Scientia Africana, Vol. 21 (No. 3), December, 2022. Pp 75-82 https://dx.doi.org/10.4314/sa.v21i3.6
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MULTI-ELEMENTAL ANALYSIS OF FREE WATER OBTAINED FROM WATER IN OIL EMULSIONS FROM NIGER DELTA REGION USING ICP-OES

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Received: 11-10-2022
Accepted: 31-11-2022

ABSTRACT

Disposal of produced water obtained from crude oil could be challenging and tough because of the effect it has on the environment. Produced water contains high levels of salt and toxic substances which must be treated before re-use or disposal to reduce their impact on the environment, people and assets. Hence, the characterization of produced water for its chemical composition is essential. This study presents the determination of heavy metals (Co, Cu, Pb, Fe, Zn, Ni, and Cd) in produced water obtained from crude oil emulsion samples via inductively coupled plasma optical emission spectrometry (ICP-OES). The samples were subjected to treatment prior to analysis. The analytical curve obtained from the calibration gave excellent correlation coefficients ranging from 0.9995-1.000 and the recovery values obtained were very good (95% - 105%). The result of the heavy metal analysis in µg/l (Co: <DL to 14.3, Cu: 114.1 to 1553.2, Fe: 492.1 to 1576.4, Ni: 52.3 to 174.5, Pb: <DL to 15.1, Zn: 92.4 to 432.9, Cd: 2.3 to 4.4) indicates that the concentrations of the metals evaluated in the produced water samples were above the recommended discharge limit (Zn - 1.0 mg/L, Co - 0.02 mg/L, Fe - 1.0 mg/L, Cu - 0.02 mg/L, Cd - 0.01 mg/L, Ni - 0.03 mg/L and Pb - 0.05 mg/L).

Keywords: Multi elemental analysis, free water, oil emulsions, Niger Delta region, ICP-OES)

INTRODUCTION

Crude oil is formed alongside gas and salt water known as formation water from the reservoir. As the reservoir is being produced, overtime it becomes depleted with a corresponding decrease in the reservoir pressure, whereby water is produced alongside. The production of water alongside crude oil creates several problems during production (Umar 2016). The water may be produced either as free water (this will later settle out of the mixture over time) or could form an emulsion (this could be a tight or loose emulsion). Produced water is a term used in the oil industry to describe water that is produced along with oil and gas (Szép & Kohlheb, 2010; Mehmet et al., 2008).

Oilfield activities generate enormous amount of wastewater (Agbalagba et al., 2013). Oilfield waste water otherwise referred to as produced water contains different organic and inorganic constituents (Lu et al., 2006). During hydraulic fracturing, large volumes of waste water is generated that require appropriate management and disposal (Vikram, 2016). Approximately, 20,000 m^3 of water will be adequate for a proper fracturing procedure, and this may be provided from local surrounding freshwater bodies or wastewater (Davarpanah, 2018). The large amount of produced water generated during oil production makes this a major environmental problem (Camarillo & Stringfellow, 2018) as a result, it must be treated and properly disposed.

At the initial stage of crude oil production, the generation of produced water could be low but the amount progressively increases with time (Lu et al., 2006). During the lifetime of a well, the volume of water produced may vary from seven to ten times the volume of crude oil that is produced (Dorea, 2007). When oil wells move from the initial stage of drilling towards the completion stage, there is the utilization of a large amount of water which is re-injected into the reservoir to cause pressure build-up and force oil to come out from the reservoir (Szép & Kohlheb, 2010). Re-injection of produced water helps in maintaining the pressure of the well (Emam et al., 2014). Additionally, produced water re-injection also helps to improve oil recoveries from the reservoir (Penha et al., 2015). The chemical composition of waste or discharged water may be complex including toxic compounds, dispersed oil, dissolved or volatile hydrocarbons, organic acids, BTEX (Benzene, Toluene, Ethylbenzene, Xylene), PAH (Polycyclic Aromatic hydrocarbons), Phenols, metals and traces of chemicals that were added to the production line (Dorea, 2007; Utvik, 1999, Guedes et al., 2020). The chemical composition of produced or discharged water is field-dependent, hence a function of geologic and geochemistry of the formation. The type of production activity associated with the well may also affect the chemical composition of produced water (Emam et al., 2014). Normally, the waters derived from gas wells contain several times greater concentrations of metals than those derived from oil wells (Emam et al., 2014).

Although, the characteristics of formation water vary from field to field, the addition of oilfield chemicals such as defoamers, corrosion inhibitors, biocides, scale inhibitors, emulsion breakers, etc further modify the composition of formation water (Santelli et al., 2012). The treatment of produced water or oilfield wastewater before discharge is important because produced water can contaminate the aquatic and terrestrial habitat. This is because of their chemical compositions which are toxic to plants and the aquatic life. Produced water is problematic to treat and its properties vary from one well to another (Szép & Kohlheb, 2010). Produced water could be a viable source of water if properly treated (Mondal & Ranil, 2008) and thereby decreasing water disposal costs.

There are many negative effects caused by untreated produced water. A few of the problems caused are (Al-Haleem et al., 2010; Emam et al., 2014):

1. Excess soluble salts which cause plants to dehydrate and die
2. Reduction in the oxygen level which threatens aquatic habitat.
3. Scaling problems thereby clogging the well-bore and impede the flow of fluid.
4. Chemical impact on the environment as a result of oilfield chemicals such as oxygen scavengers etc.

Effective treatment of produced water generally requires a series of pre-treatment operations to remove different contaminants.

Hence, treatment, as well as the knowledge of the chemical composition of produced water, is important because it can affect the effective production cost, which is a vital part of operations in the crude oil and gas industries (Penha et al., 2015). Analyzing produced water can help decision-making and reduce uncertainties during the assessment and development stages. Thus, the significance of the composition of produced water is incontestable.

MATERIALS AND METHOD

A 100ppm stock solution of the various metals (Cd, Co, Cu, Fe, Ni, Pb and Zn) was obtained from Scharlau (Spain). The various multi-element calibration standard solutions of 1 ppm, 2 ppm, 4 ppm and 6 ppm were prepared from the 100ppm stock solution. Nitric acid and Hydrochloric acid (Fischer) were used as received for wet digestion. Distilled water from a Waterstill Merit W4000 distiller connected to a resin membrane filtration unit was used throughout the study. Argon gas (99.99%) was used as plasma gas, nebulizer gas and auxiliary while Nitrogen gas (99.99%) was used as a purging gas and both gases obtained from Air Liquide Nigeria.

For basic characterization of the samples, chloride measurements were performed with a Digital Titrator (Titroline 5000 from SI Analytics). Thermo scientific Orion star A211 bench top pH meter with glass electrode was employed for pH measurements (Electrometric method). Conductivity was done with YSI 3200 conductivity machine. Elemental analysis and quantification was done with Agilent 5100 SVDV Inductively coupled plasma optical emission spectrometer (ICP-OES) with radial view, equipped with SPS4 automatic sampler, a cyclonic spray chamber and a tangential concentric nebulizer (Mira Mist) was used. The ICP instrument software version 7.4.2.10790 was used for data acquisition and management. The ICP-OES instrument operating parameters used for the metal determination is presented in **Table 1** while the wavelengths (nm) of measurement for each of the metals are as displayed: cadmium 226.502 nm cobalt 228.615 nm cupper 327.395 nm iron 238.204 nm nickel 216.555 nm lead 220.353 nm zinc 213 nm.

Table 1: Operating parameters for the determination of metals by ICP-OES

Parameters	**Settings**
Radio Frequency Power (Kw)	1.20
Plasma gas flow (L/min)	12.0
Nebulizer gas flow (L/min)	0.70
Auxiliary gas flow (L/min)	1.0
Stabilization time (s)	15
Detector	VistaChip II
Aspiration rate (ml/min)	1.2
Pump speed	12 rpm
Nebulizer chamber	cyclonic
Nebulizer Type	Mira Mist
Torch	One slot
Viewing height small window(mm)	15
Viewing height large window (mm)	51
Replicate numbers	3
Pump speed	12rpm

Source: Agilent Technologies Inc.

Sampling and Preparation

The produced free water samples used for this study were recovered from crude oil emulsions taken from well heads in two different oilfields (Obelle and Imo River) in the Niger-Delta, region of Nigeria. The free water samples were labeled OBWI, OBW3, IMR5, IMR7 and IMR 9 and preserved after collection in accordance with standard guidelines. Samples OBW1L and OBW3 were taken from Obelle while IMR5, IMR7 and IMR were from Imo River.

The samples were digested before analysis. The digestion was done using 100 ml of sample with 2 ml of (50% 1:1) nitric acid and 10 ml of (50% 1:1) hydrochloric acid and refluxed at 95^{o}C on a hot plate in an enclosed system. The digested samples were filtered under suction using the Buchner funnel and flask with a 0.45µm membrane filter. After sample preparation, the analyses were carried out using ICP-OES.

ICP-OES has been used since in the 1970s and detects elements in samples using plasma (the fourth state of matter after solid, liquid and gas) and spectrometer (Khan, 2019). The schematic of ICP-OES consist of a light source, detector, spectrometer and data processing and display unit. When plasma energy is supplied to a sample, the component elements in the sample are excited to a higher energy. When the excited atoms are return to a low energy position, emission rays are released and these emitted rays that corresponds to the photon wavelength are determined by the spectrometer. The element type is measured depending on the position of the photon rays, and the component of each element is determined based on the intensity of the rays (Khan, 2019).

RESULTS AND DISCUSSION

Table 2 presents the percentage (%) recovery from the calibration curves of multi-elemental standard solutions prepared as several diluted concentrations. From the recovery test, the recovery percentages obtained was from 95.00 % to 105.00 %. In summary, the percentage recovery results were very good for all the elements studied. However, Zn, recorded the best recovery values obtained. Meanwhile, the correlation coefficient values (r^2) obtained for respective metals from the calibration curves are presented in Table 3. From the values obtained, the calibration curves gave excellent correlation coefficient values for all the metals measured (Co-1.0000, Cu-0.9998, Pb-1.0000, Fe-0.9995, Zn-0.9999, Ni-1.0000, and Cd-0.9998). The regression coefficients show good linearity in the concentration range of concern (1 ppm, 2 ppm, 4 ppm and 6 ppm). The inverse relationship between concentration of standard (ppm) and % recovery in Table 2 showed a good confidence level of the analytical data (between 95 and 105 recovery percent).

Table 2: Percentage (%) Recovery values obtained from the analytical calibration curve prepared from 100ppm stock solution

	% Recovery values						
Conc of Standard (ppm)	Cd	Co	Cu	Fe	Ni	Pb	Zn
1.00	104.00	103.00	95.00	104.00	104.00	105.00	100.00
2.00	99.50	101.00	102.00	99.50	100.50	101.00	100.00
4.00	96.75	99.75	101.00	102.00	98.50	99.25	100.75
6.00	97.50	100.17	100.83	104.17	98.67	99.50	99.83

Table 3: correlation coefficients obtained for each of the elements from the calibration curve

Element	**Correlation coefficient (R^2)**
Cd	0.9998
Co	1.0000
Cu	0.9998
Fe	0.9995
Ni	1.0000
Pb	1.0000
Zn	0.9999

Scientia Africana, Vol. 21 (No. 3), December, 2022. Pp 75-82 *https://dx.doi.org/10.4314/sa.v21i3.6*
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The characterization results of the produced water for pH, conductivity, chloride, salinity and total dissolved solids (TDS) are presented in Table 4. The results showed that pH values of the samples fell within the basic medium and ranged from 7.61 – 9.03. A reduced pH can affect oil-water separation process and this can impact receiving waters bodies when later discharged (Chikwe & Okwa, 2016).The high pH values of the samples are indicative of scaling tendencies in addition to the large amounts of chemicals used during drilling. The Electrical conductivity (EC) – TDS (Total dissolved solids) ratio for the samples averaged 1.476. EC and TDS are water quality parameters which indicate levels of salinity (Rusydi, 2018). The TDS values of the samples evaluated varied across a wide range from 1850-49250 (mg/l). This could probably be due to the different origins of the samples, as such variation can result from the age and geology of the formations where the hydrocarbons are being produced (Souza et al., 2017).

Most crude oils' aqueous extracts have shown a variation in the salt content (TDS) that is consistent with subsurface brines (Teixeira et. al., 2017). The samples have a wide range of salinities from 1558.90 ppm to 42593.84 ppm which is typical of formation water. The dissolution of halite is the predominant mechanism that originated salinity. The values obtained for chlorides in the samples do agree with this. The variation in characterization values across the different oilfields is dependent on the geographical location of the oilfield, the geological formation and type of hydrocarbon sample being produced (Chikwe & Okwa 2016). Produced water from the same oilfield as considered in this study tend to have physicochemical properties within the same range as shown in Table 4

Table 4: Values of basic characterizations of the free water samples

Sample ID	pH	Cond (µS/cm)	TDS (mg/l)	Chloride (mg Cl/l)	Salinity (ppm)
OBW1L	7.61	45200	30750	12926.53	23353.71
OBW3	9.03	72350	49250	23576.14	42593.84
IMR5	9.41	14462.5	9,825	1474.048	2663.089
IMR7	8.31	2775.0	1850	862.0	1558.90
IMR9	8.15	15940	10850	4766.021	8610.53

Elemental analysis

Five (5) produced water samples were analyzed to determine the concentrations of heavy metals and these values are presented in Table 5.

Table 5: Metal concentrations in µg/l present in digested water samples

Sample ID	Co	Cu	Fe	Ni	Pb	Zn	Cd
OBW1L	<DL	123.2	492.1	52.3	<DL	92.4	2.3
OBW3	14.3	124.6	1576.4	134.2	<DL	229.1	3.1
IMR5	5.4	1553.2	1123.6	174.5	<DL	432.9	3.2
IMR7	5.7	114.1	1281.8	133.4	15.1	177.4	4.4
IMR9	6.1	215.1	1384.5	155.4	6.4	192.1	4.2

*The Detection limits (DL) for Co and Pb were established as below 0.004 ppm and 0.005 ppm respectively.

The concentrations of Pb and Zn are expected to be low; this is because the presence of these metals are obtained in part from galvanized steel structures of the equipment that come into contact with Produced water during oilfield processes or with other waste streams that may be treated in the oil/water separator system (Azetsu-Scott et al., 2007). As expected the concentrations of Pb for all the samples measured are very low but for Zn, the concentrations are not as low as expected. The concentration of Zn in the samples is high. This suggests that other factors such as the geological age and features as well as the injected water volume of the well may have contributed to the moderately high concentration of Zn in the produced water (Amakiri et al., 2022).

Since Cd is produced as an inevitable by-product of zinc or occasionally Lead, the concentrations are also expected to be low. From the results obtained the concentration of Cd alongside Co is observed to be low. Some analytes, such as Co and Pb, for some of the samples were below the limit of detection. For sample W1L, Co and Pb were below the Limit of detection while for samples OBW3 and IMR5, Pb was also below the limit of detection.

According to Udeagbara *et al.*, 2021, the standard disposal limit for produced water is as follows: Ca - 200 mg/L, Ba - 0.01 mg/L, Sn - 0.04 mg/L, B - 1.0–0.5 mg/L, Ar - 5 mg/L, Mn - 0.02 mg/L, Zn - 1.0 mg/L, Cr - 0.02 mg/L, Mg - 60 mg/L, Fe - 1.0 mg/L, Cu - 0.02 mg/L, Cd - 0.01 mg/L, Ni - 0.03 mg/L and Pb - 0.05 mg/L. The obtained concentration in Table 5 for the digested samples shows that some of the produced water samples have metal concentration values below the standard disposal levels while some have the values above the disposal level. The concentration of Zn, Cd, Pb and Co for the samples fell below the discharge limit. For Fe, Ni and Cu, the concentration levels in the samples were above the discharge limit. From the concentration obtained, the concentration values for most of the metals in the produced water samples exceeded the standard disposal limit. Hence, it is imperative for the samples to be treated before discharge into the environment. Similar studies, such as Onojake and Abanum, (2012), Erakhrumen (2015), and Amakiri et al., (2022) which evaluated heavy metals content and their concentration in produced water samples from different sources, also documented similar observations as those recorded in this study. If the produced water samples are to be re-used or re-injected into the reservoir for enhanced oil recovery, proper procedure should be taken to prevent crusting of the formation (Penha et al., 2015).

CONCLUSION

The chemical composition of produced water from some oilfields (Obelle and Imo River) in the Niger delta region has been determined. It is significant to highlight that the chemical determination of oilfield produced water samples is vital to properly inform and assist in deciding on the treatment of this effluent for final disposal or to reuse. Some of these metals in their present concentration in the samples evaluated could be hazardous to the environment, humans and oilfield assets.

Based on the obtained results, it is important for the produced water samples from these oilfields (OBWI, OBW3, IMR5, IMR7 and IMR 9) to be properly treated before discharge into the environment as the metal concentration present in them exceeds the disposal limit. This is important as it will aid in predicting the fate and effects of the discharges to the aquatic environment. Also, the basic characterization values obtained such as the pH (which shows that it is alkaline) and the salinity values may impart the ecosystem if discharged to the environment without treatment. It can be established that the discharge of untreated produced water may be detrimental to the surrounding environment.

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