Oil-containing wastewater treatment by means of using coarse-grained coalescing filtering materials

Naziya Urmitova, Runar Abitov and Aida Nizamova

1Kazan State University of Architecture and Engineering, Kazan, 420043, Russia
E-mail: urmitova.50@gmail.com

Abstract. A large amount of oil-containing wastewater is generated in the oil industry. Before injection into the layer, oil and mechanical impurities must be removed from the oil-containing wastewater to the specified limits for injection into the oil formation. During the purification of oil-containing waste water, the method of settling on structures of various designs is widely used. To intensify the sedimentation processes of oil-containing wastewater, pre-treatment methods are used before sedimentation in treatment plants. One of the most effective is the process of coalescence on structures with the use of granular coalescing nozzles. Granulated coalescing materials based on polymer materials and expanded clay have been developed to intensify the process of oil-containing wastewater purification. Based on the experiments, it was found that the best materials for coalescence purposes are coarse-grained coalescing hydrophobic loads for wastewater filtration at high speeds, which operate in self-regeneration mode. This increases the depth of oil-containing wastewater purification and reduces the duration of the settling process by two or more times.

Keywords: oil-containing wastewater, coalescence, coalescing loading, pretreatment, coalescence effect, purification facilities.

1 Introduction

Large volumes of oil-containing wastewater generated at oil fields of the major industrial enterprises of chemistry and petrochemistry, energy and engineering, as well as spills of oil during their transportation, make the problem of their utilization very difficult and important [1].

The most effective method of disposal of oil-containing wastewater is its reuse for flooding of oil layers, which allows solving the problems of eliminating huge volumes of oil-containing wastewater in oil fields and protecting the environment from oil pollution [2]. All types of oil-containing wastewater pose a great threat to all types of reservoirs, air, soil, and most importantly to human health [3].

In order to purify oil-containing wastewater, various facilities are used for their pre-treatment before the purification. These facilities include: methods of electrochemical treatment, membrane filtration [4], biological purification, flotation, and a number of other methods [5].

The water often accumulates dissolved and floating substances, free oil, various lubricants, phenols, aliphatic and aromatic hydrocarbons, many of these components are toxic [6].

Currently, the following methods of eliminating of the oil pollution on water bodies are used in emergency of oil spills: mechanical, physical-chemical, chemical and biological [7]. Mechanical methods include various methods of collecting the oil from the water surface, ranging from manual bailing of oil to machine complexes of oil scavengers. Initially, the floating booms located on the water surface should be concentrated and fenced. Physical and chemical methods of oil removal include the use of adsorbing materials: polyurethane foam, coal dust, rubber chips, sawdust [8], pumice, peat and peat moss. The polyurethane foam sponge material absorbs oil well and continues to float after adsorption. According to the calculations, 1 cubic meter of polyurethane foam can adsorb approximately 700 kg of oil from the water surface. The adsorbents of organic and inorganic origin before the application can granulate (powdered) and soak with water repelling agent. The technology of application consists in spraying them on an oil film. The use of granular adsorbents and liquids with...
magnetic properties, which are easily be removed by a magnet after oil adsorption, is promising. The removal of oil using chemical compounds-detergents has found application in oil spills at sea.

Microbiological decomposition of oil is a promising direction for preventing contamination of reservoirs with petroleum products. For some bacteria, oil is a nutrient medium. The main requirement for materials that sorb oil hydrocarbons is the presence of a highly developed porous structure with a hydrophobic surface. These requirements are fully met by new oil sorbents [9].

In recent years, inorganic porous ceramic membranes [10], super hydrophobic super oleophilic nano fiber membranes [11], and electro conducting ultrafiltration membranes [12] have been developed in oil-containing wastewater purification facilities. The inorganic membrane is resistant to high temperatures, pressure, acids, and alkalis [10].

Utilization of oil-containing wastewater is very often carried out to serious pollution of the environment on the surface of the earth, as well as in coastal waterways. To improve the effect of oil-containing wastewater treatment, an external electric field was used. When using electric fields, the mechanism of electro coalescence is enhanced [13]. The use of electric fields plays an important role in changing the surface particle and the rotation of droplets, which contributes to the formation of the stable droplets [14].

The granulometric composition of the coalescing load strongly affects the size of the oil particles. When the oil emulsion passes through the coalescing loading, the polydispersity of oil particles decreases [15].

Dewatering and demulsification of oil-containing wastewater is of great importance in their purification. The study of the coalescence process makes it possible to determine the size of oil particles and determine the effect of coalescence [16].

Hydrophilic nanocomposites are one of the new advanced, environmentally friendly materials for oil and water separation [17]. Biomass materials attract a lot of attention as oil adsorbents. They are biocompatible, renewable, and biodegradable [18].

Commercial felt is also used as a coalescing material. The felt is wetted under water with oil and thus it becomes effective as a coalescing material. In this case, the surface of the foam becomes superhydrophobic, its pores are reduced and the separation of water and oil becomes more efficient [19].

Oil-containing wastewater also contains a certain amount of surfactants. When coalescing with an increase in the concentration of surfactants, the stability of small drops increases significantly, and at higher concentrations of surfactants, the stability of large drops increases significantly only when using Span 80 [20].

When cleaning oil-containing wastewater, as a preliminary stage of treatment before freezing, hydrocyclones are used [21]. In the dynamic analysis of hydrocyclones, the dynamics of the effectiveness of the hydrocyclone was determined [22].

All these methods are used as a pre-treatment of oil-containing wastewater, as well as various oil wastewater in the purification facilities before their treatment.

In the modern world, there is an acute need to dispose of large volumes of oil-containing wastewater, which is formed at oil production and purification facilities and is a mixture of reservoir water, industrial waste water and surface water. The average ratio of these waters in the total volume of oil-containing wastewater: reservoir – 82-85 %, industrial wastewater – 12-15 %, surface water – 1.5-3 %.

The Republic of Tatarstan belongs to the regions of the Russian Federation with a high level of industrial development, and in particular the petrochemical, oil-producing and oil-refining industries. The developing petrochemical industry is constantly increasing the degree of water use and the load on water bodies. Industrial wastewater ranks first in terms of volume and the damage it causes to water bodies.

The largest contribution to water pollution is made by enterprises of housing and communal services, petrochemical and oil refining industries. The basin of the river Volga on the territory of the Republic of Tatarstan is experiencing a high anthropogenic impact from the major industrial hubs
located here: Kazan, Naberezhnye Chelny and Nizhnekamsk, where the bulk of industrial water consumers are concentrated. The cities of Kazan, Nizhnekamsk and Naberezhnye Chelny have concentrated a multi-industry production structure, oversaturated with technogenic objects.

On the territory of the Republic of Tatarstan are located the largest oil and gas production departments, industrial enterprises of chemistry and petrochemistry, energy and mechanical engineering, construction complex and a number of others. The economy of the Republic of Tatarstan today has a trend of sustainable development. But at the same time, the rate of environmental pollution is also increasing, primarily due to oil pollution. As of 01.01.2017, oil-producing enterprises of the Republic of Tatarstan have provided the following volumes: oil production in the amount of 35.51 million tons (with an annual plan of 33.75 million tons); production drilling – 1179.0 thousand meters (with an annual plan of 1036.0 thousand meters); exploration and evaluation drilling-39.9 thousand meters (with an annual plan of 25.6 thousand meters).

Increased development of oil fields and deposits of various ores leads to the contamination of underground water. In general, the underground water of the Republic of Tatarstan is contaminated with oil products by about 1.5 %.

The most effective method of disposal of oil-containing wastewater is to reuse it for flooding of oil reservoirs, which allows solving the problems of eliminating huge volumes of oil-containing wastewater (1.2 billion cubic meters/year) in the fields and protect the environment from oil pollution.

In the country, about 90 % of oil is extracted from fields developed using oil layers flooding methods to maintain layer pressure, which increases oil recovery.

The requirements for the quality of water injected into oil layers are determined based on the conditions of flooding technology, where the main criteria are to ensure the displacement of oil and a long and stable intake of injection wells in the specified volumes at the optimal injection pressure.

Before the injection into the layer, oil and mechanical impurities must be removed from the oil-containing wastewater to the specified limits for injection into the oil layer. In practice, only floating and emulsified oil is required to be removed from oil-containing wastewater, since the dissolved oil does not affect the pick-up rate of injection wells and its amount in the water is insignificant.

In the treatment of oil-containing wastewater, the most widely used method of sedimentation, since it is the simplest and the most economical. Various methods of pretreatment of oil-containing wastewater before settling are used to intensify treatment processes.

One of the most effective methods of pre-treatment of oil-containing wastewater before settling is the coalescence process with the use of granular coalescing materials of different diameters in coalescing nozzles of various designs, which will increase the effect and time of settling in treatment facilities [23]. The solution to this problem will allow to create highly effective technological scheme for purification of oily wastewater to clean oil and oily wastewater.

At oil fields after complex oil treatment plants, the concentration of oil in the oilfield wastewater ranges from traces to 5000 mg/l, mechanical impurities-2-420 mg/l, water temperature – +10...+70 °C, emulsified oil particles are mainly 7-81 microns in size, and 40-45 % of them do not exceed 7-15 microns.

Coalescing filters with granular loading have found the most widespread use in the treatment of oil-containing wastewater by sedimentation to intensify the treatment process. In this case, the intensification of the coalescence process of oil droplets is achieved by filtration of oil-containing wastewater through the solid granular and fibrous loads, the materials of which have high miccoalescing properties.

Coalescing material is selected based on the availability and cost in the operating conditions of treatment plants, as well as in accordance with the requirements for them: fractional composition of the load; sufficient uniformity of grain and fiber sizes; porosity and density; mechanical strength; chemical resistance to the filtered medium; heat resistance; hydraulic properties; adhesive properties. In this case, preference is given to coalescing polymer materials, which are characterized by a higher coalescence effect of oil globules.
According to the analysis, in the well-known designs of oil-containing wastewater treatment plants, porous, fibrous and granular materials are mainly used as coalescing loading: polyethylene, polopropylene, expanded clay, etc.

In general, the country's industry produces polymer materials in the form of powders and granules of a fraction of 2-5 mm, and granules of large diameters (10 mm or more) are not produced. However, with an increase in the diameter of the grains, the issue of self-regenerating coalescing nozzles is solved.

2 Materials and methods

Before selecting the most effective coalescing materials, Kazan State University of Architecture and Engineering conducted research to determine the coalescing properties of various materials: structural characteristics of polymer materials, mechanical strength, bulk mass, density, porosity, water absorption, swelling, oil resistance, chemical resistance and stability in water, adhesion and wetting, and also developed coalescing materials based on expanded clay and ceramic fillers; crushed ceramsite fractions of 3-5, 5-10 mm; unbroken ceramsite fractions of 10-15, 15-20, 20-25, 25-40 mm of a grade not lower than 500.

Hydrophobization was carried out by oil treatment. Also, for research, granules were made based on 25-40 mm ceramsite and ceramic fillers from clay and loam fractions of 15-20, 20-25 mm, which were covered with polyethylene waste in the form of powder in order to increase their mechanical strength and hydrophobicity (public joint stock company "Orgsintez", Kazan).

In the public joint-stock company "Orgsintez" pellets of 10-15 mm fraction from aluminum-containing waste along with waste of polyethylene fiber were produced.

At the Kazan plant" Polimiz", an industrial technology for producing granular polymer materials from secondary raw materials with diameters of 5 mm and a cylinder length of 15 mm.

Polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene of the secondary grade (teflon, fluoro plast) and polyformaldehyde were studied from polymer materials.

Based on the analysis of the structural characteristics of polymers, it was found that polyethylene and polypropylene are the best coalescing materials with high hydrophobic properties.

In the laboratories of the Kazan State University of Architecture and Engineering, the processes of adhesion and wetting, existing and developed coalescing materials were studied. When a liquid comes into contact with a solid surface, an adhesive interaction occurs and simultaneously the liquid wetting this surface. The adhesion process and wetting are determined by the amount of surface tension of the contacting bodies, and the wetting edge angle is a measure of wetting. The edge angle of wetting is determined by the value of the angle between the surface of the solid and the tangent to the point of contact with the liquid and is counted towards the liquid phase.

For the developed coalescing materials, the edge wetting angle is determined at the interface: "solid – distilled water", "solid – reservoir water", "solid – oil". During the experiments, reservoir water and oil from the Romashkinskoye field of the Republic of Tatarstan were used.

According to the research conducted at Kazan State University of Architecture and Engineering, it was found that the best coalescing materials for adhesion properties are hydrophobized crushed expanded clay, hydrophobized crushed expanded clay and polymers that are very well wetted with oil, and the overall adhesion work is 2-4 times less than that of crushed and non-crushed expanded clay.

Later in the laboratories of Kazan State University of Architecture and Engineering and in production conditions, i.e. on-site treatment facilities Pavlovsky plant of complex preparation and pumping of oil oil and gas department "Aktyubaneft" Public joint stock company "Tatneft" in the experimental settings investigated the processes of filtration and coalescence of the oil particles through the filter coalescing nozzles of different heights (0.6; 0.8; 1.0 m).

The following properties of the most promising existing and new developed by us coalescing materials: crushed expanded clay fractions 3-5, 5-10 mm; the uncrushed expanded clay fractions 10-15, 15-20, 20-25, 25-40 mm; hydrophobized crushed expanded clay fractions 3-5, 5-10 mm; hydrophobized uncrushed expanded clay fractions 15-20, 20-25, 25-40 mm; polyethylene fraction
3-5 mm; polypropylene fraction 3-5 mm; the uncrushed expanded clay, covered with polyethylene fraction 25-40 mm; ceramic filler coated with polyethylene fractions 15-20, 20-25 mm; polyethylene secondary grade, fractions 4-5.6; 4-6.3; 5-7; 5-10 mm; materials from polyethylene waste and aluminum-containing waste fractions of 10-15 mm.

3 Results and discussion

According to experimental data, the greatest effect of coalescence of oil particles (table. 1) obtained for polyethylene fractions of 3-5 mm at a loading height of 0.8 m and filtration rates of 18.22 and 36.43 m/h; hydrophobized crushed expanded clay fractions of 3-5 mm (Figure 1) at a loading height of 1.0 m and a filtration speed of 17.84 m/h; hydrophobized uncrushed expanded clay of 15-20 mm fractions (Figure 2) at a loading height of 1.0 m and a filtration speed of 100.3 m/h; for a ceramic aggregate coated with polyethylene fractions of 15-20 mm (Figure 3) at a loading height of 0.6 and 1.0 m and a filtration speed of 17.84 – 100.65 m/h were studied.

Figure 1. a – hydrophobized crushed expanded clay of 3-5 mm fractions; b – hydrophobized crushed expanded clay of 5-10 mm fractions.

Figure 2. a – hydrophobized uncrushed expanded clay of 10-15 mm fractions; b – hydrophobized uncrushed expanded clay of 15-20 mm fractions.
Figure 3. a – ceramic filler coated with polyethylene fractions of 15-20 mm; b – ceramic filler coated with polyethylene fractions of 20-25 mm; c – uncrushed expanded clay with polyethylene fractions of 25-40 mm.

Table 1. Characteristics of coalescing materials.

| Coalescing loading, fractional composition | Loading height, m | Filtration speed, m/h | The coefficient of polydispersity at the entrance to the nozzle | The coefficient of polydispersity at the entrance to the nozzle | The effect of coalescence |
|-------------------------------------------|-------------------|-----------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------|
| Polyethylene fractions of 3-5 mm          | 0.8               | 18.22                 | 8.22                                                          | 2.90                                                          | 2.46                      |
|                                           | 0.8               | 36.43                 | 5.92                                                          | 2.69                                                          | 1.88                      |
| Hydrophobized crushed expanded clay fractions of 3-5 mm | 1.0               | 17.84                 | 5.69                                                          | 2.18                                                          | 2.31                      |
| Hydrophobised unbroken expanded clay fractions of 15-20 | 1.0               | 100.3                 | 8.1                                                           | 3.1                                                           | 2.02                      |
| Ceramic filler coated with polyethylene of 15-20 mm | 0.6               | 17.84                 | 8.22                                                          | 3.52                                                          | 2.23                      |
| fraction                                  | 1.0               | 65.86                 | 4.29                                                          | 2.11                                                          | 1.68                      |
|                                           | 1.0               | 100.65                | 7.79                                                          | 3.22                                                          | 2.06                      |

From Table 1 it can be seen that the polydispersity coefficient at the outlet of the coalescing nozzle, depending on the type of loading, decreases from 2.1 to 2.8 times, i.e. the monodispersity of oil particles increases, which increases the settling effect.

4 Conclusion
As a result, on the basis of experiments, it was found that the best coalescing loads are coarse coalescing materials and when using coarse coalescing loads in coalescing nozzles at high filtration rates, the issue of self-regenerating coalescing nozzles is solved, which is a very important point in the operation of coalescing nozzles treatment plants. While the depth of oil-containing wastewater treatment increases and the duration of the settling process is reduced by two or more times, this gives a great economic effect in the treatment of oil-containing wastewater for injection into oil reservoirs in order to increase oil recovery and utilization of large volumes of oil-containing wastewater in order to protect the environment from pollution.

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