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Effect of Biocides Blend on Microorganisms in Produced Water

Evuensiri Onoghwarite Ohimor[1], Ambrose Onajite Akakabota[2]
[1,2]Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, P.M.B. 1221, Effurun, Delta State, Nigeria.
email:[1]ohimor.evuensiri@fupre.edu.ng, [2]ambrosegite@gmail.com

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ABSTRACT

The exploration and production of crude oil lead to the production of a significant quantity of associated gas and produce water. The produce water is either re-injected into the oil well or discharged into the environment. There is therefore a need for the water to be treated before any of the aforestated operations are carried out, as it contains a significant amount of microorganisms that pose a threat to production facilities as well as the environment. This research studies the use of a combination of two types of biocides, quaternary ammonium chloride (QUAT) and tetrakis-hydroxymethyl phosphonium sulfate (THPS), at various ratios in order to determine which is most effective. The pour-plate method for total viable bacterial enumeration was applied. It was discovered that, generally, the blends of biocide proved to be more effective in combating bacterial activities in produce water at lower concentrations and longer reaction times than the individual biocides. Thus, the 75% THPS + 25% QUAT as well as the 50% THPS + 50% QUAT were most effective at a concentration of 1000 ppm and a reaction time of 9 hrs in reducing the microbial population from 1.53 $\times 10^8$ bacterial cells/ml to 3.3$\times 10^2$ bacterial cells/ml and 3.7$\times 10^2$ bacterial cells/ml, respectively.

Keywords: Produced water; biocide; bacterial; count; crude oil; oilfield

1.0 INTRODUCTION

Crude oil is a mixture of thousands of various compounds, organic and inorganic, including aliphatic and aromatic hydrocarbons, which in average reach 75% of its content, as well as resins and asphalts. Non-hydrocarbon compounds include sulfur compounds (0.01–8%), mainly hydrogen sulfide (H_2S), mercaptans (compounds containing the -SH group), sulfides and disulfides, thiophenes, as well as benzothiophenes and naphthothiophenes that prevail in oil fractions. These compounds are unfavorable due to their chemical recalcitrance; therefore, their presence is considered in evaluating crude oil quality (Surygała, 2001).The produced oil contains a mixture of oil, gas, and water and is sent to the flow stations, where preliminary separation is carried out. The separation is carried out in separator vessels (usually a three-phase separator), which separate the mixture. The gas phase flashes to the upper portion of the vessel and is sent through pipelines for further processing while the oil forms the middle layer and the water settles at the bottom of the vessel. The separators are known as gravitational separators as they operate based on density differences. The oil is then sent through pipelines for delivery to a refinery or tanker terminal. The produced water is sent to a water treatment plant, where oil recovery is done, and it is also treated to remove other impurities before being discharged (Reed, 1990).

The water removed is either reinjected into the well or discharged into the environment (water bodies). The water separated contains dispersed or free oil, dissolved oil, and other dissolved organic compounds referred to as water-soluble organics (Odeigah *et al*., 1997). Components of the wastewater are broadly classified into three categories: dissolved mineral salts, dissolved gases, and microorganisms (Mony, 1975). The wastewater is treated by passing through stages that ensure the removal of oil from it and also by the addition of chemicals such as water clarifiers and biocides (Girling, 1989). These microorganisms present in oilfield wastewater are broadly grouped into general aerobic bacteria (GAB), sulfate-reducing bacteria (SRB), metal-reducing bacteria (MRB), metal-depositing bacteria (MDB), acid-producing bacteria (APB), and fungi (Iwona et *al*., 2000).

Oilfield wastewater is effluent co-produced with oil and gas during drilling. At the surface, oilfield wastewater is separated from the hydrocarbons, treated to remove as much oil as possible, and then either discharged into the environment or injected back into the wells (Odeiga et *al*., 1997). Oilfield wastewater is composed of formation water and injected water. Formation water is the natural water that occurs in association with oil and gas deposits in reservoirs and, being denser, lies under the hydrocarbons (Wills, 2000). Injected water is additional water usually pumped into reservoirs during the secondary stage of oil recovery to maintain reservoir pressure and help force the oil to the surface in order to achieve maximum oil recovery (Somerville *et al.,* 1987). Offshore oil production platforms as well as onshore oil fields discharge the oily water or oilfield wastewater into the environment as part of their normal operations. Oilfield wastewater contains inorganic and organic constituents (Wardley, 1979) as well as hydrocarbon components (Koons *et al.,* 1977). This is the water that is finally discharged into the environment after the oil-water separation process (Wilkinson, 1982). The wastewater is subjected to some forms of treatment. The treatment is achieved by adding chemicals such as water clarifiers and biocides, as well as passing the wastewater through stages that ensure the removal of oil from the water (Blackman et al., 1980). Part of the treated wastewater is injected into the formation to enhance oil recovery, while the remaining water is discharged into concrete pits or ponds where the operation is on shore. While in the pit, the wastewater could contaminate the soil environment as a result of overflow or seepage from faulty waste pits (Koonset et *al.,* 1997).

2.0 MATERIALS AND METHODS

2.1 Methods

The National Association of Corrosion Engineers (NACE 2006) method was employed in this research work. **T**hree biocide blends were prepared from different percentages of the contributing biocides. The first blend consists of 75% THPS and 25% QUAT. The second blend contains an equal amount of both biocides (50% THPS and 50% QUAT). The third blend contained 25% THPS and 75% QUAT. The individual biocides (i.e., 100% QUAT and 100% THPS) as well as their blends were analyzed in terms of effectiveness. The pH and specific gravity of the biocides and the blend were measured and recorded. Six (6) prescription bottles were filled with produce water up to the 100-ml graduation mark. One serves as a blank, while the other five bottles were treated with 200 ppm of the reactive biocides. The bacterial count of the blank was determined. The five prescription bottles with treated produce water were placed in a water bath at 65 $^{\circ}$C.A sample of the produced water

was withdrawn from the first, second, third, fourth, and fifth bottles after 3 hours for bacteria count determination. Produce water was also withdrawn from the prescription bottles after 6 hours and 9 hours, respectively, to determine the bacteria count. The process was repeated for biocide concentrations of 400 ppm, 600 ppm, 800 ppm, and 1000 ppm.

2.2 Determination of Sulphate-Reducing Bacteria (SRB) Count

2.2.1 Serial dilution

A ten-fold serial dilution of the NACE (2006) standard method was applied, thus reducing the concentration of the bacteria by one-tenth of the original concentration. With a micropipette, dispense 9 ml of deionized water to each of the labeled ten sterile tubes according to their dilution. A micropipette was used to transfer 1 ml of the treated produce water to the first tube, which was then mixed using a vortex mixer. This was the first ten-fold serial dilution of the initial dilution: 1:10 (1/10 = 0.1). Subsequent ten-fold serial dilution was made by transferring 1.0 ml of the last dilution to 9 ml of the deionized water up to 1:1000 (10^{-3}) = 0.001 (Harrigan et al., 1990).

2.2.2 Pour plate technique

The first step was to first dilute the sample, which has been carried out using the ten-fold serial dilution method. An aliquot of 1 ml of the produced water sample was then placed in a sterile dish, and then 15 ml of the melted agar was added to the plate and mixed thoroughly by tilting and swirling the dish. Then, allow the agar to solidify (completely gel) for about 10 minutes. It was then inverted and incubated for 48 hours at 37 °C. The number of colonies formed was then counted using a colony counter with a magnifying glass, and the values were recorded.

$$\text{The cell count (CFU/mL)} = \frac{\text{colonies counted} \times \text{dilution factor}}{\text{Aliquot}} \quad (1)$$

3.0 RESULTS AND DISCUSSION

The results of the analysis are presented in Figures 1-6. The results show the relationship between the reaction time of the biocide on the produce water sample as well as the biocide concentration on the bacteria population in the water sample. The produce water before treatment (blank) has a bacteria count of 1.53×10^{8} cells/ml.

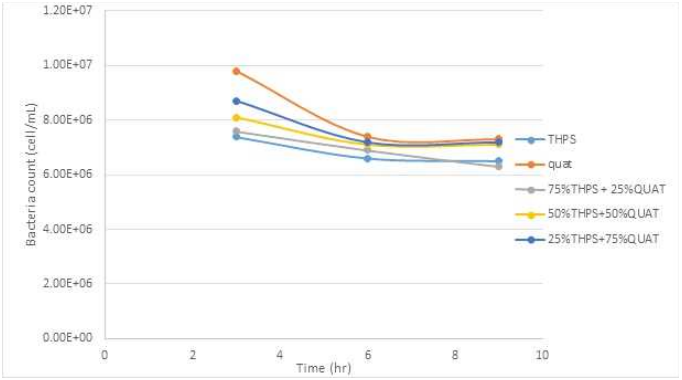

Figure 1: Bacteria count against time at 200 ppm biocide concentration

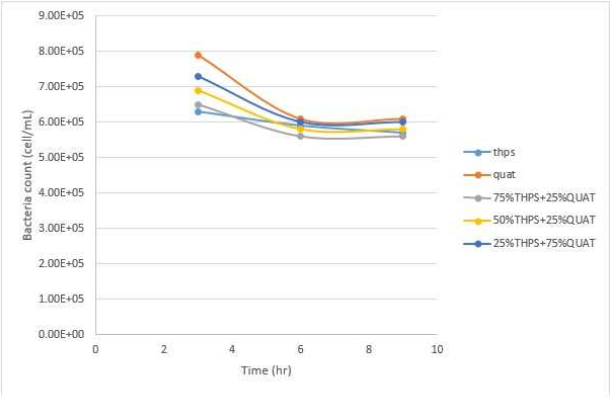

Figure 2: Bacteria count against time at 400 ppm biocide concentration

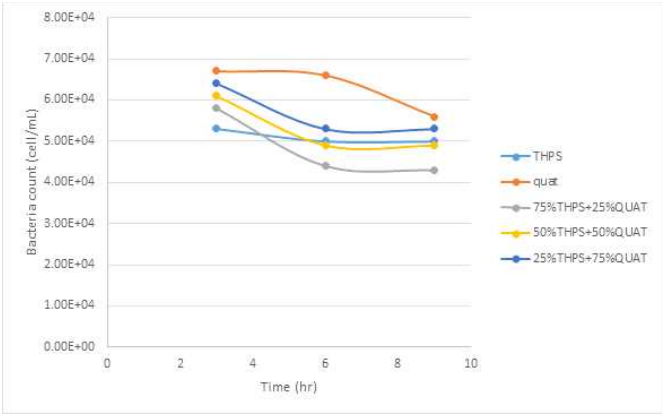

Figure 3: Bacteria count against time at 600 ppm biocide concentration

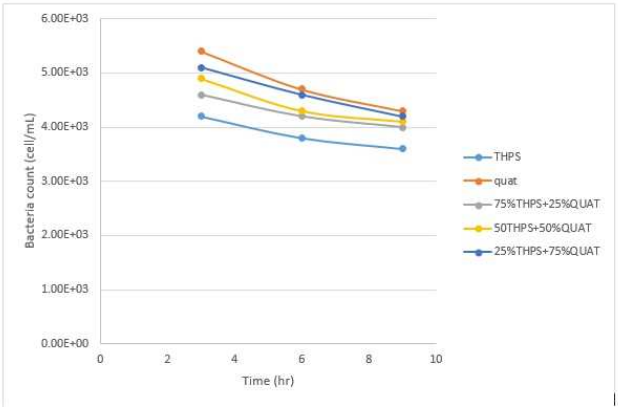

Figure 4: Bacteria count against time at 800 ppm biocide concentration

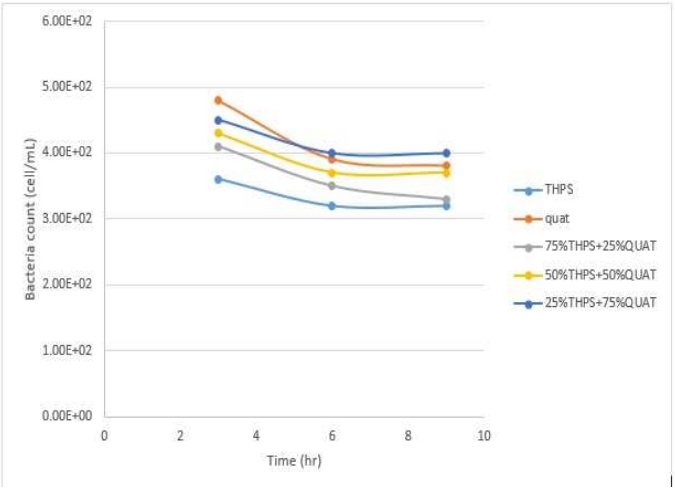

Figure 5: Bacteria count against time at 1000ppm biocide concentration

The effectiveness of the biocides as well as their blends was evaluated using the pour plate technique to determine the total viable cells remaining in the produced water after treatment with various doses of biocide. The effectiveness of the biocide on the bacteria count was evaluated at different time intervals of 3, 6, and 9 hours. Synergy among biocides used (THPS and QUAT) in the reduction of oil field general aerobic bacteria (GAB) was demonstrated. THPS were found to be more effective in reducing GAB count compared with the blends of THPS and QUAT and the QUAT biocide alone. Although various concentrations of the blends were tested to clearly demonstrate synergy, the noticeable reduction in the bacterial population by the combinations of compounds suggested that there is synergy with these biocides. The following trends were observed in the effectiveness of the individual biocides and their blends in terms of reduction of the total viable cells of GAB, using concentration of the biocides and time of reaction as major factors to determine their effectiveness. At 200 ppm biocide concentration (Figure 1), 100% THPS was found to be the most effective to reduce the total viable cells at 3 and 6 hours of reaction time, and at 9 hours of reaction time, the blend (75% THPS + 25% QUAT) was the most effective, while 100% QUAT was the least effective throughout the reaction time. At 400 ppm biocide concentration (Figure 2), 100% THPS was found to be the most effective at a 3 hour reaction time, but at an increased reaction time of 6 hours and 9 hours, 50% THPS + 50% QUAT biocide blend was more effective than THPS, and 75% THPS + 25% QUAT biocide blend was the most effective to reduce the total viable bacterial cells, while 100% QUAT was the least effective throughout the reaction time. At 600 ppm biocide concentration (Figure 3), 100% THPS was the most effective to reduce the total viable bacterial cells at 3 hours of reaction time, and at 6 hours and 9 hours of reaction time, the blend (75% THPS + 25% QUAT) was the most effective, while 100% QUAT was the least effective throughout the reaction time. At 800 ppm (Figure 4), 100% THPS was the most effective throughout the reaction time, while 100% QUAT was the least effective throughout the reaction time. At 1000 ppm (Figure 5), 100% THPS was the most effective throughout the reaction time, while 100% QUAT was the least effective at 3 hours of reaction time, and 25% THPS + 75% QUAT biocide was the least effective at 6 hours and 9 hours of reaction time. It was observed that the effectiveness of the QUAT, THPS, and their blend increased as the reaction time increased.

4.0 CONCLUSION

The research work shows that the time of reaction of the individual biocides and their blends affects their effectiveness. It would be observed from the graph that the least number of bacteria count was recorded at a 9-hour reaction time for any dose of biocide used in treating the produced water sample. Hence, allowing more time for the reaction of the biocide with the produced water will give better results in terms of reducing the number of bacteria in the produced water. The concentration of the individual biocide and the blends is also a factor that affects its effectiveness. It would be observed that the blends function at relatively lower concentrations than the individual biocides. At higher reaction times, the 75% THPS + 25% QUAT and also the 50% THPS + 50% QUAT blend proved to be more effective for concentrations of 200 ppm, 400 ppm, and 600 ppm, but increasing the concentration to 800 ppm and also 1000 ppm results in 100% THPS being more effective than any blend or 100% QUAT. Hence, allowing more reaction time for the biocide blends at a lower concentration (dose) is a more cost-effective approach to reducing the bacteria population in the produced water.

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