

Effectiveness and Toxicity of Chemical Dispersant in Oil Spill Aquatic Environment

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Received January 5, 2021; revised and accepted March 25, 2021

Abstract: Pollution of the marine ecosystem by crude oil spill endangers marine species. The use of chemical dispersants in removing spilled oil from the marine environment by forming oil-in-water emulsions proves to be relatively effective, but the effectiveness is influenced by a number of factors. However, the successful use of these dispersants depends, to a great extent, on the toxicity of the oil-dispersant mixture that forms when dispersants are applied to combat oil spills. In this review, the type and quantity of dispersant used were reported to influence the toxicity of the oil-dispersant mixture on aquatic organisms relative to both the crude oil and the dispersant. The viscosity of oil, the salinity of water and the quantity of dispersants used were discussed as major factors influencing the effectiveness of dispersants. With contrasting results in assessing the overall toxicity of oil-dispersant mixtures on marine life, recommendations were suggested at the end of this review.

Key words: Crude oil, oil spill, dispersants, toxicity.

Introduction

The need to increase our petroleum reserves in Nigeria led to exploration into geographically and geologically complex environments such as ultra-deep waters. Major crude oil reserves in Nigeria are located along the Niger Delta River, Gulf of Guinea, offshore Bight of Benin, the Bight of Bonny, as well as in the deep and ultra-deep offshore and some activities in the Chad Basin (Iniaghe et al., 2013). However, various stages in oil exploration—drilling, production, refining and distribution—can create enormous challenges for the environment (Aghalino, 2009). There are documented environmental and social implications due to oil exploration activities, including oil spill contamination

of land, rivers and streams, loss of biodiversity, etc. (Celestine, 2003).

Crude oil spills often accompany oil exploration activities, but crude oil can also find its way into the environment during transportation, storage, processing and distribution. Half of Nigeria's spilled crude oil is reportedly attributed to corrosion, sabotage makes up 28%, oil production contributes 21%, while engineering drills, equipment breakdown, and carelessness in handling oil vessels during loading and unloading, as well as failure to control wells effectively, contribute 1% (Odokuma and Williams 2012, 2013; Odokuma and Ugboma, 2013). The oil spill has also been the result of restiveness by youths in some oil-producing regions of the Niger Delta area when they engage in cutting of oil

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pipelines, aided by hacksaws and blades for the purpose of illegal oil refining, otherwise known as 'oil theft'.

Four categories of oil spill have been identified: minor (wherein oil spillage is not up to 25 barrels in—land/inland waters, offshore or coastal waters, and is of no significant health concern), medium (here, spilled oil is less than or equal to 250 barrels in inland water/ 250 to 2,500 barrels on land, offshore and coastal water), major (in this case, the spilled oil exceed 250 barrels on land, offshore or coastal waters) and disaster (this refers to any uncontrollable well blow-out, storage tank failure or pipeline rupture, which potentially threatens the health and welfare of the public) (Egberongbe et al., 2006).

Pollution of the Marine Environment due to Oil Spill

Marine pollution can be defined as the introduction by many, directly or indirectly, of substances or energy into the marine or estuarine environment resulting in deleterious effects which are harmful to living resources, hazards to human health, a hindrance to marine activities including fishing and impairment of quality for the use of seawater (GESAMP, 1991). Oil spill in the marine environment is caused chiefly by accidents during oil extraction offshore, transportation by ocean vessels and ocean oil tanker (Haapkylal et al., 2007). Offshore oil well blowout, leaking pipelines, manifolds, colliding or grounding vessels, etc. also contribute significantly to oil spills in the marine ecosystem (Azadeh et al., 2012).

In Nigeria, there are recorded oil spill cases in different areas and on various occasions along the Nigeria coast. Some of the common cases are the Idoho Oil Spill in 1998, which recorded a loss of around 40,000 barrels of crude oil, the Funiwa 5 seaward station spill in 1980 with an aggregate of about 37.0 million liters of unrefined petroleum (Badejo and Nwilo, 2004), the Ogoniland oil spill, which according to the United Nations, could demonstrate to be the world's most comprehensive and long term oil remediation exercise (UNEP, 2017). When oil spills get close to shorelines, they have adverse effects on shoreline vegetation, local wildlife, fishing gear, boat damage and also, severely diminish the shores' value for recreational purposes (Ventikos et al., 2004). The formation of oil film on surface water restricts vertical dissolution of oxygen from the air into the water, impairs the activities of surface water organisms, pollutes water and increases the content of water soluble materials, which may be toxic to aquatic organisms, etc. (Shore and Douben,

1994). When oil spills occur and are left unattended, it takes a long period of time for the spilled oil to naturally degrade (biodegradation, chemical degradation and physical degradation), with reports suggesting that, up to 22 years is required for total degradation of 1 kg of crude oil (Anson and Mackinnon, 1984).

Dispersants and Oil Spill Cleanup

Oil spills pose a great threat to the marine environment, mainly because, crude oil is less dense than water and as such, it floats on the surface of the water, thereby affecting aquatic species by limiting the oxygen dissolution rate into the water (<https://www.britannica.com/science/oil-spill>; Saadoun, 2015). After an oil spill incident occurs, the oil disperses itself via natural agitation of the water body, but this process takes a lot of time and is dependent on wave action and turbulence. For this reason, a number of cleanup methods were developed to reduce the impact of oil spills on the marine environment. There are several methods (physical, chemical and biological) used for removing oil spills from water, with each method having its own merits and demerits. For example, physical methods such as containment and recovery techniques using booms and skimmers offer the benefit of eliminating spilled oil, but the process is extremely slow. Burning floating slicks of crude oil potentially removes a significant amount of oil, but this technique often demands that the slicked oil is freshly spilled and sufficiently thick. The use of chemical dispersants as a countermeasure for combating oil spills is by far the commonly used remediation method because they disperse the oil throughout the water, thus, decreasing probable pollution, and, they can swiftly spread on to huge volumes of spilled oil, and is also cost effective (Liu and Callies, 2019; Nnadozie and Odokuma, 2017a and b).

Chemical dispersants are a mixture of surface-active substances, solvents and other additives which can reduce/prevent the formation of surface oil slicks, i.e., they help to break up crude oil into smaller particles (oil-in-water emulsions), thereby allowing them to be easily degraded by natural processes by increasing their surface area exposed to bacteria action, this ensures minimal recoalescence and slow resurfacing (Lessard and DeMarco, 2000). In this manner, the spilled oil is prevented from reaching the shorelines (Wise and Wise, 2011). However, their efficacies depend on microbial biodegradation for effective removal, oil characteristics, sea and weather conditions (Liu and Callies, 2019). In

Nigeria, the use of oil spill dispersants as a counter measure for oil spills is permitted offshore (EGASPIN, 2018).

The complete composition of most chemical dispersants is not made public (Wise and Wise, 2011), but the United States Environmental Protection Agency (USEPA) posted the chemical composition of two commonly used dispersants—Corexit 9527 and 9500—produced by NALCO, to include (USEPA, 2010):

- 1,2-propanediol
- Ethanol, 2-butoxy- (not included in Corexit 9500)
- Butanedioic acid, 2-sulfo-1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)
- Sorbitan, mono-(9Z)-9-octadecanoate, poly(-1,2-ethanediyl) derivatives
- Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives
- 2-Propanol, 1-(2-butoxy-1-methylethoxy)-
- Distillates (petroleum), hydro treated light

There are a variety of chemical dispersants available, and the major manufacturers and their corresponding products are as follows (Wise and Wise, 2011):

- Nalco: Corexit 9500, 9527, 7604, etc.
- BP: BP1100X, BP1100WD, BP1002.
- Shell: Shell SD LTX, Shell SD LT.
- Total special fluids: Finasol ESK, Finasol OSR-2, Finasol OSR-5
- Miscellaneous: Actusol, Atlas and Basol AD6, Biosolve, Conco-K, Cleaner crystal Simple Green, D-tar, Duosol, Foremost, Hiclean II, Houghtoslov, Nokomis 3, Oilspere 43, Penetone 861, Slik-A-Way, Slix, Su-Gee2, Superdispersant-25 and Supersonic OSD.

The major motivations for utilising dispersants are to lessen the effect of spilled oil on coastlines, decrease the impact of oil on birds and mammals on the surface of the water and promote the degradation of oil in the water column. Although the impact of dispersants on wildlife is being investigated, the effect of dispersants on the biodegradation of crude oil is still disputed (Fingas and Banta, 2019) because they can accumulate in the environment, thereby becoming a secondary source of water pollution (Ventikos et al., 2004). However, the major issues surrounding the use of dispersants in oil spill remediation exercises are basically effectiveness, toxicity and long-term considerations.

Effectiveness of Chemical Dispersants

The quantity of spilled oil a dispersant placed into

the water column compared to the quantity of oil that remains on the water surface is its effectiveness (Fingas and Banta, 2019). The effectiveness of a dispersant depends on the viscosity of the oil, dispersant type and quantity used, salinity of the water, amount of surfactant available at the oil-water interface (Chapman et al., 2007), sea energy, temperature, etc (Fingas, 2014).

Factors Influencing Effectiveness of Chemical Dispersants

Viscosity of Oil

A general thumb rule states that “oil with high viscosity and pour point tend to be much less dispersible as delivery of the surfactant to the oil/water interface becomes more difficult. Since weathering will increase the viscosity of the oil, it, therefore, follows that the longer the oil is left to weather, the less likely it is to disperse effectively” (Chapman et al., 2007). Chemical dispersants are reportedly used for oil spill clean-ups when the oil’s viscosity does not exceed a viscosity of 5,000 cSt; beyond this value, the success rate drops rapidly and it is not applicable when viscosity exceeds 10,000 cSt. Furthermore, the viscosity of spilled oil rises with prolonged stay in the environment; this is so because, under the influence of ageing (emulsification, evaporation), the extent of dispersion of the oil drops with time (REMPEC, 2011).

Type of Dispersant

Biodegradation is the chief mechanism of oil removal when dispersants are applied. Dispersants thus support biodegradation when tiny oil droplets (oil-in-water emulsions), typically <100 microns are formed, thereby increasing their surface areas and allowing them to be readily available for microbial attack (Mulyono et al., 1994). Natural processes, including wave action, wind and turbulence also aid this process. There have, however, been conflicting reports as to the effectiveness of dispersants in aiding oil degradation; in some cases, minimal effects ranging from positive to negative results were recorded (Varadaraj et al., 1995).

Laboratory scale experiments are commonly used in gaining insights into the possible effects of one dispersant compared to others. Some regulatory organisations inaugurated the standard Swirling Flask Test for assessing relative effectivity of dispersants (Blondina et al., 1997), but actual field performance of the dispersant is not guaranteed since this test does not take into account, the specific conditions of the marine environment and their influence on the overall effectiveness of the various dispersants (Chapman et al.,

2007). For instance, the effectiveness of three different dispersants (Pars 1, Pars 2, and Gamlen) on the removal of spilled oil was comparatively studied using the Well method (i.e., fungi and bacteria's abilities to grow on the sides of a well), and the growth rate of isolated bacteria and fungi in a laboratory-scale experiment (Azadeh et al., 2011). The authors showed that both Pars 1 and Pars 2 dispersants proved to be of better effectiveness in crude oil biodegradation compared with the Gamlen dispersant using measurements from biochemical and chemical oxygen demands.

Salinity of Water

At some point in time in the U.S, oil spill dispersants were predominantly used in offshore marine waters having very high salinities. Later on, there became growing interest in using these dispersants near-shore, wherein the water could be brackish or fresh (SL Ross Environmental Research, 2010). Therefore, dispersants designed for use in the marine environment were highly effective when the salinity of the water was between 30-35 ppt, and they became less effective with salinity >40 ppt or <20 ppt. Conversely, freshwater dispersants are reportedly more effective than marine dispersants when salinity is between 10-20 ppt. In other cases, the effectiveness of dispersants has been improved for both brackish and freshwater by increasing the salt content in the formulation of dispersants using CaCl_2 (George-Ares et al., 2001).

Again, dispersants appear to be the most efficient cleanup method but are not environmentally friendly. Hence, there are documented specialized settings where chemical dispersants are used. They are not commonly used in areas where a high possibility of mixing of water does not allow for quick dilution of the dispersed oil, or in ecologically vulnerable/sensitive areas (REMPEC, 2011).

Toxicities Associated with the Use of Dispersants

'Toxicity' in this regard, refers to the adverse nature of both dispersant and the dispersed oil droplet (Fingas, 2014; Uffort and Odokuma, 2018). With the recent improvement in the formulation of dispersants, the toxicity of the dispersed oil is of greater importance than the dispersant itself (Chapman et al., 2007). The toxic effects of dispersants used in combatting oil spills are of serious importance to organisms within the recipient aquatic system of the oil spill incident. A standard toxicity test measures the acute lethal concentration

(LC_{50}) to standard species using a 96 h time frame (Wise and Wise, 2011).

When dispersants are applied to spilled oil in the marine environment, a synergistic interaction occurs between the oil and the dispersant, which may make the oil-dispersant mixture more toxic; and, up to 52-fold increased toxicity of oil-dispersant mixture relative to the crude oil itself has been reported using Corexit 9500A dispersant (Rico-Martinez et al., 2013). Almeda et al. (2014) investigated the acute toxicity of Corexit 9500A dispersant and dispersant-crude oil mixture to marine microzooplankton. The results showed that the dispersant itself was inherently toxic to the studied species, and the toxicity increased significantly when the dispersant was combined with crude oil. Adams et al. (2014) investigated exposure of *Clupeaharengus* embryos to water-accommodated fractions (WAFs) and chemically-enhanced water-accommodated fractions (CEWAFs) with Corexit 9500A of Medium South American crude oil. The CEWAF was roughly 100-fold more harmful than WAF. A study on Nigerian crude oil using dispersants and crude oil-dispersant mixtures indicated that the oil dispersants Teepol and Conco-k were highly toxic to *Barbus* fingerlings than crude oil (Alade and Anyachukwu, 1990).

Fuller et al. (2004) evaluated the toxicity of oil, dispersant (Corexit 9500), and oil-dispersant mixture to different species of *A. bahia*. Results from the study showed that oil-dispersant mixture seemed to be approximate or less toxic than the oil alone. Milinkovitch et al. (2011) assessed the exposure of *Liza aurata* to dispersant alone, mechanically and chemically dispersed oil. The result indicated no significant difference between mechanically and chemically dispersed oil. The quantity of dispersant used in combatting oil spills also plays a major role in assessing the toxicity of the oil-dispersant mixture. Otitolaju (2005) evaluated the toxicities of Forcados Light crude from Nigeria to a recently endorsed dispersant for use (Biosolve) and their blends against the juvenile phase of *Macrobrachium vollehovenii* (prawn). Raw petroleum was discovered to be around multiple times more harmful than the dispersant itself against *M. vollehovenii*, while the effect of the crude oil-dispersant mixture varied, as mixture proportions of 9:1 and 6:1 were of lower toxicities than crude oil. The toxicity of three newly formulated oil spill dispersants- Nalco D4106, Corexit 9527 and Goldcrew, as well as their combined forms with brent crude oil, to *Chironomus* sp., was evaluated (Rotimi and Ogedegbe, 2011). The 96 h LC_{50} values indicated varied toxicity levels amongst the dispersants;

however, crude oil-dispersant mixtures were reportedly less toxic than the crude oil alone.

Conclusion

The low density of crude oil relative to water allows it to float on the surface of water when the oil spill occurs. The presence of oil in the marine environment poses a great threat to the marine ecosystem, mainly because it limits the amount of oxygen that dissolves into the water, thereby endangering aquatic lives. The use of chemical dispersants for combatting oil spills in the marine ecosystem became necessary in order to prevent the spilled oil from reaching shorelines, and also, to enable the formation of an oil-in-water emulsion, which could easily be degraded by natural forces and hydrocarbon-degrading bacteria. The effectiveness of these dispersants matters a lot but is dependent on the viscosity of the spilled oil, the salinity of water in which the spill occurred, as well as the type and quantity of dispersant used. However, while effective cleanup of spilled oil is highly sought after, the toxicity of the crude oil-dispersant mixture calls for serious concern. Since the effectiveness and toxicities of dispersants depend on several factors, there is the need for more comparative, simulative and laboratory-scale studies, wherein actual water samples are obtained from different marine environments to determine the effectiveness and toxicities of specific dispersants and oil-dispersant on different aquatic organisms.

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