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Possible Synergistic Toxicity of Oxygen Scavenger and Defoamer on the Niger Delta Freshwater *Tilapia guineensis*

Ikechukwu Kingsley Anyanwu[1*], Ogbonna Friday Joel[1], Owunari Abraham Georgewill[2]

[1]World Bank Africa Centre of Excellence in Oilfield Chemical Research (ACE-CEFOR), University of Port Harcourt, Rivers State, Nigeria
[2]Department of Pharmacology, Faculty of Basic Medical Science, University of Port Harcourt, Rivers State, Nigeria
Email: *anyanwu.kingsley@aceuniport.org, ike4moni@gmail.com, ogbonna.joel@uniport.edu.ng, owunari.georgewill@uniport.edu.ng

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Abstract

Globally, the generation of produced water keeps increasing due to depleting wells and about 40% of this wastewater is disposed of into the environment. Produced water is made up of several components that are toxic in nature, like production chemicals that are used for oil and gas production activities. Oxygen scavenger and defoamer are commonly used for corrosion prevention as both are applied at different stages of corrosion prevention. Evaluation of the possible synergistic toxicity contribution of oxygen scavenger and defoamer formed the basis of this research and was conducted using the *Tilapia guineensis* as bio-indicator. The toxicity test was carried out using the ELIMINOX (oxygen scavenger) and EC9017A (defoamer) individually and both chemicals were combined together. The choice of these chemicals was premised on previous researches that have confirmed that they are toxic individually, without further research on how they interact when they are combined. These chemicals and freshwater were used to generate produced water samples in the laboratory. The experiment was set up by adding ten fishes into each of the glass containers, containing the produced water samples at different concentrations and a control sample without the chemicals. The rate of mortality of the fish for the individual chemicals ranged from 100% to 10% for the different percentage concentrations. While on the other hand, a combination of the two chemicals had more survival than mortality, the percentage survival rate ranged from 100% to 90% across all the percentage concentrations. The lethal concentration also showed that the oxygen scavenger was more toxic than the defoamer, however, when they were combined; they showed an antagonistic relationship as the toxicity of the oxygen scavenger drastically reduced. The research findings intend to create awareness of the possible interaction of production chemicals when they are used for oil and gas activities and their combined toxicity contribution to produced water. This will in turn aid government regulators in their decision-making for disposal of produced water.

Keywords

Produced Water, Oxygen Scavenger, Defoamer, *Tilapia guineensis*, Toxicity, Lethal Concentration, Synergetic Effects

1. Introduction

The water in oil and/or gas reservoirs are usually referred to as connate or formation water and they can be either fresh or saltwater. This connate water is easily trapped in the reservoir because water is heavier than oil and/or gas and the water characteristics are largely determined by the type of chemicals used for the drilling and production activities [1] [2].

Produced water is a mixture of the connate water and drilling/production enhancement chemicals, and it's the highest form of waste generated in the petroleum industry. This waste can be as high as 80% during natural gas production from gas reservoirs [3] [4].

The main means of disposal of oilfield produced water world over is through discharge into the ocean, there is however concerns to this means of disposal, considering that produced water discharge is continuous and the volume generated keeps increasing as the oil and gas from the reservoirs keeps depicting. Aside from the volume of produced water disposed of into these water bodies, the produced water contains concentrations of heavy metals and toxic compounds that are higher than that in the recipient water bodies, which can have potentially toxic effects on the aquatic environment [4].

Globally it is estimated that 250 million barrels of produced water are generated daily and about 40% of this produced water is being discharged into the aquatic environment [5]. In the Nigerian oil fields, the estimated average ratio of oilfield produced water to oil is 1:1 and about 1 billion barrels of oilfield produced water is generated yearly from oil and gas production activities [6].

Produced water is made up of different components, these components include dissolved solids, heavy metals, residual hydrocarbons, suspended solids, chemicals used during the oil and gas production, organic and inorganic species and naturally occurring radioactive materials [7]. Oil and grease and other dissolved compounds are the major constituents of organic compounds of oilfield-produced water [7]. The authors [8] and [9] went further to state that produced water components vary with time from one location to the other and depend on the production activity, whether it is oil production or gas production or in their associated state.

There are different drill chemicals used or applied to oil and gas production systems during production activities. These chemicals serve their unique purposes, like prevention of corrosion, enhanced separation of the water from oil and/or gas, and prevention of formation of methane hydrate in gas production systems [4]. The common ones are emulsion breakers, gas treating chemicals, oxygen scavengers, defoamers, corrosion inhibitors and biocides. Oxygen scavengers are used in water injection systems to reduce corrosion and to reduce microbial activities and hydrogen sulfide production, biocides can be used. To increase flow rates, reduce scales, corrosion and foam production, corrosion inhibitors and anti-foams can be used. Surfactants and polymers can also serve as chemicals for enhanced oil recovery [10]. For instance, to reduce corrosion or microbial activities, there is a need to eliminate oxygen, and oxygen scavengers capture all the dissolved oxygen present when it is introduced in a production system in a safe reaction and leaves no oxygen for corrosion or microbial aerobic reactions [11].

Defoamers also referred to as anti-foam is usually introduced into saline waters during treatment (desalination). These saline waters are prone to foaming and scaling that affects the efficiency of desalination equipment, to overcome this effect defoamers are introduced to the saline water to remove the foams [12].

The concentration of production chemicals in oilfield produced water from any production system that had need of any of them are usually high. Despite their importance, there are however some environmental concerns associated with their usage, as studies have shown they are toxic in nature and the concentration of the chemicals determines their level of toxicity contribution to the produced water, and when they are disposed of into the aquatic environment can lead to mortality of the aquatic organisms [4].

These authors [13] in their work demonstrated the possible combined toxic effect of graphene oxide and trace elements like Zinc (Zn) and Cadmium (Cd) on the freshwater fish *Geophagus iporangensis*. Their research showed that the combination of graphene oxide and trace elements had synergetic effects on the fish.

These authors [14] in their work sought to understand the interaction of lead (Pd) and carbon nanotubes and their synergistic toxic effect on Nile tilapia (*Oreochromis niloticus*). They concluded that the carbon nanotubes increased the toxicity of the lead which was evident in the increased damage to the gills of the fishes, showing a synergetic effect. In a related work by these authors [15] using carbofuran and carbon nanotubes, it was also observed that the toxicity effect of the carbofuran on the Nile tilapia (*Oreochromis niloticus*) was increased by 25% after the interaction of the two toxicants, showing a synergistic effect.

These authors [12] carried out a chronic toxicity test of defoamers on rats for a 90-day test period and concluded from their research that the livers of the rats, especially the female rats were severely damaged by the defoamer which indicates that its toxic living organisms. This author [16] stated that defoamer when introduced into water has the potentials to affect the rate of oxygen transfer in the water and hence affect the dissolved oxygen.

This research will seek to understand how production chemicals (oxygen scavenger and defoamer) interact with each other when present in produced water and to confirm their possible synergistic toxic effects on *Tilapia guineensis*, a common fish species in the Niger Delta environment.

2. Research Methodology

2.1. Chemicals Used

ELIMINOX (oxygen scavenger) and EC9017A (de-foamer) were used in the experimental study. The chemicals are already prepared sourced products from the market within Nigeria and have been approved by the Department of Petroleum Resources (DPR) for use in oilfields within the Nigerian environment.

2.2. Apparatus/Instruments

100 Beaker, hand gloves, weighing balance, filter paper, DO meter, thermometer, multi-parameter photometer, glass container, holding tank small hand net mesh and electrical conductivity.

2.3. Sampling Collection and Handling

Tilapia guineensis (fishes) were purchased from the Aluu, Rivers State outstation of the Nigerian Institute of Oceanography and Marine Research (NIOMR) in 2019. The fishes were transferred immediately into marked plastic containers (50.00 cm diameters by 7.00 cm height with the top opened) each containing its habitat water. Collected samples were later transported to an external laboratory in Port Harcourt, Rivers State with the temperature of the water maintained between 24˚C to 27˚C. Ten (10) actively kicking *Tilapia guineensis* fishes that survived after ten days of acclimatization were randomly selected with a small hand net mesh from the appropriate holding tank and added to each glass container. Hand was not used to avoid stress to the organisms.

2.4. Description of Sampling Location

The Nigerian Institute for Oceanography and Marine Research (NIOMR) was established in November 1975 by the Research Institutes' Establishment Order 1975. The main research departments in the institute are: Aquaculture, Biological Oceanography, Biotechnology, Fisheries Resources, Fish Technology & Product Development, Marine Geology/Geophysics and Physical/Chemical Oceanography. The outstation location in Aluu, Rivers State, Nigeria is majorly into Fisheries Resources.

2.5. Toxicity Test of ELIMINOX and EC9017A

Toxicity test of ELIMINOX (oxygen scavenger) and EC9017A (de-foamer) was carried out in the laboratory for a 96hours test period using *Tilapia guineensis* as bio-indicator. The *Tilapia guineensis* was acclimatized for ten (10) days in freshwater sample and the actively kicking fishes were selected for test. Five (5) of the fishes were used for range finding test to determine the appropriate percentage concentration for the main experiment. Subsequently, ten (10) of the *Tilapia guineensis* were selected and used for the toxicity test proper. Hand was not used during the selection of the fishes to avoid stress on the organisms.

The experiment was set up using glass containers in the laboratory. 2000 ml of freshwater was added into each of the containers, as well as the chemicals of different percentage concentrations. From the range-finding the following percentage concentrations were used for the toxicity test; for oxygen scavenger 0.031%, 0.016%, 0.008% and 0.004%, for the de-foamer 0.5%, 0.25%, 0.125% and 0.0625%, a further test was carried out on the defoamer using same concentrations as the oxygen scavenger for ease of comparison. A control sample was also set up that contained only 2000 ml of freshwater.

Furthermore, another investigation was carried out to determine the synergistic effects of the two chemicals, considering their individual toxic effects. For this investigation, 0.0625% percentage concentration of the de-foamer was mixed with the individual concentrations of the oxygen scavenger used for the individual toxicity test.

For each of the experimental sets up, the pH, temperature, dissolved oxygen and electrical conductivity measurement were carried out at the beginning of the experiment and at the 96th hour for each of the different concentrations of the production chemicals.

The percentage survival and mortality of the *Tilapia guineensis* were monitored at an interval of one (1) hour for the ninety-six (96) hours test period. The median lethal concentration (LC50) of the oxygen scavenger and defoamer (individually and combined) on the test organisms in freshwater were determined by subtracting the value of the highest concentration used from the sum of concentration difference, multiplied by mean percentage mortality and divide by the control (100).

$$\text{LC50} = \text{LC100} - \frac{\sum \text{conc. Diff.} \times \text{mean \% mortality}}{\text{\% control}}$$

The (LC50) for the individual chemicals and when they were combined was calculated and compared with one another to ascertain their toxic effects on the *Tilapia guineensis*. The lethal concentration (LC50) is the percentage concentration that is required to kill half the *Tilapia guineensis*.

3. Results and Discussions

The results of the range-finding and the toxicity test for the 96 hours period are presented in **Tables 1-3** and **Figures 1-3**. The pH, temperature, dissolved oxygen and electrical conductivity values measured for the simulated produced water at different concentrations of the ELIMINOX (oxygen scavenger) ranged

Table 1. Range finding results for oxygen scavenger and defoamer.

Concentration/Time	Defoamer (% Conc.)			Oxygen Scavenger		
	0	0.0625	1	0	0.0625	1
No. of individual	5	5	5	5	5	5
% Mortality 4 hrs	0	0	100	0	60	100
% Mortality 8 hrs	0	0	100	0	100	100
% Mortality 12 hrs	0	0	100	0	100	100
% Mortality 16 hrs	0	0	100	0	100	100
% Mortality 20 hrs	0	0	100	0	100	100
% Mortality 24 hrs	0	0	100	0	100	100

Table 2. Percentage mortality of freshwater *Tilapia guineensis* at Various concentrations of oxygen scavenger combined with 0.0625% defoamer.

Concentration/Time	Control	0.031	0.016	0.008	0.004
No. of individual	10	10	10	10	10
4 hrs (% Mortality)	0	0	0	0	0
8 hrs (% Mortality)	0	0	0	0	0
12 hrs (% Mortality)	0	10	0	0	0
24 hrs (% Mortality)	0	10	0	0	0
48 hrs (% Mortality)	0	10	0	0	0
72 hrs (% Mortality)	0	10	0	0	0
96 hrs (% Mortality)	0	10	0	0	0

Table 3. LC50 Values for the production chemicals (individually and combined) on *Tilapia guineensis.*

Chemicals	*Tilapia guineensis*
Oxygen Scavenger	0.010%
Defoamer	0.176%
Oxygen Scavenger + Defoamer	0.030%

from 3.5 - 7.3, 28.1˚C - 30.1˚C, 2.56 mg/l - 5.79 mg/l and 290 mg/l - 500 mg/l respectively, while the values at different concentrations of EC9017A (anti-foam) ranged from 5 - 7.6, 28.4˚C - 30.3˚C, 2.94 mg/l - 6.36 mg/l and 230 mg/l - 390 mg/l respectively.

Table 1 shows the result of the range finding. For the defoamer, at the 0.625% percentage concentration, there was 100% survival of the *Tilapia guineensis* at the end of the 24 hours test period, while there was 100% mortality within 8hours of the test period for the oxygen scavenger. This was the basis for the choice of the percentage concentrations of 0.5%, 0.25%, 0.125% and 0.0625% for the defoamer and 0.031%, 0.016%, 0.008% and 0.004% for the oxygen scavenger.

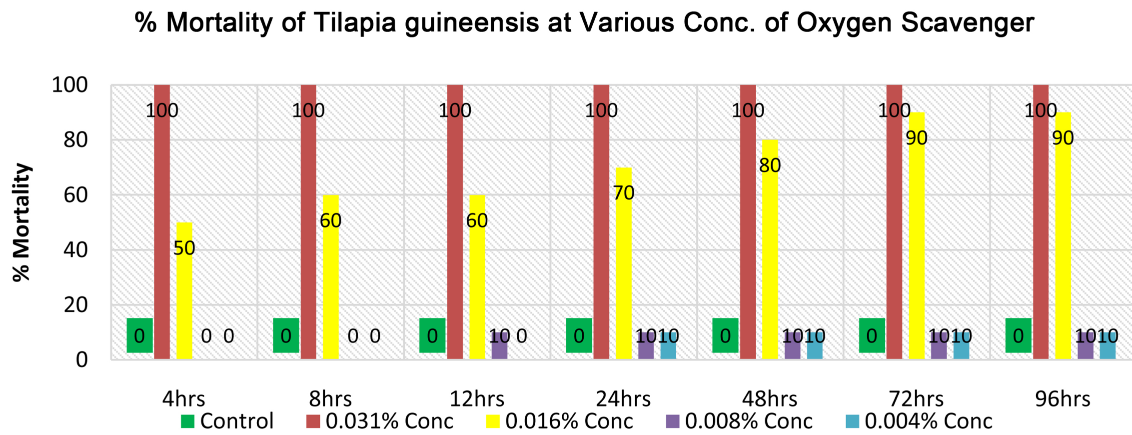

Figure 1. Percentage mortality of freshwater *Tilapia guineensis* at various concentrations of oxygen scavenger.

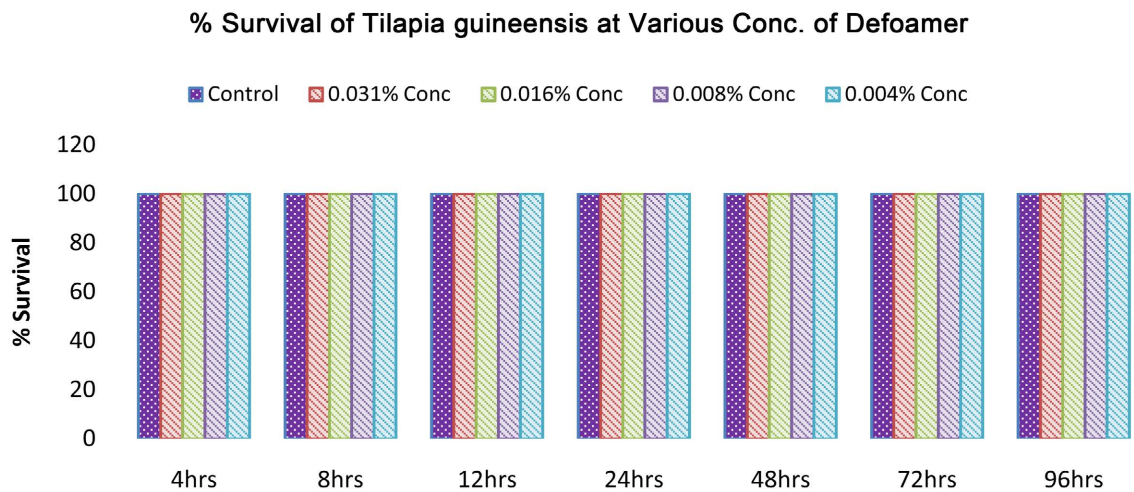

Figure 2. Percentage survival of freshwater *Tilapia guineensis* at various concentrations of defoamer.

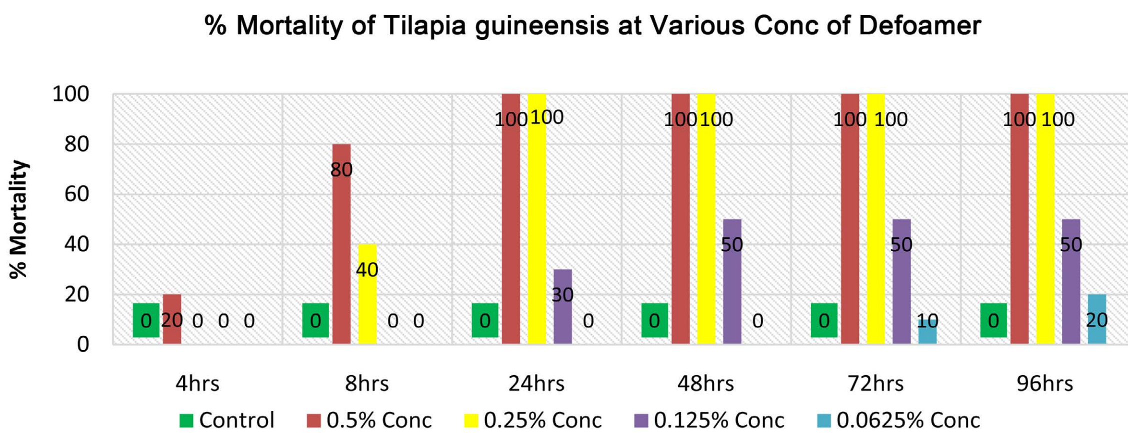

Figure 3. Percentage mortality of freshwater *Tilapia guineensis* at various concentrations of defoamer.

It was observed that the dissolved oxygen values kept reducing across all the concentrations of the production chemicals for the test period, hence the lowest values of the DO were the values measures at the 96th hour. Concerns that temperature of the test medium might have led to the mortality of the fishes was eliminated because the temperature range (28.1˚C - 30.1˚C and 28.4˚C - 30.3˚C) for both production chemicals at the different concentrations were suitable for the survival of the *Tilapia guineensis* [17].

Figure 1 shows the percentage mortality of the freshwater *Tilapia guineensis* at different concentrations of oxygen scavenger. There was 100% mortality of the *Tilapia guineensis* at the 0.031% percentage concentration within 4hours of the test period; however, the 0.016%, 0.008% and 0.004% concentrations had 10%, 90% and 90% survival percentage respectively at the end of the 96 hrs test period. The LC50 of the oxygen scavenger on the *Tilapia guineensis* was 0.01% which is the percentage concentration of the oxygen scavenger required to kill at least 50% of the *Tilapia guineensis*. The mortality of the *Tilapia guineensis* indicates that the oxygen scavenger is lethal to the aquatic organism, this can be associated with the reduction of dissolved oxygen in the sample due to the elimination of oxygen by the chemical [11] [18].

Figure 2 shows that there was 100% survival of the *Tilapia guineensis* across all the percentage concentrations within the 96hours test period of the defoamer. The test was repeated with higher concentrations of the defoamer based on the range finding results. **Figure 3** shows the percentage mortality of the freshwater *Tilapia guineensis* at the different concentrations of the defoamer. There was 100% mortality of the *Tilapia guineensis* at the 0.5% and 0.25% percentage concentrations of the defoamer respectively within 24 hours of the test period. While the percentage survival for 0.125% and 0.0625% percentage concentrations at the end of the 96 hours test period were 50% and 80% respectively. The LC50 of the defoamer on the *Tilapia guineensis* was 0.176% derived from the formula stated in research methodology section.

The mortalities recorded at the higher concentrations of the defoamer showed that the defoamer is lethal to the *Tilapia guineensis*. The mortality recorded collaborate previous findings that defoamers are toxic and have potentials to reduce the amount of oxygen flow in water bodies thereby reducing the dissolved oxygen required by aquatic organisms for survival [12] [16]. This also collaborates this author [10] that the breakdown of bubbles by defoamers usually leads to the release of gases in water (oxygen inclusive), leading to the reduction of available oxygen in the samples.

Table 2 shows the percentage mortality of the freshwater *Tilapia guineensis* at the different concentrations of the oxygen scavenger combined with 0.0625% of defoamer. There was only a 10% mortality of the *Tilapia guineensis* at the end the of the 96hours test period for the 0.031% percentage concentration of the oxygen scavenger combined with 0.0625% of the defoamer. The other percentage concentrations 0.016%, 0.008% and 0.004% of the oxygen scavenger combined with defoamer, had 100% survival. The LC50 of the oxygen scavenger combined with defoamer on the *Tilapia guineensis* was 0.03%.

The combination of the oxygen scavenger with defoamer showed less lethal effect on the *Tilapia guineensis*. The LC50 value of 0.03% for the oxygen scavenger combined with defoamer has lesser lethal effect than LC50 value of 0.01% for oxygen scavenger alone. This shows that the combination of the oxygen scavenger with defoamer had antagonistic effects on the fish [19].

Comparing the different lethal concentrations (**Table 3**) it was observed that oxygen scavenger was more toxic to the *Tilapia guineensis* than the defoamer. Furthermore, there was a significant drop in the lethal concentration of the oxygen scavenger when the two chemicals were mixed.

4. Conclusion

The *Tilapia guineensis* when exposed to a combination of ELIMINOX (oxygen scavenger) and 0.0625% of EC9017A (defoamer) do not have synergetic effects; rather they are antagonistic to each other, thereby reducing their toxicity level. This could be attributed to the fact that while the oxygen scavenger is taking up the oxygen present in the water, the defoamer is breaking the bubbles carrying the oxygen and releasing it back into the water, hence the abundance of the oxygen in the water and the less-lethal effect on the *Tilapia guineensis*.

Recommendation

We recommend that further researches should be carried out on other production chemicals to help understand how they interact with one another and their possible synergistic or antagonistic toxicity contribution to produced water.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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