 The Open Petroleum Engineering Journal, 2015, 8, 90-92

Stability Research on the Effect of Oil Spill Dispersant I-Separation Characteristics of Oil Spill Dispersant

Qiao-min Wang, Bing Sun*, Zhi-yu Yan, Xiao-mei Zhu, Hui Liu and Yan-bin Xin

Environmental Science and Engineering College, Dalian Maritime University, Dalian, 116026, China

Abstract: With the continuous research and development of the low-toxic and high-efficiency oil spill dispersants (OSDs), there are an increasing number of evaluation methods for the effect of the OSDs. Currently, the majority of the OSDs effect evaluation is related with the testing of the emulsification in the laboratory, while the stability researches on the OSDs effect are still few. In this paper, the separation characteristics of the oil spill dispersant (OSD) and the oil were investigated, and the stability of the effect of the OSD was also studied. Firstly, the mixture of the oil and the OSD, which have been poured into the seawater, was thoroughly stirred, left to stand and observed. Later, the greatest separation degree with the oil and the final stability of the OSD was obtained through the analysis. Then, the stability of the combination between the oil and the OSD was studied under the conditions of the no wave, intermittent wave and continuous wave. The study shows the OSD will gradually move away from the oil, which is influenced by the time and duration of the wave action. This study provides experimental basis and methods for the research on the stability mechanism of the OSD effect, as well as the theoretical basis for the comprehensive evaluation and the rational use of the OSD.

Keywords: Effect, oil spill dispersant, separation characteristics, stability.

1. INTRODUCTION

Large-scale oil spills happened frequently, in spite of the international agreements on oil pollution with strict preventive strategies [1]. The oil spill dispersants (OSDs) play an important role in dealing with the frequent oil spills in the marine environment, which can effectively reduce the interfacial tension between the oil and the seawater, greatly speed up the oil dispersing into the seawater from the surface, rapidly clean up the oil spills in the sea, and significantly reduce the impact on shorelines and habitats [2]. In order to better develop and select the appropriate OSDs, some standardized effect tests in the laboratory are often used to evaluate different kinds of OSDs' effect [3].

Currently, the majority of the OSDs' effect evaluation in the laboratory is concerned with the testing of the OSDs' emulsification while the researches on the emulsion stability are few. The OSDs' effect is evaluated on the laboratory scale, which mainly means the OSDs' effect is evaluated in the controlled environment. The mixing approach of the oil and the OSDs used in the laboratory differs even with the slightly different testing method. The reason why emulsification decreases in the experiment is generally considered to be due to the emulsion oil floating. Therefore, the OSDs have been mistakenly assumed to be of continuously good effect because the emulsification test is not based on the timeliness and dynamics in a long time under the wave action. Many research results show that the OSDs effect value in the laboratory is higher than that in the field. It is mainly because the surfactant is separated from the spilled oils during the initial usage period or the mixing period after the spraying, and the hydrophilic part of the surfactant directly merges with the seawater, that is, there is an exchange of surfactants between the oil droplet and the surrounding seawater [4, 5] and the removal of surfactants was equivalent to a proportional loss of the entire dispersant [6]. There is a study showing the rate of dispersant loss, and decline in the dispersion potential was related to slick thickness or the quantity of the test oil used [7]. Moreover, the behavior of the oil is also determined by the chemical composition and physical properties of the crude oil, and the way its properties will change when the oil is spilled in the sea [8]. For that reason, the accurate effect of the OSDs is determined by the actual number of the OSDs in the oils instead of the total number of the OSDs that have been used. Therefore, determining the actual number of the OSDs in the oil spills under different conditions is a new focus of the OSDs effect, which overcomes the former shortcomings that only the OSDs emulsifying efficiency is taken into consideration. This approach is also an important means to determine whether the OSDs suffer physical failure directly. In addition, whether the OSD is constantly evaluated in the long-term with the same effectiveness will arise the concerns on the consequence of using OSDs, namely, whether the dispersive oil will be floating in the remote place after a period of time. This will pose a latently great threat to the marine, which may appear abruptly at any time. Besides, it is difficult to ascertain where the responsibility lies for the oil spills.

Taking into account the internal and external factors described above, representative crude oil and the oil spill dispersant (OSD) were selected as the experimental subjects in this paper, that is, Bohai crude oil which is suitable to be disposed with the OSDs and the common OSD. The standing experiment and the dynamic experiment were performed to study the stability of the OSD and the characteristics of the wave impacting on the stability. Firstly, the OSD and the oil

*Address correspondence to this author at the Linghai Road, Dalian, China. Postcard: 116026; Tel: 0086-0411-84725275;
E-mail: sunb88@dlmu.edu.cn

1874-8341/15 2015 Bentham Open

were thoroughly mixed, poured into the seawater, stirred, and then left standing. Its stability was observed and analyzed. Also, whether or not the time and duration of the wave action impacted the stability of the OSD effect, was studied, based on which the stability of the OSD in combination with the oil is also discussed. In this study, the analysis methods focused on the relative content of the OSD in the oil slick and the concentration of the dispersive oil in the seawater.

2. MATERIALS AND METHODS

2.1. Materials

The experimental oil was from a platform in Bohai and is of medium viscosity. The OSD was the FuKen-II OSD from Qingdao Huahai Environmental Protection Industry Co., Ltd. The salinity of the artificial seawater was about 34 ‰.

2.2. Methods

2.2.1. The Experiments About the Stability

The mixture of the oil and the OSD was prepared by the volume ratio about 0.1, 0.2, 0.4 and 0.6 according to the use range of the OSD. The mixture described above was respectively poured into the seawater (V_{oil}: $V_{seawater}$ = 1:80). After being sufficiently stirred, the mixture was left standing for 72h. The floating oil formed after standing was moved to the clean seawater (V_{oil}: $V_{seawater}$ = 1:200), followed by sufficiently stirring, and let stand for 48h. The process was repeated three times. The ratio of the oil and seawater were 1:500 and 1:1000 respectively. The proportion of seawater was increased to simulate the process that the oil diffuses into the seawater.

2.2.2. The Experiments About the Waves Impacting the Stability

The mixture of the oil and the OSD was poured into the seawater tank, and three conditions were provided, which were respectively the no wave, the intermittent wave (the vibration frequency was 33±1 times/min; the wave had been on for 2 hours and off, for 1 hour), and the continuous wave (the vibration frequency was identical to the intermittent wave). Each experimental group had been maintained for 12 hours. During the experiment, the oil slick was sampled for gas chromatography analysis every three hours, which were aimed at measuring the relative content of the OSD in the oil slick. All the experiments were finished in the laboratory of 15±1 ^{o}C.

2.3. Test Methods

The relative content of the OSD in the oil slick was measured by the gas chromatography (Shimadzu Co., Ltd. GC-2010 gas chromatography). The pretreatment of the oil slick: the chromatography column was successively filled with cotton, 5.5g silica gel with column chromatography reagent grade, and 1.2g anhydrous sodium sulfate placed on the top. Each sample accurately weighed was fully dissolved in the 15mL configured mixed solution of dichloromethane and n-hexane. The filled column was rinsed with 10mL hexane. As soon as anhydrous sodium sulfate was exposed, the dissolved oil sample prepared into the column was immediately poured and the chromatography liquid was collected for testing.

Testing conditions of the GC: the temperature of the inlet and the detector were respectively 280 ^{o}C and 300 ^{o}C, and the carrier gas was high purity N_2. Temperature program: the initial temperature was 60 ^{o}C at first, then increased to 100 ^{o}C by 20 ^{o}C/min, and kept for 2 min; then increased to 280 ^{o}C by 8 ^{o}C/min, and kept for 50 min.

3. RESULTS

3.1. The Stability Results of the Oil in Combination with the OSD

The standing experimental investigation was performed to study the OSD's stability, which was completed by intermittently increasing the amount of seawater and alternately stirred during the standing operation. In other words, the floating mixture at the surface of the seawater was poured into the seawater, stirred, and then left standing. Finally, the sampling analysis was conducted. The floating mixture in last experiment was transferred to the clean seawater, and the above operation was constantly repeated in the different amount of the seawater. Stirring adequately, intermittently increasing seawater and letting it stand for a long time were done to find the value of maximum dispersion (the degree of the dispersion and the amount of the dispersion), the greatest separation degree with the oil, and the final stability of the OSD. The relative content of the OSD was measured by the gas chromatography. The test result is shown in the Fig. (**1**).

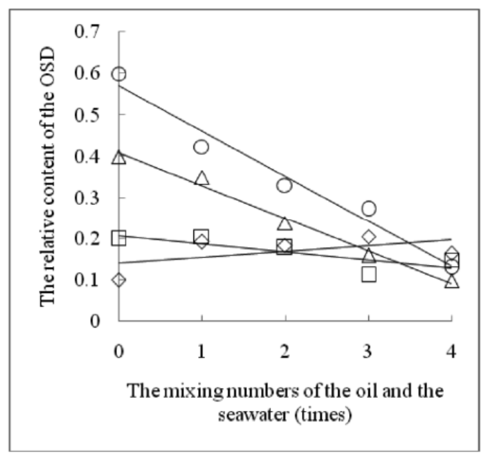

Fig. (1). The change of the relative content of the OSD in the oil slick with the time in the standing experiment.

As can be seen from the Fig. (**1**), with the increase of the operation times, the trend line is slightly rising: when the ratio of the OSD and the oil is 0.1(the ratio of the OSD used is below the use range), and the relative content of the OSD in the oil slick is linearly declining; when the ratio of the OSD and the oil are 0.2, 0.4 and 0.6, it indicates that the OSD will be away from the oil slick. The degree of the separation varies with the initial ratio of the OSD and the oil. The larger the initial ratio is, the greater the loss of the OSD will be. For example, when the relative content of the OSD is 0.6 initially, about 7.5% floating oil slick will be lost each time when mixed with the clean seawater.

In the case of approximating OSD effect, the OSD usage principle "as little as possible" should be followed in order to avoid the secondary pollution to the marine environment. As is shown in Fig. (**1**), in this experiment when the ratio of the OSD and the oil is 0.4, the best amount of the OSD is obtained, so the following experiment is controlled by this ratio.

3.2. The Experimental Results of the Wave Impacting on the Stability

The relative content of the OSD in the oil slick is measured under the condition of the no wave, intermittent wave and continuous wave, which is mainly used to study the effect of the wave's continuity and shows different relative contents of the OSD of the oil slick contrasted among these three cases. The results are shown in Fig. (**2**).

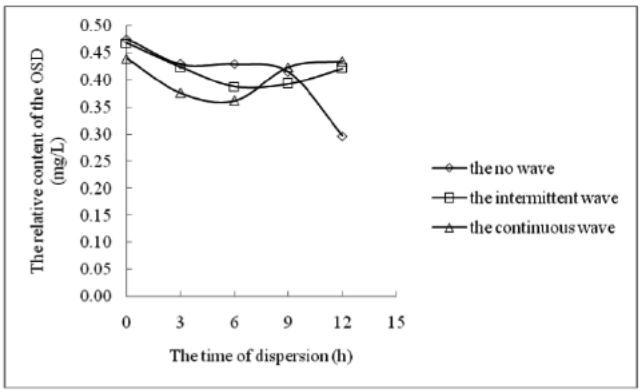

Fig. (2). The change of the relative content of the OSD in the oil slick under the condition of the no wave, intermittent wave and continuous wave.

As can be seen from Fig. (**2**), the relative content of the OSD is significantly decreased under the condition of the no wave; when the wave exits, the continuous wave is better than the intermittent wave at keeping the OSD in the oil slick; the OSD has decreased under the different wave action, but with the wave time increasing, the relative content of the OSD decreases, which may be relative to the increase of the entrained seawater.

From what has been discussed above, the wave plays a key role in the combination stability of the oil and the OSD. The wave is not only beneficial to the mixing of the OSD and the oil, which fully interact with each other, but also can help the OSD remain for a long retention time in the oil.

CONCLUSION

The stability of the OSD effect was investigated by the standing experiment, and the dynamic characteristics of the OSD being away from the oil were also studied under the different wave actions. The conclusions are listed below.

The changes of the OSD in the oil slick were analyzed by the gas chromatography, which manifested the OSD will move away from the oil slick whatever the conditions are.

Waves play a key role in the combination stability of the OSD and the oil, which mainly reflects the duration and the action time. The longer the time of the wave is, the harder it is to separate the OSD from the oil slick.

The study preliminarily shows that the stability of the OSD effect is influenced by the wave complexity and repeated occurrence, which is possibly related with the emulsified oil Entrained with water.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The work was supported by the National Natural Science Foundation of China (41206095), Ph.D. Programs Foundation of Ministry of Education of China (20122125120010), and the Fundamental Research Funds for the Central Universities (No.3132013091). The work was also supported by the project "Research on the characteristics, drifting prediction and recovery technology of the Bohai submerged and sunken oil". The authors wish to thank the Hebei Maritime Safety Administration of China for their help.

REFERENCES

[1] ITOPF, *The International Tanker Owners Pollution Federation Limited*, 2011/2012 Handbook, London, UK, 2011.

[2] R.R. Lessard, and G. Demarco, "The significance of oil spill dispersants," *Spill Science and Technology Bulletin*, vol. 6, pp. 59-68, Feb 2000.

[3] National Research Council (NRC), *Understanding Oil Spill Dispersants: Efficacy and Effects*. The National Academies Press: Washington, DC, 2005.

[4] M.F. Fingas, and E. Decola, "*Oil Spill Dispersant Effectiveness Testing in OHMSETT February-March 2006*," A Report for Prince William Sound Regional Citizens' Advisory Council (PWSRCAC): Anchorage, Alaska, May 2006.

[5] P.C. Heimenz, R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, Inc.: New York, NY, 1997.

[6] J.L. M. Resby, P.J. Brandvik, P.S. Daling, J. Guyomarch, and I. Eide, "*Effects of Time on the Effectiveness of Dispersants*," Report to PERF (Petroleum Environmental Research Forum) Report STF80MKA07143, 15th December 2007.

[7] A. Lewis, B.K. Trudel, R.C. Belore, and J.V. Mullin, "Large-scale dispersant leaching and effectiveness experiments with oils on calm water", *Marine Pollution Bulletin*, vol. 60, pp. 244-254, Feb 2010.

[8] T.S. Kristiansen, A. Lewis, P.S. Daling, J.N. Hokstad, and I. Singsaas, "Weathering and dispersion of naphthenic, asphaltenic, and waxy crude oils," In: *Proceedings of the International Oil Spill Conference,* American Petroleum Institute: Washington, DC. 1997.

Received: December 15, 2014 Revised: January 04, 2015 Accepted: February 25, 2015