

Original Research Article

EVALUATION OF TOXIC EFFECTS OF SELECTED PRODUCTION CHEMICALS ON THE NIGER DELTA FRESH WATER TILAPIA *GUINEENSIS*

ABSTRACT

The energy need of the world is expected to keep increasing in the years to come, while mono-economies like that of Nigeria that depends on the revenues from oil and gas production to thrive will continually search for more oil fields to explore and produce from. However, there are numerous environmental concerns associated with oil and gas activities, especially with respect to management of the wastes generated during the oil and gas activities. One of the concerns is the environmental issues associated with produced water arising from completion and production operations. 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 (LC₅₀) 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 24hours 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 will aid government regulators to put stricter measures with respect to chemicals to be approved for oil and gas production activities and how best produced water should be discharged depending on the constituent chemicals.

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 despite the existing regulatory limits and standards to be met before disposal. They went further to demonstrate that most of the 'treated' produced water being discharged by Oil Producing companies within the Niger Delta of Nigeria are not within the set regulatory limits, despite that the limits are below international standards, this findings collaborates 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 RESEARCH METHODOLOGY

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 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) 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.

2.4 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.

3.0 RESULTS AND DISCUSSIONS

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 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 0hr and 96hrs 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.

Median Lethal Concentration (LC₅₀)

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).

$$LC_{50} = LC_{100} - \frac{\sum \text{conc. Diff.} \times \text{mean \% mortality}}{\% \text{ control}}$$

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°C – 30.9°C, 3.5 – 7.6, 230mg/l – 500mg/l and 2.56mg/l – 7.32mg/l respectively. At the end of the 96hours 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.

Table 1: Percentage Mortality of Freshwater *Tilapia guineensis* at Various 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 2: Percentage Mortality of *Tilapia guineensis* at Various 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 3: Percentage Mortality of Freshwater *Tilapia guineensis* at Various 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 4: Percentage Mortality of Freshwater *Tilapia guineensis* at Various 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 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

The lethal concentration (LC₅₀) 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 (LC₅₀) for the Production Chemicals for Freshwater Tilapia *guineensis*

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

The temperature range 28°C – 30.9°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 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 4hours 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 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 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.

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).

Table 6 shows the LC_{50} 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

Within the limits of this research the following conclusions were drawn:

1. The four chemicals corrosion inhibitor, biocide, oxygen scavenger and defoamer are toxic in nature.

2. FLOGARD MS 6208 (corrosion inhibitor) amongst the four chemicals had the highest lethal effect on the *Tilapia guineensis*.
3. The EC9017A (anti-foam) was the least toxic amongst the four chemicals, there was 100% survival of the *Tilapia guineensis* at the comparative percentage concentrations, and very significant survival at the higher percentage concentrations.
4. The FLOGARD MS 6208 (corrosion inhibitor) might be contributing more to the toxicity of produced water.

5.0 RECOMMENDATION

1. Researches on other production chemicals 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.
2. 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.

3. COMPETING INTERESTS DISCLAIMER:

- 4.
5. Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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