https://chemclassjournal.com/
ChemClass Journal Vol. 8 Issue 1 (2024); 303-319
e-ISSN:0198-2734 p-ISSN:0198-5680
doi.org/10.33003/chemclas_2024_0801/026

Physico-chemical Evaluation of Produced Water of Umuechem Oil Fields in Niger Delta

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Abstract

Management of produced water presents environmental challenges and costs to drilling, oil exploration, and refining operations. Both the formation water and injected water are eventually produced along with oil. Therefore, as the field becomes depleted with, the produced water content of the oil increases. The research was carried out to assess the physico-chemical composition of produced water from Umuechem oil field in Etche, Rivers State, Nigeria. Samples of produced water were obtained from the oil field were tested for Conductivity, TDS, Cl^-, SO^{4-}, Turbidity, Oil and grease, Alkalinity, PO^{4-}, Phenol and Ammonia Hydrogen. The study confirms that the produced water of Umuechem oil field is acidic and has pH values ranging from 5.15-6.37 shown to be above the W.H.O permissible limits and therefore are toxic and deleterious to the environment. The trace heavy metals Cu, Fe, Pb, Zn, Mn in produced water have mean concentrations of 0.09795ppm, 0.4778ppm, 0.0337ppm, 0.263ppm and 0.04025ppm respectively. Only Fe and Pb showed concentrations above the US EPA permissible limits for discharge of produced water into the environment. At the moment, proper management practices are not only required for Produced Water treatment to meet regulatory agencies' specified water quality limits for safe discharge and/or reuse.

Keywords: Discharge, Effluent, Physicochemical, Produced water, Wastewater

Introduction

The term Produced water refers to the water extracted during the production of oil and gas Brine, Hydrocarbons, and other impurities such as aliphatic hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX) and polyaromatic hydrocarbons and contaminants are frequently present in Produced water. Produced water is that water that has been trapped in subterranean formations that is brought to the surface along with gas and oil [1]. "It is by far the most significant quantity of by-product or waste stream related to crude oil production".

The degradation of the ecosystem ranging from high mortality of aquatic animals, loss of biodiversity in breeding grounds, vegetation hazards, loss of portable and industrial water resources are amongst the many problems associated with the vast volume and complex toxic constituents of produced water to both oil producers and man's health has necessitated varying studies on it.

The aim and objective of this research are to evaluate trace heavy metals present, to assess the physicochemical characteristics and to briefly investigate the detrimental effect associated with their discharge because it is often the largest by-product of oil and gas extraction. Secondly, is to discuss the composition of produced water.

Produced water has been in contact with geological formations for millions of years [2], contains a wide variety of dissolved inorganic salts, organic compounds and trace amounts of heavy metals. The type and amount of these constitutes characteristics of the reservoir and the geological formation from which the water has been produced. Numerous factors, including reservoir geology, hydrocarbon content, geological location, water injection history, and maturity, influence the physical and chemical characteristics of produced water, which is a complex cocktail of dangerous substances. These harmful substances, which include inorganic salts and trace metals, are harmful to both humans and the environment.

Naturally occurring rocks in subterranean formations are typically permeated with fluids like gas, oil, or water (or some combination of these fluids). It is thought that the rock in the majority of oil-bearing formations was fully saturated with water before petroleum invaded and trapped it [3] Some of the water in the formation was displaced by the less dense hydrocarbons when they moved to trap places, forming hydrocarbon reservoirs. These rocks typically contained water as well as liquid and gaseous petroleum hydrocarbons. This water is derived from injected fluids and additives that are the outcome of production processes, either above or below the hydrocarbon zone. This water is frequently referred to as "connate water," "fossil water," or "formation water."

However, when it is pushed to the surface with the natural gas or crude oil, it is referred to as produced water. Therefore, by definition, produced water is any water that forms in the rocks of an oil reservoir and rises to the surface in connection with natural gas or crude oil. Produced water is defined by the US Environmental Protection Agency (USEPA) as the water (brine) that is drawn up from the hydrocarbon-bearing formation strata during the extraction of oil and gas [1]. This can include either formation water, chemicals injected down completely or during the process of separating water and oil.

The water produced alongside with the crude oil may exist in one of several forms as shown in the Figure 1.0 below.

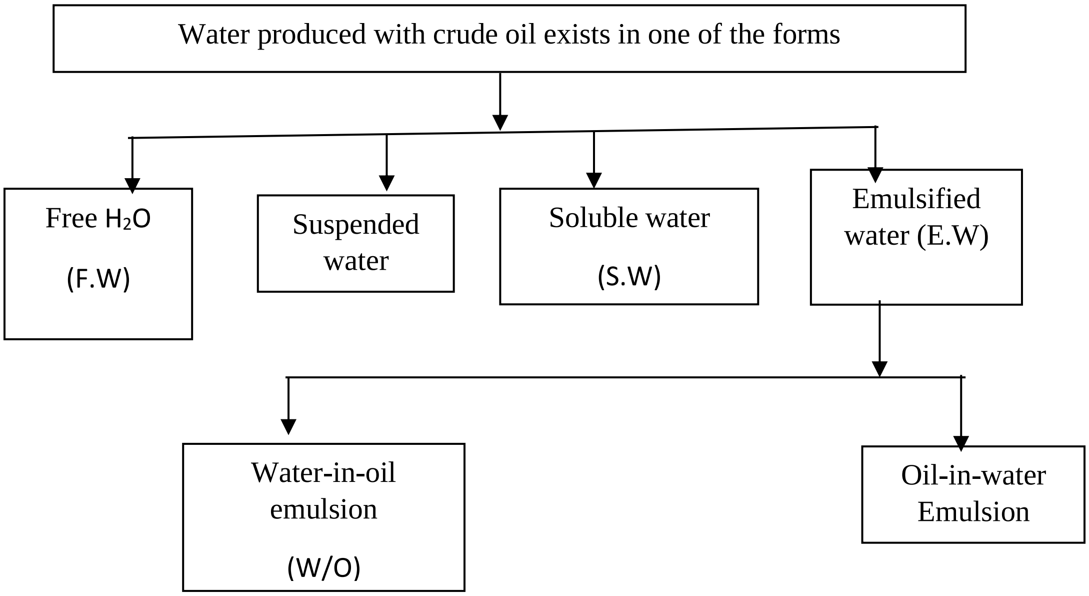

Fig 1.0 Forms of Saline water produced with crude oil [4].

When water is produced alongside with crude oil, separation is usually carried out to remove the water from oil. However, because of inadequate separation, it often contains a variety of harmful substances, including naturally occurring radioactive materials (NORM) predominantly 226Ra, 228Ra and 210Pb [5], produced solids, metals in trace amounts, production and processing chemicals, and dispersed and dissolved hydrocarbons.

Produced water discharges on the immediate near shore environment and the target microorganisms are the hydrocarbon degrading organisms and sulphate reducing bacteria which seems to be indigenous to produced water. Hydrogen sulphide, sulphate reducing bacteria have been known to be responsible for corrosion of iron and steel in the form of storage tanks, pipelines and pumps.

A significant concentration of hydrocarbon utilizing microorganisms have also been isolated from produced water, and the studies conducted thereafter showed that produced water is easily biodegradable [6], the presence of hydrocarbon degrading bacteria in produced water therefore can be of immense benefit to the receiving environment especially in the degradation of recalcitrant organic compounds in the receiving environment [7].

Impacts are related to the exposure of organisms to concentrations of various chemicals. Factors that affect the amount of produced water constitutions and their concentration in seawater, and therefore their potential for impact on aquatic organism include the following [8].

1. Dilution of the discharge into the receiving environment.
2. Instantaneous and long-term precipitation/
3. Volatilization of low molecular weight hydrocarbons.

4. Physico-chemical reactions with other chemical species present in sea water that may affect the concentration of produced water components
5. Adsorption onto particulate matter
6. Biodegradation of organic compounds into other simpler compounds
7. Salt tolerant aquatic habitat in ponded waters and surface reservoirs may increase within the marine environment.

On offshore operations, key factors include concentration of constituents and other characteristics of the constituent such as toxicity. Actual fate and effects vary with volume and composition of the discharge and the hydrologic and physical characteristics of the receiving environment. New plant species may take over from native plants as a result of changes in soil resulting from contact with produced water. Local environments can be altered as a result of excess soluble salt, which can cause plants to dehydrate.

Generally, the effects of discharged produced water impacts negatively on the environment by:

1. Causing high mortality of aquatic animals, impairment of human, Loss of biodiversity in breeding grounds, Vegetation hazards, loss of portable and industrial water resources
2. Reducing fishing and farming activity and
3. Giving room to poverty, rural underdevelopment and bitterness due to lack.

Materials and Methods

The physical properties considered for the purpose of this research were: pH, Conductivity, Total Dissolved Solids, Chloride, SO_4^- , PO_4^-, Turbidity, Phenolphthalein Alkalinity, Oil & Grease, Methyl orange Alkalinity, Ammonia nitrogen and Phenol. This will aid to evaluate the physicochemical characteristics of the field. 1.1 litres of Conc. Hydrogen Trioxonitrate (IV) acid (HNO3) was placed in a sterilized one (1) litre plastic container. Random sampling was employed to collect the samples, three samples each were taken from Six (6) oil wells in the Umuechem oil field. The investigations were conducted using the American Standard for Testing and Materials (ASTM) and APHA methodologies being used as a guide, The test methods employed are colorimetric, gravimetric or trimetric.

pH Value

Method: Measurement of pH by Electrometric Method
Using Lab pH Meter (ASTM D1293-84)

Apparatus: pH Meter

Procedure: The pH meter was standardized using the pH buffer solution after which the electrodes were thoroughly rinsed with distilled water. The samples were allowed to cool to ambient temperature and were then poured into a plastic container, one after another the electrode was thereafter, and immersed into the sample such that the electrode tips are covered. The instrument was powered on and the meter reading allowed to stabilize. Upon meter stabilization, the reading on the meters was read and recorded as the pH of the samples.

Electrical Conductivity

Method: Measurement of Electrical Conductivity using Orion Conductivity Meter (ASTM D1125-82)

Principle: The magnitude of the conductivity is an indication of total concentration of the ionic solutes.

Procedure: The meter was switched on and allowed to stabilize. It was afterwards, standardized using standard solutions. The plastic sample receiving container was rinsed thoroughly with distilled water followed by the test sample. Some quantity of the sample was then poured into the receiving container and the electrode completely immersed into the sample. Adjusting buttons and then the meter was allowed to achieve equilibrium. The reading (i.e., the digital display on the meter) was recorded as the conductivity of the sample in Micro Siemens per centimetre (μS/cm).

Total Dissolved Solids (TDS)

Method: Determination of Total Dissolved Solids (TDS) in the Waste water by Gravimetric method (APHA 208C)

Apparatus: Electric heater (Hot Plate), Tong, Oxford weighing balance (G2104), Beakers, oven, Desiccators

Reagent: Chromic acid

Procedure: A 100m beaker was used for each sample. All was washed with chromic acid and rinsed with distilled water. It was thereafter dried in an oven at 105^{0}C for 1hr after a period of 1hr, the breakers were transferred with a tong into a desiccator with desiccant at room temperature. The beakers were weighed on a weighing balance and their respective weights recorded as weight A (Wt. A).

The samples were filtered and 25ml of the filtrate introduced into the weighted beaker. The beakers with the sample were heated to dryness on a hot plate without allowing the samples to boil (90-95^{0}C). The dried beaker was transferred with a tong into a desiccator and allowed to cool for 1hr (at room temperature). The beaker was again weighed and the new weight recorded as weight B (wt. B).

Turbidity

Method: Determination of Turbidity in water sample (ASTM)

Apparatus: Turbidity Meter

Principle: This method is based on the comparison of the intensity of light scattered by a given sample under a defined condition with the intensity of light scattered by a standard reference sample under the same condition. The higher the turbidity the higher the intensity of scattered light and the more turbid is the sample.

Procedure: The Turbidity Meter was switched on and allowed to stabilize for 30 mins. The instrument was calibrated with distilled water in the sample cell, the transparent path of the cell was inserted into the compartment, and another standard cell marked 614 was also inserted in its compartment carrier. The sample cell containing distilled water was adjusted to zero using the zero adjustment knobs.

The standard was also adjusted to the 614-value using the standard adjustment knob. To measure, a small quantity of sample was introduced into the sample cell after discarding the distilled water. Replaced in the open channel compartment and covered. The reading was allowed to stabilize and recorded as the turbidity of the sample in the Nephelometric Turbidity Unit (NTU).

Alkalinity

Method: Determination of Alkalinity by Titration (ASTM 01067-02, APHA 2320 B (1998)

Apparatus: Retort stand, burette, conical flask, measuring cylinder

Reagents: Standard 0.02N H_2SO_4, Phenolphthalein indicator, Methyl orange indicator

Principle: Carbonate and hydroxide, $CO_3^{2-} + OH^-$, are determined by titration with standard acid to PH about 8.3; the end – point is detected using phenolphthalein indicator. The hydrogen carbonate, HCO^-_3, is determined by further titration with standard acid to an end–point pH between 4.2 and 5.4 using methyl orange indicator.

Procedure: (A) Phenolphthalein Alkalinity (P_A)

A 100 ml portion of the filtered sample was measured using a measuring cylinder and introduced into a 250 ml conical flask, and 10 drops of Phenolphthalein indicator was added. When the sample turns pink, it is titrated with the 0.02N H_2SO4 till colour disappeared and the titre value was recorded.

(B) Methyl Orange Alkalinity (P_M)

Where sample remains colourless with the addition of Phenolphthalein as above, 3 drops of methyl orange was further, added and then titrated with 0.02N H_2SO_4 and stirred continuously until colour changes from yellow to orange.

Calculation:

$$= \frac{N \times 1000 \times \text{Eq. wt } CaC0_3 \times \text{titre value}}{\text{Volume of sample used}}$$

$$P_{A/M} = N \times 500 \times \text{Titre value}$$

$$= 10 \times \text{Titre value as } CaC0_3$$

Chloride

Method: Mohr's Method for Determination of Chloride Ion (ASTM D512-81)

Apparatus: Retort stands, beaker, burette, conical flask

Reagents: Silver nitrate solution (0.025N $AgNO_3$), Potassium chromate solution

Principle: The Mohr's method employs silver nitrate as titrant and potassium chromate as the end point indicator. The chloride ion present in the water/waste water sample is precipitated as silver chloride.

$$Ag^+ + Cl^- \longrightarrow AgCl \qquad (Ksp = 3x10^{-10})$$

As the chloride ions in the sample are being wholly precipitated, any addition of silver nitrate solution will lead to a level at which the solubility product of silver chromate is exceeded and it begins to form a reddish- brown/ brick-red precipitate.

$$2Ag + CrO^-_4 \longrightarrow Ag_2CrO_4 \ (Ksp = 5x10^{-12})$$

(reddish- brown)

This is taken as the end-point.

Procedure: The titration was carried out on two separate samples; a blank (reference) sample and the produced water sample. For blank, a 50 ml burette was properly placed and clamped on a retort stand. The 0.025N $AgNO_3$ was transferred into the burette using a beaker and funnel to the 50 ml mark. 25 ml of the first produced water sample was measured into a 250 ml conical flask using a measuring cylinder, and was topped up to 50 ml mark with distilled water. 1ml of the indicator, potassium chromate was then added and shaken to mix uniformly. The sample was then titrated with $AgNO_3$ drop wise from the burette until a reddish-brown colour was observed as the end-point and titre value was recorded.

For the sample, 50 ml of each produced water sample was measured into another 250 ml conical flask respectively. This was followed by the addition of a 1.0ml potassium chromate indicator and shaken to mix thoroughly. This was titrated with $AgNO_3$ from the burette in drops until a reddish- brown end point was noticed. The titre was recorded as sample titre.

Calculation:

$$\text{Chloride, mg/l} = \frac{\text{sample titre} - \text{blank titre x N x 71}}{\text{Volume of sample used}} \text{ x 1000}$$

Cl^- (mg/l) = titre value x factor

Titre value = sample titre- blank titre

$$\text{Factor} = \frac{\text{Nx71X1000}}{\text{Vol. of sample used for standardization}}$$

Standardization volume = 100ml

Phosphorus In Water (Phosphate)

Method: Vanado-Molybdo-Phosphoric acid Colorimeter Method (ASTM D515-82)

Apparatus: UV spectrophotometer (Specord 200)

Reagents: Phosphate reagent = Ammonium trioxo-vanadate(V) (ammonium metavanadate); NH_4VO_3

Principle: In dilute orthophosphate solution, ammonium molybdate ($NH_{4)2}$ MO_4) reacts under acidic condition to from a heteropoly acid: Molybdo-phosphoric acid ($(NH_4)_3PO_4$ $3MoO_3$). In the presence of vanadium, used as soluble ammonium trioxo-vanadate (V) (ammonium metavanadate), NH_4VO_3; yellow colour Vanado-molybdo-phosphoric acid is formed.
$4(NH_4)_3PO_{4.}$ $3MoO_3 + NH_4VO_3$ —> Vanado – molybdo- phosphoric acid (yellow).

The intensity of the colour is proportional to the phosphate concentration in sample solution.

Procedure: 50 ml of distilled water was measured with a measuring cylinder into the plastic bottle and 50 ml of the produced water sample was also taken each into separate containers. 25ml phosphate reagent (ammonium metavanadate solution) was added into each container and allowed to stand for 2 mins. The UV spectrophotometer was used to read off the concentration at a wavelength of 400mm.

Calculation:

$PO^{3-}{}_4$, mg/l = instrumental concentration x factor.
Factor = 3.066

Nitrates- Ammonia Nitrogen

Method: Determination of Ammonia – Nitrogen by Direct Nesslerization (ASTM D1426-79, Method B)

Apparatus: Nessler reagent (K_2HgI_4), $ZnSO_4$ solution.

Principle: Ammonium ion, NH_4^+, reacts with the Nessler reagent in a strongly alkaline solution to form a yellowish-brown colloidal substance. The intensity of the colour is proportional to the amount of ammonia, NH_3, present in produced water samples.

Procedure:

The samples were filtered and 1ml of $ZnSO_4$ added to make turbid. NaOH was added to adjust the pH to about 10.5, again the sample was filtered. 100 ml of the filtered sample was then measured into sample bottles. 1ml of Nessler reagent was added to all samples and to the blank sample as well, it was mixed and allowed to stand for 5 mins. The solution was transferred into a 10mm (1cm) curve cell and measured against blank (reference sample) at 425 nm (ammonia wavelength). The concentration was read and recorded as result in ppm.

Phenols

Method: Determination of phenols in water sample (ASTM D 1783-01)

Apparatus: UV-spectrophotometer (specord 200), SUGIYAMA-GEN Distillation Apparatus, Measuring cylinder, conical flask.

Reagents:

(i) methyl red indicator

(ii) phosphoric acid (H_3PO_4)

(iii) copper sulphate ($CuSO_4$)

(iv) ammonium chloride buffer

(v) 4-amino-antipyrine

(vi) Potassium ferro-cyanide

Principle: Phenol reacts under conditions specified in this test method with 4-amino-antipyrine at about pH 10 and in potassium ferro-cyanide medium to from a coloured dye called antipyrine (phenazone; 2.3-dimethyl -1- phenyl – pyrazol -5-one). This dye can be measured on a spectrophotometer at 510 nm. The higher the concentration of the phenol, the deeper the colour of the dye, and the higher the absorbance.

Procedure: A 100 ml portion of each sample was measured into a 250 ml conical flask and 3 drops of methyl red indicator (having pH range of about 4-3) added to test for acidity, colour changes to yellow (for acidic samples). For acidic samples; H_3PO_4 was added in drops to obtain a pink colour end point (indicating that the sample is acidic). 1 ml of $CuSO_4$ solution (160 g/l) was added. A 15 ml portion of distilled water was also added. The sample solution was distilled and the distillate received with a measuring cylinder and introduced into labelled bottles. 100ml distilled water was measured as a blank sample. 3 ml of ammonium chloride buffer was added to the samples and to blank as well. 2 ml of 4-amino-antipyrine was added as an indicator. 2 ml potassium ferro-cyanide was also added and shaken to mix thoroughly. The solutions were allowed to stand for 10mins to allow the colour to develop. The phenols concentration was measured with the blank (as reference) using a 10 mm (1cm) curve cell at a wavelength of 510 nm.

The UV concentration was recorded as the phenolic concentration in ppm.

Oil and Grease

Method: Determination of Oil and Grease in the polluted water (ASTM D4281) by gravimetric method.

Principle:

In the determination of oil and grease, an absolute quantity of specific substances is not measured; rather groups of substances with physical characteristics are determined quantitatively on the basis of their common solubility in a specific solvent. Oil and grease may therefore include hydrocarbons, fatty acids, soaps, fats, waxes, oils and other materials that are extracted by the solvent.

Apparatus:

(i) An oven
(ii) A desiccator
(iii) Separator funnel
(iv) Filter paper
(v) Beakers

Reagents: Extraction solvent (chloroform), sodium sulphite ($NaSO_3$); anhydrou**s.**

Procedure: Beakers were washed and dried in an oven at 105^0C for 1hr and cooled in a desiccator for 1hr. The beakers were weighed and the weights recorded as weight. A 200ml of each sample was measured into a separatory funnel. 5 ml of concentrated HCl and 40ml Trichloromethane (chloroform) was added. The funnel was opened and shaken vigorously and the tap opened at intervals to expel any produced gas. The funnel was placed in a rack and the stopper removed. The filter paper was folded into a cone and 2g of anhydrous Na_2SO_3 was added on the filter. The weighted beaker was then placed under the separatory funnel in the rack. The chloroform (containing the extract) is received into the weighted beaker and heated to dryness. The heated beaker was cooled in a desiccator with a desiccant for 1hr (room temperature). It was reweighed and the weight recorded as weight B.

Calculation: Oil and crease (ppm) =

$$\frac{\text{Final weight (B)} - \text{initial weight (A)} \times 10^6}{\text{Volume of Sample}}$$

Sulphate

Method: Determination of sulphate ion in waste water by gravimetric method (ASTM D516-02)

Principle: Sulphate is precipitated in hydrochloric acid medium as barium sulphate ($BaSO_4$) by the addition of barium chloride solution.

$$BaCl_2 + SO_4^- \longrightarrow BaSO_4 + 2CL^-$$

This method is based on the formation of barium sulphate in the colloidal form by a sulphate in the presence of (acidified HCl) barium chloride. The absorbance of the colloidal solution is measured as the concentration of $SO_{4.}^-$ on a standard spectro-photometer.

Reagents:

(i) Barium chloride ($BaSO_4$)
(ii) Sulphur conditioning reagent

Procedure: A 50 ml portion of distilled water was measured into a 25 ml Erlenmeyer flask as blank. 50 ml of the sample was measured as well into another 25 ml flask. 10ml of sulphur conditioning reagent was added to each of the flasks. 0.3 g of $BaSO_2$ solution of 30-40 mesh was then added and the solution was stirred for 1 min and allowed to stand for 4mins. After 4 mins, the solution was again stirred for 2 sec. Some of the solution was poured into an absorption cell of path length 40 mm and absorbance (concentration) read at 420 nm. This is recorded as the concentration of $S0_4^-$ in mg/l.

Trace Metals

Method: Atomic Absorption Spectrophotometer (AAS)

Principle: A sample is introduced (aspirated) into a flame where it becomes atomized. A light beam is directed through the flame into a monochromator and then onto a detector that measures the intensity of the light absorbed. The amount of light intensity absorbed in the flame is proportional to the concentration of the element in the sample. Each metallic element has its own characteristic absorption wavelength, a source lamp made of that element is employed which makes the method free of spectral or radiation interferences. AAS depends on the presence of free unexcited atoms, of an element in a sample.

Apparatus: (i) Shimadzu Atomic Absorption Spectrophotometer (AAS) (AA-6300 series).

(ii) Pressure filter pump

(iii) Glass sample bottles

Reagents:

(I) Conc. HNO_3, (ii) Distilled water

Procedure: The samples were filtered using the pressure filter pump and the filtrate was poured into the sample bottle. Few drops of Concentrated $HN0_3$ were added to acidify the sample. The distilled water was first aspirated into the AAS to clear the line and make it free of contamination. The appropriate cathode lamp was set for each metal to be analysed and the AAS was set to the appropriate wavelength. And the concentration of the metals was determined, one after another in all samples.

Results

Table 1: Physico-chemical Properties of Produced Water in Umuechem field

S/N	Parameter	PWW1	PWW 2	PWW3	PWW4	PWW5	PWW6	Mean
1	Ph	5.76	6.37	6.35	6.00	5.15	6.11	5.9566
2	Conductivity (µS/cm)	141	75	129	75	105	72	99.5
3	TDS (mg/l)	366	502	734	431	653	1788	745.66
4	CL^- (mg/l)	1.54	3.53	5.10	3.51	7.41	1.72	3.8016
5	SO_4^- (mg/l)	1.21	3.89	2.59	3.52	6.99	5.15	3.8916
6	PO_4^- (mg/l)	3.47	6.17	3.18	7.18	2.81	3.55	4.3933
7	Turbidity (NTU)	125	129	139	135	138	177	140.5
8	Phenolphthalein Alkalinity (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
9	Oil & Grease (mg/l)	0.6	0.6	1.8	0.7	0.9	4.4	1.5

10	Ammonia nitrogen (mg/l)	1.28	1.03	0.91	1.24	1.55	2.42	1.405
11	Phenol (mg/l)	0.07	0.06	0.32	0.09	0.38	0.33	0.2083
12	Temp ºC	24..21	24.24	24.05	24.03	24.71	24.8	24.34
13	Methyl orange Alkalinity (mg/l)	1.38	2.84	2.45	2.88	3.58	1.87	2.5

PWW: Produced Water Well.

Table 2: Concentration of trace metals in produced water of Umuechem field.

S/N	**Metal (mg/l)**	**PWW1**	**PWW 2**	**PWW 3**	**PWW4**	**PWW5**	**PWW 6**	**Mean**
1	Cu	0.1097	0.0357	0.0426	0.0239	0.1473	0.2285	0.09795
2	Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
3	Fe	0.3352	0.4924	0.7671	0.7612	0.1354	0.3755	0.4778
4	Pb	0.3345	0.7424	0.1193	0.1922	0.5520	0.2540	0.3337
5	Ni	0.05	<0.01	0.06	<0.01	<0.01	0.06	<0.07917
6	Zn	0.3317	0.3725	0.075	0.427	0.2732	0.1313	0.2683
7	Mn	0.074	0.022	0.053	0.059	0.030	0.0035	0.04025

PWW: Produced Water Well

Discussion

Concentration Variation of Trace Metals:

The mean concentrations of Cu, Cr, Mn, Fe, Zn, Pb and Ni were analysed from six (6) wells of produced water all of Umuechem oil fields. The results of the concentration of trace metals are presented in Table 2. Iron (Fe) and Lead (Pb) show highest concentration in all wastewater samples (oil wells) with mean concentration of 0.4778 and 0.3337 mg/l. This concentration is above the EPA permissible limit of 0.10mg/l and 0.05mg/l for Fe and Pb respectively. These may have risen from natural and anthropogenic sources and activities for example the historical use of lead additives in gasoline. High concentrations of lead (Pb) and iron (Fe) in the environment can have many negative consequences, including Heavy metals like Pb and Fe can accumulate in the food chain and become toxic to humans and the environment. It can also reduce the growth of plant roots and shoots. Lead can cause a number of health issues in humans, including kidney, brain, and reproductive organ damage. It can also cause neurological problems and bone loss. Heavy metals can alter the properties of soil, such as its pH, colour, porosity, and natural chemistry. The high concentration of these metals could also contribute to corrosion in oil and gas production equipment.

Other trace metals show mean concentrations of 0.09795 mg/l Cu, 0.02683mg/l Zn, <0.07917mg/l N_i, and 0.04025mg/l Mn while Cr occurs in undetectable amounts. Generally, trace metals from Umuechem field show low concentrations, the variation in physicochemical values accounts for the differences in reservoir geology, water injection history and filled maturity. Toril I. [9] reported that concentrations of metals in produced water depend on the field, particularly with respect to age and geology of the formation from which the oil and gas are produced. The results of physicochemical parameters of produced water are presented in Table 1.

Results of pH analysis indicated PWW-01-PWW-06 ranged from 5.15-6.35. These values did not conform to the WHO specification of 6.50-8.50 and 6.00-9.00 for both drinking water and discharged wastewater into the stream respectively. *Bhatia* [10] reported that a high concentration of pH of either an acid (pH << 7) or an alkali (pH >>7) in wastewater is an indication of industrial waste. Conductivity, which is a useful indicator of its salinity or total salt content, is low in the produced water of Umuechem oil field.

Turbidity values are 125NTU for PFW-01, 129NTU for 02, and 139NTU for 03, 1135 for 04, 138NTU for 05, 177NTU for 06, The mean value obtained is 140.5NTU all the values obtained for turbidity are above the WHO standard of 5NTU for discharge of wastewater into stream. The higher turbidity value indicates the presence of suspended matter, organic matter, silt and metal oxides, etc.

Table 1, also represents results for anions such as SO_4^-, NO_3^-, $Cl^{-,}$ their concentrations vary between 0.55 to 4.13 mg/l SO_4^-, 0.37 to 6.22mg/l PO_4^-, and 0.41 to 2.50mg/l Ammonia-nitrogen (nitrate).

The levels of sulphate were below the W.H.O limit of 45 mg/l for discharge of wastewater into the river. The levels of phosphate only exceed the WHO standards of 5 mg/l in sample PFW-02 and PWW-04. The levels of nitrate are below the W.H.O specification of 45 mg/l nitrate in wastewater. But the mean chloride concentration of 3.8016mg/l is below the W.H.O guideline for discharge of wastewater into rivers.

Oil and grease concentrations are low in samples PWW01-PWW-06. Phenol's concentration is low in Umuechem produced water samples with a mean concentration of 0.2083mg/l. This is favourable for discharge into the river.

Conclusion

Produced water varies inconsistently due to its widely dependent factors such as the geology of the well, hydrocarbon composition, geological location and injection history. It is therefore pertinent to conclude that the produced water of Umuechem fields, Nigeria has been treated but the treatments were never perfect as it still contains high concentration of some toxic chemicals that will be deleterious to marine organisms and human consumers of marine product if discharged.

The study reveals low concentration of physicochemical parameters, and high concentration of metal which is not W.H.O standard permissible limit for discharge of waste water into the river.

Recommendation

The following recommendations are therefore made from the study conducted:

- The produced water of Umuechem oil field should be further treated.
- The following treatment technologies are recommended to remove these toxic chemicals: carbon adsorption, air stripping, chemical oxidation and ultraviolet light.
- The authorities concerned should set-up/enforce Environmental Protection Agency (EPA) that will regulate and monitor produced water discharges.
- Oil and gas producers should carry out the following produced water management options.
- Water minimization option-using mechanical blocking devices, water shut-off chemicals, etc.
- Water recycles and Reuse options-underground injection for increasing oil recovery
- Water disposal options-treatment before disposal/injection.

At the moment, proper management practices are not only required for Produced Water treatment to meet regulatory agencies' specified water quality limits for safe discharge and/or reuse [11,13], but also to accomplish pertinent SDGs (Clean water and sanitation, Climate Action, Life below water, and Life on land) that are strategic to water use and environmental sustainability [12].The creation of an economical, environmentally friendly technology that emits no pollutants should be a top priority for Produced Water management both now and in the future.

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