# Original Research Article

# EVALUATION OF SELECTED CHEMICALS USED FOR OIL AND GAS PRODUCTION AND THEIR TOXIC EFFECTS ON THE NIGER DELTA FRESH WATER TILAPIA GUINEENSIS

#### **ABSTRACT**

There are projections of continuous increase in the world's energy demand, which might result to increase in oil and gas exploration and production activities. Nigeria for instance, runs a monoeconomy that largely depends on the revenues from her rich oil and gas deposits. Oil and gas exploration and production activities are expected to increase over the years in Nigeria to meet her economic needs, as well as the global energy need. However, oil and gas production activities are associated with environmental concerns, especially with respect to management of the kind of wastes it generates. A major waste generated during oil and gas completion and production operations is the Produced Water (composed of water, different production chemicals and other constituents). This study is focused on evaluation of the toxic effects of selected production chemicals on the Niger Delta freshwater Tilapia guineensis. Among the chemicals evaluated include: SPECTRUS NX1173 (Biocide), FLOGARD MS 6208 (Corrosion inhibitor), ELIMINOX (Oxygen scavenger) and EC9017A (anti-foam), while Tilapia guineensis was used as the bioindicator. Whereas there are past researches on the individual chemicals and confirmation that they are toxic in nature, there are no adequate researches on the comparative toxicity effects of these chemicals, especially on the Niger Delta environment. Produced water samples were simulated in the laboratory using the production chemicals (at different concentrations) and 2000ml of freshwater sample for each experimental setup. The fishes were acclimatized for ten days using same freshwater sample, those that survived were selected for the experiment. The mortality and survival rate of the test organism was monitored at a constant interval of one (1) hour for Ninety-six (96) hours and the percentage mortality of the test organism recorded for all the chemicals at different concentrations ranged from 100% to 10%. The lethal concentration (LC<sub>50</sub>) calculated for each of the chemicals are as follows: Corrosion inhibitor 0.002%, biocide 0.003%, oxygen scavenger 0.01% and defoamer 0.176%. The corrosion inhibitor was the most toxic as there was 100% mortality of the Tilapia guineensis within 24 hours of the test period, while the defoamer was the least toxic as there were more survival of the test organism at the end of the test period. The test results indicated that all the production chemicals used in this research were toxic, their lethal concentrations differed from one chemical to the other, and the corrosion inhibitor and biocide had the highest toxicity effect on the organisms. The research findings could be used as a basis by the Nigerian regulatory agencies for possible review of currently approved completion and production chemicals for oil and gas activities, as well as produced water disposal options, especially discharge in water bodies in the Niger Delta.

Keywords: Produced water, biocide, corrosion inhibitor, oxygen scavenger, defoamer, Tilapia *guineensis*, toxicity, lethal concentration

## 1.0 INTRODUCTION

Globally, the world's energy need keeps increasing, with Asia-pacific leading in the oil demand (IOGP 2019). The world's daily petroleum consumption is estimated to increase from 95 million barrels in 2015 to 113 million by 2040 (International Energy Outlook, 2017).

However, oil and gas exploration and production are associated with large waste generation which are in gaseous, liquid and solid forms; the greatest portion of these wastes are in liquid form (Obunwo and Chukwudi, 2015). The liquid wastes also referred to as produced formation water is the highest stream of waste from the oil and gas exploration and production activities. Its management poses a serious environmental threat both globally and locally (Isehunwa and Onovae, 2011, Neff *et al*, 2011). Chikwe and Okwa, (2016) stated that an estimated one billion barrels of oilfield produced water is generated yearly from oil and gas production activities from Nigerian oil fields. The volume of water produced from oil and gas wells increases as the wells age, and produced water could be up to 80% of the total amount of waste generated during gas production (Neff *et al*, 2011).

Oil and gas formations in geologic reservoirs are usually combined with water. The water in these formations is called "formation water" or "connate water" which can either be salt or fresh water and is usually trapped for a long time in the formation by the oil and/or gas in the reservoir (Collins, 1975). The formation water is easily trapped in the reservoirs because oil and gas are less dense than water, making them stay above water in the formation. The content of the formation water is also dependent on the reservoir formation whether its oil or gas formation and the type of chemicals injected into the well during the drilling activities (USEPA, 2009). The water produced to the surface along the oil and/or gas during production activities from the reservoirs is referred to as produced water (Neff *et al*, 2011).

The components of oilfield produced water are residual hydrocarbons, heavy metals, dissolved solids, suspended solids, chemicals used during the oil and gas production, organic and inorganic species and naturally occurring radioactive materials (Somerville *et al*, 1987). Somerville *et al*, (1987) further stated that oil and grease and other dissolved compounds are the major constituents of organic compounds of oilfield produced water. These components vary with time from one location to the other and depending on the production activity, whether it is oil production or gas production or in their associated state (Al-Haleem *et al*, 2010).

Okogbue *et al* (2017) carried out an assessment to ascertain the possible pollution from produced water discharges on offshore waters in the Niger Delta area of Nigeria. From their findings, they concluded that pollutant parameters (like heavy metals and the hydrocarbon constituents) in the produced water have the capacity to alter the composition and quality of seawater and in turn pose severe threat to the Niger Delta aquatic environment.

Isehunwa and Onovae (2011) in their work on discharge of produced water in the Niger Delta environment stated that the components of oilfield produced water makes them toxic and not good for discharge into any aquatic environment, notwithstanding the required regulatory limits to be met before disposal. They went further to demonstrate that most of the 'treated' produced water being discharged into the Niger Delta aquatic environment by Oil Producing companies are usually not treated to the required limits before disposal. This is besides the fact that produced water regulatory limits for disposal into aquatic environment in Nigeria are below international standards, these findings collaborate the research by Onojake and Abanum (2012) and Ajuzieogu *et al* (2018).

Production chemicals such as corrosion inhibitors, biocides, oxygen scavengers, anti-foam and reverse emulsion breakers, used for production processes and for the treatment of oilfield produced water before discharge into oceans and other, can themselves pose a serious toxicity threat to the aquatic environment, if they are not properly handled (Oilfieldwiki, 2016).

Neff *et al* (2002) stated that the concentration of production chemicals present in any produced water sample is usually determined by the point in the production process when they were added. They further stated that among the production chemicals used for oil and gas production, corrosion inhibitor and biocide are the most toxic. Uche *et al* (2015) in their work on the biological and chemical changes associated with the exposure of Cyprinid fishes to oilfield chemicals concluded that production chemicals have individual and synergetic toxic effects on the fish.

Henderson *et al* (1999) in their research to determine the impact of production chemicals on produced water toxicity stated from their findings that the chemicals at their normal concentrations in the North Sea oilfield produced water did not show any acute toxicity effect on the marine bacterium used for the test. They however recommended for further research to be carried out using other test organisms. Ibrahim and Odelele (2018) however, stated that different studies have shown that production chemicals used in oil and gas activities are toxic in nature.

Researches on the toxicity of production chemicals especially in the Niger Delta environment have been standalone without possible link to produced water and how they contribute to its toxicity. This research is aimed at evaluating the possible toxic effects of selected production chemicals on the Niger Delta aquatic environment and collaborate findings in other regions of the world and also seek to understand how they possibly contribute to the toxicity of produced water.

#### 2.0 Materials and Methods

#### 2.1 Chemicals Used

SPECTRUS NX1173 (Biocide), FLOGARD MS 6208 (Corrosion inhibitor), ELIMINOX (Oxygen scavenger) and EC9017A (anti-foam) were used in the experimental study. The chemicals are already prepared sourced products from the market within Nigeria and have approved by the Department of Petroleum Resources (DPR) for use in oilfields within the Nigerian environment.

# 2.2 Sampling Collection and Preservation

Tilapia *guineensis* (fishes) and Macobrachium *vollenhovenii* (Shrimps) were purchased from the Aluu, Rivers State outstation of the Nigerian Institute of Oceanography and Marine Research (NIOMR) in 2019. The fishes and shrimps 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 and Eight (8) Macobrachium *vollenhovenii* Shrimps 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.

# 2.3 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.

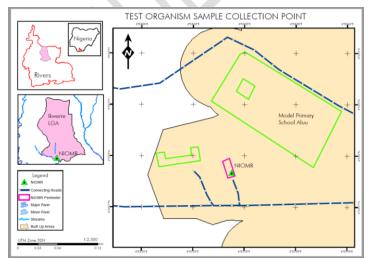


Figure 1: The Nigerian Institute of Oceanography and Marine Research (NIOMR), Aluu, Rivers State, Outstation.

# 2.4 Median Lethal Concentration (LC<sub>50</sub>)

The median lethal concentration of the respective chemicals 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).

$$LC_{50} = LC100 - \sum conc. Diff. \times mean \% mortality$$
 % control

# 2.5 Laboratory Experiment

Acute toxicity test was carried in the laboratory using four production chemicals, SPECTRUS NX1173 (Biocide), FLOGARD MS 6208 (Corrosion inhibitor), ELIMINOX (Oxygen scavenger) and EC9017A (anti-foam). The bio-indicator used for the research was freshwater Tilapia *guineensis*. The Tilapia *guineensis* was acclimatized for Ten (10) days in freshwater sample and Ten (10) actively kicking Tilapia *guineensis* that survived after the 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.

Produced water was generated in the laboratory via simulation using 2000ml of the freshwater sample used for the acclimatization of the Tilapia *guineensis* and production chemicals with known percentage concentrations. Preliminary range finding was first carried out to determine the percentage concentrations of the biocide, corrosion inhibitor and oxygen scavenger to be used for the test. The percentage concentrations used for the toxicity test as derived from the range finding for all the chemicals was 0.031%, 0.016%, 0.008% and 0,004%, however, the following higher concentrations of the defoamer were also used 0.5%, 0.25%, 0.125% and 0.0625%. A sample that contained 2000ml of the freshwater sample only was set up as the control sample.

Tilapia *guineensis* was added to the toxicity test samples for the production chemicals at the four different concentrations and to the control sample. The mortality and survival rate of the test organisms were monitored at a constant interval of one (1) hour for (96) Ninety-six hours. The pH, temperature, electric conductivity and dissolved oxygen at 0 hour and 96 hours were measured.

The percentage mortality was determined by dividing the number of organisms that died at each exposure hour by the total test organisms and multiplied by 100, while percentage survival was determined by dividing the number of organisms that survived at each exposure hour by the total test organisms and multiplied by 100.

The physiochemical parameters were determined in the laboratory using pH meter, DO meter and multiparameter photometer. The sensor of the instruments was dipped into a portion of the freshwater sample and the readings recorded.

#### 3.0 Results and Discussions

The range of values for temperature, pH, electric conductivity and dissolved oxygen for each of the simulated produced water at different concentration of the production chemicals are  $28^{\circ}\text{C} - 30.9^{\circ}\text{C}$ , 3.5 - 7.6, 230mg/l - 500mg/l and 2.56mg/l - 7.32mg/l respectively. At the end of the 96 hours test period, the mortality and survival of the Tilapia *guineensis* were recorded and the percentage mortality calculated. Tables 1 to 5 show the percentage mortality for the different production chemicals.

The temperature range  $28^{\circ}\text{C} - 30.9^{\circ}\text{C}$  was within the suitable temperature required by the Tilapia *guineensis* for survival, hence it was ruled out as the possible cause of the mortality of the fishes (Campbell, 1987).

Table 1: Percentage Mortality of Freshwater Tilapia *guineensis* at Various Percentage Concentrations of Corrosion Inhibitor

Concentration/Time	Control	0.031	0.016	0.008	0.004
4hrs (% Mortality)	0	100	100	10	0
8hrs (% Mortality)	0	100	100	90	30
12hrs (% Mortality)	0	100	100	100	80
24hrs (% Mortality)	0	100	100	100	100
48hrs (% Mortality)	0	100	100	100	100
72hrs (% Mortality)	0	100	100	100	100
96hrs (% Mortality)	0	100	100	100	100

Table 1 shows the percentage mortality of the freshwater Tilapia *guineensis* at the different concentrations of the corrosion inhibitor. There was 100% mortality of the Tilapia *guineensis* in all the percentage concentrations within 48hours of the test period. The percentage concentration of 0.031% and 0.016% achieved 100% mortality within 4 hours of the test period. The corrosion inhibitor showed significant lethal effects on freshwater Tilapia *guineensis*, this collaborates previous research that corrosion inhibitors are toxic to fish and other aquatic organisms (Osagie *et al*, 2016, Uche *et al*, 2015).

Table 2: Percentage Mortality of Tilapia guineensis at Various Percentage Concentrations of Biocide

Concentration/ Time	Control	0.031	0.016	0.008	0.004
4hrs (% Mortality)	0	100	60	0	0
8hrs (% Mortality)	0	100	100	40	30
12hrs (% Mortality)	0	100	100	60	40
24hrs (% Mortality)	0	100	100	100	80
48hrs (% Mortality)	0	100	100	100	100
72hrs (% Mortality)	0	100	100	100	100
96hrs (% Mortality)	0	100	100	100	100

Table 2 shows the percentage mortality of the freshwater Tilapia *guineensis* at the different concentrations of the biocide. There was 100% mortality for 0.031% percentage concentration of the biocide within 4 hours of the test period. For the other percentage concentrations, there was 100% mortality within 48 hours of the test period. The mortality of the Tilapia *guineensis* recorded within the test period, shows that the biocide is toxic and hence collaborates the findings of Hernandez-Moreno *et al* (2019) that Biocides are toxic to aquatic organisms.

Table 3: Percentage Mortality of Freshwater Tilapia *guineensis* at Various Percentage Concentrations of Oxygen Scavenger

Concentration/ Time	Control	0.031	0.016	0.008	0.004
4hrs (%Mortality)	0	100	50	0	0
8hrs (% Mortality)	0	100	60	0	0
12hrs (% Mortality)	0	100	60	10	0
24hrs (% Mortality)	0	100	70	10	10
48hrs (% Mortality)	0	100	80	10	10
72hrs (% Mortality)	0	100	90	10	10
96hrs (% Mortality)	0	100	90	10	10

Table 3 shows the percentage mortality of the freshwater Tilapia *guineensis* at different concentration of oxygen scavenger. There was 100% mortality of the Tilapia *guineensis* at the highest concentration of 0.031% within 4 hours of the test period, however, the 0.008% and 0.004% concentration had 80% and 90% survival percentage respectively at the end of the 96hrs test period. The mortality of the Tilapia *guineensis* can easily be associated with the reduction of dissolved oxygen in the freshwater sample due to the elimination of oxygen by the chemical (Schlumberger, 2020) and collaborates the findings of Uche *et al* (2015) that production chemicals are toxic on aquatic organisms.

Table 4: Percentage Mortality of Freshwater Tilapia *guineensis* at Various Percentage Concentrations of Defoamer

Concentration/Time	Control	0.031	0.016	0.008	0.004
4hrs (% Mortality)	0	0	0	0	0
8hrs (% Mortality)	0	0	0	0	0
12hrs (% Mortality)	0	0	0	0	0
24hrs (% Mortality)	0	0	0	0	0
48hrs (% Mortality)	0	0	0	0	0
72hrs (% Mortality)	0	0	0	0	0
96hrs (% Mortality)	0	0	0	0	0

Table 5: Percentage Mortality of Freshwater Tilapia *guineensis* at Various Percentage Concentrations of Defoamer

Concentration/ Time	Control	0.5	0.25	0.125	0.0625
4hrs (% Mortality)	0	20	0	0	0
8hrs (% Mortality)	0	80	40	0	0
12hrs (% Mortality)	0	90	50	10	0
24hrs (% Mortality)	0	100	100	30	0
48hrs (% Mortality)	0	100	100	50	0
72hrs (% Mortality)	0	100	100	50	10
96hrs (% Mortality)	0	100	100	50	20

Tables 4 and 5 show the percentage survival and mortality of the freshwater Tilapia *guineensis* at the different concentrations of the defoamer. In Table 4 there was a 100% survival of the Tilapia *guineensis* at the end of the 96 hours test period for all the percentage concentrations. The analysis was repeated with higher concentrations of the defoamer in Table 5, there was 100% mortality of the Tilapia *guineensis* at the 0.5% and 0.25% percentage concentrations of the defoamer respectively within the 24 hours of the test period. While the percentage survive for 0.125% and 0.0625% percentage concentrations at the end of the 96 hours test period were 50% and 80% respectively. The defoamer showed significant lethal effects on the Tilapia *guineensis* at the higher concentration. The mortality recorded collaborates 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 (Lian *et al*, 2019, Routledge 2012).

The lethal concentration (LC<sub>50</sub>) which is the percentage concentration of the chemicals required to kill at least 50% of the Tilapia *guineensis* were calculated for each of the production chemicals and the results are as shown in Table 6.

Table 6: Median Lethal Concentration ( $LC_{50}$ ) for the Production Chemicals for Freshwater Tilapia *guineensis* 

<b>Production Chemical</b>	<b>Lethal Concentration (LC<sub>50</sub>)</b>
Corrosion Inhibitor	0.002%
Biocide	0.003%
Oxygen Scavenger	0.01%
Defoamer (for higher conc.)	0.176%

Table 6 shows the LC<sub>50</sub> for each of the production chemicals calculated using the formula presented under materials and methods. All the chemicals showed that they are lethal to the Tilapia *guineensis*. However, the corrosion inhibitor and biocide had the least mean lethal concentration for the test organism, indicating they are the most toxic. This collaborates the findings by Neff *et al* (2002) that corrosion inhibitors and biocides are the most toxic production chemicals.

#### 4.0 Conclusion

While the world's need for energy persist and in turn the need for continuous exploration and production of oil and gas to meet the energy demands. There are however environmental concerns relating oil and gas production activities as this research has revealed. The production chemicals (corrosion inhibitor, biocide, oxygen scavenger and defoamer are toxic) used for this research showed they are toxic to the Tilapia *guinnesis*, and possibly to other related aquatic organisms. The corrosion inhibitor (FLOGARD MS 6208) had the highest lethal effect on the Tilapia *guineensis*, while anti-foam (The EC9017A) had the least toxic effect among the four (4) chemicals evaluated.

The corrosion inhibitor, biocide, oxygen scavenger and anti-foam showed that they significantly contribute to the toxic nature of oilfield produced water, with corrosion inhibitor contributing the most among the four (4) chemicals.

# 5.0 Recommendation

- Researches on other production chemicals such as scale inhibitor, scale dissolver, hydrogen sulfide scavenger, calcium nitrate, hydrogen scavenger, demulsifier, water clarifier, and emulsion breaker, should be carried out and results compared with the findings of this research to confirm the production chemical that contributes the most to the toxicity of produced water.
- Further research should also be carried out on the synergetic effects of these chemicals. This will show how they interact in the wells during the production operations activities,

- as different chemicals are injected into wells at different times depending on the operations need, leading combination of different chemicals in the well.
- > Stricter environmental measures should be put in place by the Nigerian Upstream Petroleum Regulatory Commission (NUPRC) for the use of production chemicals and in turn discharge of produced water, especially in the zero discharge zones.

# **6.0 Competing Interests Disclaimer:**

The authors declare that there are no competing interests and do not intend to use the research findings as an avenue for any litigation but for the advancement of knowledge. The research was fully funded by the authors without any form of sponsorship.

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