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Research Article

Management of Produced Water from Oil Fields in Niger Delta using Selected Agricultural Wastes

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ABSTRACT

Produced water, which is the biggest waste output from oil and gas well production, contains a number of hazardous components, ranging from heavy metals to soluble hydrocarbons and numerous contaminants. To guarantee compliance with best worldwide practices, it is suggested that sufficient treatment, monitoring, and re-use as the case may be for this waste water in the Niger Delta region be implemented.

Produced water samples were taken from different oil fields in Niger Delta region of Nigeria. Samples R was taken from an oil field in Imo River; sample X was taken from an oil field in Nembe, sample Y was picked from an oil field in Kolo creek, while sample Z was taken from Awoba oil field, all in Niger Delta region (4). The contaminants analyzed in these samples were chloride, carbonates and bicarbonates, sulphate as well as the Total Dissolved Solids (TDS).

The local materials (agricultural wastes) were thoroughly washed with water to remove unwanted materials that may stick on them. The materials were slice into pieces; dried under the sun for over 72 hours during hammer time season, and were further dried in an oven at 105°C for 3 hours for orange and banana peels, 150°C for 30 minutes for *luffa cylindrica*, and 3 hours for palm kernel fiber at 80°C to remove any adsorbed gas(s). Each was milled and sieved into 150 and 300 micron sizes and stored for the analysis.

For sample R treated with banana peels, orange peels, palm kernel fiber and *luffa cylindrical* in that order, the percentage reduction in the chloride concentrations were 52.94%, 60.78%, 37.25% and 43% respectively, for sample X the reductions were 54.54%, 63.64%, 45.45% and 50.90% respectively, for sample Y the reductions were 57.61%, 64.27%, 46.56% and 48.16% respectively while for sample Z, it was found to be 56.60%, 52.28%, 46.08% and 50.28% respectively. The finer local material (adsorbent) having more surface area was more efficient in the treatment. Similar results were as well obtained for carbonate and bicarbonate, sulphate and Total Dissolve Solids (TDS) from samples obtained from other oil fields.

Produced water samples obtained from oil fields in Niger Delta were successfully treated of impurities using the selected local materials. 150 micron size gave the best results.

Keywords: Produced water; Adsorption chamber; Pollution; Treatment

INTRODUCTION

Study background

Produced water is the most waste steam resulting from oil field operations. Produced water production is calculated to be above 60 million barrels per day across the world. 'The quantity of crude oil extracted from a hydrocarbon reservoir depends on certain factors like geological feature of the formation, reservoir energy drive, well completion method, depletion stage as well as production practices' [1]. Management of produced water is very essential because of the large volume extracted, the financial involvement in the treatment and environmental effect of chemicals contained in the waste stream. Numerous oil producing countries across the globe have enacted some laws and regulations on the level of treated produced water to be discharged on the environment. During the early days

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of oil production from the subsurface, absolutely no measure was put in place in managing produced water. The waste stream in some instances was released to rivers, ocean, and lakes with absolutely no treatment; it was spilled and discharged on the ground surface with no consideration of its effect to the environment. As time went on, petroleum engineers came to terms that this waste stream if properly treated could be injected into the formation to promote production' [2].

Nigeria is one of the Organization of Petroleum Exporting Countries (OPEC), second-largest producer of crude oil in Africa and sixth-largest nation known for oil-production in the world generating crude oil capacity of about 2.5 million barrels per day (Oil Production, n.d.). In 2003, oil extracted from the Niger Delta region accounted for over 96.7% of the Nigerian government's revenue and 97% of its total export [3]. The importance of the Niger Delta region in the country is indubitably essential to the economy and growth of the nation which is why the government has invested resources into the development and cleaning of environmental pollution resulting from oil exploration in the area.

Produced water as an inevitable associate of crude oil, the advent of the oil and gas sector in Nigeria has undoubtedly brought about economic reform in the country. However, this has come at the cost of dilapidating the region of the Niger Delta, causing severe water pollution, lifestyle difficulty in farming, and sourcing of clean water. In oil and gas production process, a considerable volume of water is injected down hole into the formation to improve the subsurface pressure and enhance more oil recovery. As the injected fluid comes back to the surface again, it comes along side with some hydrocarbons and is called produced water. The world extraction of produced water is over 250 mbpd. This waste stream (produced water) consist of numerous inorganic and organic composition of varying concentrations, which needs a composite design in terms of economical, more flexible system, and efficient plants to sort out the crude oil and also acheive a high quality treated water effluent [4].

A major challenge is the cleaning of the environmental degradation in the Niger Delta due to the vast quantity of oil exploration and in turn spillage that occurs. Numerous efforts and researches are being applied and developed to tackle the issues of environmental pollution. However; the focus of this paper will be on the management of produced water using local materials to minimize the concentration of contaminants (Figure 1).

Produced water is kwon to be a by-product of oil exploration and it is the most waste stream emanating from oil and gas activates. 'It is a combination of organic (soluble and insoluble) and inorganic components. It also composed of drilling chemicals, well stimulation chemicals with elevated hydrocarbons, salts, metals table as typical examples. It also has some radioactive materials' McLaughlin 2020. The large variation composition of produced water as seen on Table 1 results in pollution and is a great concern for the environment due to the convoluted nature of harmful chemicals and uncertainty of presumed ecological impact in future.

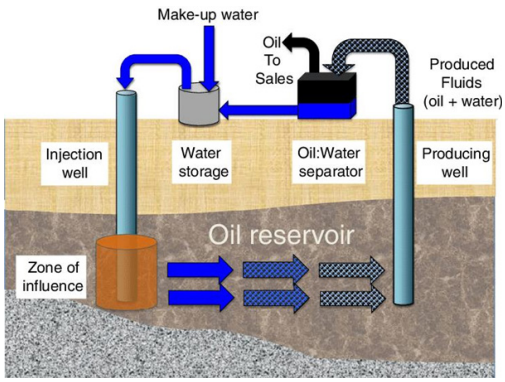

Figure 1: Formation of produced water.

Table 1: Composition of produced water.

Parameter	Unit (mg/l)	Parameter	Unit (mg/l)
Aluminium	310-410	Manganese	0.004-175
Ammonia nitrogen	10-300	Mercury	0.001- 0.002
Arsenic	0.005-0.3	pH (-)	4.3-10
Barium	1.3-650	Phenols	0.009-23
Beryllium	0.001-0.004	Potassium	24-4300
Bicarbonate	77-3990	Silver	0.001-0.15
Boron	5-95	Sodium	132-97000
Cadmium	0.005-0.2	Strontium	0.02-1000
Calcium	13-25800	Sulfate	2-1650
Chemical oxygen	1220	Sulfite	10
Chloride	80-200000	Surface tension (dynes/cm)	43-78
Chromium	0.02-1.1	Titanium	0.01-0.7
Copper	0.002-1.5	Total Organic Carbon (TOC)	0 -1500
Density (kg/m^3)	1014-1140	Total oil	2-565
Higher acids	1-63	Total polar	9.7-600
Iron	0.1-100	Total Suspended Solids (TSS)	1.2-1000
Lead	0.002-8.8	Volatile	0.39-35
Lithium	3-50	Volatile fatty acids	2-4900
Magnesium	8-6000	Zinc	0.01-35

Pointed out that produced water is made up of so many things among which is crude oil, which is composed of aromatic and aliphatic compounds, minerals, toxic metals as well as radioactive materials [4]. Others include production chemicals, synthesized additives; formation solids, scale materials, corrosion materials, bacteria growth, wax materials. with asphaltenes and dissolved gases present (Table 1).

Produced water is composed of organic and inorganic substances in varying concentrations as seen in Table 1. The location, nature of formation rock, reservoir lifetime as well as the type of crude produced tells the physiochemical characteristics shown by produced water [5,6]. Produced water features are shown by the type of formations from which it is produced; the conditions and chemical materials applied also define the contents of produced water. Compounds mostly found in this waste stream (produced water) are crude oil, minerals within the formation, chemical substances used in production process, production solids such as metals, corrosion products, waxes, bacteria, gases, etc. Taleb H. Ibrahim 2016.

Produced water volume extracted from a particular reservoir is not always constant. It's less at the initial time of production and gradually increases as production continues and because of this, the volume of produced water extracted will eventually be much [7].

Environmental effects of produced water

'The impact of produced water in the environment always depends on the biological, chemical as well as the physical constituent of the environment. Research shows that upon the amount of toxicity of produced water, there is insufficient information on the actual effect on the ecology' Odeigah 1997. In offshore drilling, produced water is always discharged to the aquatic environment within. Organic and inorganic compounds in produced water contain more harmful compounds compared to that in crude oil. The discharge of these harmful compounds contained in the extracted effluent to the aquatic system poses a big threat to the agricultural activities within the region as well as aquatic life.

Ayotamuna 2012 observed that discharge of produced water effluent to fresh water environment has a great negative impact to the agricultural activities within the region and also affect aquatic life adversely. Research has shown that produced water contains a substantial quantity of Biological Oxygen Demand (BOD) as well as Chemical Oxygen Demand (COD) which has fatty acids origin. Salinity is more pronounced in produce water compared with sea water which could lead to destruction of aquatic life in fresh water [1]. Toxic metals, contaminants and certain radioactive materials found in produced water is always unfriendly environment.

Niger Delta region of Nigeria is found within the coastline, it's a tropical rainforest with diverse ecosystems comprising of different species of plants and animals. 'This region is ecologically divided into four (4) classes namely: coastal inland zone, lowland rainforest, freshwater zone as well as mangrove swamp zone [3]. This region has a vast human populace whose means of survival re mainly fishing and farming.

El-Din 2018 conducted a study in which they used aquatic plant species for produced water management. The plants employed in the study were green algae, duckweeds, as well as water hyacinth. Among the parameters given consideration in the work was Biological Oxygen Demand (BOD) as well as Chemical Oxygen Demand (COD). From the outcome of the analysis, duckweed brought down the concentration of chemical and biological oxygen demand in the produced water sample to 43% and 42% respectively, water hyacinth brought down the concentrations to 28% and 33% respectively while green algae gave 33% and 38% respectively. From the results obtained, duckweed is more efficient than other plants.

Alcione, 2018 looked into technologies available for waste water management. The rising output of water containing much oil and the problems associated with the management of such effluent was what prompted the research. This effluent requires proper management to make sure it's at its disposable condition otherwise it will pose a serious danger to the entire ecosystem. Not only does the review look into means of extracting the oil and other impurities out of the effluent, it also considered the cost effectiveness of these technologies.

Talab, 2016 conducted a research on produced water management with pomegranate peel. Extracted powder of Pomegranate peel was used for the extraction of oil from produced water (simulated). The effects of contact time, quantity of adsorbent, acidity and temperature were considered in the analysis. Results obtained revealed that as these parameters into consideration are increased, the more the oil content of the simulated water is removed. Crude oil adsorption by pomegranate peel was established to obey Langmuir sorption model. The result indicated that the peel did a great job in extracting the oil content of the produced water sample with efficiency as high as 95% in less than an hour.

Mar, 2015 did a research on waste water (industrial) with Eucalyptus wood saw dust activated carbon powder to remove chemical oxygen demand and total dissolve solids from the waste water. The material was properly prepared before use and at the end of the work, it was observed to be very effective in removing Chemical Oxygen Demand (COD) and Total Dissolve Solids (TDS) in the effluent. The efficiency of the material in this treatment was found to be 94.8% for COD and 89.2% for TDS respectively.

Kingdom 2012 presented a research on management of produced water from Niger delta oil field region using phytoremediation. Phytoremediation entails managing wastewater with living plants in order to get rid of pollutants. The plants assist in removal of the contaminants in the waste water by adsorption. The plant used in the research was hyacinth. Result obtained indicated a high effluent quality with a pronounced achievement due to the high adsorbing power of water hyacinth plant. Remarkable improvement was recorded on Biological Oxygen Demand (BOD) having 5.0% efficiency while 50% removal was recorded for sulphate (SO_4^{2-}). It was a huge success using the plant to extract contaminants from waste water.

Sulphate Reducing Bacteria (SRB) are the most biological problems encountered in oil production facilities as established by Hayward Gordon Limited (2000). These organisms reduce the sulphate ion to sulphide of hydrogen which brings about chemical corrosion, steel rupture, as well as fouling of equipment when iron sulphide is produced. Quaternary amine salt, amine acetate, and gluteraldehyde are the most commonly used chemical bactericides in production facilities. They are water soluble bactericides and mostly present as aqueous solutions having bulk concentrations in the range of 10%-50%. Slug treatments or continuous process are methods of applying bactericides. For slug treatments, concentrations are within 100-200 mg/l for 3-7 hours, once in a week or thereabout, though it depends on the nature and type of production, nature

of produced water, and how complex the production system been handle is. Continuous treatment concentrations are found within the range of 4-21 mg/l which also depends on the same factors mentioned earlier. These chemicals proved worthwhile in reducing the concentration of such bacteria in produced water.

Isehunwa, 2011 did a work on evaluation of produced water released in the Niger Delta area of Nigeria. The research was targeted at evaluating if companies in the region are actually observing the treatment and discharge laws pertaining produced water management in the region. The samples of produced water were picked from oil terminals and flow stations in the region, and among the items investigated in the samples were cations, anions, as well as acidity, oil/grease content, dissolve solids, suspended solids, BOD, etc., The research indicated that some parameters investigated were above the standard limit. Such parameters are oil and grease content, chloride, dissolve and suspended solids, whereas the rest are within the limit.

The Nigerian government is committed to developing a sustainable system for providing water and wastewater systems throughout the country [8].

Life cycle assessment of water incorporates water source, water use, and cleaner production [9].

Environmental laws and regulations must be enacted for sustainability and improvement of Nigerian Environment [10].

Management of produced water

There are many options available for managing produced water extracted form an oil production. Among these options are [11]:

Prevention of water into surface facility: This is done by using separator at the subsurface to extract the water in crude oil and channel the water back to the formation.

Produced water injection: This entails re-directing the waste effluent back to the formation or even other formations; it involves transporting the waste stream (produced water) from the production site to a new site for re-injection purpose, and at same time the water should be purified to reduce the growth of organisms and other possible problems in the system.

Discharging of produced water: This entails treatment of waste stream (produced water) to measure up with the discharge limits in offshore and onshore environments, and it should also be noted that certain areas never need treatment before it can be discharged.

Application of wastewater for oil field operations: Drilling as well as work-over maintenance require water for effective operation. Produced water can be treated and channeled into these areas.

Produced water extracted from oil/gas production facility is common effluent water in oil and gas operations. It varies in quality and quantity with so many constituents. The waste water is most times a useful product which can be applied in certain areas. The waste water could as well be a marketable commodity as the case may be. Produced water that was initially regarded as a waste stream has be proved to be a useful product as many oil producing companies have realized that the waste is actually a profit making stream. Knowing produced water to be a waste or a commodity stream goes with some cost effects, and this needs to be put into consideration in relation to the plans of each production work [12]. If this is not well managed, the age of the producing well will be affected, which can lead to unrecovered resources left in the subsurface. Produced water management and discharge should be guided by some laws to project the ecosystem and the environment at large, and any defaulting operator should be made to pay a fine, otherwise the environment will be messed up. The technique for handling produced water stream depends on the constituent and the nature of the produced water, formation location, and the volume of reserves as well as the available facilities (Table 2) [2].

Table 2: Effluent discharge range in Nigeria oil industry [1].

Characteristic of effluent	Inland area	Near shore	Offshore
pH	6.5-8.5	6.5-8.5	No limit
Temperature °C	25	30	-
Oil/Grease content	10	20	40
Salinity	600	2000	No limit
Turbidity	>10	>15	-
Dissolved solid	2000	5000	-
Suspended solids	>30	>50	-
Chemical Oxygen Demand (COD)	10	125	-
Biochemical Oxygen Demand (BOD)	10	125	-
Lead	0.05	No limit	-
Iron	1	No limit	-
Copper	1.5	No limit	-
Chromium	0.03	0.05	-
Zinc	1	5	-
Sulphide mg/1	0.2	0.2	0.2
Sulphate (SO_4^-) mg/1	200	200	300
Mercury mg/1	0.1	-	-
Turbidity	10 NTU	10 NTU	10 NTU

MATERIALS AND METHODS

Materials

The following materials were used: Produced water, Sponge gourds (*Luffa cylindrica*), Banana peels, Orange peels, Palm kernel fiber, Reagents, and other Laboratory glass wares.

Equipment

The following were employed in this research: Adsorption column, Mechanical Shaker, milling machine, sieves, balance, pH meter, etc. The equipment were cleaned very well to remove any possible dirt that may affect the results

This research involves the determination of chloride, carbonates and bicarbonates, sulphate as well as total dissolved solids in the samples of produced water stream before and after treatment using the local materials.

Collection of samples and materials

The samples (produced water) were picked from oil fields in Niger Delta. Sample R was collected from Imo River; Sample X was picked from Nembe, sample Y came from Kolo creek, while sample Z was picked from Awoba. The samples were stored at ambient temperature from the field and also in the laboratory where the analysis was done. The local materials (*Luffa cylindrica*, Orange and Banana peels) were sourced from a market in Ado-Ekiti, while the palm-kernel fiber was picked from a farm in Ado-Ekiti state. Other materials and reagents used in the research were of analytical and standard grade.

Preparation of materials

The local materials were thoroughly washed with tap water to eliminate dirty substances. The materials were sliced; dried under the sun for 72 hours or thereabout on hammer time season, oven dried for 3 hours at 105°C for Orange and Banana peels, 30 minutes at 150°C for *luffa cylindrica*, and 3 hours at 80°C for palm kernel fiber. Oven drying is necessary to remove unnecessary adsorb gas. Each was milled and sieved into 150 and 300 micron sizes and stored for the analysis (Figures 2-4).

Figure 2: Raw *Luffa cylindrica* and palm kernel fiber.

Figure 3: Raw banana and orange peels.

Figure 4: Filtrates from adsorption process.

Produced water treatment procedure

The sieved local materials were treated with 200 ml of 0.4 mol L^{-1} HNO_3 for a day, filtered and rinsed with clean water until the filtrates were close to neutral. The essence of this is to get rid of any coloring agent that may affect the result. The residues (adsorbents or local materials) were further dried before used for the treatment. 8-gram of the residue (Orange peels-150 micron) was packed in one column of the adsorption chamber; about 250 ml of sample R was allowed to flow through the chamber containing the local materials for adsorption to occur. Filtrate was picked after three hours of treatment and subjected to analysis using AAS. The local material on the column was replaced with 300 micron of the same Orange peels, the process was repeated and the filtrate was collected and analyzed. Same process was repeated once again with other local materials (Banana peels, *luffa cylindrica*, and Palm kernel fiber) of the same particle sizes of 150 and 300 micron respectively. Results were obtained and recorded [13-20].

Determination of chloride concentration (mg/l) in the produced water samples

Preparation of reagents: Standard sodium chloride (NaCl) solution:

- NaCl (1.648 g) was weighed using the weighing balance.
- The NaCl was transferred into a beaker containing distilled water and was stirred thoroughly using a glass rod until it was dissolved.
- The NaCl solution in the beaker was transferred to a standard flask of 100 ml capacity, and filled with distilled water up to 100 ml.
- Silver Nitrate (4.791 g) was measured and poured into a beaker containing distilled water.
- The contents in the beaker was transferred to a standard flask of 100 ml capacity, and was filled with distilled water up to 100 ml
- The content in the standard flask was standardized against 0.0282 N NaCl solutions and stored in an amber bottle.

Procedure for preparation of potassium chromate indicator

- Potassium Chromate (25 g) was measured and transferred into a beaker with distilled water. Some drops of Silver Nitrate solution were pouted into the potassium chromate until a slight red precipitate was formed.
- The solution was left for 12 hours, and then filtered using a filter paper. The filtrate was diluted to 1000 ml with distilled water.

Procedure

- NaCl (1.5 g) was measure and transferred into a volumetric flask. of 250 ml capacity
- The content in the flask was dissolved with a small volume of distilled water and the solution was thoroughly mixed.
- The burette was filled with the silver nitrate solution.
- NaCl solution (25 mL) was pipetted into a conical flask of 250 ml capacity
- Few drops of potassium chromate (5% aqueous solution) were added to the flask containing NaCl solution and the contents were mixed thoroughly.
- The Silver Nitrate solution from the burette was run down into the conical flask gradually till a reddish brown precipitate appears which indicated the end point.
- The experiment was repeated until consistent titration values were acquired. The average value was recorded.
- The volume of chloride concentration in each produced water sample was estimated using the formula.
- Chloride content (mg/l)=(Vs–Vb)* normality*35.45*1000/ vol. of sample taken (1)

Where Vs=volume of silver nitrate for sample, Vb=volume of silver nitrate for blank, Normality of EDTA=0-028 N. volume of sample taken=volume of produced water taken.

Determination of concentration of carbonates and bicarbonates in the produced water samples

Preparation of reagents: Sulphuric acid solution (0.02 N):

• Distilled water (500 ml) was poured into a standard flask of 1000 ml capacity

• Concentrated (20 mL) 0.1 normality sulphuric acid was measured and poured gradually along the side of the standard flask.

• The volume of the standard flask was made up to 1000 ml with distilled water.

Phenolphthalein indicator preparation:

• Phenolphthalein (1 g) was weighed and added to 100 ml of 95% ethyl alcohol solution

Preparation of mixed indicator:

• Bromocresol green (100 mg) and methyl red (20 mg) were dissolved in 100 ml of 95% ethyl alcohol.

Procedure

• Sulphuric acid (0.02 N) was used to rinse the burette and it was discarded.

• Sulphuric acid (0.02 N) was used to fill the burette and the burette adjusted to the zero mark.

• The burette was fixed on the tripod stand.

• The sample (100 ml) was measured and poured in a conical flask of 250 ml volume.

• Few drops of phenolphthalein indicator were poured to the sample in the flask with a resulting pink color change.

• The solution was titrated against 0.02 N sulphuric acid from the burrette till the pink color disappears.

• Few drops of mixed indicator were poured into the solution in the conical flask with a resulting blue color change.

Titration was started again from the point it stopped for the phenolphthalein alkalinity and it went on until the solution turns red. The burette reading was then taken.

Determination of sulphate concentration in the produced water samples

Preparation of reagents:

Reagent conditioning:

• Glycerol (25 ml) was weighed and put into a beaker.

• Conc. HCl (15 ml) was measured and added into the same

beaker.

• Isopropyl alcohol 95% (50 ml) was weighed and added into same beaker and then thoroughly mixed.

• NaCl (37.5 g) was measured and dissolved in water (distilled water).

• The contents in the beaker were mixed very well and the volume of the final solution was made up to 250 ml with distilled water.

Standard sulphate solution:

• Anhydrous sodium sulphate (1.479 g) was weighed and dissolved in distilled water.

• Measuring cylinder (1000 ml) was used and an anhydrous sodium sulphate solution was transferred to the cylinder and the solution was brought to 1000 ml with distilled water.

Preparation of blank, standards and sample for testing:

• Six glass stopper standard flasks (50 ml each) were used (four for standards, one for sample and the other for blank).

• Standard sulphate solution of 10 ml was poured into the first flask, 20 ml to the second, 30 ml to the third and 40 ml to the fourth respectively

• The sample (produced water) 20 ml was poured into the fifth flask.

• Distilled water was poured into the sixth flask which is meant for blank.

• Conditioning reagent (5 mL) was added to each of the standard flasks. All the flasks were made up to 100 mL with distilled water.

• The absorbance was estimated with UV-Vis Spectrophotometer and the results were taken. The results were used to generate a calibration curve, which was used to estimate the concentration of sulphate in the samples.

Procedure

• A volume of the sample that will give rise to between 2.5 mg-200 mg of residue was selected.

• The sample was well mixed and transferred into a graduated cylinder to the selected volume.

• The evaporating dish was weighed and the measured volume was poured into the pre-weighed dish.

• The evaporating dish and the content were dried for about 1 hour at 103-105°C in an oven.

• The dish was retrived from the oven and cooled in a desiccator to room temperature.

• The dish and residue was weighed and the weight was recorded.

Total dissolved solid in a liquid sample is estimated with the formula

TDS=((wt.of evaporating dish+residue–wt.of evaporating dish)*1000)

TDS Content (mg/l)=(TDS*1000)/vol.of sample (2)

RESULTS AND DISCUSSION

Concentrations of chloride in the produced water samples

Table 3 presents the volume of sample used and chloride concentrations in the untreated samples R, X Y and Z. Chloride concentrations in the untreated samples increases in this order Z>Y>X>R.

Table 4 presents the chloride concentrations in the treated samples after 3 hours of treatment. From the results obtained, the chloride concentrations in untreated samples R, X, Y and Z reduced drastically compared with the results of treated samples in Table 4. The order of the reduction are R>X>Z>Y. The orange peels was the best for treating the chloride content in the produced water samples, while the palm kernel fiber was the least effective though it reduced the chloride content to an appreciable level when compared to its original concentration as seen in Table 2.

From the table, the best size of the adsorbent used in the treatment of samples is 150 microns especially for sample R and X. The average of the results confirms that 150 micron is the best for the treatment, and this could be because it's finer compared to 300 micron particle. For samples Y and Z, neither of 150 nor 300 micron particles size could be declared as the best as both of them gave almost the same range of result. The effectiveness of the adsorbents when used individually as shown on the table is in this order, orange peels>banana peels>*luffa cylindrical*>palm kernel fiber. This could be attributed to the high content of fiber, lignin, tanin and some other functional groups responsible for the adsorption. It could be said that orange peels contains more of these fiber, tannin, lignin and other functional groups more than other adsorbents, followed by banana peels, *luffa cylinderica* and palm kernel fiber in that order.

For sample R treated with peels of banana, orange, palm kernel fiber and *luffa cylindrical* in this order, the percentage reduction in the chloride concentrations were found to be 52.94%, 60.78%, 37.25% and 43% respectively, for sample X the reductions were 54.54%, 63.64%, 45.45% and 50.90% respectively, for sample Y the reductions were 57.61%, 64.27%, 46.56% and 48.16% respectively while for sample Z, it was found to be 56.60%, 52.28%, 46.08% and 50.28% respectively. Similar results were obtained with other adsorbents and samples.

Sulphate concentrations in the produced water samples

Table 5 present the absorbance and solution of known concentrations containing sulphate while Figure 5 presents the calibration curve obtained from the table. Table 5 indicates that the higher the concentration, the higher the absorbance of the sulphate concentration in the solution. In Figure 5, which is a linear plot supports the behavior of the parameters on Table 5. The calibration curve of the plot was determined by finding the slope and intercept of the graph. The sulphate concentrations as contained in the samples were estimated with BEER'S equation which says:

Y=MX+C (3)

Where Y=Produced water samples absorbance, M=slope of the plot, X=concentration of the ion (mg/l), C=intercept of the plot

Table 6 presents the volume of samples used and the sulphate concentrations in the untreated samples (R, X, Y and Z). The sulphate concentration in untreated sample R is higher than sample X, Y and Z in that order. This shows that the location where sample R was collected has more sulphate containing formation than other samples locations, it could also be as a result of drilling and well completion fluid used.

Table 3: Chloride concentrations in the untreated produced water samples.

Sample	Volume of sample (ml)	Conc. of chloride (mg/l)
Sample R	20	254.92
Sample X	20	274.91
Sample Y	20	279.21
Sample Z	20	282.53

Table 4: Chloride concentration in the treated samples.

Adsorbents	Particle size (microns)	Volume of sample (ml)	Conc. of Chloride in sample R (mg/l)	Conc. of chloride in sample X (mg/l)	Conc. of chloride in sample Y (mg/l)	Conc. of chloride in sample Z (mg/l)
Banana peels	300	20	109.97	119.96	112.72	115.97
	150	20	119.97	124.96	118.34	122.61
Orange peels	300	20	104.97	109.97	107.28	110.05
	150	20	99.97	99.97	99.75	97.48
Palm kernel fiber	300	20	154.95	139.96	142.15	141.92
	150	20	159.95	149.95	149.20	152.35
Luffa cylindrica	300	20	139.96	139.96	140.48	148.01
	150	20	144.96	134.96	144.73	140.46

Table 5: Absorbance readings for sulphate concentrations.

Sample	Conc. of sulphate (mg/l)	Absorbance
Blank	0	0
A	10	0.07
B	20	0.16
C	30	0.35
D	40	0.51
E	50	0.72

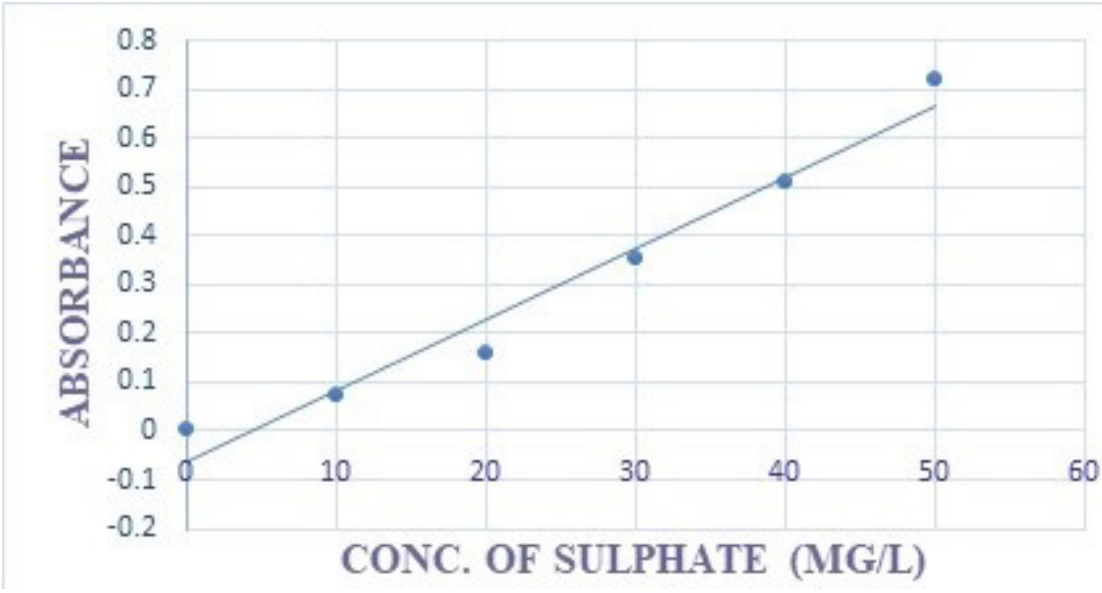

Figure 5: Calibration curve of absorbance vs. concentration of sulphate.

Table 6: Sulphate concentration in the untreated produced water samples.

Sample	Volume of samples (ml)	Conc. of sulphate (mg/l)
R	20	1608
X	20	1501
Y	20	1406
Z	20	1284

Table 7 presents the sulphate concentrations in the treated produced water samples after 3 hours of treatment. From the results, the sulphate concentrations reduced drastically when compared with the concentrations in the untreated samples. The sulphate concentration reduced more in sample Y followed by Z, R and X in that order. The concentrations as determined from each of the sample depend on the location from which it was collected. Some formations are known to contain more surphates than others. The sulphate could also find its way into the formation through the drilling fluid as well as some well completion fluid used in the process.

Also from the table, the palm kernel fiber was the best adsorbent for treating the sulphate content in sample R, followed by *luffa cylinderica*, banana peels and orange peels in that order. In sample X, orange peele was the best adsorbent for the treatment followed by palm kernel fiber, banana peels, *luffa cylindrica* in that order. In sample Y, *luffa cylinderica* was the best adsorbent followed by palm kernel fiber, banana and orange peels in that order. For sample Z, the best adsorbent for the treatment was orange peels, with banana peels the next, and then palm kernel fiber comes next with *luffa cylinderica* the least.

In general, 300 micron size was found to be more efficient in management of produced water sample containing sulphate. The percentage reductions in sample R when treated with banana peels, orange peels, palm kernel fiber, and *luffa cylindrical* in that order were found to be 29,85%, 23.22%, 43.31% and 41.46% respectively. For sample X, it was 31.96%, 37.29%, 33.73% and 28.40% respectively. For same Y. the reductions were 30.26%, 30.52%, 50% and 55.58% respectively, and finally for sample Z, the reductions were 36.43%, 52.16%, 34.57% and 28.76% respectively. Similar results were obtained in other samples.

Carbonates and bicarbonates concentrations in produced water samples

Table 8 presents concentrations of carbonates and bicarbonates in untreated samples of produced water. From the results, concentrations of carbonates and bicarbonates in the samples increases in this order, Z>Y>X>R. This could be as a result of the location where the samples were obtained. It could as well be as a result of traces of carbonates and bicarbonates within the fluids used in the well completion

Table 9 presents the concentrations of carbonates and bicarbonates in treated samples. From the results, concentrations of carbonates and bicarbonates reduced very well compared with the results obtained from the untreated samples which are 470 for sample R, 524 for sample X, 552 for sample Y and 598 (mg/l) for sample Z. The concentration reduction was more in sample Y, followed by Z, X and R in that order.

Table 7: Sulphate concentration in the treated samples.

Adsorbents	Particle size (microns)	Volume of sample (ml)	Conc. of sulphate in sample R (mg/l)	Conc. of sulphate in sample X (mg/l)	Conc. of sulphate in sample Y (mg/l)	Conc. of sulphate in sample Z (mg/l)
Banana peels	300	20	994.7	941.3	840.06	760.35
	150	20	1128.0	1021.3	980.50	816.20
Orange peels	300	20	1154.7	888.0	964.71	578.30
	150	20	1234.7	941.3	976.82	614.25
Palm kernel Fiber	300	20	861.3	914.7	782.91	806.21
	150	20	914.7	994.7	816.32	840.16
Luffa cylindrica	300	20	888.0	1048.0	562.39	905.83
	150	20	941.3	1074.7	624.58	914.70

Table 8: Concentration of carbonates and bicarbonates in the untreated produced water samples.

Sample	Volume of sample (ml)	Conc. of carbonates and bicarbonates (mg/l)
R	20	470
X	20	524
Y	20	552
Z	20	598

Table 9: Concentration of carbonates and bicarbonates in the treated sample.

Adsorbents	Particle size (microns)	Volume of sample (ml)	Conc. of carbonates and bicarbonates in sample R (mg/l)	Conc. of carbonates and bicarbonates in sample X (mg/l)	Conc.of carbonates and bicarbonates in sample Y (mg/l)	Conc.of carbonates and bicarbonates in sample Z (mg/l)
Banana peels	300	20	180	170	172.00	160.30
	150	20	166	164	150.50	151.00
Orange peels	300	20	190	180	180.20	170.20
	150	20	174	186	164.00	178.51
Palm kernel fiber	300	20	170	168	159.40	154.90
	150	20	172	170	180.60	178.65
Luffa cylindrica	300	20	244	238	196.00	191.62
	150	20	260	244	182.35	184.30

All the adsorbents used in the treatment proved worthwhile in the treatment and are highly recommended for produced water samples containing carbonates and biacarbonates. Also from the table, palm kernel fiber, orange peels, banana peels proved to be the best adsorbents for treating the carbonates and bicarbonates content in sample Y and Z, with *luffa cylinderica* been the least. In sample R and X, the same *luffa cylinderica* was the least effective when compared with other adsorbents. The palm kernel fiber seems to contain more lignin and tannin and other necessary functional groups responsible for the adsorption. It can also be concluded that other adsorbents used in the treatment proved worthwhile in the treatment as they were all able to reduce the concentrations of the carbonates and bicarbonates to some reasonable extent as recommended by the regulatory bodies.

The best particle size for the adsorption as seen from the results was 150 micron, possibly because it's finer. The effectiveness of the adsorbents as used individually are in the order, palm kernel fiber>banana peels>orange peels>*luffa cylindrica*.

The percentage reductions in sample R (150 micron size) when treated with banana peel, orange peel, palm kernel fiber and *luffa cylindrical* in that order were found to be 64,65%, 62.98%, 63.40% and 44.69% respectively, for sample X, it was found to be 68,70%, 64.50%, 67.56% and 53.44% respectively, for sample Y, it was found to be 72.74%, 70.29%, 67.28% and 66.97% respectively, and finally for sample Z, it was found to be 74,75%, 70.15%, 70.11% and 69.16% respectively. Similar results were obtained with other adsorbents.

Total dissolved solids concentrations in produced water samples

Table 10 presents volume of sample used and the amount of total dissolved solids present in untreated samples R, X, Y and Z respectively. From the analysis, the amount of TDS in the samples increases in this order X>Z>Y>R. This could possibly be as a result of sample location and the activities around such location. Table 11 presents the amount of Total Dissolved Solids (TDS) treated samples after three hours of treatment.

Table 10: Total dissolved solids in untreated produced water samples.

Sample	Volume of sample (ml)	TDS (mg/l)
R	20	100
X	20	250
Y	20	180
Z	20	210

Table 11: Amount of total dissolved solids (TDS) in treated produced water samples.

Adsorbents used	Particle size (microns)	Volume of sample (ml)	Sample R TDS (mg/l)	Sample X TDS (mg/l)	Sample Y TDS (mg/l)	Sample Z TDS (mg/l)
Banana peels	300	20	100.00	98.30	90.50	88.00
	150	20	98.20	97.20	88.00	87.00
Orange peels	300	20	97.30	80.00	84.50	70.00
	150	20	95.00	82.50	82.00	70.50
Palm kernel fiber	300	20	98.00	93.00	86.00	86.50
	150	20	92.00	94.00	80.00	97.00
Palm kernel fiber	300	20	83.20	78.90	70.50	72.00
	150	20	80.00	76.30	59.50	56.50

From the analysis, the TDS reduced very well in both samples compared with the values of the untreated samples. The untreated values were 100 (mg/l) for sample R, 250 (mg/l) for sample X, 180 (mg/l) for sample Y and 210 (mg/l) for sample Z respectively. The reductions observed in the samples were really encouraging. This indicates that the local materials (adsorbents) were extremely good in managing produced water containing dissolved solids. Generally, more reduction was recorded in sample Z followed by Y, X and R in that order.

From the table, all the adsorbents proved worthwhile in the treatment, though some were better than the others. In same R, *luffa cylindrica* proved to be the best adsorbent for reducing the level of dissolved solids in the samples, followed by, orange peels, palm kernel fiber and banana peels respectively. Also, the best particle size for the adsorption was 150 micron which could be because of its large surface area as earlier stated. In sample X, the same *luffa cylinderica* was found to be the best adsorbent followed by orange peels, palm kernel fiber and banana peels in that order. In sample Y, *luffa cylinderica* was still the best adsorbent among others. It was followed by orange peels, palm kernel fiber and banana peels respectively. In sample Z, *luffa cylinderica* was still the best followed by orange peels, banana peels with palm kernel fiber the least [21-25].

One good thing about the whole adsorbents was that all of them gave very good and encouraging results not minding the particle size used. The results obtained were able to meet the regulatory discharged limit as set by the regulatory bodies. It is also important to note that any of the adsorbents could be used in the treatment, but it's advisable to use *luffa cylinderica* for the treatment as it gives the best result. In the absence of *luffa cylinderica*, any other available adsorbents as used in this research can comfortably be used for the treatment. Though 150 microns particle size seems to be the best, 300 micron particle size can as well be used since the result obtained with it was good as well.

Another point to note about these adsorbents is that they are economical, cheap, and readily available to be used unlike the conventional methods that are expensive with complex operational methods and procedures. These adsorbents can be locally sourced as they are all our agricultural wastes available in large quantities any time any day, and they do not necessarily require regeneration after use since they are readily available. The percentage reductions in sample R (150 micron size) when treated with banana peels, orange peels, palm kernel fiber and *luffa cylindrical* in that order were found to be 1.8%, 5%, 8% and 20% respectively, for sample X, it was found to be 61,12%, 67%, 62.4% and 69.48% respectively, for sample Y, it was found to be 51.11%, 54.44%, 55.55% and 66.94% respectively, and finally for sample Z, it was found to be 58,57%, 66.43%, 53.89% and 70.09% respectively. Similar results were obtained with other adsorbents (Tables 3-11).

Contribution to knowledge

This research proved that use of selected local materials or adsorbents (Orange and Banana peels, Palm kernel fiber and *luffa cylindrical*) were very efficient in reducing inorganic substances and other impurities in produced water than conventional methods. The local materials (adsorbents) employed for this treatment of produced water are very cheap, environmentally friendly and readily available unlike the conventional methods that are very expensive and produce by-products that are detrimental to man the environs. Attention should therefore be shifted to these local materials for wastewater treatment and again, it's a means of keeping our environment clean and tidy.

CONCLUSION

Produced water samples considered in this research were found to have traces of inorganic substances as well as toxic and heavy metals. The laboratory procedures applied in analysis of these inorganic substances (chloride, sulphate, carbonates and bicarbonates, Total Dissolved Solid (TDS)), were carried out with standard solutions of anions involved which were prepared at room temperature. The experiments were successful; the concentration of each substance before and after treatment with the bioadsorbents was analyzed with the help of the listed materials and equipment in the laboratory.

Samples of produced water were selected from four oilfields in Niger Delta region of Nigeria as outlined above. The local materials picked for the produced water treatment were *Luffa cylindrica*, Banana peels, Palm kernel fiber and Orange peels. The local materials (bio-adsorbents) were properly dried and treated to remove any dirty material or substance that is likely to affect the result. Treatments were carried out successfully in the chamber using the bioadsorbents individually to minimize the concentration of inorganic and solid contents present in produced water samples.

Laboratory analysis showed that concentrations of these inorganic materials in the samples were more than expected. After treatment, concentrations of these substances (chloride, sulphate, carbonates and bicarbonates, Total Dissolved Solid (TDS)) were drastically brought to the desired limits as can be seen on the results. Averagely, 150 micron size gave a better result in almost all the treatments probably because of it large surface area. From literature, we were meant to understand that finer particles with big surface area give the best result in an adsorption system. This is in line with the results presented in this research.

One thing about these local materials is that they are economical, cheap, and readily available to be used, and need no regeneration as the supply is in abundant. They are all agricultural wastes that litter the environment. Use of these wastes as adsorbents is a good way of putting the wastes into use thereby keeping the environment clean and safe.

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