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Estimation of “environmentally sensitive” dispersal ratios for chemical dispersants used in crude oil spill control

Adebayo A. Otitoloju · Temitope O. Popoola

Abstract The toxicities of two dispersants (Biosolve and OSD 9460), Forcados light crude oil and their mixtures based on ratios 6:1, 9:1, and 12:1 (v/v) were evaluated against the juvenile stage of African catfish, *Clarias gariepinus*, in laboratory bioassays. On the basis of the derived toxicity indices, Biosolve (96-h $LC_{50} = 0.211$ µl/l) was found to be about 27,284 times more toxic than crude oil (96-h $LC_{50} = 5.757$ ml/l) and 6,450 times more toxic than OSD 9460 (96-h $LC_{50} = 1.361$ ml/l). OSD 9460 was also found to be four times more toxic than crude oil when acting alone against *C. gariepinus*. Toxicity evaluations of the mixtures of crude oil/dispersants mixtures varied, depending largely upon the proportion of addition of the mixture components. The interactions between mixture of crude oil and Biosolve at the test ratios of 6:1, 9:1, and 12:1 were found to conform with the model of synergism (SR = 7,655, 14,876, and 8,792, respectively), and the mixtures were therefore more toxic than the crude oil acting singly. Similarly, the interactions between mixture of crude oil and OSD 9460 at the test ratios of 6:1 and 9:1 also conformed to the model of synergism (SR = 2.2 and 1.84, respectively). Interactions between the dispersant OSD 9460 and the crude oil at test ratio 12:1, however, conformed to the model of antagonism (SR = 0.84), indicating that the mixture was less toxic than crude oil acting alone. The results of the emulsification potential of OSD 9460 and Biosolve [measured in terms of optical transmittance (%)] prepared at the dispersal ratios 6:1, 9:1, and 12:1 revealed that the dispersal ratio of 6:1 achieved the highest emulsification of the crude oil with optical transmittance value of 4% and 6%, respectively. Estimation of an “environmentally sensitive” dispersal ratio for OSD 9460 and Biosolve revealed the optimum dispersal ratio for OSD 9460 range between ratios 7.5:1 and 9:1, while for Biosolve such an optimum dispersal ratio was indeterminate within the range of test dispersal ratios. The implications of these results in setting manufacturer’s and regulatory dispersal ratios for chemical dispersants used for oil spill control were discussed.

Keywords Crude oil · Dispersants · Dispersal ratios · Spill control · Joint action

1 Introduction

The spillage of crude oil into the environment and its far-reaching negative effects on the environment demands the development of various control strategies, such as containment and recovery using booms, skimmers or pumps, sinkers, burning, or dispersants (Westermeyer 1991). The volume of crude oil spilled, the sensitivity of the receiving environment, the topography of the area, etc. will always dictate the type of control strategies deployed. Dispersants are usually deployed when there is need to urgently eliminate the floating mass of oil slick, especially when the spillage is close to shorelines (NRC 1989). They are thus defined as specially designed oil spill products that are composed of detergent-like surfactants in low toxicity solvents. The dispersants act by emulsifying or breaking up the oil slick into smaller pieces, thus ensuring easy dispersal and/or mixing in aquatic ecosystems. It is however important to note that most of the dispersants that have been initially introduced into the market were found to be either very toxic on their own against organisms inhabiting

A. A. Otitoloju (✉) · T. O. Popoola
Department of Zoology, University of Lagos,
Akoka, Lagos, Nigeria
e-mail: bayotitoloju@yahoo.com

the receiving ecosystems or, in some cases, enhance the toxicity of the spilled crude oil to the exposed organisms when deployed or utilized to control oil spills (Oyewo 1986; Otitoloju 2005).

According to Lindstrom and Braddock (2002), chemical dispersants can be very effective tools in the management of crude oil spilled in aquatic environments; however, several important factors must be considered in deciding whether to use them. Some of the factors highlighted include the physical effectiveness of the dispersant under conditions of expected use (Laux et al. 2000; Sterling et al. 2004), toxicity of dispersant and dispersed oil to local flora/fauna (Mitchell and Holdway 2000), the effect of dispersants on the fate of spilled petroleum hydrocarbon products (Moles et al. 2002) and the type of joint action toxicity exhibited by the mixtures (Otitoloju 2006). Studies on the toxicity of mixtures of crude oil and dispersants tend to indicate that there is usually an enhancement of the toxicity of the mixture (Akintonwa and Ebere 1990; Fisher and Foss 1993). This increase in the biological response of exposed organisms has been attributed to increased hydrocarbon availability in the water column following dispersion (Fisher and Foss 1993). A few other studies have also reported a decrease in toxicity of crude oil following dispersant application. For instance, Fabregas et al. (1984) working on Corexit 8667 and Corexit 7664 reported that non-dispersed crude oil was more toxic to prasinophycete, *Tetraselmis suecica*, than the dispersed oil.

Recent information on joint action toxicity of mixtures of compounds has shown that the types of interactions exhibited by components of mixtures are largely dependent on the proportion of their occurrence in the mixture (Otitoloju 2002, 2003). Basically, when two or more chemicals are exposed simultaneously against a living system, the interactions between the constituents may result in an enhancement (synergism), addition (additive action), or reduction (antagonism) of the toxic effects of the chemicals (Enserik et al. 1991; Don-Pedro 1996; Otitoloju 2002, 2003). Therefore, it is not impossible that those dispersants, which in the past were found to have enhanced (synergism) the toxic effect of crude oil to exposed organisms, could actually have caused a reduction (antagonism) in the toxic effect at other dispersal ratios. Indeed, it is a fact that the recommended mixture or dispersing ratio of previously introduced dispersants took into consideration mainly the optimum dispersal ratio that could achieve the greatest emulsifying capabilities with minimal consideration for the type of joint action that may be exhibited by the mixtures at the proposed mixing ratio (Kingham 1981). It is therefore important to carry out extensive toxicity evaluation of dispersants and crude oil in various mixing ratios before permits are given to allow the use of such chemicals in managing oil spills in aquatic resources.

On the basis of the above, the objective of this study is to estimate an environmentally safe dispersal ratio for two dispersants used for crude oil spill control, which can achieve optimum dispersal of spilled oil at a minimal level of toxicity or damage to the ecosystem.

2 Materials and methods

2.1 Materials

2.1.1 Test animal, acclimatization, and selection of test animals

Clarias gariepinus (air breathing catfish): Chordata, Osteichthyes, Siluriformes, and Clariidae. Juvenile stages of *C. gariepinus* (weight range 18–25 g; length range 14.5–17.1 cm) were used for the experiment. The source of the fish was a fish farm in Lagos, Nigeria. The fishes were caught early in the morning and transported to the research laboratory in oxygenated polythene bags (containing borehole or dechlorinated water) between 6:30 a.m. and 7:30 a.m. In the laboratory, about 50 juveniles were transferred into a plastic holding tank (28 × 51 × 29 cm) that had been three-quarter filled with dechlorinated water. In the holding tank, the juveniles were fed twice (morning and evening) daily and the stock water changed every other day to prevent the accumulation of waste metabolites and decaying food materials. The acclimatization period was 7 days during which the fishes were stabilized to the laboratory environment (temperature 28 ± 2°C; relative humidity 78 ± 4%) before being used for laboratory bioassays.

Juveniles of similar sizes, 8–10 weeks old, were caught with the aid of a hand net from the stock tank. They were then transferred to the test media in the bioassay tanks. Mortality assessments were made every 24 h over 4 days. Test animals were taken to be dead when they failed to respond to mechanical stimulation. Dead fish was removed at each observation.

2.1.2 Test chemicals/compounds

Crude oil. Fresh Forcados light crude oil used for this experiment was obtained from Shell (SPDC) production platform in Forcados, Port-Harcourt, Nigeria. Some of the physico-chemical characteristics of the Forcados light brand of crude oil include: sulfur content 0.2%; API gravity 60/60F; rapid vapour pressure 2.5 psi; and pour point 25.

Dispersant I. Biosolve is a water-based, biodegradable hydrocarbon mitigation agent.

Properties: flash point, NA; water-based > 93.3°C; pour point, 0.5°C; viscosity, 490 cP; specific gravity, 1.025 at

15.5°C; pH, 9.37 ± 0.5; surface active agent, confidential; solvents, confidential; additives, confidential; and solubility in water, complete.

Dispersant II. OSD 9460 is a water-based, biodegradable hydrocarbon mitigation agent.

Properties: flash point, none; pour point, 0°C; viscosity, 700 cP; specific gravity, 1.03 at 15.5°C; pH, 7.5; surface active agent, confidential; solvents, water; additives, confidential; and solubility in water, complete.

2.2 General bioassay procedures

2.2.1 *Preparation of test media*

Single action bioassays. A measuring cylinder was used to measure one litre of dechlorinated water and added into each bioassay tank. Predetermined amounts of the test chemicals, crude oil, Biosolve, OSD 9460, were measured out using pipette and then introduced into each bioassay tank by removing the same amount of water first and making it up to one litre to achieve the given concentration of the test medium. The mixture was shaken or mixed vigorously for about 15 s before introducing the animals.

Joint action bioassays. Mixtures involving binary constituents (oil:dispersant) in predetermined ratios of 9:1 (prescribed by regulators for oil spill control in Nigeria), 6:1 (prescribed by the manufacturers) and 12:1 of the test compounds were prepared. At each predetermined concentration of a mixture to be tested, the proportion of each constituent compound dictated by the predetermined ratio was computed and measured out. Crude oil was applied to the substrate before transferring the dispersant at the desired concentration into the bioassay container.

2.2.2 *Measurement of physico-chemical characteristics of test media*

Physico-chemical characteristics measurements were made at the beginning of the experiment and at the end (i.e., before change of test media) after 48 h. The parameters measured are: dissolved oxygen (using Jenway instruments), pH (using Hanna instruments), total dissolved solids (using Hanna instruments), conductivity (using Hanna instruments), and salinity (using an automatic compensation salinity refractometer made by Atago).

2.3 Bioassay

2.3.1 *Single action toxicity of crude oil and dispersants against juveniles of C. gariepinus*

Four active catfishes, *C. gariepinus*, of similar sizes in two replicates were introduced randomly into the test media in bioassay containers. A total of eight juveniles were exposed per treatment including untreated or control [without test chemical(s)]. Test animals were exposed to graded concentrations of crude oil and dispersants acting singly as follows:

Crude oil: 0.5, 2.5, 5, 8, 10, 12 ml/l, and untreated control.
Dispersant 1: Biosolve; 0.25, 0.50, 0.75 μl/l, and untreated control.
Dispersant 2: OSD 9460; 0.5, 1.5, 3, 5, 8, 10 ml/l, and untreated control.

Mortality was assessed as described in Sect. 2.1.1 once in every 24 h for a period of 96 h (4 days).

2.3.2 *Joint action toxicity of mixtures of crude oil and dispersants against juveniles of C. gariepinus*

A similar procedure as described in Sect. 2.3.1 was carried out in these bioassays; the test media contained both crude oil and dispersants in ratios 6:1, 9:1, and 12:1. The juveniles were exposed to varying concentrations of the mixtures as follows:

Crude oil/Biosolve: 0.5, 0.8, 1, 1.2, 1.6, 2.5, 4, 6, 8, 12, 15 μl/l, and untreated control.
Crude oil/OSD 9460: 0.5, 2, 2.5, 4, 6, 8, 10, 12, 15 ml/l, and untreated control.

Mortality was assessed as described in Sect. 2.1.1 once in every 24 h for a period of 96 h (4 days).

2.3.3 *Determination of dispersant efficacy by measurement of optical transmittance*

The optical transmittance of crude oil and dispersants, OSD 9460 and Biosolve, singly and in binary mixtures (6:1, 9:1, 12:1) obtained within the visible wavelength spectrum of 540 nm was used a measure of emulsification of the crude oil. This was carried out by pipetting a given volume of crude oil, OSD 9460 and Biosolve, and their binary mixtures (6:1, 9:1, 12:1) into a cuvette, vortexed for 5 min, and allowed settling for 5 min, and then the optical transmittance of the dispersed oil in the water column with the aid of a colorimeter set at wavelength of 540 nm was measured.

2.4 Statistical analysis

2.4.1 *Probit analysis*

Toxicological data involving quantal response (mortality) for both single and joint action studies were analyzed by probit analysis—including equation for probit lines (Finney 1971). This was executed via a computer program by Ge Le Pattorel, Imperial College, London, run by an IBM computer system as adopted by Don-Pedro (1989). The indices of toxicity measurement derived from these analyses were LC_{50}, LC_{95}, TF, and their 95% confidence limits were employed as follows:

LC_{50}	Median lethal concentration that causes 50% response (mortality) of exposed organisms.
LC_{95}	Lethal concentration that causes 95% response (mortality) of exposed organisms.
TF	Toxicity factor for relative potency measurements, e.g., ratio of 96-h LC_{50} of a compound to LC_{50} values at equivalent time intervals.

2.4.2 *Analysis of data and measurement of joint action toxicity of multiple mixtures of test compounds*

For the joint action toxicity of heavy metals mixtures, the two models employed for the classifications are the concentration-addition model by Anderson and Weber (1975) with slight modification [relative toxic units (RTU) estimations; Otitoloju (2001)] and the synergistic ratios (SR) model after Hewlett and Plackett (1969).

Model 1. The concentration-addition model assumes that when similarly acting toxicants are mixed in any proportion, they will add together to give the observed response. In evaluating the joint action, a predicted response value(s) (e.g., LC_{50}) is derived by summing-up the LC_{50} values of the separate toxicants according to the proportion of their contribution in the mixture. The predicted LC_{50} value(s) is then compared to the observed LC_{50} value of the mixture so as to classify the type of interaction among the components of the mixture as follows:

Additive if the observed LC_{50} value of the mixture is equal to the predicted LC_{50} value.
Synergistic if the observed value of the mixture is less than the predicted LC_{50} value.
Antagonistic if the observed LC_{50} value of the mixture is greater than the predicted LC_{50} value.

The relationship of observed LC_{50} values to predicted LC_{50} (RTU) values is estimated as follows:

$$RTU = \frac{\text{predicted } LC_{50} \text{ value}}{\text{observed } LC_{50} \text{ value}}$$

where $RTU = 1$ describes additive action, $RTU < 1$ describes antagonism, and $RTU > 1$ describes synergism.

Model 2. The SR model is as follows:

$$SR = \frac{LC_{50} \text{ of a chemical acting alone}}{LC_{50} \text{ of chemical} + \text{additive (mixture)}}$$

where $SR = 1$ joint action is described as additive, $SR < 1$ joint action is described as antagonistic, and $SR > 1$ joint action is described as synergistic.

3 Results

3.1 Physico-chemical characteristics of test media

The results of the physico-chemical parameters of the test media are given in Table 1. The dissolved oxygen level ranged from 5.8 (after 2 days of exposure) to 9.7 mg/l (after each change to a clean media). The pH and salinity of the test media remained constant with values ranging from 7.2 to 7.3 and 2 to 3‰, respectively. The conductivity and total dissolved solids in the test media increased from 0.12 mS/cm and 0.06 mg/l to 0.26 mS/cm and 0.13 mg/l, respectively over the period of observation.

3.2 Relative acute toxicity of crude oil and dispersants against *C. gariepinus*

On the basis of the 96-h LC_{50} value, the dispersant Biosolve (96-h $LC_{50} = 0.211$ µl/l) was the most toxic followed by the dispersant OSD 9460 (96-h $LC_{50} = 1.361$ ml/l), and crude oil (96-h $LC_{50} = 5.757$ ml/l) was the least toxic of the test compounds (Table 2). The computed toxicity factor revealed that Biosolve was about 27,284 times more toxic than crude oil and 6,450 times more toxic than OSD 9460. OSD 9460 was also found to be four times more toxic than crude oil (Table 2). Probit–log concentration graph depicting the relative profile of the test compounds against *C. gariepinus* was non-parallel. This implies that comparison of toxicity levels or relative potency is statistically restricted to only a particular response level and concentration (LC_{50} values).

Table 1 Physico-chemical characteristics of test media

Physico-chemical parameters	Unit	At the beginning of the experiment	Before change to a clean media
Conductivity	mS/cm	0.12	0.26
Dissolved oxygen (DO)	mg/l	9.7	5.8
pH at 25°C	–	7.3	7.2
Salinity at NaCl ppt	‰	2	3
Total dissolved solids (TDS)	mg/l	0.06	0.13

Table 2 Relative acute toxicity of crude oil, Forcados light, and dispersants, OSD 9460 and Biosolve, acting singly against *Clarias gariepinus* based on 96 h mortality data

Treatment	LC_{50} (95% CL)	LC_{95} (95% CL)	Slope ± SE	Probit equation	*df*	TF
Crude oil (ml/l)	5.757 (7.571–4.365)	13.725 (24.491–7.914)	4.373 ± 1.355	$Y = 1.676 + 4.373X$	2	1
OSD 9460 (ml/l)	1.361 (4.085–0.187)	11.133 (44.517–2.318)	1.000 ± 0.820	$Y = 4.758 + 1.808X$	2	4.2
Biosolve (μl/l)	0.211 (0.411–0.093)	0.592 (1.384–0.298)	3.687 ± 1.908	$Y = 7.489 + 3.687X$	1	27,284

CL confidence limit, *df* degree of freedom, *SE* standard error, *H* hours

Toxicity factor (TF) $= \frac{\text{96-hLC}_{50}\text{ of crude oil}}{\text{96-h LC}_{50}\text{ ofdispersant}}$

3.3 Joint action toxicity of binary mixtures (6:1, 9:1, and 12:1) of crude oil and dispersants, OSD 9460 and Biosolve, against *C. gariepinus*

3.3.1 Crude oil:OSD 9460 mixtures

The analysis of dose–response data for the mixture of crude oil and dispersant OSD 9460 at mixture ratios of 6:1, 9:1, and 12:1 showed that the 96-h LC_{50} values of the mixtures were 2.582, 3.126, and 6.813 ml/l, respectively, compared with the 96-h LC_{50} values of 5.757 and 1.361 ml/l for crude oil and OSD 9460 when acting singly (Table 3). On the basis of the derived LC_{50} values, two of the mixtures (ratios 6:1 and 9:1) were more toxic than crude oil when acting singly.

Comparison of the predicted toxicity of the mixtures (based on the concentration–addition model) and their experimentally observed toxicity levels (96-h LC_{50}) revealed that the interactions between crude oil and OSD 9460 were in agreement with the model of synergism ($RTU > 1$) for dispersal mixture ratios 6:1 and 9:1, while for mixture ratio of 12:1 interactions between the test chemicals were antagonistic ($RTU < 1$).

Further analysis of the dose–response data by the SR model revealed that interactions between the test compounds conformed with the model of synergism, with SR ranging between 2.23 and 1.84 for ratios 6:1 and 9:1, respectively, while for dispersal ratio 12:1, interaction between the constituent was antagonistic ($SR < 1$).

3.3.2 Crude oil:Biosolve mixtures

The analysis of dose–response data for the mixture of crude oil and dispersant Biosolve at mixture ratios of 6:1, 9:1, and 12:1 showed that the 96-h LC_{50} values of the mixtures were 0.752, 0.387, and 6.548 μl/l, respectively, compared with the 96-h LC_{50} values of 5.757 ml/l and 0.211 μl/l for crude oil and Biosolve when acting singly (Table 4). On the basis of the derived LC_{50} values, all of the mixtures (ratios 6:1, 9:1, and 12:1) were more toxic than crude oil when acting singly.

Comparison of the predicted toxicity of the mixtures (based on the concentration-addition model) and their experimentally observed toxicity levels (96-h LC_{50}) revealed that the interactions between crude oil and Biosolve were in agreement with the model of synergism ($RTU > 1$) for the dispersal ratios 6:1, 9:1, and 12:1.

Further analysis of the dose–response data by the SR model revealed that interactions between the test compounds conformed to the model of synergism, with SR ranging between 879 and 14,876 for the dispersal ratios 6:1, 9:1, and 12:1.

Table 3 Analysis (based on concentration-addition or synergistic ratio models) of the 96-h LC_{50} values of crude oil and OSD 9460 when acting jointly or singly against *C. gariepinus* juveniles

Treatment (ml)	Observed 96-h LC_{50} (95% CL)	Predicted 96-h LC_{50} (95% CL)	Probit line equation	RTU	SR
Crude oil/OSD (6:1)	2.582 (6.078–0.929)	5.129 (7.073–3.768)	$Y = 3.81 + 2.889X$	1.99	2.23
Crude oil/OSD (9:1)	3.126 (4.184–2.319)	5.317 (7.222–3.947)	$Y = 1.232 + 7.612X$	1.70	1.84
Crude oil/OSD (12:1)	6.813 (10.938–4.174)	5.419 (7.303–4.044)	$Y = 1.873 + 3.752X$	0.79	0.84
Crude oil acting singly	5.757 (7.571–4.365)		$Y = 1.676 + 4.373X$		

CL confidence limit

Predicted 96-h LC_{50} = sum total of the single action 96-h LC_{50} values of constituent toxicants according to proportion of contribution in the test mixture

Synergistic ratio (SR) $= \frac{96-\text{h LC}_{50}\text{ of crude oil acting singly}}{\text{96-hLC}_{50}\text{ ofthemixture}}$

Relative toxic units (RTU) $= \frac{\text{predicted }96-\text{h LC}_{50}}{\text{observed}96-\text{hLC}_{50}}$, where $RTU = 1$ describes additive action, $RTU < 1$ describes antagonism, and $RTU > 1$ describes synergism

Table 4 Analysis (based on concentration-addition or synergistic ratio models) of the 96-h LC_{50} values of crude oil and Biosolve when acting jointly or singly against *C. gariepinus* juveniles

Treatment	Observed 96-h LC_{50} (95% CL)	Predicted 96-h LC_{50} (95% CL)	Probit line equation	RTU	SR
Crude oil/Biosolve (6:1) μl/l	0.752 (1.116–0.242)	4,934.602 (6,489.487–3741.442)	$Y = 5.553 + 4.462X$	6,561.970	7,655.58
Crude oil/Biosolve (9:1) μl/l	0.387 (1.424–35.206)	5,181.321 (6,813.941–3,928.509)	$Y = 5.441 + 1.070X$	13,388.462	14,875.97
Crude oil/Biosolve (12:1) μl/l	6.548 (14.582–2.851)	5,314.170 (6,988.647–4,029.238)	$Y = 2.708 + 2.808X$	811.571	879.2
Crude oil (μl/l) acting singly	5.757 (7.571–4.365)		$Y = 1.676 + 4.373X$		

CL confidence limit

Predicted 96-h LC_{50} = sum total of the single action 96-h LC_{50} values of constituent toxicants according to proportion of contribution in the test mixture

Synergistic ratio (SR) $= \frac{96\text{−h LC}_{50}\text{ of crude oil acting singly}}{96\text{-hLC}_{50}\text{ ofthemixture}}$

Relative toxic units (RTU) $= \frac{\text{predicted 96−h LC}_{50}}{\text{observed96−hLC}_{50}}$, where RTU = 1 describes additive action, RTU < 1 describes antagonism, and RTU > 1 describes synergism

3.4 Emulsification potential of crude oil by dispersants, Biosolve and OSD 9460, prepared at dispersal ratios 6:1, 9:1, and 12:1

3.4.1 *Dispersant OSD 9460*

The results of the emulsification potential of OSD 9460 [measured in terms of optical transmittance (%)] prepared at the dispersal ratios 6:1, 9:1, and 12:1 revealed that the ratio dispersal 6:1 of crude oil:OSD 9460 achieved the highest emulsification of the crude oil with optical transmittance value of 4% compared with dispersal ratios 9:1 (3%) and 12:1 (1%), while the reference materials, dechlorinated tap water and crude oil, had optical transmittance values of 63.5 and 0%, respectively (Table 5).

3.4.2 *Dispersant Biosolve*

The results of the emulsification potential of Biosolve [measured in terms of optical transmittance (%)] prepared at the dispersal ratios 6:1, 9:1, and 12:1 revealed that the ratio dispersal 6:1 of crude oil:Biosolve achieved the highest emulsification of the crude oil with optical transmittance value of 6% compared with dispersal ratios 9:1 (4%) and 12:1 (4%), while the reference materials, dechlorinated tap water and crude oil, had optical transmittance values of 63.5 and 0%, respectively (Table 6).

3.5 Estimation of environmentally sensitive dispersal ratios for dispersants, OSD 9460 and Biosolve

3.5.1 *Dispersant OSD 9460*

Estimation of the optimum emulsification potential of OSD 9460 by plotting the toxicity indices (96-h LC_{50}) values of the crude oil, dispersants, and dispersal ratios (6:1, 9:1, and 12:1) of crude oil to dispersant against the optical transmittance values on a log scale revealed that the dispersal ratio, which would be environmentally safe by achieving optimum emulsification of the crude oil at an acceptable level of toxicity, is between 7.5:1 and 9:1 (Fig. 1).

3.5.2 *Dispersant Biosolve*

Estimation of the optimum emulsification potential of Biosolve by plotting the toxicity indices (96-h LC_{50}) values of the crude oil, dispersants, and dispersal ratios (6:1, 9:1, and 12:1) of crude oil to dispersant against the optical

Table 5 Emulsification potential (optical transmittance %) of dispersant OSD 9460 and the toxicity indices (96-h LC_{50} values) of the test compounds acting singly and jointly

Test compound(s)	96-h LC_{50} value (ml/l)	Mean transmittance (%) ±SD
Dechlorinated tap water	–	63.5 ± 0.5
Crude oil alone	5.757	0 ± 0.0
OSD alone	1.361	0 ± 0.0
Crude oil/OSD (6:1)	2.582	4 ± 0.1
Crude oil/OSD (9:1)	3.126	3 ± 0.1
Crude oil/OSD (12:1)	6.813	1 ± 0.1

Table 6 Emulsification potential (optical transmittance %) of dispersant Biosolve and the toxicity indices (96-h LC_{50} values) of the test compounds acting singly and jointly

Test compound(s)	96-h LC_{50} values (ml/l)	Mean transmittance (%) ±SD
Dechlorinated tap water	–	63.5 ± 0.5
Crude oil alone	5.757	0 ± 0.0
Biosolve alone	0.000211	4 ± 0.1
Crude oil/Biosolve (6:1)	0.000752	6 ± 0.2
Crude oil/Biosolve (9:1)	0.000387	4 ± 0.1
Crude oil/Biosolve (12:1)	0.006548	4 ± 0.1

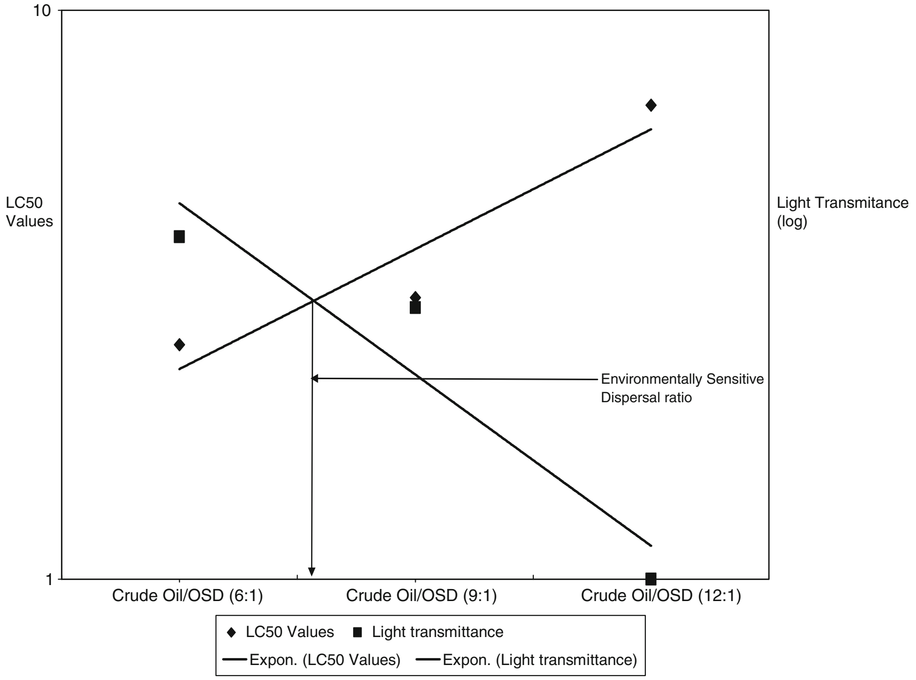

Fig. 1 Estimation of environmentally sensitive dispersal ratio for dispersant OSD 9460 in crude oil spill control

transmittance values on a log scale revealed that the dispersal ratio, which would be environmentally safe by achieving optimum emulsification of the crude oil at an acceptable level of toxicity, was not derivable within the range of dispersal ratios tested (Fig. 2).

4 Discussion

In this study, the dispersants, Biosolve and OSD 9460, were found to be about 27,000 and four times, respectively, more toxic than crude oil when tested against *C. gariepinus*, based on the 96-h LC_{50} value. This is consistent with the report of Oyewo (1986), which stated that some dispersants used in Nigeria were relatively highly toxic to some aquatic organisms. Ross (1997) also stated that the dispersant used for treating the Torrey canyon oil spill that occurred in Britain in 1967 turned out to be highly toxic and resulted in the mortality of crustaceans, molluscs, and other animals in the dispersant treated areas. Similarly, Nelson-Smith (1967) also reported that one of the most serious problems associated with the early use of dispersants was the toxicity of

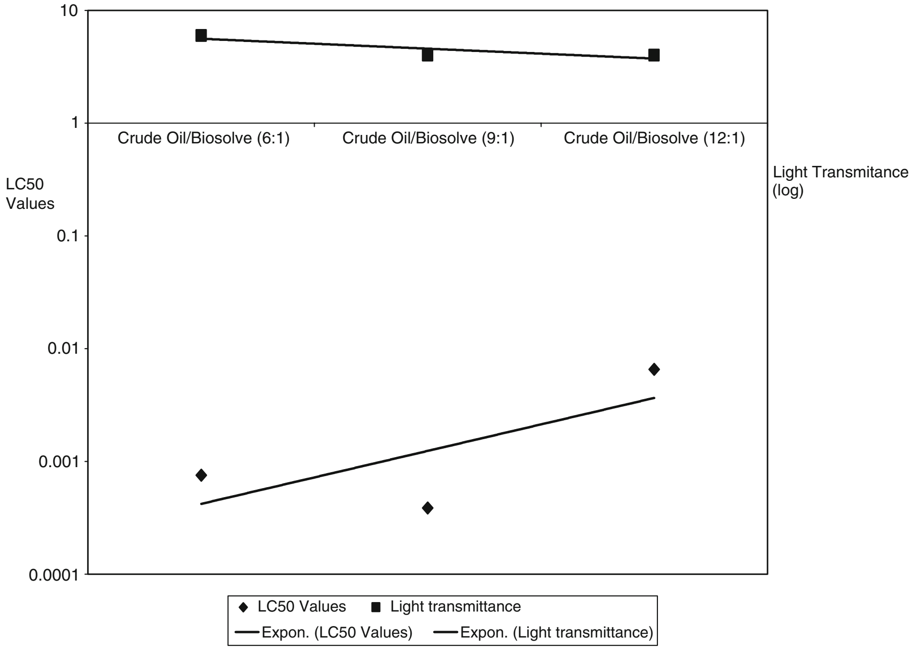

Fig. 2 Estimation of environmentally sensitive dispersal ratio for dispersant Biosolve in crude oil spillage control (environmentally safe dispersal ratio for the dispersant Biosolve is indeterminate within the range of test dispersal ratios)

the dispersants themselves, particularly those whose solvent fractions consisted of a mixture of hydrocarbons. For example, Corexit 9527 that has been found to be very toxic to aquatic organisms contains the hydrocarbon solvent ethylene glycol monobutyl ether (Mitchell and Holdway 2000), which has now been reformulated and likely to be replaced by a less toxic Corexit 9500. The trend generally is the introduction into the market of more water-based dispersants such as OSD 9460 and Biosolve that are believed to be generally less toxic (Moles et al. 2002).

Comparison of the toxicity of both the dispersants, OSD 9460 and Biosolve, also revealed that Biosolve was about 6,805 times more toxic than OSD 9460 when acting singly against *C. gariepinus*. The differential toxicity observed between these two water-based dispersants indicates that the type of surfactants, either anionic or ionic or combination of both, also contributes significantly to the toxicity observed in exposed organisms. The types of surfactants and physical characteristics of the eventual product will dictate their penetrability into living organisms, site of action of metabolism, and hence the toxic actions they exert on exposed organisms. Generally, it has been well established that most dispersants act on the surface membrane of exposed organisms thereby disrupting the membrane barrier and thus causing easier influx of toxicants.

The studies on the joint action toxicity of crude oil and the dispersant OSD 9460 when prepared at the dispersal ratios 6:1, 9:1, and 12:1 and tested against *C. gariepinus* revealed that the type of interactions between the constituent compounds varied, depending on the proportion of the mixture components. Interactions between constituent compounds prepared according to ratios 6:1 and 9:1 were found to be synergistic (SR ranging from 1.84 to 2.23), and consequently the mixtures were more toxic than crude oil when acting singly against the test animal *C. gariepinus*. Interactions between the constituents prepared based on dispersal ratio 12:1 was however found to be antagonistic and consequently the mixture was less toxic than crude oil acting singly. Therefore, indicating that the dispersant OSD 9460 would be a potentially safer dispersant when deployed at the 12:1 ratio.

The studies on the joint action toxicity of crude oil and the dispersant Biosolve when prepared at ratios 6:1, 9:1, and 12:1 and tested against *C. gariepinus* revealed that the interactions between the constituent compounds were in conformity with the model of synergism (SR ranging from 879 to 14,875), and consequently the mixtures were more toxic than crude oil when acting singly against the test animal, *C. gariepinus*. In fact, the mixture prepared according to the prescribed dispersal ratio (6:1) by the manufacturers was about 8,000 times more toxic than crude oil acting alone against the catfishes. The implication of this observation is that in terms of toxicity and potential of causing damage to aquatic lives, it would be better-off not to control spilled oil than to deploy the dispersant Biosolve oil at the manufacturer's recommended or other test dispersal ratio, since the results have shown that the mixture of the dispersant and crude oil have the potential to cause more harm in the environment than the crude oil itself.

Determination of the emulsification potential of both dispersants showed that Biosolve has higher capacity to emulsify crude oil than OSD 9460. The optical transmittance values obtained for Biosolve at dispersal ratios of 6:1, 9:1, and 12:1 ranged from 4 to 6% while for OSD 9460 it ranged from 1 to 4%. Comparison of the obtained values with the optical transmittance values obtained for crude oil alone (0%), OSD 9460 (0%), Biosolve (4%), or dilution waters (63.5%) showed that the optical transmittance measurement did give an indication of dispersion of the crude oil into the water column. Other test protocols, which have been used to evaluate the effectiveness of dispersants to emulsify crude oil, include the swirling flask test (Fingas et al. 1995), baffle flask test (Moles et al. 2002), EPA method, CAL SFT method, and many other variations of the swirling flask test (Blodina et al. 1997). The various methods involve the use of different analytical instruments such as the gas chromatography, nitrogen–sulfur–carbon analyzers, oil content meters, and TOC analyzers. According to Blodina et al. (1997), all these techniques suffered similar biases though they gave an indication of the dispersion of oil into the water column. So like other dispersant effectiveness tests, the optical transmittance test may have its biases but it gave a good indication of dispersion of the crude oil into the water column.

Most manufacturers of chemical dispersants set the recommended dispersal ratios for their products on the basis of the economics and effectiveness of the dispersant to disperse the crude oil with minimal consideration for the potential harm that can be caused in the receiving ecosystem (Laux et al. 2000). As a result, the deployments of dispersants in the past have always come at a great loss of organisms inhabiting the already impacted habitat. Proper risk assessment and quantification of hazard would, however, be required if an "environmentally sensitive" dispersal ratios for chemical dispersants are to be prescribed. The estimation of such safe dispersal ratio, which would be capable of achieving desirable level of dispersion of crude oil at a corresponding acceptable level of toxicity, would therefore need to be determined in order to achieve a "safer" deployment of dispersants in oil spill control. An attempt in this study to estimate such an "environmentally sensitive" dispersal ratio for OSD 9460 and Biosolve revealed that such an optimum dispersal ratio for OSD 9460 would range between ratios

7.5:1 and 9:1 which are quite within the recommended dispersal ratio for dispersants by the regulatory body (Department of Petroleum Resources) in Nigeria. However, for the more toxic Biosolve, such estimation of an optimal dispersal ratio which takes into consideration both emulsification capacity and the toxicity of the mixtures could not be determined within the range of test dispersal ratios. Therefore, both the manufacturer's prescribed ratio of 6:1 and regulatory body recommended ratio of 9:1 are environmentally insensitive, and the deployment of this dispersant Biosolve at any of these dispersal ratios is likely to cause more harm in the receiving ecosystem than if the spilled oil was left uncontrolled.

On the basis of these results, it is important for the manufacturers and regulatory bodies involved in oil pollution control to revise the existing dispersal ratios currently being used for spill control in order to accommodate the need to protect organisms inhabiting the receiving ecosystem. Furthermore, regulatory bodies especially in the developing countries like Nigeria must also desist from setting a blanket dispersal ratio for all dispersants because of the differences in their potential to cause harmful effects in the environment as observed between the two dispersants tested in this study.

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