UDC: 504.4.054:665.61
DOI: https://doi.org/10.30546/2521-6341.2026.01.927

HYDROSPHERE POLLUTION BY OIL AND PETROLEUM PRODUCTS: SOURCES, IMPACTS, AND REMEDIATION METHODS

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ARTICLE INFO

Article history:
Received:2025-07-29
Received in revised form:2025-08-16
Accepted:2025-10-19
Available online :2026-06-26

Keywords:
oil pollution;
oil spills;
dispersants;
sorbents;
surfactants

ABSTRACT

The article is devoted to the sources of hydrosphere pollution by oil and petroleum products, their environmental impacts, and modern methods for oil spill remediation. It is shown that the main pathways of oil contamination in aquatic environments include ship discharges, port operations, industrial and municipal wastewater, river runoff, atmospheric deposition, as well as accidents involving offshore drilling platforms and vessels. The processes of oil transformation on the water surface and the factors governing its spreading and degradation are discussed. An analysis of mechanical, chemical, and sorption-based cleanup methods is presented, including the use of skimmers, containment booms, dispersants, oil collectors, and sorbents of various origins. Particular attention is given to the Corexit family of dispersants and other commercial reagents, with emphasis on their effectiveness, application limitations, and potential toxicity. Promising surfactant-based reagents and polymer–surfactant complexes capable of providing long-term localization of oil slicks are also reviewed. The study concludes that the selection of oil spill response technologies should be based on specific hydrometeorological conditions and pollution characteristics, which is especially important for the protection of the Caspian Sea ecosystem.

INTRODUCTION

Rapid economic development has led to the emergence of new technologies. Due to their efficiency and practicality, these technologies are widely used in various industrial sectors to meet growing demand. However, despite their modern design and advanced capabilities, they cannot completely eliminate the risk of accidents. As a result, industrial accidents can lead to severe environmental and economic consequences.

Approximately three-quarters of the Earth's surface is covered by water. Water is one of the most valuable, irreplaceable, and inexhaustible resources for humanity. Oceans and seas play a crucial role in the economic development of countries with direct access to marine waters. Maritime transportation, as well as the utilization of marine flora and fauna, contributes significantly to national economies.

In recent years, incidents such as mass strandings of whales and dolphins and the formation of thousands of cubic meters of foam along coastlines after storms have indicated increasing levels of water pollution. Preventing water pollution and treating contaminated water remain among the most important global environmental challenges [1-3]. Water pollution has many causes, and consequently, various remediation methods have been developed. One of the major pollutants of aquatic environments is oil. The irrational exploitation of natural resources, together with the use of outdated technologies and equipment that fail to comply with modern technological and environmental standards during resource extraction, transportation, and processing, constitutes one of the primary sources of environmental pollution. In particular, contamination arising from oil and gas extraction, refining, and transportation activities is recognized as a major anthropogenic factor exerting adverse impacts on ecosystems and environmental quality [4-7].

It is well known that modern economic development is impossible without petroleum. Every year, between 4 and 10 million tons of oil enter the world's oceans. Depending on its viscosity and ambient temperature, spilled oil usually spreads over the water surface as a thin film several millimeters thick

The physical and chemical transformation of oil spilled into marine environments depends mainly on the oil's viscosity, water temperature, and turbulence. After oil is released onto the water surface, it undergoes a series of transformations (Figure 1).

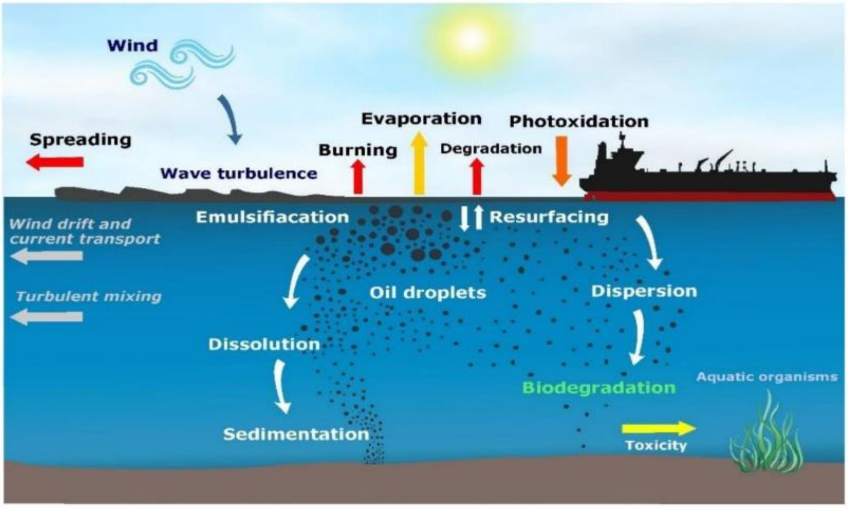

Fig. 1. *Processes of Transformation Experienced by an Oil Slick on the Water Surface*

Oil pollution can originate from various sources, which can be divided into two categories:

1. Continuous pollution sources
2. Accidental pollution sources

The main pathways through which oil and petroleum products contaminate water include:

- Discharge of ballast water, oily wastewater, and tank washing residues from ships (23%);
- Waste releases into ports and port waters, including losses during tanker bunkering operations (17%);
- Industrial wastewater and sewage discharges (10%);
- Stormwater runoff (5%);
- Accidents involving offshore drilling platforms and vessels (6%);
- Offshore shelf drilling activities (1%);
- Atmospheric deposition (10%);
- River runoff in various forms (28%).

During the last 30 years, nearly 2,000 wells have been drilled in the world's oceans. Since 1964, approximately 1,000 of these wells have been drilled in the North Sea alone, with around 350 production wells being developed. Small leaks from drilling platforms result in annual oil losses of approximately 0.1 million tons, while major accidents occur periodically.

A significant amount of oil reaches seas from land via domestic wastewater, stormwater, and river systems. This source contributes more than 2 million tons of oil pollution annually. In addition, industrial facilities and oil refineries discharge approximately 0.5 million tons of oil into marine environments every year.

Examples of accidental pollution sources include the 2010 oil spill in the Gulf of Mexico and tanker accidents. On April 20, 2010, during the cementing operation of an offshore oil well in the central Gulf of Mexico, an oil platform exploded and caught fire. Estimates indicate that approximately 5,000 barrels (700 tons) of oil per day leaked from the uncontrolled well into the Gulf of Mexico [8].

The methods used to remove oil from water depend on the source of contamination and the amount of oil released. Following major spills, oil begins spreading across the water surface, depending on weather conditions. Strong winds accelerate the dispersion process.

Oil spilled on water can be removed using mechanical, physical, and chemical methods. Thick oil layers are generally best removed mechanically. Mechanical recovery of oil slicks is typically performed using skimmers [9-11]. Skimmers are most productive and efficient when the oil layer thickness exceeds 10 mm.

However, during large-scale spills, weather conditions often cause oil slicks to spread over extensive areas, forming very thin films. This significantly reduces skimmer efficiency, allowing recovery of only 10–15% of the spilled oil. To improve performance, floating booms arranged in V-, J-, or U-shaped configurations are used to concentrate oil and facilitate collection. Nevertheless, strong winds substantially reduce the effectiveness of this approach.

Mechanical methods cannot effectively remove oil films thinner than 0.1 mm. After mechanical recovery, a thin residual oil layer often remains on the water surface. This layer forms a barrier between the atmosphere and hydrosphere, hindering oxygen and carbon dioxide exchange, reducing water evaporation, and limiting sunlight penetration into deeper water layers. Consequently, it has a highly detrimental effect on aquatic flora and fauna.

Surfactants for Thin Oil Film Removal

Various surfactants are widely used to remove thin oil films. According to their mode of action, these substances are classified into two groups:

1. Oil dispersants
2. Oil collectors (oil herders)

Oil Dispersants

Dispersants are sprayed onto thin oil films on the water surface. They break the oil into microscopic droplets that become distributed throughout the water column. These fine oil emulsions undergo relatively rapid biodegradation (Figure 2).

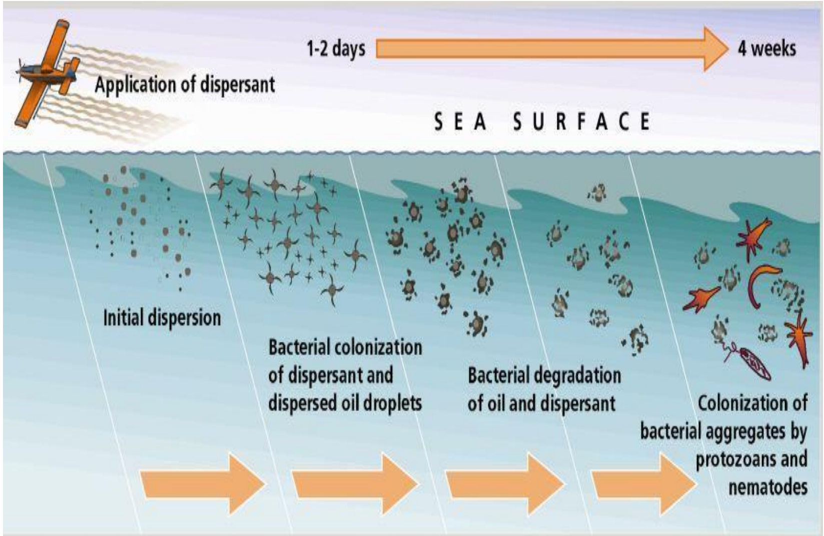

Fig. 2. *Mechanism of Oil Spill Dispersion by a Dispersant on the Water Surface*

Dispersants are generally most effective within 72 hours after a spill and at temperatures above 5°C. Their penetration beyond 10 meters below the water surface is undesirable. Application by aircraft or helicopters is considered most effective. Windy conditions often enhance dispersant performance, making them particularly useful when mechanical recovery is impractical.

Since dispersants exhibit some degree of toxicity, they should be applied in controlled dosages rather than excessive quantities.

One of the most widely used dispersants is Corexit, produced in several formulations by Nalco Holding Company, including:

- COREXIT 9527 [12]
- COREXIT 9580 [13]
- Corexit EC9500A [14]
- Corexit EC9527A [15]

The complete chemical composition of these products has not been fully disclosed.

Following the 2010 Deepwater Horizon disaster in the Gulf of Mexico [16], unprecedented quantities of Corexit EC9500A and Corexit EC9527A were used. Corexit EC9527A primarily contains 2-butoxyethanol, proprietary organic sulfonates, and small amounts of propylene glycol.

Corexit 9500 mainly consists of:

- Sorbitan compounds
- Succinic acid derivatives
- Petroleum distillates

Corexit EC9500A is based on hydrotreated light petroleum distillates, propylene glycol, and proprietary organic sulfonates.

The dispersant Corexit 9580 had previously been used during the 1989 Exxon Valdez oil spill in Alaska.

Other well-known dispersants include:

- Finasol OSR51 [17]
- Superdispersant 25 [18]
- Slickgone NS [19]
- Inipol IP90 [20]

The dispersing efficiency of various dispersants toward Chirag crude oil spilled on the surface of the Caspian Sea was experimentally investigated [21].

Oil Collectors and Dispersants

Oil-collecting and oil-dispersing reagents differ in raw materials, chemical structure, and properties. They can be synthesized from higher alcohols and epoxy compounds, higher fatty acids and epoxy compound, amines, orthophosphoric acid, epoxy compounds, and alkyl halides [22-27].

All dispersants can be either oil-soluble or water-soluble.

Oil-soluble dispersants generally require concentrations of 3.5% or higher, have densities lower than water, and viscosities below 50 cP.

Water-soluble dispersants contain surfactant mixtures rich in hydrophilic components and are typically used at concentrations up to 10%.

Before use, both oil- and water-soluble dispersants are commonly diluted to approximately 15% concentration with water or organic solvents.

One of the classic dispersants developed in the previous century is which produces highly dispersed oil emulsions with droplet diameters below 1 μm. Its distinctive feature is its versatility: it can function both as a dispersant and as an oil collector.

When used as a dispersant, an aqueous DN-75 solution is sprayed onto floating oil slicks. The surfactants in the formulation reduce the oil-water interfacial tension to approximately 2 mN/m, promoting the formation of fine oil emulsions that subsequently undergo rapid biodegradation.

The primary disadvantage of dispersion is that the oil remains within the aquatic environment.

When DN-75 is used as an oil collector, it is applied around the perimeter of the oil slick. It forms a stable monomolecular film on the water surface. This film increases surface tension at the seawater interface to approximately 45 mN/m, significantly higher than the oil-water interfacial tension. As a result, the reagent exerts greater spreading pressure than the oil itself, causing the slick to contract and become localized.

The reagent can concentrate dispersed oil into isolated slicks up to 6 mm thick and prevent further spreading. Successful localization and collection generally require approximately 5 kg of reagent per square kilometer of contaminated surface.

Different oil-collecting and dispersing agents exhibit varying efficiencies, toxicities, and durations of action. Compounds derived from higher alcohols often demonstrate high effectiveness but may possess moderate toxicity. Reagents synthesized from individual fatty acids can be relatively expensive.

Replacing pure higher fatty acids with acid fractions derived from natural triglycerides significantly reduces production costs while enhancing oil-collecting and dispersing performance through synergistic effects [28,29].

Polymer–Surfactant Complexes

Another important class of oil spill response agents consists of polymer–surfactant complexes. These materials differ from conventional surfactant-based reagents in several respects [30-32].

Their effect on oil slicks develops more gradually; however, they are capable of maintaining localized oil accumulations for significantly longer periods than conventional surfactants.

Sorbent-Based Cleanup

Another widely used oil spill remediation method is sorption. Sorbents can be classified into three categories [33-36]:

1. Natural sorbents (cotton, peat, sawdust, perlite, clay, etc.);
2. Artificial sorbents;
3. Synthetic sorbents.

Plant-based sorbents can absorb up to twenty times their own weight in oil and may achieve removal efficiencies as high as 99%.

Conclusion

The Caspian Sea is one of Azerbaijan's most valuable natural resources. A portion of Azerbaijan's oil production originates from offshore wells located in the Caspian Sea. In addition, the Caspian Sea serves as an important transportation route for crude oil from Central Asia to Europe.

These activities inevitably contribute to oil contamination of the Caspian Sea. In order to minimize the environmental impacts of existing and future pollution events, it is essential to apply appropriate oil spill response technologies based on a thorough assessment of the specific conditions. The implementation of mechanical, chemical, and sorption-based cleanup methods plays a critical role in protecting marine ecosystems and reducing the ecological consequences of oil pollution.

This research was supported by the Azerbaijan Science Foundation Grant № AEF-MGC-2025-1(54)-20/15/4-M-15

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