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Induction of Souring and Corrosion by Anaerobic Microbial Activities in Offshore and Nearshore Oil-Producing Facilities in Nigeria

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Induction of Souring and Corrosion by Anaerobic Microbial Activities in Offshore and Nearshore Oil-Producing Facilities in Nigeria

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Anaerobic microbiological activities of two oil-producing facilities were determined by monitoring microbial activities in CSB-K medium and MPN counts of SRB in API RP-38 broth medium and APB in ZPRA-5 broth medium. Corrosion measurements were also carried out by weight loss method. Our investigation revealed that microbial activities at the near-shore facility were dominated by both sulfate reduction and methanogenesis with potential for souring and corrosion, while that of offshore was dominated by sulfate reduction, but the potential for souring and corrosion were reduced by frequent application of a combination of biocides by the operators.

Keywords: anaerobic microbiological activities, SRB, APB, souring, corrosion

INTRODUCTION

Microorganisms thrive in oil reservoirs under strict anaerobic conditions and the major metabolic processes in oil reservoirs are sulfate reduction, methanogenesis, fermentation, and to some extent nitrate reduction (Magot, 2005). The anaerobic food chain of oil field microorganisms is therefore based on the use of organic compounds by the fermentative bacteria and sulfate-reducing bacteria (SRB) that oxidize organic matter under anaerobic conditions and methanogenesis through carbon dioxide reduction and hydrogen scavenging may be the dominant terminal metabolic process (Magot et al., 2000). The potential electron donors for fermentation and sulfate reduction include numerous organic molecules such as acetate, formate, propionate, butyrate, and benzoate (Voordouw, 2011). SRB and Archaea constitute a large and heterogeneous physiological group of strictly anaerobic prokaryotes that are commonly found in oil fields. They share the ability of anaerobic respiration using sulfate as a terminal electron acceptor and organic compounds or hydrogen as electron donors in a process known as dissimilatory sulfate reduction as opposed to assimilatory sulfate reduction (Birkeland, 2005).

In the present study, detailed anaerobic microbiological activity analysis were carried out in oil/water mixtures, produced water, injection water and sea water samples collected from a near shore and an offshore oil production facilities operated by Chevron in the Nigerian oil-rich Niger

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delta. Chevron is the third largest oil producer in Nigeria with an average daily oil production of 524,000 barrels, 206 million cubic feet of natural gas, and 5,000 barrels of liquefied petroleum gas (Nigerian Fact Sheet, 2000). Of particular interest in our study is the analysis of the anaerobic microbiological activities of Chevron's oil production skimmer pit located at its Escravos tank farm. A skimmer pit is a short-term storage facility of liquid oily wastes arising from oil production activities. The pits are dug on the ground and the base of the walls are lined with heavy gauge oil impermeable materials such as PVL, polythene, or oil-resistant rubber sheeting to prevent ground water and soil contamination. The sheets are prelined with sands to prevent the plastic sheet from being punctured by sharp objects. As a result of frequent movement of hot liquids used for washing, flushing, and cleaning of oil facility into the skimmer pit, its temperature is usually elevated ranging between 45 and 60°C (Margesin and Schinner, 2001).

The major parameters we used to quantify the activities of anaerobic microorganisms from the oil fields under investigation are the functional group activities such as the ability to reduce sulfate and produce sulfide by SRB, reduce nitrate by the heterotrophic nitrate-reducing bacteria (hNRB), and oxidize sulfide and reduce nitrate by sulfide oxidizing, nitrate-reducing bacteria (so-NRB). We also tested the samples for the production of methane gas by methanogens and corrosion tests were conducted by weight loss method.

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EXPERIMENTAL

Sample Collection

A total of eight samples were collected from two oil production facilities (Escravos terminal and Meren offshore) operated by Chevron as shown in Table 1. Sampling points were initially flushed to remove any local line microbial contamination.

Chemical Analysis of Samples

The pH of the samples was measured using an Orion pH meter. Aqueous sulfide was analyzed using the diamine method (Trüper and Schlegel, 1964) and NH_4^+ with the indophenol method (American Public Health Association, 1992). Sulfate, NO_3^-, NO_2^- and the volatile fatty acids (VFA) acetate, propionate, and butyrate were analyzed by high-pressure liquid chromatography (HPLC), as described elsewhere (Grigoryan et al., 2008). For analysis of inorganic anions, 100 μL of sample was combined with 400 μL HPLC anion buffer, while for analysis of VFA, 300 μL of the sample were combined with 20 μL 1 M phosphoric acid.

Bacterial Activity and Viable Cell Counts for SRB and APB

The activities of SRB, as well as of heterotrophic (hNRB) and of so-NRB were measured in Coleville synthetic brine (CSB-K) medium as described elsewhere (Okoro et al., 2014). Counts for SRB and acid producing bacteria (APB) were also taken as previously described (Okoro et al., 2013).

Methane Production Test and Corrosion Rate Measurements

CSB-K medium inoculated with 5% sample or 1 g of solid sample were used to determine the ability of viable organisms in the samples to produce methane; 30 mL medium was poured into an 80 mL bottle and inoculated with 2.5 mL sample. Each sample was incubated with and without two carbon steel coupons (5 × 0.5 × 0.1 cm). The head space of each bottle was filled with 10% N_2 and 90% CO_2 gas. A serum bottle with medium only served as a control. Each sample was incubated

TABLE 1
Sample Description and Water Chemistry (mM [ppm])

S/N	*Samples*	*pH*	**NaCl*	*Conductivity (mS/cm)*	*Sulfate*	*Sulfide*	*Ferrous iron*	*Ammonium*	*Ace.*	*Pro.*	*But.*
1	Water from Escravos terminal	7.84	246	25.35	0.12 (11.99)	0	0.73 (13.25)	7.28 (436)	0.52 (38.53)	0	0
2	Escravos Skimmer Pit Water	7.95	120	12.38	0 (0.15)	0.029 (0.97)	0	0.22 (3.93)	3.72 (223)	0	0
3	Injection water from MEREN	7.36	469	48.30	3.10 (297)	0.043 (1.41)	0	0.04(0.75)	0.02 (1.50)	0	0
4	Produced Water from MEREN	7.81	449	46.23	2.30 (220)	0.045 (1.50)	0	1.72 (31.02)	2.87 (172)	0.38 (23.04)	0.07 (4.24)
5	Sludge sample from Escravos Tank Farm	8.25	223	23.03	0	0.045 (1.50)	0	0.65 (11.79)	0.05 (2.82)	0	0.07 (4.24)
6	Produced oil from Meren	7.93	442	45.57	2.31 (222)	0.078 (2.56)	0.002 (0.11)	0.67 (12.15)	2.96 (177)	0.40 (23.90)	0.14 (8.29)
7	Skimmer pit sediment	7.62	171	17.68	0	0.07 (2.29)	0.049 (2.74)	0.62 (11.30)	0.08 (4.72)	0	0
8	*Pig-runs sample from Meren	7.83	13	1.41	0.19 (18.45)	0.075 (2.47)	0	0.011 (0.19)	0.07 (4.07)	0	0

*The sample mixed with mili Q water by equal ratio and water phase used for analyses
Ace = Acetate; Pro = Propionate; But = Butyrate

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at 32°C and 100 rpm shaking. Methane production was detected by injection of 0.2 ml of culture headspace into an HP 5890 gas chromatograph equipped with a stainless steel column (0.049 cm × 5.49 m) Porapak R 80/100. Injector and temperatures were 150 and 200°C, respectively. After culturing, corrosion rates were determined by the weight loss method described previously (Okoro et al., 2014).

RESULTS

Chemical Analysis of Samples

The pH of the samples ranged from 7.3 (water sample of Meren platform) to 8.2 (sludge sample, Escravos tank). The sulfate concentration was negligible in the Escravos samples except in sample 1. Sulfate concentrations in Meren platform samples ranged from 2.30 to 3.10 mM and 0.19 mM sulfate was found in the solid deposit (Table 1). Sulfide concentrations were low (0.02–7 mM) in all samples. The nitrite and nitrate concentrations were below the detection limit in all samples. The ammonium concentration in all samples ranged from 0.01 (Solid samples) to 1.72 mM (water sample

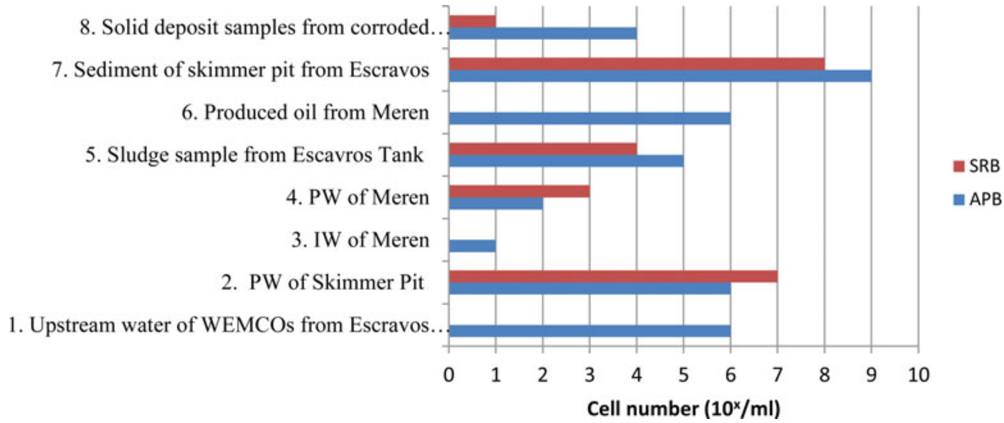

FIGURE 1 Viable cell counts for SRB and APB in samples from Meren platform and Escravos terminal.

from Meren). Ferrous iron was found mainly in the sediment of skimmer pit at a concentration of 0.049 mM. Conductivities of the samples were around 46 mS/cm in the Meren samples due to the use of seawater for injection and Escravos terminal samples from 12 mS/cm (Sample 2) to 25 mS/cm (Sample 1). The NaCl concentrations were equivalent to conductivity value.

VFA analysis results are also shown in Table 1. The highest acetate concentration was found in sample 1 (7.28 mM) and the skimmer pit water also had a considerably high acetate concentration (3.72 mM). Meren platform water and the water phase of the oil sample had 2.87 mM and 2.96 mM acetate, respectively (Table 1). Propionate concentrations of 0.38–0.52 mM were found in produced water, water in oil of Meren and upstream water of Escravos, but were not detected in the other samples. Produced water and the water phase in oil of Meren samples had 0.07–0.14 mM butyrate, respectively.

Viable Cell Counts for SRB and APB and Bacterial Activity Tests

SRB and APB Numbers

The numbers of SRB and APB in the samples were determined using a commercial MPN kit. Produced water and sediment of skimmer pit sample from Escravos terminal had 10^{7}–^{8}/mL of SRB and 10^{6}–^{9}/mL of APB. The water phase of oil, injection water in Meren, and upstream water from Escavros did not show any SRB growth. The injection water had 10^{1}/mL APB count. The solid deposit sample had cell counts of 10^{4}/mL of APB and 10^{1}/mL of SRB (Figure 1).

Bacterial Activity

Bacterial activity was assayed for SRB, hNRB and so-NRB in the samples. Sample 1, had high SRB activity with lactate (111 units/day) and hNRB activity (167 units/day) but did not show so-NRB activity and had low SRB activity with VFA (2.8 units/day; Figure 2). Produced water from the skimmer pit (No. 2) showed the highest hNRB activity (222 units/day). Injection water from Meren (No. 3), the solid deposit (No. 8), the sludge sample (No. 5) and the sediment of the skimmer pit (No. 7) had very high hNRB activity as well. Produced water from Meren (No. 4) did not any

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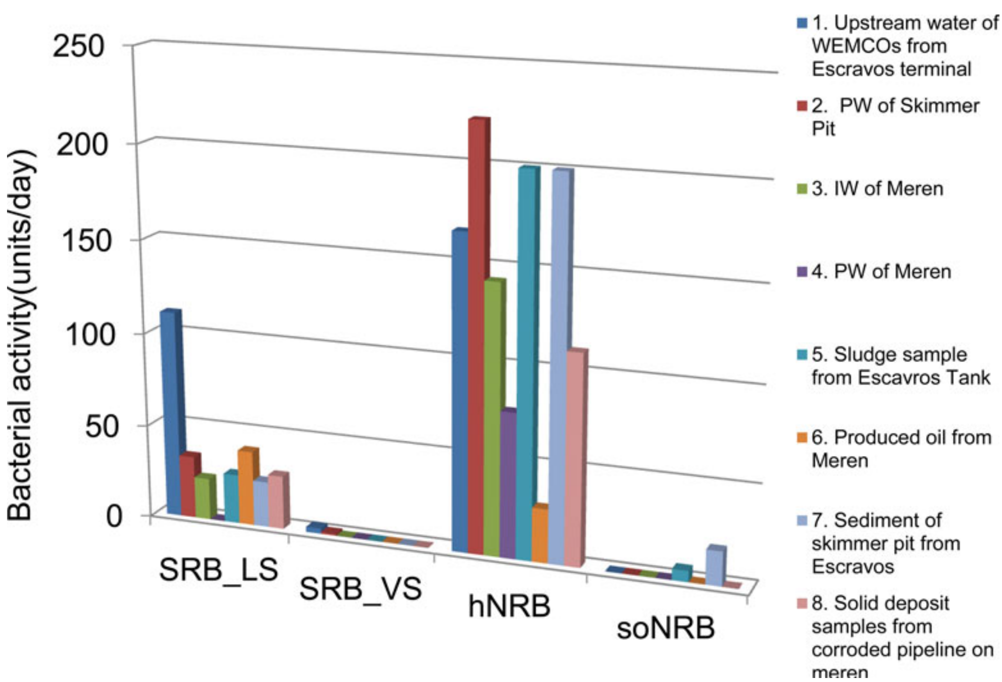

FIGURE 2 Bacterial activity for SRB, hNRBm and so-NRB in samples.

observable activity except for hNRB activity (77 units/day). In the so-NRB activity results, sediment from the skimmer pit (No. 7) showed considerable activity (18 units/d). Most samples had no SRB activity with VFA and sulfate.

Corrosion Rate Measurements Under Methanogenic Conditions

Sample 1 had the highest methane formation of 7.38 mM after 6 weeks incubation. The water sample from skimmer pit had (5.22 mM) and sediment of skimmer pit samples had (3.26 mM) Sludge sample from the Escravos facility recorded (0.43 mM). Other samples showed less than 10 uM of methane production (Figure 3A). In the bottles with coupons, methane production of sample 1 was (2.57 mM) while that of skimmer pit was (2.43 mM), these were lower than those without coupons (Figure 3B), but sediment of skimmer pit sample had higher methane formation (5.05 mM) when no coupon was present. The methane production from the solid deposit from a corroded pipeline sample increased to 1.59 mM when a coupon was added (Figure 3B). No methane was produced in the control bottles (CSB-K medium only).

The highest corrosion rate was seen in the sediment of skimmer pit (0.0164 $\pm$ 0.0008 mm/year) and followed respectively by the sludge sample (0.0151 $\pm$ 0.002 mm/year), upstream water (0.0129 $\pm$ 0.003 mm/year), and skimmer pit water (0.0114 $\pm$ 0.0009 mm/year; Figure 4). Injection water (0.006 $\pm$ 0.001 mm/yr) and produced water (0.002 $\pm$ 0.0005 mm/year) of Meren had lower corrosion rate than other samples. The corrosion rate of solid sample from corroded pipe was 0.004 $\pm$ 0.0008 mm/year while that of control (medium only) sample was 0.003 $\pm$ 0.001 mm/year.

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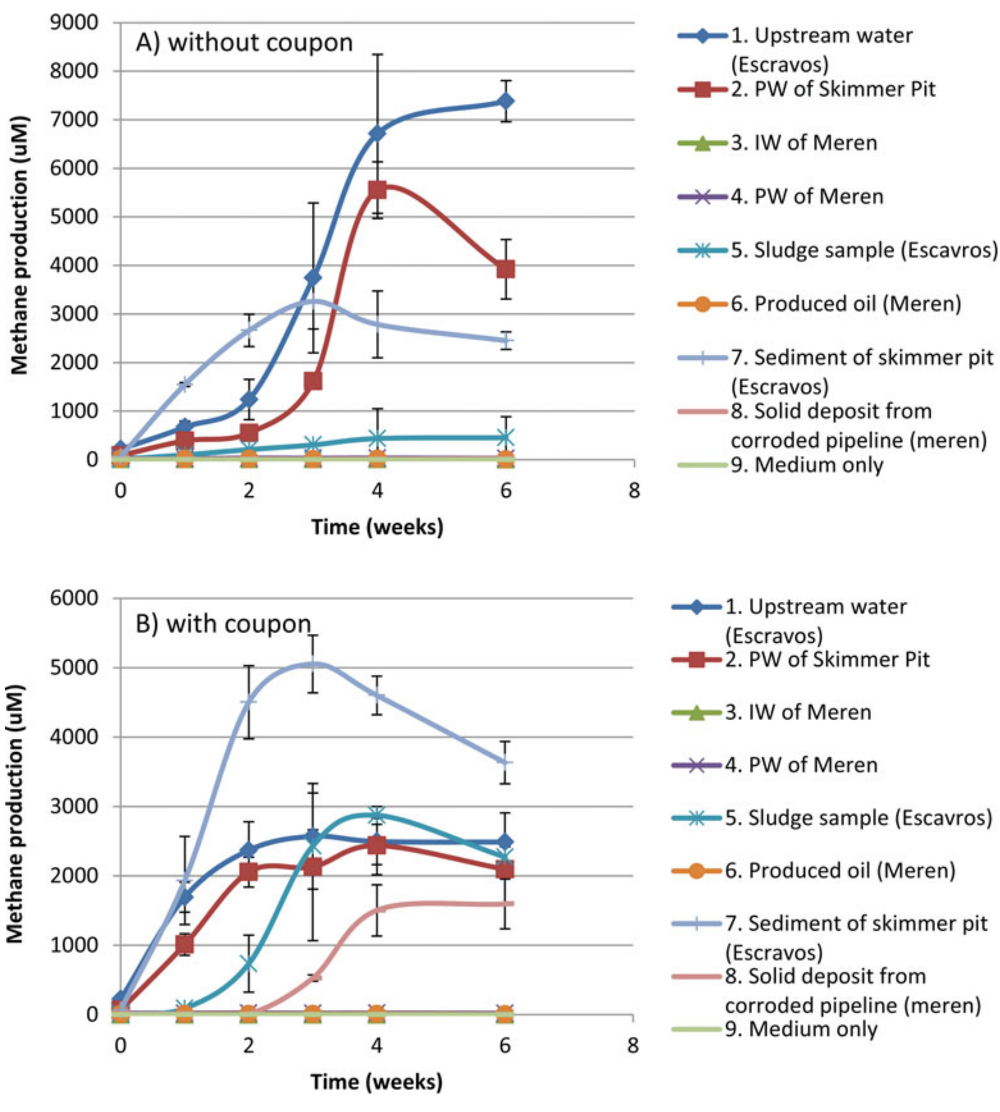

FIGURE 3 Methane production tests in samples. (A) Methane production without coupon. (B) Methane production with coupon.

DISCUSSION

In the present study, we used cultivation based mechanism and functional group activities to monitor the anaerobic microbiological activities of two Nigerian oil fields with an objective to determine their souring and corrosion potentials. Relatively high acetate concentration for instance was found in some samples such as the Escravos upstream water (7.28 mM), Skimmer pit water (3.72 mM), Meren produced water (2.87 mM), and Meren produced oil (2.96 mM). This results indicate the availability of sufficient organic nutrients for the growth and proliferation of anaerobic bacterial and archaeal communities in the oil fields concerned (Head et al., 2003; Okoro et al., 2014).

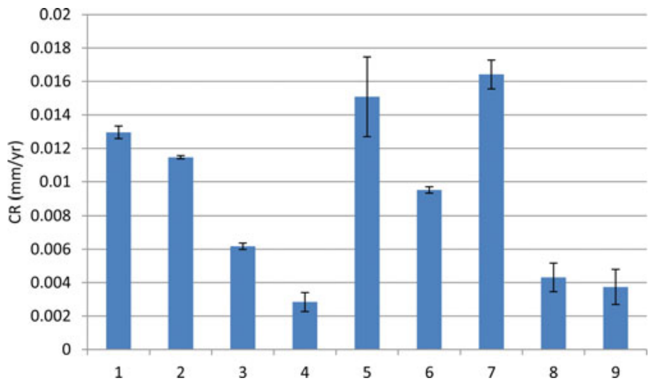

FIGURE 4 The corrosion rate measurements under methanogenic conditions. 1. Water from Escravos terminal. Upstream of WEMCOs after surge tank. 2. Water from Escravos terminal. Skimmer Pit. 3. Water from MEREN WIP. Water injector before injection point. 4. Water from MEREN. 5. Sludge sample from Escavros Tank Farm. 6. Oil from MEREN. Produced oil. 7. Sediment of skimmer pit. Escavros Terminal Produced Water Discharge Point. 8. Solid deposit samples after pig-runs from corroded pipeline.

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The biological counts and activity data indicated that the Escravos skimmer pit had the highest SRB (10^{7-8}/mL) and APB (10^{6-9}/mL) counts. High concentration of SRB at the skimmer pit with sulfate almost depleted and the production of sulfide is an indication that souring is already taking place (Nemati et al., 2001; Voordouw, 2011).

Escravos upstream water recorded the highest SRB activity with lactate (111 units/day) and relatively high corrosion rates under methanogenic conditions (0.0129 $\pm$ 0.003 mm/year). The hNRB activity was also high (167 units/day). Escravos skimmer pit also recorded relatively high bacterial activity and corrosion rates under methanogenic conditions (26 units/day and 0.0164 $\pm$ 0.0008 mm/year, respectively). These results indicate that the Escravos skimmer pit and the upstream water have high potential for souring and corrosion.

Meren produced and injection waters recorded low SRB counts and activity though the major microbiological activity at Meren was sulfate reduction. Low SRB counts and activity at Meren may be attributed to continuous treatment of the facility with combination of biocides (hypochlorite, glutaraldehyde, and quaternary ammonium salts), which may have drastically reduced SRB activities (Adetoba 1985; Lumley et al., 2000).

CONCLUSION

The present study have clearly demonstrated that microbiological activities at Escravos was dominated by both sulfate reduction and methanogenesis with high potential for both souring and corrosion while that of Meren were dominated by sulfate reduction but the potential to induce souring and corrosion at Meren was reduced by frequent application of a combination of biocides by the operators.

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