOI: 10.20535/2617-9741.3.2023.288252

* Corresponding author: dsts1@ukr.net

Received 12 July 2023; Accepted 14 September 2023

Formulation of the problem. Over the past 50–60 years, there has been a rapid development of shipping [1]. To date, high-tonnage transportation is carried out almost entirely by world shipping [2]. The increase in the tonnage of the sea fleet and the reduction of transportation time have led to the emergence and development of anthropogenic influence on the ecology of aquatic ecosystems, especially in the areas of sea routes.

The problems associated with the pollution of the water environment by oil and oil products cause a special danger. In this regard, the issues of increasing man-made safety of objects contaminated with oil products and minimizing the man-made load on the components of the natural environment are becoming more and more relevant.

The analysis of sources [3] and forms of oil pollution made it possible to establish that in the total amount of incomes:

- 23 % are discharges from ships into the sea of washing and ballast water, i.e. pollution associated with the normal operation of ships;
- 17 % is due to discharges of oil and oil products in ports or near-port water areas, including losses when loading bunkers of bulk vessels;
- 10 % comes from the shore together with industrial waste and wastewater containing emulsified, dissolved and film oil;
- 5 % is brought by storm drains in the form of emulsified, dissolved and film oil;
- 6 % is associated with disasters of ships, drilling stations at sea, when continuous fields and films of emulsified or dissolved oil are formed;
- 1 % from offshore drilling, these contaminants consist of emulsified, dissolved and film oil;
- 10 % is oil that comes from the atmosphere in a dissolved and gaseous state;
- 28 % are brought by river waters containing oil in all its various forms.

The last two sources are "transporters": they collect oil pollution from various objects located far from the sea and carry it to the ocean.

Therefore, the largest part of pollution of the hydrosphere by oil and oil products relates to the discharge of washing, ballast and bilge waters.

On the one hand, oil is a natural component, and on the other hand, it acts as a serious pollutant if it enters the environment. Pollution of the environment with oil and oil products leads to a violation of the ecological balance and natural balance of ecosystems, changes in the ecological and trophic groups of biocenoses, toxic effects on all living organisms, including negative consequences for humans.

Analysis of previous studies. The US Environmental Protection Agency describes the effect of an oil spill as follows: 10 minutes after 1 ton of oil enters the water, an oil slick 10 mm thick forms. In the future, the thickness of the film decreases (to less than 1 mm), but the spot expands – 1 ton of oil can cover the area of the water mirror up to 12 km². The environmental effects of oil spills are usually felt over months or even years, especially in cold waters where the microbiological transformation of oil is slow.

The legal basis for protecting the marine environment from pollution is reflected in the International Convention for the Prevention of Pollution from Ships (MARPOL-73/78) [4]. The convention served as an incentive for the implementation of a technical solution for the indication and ranking of pollution sources, the development and implementation of installations and systems for the purification and disinfection of wastewater on ships.

Thus, according to the 1978 protocol (MARPOL Convention 73/78), it is allowed to discharge purified sewage water with a concentration of petroleum products of no more than 15 ppm (15 mg/dm³) overboard in international waters. In the future, it is planned to further strengthen the requirements to reduce the permissible content of petroleum products in water discharged into the sea to 5 ppm.

There are two main types of oil-containing water coming from a ship: ballast water and bilge water.

To ensure the stability of the vessel, after they are freed from oil, the tanks are filled with onboard water (ballast), as a result of which this water eventually mixes with oil residues, and polluted oil-containing waters are formed.

The amount of dirty ballast is usually much greater than the amount of fresh water. Bilge waters are a collection of waters from the ship's sewage wells, which are located in the lower part of the ship. They may contain contaminants that come during disassembly, washing, repair and filling of various mechanisms. Also, these waters may contain surface-active substances used for washing mechanisms. The presence of surfactants causes the formation of stable oil-water emulsions. A characteristic feature of bilge waters is the small content of suspended substances in them.

It is the discharge of the listed wastewater that causes great damage to the hydrosphere.

Due to the lack of reliable and effective technical means of treating large volumes of ballast water and highly polluted bilge water in world shipping, these waters are most often sent to coastal treatment facilities. However, in accordance with the requirements of MARPOL, water treatment facilities are installed on sea vessels, which are intended for the treatment of drinking water only. It is assumed that, depending on the size of the vessel and its age, polluted water in the amount of no more than 50 m³/hour can accumulate in the vessel's bilges every day [5–7]. Therefore, according to recommendations, the productivity of local sewage treatment plants should not exceed 50 m³/h.

The content of oil products in bilge waters depends on the age of the ship and the type of ship's power plant and, on average, is 2000–3000 ppm (2–3 g/dm³). The relative density of oil products contained in the drinking water is within 0.84–0.99 g/cm³. The hydrogen index (pH) of these waters is in the range of 5.9–8.5.

Bilge waters are characterized by a wide morphological composition, which determines the methods of their purification. Thus, petroleum products can be in an insoluble state (particle size greater than 100 μm), in an emulsified state (particle size 0.1–100 μm), in a colloidal state (particle size 0.001–0.1 μm), in a dissolved state (particle size less than 0.001 μm).

The market offers many technologies for the treatment of oil-containing waters generated on ships. However, such limitations as: purification efficiency, availability of space, cost of implementation and level of environmental friendliness play an important role in using a specific type of water treatment system.

Among the main methods of oil-containing waters treatment are physical, chemical, and biological methods [8]. Each method has its advantages and disadvantages. Therefore, combined methods are often used to increase the efficiency of purification.

Physical purification methods are characterized by ease of implementation and low cost. However, the limiting feature of these methods is the limitation of isolating particles of different morphological composition [9]. In particular, the efficiency of removing emulsified oil, the fraction of which is the largest in oil-containing waters, and surface-active substances is too low. In addition, in the case of applying filtration, the issue of generation and disposal of washing water arises [10].

Sorption methods are characterized by high purification efficiency and compact placement of equipment. However, it should be noted that among the disadvantages of these methods are the high cost of technological equipment and the need to regenerate spent adsorbents [11].

Among the advantages of biological methods of water purification from oil and oil products [12–14] highlight the absence of additional chemical pollution and the low cost of the process. Among the shortcomings of this group of methods, the low efficiency of water purification, the duration of the process, and the difficulty of purifying large volumes of water are noted.

Electrochemical methods, electrocoagulation in particular, [15–18], and electroflotation [19], meet all the main requirements: a high degree of pollutant removal, processing speed, small size of the equipment [20]. The disadvantages of electrochemical methods include energy costs, the high cost of consumables, and the likelihood of electrochemically dissolved substances entering the environment. Aluminum and iron [15, 17] plates or cylinders are usually used as soluble anodes [21, 22]. To some extent, the degree of water purification depends on its mineralization [18], and this must also be considered during water treatment.

In general, due to the ease of carrying out the process of water purification from oil and oil products by electrochemical methods, the latter are promising. To overcome the shortcomings inherent in electrochemical methods, it is advisable to conduct additional research on the influence of operating parameters on the process.

The purpose of this work was to evaluate the effectiveness of electroflotation treatment of water from oil using aluminum and iron electrodes.

To achieve the set goal, the following scientific tasks must be solved:

1. To determine the efficiency of electroflotation removal of oil from water using aluminum electrodes, depending on the anode current density and the initial water mineralization.
2. To establish the dependence of the efficiency of water purification from oil by the electroflotation method using iron anodes on the salinity of dissolved substances in water and the anode current density.
3. To evaluate the effectiveness of using iron and aluminum anodes for purification of oil-containing waters by the electroflotation method.

Methodology of work. In this work, a single-chamber 500 cm³ electrolyzer was used. The areas of the electrodes were the same – SA=SK=0.26 dm². The distance between the plates was 0.065 m. A metal plate made of alloy steel 12X18H10T was used as the cathode. Aluminum or iron plates were used as anodes. In a number of studies, the iron electrode was covered with a layer of magnetite. For this, the iron plate was boiled in a solution of alkali (pH 9.5) at a temperature of 100 °C for three hours.

A direct current source was used for electrolysis. Research was conducted on model water-oil solutions, the salinity of which is similar to fresh and sea water: 1 – 100 mg/dm³ of oil, 200 mg/dm³ of sodium chloride; 2 – 100 mg/dm³ of oil, 30 g/dm³ of sodium chloride.

Electrolysis was performed at a fixed voltage in the range of 10–20 V. At the same time, the anodic current density was in the range from 0.07 A/dm² (0.02 A) to 7.39 A/dm² (2.02 A). The total time of electroflotation was 60 minutes. Samples for analysis were taken from the lower part of the electrolyzer every 15 minutes and after filtering, the following were determined in them:

- residual oil concentration by spectrophotometric method;
- concentration of chloride ions by argentometric titration;
- pH of the medium by the potentiometric method.

The degree of purification of water from oil (Z , %) was calculated according to the formula:

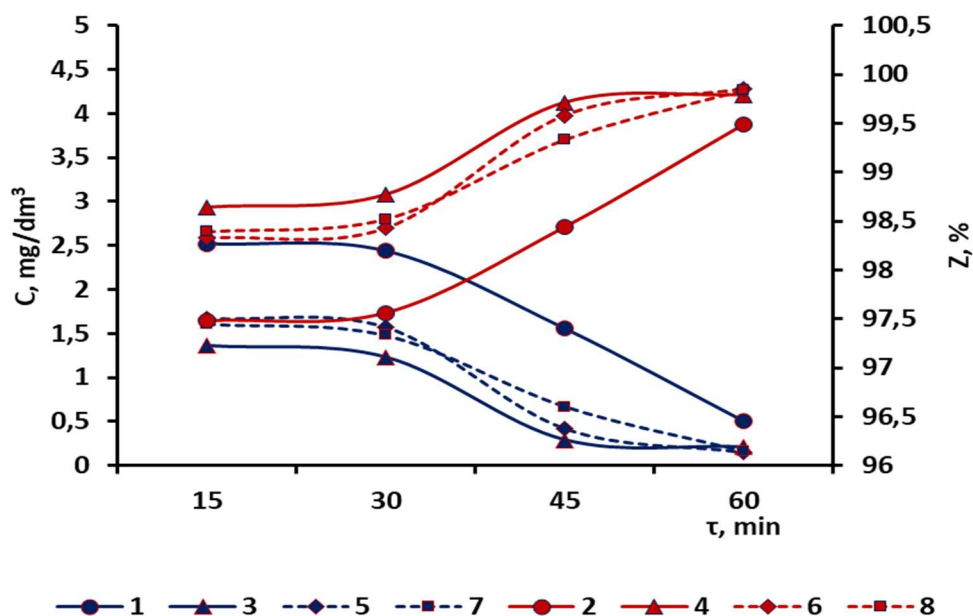
$$Z = \left(1 - \frac{C}{C_0}\right) \cdot 100, \% \quad (1)$$

where C – final concentration of the component after water treatment, mg/dm³; C_0 – initial concentration of the component after water treatment, mg/dm³.

Presentation of the main material. Due to the high efficiency of water purification and the ease of implementation of the process, electrochemical methods are considered to be one of the most promising methods of water purification from oil and petroleum products both in ship and stationary purification systems.

At the first stage of the work, research was conducted to determine the efficiency of using aluminum electrodes in the processes of electroflotation water purification.

Electroflotation treatment of oil-containing water ($C_{oil}=100$ mg/dm³) in a single-chamber electrolyzer with an aluminum anode allows to achieve a high degree of pollutant removal (Fig. 1.).



1, 2 – sea water, $U=10\text{ V}$; 3, 4 – sea water, $U=20\text{ V}$; 5, 6 – fresh water, $U=10\text{ V}$; 7, 8 – fresh water, $U=15\text{ V}$

Fig. 1 – Reducing the concentration of oil in water (1, 3, 5, 7) and increasing the degree of water purification (2, 4, 6, 8) with the time of electroflotation of water-oil solutions (100 mg/dm^3 oil, 30 g/dm^3 NaCl (1, 2, 3, 4); 100 mg/dm^3 oil, 200 mg/dm^3 NaCl (5, 6, 7, 8)) in single-chamber electrolyzer ($V=500\text{ cm}^3$, $U=10\text{ V}$ (1, 2, 5, 6); 15 V (7, 8); 20 V (3, 4); $j=1,65\text{ A/dm}^2$ (1, 2); $6,69\text{ A/dm}^2$ (3, 4); $0,37\text{ A/dm}^2$ (5, 6); $0,36\text{ A/dm}^2$ (7, 8)) when using an aluminum anode

During 15 minutes of electroflotation of a model mineralized solution that imitated polluted sea water (30 g/dm^3 of sodium chloride, 100 mg/dm^3 of oil), at a voltage of 10 V ($j=1.65\text{ A/dm}^2$), the concentration of oil decreased from 100 mg/dm^3 to 2.52 mg/dm^3 , which corresponded to a degree of water purification of 97.48% .

As the electroflotation time increased to 1 hour, the concentration of oil in water decreased to 0.51 mg/dm^3 , while the degree of oil removal was ensured at the level of 99.49% .

Increasing the voltage in the system to 20 V ($j=6.69\text{ A/dm}^2$) significantly improved the purification process. Residual oil concentrations decreased by half compared to the results of the water treatment process at a voltage of 10 V . Thus, in the first 15 minutes, the oil concentration decreased to 1.36 mg/dm^3 ($Z=98.64\%$), and then within an hour the concentration of the pollutant decreased to 0.21 mg/dm^3 ($Z=99.49\%$).

Under the same initial conditions ($U=10\text{ V}$, aluminum anode, $C_{\text{oil}}=100\text{ mg/dm}^3$), the purification of fresh water from oil was much better than in the case of mineralized water purification. Thus, in the first 15 minutes, the concentration of oil in lightly mineralized water decreased to 1.67 mg/dm^3 ($Z=98.33\%$), and in seawater decreased during the same period to 2.52 mg/dm^3 ($Z=97.48\%$).

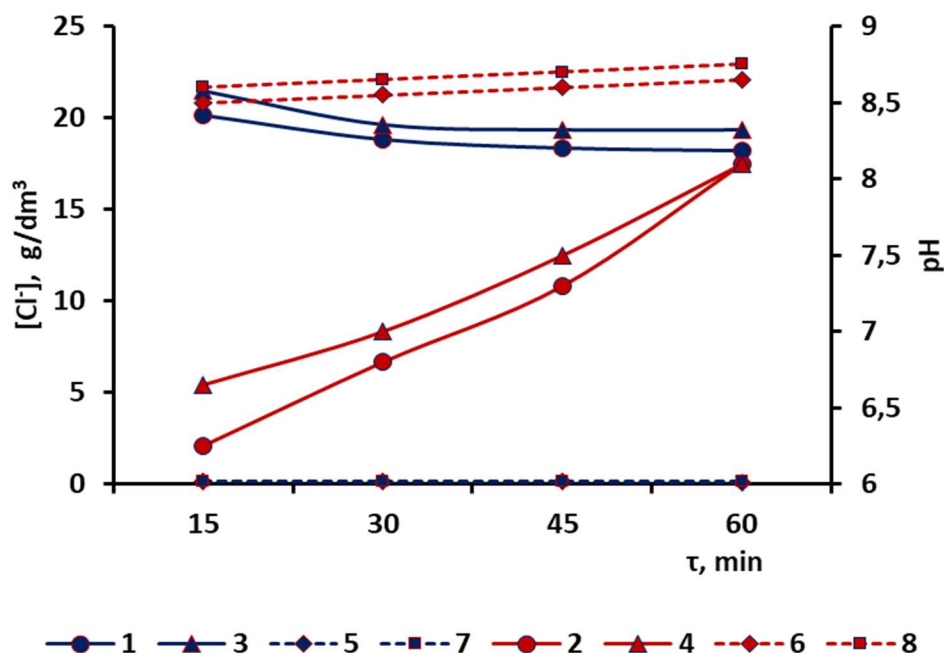
Increasing the electroflotation time to 60 minutes, as in the case of seawater, contributed to the reduction of the residual oil concentration. In fresh water, after an hour of treatment, the residual concentrations of the pollutant were significantly lower compared to mineralized water. Thus, after 1 hour of electroflotation of weakly mineralized water, the residual concentration of oil was 0.15 mg/dm^3 ($Z=99.85\%$), at the same time, the residual concentration of the pollutant in salt water was 0.51 mg/dm^3 ($Z=99.49\%$).

In the case of freshwater treatment by the electroflotation method, increasing the voltage from 10 V to 15 V ($j=0.36\text{ A/dm}^2$) did not contribute to an increase in the degree of purification, which remained at the level of 99.84% ($S_{\text{res}}=0.16\text{ mg/dm}^3$).

It should be noted that significant resistance in the system was observed in freshwater solutions. The current strength was at the level of $0.07\text{--}0.1\text{ A}$ (anode current density was 0.36 A/dm^2 on average) at a voltage of $10\text{--}15\text{ V}$.

Regardless of the mineralization of the source water, the maximum decrease in oil concentration took place in the first 15 minutes. However, with the duration of the water treatment process up to 60 minutes, active removal of oil was observed.

During electroflotation, the residual concentration of chloride ions and the pH of the medium were simultaneously determined in the samples (Fig. 2).



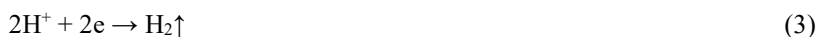
1, 2 – sea water, $U=10$ V; 3, 4 – sea water, $U=20$ V; 5, 6 – fresh water, $U=10$ V; 7, 8 – fresh water, $U=15$ V

Fig. 2 – Changes in the concentration of chloride ions in water (1, 3, 5, 7) and pH (2, 4, 6, 8) with the time of electroflotation of water-oil solutions (100 mg/dm³ oil, 30 g/dm³ NaCl (1, 2, 3, 4); 100 mg/dm³ oil, 200 mg/dm³ NaCl (5, 6, 7, 8)) in single-chamber electrolyzer ($V=500$ cm³, $U=10$ V (1, 2, 5, 6); 15 V (7, 8); 20 V (3, 4); $j=1,65$ A/dm² (1, 2); 6,69 A/dm² (3, 4); 0,37 A/dm² (5, 6); 0,36 A/dm² (7, 8)) when using an aluminum anode

During electroflotation of a salty water-oil emulsion at a voltage of 10 V and 20 V (the current density was, respectively, 1.65 A/dm² and 6.69 A/dm²) in the first 15 minutes, the concentration of chloride ions significantly decreased from 30.0 g/dm³ down to 20.1 g/dm³ and 21.5 g/dm³, respectively. In the next 45 minutes of the water treatment process, the chloride concentration decreased slowly to 18.2 g/dm³ and 19.3 g/dm³, respectively. In fresh water, the concentration of chloride ions decreased from 200 mg/dm³ to 100–113 mg/dm³ within 1 hour at a voltage of 10–15 V and an anodic current density of 0.36 A/dm². A decrease in the concentration of chloride ions is caused by electrochemical reactions accompanied by the formation of oxygen and/or active chlorine:

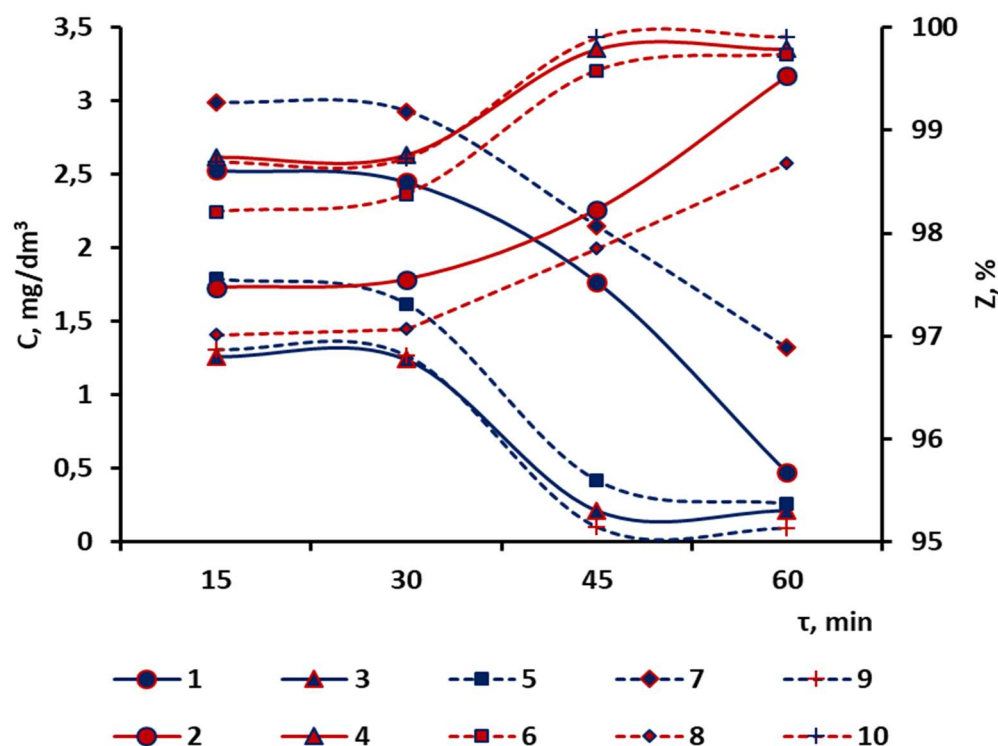


During the electrochemical treatment of water, the pH of the medium increased. Thus, during an hour of electroflotation of highly mineralized water at a voltage of 10–20 V, the pH increased from 6.25 and 6.65 in the first 15 minutes to 8.1 at the 60th minute. In weakly mineralized water at a voltage of 10–15 V, the pH increased from 8.5 and 8.6 in the first 15 minutes to 8.65 and 8.75 at the end of an hour. The increase in pH in the process of electrochemical water treatment is explained by electrochemical reactions that occur at the cathode with the formation of hydrogen and hydroxide anions:



During the second stage of the work, research was carried out to determine the efficiency of iron anodes in the processes of electroflotation purification of water-oil solutions of different initial mineralization.

The use of an iron anode in the processes of electroflotation removal of oil from a water-oil emulsion in a single-chamber electrolyzer ensured a high degree of purification - at the level of 97.5–99.8 % (Fig. 3).



1, 2 – sea water, $U=10\text{ V}$; 3, 4 – sea water, $U=20\text{ V}$; 5, 6 – fresh water, $U=10\text{ V}$; 7, 8 – fresh water, $U=15\text{ V}$

Fig. 3 – Decrease in the concentration of oil in water (1, 3, 5, 7, 9) and increase in the degree of water purification (2, 4, 6, 8, 10) with the time of electroflotation of water-oil solutions (100 mg/dm³ of oil, 30 g/dm³ of NaCl (1, 2, 3, 4); 100 mg/dm³ of oil, 200 mg/dm³ of NaCl (5, 6, 7, 8, 9, 10)) in a single-chamber electrolyzer ($V=500\text{ cm}^3$, $U=10\text{ V}$ (1, 2, 5, 6); 15 V (9, 10); 20 V (3, 4, 7, 8); $j=2.51\text{ A/dm}^2$ (1, 2); 7.39 A/dm^2 (3, 4); 0.07 A/dm^2 (5, 6); 0.13 A/dm^2 (7, 8); 0.49 A/dm^2 (9, 10)) when using an iron anode

In the first 15 minutes of electrolysis of a water-oil emulsion with a high salt content at a voltage of 10 V and an anodic current density of 2.51 A/dm², there was a significant decrease in the concentration of oil in water from 100 mg/dm³ to 2.53 mg/dm³. The degree of water purification was ensured at the level of 97.47 %.

Increasing the time of electroflotation to 1 hour contributed to the further reduction of the oil content in water to the values of 0.47 mg/dm³, and at the same time the degree of oil removal reached 99.53 %.

As in the case of using an aluminum anode, increasing the voltage to 20 V ($j=7.39\text{ A/dm}^2$) significantly increased the degree of water purification when using an iron anode. Compared to the results of the purification process at a voltage of 10 V, the effect of water treatment at a voltage of 20 V has improved twice. Thus, in the first 15 minutes of water treatment, the oil concentration decreased to 1.26 mg/dm³ ($Z=98.74\%$), and during the hour of electroflotation, the oil concentration decreased to 0.21 mg/dm³ ($Z=99.79\%$).

Despite the high resistance in the system, which is explained by the small content of dissolved substances in the water ($j=0.07 \text{ A/dm}^2$, 0.13 A/dm^2), weakly mineralized waters are also subject to electrochemical water purification.

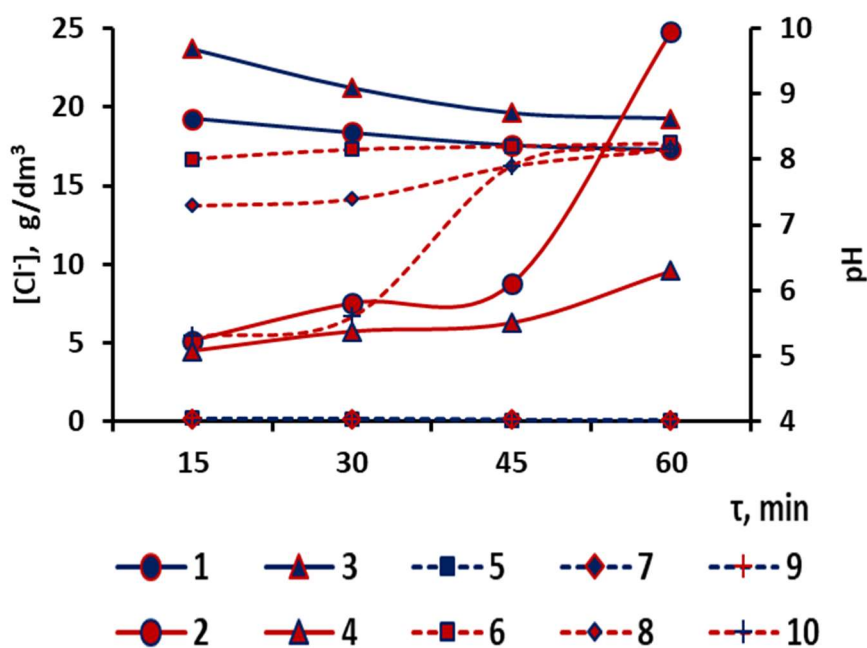
Thus, under the same initial conditions ($U=10 \text{ V}$, iron anode, $C_{\text{oil}}=100 \text{ mg/dm}^3$), in the first 15 minutes the concentration of oil in fresh water decreased to 1.79 mg/dm^3 ($Z=98.21\%$), and in sea water decreased over the same period to 2.53 mg/dm^3 ($Z=97.47\%$).

As in all previous studies, increasing the time of electroflotation made it possible to reduce the oil content in the water. Thus, the result of one-hour electroflotation of weakly mineralized water is a decrease in oil content from 100 mg/dm^3 to 0.26 mg/dm^3 ($Z=99.74\%$).

A further increase in the voltage in the system to 20 V ($j=0.13 \text{ A/dm}^2$) did not lead to an increase in the efficiency of oil extraction, although a high degree of its removal was ensured, at the level of $97\text{--}98\%$.

High results in the purification of water from oil were obtained when using an iron anode, which was previously covered with a layer of magnetite. Thanks to its use during electroflotation of fresh water for 1 hour ($U=15 \text{ V}$, $j=0.49 \text{ A/dm}^2$), the concentration of oil decreased from 100 mg/dm^3 to 0.09 mg/dm^3 . The use of this type of anode ensures a degree of purification of 99.9% .

The decrease in chloride concentration in water during electrochemical water treatment is explained by reactions 1–2 (Fig. 4). Due to the high initial concentration a more significant decrease in their content was noted in highly mineralized waters. Thus, in the first 15 minutes, a decrease in chloride content was noted from 30.0 g/dm^3 to 19.3 g/dm^3 at a voltage of 10 V and an anodic current density of 2.51 A/dm^2 . When the voltage increased to 20 V ($j=7.39 \text{ A/dm}^2$), the content of chloride ions decreased to 23.7 g/dm^3 . In the next 45 minutes, a slow decrease in chloride concentration was observed to 17.3 g/dm^3 and 19.3 g/dm^3 , respectively. In fresh water, the content of chloride ions per hour decreased from 200 mg/dm^3 to trace amounts at the level of 10 mg/dm^3 at voltages of 10 and 20 V ($j=0.07 \text{ A/dm}^2$, 0.13 A/dm^2 , respectively). When using a processed iron anode ($U=15 \text{ V}$, $j=0.49 \text{ A/dm}^2$) during 1 hour of electroflotation, the concentration of chloride ions decreased to the level of 110 mg/dm^3 .



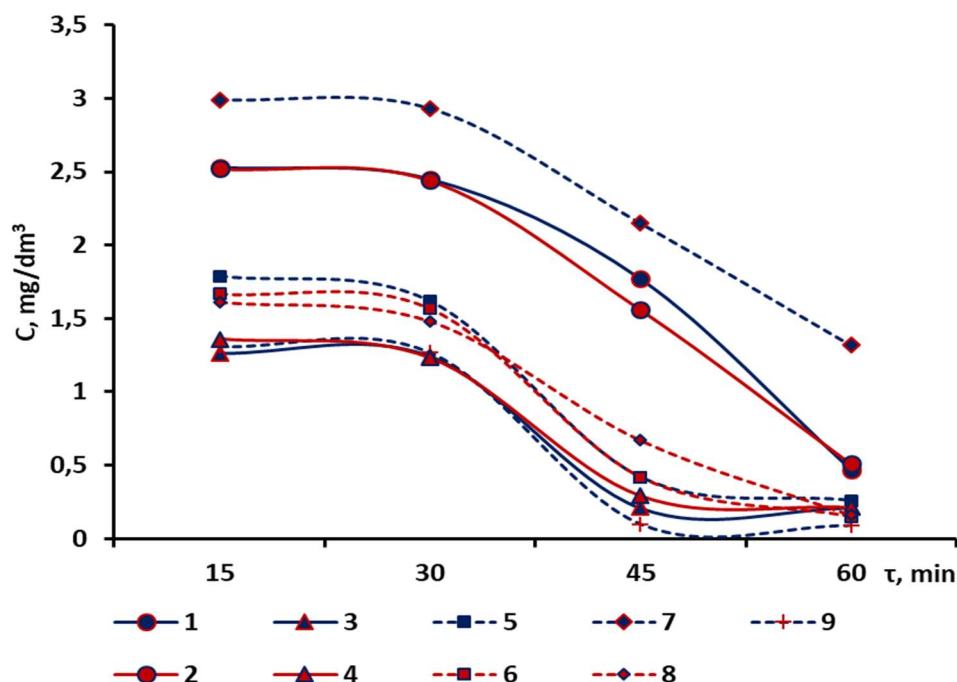
1, 2 – sea water, $U=10 \text{ V}$; 3, 4 – sea water, $U=20 \text{ V}$; 5, 6 – fresh water, $U=10 \text{ V}$; 7, 8 – fresh water, $U=15 \text{ V}$

Fig. 4 – Changes in the concentration of chloride ions in water (1, 3, 5, 7, 9) and the pH of the medium (2, 4, 6, 8, 10) with the time of electroflotation of water-oil solutions (100 mg/dm^3 of oil, 30 g/dm^3 of NaCl (1, 2, 3, 4); 100 mg/dm^3 of oil, 200 mg/dm^3 of NaCl (5, 6, 7, 8, 9, 10)) in a single-chamber electrolyzer ($V=500 \text{ cm}^3$, $U=10 \text{ V}$ (1, 2, 5, 6); 15 V (9, 10); 20 V (3, 4, 7, 8); $j=2.51 \text{ A/dm}^2$ (1, 2); 7.39 A/dm^2 (3, 4); 0.07 A/dm^2 (5, 6); 0.13 A/dm^2 (7, 8); 0.49 A/dm^2 (9, 10)) when using an iron anode

The increase in the pH of the medium during electroflotation is explained by reactions 3–4. The increase in the pH of the medium with the time of electrolysis occurred slowly to values of 6.3–9.9 with a smoother increase in weakly mineralized water. Mineralized waters were characterized by a significant increase in pH after 45 minutes of water treatment. In the case of using an iron anode covered with magnetite, sharp alkalization occurred after 30 minutes of electroflotation.

The process of electroflotation occurs in several stages. At the first stage, the anode is electrochemically dissolved with the formation of metal cations (aluminum or iron), which later form sparingly soluble compounds. Processes of electrochemical dissolution of aluminum and iron anodes are described in detail in [18].

When comparing the efficiency of water purification from oil with the use of aluminum and iron anodes (Fig. 5), the following can be noted:



1 – sea water, $U=10$ V, Fe-anod; 2 – sea water, $U=10$ V, Al-anod; 3 – sea water, $U=20$ V, Fe-anod; 4 – sea water, $U=20$ V, Al-anod; 5 – fresh water, $U=10$ V, Fe-anod; 6 – fresh water, $U=10$ V, Al-anod; 7 – fresh water, $U=20$ V, Fe-anod; 8 – fresh water, $U=15$ V, FAI-anod; 9 – fresh water, $U=15$ V, Fe-anod with magnetite layer.

Fig. 5 – Reduction of oil content in water with time of electroflotation of water-oil solutions (100 mg/dm^3 oil, 30 g/dm^3 NaCl (1, 2, 3, 4); 100 mg/dm^3 oil, 200 mg/dm^3 NaCl (5, 6, 7, 8, 9)) in a single-chamber electrolyzer ($V=500 \text{ cm}^3$, $U=10$ V (1, 2, 5, 6); 15 V (8, 9); 20 V (3, 4, 7); $j=2.51 \text{ A/dm}^2$ (1); 1.65 A/dm^2 (2); 7.39 A/dm^2 (3); 6.86 A/dm^2 (4); 0.07 A/dm^2 (5); 0.37 A/dm^2 (6); 0.13 A/dm^2 (7); 0.36 A/dm^2 (8); 0.49 A/dm^2 (9)) when using iron (1, 3, 5, 7, 9) and aluminum (2, 4, 6, 8) anodes

Iron and aluminum anodes ensure high efficiency of oil removal from both fresh and salt water. In the first 15 minutes of electroflotation, the pollutant is actively removed from the water, almost regardless of the type of anode. Basically, the degree of purification depends on the initial mineralization of the water: greater efficiency is observed for mineralized water. Thus, at an output voltage of 20 V, the oil content in mineralized water decreases in the first 15 minutes from 100 mg/dm^3 to 1.26 mg/dm^3 for an iron anode and to 1.36 mg/dm^3 for an aluminum anode. At the end of 1 hour of electroflotation for all anodes, the residual oil content is 0.21 mg/dm^3 .

Aluminum anode shows better in freshwater. At a voltage of 10–15 V, the residual content of oil in water after one hour of treatment is $0.15\text{--}0.16 \text{ mg/dm}^3$. An iron anode covered with magnetite provided the best results for the treatment of fresh oil-bearing waters. In 15 minutes of processing, the oil content decreases from 100 mg/dm^3 to 1.31 mg/dm^3 , and after an hour of processing, its content drops to 0.09 mg/dm^3 .

Conclusions. The efficiency of using electroflotation for the purification of water-oil emulsions with different mineralization using aluminum and iron anodes was investigated.

Electroflotation of water-oil solutions provides 98.6–99.9 % oil removal using these electrodes at an anodic current density of 1.65–7.39 A/dm² for highly mineralized waters and 0.07–0.50 A/dm² for fresh waters.

Water treatment during the first 15 minutes provides a significant reduction of oil concentration from 100 mg/dm³ to values at the level of 1.31–2.52 mg/dm³, almost regardless of the type of anode metal. Basically, the efficiency of pollutant removal from water depends on its mineralization, where mineralized (salty) water is dominant. Aluminum anode is more effective than iron anode in fresh water. However, in the case of preliminary treatment of the iron anode with the formation of a magnetite layer on it, this anode is characterized by the highest treatment efficiency for low-salt waters.

Prospects for further research. In the future, the authors plan to conduct process research removal of oil from water by magnetite-based sorbents.

References

1. Nugroho, T.F., Baheramasyah, A., Trikurnia, N.A. (2019), “Analysis of port-based discharge water treatment of ships, case Study: PT. TPS”, *International Journal of Marine Engineering Innovation and Research*, 3(4). pp. 141–147.
2. PT. TPS. (2017). Data Asset. Surabaya: PT. TPS
3. Dembovych, B. I., Yavorska, S. V. (2013), “Pollution of oceans by oil and oil products”, *Proceedings of the VII International Scientific Conference. Dnipropetrovsk: Adverta*. pp. 45–48. (In Ukrainian).
4. International convention for the prevention of pollution from ships, 1973 as modified by the Protocol of 1978, or “MARPOL 73/78”.
5. Resolution MEPC.60(33). Guidelines and specifications for pollution prevention equipment for machinery space bilges of ships. – London: IMO, 1992. – 132 p.
6. Resolution MEPC.107(49). Revised guidelines and specifications for pollution prevention equipment for machinery space bilges of ships. – London: IMO, 2003. – 25 p.
7. Resolution A.393(X). Recommendation on international performance and test specifications for oily-water separating equipment and oil content meters, – London: IMO, 1978. – 32 p.
8. Mysore, D., Viraraghavan, T., Jin, Y.C. (2017), “Oil/water separation technology-A review”, *Journal of Residuals Science and Technology*, 3. pp. 5–14.
9. Yong, Li, Zhaozhu, Zhang, Bo, Ge, Xuehu, Men, Qunji, Xue. (2017), “A versatile and efficient approach to separate both surfactant-stabilized water-in-oil and oil-in-water emulsions”, *Separation and Purification Technology*, 176. pp. 1–7.
10. Rana, M., Chen, J.T., Yang, S.D., Ma, P.C. (2016), “Biomimetic superoleophobicity of cotton fabrics for efficient oil-water separation”, *Advanced Materials Interfaces*, 3.
11. Kratochvil, M.J., Manna, U., Lynn, D.M. (2017), “Superhydrophobic polymer multilayers for the filtration- and absorption-based separation of oil/water mixtures”, *Journal of Polymer Science*, 55. pp. 3127–3136.
12. Ma, C., Liu, J., Zhou, T. (2015), “Study on characteristics of marine petroleum-degrading strains and their bioremediation utilization of carbon source spectrum”, *Journal of Bionanoscience*, 9. pp. 127–134.
13. Uma, V., Gandhimathi, R. (2018), “Organic removal and synthesis of biopolymer from synthetic oily bilge water using the novel mixed bacterial consortium”, *Bioresource Technology*, 273. pp. 169–176.
14. Vyrides, I., Drakou, E.M., Ioannou, S., Michael, F., Gatidou, G., Stasinakis, A.S. (2018), “Biodegradation of bilge water: Batch test under anaerobic and aerobic conditions and performance of three pilot aerobic Moving Bed Biofilm Reactors (MBBRs) at different filling fractions”, *Journal of Environmental Management*, 217. pp. 356–362.
15. Aswathy, P., Gandhimathi, R., Ramesh, S.T., Nidheesh, P.V. (2016), “Removal of organics from bilge water by batch electrocoagulation process”, *Separation and Purification Technology*, 159. pp. 108–11.
16. Karhu, M., Kuokkanen, V., Kuokkanen, T., Ramo, J. (2012), “Bench scale electrocoagulation studies of bio oil-in-water and synthetic oil-in-water emulsions”, *Separation and Purification Technology*, 96. pp. 296–305.

17. Cerqueira, A.A., Souza, P.S.A., Marques, M.R.C. (2014), "Effects of direct and alternating current on the treatment of oily water in an electroflocculation process", *Brazilian Journal of Chemical Engineering*, 31. pp. 693–701.
 18. Vozniuk, M., Shablii, T., Gomelya, M., Sirenko, L., Sidorov, D. (2023), "Electrochemical purification of oil-Containing shipping waters", *Journal of Ecological Engineering*, 24(7). pp. 246–253.
 19. Nonato, T.C.M., Alves, A.A.A., Broock, W.F., Dalsasso, R.L., Sens M.L. (2017), "The optimization of the electroflotation process using DSA® electrodes for treating the simulated effluent of produced water from oil production", *Desalination and Water Treatment*, 70. pp. 139–146.
 20. Ulucan, K., Kurt, U. (2015), "Comparative study of electrochemical wastewater treatment processes for bilge water as oily wastewater: A kinetic approach", *Journal of Electroanalytical Chemistry*, 747. pp. 104–111.
 21. Gobbi, L.C.A., Nascimento, I.L., Muniz, E.P., Rocha, S.M.S., Porto, P.S. S. (2018), "Electrocoagulation with polarity switch for fast oil removal from oil in water emulsions", *Journal of Environmental Management*, 23. pp. 119–125.
 22. El-Ashtouky, E-S. Z., Fouad, Y.O. (2014), "Oil removal from oil-water emulsion by electrocoagulation in a cell with rotating cylinder anode", *Electrochemistry*, 82, 11. pp. 974–978.
-

Вознюк М. Б., Шаблій Т. О.

ОЦІНКА ЕФЕКТИВНОСТІ ЗАСТОСУВАННЯ ЕЛЕКТРОФЛОТАЦІЇ ДЛЯ ОЧИЩЕННЯ НАФТОВІСНИХ ВОД СУДНОПЛАВСТВА

В статті охарактеризовані проблеми утворення та очищення судових нафтовісних вод. Проведена оцінка ефективності застосування електрофлотації із використанням алюмінієвих та залізних анодів для вилучення нафти з воднонафтових емульсій, що відрізняються різною мінералізацією.

Електрофлотаційна обробка воднонафтових розчинів забезпечує 98,6–99,9 % видалення нафти із застосуванням алюмінієвих або залізних електродів при анодній щільності струму 1,65–7,39 А/дм² для високомінералізованих вод та 0,07–0,50 А/дм² для прісних вод.

Обробка води протягом перших 15 хвилин забезпечує різке зниження вмісту нафти зі 100 мг/дм³ до 1,31–2,52 мг/дм³ практично незалежно від типу металу аноду. Ефективність вилучення нафти з води, в основному, залежить від її мінералізації. В мінералізованій (солоній) воді процес очищення проходить ефективніше. В прісних водах вищу ефективність очищення води забезпечує алюмінієвий анод, в порівнянні із залізним. Проте, в разі попередньої обробки залізного аноду розчином луку з утворенням на ньому шару магнетиту, даний анод відзначається найбільшою ефективністю очищення для слабкосолоних вод, забезпечуючи ступінь очищення води на рівні 99,9 %.

Ключові слова: *нафтовісні води, лляльні води, електрофлотація, судові стічні води, електроліз, алюмінієвий анод, залізний анод*

Список використаної літератури

1. Nugroho T.F., Baharamsyah A., Trikurnia N.A. Analysis of port-based discharge water treatment of ships, case Study: PT. TPS. // *International Journal of Marine Engineering Innovation and Research*. – 2019. – №3(4). – P. 141–147.
2. PT. TPS. (2017). *Data Asset*. Surabaya: PT. TPS
3. Дембович Б.І., Яворська С.В. Забруднення океанів нафтою та нафтопродуктами. // *Матеріали VII Міжнародної наукової конференції*. – Дніпропетровськ : Адверта, 2013. – С. 45–48.
4. *International convention for the prevention of pollution from ships, 1973 as modified by the Protocol of 1978, or "MARPOL 73/78"*.

5. Resolution MEPC.60(33). Guidelines and specifications for pollution prevention equipment for machinery space bilges of ships. – London : IMO, 1992. – 132 p.
6. Resolution MEPC.107(49). Revised guidelines and specifications for pollution prevention equipment for machinery space bilges of ships. – London : IMO, 2003. – 25 p.
7. Resolution A.393(X). Recommendation on international performance and test specifications for oily-water separating equipment and oil content meters, – London : IMO, 1978. – 32 p.
8. Mysore D., Viraraghavan T., Jin, Y.C. Oil/water separation technology-A review // *Journal of Residuals Science and Technology*. – 2017. – №3. – P. 5–14.
9. Yong Li, Zhaozhu Zhang, Bo Ge, Xuehu Men, Qunji Xue. A versatile and efficient approach to separate both surfactant-stabilized water-in-oil and oil-in-water emulsions // *Separation and Purification Technology*. – 2017. – №176. – P. 1–7.
10. Rana M., Chen J.T., Yang S.D., Ma P.C. Biomimetic superoleophobicity of cotton fabrics for efficient oil-water separation // *Advanced Materials Interfaces*. – 2016. – №3.
11. Kratochvil M.J., Manna U., Lynn D.M. Superhydrophobic polymer multilayers for the filtration- and absorption-based separation of oil/water mixtures // *Journal of Polymer Science*. – 2017. – №55. – P. 3127–3136.
12. Ma C., Liu J., Zhou T. Study on characteristics of marine petroleum-degrading strains and their bioremediation utilization of carbon source spectrum // *Journal of Bionanoscience*. – 2015. – №9. – P. 127–134.
13. Uma V., Gandhimathi R. Organic removal and synthesis of biopolymer from synthetic oily bilge water using the novel mixed bacterial consortium // *Bioresource Technology*. – 2018. – №273. – P. 169–176.
14. Vyrides I., Drakou E.M., Ioannou S., Michael F., Gatidou G., Stasinakis A.S. Biodegradation of bilge water: Batch test under anaerobic and aerobic conditions and performance of three pilot aerobic Moving Bed Biofilm Reactors (MBBRs) at different filling fractions // *Journal of Environmental Management*. – 2018. – №217. – P. 356–362.
15. Aswathy P., Gandhimathi R., Ramesh S.T., Nidheesh P.V. Removal of organics from bilge water by batch electrocoagulation process // *Separation and Purification Technology*. – 2016. – №159. – P. 108–11.
16. Karhu M., Kuokkanen V., Kuokkanen T., Ramo J. Bench scale electrocoagulation studies of bio oil-in-water and synthetic oil-in-water emulsions // *Separation and Purification Technology*. – 2012. – №96. – P. 296–305.
17. Cerqueira A.A., Souza P.S.A., Marques M.R.C. Effects of direct and alternating current on the treatment of oily water in an electroflocculation process // *Brazilian Journal of Chemical Engineering*. – 2014. – №31. – P. 693–701.
18. Vozniuk M., Shabliy T., Gomelya M., Sirenko L., Sidorov D. Electrochemical purification of oil-Containing shipping waters // *Journal of Ecological Engineering*. – 2023. – №24(7). – P. 246–253.
19. Nonato T.C.M., Alves A.A.A., Broock W.F., Dalsasso R.L., Sens M.L. The optimization of the electroflotation process using DSA® electrodes for treating the simulated effluent of produced water from oil production // *Desalination and Water Treatment*. – 2017. – №70. – P. 139–146.
20. Ulucan K., Kurt U. Comparative study of electrochemical wastewater treatment processes for bilge water as oily wastewater: A kinetic approach // *Journal of Electroanalytical Chemistry*. – 2015. – №747. – P. 104–111.
21. Gobbi L.C.A., Nascimento I.L., Muniz E.P., Rocha S.M.S., Porto P.S. S. Electrocoagulation with polarity switch for fast oil removal from oil in water emulsions // *Journal of Environmental Management*. – 2018. – №23. – P.119–125.
22. El-Ashtoukhy E-S. Z., Fouad Y.O. Oil removal from oil-water emulsion by electrocoagulation in a cell with rotating cylinder anode // *Electrochemistry*. – 2014. – №82 (11). – P. 974–978.