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Refinery effluent water treatment: An integrated approach

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Abstract

This study has successfully investigated the use of an integrated approach to refinery effluent water treatment. To achieve this, a multistage system was used for the treatment of refinery effluent water from Port Harcourt Refining Company, Rivers State Nigeria. The physicochemical and microbial properties of the treated effluent water were used to assess the efficacy of the treatment process. Properties investigated include temperature, pH, chlorine content, bacterial count, chemical and biological oxygen demand, dissolved oxygen, amount of oil and grease in the water, turbidity, and the amount of metal content in the water. The results for the treated effluent water sample were pH 7.84, Turbidity 3.47NTU, Total Dissolved Solid 69.96 ppm, Total Suspended Solid 14.82 mg/L, Total salinity 29.21 ppm, Biochemical Oxygen Demand 0.65 mg/L, Chemical Oxygen Demand 1.87 mg/L, and Dissolved Oxygen 4.13 mg/L. The results showed an impact of this process on refinery effluent water treatment.

Keywords: Wastewater; Refinery; Environment; Integrated Approach

1. Introduction

One of the challenges of industrial operations particularly the oil and gas industry is that of water pollution. These operations involve many dissolved ions and solids getting into the water samples thereby making them unfit for consumption and leading to other problems such as scale and corrosion formation among other problems. The refinery effluent water is one of the biggest contaminants of the ecosystem [1]. Although both the petroleum and petrochemical industries are essential components of our everyday life for enhanced quality of life and national development, the huge volume of wastewater coming out of these industries and emptied into the water bodies and the environment remains a source of serious concern. These pollutants are naturally lethal and can provoke environmental and health hazards like skin cancer, renal diseases, cardiac arrhythmias and even death [2].

Based on the nature of the activities, these effluents contain extremely high level of dissolved salts, oil grade and other microbial pollutants. Though tremendous efforts have been made to curtail such pollutants, the refinery effluent water remains a major concern [3]. The projected rise of demand for petroleum products in the forthcoming years especially for the light olefins has been put at 44% and this could further exacerbate the growing concern on the pollution impact that these heightened activities could cause. Crude oil refining operation involves huge volume of water and disposal of such; thus, accounting for the huge volume of refinery effluent water across the world especially in Nigeria where most of these effluent waters end up in water bodies [4]. Studies have shown that the refinery effluent water produced from the crude oil refining process is about twice the quantity of oil being processed, approximately 33.5 mbpd of wastewater effluent from refineries [5]. It is projected that within the next 20 years, the demand for crude oil refined products will exceed 107 mbpd with a proportionate increment of effluent water discharge from these refineries. The world energy output by 2030 is predicted to be accounted for from 32% of crude oil production while other renewable energy sources such as solar, and biofuel will account for the rest. This implies that the menace caused by effluent water discharge will

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remain persistent for some time, hence the heightened interest in effluent water study and treatment. Effluent water is causing a huge menace in the environment, and the constituents of these effluents vary from one refinery to another [6]. These effluent waters pollute water bodies, affect aquatic lives, reach long distances and negatively impact the water quality.

Different methods such as adsorption, chemical oxidation, biological processes etc. have been utilized for the effective treatment of effluent water [7]. Others include membrane and catalytic microwave oxidation. Chemical oxidation is characterized by low performance and heavy sludge generation and this work best in a low pH condition; moreover, its usage is also characterized by slow reaction rate [8, 9]. Other treatment methods also have their peculiar limitations [10]. Following the inadequate performance of the existing effluent treatment methods to degrade the pollutants completely, there is a paradigm shift towards using novel cost-effective techniques that will effectively degrade the pollutants.

Hence, for adequate success to be achieved in effluent water treatment from refineries, there is a need to explore other alternative methods of wastewater treatment by possibly integrating different mechanisms. This study seeks to explore the use of an integrated approach to refinery effluent water treatment using a commercial refinery in Nigeria.

2. Material and methods

2.1. Materials

The materials used in this study include silicate glass bottles, oven, reflux flask, pH meter, digital thermometer, glass fiber filter paper, water bath, pre-calibrated handheld meter Hannah Instrument (HI 9142) and several pure grade reagent chemicals obtained from Sigma-Aldrich Chemicals.

2.2. Methods

This study involved the characterization of the wastewater sample to determine its physicochemical properties as well as water standard treatment method.

2.2.1. Sample collection and preparation

Refinery effluent water samples were collected with pre-sterilized borosilicate glass bottles prescribed for this purpose at the designated sampling stations, in accordance with the American Public Health Association (APHA). The oven was set to a temperature of 160 ˚C to sterilize the bottles for an hour. Thereafter, the sterilized bottles were used for the wastewater collection. Aseptic technique was used in a bid to ensure that the samples were not contaminated while transporting them from the field to the laboratory, they were also secured in an ice-chest. Laboratory investigation was conducted on the samples within a period of 8-12 h.

2.2.2. Water treatment

A multistage wastewater process was adopted in this work to eliminate impurities such as organic matter, solids, and other pollutants. The pre-treatment process involved filtration with a sieve to remove solid particles which were treated and safely disposed in a landfill. Thereafter, the wastewater went through a reactor where the suspended solids and grease samples from the water were separated. The sample was dozed in a reactor for about 2hrs to allow the grease settle on top while the particles settle at the base and afterwards, they are drawn off. Dead organic matters were alienated from the water sample using micro-organisms in an aerated lagoon system. Finally, the process of removing the disease-causing organisms from the water sample was attained through the addition of chlorine dioxide as well as the use of ultraviolet (UV) light. Chlorine-neutralizing chemicals, Sodium Sulphite ($Na_2S_2O_5$) was also added for neutralization to aid safe disposal of the sludge. The schematic of the process is shown (Figure 1).

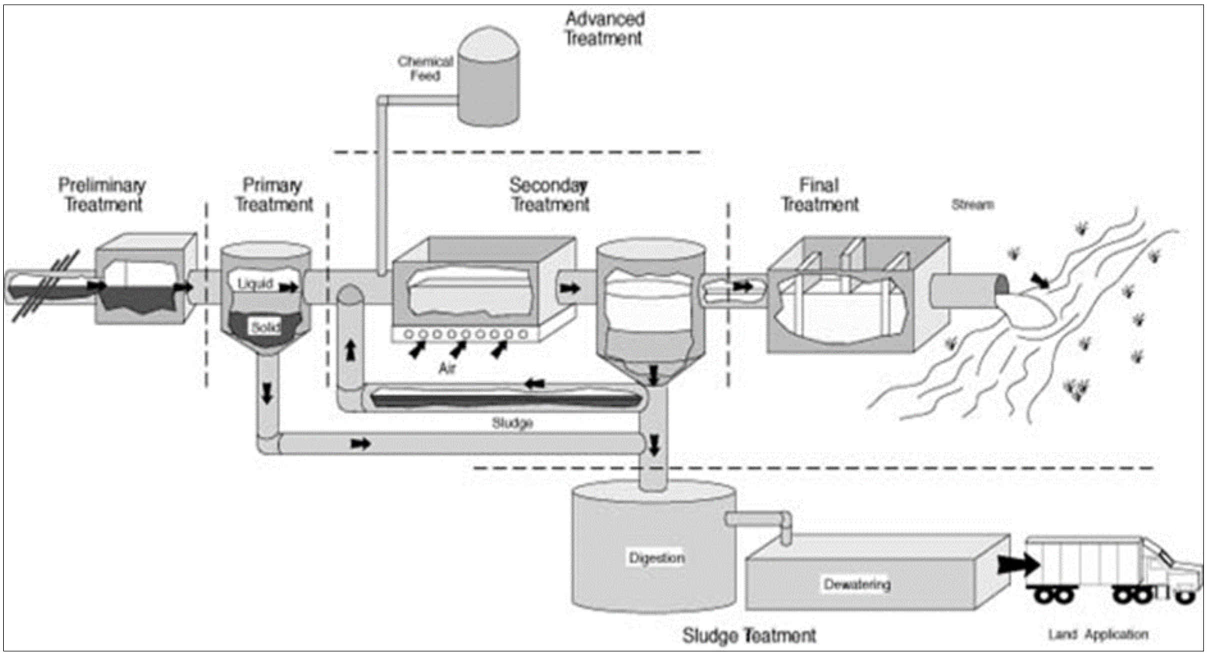

Figure 1 Schematic of Wastewater treatment Process

2.2.3. Physicochemical properties

In accordance with ASTM standards, the following physicochemical properties of the recovered water bodies were determined.

pH

This was measured using an electronic pH meter (Atiorin pH model 310 series) at ambient temperature. Using three buffer solutions at pH of 4, 7 and, 10, the pH meter was standardized. To ensure accuracy in each measurement, the probe was constantly flushed with distilled water and wiped at the end of each measurement.

Chlorine Content

A HACH test kit was used to evaluate the residual chlorine content in the water sample. Using pre-calibrated cell bottles, 25 ml of the water sample was measured into two different cell bottles, then DPD powder pillow was added to cell bottle 'A' to meet up the graduated mark while cell bottle 'B' had no powder pillow in it and both bottles were swirled. The two cell bottles were inserted into the test kit with a graduated colour comparator and allowed to stand for about 6 minutes to estimate the chlorine content.

Temperature

The temperature readings at regular intervals were carried out with the aid of a handheld digital thermometer (model: API-RP 45).

Total/Faecal Coliform Bacteria

The multiple test tube method (model: APHA 9221 E) was employed to determine the coliform bacterial count in the water sample.

2.2.4. Biochemical Oxygen Demand (BOD_5)

The initial DO of the BOD sample collected in amber bottle were fixed with Winkler 1 & 2 solution in the field and the concentration was determined by acidifying 250ml of the fixed sample and titrating fixed samples using 0.25N sodium thiosulphate solution. Readings to evaluate the BOD content were taken on the 1st and 5th day and recorded as required.

Chemical Oxygen Demand (COD)

This was estimated by redox titrimetric process via sample digestion and refluxing. A measure of the sample (25 ml to 50 ml) was placed in a reflux flask, this was followed by the addition of 1 g of mercuric sulphates in an ice bath alongside 5ml of conc. H_2SO_4 and the mixture was stirred thoroughly. Also, 25ml of 0.025N potassium dichromate solution was slowly added to the reflux flask amidst continuous agitation in the ice bath, after which 10 ml sulphuric acid- silver sulphates solution was gradually added. The solution was then refluxed for 2 hrs and the resultant digest was diluted to about 300ml with water and allowed to cool to room temperature. Furthermore, 8 to 10 drops of phenolphthalein indicator were added as well as ferrous sulphates solution while the excess dichromate was titrated with 0.025N ferrous ammonium sulphates (FAS).

Dissolved Oxygen (DO)

This was evaluated using a pre-calibrated handheld meter Hannah Instrument (HI 9142). The DO probe consists of a thin permeable membrane which aids the flow of oxygen and covers the polarographic sensors coupled with a built-in thermistor for temperature measurements. The voltage applied across the sensors facilitates the evaluation of the dissolved oxygen.

Total Dissolved Solids (TDS)

With the aid of a vacuum pump and a filter paper, 50ml of the water sample was filtered into a pre-weighed glass beaker. This was gently evaporated in a water bath to dryness and then to a constant weight. The weight difference was used to compute the TDS.

Total Suspended Solid (TSS)

The residue obtained from the glass fibre filter paper was placed in an oven at a temperature of 105 ^{o}C and allowed to dry to a constant weight. The weight difference of the filter paper was used in estimating the TSS.

Oil and Grease

The concentration of oil and grease in the stream were estimated with the aid of a phase extraction/spectrophotometry. A known volume of the sample was shaken vigorously with an organic solvent – xylene as an extracting agent in a separating funnel. The extract alongside with xylene and the absorbance read at 425 nm from a spectrophotometer. The concentration of oil and grease in the extract was extrapolated from a 1:1 standard Bonny Light and Medium crude calibration curve. Xylene was used as blank.

Turbidity

The nephelometric method was employed in the determining the turbidity of the obtained water sample. The turbidity was read directly from the turbidimeter which was calibrated with diluted turbidity formazin suspension solutions of known NTU according to the manufacture's specifications, while the sample was shaken thoroughly after dilution. Air bubbles were expelled before pouring the samples into turbidimeter tube.

Metals

Sample preparation was carried out through acid digestion, which was preceded by filtration through a 0.45-micron membrane filter. Aliquots of the filtrate were used to analyze for iron, copper, chromium, lead, and zinc.

3. Results and Discussion

Table 1 outlines the results obtained for the physicochemical and microbial properties of the treated and untreated refinery effluent water.

The pH obtained from the analysis would not impact negatively. The pH values in this study fell within the WHO limits (6.5 – 9.7) for effluents prior to their disposal to the water bodies [11]. The pH level indicates that the wastewater might not have any negative influence on the environment where it is disposed. These findings are in line with the reports for both treated and untreated effluent water from Osuoha *et al.* [2] and Nwaichi *et al.* [12] on Port Harcourt Refining Company and Warri Refining and Petrochemical Company. The resultant temperature of the effluent water was within permissible range as such it is considered suitable for aquatic life.

The turbidity values at the point of discharge (7.55 NTU) were not within the permissible limit (5.81 NTU) for effluents as stipulated by the WHO [11]. These extremely high values may portend danger to the environment and aquatic life [13]. The marked difference between the turbidity of the untreated effluent sample with that of the treated effluent sample is attributable to accumulated debris [14].

Table 1 Physicochemical and microbial properties of treated and untreated refinery effluent water

S/N	PARAMETER	Untreated	Treated	WHO standard
1.	pH	8.39	7.82	6.5 – 9.2
2.	Temperature (^oC)	28.2	26.82	30
3.	DO mg/l	3.52	4.2	4-5
4.	Conductivity (µs/cm)	212	140	500
5	Turbidity (NTU)	7.55	3.47	5.82
6	Total Dissolved solid (mg/L)	172	69.93	500
7.	Total Suspended Solid (mg/L)	42	14.82	30
8.	Salinity (mg/L)	11.54	29.21	NA
9.	Oil and Grease (mg/l)	1.4	0.04	-
10.	BOD_5 (mg/l)	1.75	0.65	1.0
11.	COD (mg/l)	1.83	1.87	40
12	Iron (mg/l)	3.4	2.3	1.0
13	Chromium (mg/l)	0.03	0.02	-
14	Copper (mg/l)	3.57	2.36	
15	Lead (mg/l)	0.06	0.04	-
16	Zinc (mg/l)	0.69	0.09	-
17	Coliform Bacteria (MPN/100 ml)	200		-

The total dissolved solids (TDS) values were well within the WHO tolerable range (500 mg/L) although the values for the treated samples were much lower. The high concentration of the total suspended solids (TDS) observed in the untreated wastewater sample was much higher than the tolerable limits (30 mg/L) reported by WHO for effluents but was more than halved with treatment. The biological oxygen demand (BOD) values indicate that the microorganisms utilize some part of the product from decomposition of organic matter within 48 hours while the other counterpart complex portion commonly referred to as chemical oxygen demand, COD, gets decomposed slowly. These markers are fundamental in the determination of the quality of wastewater because they provide useful information about the total organic load of the sample. The BOD and COD levels obtained for the treated wastewater samples fall within the limits as stipulated by the WHO. Dissolved oxygen is said to be the amount of oxygen used during organic matter oxidation under aerobic conditions [14]. The DO values obtained for the untreated and treated wastewater samples are 3.21 mg/L and 4.23 mg/L, respectively. The DO of the untreated wastewater fell below WHO acceptable range and is indicative of organic pollution. Electrical conductivity is a fundamental property that is used to control the level of pollution of wastewater effluents. The high conductivity value observed in the untreated wastewater sample might is indicative of the amount of chemical impurities released into the water during crude oil refining operation. After treatment, this value greatly reduced hence the value recorded for the treated effluent was significantly lower.

The total coliform bacteria (MPN/100 ml) and faecal coliform (MPN/100 ml) of the water samples were all obtained as zero. Based on this, it therefore stands that the effluent was generally free from bacteria on an MPN/100 ml count.

The treatment of the effluent water significantly improved the water quality while reducing the toxic level of the water sample to ensure that its discharge to the environment causes no significant environmental or health threats.

Furthermore, the physicochemical and microbial properties of the water sample maintained the stipulated levels of World Health Organization (WHO) even after treatment.

4. Conclusion

The study adopted an integrated approach for the treatment of refinery effluent water. Results showed a significant reduction of contaminants in the effluent water. Based on its performance, the integrated approach has been found to be effective in the elimination of the physical, chemical and microbial pollutants. Future and more advanced studies should be conducted in this research area to further assess this method. Moreover, the use of this method can be explored with other available methods and used to assess the treatment of effluent water from other locations.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors, Amalate Ann Obuebite and Obumneme Okwonna declare that they have no competing interest neither is there any conflict of interest.

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