

# Petroleum products in wastewater and their properties

*Evgeny Valerevich Alekseev*<sup>1\*</sup> and *Olga Valentinovna Bukina*<sup>1</sup>

<sup>1</sup>Moscow State University of Civil Engineering, 26, Yaroslavskoye shosse, Moscow, 129337, Russia

**Abstract.** Water bodies are polluted by oil and petroleum products from various sources. The primary sources are navigation, accidents on ships and coastal areas, industrial wastewater discharges, surface wastewater from settlements, and transportation crossings of water bodies. Reducing the content of oil products in water bodies is an important task of nature protection, requiring the development of new effective methods of wastewater treatment from oil products. A systematic approach is proposed to solve this problem, including analysis of conditions of wastewater formation, study of phase-disperse composition of pollutants and their physical and chemical properties, and analysis of possible water treatment methods. According to the formation conditions, oily wastewater can be divided into domestic wastewater, surface runoff, and industrial wastewater. Depending on the formation conditions, oil products in wastewater are in different phase-disperse states with different sedimentation and aggregative stability values. Separation methods are most effective for sediment-unstable petroleum product systems and are sufficiently simple and reliable. Sedimentation stable systems of petroleum products in water need to be preliminarily destabilized. This is achieved by adding alkaline acids, mineral coagulants, or organic polyelectrolytes. Wastewater characterized by aggregative stable systems of petroleum products can be treated by degradation methods such as ozonation or sorption.

**Keywords:** oil products, wastewater, phase-disperse state, sedimentation stability, aggregative stability, wastewater treatment.

## 1 Introduction

The primary sources of water body pollution by oil products are navigation, emergency spills during transportation by water transport, discharge of insufficiently treated wastewater from industrial enterprises, surface wastewater from coastal settlements, and transport crossings of water bodies.

Petroleum products are classified as hazardous anthropogenic pollutants [1]. For example, the self-cleaning process of 1dm<sup>3</sup> of oil products in a water body consumes dissolved oxygen in more than 400 m<sup>3</sup> of water. Spill, 1 ton of oil products covers up to 12 km<sup>2</sup> of water surface with oil film. At the concentration of oil products in water 0.2-0.4

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\*Corresponding author: [AlekseevE@mgsu.ru](mailto:AlekseevE@mgsu.ru)

mg/dm<sup>3</sup>, organoleptic indicators are disturbed, which are not eliminated by traditional water treatment methods.

Petroleum products entering a water body as part of wastewater have various forms of pollutant impact [2].

The film of oil products on the water surface significantly reduces diffusion processes at the interface “air-water”, disrupting gas exchange processes in the reservoir. As a result, the oxygen deficiency in the water increases, while at the same time, the hydrogen sulfide, carbon dioxide, and methane content increases.

Micro-dispersions and emulsions of petroleum products in water have a negative impact on the biota of the reservoir:

- covering the surface of fish gills with a thin film disrupts gas exchange and leads to the death of fish;
- emulsified mixtures and water-soluble compounds readily penetrate the bodies of fish and other amphibians;
- heavy fractions settling on the bottom disturb the food base of water bodies;
- dissolved components of oil and petroleum products often contain the most toxic substances.

This leads to disturbance of the general ecological condition of water bodies. Consequently, bioproductivity decreases, chemical, physical and organoleptic properties of water change, and the biocenosis of water bodies, including the composition of higher aquatic vegetation, is disturbed.

As a result of the action of these processes, the water body becomes a source of toxic substances to humans through four water-trophic chains [2]:

- (water) → (human);
- (water) → (animals) → (human);
- (water) → (soil) → (plant) → (human);
- (water) → (soil) → (plant) → (animals) → (human).

Reducing the content of oil products in water bodies is currently one of the target tasks of nature protection. The relevance of this issue determines the search for new directions for its solution.

The target direction of research is improving wastewater treatment technology and developing new, more efficient, cost-effective methods of wastewater treatment from oil products.

## **2 Materials and methods**

The realization of the target direction of research implies a systematic approach based on the study of the current state of the problem and promising ways of its solution. Research objectives included analysis and systematization of wastewater formation conditions containing oil products, analysis of phase-disperse composition of pollutants and their physical and chemical properties, and analysis of possible water treatment methods from oil products.

## **3 Results and discussion**

According to the formation conditions, wastewater containing oil products can be divided into three types:

*Domestic wastewater* is generated by processes that support human activity in residential, administrative, office, commercial, and industrial buildings. The concentration of petroleum products in this type of wastewater is low, in the range of 0.5-10 mg/l [3].

Domestic wastewater is discharged to the municipal treatment facilities, providing normative indicators on the composition of pollutants. After the treatment process, the water is discharged into a water body.

*Surface wastewater (of residential areas) of settlements* is generated from precipitation, meltwater, and irrigation water. Drainage water discharged from buried parts of buildings and structures is often referred to as the category of surface wastewater [4]. The concentration of petroleum products in surface wastewater can be significantly higher than in domestic wastewater and mainly depends on the water collection area. The concentration of petroleum products in the composition of atmospheric wastewater from residential areas can vary in the range of 0.12-125 mg/l depending on the nature and density of buildings, the presence of main streets with heavy traffic, the remoteness of the territory from industrial enterprises [5]. As a rule, surface wastewater is disposed of after treatment into a water body.

A promising direction for the prevention of oil product inflow with surface runoff into water bodies is to use it within the territory of formation.

*Wastewater of industrial enterprises* is formed due to the realization of production cycles accompanied by technological processes using oil, oil products, and water. This type of wastewater includes:

- wastewater from refinery production processes;
- wastewater from storage and transportation enterprises and oil products (oil depots, pumping stations, and loading points);
- oily and oiled wastewater from thermal power plants (operation of fuel oil farms, turbine oil systems, lubrication of bearings of rotating mechanisms, flushing from floors of turbine and boiler rooms);
- wastewater from machine-building enterprises (water for cooling parts, preparation of aqueous solutions, compressor cooling systems);
- wastewater from motor transport and car repair enterprises (external washing of cars and parts, battery washing);
- oil-containing wastewater from production processes of metallurgical plants (cooling of metallurgical units, washing of products);
- wastewater from production processes of textile enterprises.

Three main categories of wastewater are formed at industrial enterprises that use oil or petroleum products in their production technology, such as oil refineries (refineries) [5]:

- concentrated industrial wastewater – directly from technological processes with high content of oil products (up to 15.0 g/l) [6, 7];
- moderately polluted wastewater from auxiliary industries (up to 500 mg/l) [4];
- surface wastewater (10-70 mg/l) [4].

At the same time, surface runoff discharged from the production sites of processes with the use of oil products, for example, surface-industrial runoff, differs significantly in the quantity and composition of pollutants from the surface runoff from the site adjacent to the territory of the administrative building of the same enterprise. Accordingly, in this flow, the oil product content will be close in magnitude to the surface water discharged from the residential areas.

Industrial wastewater flows are discharged through separate wastewater disposal networks to treatment facilities and then, after treatment, are returned to the technological process, where they are reused or discharged into the city's centralized wastewater disposal system. Surface wastewater collected from the territories and sites of industrial enterprises, through the drainage network, enters the surface runoff treatment facilities and then, after treatment, is discharged into a water body.

*Analysis of the phase-disperse composition of oil products* in wastewater is necessary to determine the conditions for the effective application of methods of water treatment and recovery of utilized components.

Oil and oil products in water are a heterophase polydisperse system. In wastewater, petroleum products may be in different phase-dispersed states.

Sedimentation stability of coarsely dispersed particles of petroleum products depends on their density relative to the water density. When the density of the particles is less than the water density, they appear as a film (slick) on the surface. Heavy fractions of solid and viscous components settle out at particle densities greater than the water density. In the suspended state (floating in the water column), residual oil-oil aggregates may be sorbed on other micro-dispersed impurities.

Microdispersed particles forming emulsions of direct type “oil product in water” have high aggregative stability. Microdispersed particles of “light” petroleum products represent the so-called “soluble” petroleum products [8, 9].

The choice of methods of wastewater treatment from oil products is conditioned by a number of aspects. The main ones include the amount of wastewater, the content of oil products in it, the phase-disperse state of pollutants, the intended purpose of treated water, and the feasibility of using separated oil products [10, 11].

The phase-disperse state of oil products in water is the basis for the choice of water treatment methods and the technological sequence of their application [12]. The most widespread technology of oily wastewater treatment is separation methods. As a result of their application, pollutants are extracted from water, and the extracted product may have a recyclable potential. The separation methods currently used for *sedimentation-unstable petroleum product systems* are simple and reliable. These include gravity settling, using skimmers to capture oil films (slicks), filtration through granular loads, and flotation.

*Gravitational separation.* Technically simple and economical water purification methods from oil products are based on gravity separation [13]. Oil products, as lighter in the oil-water mixture, float to the open surface of the structure, where special devices collect them. Gravity separation allows the extraction of practically all coarse dispersed particles of oil products from oily waters. When oil products and heavily dispersed impurities are present together in wastewater, the latter may become coated with oil films, resulting in neutral floatability. The efficiency of gravity separation is reduced in this case. In addition, such agglomerates overlap filter elements’ pore space, significantly reducing their operation duration. Currently, gravity sedimentation and separation in the field of centrifugal forces are used as the first stage of the technological process of water purification [14].

*Flotation.* The flotation method is based on the floating of flotation complexes formed due to the adhesion of oil product particles with air or other gas bubbles. Mechanical, hydraulic, pneumatic, compression, and electrochemical flotation are distinguished according to the method of obtaining dispersed gas phase in water [15]. The flow of surfacing flotation complexes forms a gradient separation of oil product content along the height of the flotation chamber – concentrate (flotation sludge, foam) on the upper surface and purified water in its lower part. Gravity sedimentation and flotation are used to treat wastewater containing large amounts of petroleum products in the form of sedimentation unstable systems.

If the oil products in water form a *sediment-stable system*, directly applying these methods becomes ineffective. In this case, water pretreatment is necessary to disrupt the sedimentation stability of the system of petroleum products in water.

The most common technology in oily wastewater treatment is chemical additives that reduce the sedimentation stability of the system, after which it becomes possible to apply the separation methods of water treatment discussed above effectively. The action of such

additives is based on destroying the barrier monolayer at the “particle-water” interface due to the structure of the electric double layer or the presence of adsorption shells with high structural viscosity. In the first case, the violation of sedimentation stability is achieved by the addition of acid or alkali, changing the pH value; in the second case – by the addition of mineral coagulant or organic polyelectrolyte, changing the adsorption equilibrium at the interface.

Compression flotation with preliminary wastewater coagulation is an example of such a technological method. Heterophase flotation complexes formed in this process contribute to the extraction of oil products and other dispersed pollutants from water in addition to microparticles.

Wastewater, characterized by the *aggregative stable* state of petroleum products in water, presents the greatest difficulties in its treatment. Aggregative stable systems are often characterized by wastewater containing small amounts of petroleum products. The methods of coalescence, sorption, and chemical degradation are used to treat such waters.

*Coalescence.* The coalescence method is based on the enlargement and fusion of oil product particles in contact with the developed surface of hydrophobic material. When water passes through the coalescing device, the electrostatic interaction of petroleum product particles and their consolidation occurs. Further, the consolidated particles of oil products are separated by gravity separation and discharged to the oil collector [16-18].

There are three types of coalescence:

- pore, when the aggregation of petroleum product particles occurs in a porous material;
- surface, when coalescence occurs on the surface of the coalescing material;
- volumetric, when the fusion of oil product micro-particles occurs when they collide.

Synthetic fiber, polypropylene, polyurethane, granular-polystyrene foam, polyurethane foam, natural – silk, and wool can be used as coalescing materials.

*Adsorption.* The method is based on the absorption of pollutants by the developed surface of adsorption material (sorbent). Natural, artificial, and synthetic materials, as well as some types of industrial wastes, can be used as sorbents. The main requirement for the sorbent used for water purification from oil products is hydrophobicity and developed pore surface. The best sorbents are different grades of active carbons. [19, 20]. Static and dynamic sorption processes can be used for wastewater treatment. Dynamic sorption processes provide water treatment’s greatest stability and quality [21].

Wastewater characterized by aggregative stable systems of oil products with relatively low oil content can be treated with destructive effects. These methods include ozonation and ultraviolet irradiation. The most versatile is the ozonation method.

*The water ozonation method* is based on the high oxidizing power of ozone. Ozone destroys many organic substances in wastewater over various temperatures and content. During the process of water ozonation, there is a significant improvement in the water quality in many respects. The degradation of organic pollutants results in discoloration, deodorization, disinfection, and water oxygenation. The use of ozone as a destructor of organic pollutants usually does not require the addition of other reagents to the treated water. However, it should be considered that ozone is a rather toxic gas; its maximum permissible concentration in the air of the service area should not exceed 0.1 mg/l of air.

The scope of application of this or that method, in addition to the economic and environmental component and the requirements for discharge into a water body or the conditions for receiving treated effluent by the consumer, may be determined by the feasibility of collecting and recovering petroleum products [22]. In the presence of highly concentrated oily wastewater, it is advisable to use mechanical and physical-chemical treatment methods.

Destructive methods are used to reduce the concentration of petroleum products in wastewater. As a rule, these are systems installations for additional wastewater treatment that has passed earlier stages of mechanical and physical-chemical treatment.

Thus, the composition of oily wastewater treatment facilities depends on the type and quantity of pollutants and the requirements for the quality of treated water, for example, for a process with reuse or recycling of water or regulatory requirements for water to be discharged into water bodies.

## 4 Conclusion

Petroleum products are among the most harmful chemical pollutants in water bodies and oceans.

Wastewater-containing oil products can be classified by the conditions of formation and by the phase-disperse state of the oil products they contain.

Wastewater treatment from oil products is an urgent task of nature protection and requires the development of new effective and economically favorable methods.

The choice of wastewater treatment methods from oil products depends on the amount, content, and phase-disperse state of pollutants, as well as the intended purpose of treated water and utilization of separated oil products.

Petroleum products in wastewater can be in coarse-dispersed, micro-dispersed, and highly dispersed states.

The greatest difficulty in the technology of oily wastewater treatment is the extraction of emulsified micro dispersions of petroleum products with high sedimentation and aggregation stability.

Methods of wastewater treatment from oil products should be focused on the peculiarities of the phase-disperse state of oil products in water and their sedimentation and aggregative stability. Destructive wastewater treatment methods are expedient to apply in the case of highly dispersed aggregate stable forms of petroleum products in small concentrations.

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