

# Physical-Chemical Remediation of Oil-Polluted Sea Waters

Abdul Hamid

Head of East Java Province Library and Archives Service, Jalan Menur Pumpungan 32, Surabaya, Indonesia

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## ABSTRACT

Oil spills have given extraordinary treatment and caused short and long term damage to the sea ecosystem. Characteristics of oil and polluted site conditions are limiting factors for the physiochemical fate of oil compounds in ecosystems. Furthermore fate determines risk based approach in controlling pollution. Therefore, physical-chemical improvements are site-specific technologies for remediating oil contaminated oil marine ecosystem. A preliminary study must be carried out to choose the suitable one technology and monitoring methods must be provided for the technology chosen.

**KEYWORDS:** oil spills, fate, marine ecosystem, remediation, monitoring

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## 1. INTRODUCTION

The energy needs of human life activities continue to use hydrocarbon (fossil) energy sources. Various exploration, exploitation, transportation, storage, processing and distribution activities of crude oil and refined oil often produce leakage and / or oil spills into the environment. Particularly in the chain of exploitation - distribution through sea media, oil spills in the sea have impacted multidimensional pollution for marine life itself, fisheries, tourism businesses, to the extent of sea damage [1]. Oil is still widely used, although security measures are developed, leakage and / or oil spills in the sea are almost certain to continue. Therefore, pro-active action to prepare for the recovery of marine pollution is necessary for the purpose of: responding to pollution, or reusing it as a place for oil exploitation activities.

Crude oil and refined oil are complex hydrocarbon compounds which have thousands of variations of compounds. The diversity of oil compounds produces a variety of physical chemical qualities [2]. Knowledge of oil characteristics, and ocean characteristics, is a prerequisite for predicting the behavior of oil spills at sea and treatment for pollution recovery.

The diversity of oil characteristics and experiences of oil pollution events at sea shows that the methodology for pollution recovery is site-specific [3]. This is a challenge in the efforts to restore oil pollution at sea required local pre-study to establish appropriate recovery technology. Recovery technology can be carried out both physically chemically, and in combination. The difference in the application of recovery technology requires an appropriate method of monitoring and evaluation. The match between the pre-study, the application of technology, and monitoring and evaluation will result in an effective and efficient performance in the recovery of oil pollution at sea.

## 2. Oil characteristics

The physical properties of oil which affect the behavior of oil in the sea and its recovery. Important physical properties are density, viscosity, pour point, and water solubility. Density is expressed as specific gravity and American Petroleum Institute (API) gravity. Specific gravity [3] is the ratio of the weight of the oil mass and the mass weight of water at a certain temperature. API gravity is expressed in numbers  $10^\circ$  in pure water  $10^\circ$  C. API gravity can be calculated from specific gravity using the formula:  $AP\ Gravity(o) = (141.5 / Specific\ Gravity\ 10oC) - 131.5$ . Crude oil has a specific gravity in the range 0.79-1.00 (equivalent to API 10 - 48). Oil density is important for predicting oil behavior in water.

Viscosity is a trait that shows resistance in shape and movement changes. Low viscosity means it is easy to flow. Viscosity factors are oil composition and temperature. This viscosity is important for predicting the spread of oil in water.

The point of change is the temperature level that changes the oil to solidify or stop flowing. The point of change of crude oil varies between  $-57^\circ$  C to  $32^\circ$  C. This point of change is important for predicting oil behavior in water and establishing environmental cleaning strategies.

The solubility of oil in water is low around 30 mg / L [4] and depends on the chemical composition and temperature. The amount of solubility is achieved by aromatic oils with small molecular weights such as benzene, toluene, ethylbenzene, and xylene (BTEX). This solubility is important for predicting oil behavior in water, bioremediation processes, and oil ecotoxicity.

The chemical characteristics of oil are different between crude oil and refined oil. Crude oil contains about 50-98% hydrocarbon compounds and the rest are non-hydrocarbon compounds (sulfur, nitrogen, oxygen, and some heavy metals). Classification of oil based on solubility in organic solvents, namely:

- 1) Saturated hydrocarbons. Included in this class are alkanes with the structure of  $C_nH_{2n+2}$  (aliphatics) and  $C_nH_{2n}$  (alicyclics), where  $n > 40$ . This saturated hydrocarbon is the highest content in crude oil.
- 2) Aromatic hydrocarbons. Included in this class are monocyclic aromatics (BTEX) and polycyclic aromatic hydrocarbons (PAHs: naphthalene, anthracene, and phenanthrene). PAHs are carcinogens, or can be transformed by microbes into carcinogenic compounds, so they become important compounds in maintaining environmental quality.
- 3) Resin. Included here are polar compounds containing nitrogen, sulfur, oxygen (pyridines and thiophenes), so they are also referred to as NSO compounds.
- 4) Asphalt. Included here are compounds with large molecular weight and heavy metals nickel, vanadium, and iron. Of course variations in the composition of crude oil are different in various places, which is why remediation technology is site-specific.

Refined oils such as gasoline, kerosene, jet oil, and lubricant are processed crude oil products through catalytic cracking and fractional distillation processes. As a processed product, refined oil has different physical chemical properties from crude oil. Refined oil contains crude oil and unsaturated hydrocarbon compounds such as olefins (alkenes and cycloalkenes) from the catalytic cracking process. Olefins content is quite large to 30% in gasoline and about 1% in jet fuel [4].

### 3. Oil behavior in the sea

When oil is exposed to the marine environment, oil will immediately change its physical chemical and biological properties. This change in nature will change / determine the remediation strategy. The process of changing physical properties includes:

- 1) Expansion. This expansion is perhaps the most important process during the initial exposure to oil in water, as long as the oil change point is lower than the ambient temperature. This process will expand the distribution of oil thereby increasing mass transfer through the process of evaporation, dissolution and biodegradation.
- 2) Evaporation. This process can be relied upon to remove oil fractions with toxic content and low molecular weight. Alkane ( $<C_{15}$ ) and aromatic evaporation takes place between 1 - 10 days. Environmental factors that influence evaporation are wind, water waves and temperature. Evaporation causes oil to be left in the water to increase in density and viscosity.
- 3) Dissolution. This process is not significant in terms of mass transfer but is important in the biodegradation process. Aromatic with a small molecular weight and is the most toxic is the most water-soluble compared to other oil compounds. The speed of dissolution is influenced by the photo-oxidation process and biological processes.
- 4) Photo-oxidation. In aerobic conditions and exposed to sunlight, aromatic oils can be transformed into simpler compounds. These simpler compounds (hydroperoxides, aldehydes, ketones, phenols, and carboxylic acids) are more water-soluble thus increasing the rate of biodegradation but more toxic [5].
- 5) Dispersion. This spread occurs because of the concentration gradient process by forming an oil-water emulsion formation (oil droplets in the water column) thereby expanding the surface of the oil grain. Oil-water emulsions can be maintained by agitation (wind and waves are examples of natural agitation), or by the addition of dispersants.
- 6) Emulsification. Emulsification is the process of changing the status of oil droplets in water into water droplets in oil (also called chocolate mousse). Asphaltic ingredients can increase emulsification. But emulsification will make cleaning oil difficult.
- 7) Others. Included here is the process of oil adsorption on water solids, sedimentation and tar grain formation.

### 4. Physical-chemical remediation

Physical chemical remediation is effective for short-term / immediate goals of localizing and taking as much oil as possible from the sea. Physical remediation that has been practiced in general [6] are:

- 1) Boom and skimming. Booms are used to localize and control the movement of oil. Skimmer is used to take oil.
- 2) Wiping with absorbent. Hydrophobic material is used to wipe oil from the surface of the water.
- 3) Mechanical. Mechanical equipment is used to collect and dispose of oil-contaminated sediment. This is mainly done in coastal areas.
- 4) Washing. Washing uses low pressure cold water to high pressure hot water.
- 5) Relocation of sediment and tilling. Transfer of oil-contaminated sediment to another place or mixing with other sediment. This method is analogous to polluting dilution.
- 6) Local burning. Combustion of oil-contaminated sites is usually carried out together with flammable substrates (dry plants, dry waste). This is especially true for coastal areas.

Chemical remediation that has been practiced in general are:

- 1) Dispersants. The surfactant content is used to disperse oil into granules in water. The oil droplets have a total surface area of the granules thus accelerating the process. This method is used routinely in many countries, especially when facing physical remediation constraints.
  - 2) Demulsifiers. This material is used to break oil-water emulsions to speed up natural disperse.
  - 3) Solidifiers. This material is used to improve oil polymerization so that the oil becomes stable, minimizes spread, and increases the effectiveness of physical remediation.
  - 4) Surface film chemicals. Film-forming agents are used to prevent oil from being attracted to the open sea substrate, and to increase the removal of oil bound to the surface of pressure washers.
- Physical chemical remediation is short term [7] and incomplete remediation (mass transfer between environmental media). About 10-15% of pollutants can be removed from marine media.

## **5. Pre-study and monitoring**

Pre-study and monitoring of remediation of oil-polluted seas is a must because it is site-specific and for the determination of appropriate and effective techniques for remediation activities. The minimum pre-studies and monitoring required include the following [8].

Predictive hazard assessments. This study is the first step in establishing remediation technology. This study aims to determine predictive behavior of oil in seawater both regarding the distribution of oil concentrations in water, air, solids / sediment and biota media. This study model can be used multi media fugacity models or release from the technosphere, and there are still many models that can be developed.

Treatability study. This study is a continuation of predictive hazard assessments. After knowing the distribution of oil concentration in environmental media, the amount of oil concentration in each media was tested by physical, chemical, microbiological, and plant remediation techniques.

The monitoring function is based on the intended use of monitoring, namely:

- 1) Retrospective monitoring. Retrospective monitoring is monitoring which results are used to make corrections or justifications for the predictive hazard assessments and application of technology. Both are monitored physically and / or using physical, chemical and biological indicators.
- 2) Prospective monitoring. Perspective monitoring is monitoring which results are used to make predictions. Ecotoxicity testing is an example of prospective monitoring. One indicator of the level of organic toxicity is the BOD / COD ratio. The results of monitoring of the BOD / COD ratio are increasing indicating the level of toxicity decreases.

## **CONCLUSION**

The characteristics of crude oil are different according to the source, refined oil different characteristics according to processing, and if spilled on the ecosystem then the physical behavior of oil chemistry is site-specific. The specificity of the place determine the approach to pollution risk control and technology choices remediation. Physical chemical remediation is first aid to remove oil from environmental media.

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