

Characterization of Effluent from the Fuels Plants and Its Contribution to the Overall Effluent Characteristics of Kaduna Refinery

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ABSTRACT: Effluent samples were collected from the Fuels Plants (CDU-1, NHU and CRU) of Kaduna Refining and Petrochemical Company (KRPC) as well as Waste Water Treatment plant and the Effluent Outfall to the environment. The physicochemical properties of the Effluents samples were determined using various analytical techniques based on American Society for Testing and Measurement (ASTM) methods. The metals (Mercury, Cadmium, Iron, Lead, Zinc, Copper, Vanadium, and Chromium) were determined using Atomic Absorption Spectroscopy (AAS) method. The study showed that the Conductivities, the Biochemical Oxygen Demand (BOD), the Chemical Oxygen Demand (COD), the Oil and Grease, Sulphide, Temperature and pH of the effluent samples from these fuels plants were higher than the NESREA acceptable standard. Heavy metals concentrations in the effluents samples were also determined. It was observed that mercury, cadmium and lead concentrations were higher than the NESREA limit in the samples from these plants, and therefore contributes heavily to the overall effluent characteristics of the refinery. It was recommended that the treatment of effluent samples for Conductivity, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Oil and grease, pH, Temperature, Sulphide, Mercury, Cadmium and Lead should start at the fuels plants where they are generated. This will reduce contaminants in the effluent at source which will in turn result to increase in efficiency and quality of treatment at the waste water treatment plant.

1.0 INTRODUCTION

Pollution can be defined as the direct or indirect alteration of the physical, chemical, thermal, biological or radioactive properties of any part of the environment which creates a hazard to health, safety or welfare of any living species. Pollution may occur naturally but mostly occurs due to changes brought by emission of pollutants by discharge of industrial and humans' domestic wastewater or sewage and release of excessive heat from industries [1][2].

Over 70% of our Earth's surface is covered by water. Although water is seemingly abundant, the real issue is the amount of fresh water available. 97.5% of all water on Earth is salt water, leaving only 2.5% as fresh water. Nearly 70% of that fresh water is frozen in the icecaps of Antarctica and Greenland; most of the remainder is present as soil moisture, or lies in deep

underground aquifers as groundwater not accessible to human use. Only ~1% of the world's fresh water is accessible for direct human uses. This is the water found in lakes, rivers, reservoirs and those underground sources that are shallow enough to be tapped at an affordable cost. Only this amount is regularly renewed by rain and snowfall, and is therefore available on a sustainable basis [3] The situation is worse in developing countries where about half of the population do not have access to safe drinking water and 73% have no sanitation, some of their wastes eventually contaminate their drinking water supply leading to serious health problems [4]. In many places both surface and ground water is polluted with industrial, agricultural, and municipal wastes. In addition to making water unavailable for drinking and other

domestic uses, industrial water pollution also leads to severe economic and social consequences such as the destruction of aquatic life, rendering the water unfit for agricultural purposes or unsafe for recreational activities like swimming.

Although industrialization is inevitable, many environmental degradation and human disasters which have continuously occurred over the years could be linked to industries as major contributor [5]. Industrial waste and emissions contain toxic and hazardous substance most of which can be detrimental to human health [6]. Effective management of such waste generated by industrial processes involves, but not limited to reduction, re-use or recycling of these industrial wastes, employing the best practice and technology. When this is done it will leave little or no waste to be treated, which will in turn result to clean environment and better industry-community relationship.

Studies conducted on River Romi, Kaduna Nigeria shows evidence of pollution of the water body by the activities of the Kaduna Refining and Petrochemicals Company Ltd. An example of such documented evidence was a research conducted on the water quality of River Romi (Nigeria), in which industrial effluent from Kaduna Refining and Petrochemical Company limited is discharged. It was reported that the water in River Romi has been contaminated by effluent discharge from the refinery, because there was difference of concentration of the pollutants at the upstream, point of entry and downstream. Despite the fact that the refinery has a waste water treatment plant, the waste released into the river from the refinery contaminated the water. Many of the parameters measured were still higher than the acceptable limit set by Nigerian National Standard and World Health Organization. It was found that these pollutants present in the river reduced the effects of solar energy absorption, resulting in a lower rate of photosynthesis and slowed down natural water

purification processes. And the long effect of this is environmental degradation. The researchers recommended that Kaduna Environmental Protection Authority (KEPA) should ensure that Kaduna refinery complies with Federal Environmental Protection Agency and National Standard Drinking Water Quality guidelines of industrial effluent discharge[4].

Evidence of the harmful effect of refinery effluent on human food chain was seen in the study conducted on fish from Kaduna River. Accumulation of heavy metals and histopathology were observed in *Oreochromis niloticus* exposed to treated petroleum refinery effluent from the Nigerian National Petroleum Corporation, Kaduna. Analysis of fish metal burden showed that the fish concentrated trace metals a thousand times above the levels existing in the exposure medium. Some metals were preferentially accumulated more than others and the accumulation was, in decreasing order, Pb, Fe, Zn, Cu, Mn, Cr, Ni, and Cd. The extent of metal accumulation and histopathological damage were directly related to the effluent concentrations [7].

The physicochemical qualities of a refinery effluent and water and sediment of an effluent receiving water body were investigated by Otokunefor and Obiukwu in 2005 [8]. The treated refinery effluent contained very high concentrations of phenol (11.06 mg/l), oil and grease (7.52 mg/l), ammonia (8.52 mg/l), COD (91.76 mg/l), TDS (390.6mg/l) and phosphate (6.2 mg/l), but low in sulphide, nickel, lead, copper and chromium, which were undetectable. High concentrations of phenol (5.13–16.38 mg/l), oil and grease (10.56–15.23 mg/l), and ammonia (4.31–13.17 mg/l) were observed in water and sediment samples respectively, at the point of effluent impact. A high concentration of sulphide (3.74 mg/l) was accumulated in the sediment at the point of impact of the refinery effluent, though it was undetectable in the effluent itself or water

sample. The concentrations of these parameters as well as of phosphate, nitrate, zinc and COD declined progressively with distance from the point of impact but were still significantly higher than in control water and sediment in samples 1.5 km downstream from the point of impact. Higher concentrations of the pollutants were recorded in the dry season than rainy season except for phosphate and nitrate, which showed the reverse trend. Nickel, lead, copper, chromium and cyanide were neither detected in the effluent nor impacted water body.

The research conducted by Aderogba in 2011 on the Significance of Kaduna River to Kaduna Refining and Petrochemicals Complex, mentioned among other observations that the Sour Water Stripper (SWS) was not functioning. Consequently, the polluted wastewater is discharged directly to the environment. It was recommended that the Sour Water Stripper be resuscitated and made to function. Also recommended was the use of Ultra Filtration Membrane System for the treatment of desalter effluent [9].

In 2011, Uzoekwe and Oghosanine, investigated the effects of treated effluent discharge on the water quality of Ubeji Creek, Warri. Water and sediment samples were collected from upstream and downstream sections of the creek. Physicochemical parameters and concentrations of heavy metals of the receiving water body (upstream and downstream) were compared with that of the treated effluent. Recorded mean pH values of the effluent, receiving water body and sediment were 6.26 ± 0.04 , 6.90 ± 0.06 (upstream), 6.87 ± 0.01 (downstream) and 6.54 ± 0.44 respectively. Electrical conductivity ranged from $1150.41 \pm 0.01 - 151.50 \pm 0.71 \mu\text{S}/\text{cm}$ for water samples and mean value of $1870.00 \pm 1117.23 \mu\text{S}/\text{cm}$ for sediment. THC (Total hydrocarbon) and TDS varied from maximum values of $8.81 \pm 0.01 - 2.83 \pm 0.04 \text{ mg/l}$ and $575.15 \pm 0.07 - 75.72 \pm 0.26 \text{ mg/l}$ respectively.

Nitrate and phosphate level was observed to be higher in the sediment ($45.30 \pm 3.96 \text{ mg/l}$ and $9.62 \pm 2.57 \text{ mg/l}$ respectively) than the level obtained for upstream (0.35 ± 0.01 and $0.01 \pm 0.00 \text{ mg/l}$) and downstream (0.25 ± 0.03 and $0.01 \pm 0.00 \text{ mg/l}$). The ranges for exchangeable ions were; Na ($7.73 \pm 0.24 - 6.61 \pm 0.24 \text{ mg/l}$), P ($5.26 \pm 0.04 - 2.25 \pm 0.03 \text{ mg/l}$), Ca ($34.74 \pm 0.09 - 13.45 \pm 0.33 \text{ mg/l}$) and Mg ($2.74 \pm 0.18 - 1.80 \pm 0.06 \text{ mg/l}$) for water samples; for the sediment, the range is $36.33 \pm 2.50 - 2.76 \pm 0.96$ (Na > P > Ca > Mg). The results obtained, ranges from Fe ($4.29 \pm 0.00 - 2.76 \pm 0.03$) to Pb ($0.01 \pm 0.01 - 0.01 \pm 0.00$) for water samples and Zn (9.40 ± 1.50) to Cd (0.05 ± 0.00) for sediment. The value obtained for sediment was observed to be higher than that in the water samples. This shows that most of the pollutants in an effluent receiving water body may settle as sediments which may give a false impression on the purity of the water [10].

In 2000, Abdul [11] studied the "Effects of oil industry effluent on water quality," (Kaduna Refining and petrochemical company as a case study) to determine the nature of the effluent discharged into Romi River by Kaduna Refining and Petrochemical Company (KRPC), and to see the effects on water quality and conformity with National Environmental Standards and Regulations Enforcement Agency (NESREA) standard. At the end of the work, it was found that industrial effluent of KRPC contained some hazardous chemicals which could cause kidney damage, corrosion, stains in clothes and which is capable of rendering the water unsuitable for aquatic and human use.

Another evidence of pollution of oil refinery on host community was the research conducted by Nduka *et al.*, in 2009 [12]. That research investigated the "Effect of Effluents from Warri Refining and Petrochemical Company (WRPC) on "Water and Soil Qualities of Contiguous Host and Impacted Communities of Delta

State, Nigeria.” Since open and underground water bodies are regarded as final recipient of most environmental pollutant, the study provided data on pollutant load of potable water supply of the study area. Surface water of Aja-Etan and Ijala had highest levels of cadmium (1.45 ± 0.01 and 1.20 ± 0.0 (mg/l), that of ifie-kporo and Ekpan had highest lead (1.00 ± 0.01 mg/l). Ekpan borehole water is more acidic (4.79 ± 0.01) than others. Agigba and Ajamimogha surface water had highest level of manganese (2.40 ± 0.03 and 2.20 ± 0.03 mg/l). With the exception of Ekpan shallow well, BOD and hardness were in highest concentration in surface water. Some of the parameter were above WHO standards and USEPA maximum contaminant level (MCL). The levels of lead, cadmium, manganese and chromium exceeded the threshold limits (0.01, 0.003, 0.4 and 0.05 mg/l respectively) set by the WHO health-based guideline for drinking water; and this could portend environmental hazards. The manganese levels of potable water supply in the impacted communities were higher than that of the contiguous host communities. The metal levels of soil from contiguous host communities were low; this is because of the washing of soil into surface water by flood and infiltration into underground water. High level of these

metals was also attributed to other relevant occupational fields (steel making, foundry work, thermal cutting, welding, glass and ceramic production etc.) within the study area. Physicochemical parameters of potable water of the contiguous host communities shows serious pollution burden. The pH of all surface water was within the internationally recommended standard (pH for surface water systems: 6.50-8.50, for underground water systems: 6.00-8.50). The pH of underground water (shallow well and borehole) in this study was acidic ranging from 4.79-5.91.

A possible solution to refinery effluent treatment problems was the use of Fed Batch Reactor (FBR), followed by coagulation and sand filtration as suggested by the study conducted by Ghulam *et al.*, in 2013 [13]. The researchers observed that the total reductions in COD, BOD, oil contents and phenol were 95.11%, 94.30%, 99.47% and 100%, respectively, with FBR followed by coagulation and sand filtration. This FBR-coagulation-sand filtration treatment system also removed the toxicity from the oil refinery wastewater. Treated wastewater by this approach meets National Environmental Quality Standards (NEQS) of Pakistan, and can be safely released into the environment.

2.0 RESEARCH METHODOLOGY

2.1 Study Area

Kaduna Refining and Petrochemicals Company (KRPC) limited is one of the four refineries owned by The Federal Republic of Nigeria and operated by the

2.1.1 Sample Collection/Preservation

Composite samples were manually collected and thoroughly mixed. Four (4) litres of each of the samples was collected in plastic containers for the analysis of the metals, temperature, pH, conductivity, turbidity, sulphide, nitrate and hardness, while two (2) litres of each sample was

Nigerian National Petroleum Corporation (NNPC). It is located in the southern part of Kaduna metropolis between latitude 10° North and longitude 7° East.

collected with glass containers for the analysis of oil and grease and COD. Samples for the analysis of DO and BOD were collected using a special BOD bottle: a glass bottle with a "turtleneck" and a ground glass stopper.

Replicate samples were also collected. The samples were collected and identified as;

Sample A: The effluent of Crude Distillation Unit 1 (CDU 1) which is made up of desalter effluent and sour water from the reflux drum (Figure 2.2).

Sample B: The effluent from the surge (feed) drum of Naphtha Hydrotreating Unit (figure 2.3) and Catalytic Reforming Unit (Figure 2.4)

Sample C: Effluent from the Waste Water Treatment Plant.

Sample D: Effluent from the outfall of Kaduna Refinery to the environment (Figure 2.5).

The analysis of the samples started immediately after collection and continued till the next day. The samples were preserved in a refrigerator at 4°C. But the samples for the determination of BOD₅ were incubated at 20°C for five days.



Figure 2.1 Map of Kaduna Refinery

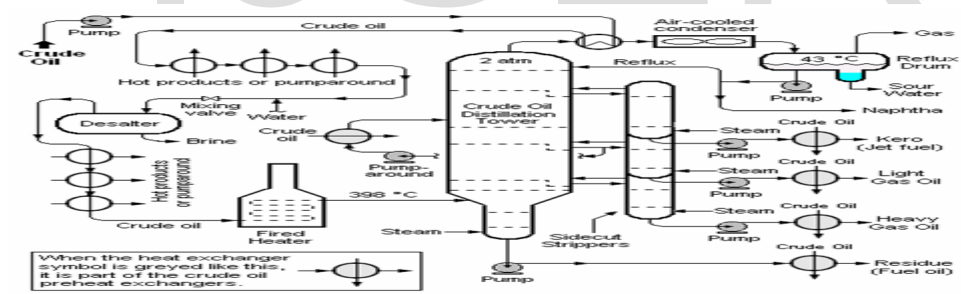
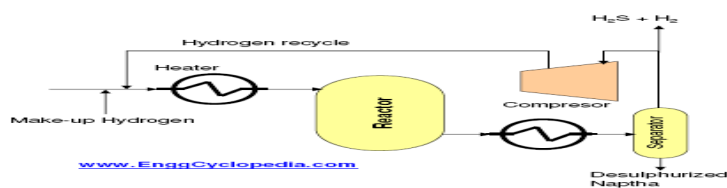


Figure 2.2 Crude distillation unit flow diagram



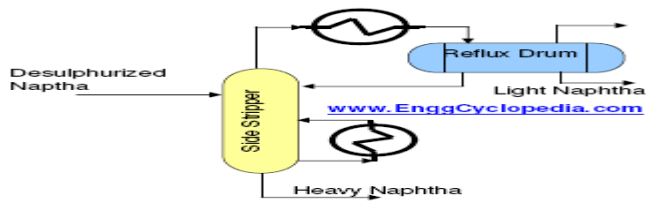


Figure 2.3 Naphtha Hydrotreating Unit

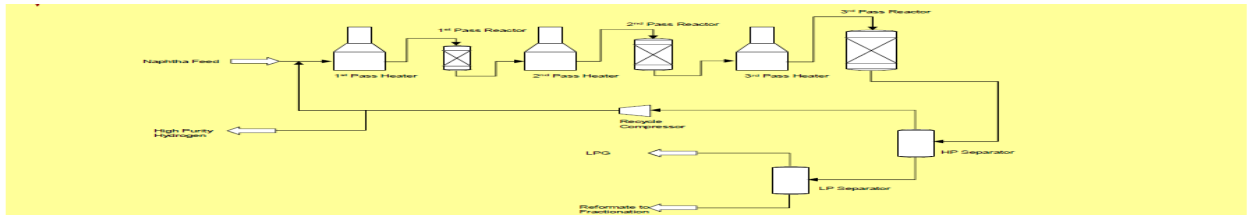


Figure 2.4 Catalytic Reforming Flow Diagram



Figure 2.5. Effluent outfall from the Refinery.

2.2 Method of Analysis

The characteristics determined are Turbidity, Conductivity, DO, BOD, COD, Temperature, pH, Oil and Grease,

Sulphide, Nitrate, Hardness, Mercury, Cadmium, Iron, Lead, Zinc, Copper, Vanadium, and Chromium.

Table 2.1 Sample Identification

2.2.3 Determination of pH of Effluent (Astm D1293).

Procedure

The pH electrode was standardized with buffer solution and rinsed by means of flowing stream of distilled water from a wash bottle. Then the sample was placed

in a clean plastic beaker equipped with a small laboratory-type mechanical stirrer and stirred thoroughly. Then the pH electrode was inserted into the sample and the pH value recorded.

2.2.4 Determination of Turbidity (Astm D1889)

Procedure

solution was replaced with the sample in a

Mean Sample	Sample	Name
A	A1 and A2	CDU-1 Effluent
B	B1 and B2	NHU/CRU Effluent
C	C1 and C2	Waste Water Treatment (WWT) Plant Effluent
D	D1 and D2	OUTFALL Effluent

The instrument was calibrated with the standard solution. Next, the standard

sample cell and the value was recorded.

2.2.5 Determination Of Conductivity Of The Water (Astm D1125)

Procedure

The platinized electrode was rinsed with distilled water before it was inserted inside the beaker containing the sample. Next, the conductivity power button was pressed and

sufficient time was allowed for the equalization of temperature until a constant reading was obtained. Then the instrument reading was recorded.

2.2.6 Determination of Hardness in Water (Astm D1126)

Procedure for Reagents Preparation

Buffer solution.

40 g of Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) was dissolved in 800

cm^3 of water. Then 10 g of sodium hydroxide (NaOH), 10 g of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and 10 g of potassium sodium tetraborate

(KNaC₄H₄O₄·4H₂O) were dissolved in 100 cm³ of water. Next, the two solutions were mixed and made up to 1000 cm³ (1 litre) with distilled water.

Calcium indicator

0.2 g of ammonium purpurate (murexide) and 100 g of sodium chloride (NaCl) were mixed and ground together to a 40-50 mesh size.

Hardness indicator

0.5 g of chrome black T and 100 g of powdered sodium chloride were mixed,

Procedure

TOTAL HARDNESS (TH)

50 cm³ of each of sample was measured into different beakers. Then, 0.5 cm³ buffer solution and 0.2 g chrome black-T were added and stirred. Next the solution was titrated with standard EDTA. The stirring continued until the colour changed from red to blue.

CALCIUM HARDNESS

50 cm³ of each sample was measured into different beakers. Then, 2 cm³ of NaOH

3.2.7 Determination of Nitrate

Preparation of Brucine Solution

1 g of brucine sulphate was dissolved in 70 cm³ of distilled water. Then 0.1 g sulfanilic acid was added. Next the solution was mixed and heated. Finally, 3 cm³ of conc. H₂SO₄ was added gently to the mixture. Then the solution was cooled and diluted to 100 cm³ with distilled water.

2.2.8 Determination of Sulphide

Preparation of Sample

50 cm³ of filtered sample was measured into a beaker. Also 50 cm³ of distilled water (blank) was measured into another beaker. Then 50 cm³ of NaOH solution and 0.5 cm³ NH₄OH solution were added into sample and blank, and mixed.

Procedure

2.2.9 Determination of Biochemical Oxygen Demand

Reagents Preparation

i. Solution A (Buffer solution).

21.75 g of dipotassium phosphate, 8.5 g of potassium phosphate, 33.4 g of disodium

phosphate (heptahydrate) and 1.7 g of ammonium chloride were dissolved in distilled water and made up with distilled water to 1000 cm³ (1 litre.)

ground and stored in a dark coloured bottle.

Disodium Ethylenediamine Tetra-acetate (Na₂H₂ EDTA) solution standard.

3.8 g of disodium ethylene-diamine tetra-acetate dehydrate was dissolved in 800 cm³ of distilled water.

Sodium hydroxide solution (50 g/L).

50 g of sodium hydroxide (NaOH) was dissolved in distilled water and diluted to 1000 cm³ (1 litre).

solution was added and stirred before adding 0.2 g of calcium indicator. Then, the solution was continuously stirred and titrated slowly with standard EDTA solution until the colour changed from salmon pink to orchid purple.

MAGNESIUM HARDNESS

Magnesium hardness was calculated as follows;

Magnesium hardness = Total hardness (mg/l) – Calcium hardness in (mg/l)

Procedure

25 cm³ of the sample was filtered and measured into Cuvette1. Also 25 cm³ of distilled water (blank) was measured into cuvette 2. Then 1 cm³ brucine sulphanic acid solution was added into the Sample and the Blank. Next the Spectrophotometer was set to program number 353 and wavelength of 400 nm. Then, the blank was used to auto-zero the instrument. And then the sample was read and recorded.

Sample was filtered and 25 cm³ of the sample was measured into Cuvette1. Also 25 cm³ of distilled water (blank) was measured into cuvette 2. Then the Spectrophotometer was set to program number 690 and wavelength of 665 nm. Next, the blank was used to auto-zero the instrument. And then the sample was read.

phosphate (heptahydrate) and 1.7 g of ammonium chloride were dissolved in distilled water and made up with distilled water to 1000 cm³ (1 litre.)

Solution B (Magnesium sulphate solution).
22.5 g of magnesium sulphate was dissolved in water and made up to 1000 cm³ (1 litre).

Solution C (Calcium chloride solution).
27.5 g of calcium chloride (anhydrous) was dissolved with distilled water and diluted to 1000 cm³ (1 litre).

Solution D (Ferric chloride solution).
0.25 g of ferric chloride (hexahydrate) was dissolved in water and made up to 1000 cm³ (1 litre).

2 cm³ of solutions A, B, C and D were added to 1000 cm³ (1 litre) of the aerated water. The aerated water was then ready for the determination of Dissolved Oxygen before and after incubation.

Manganous sulphate solution.
364g of manganous sulphate (MnSO₄.H₂O) was dissolved in water, filtered and diluted to 1000 cm³ (1 litre).

Alkaline iodide – sodium azide solution.
500 g of sodium hydroxide and 135 g of sodium iodide were dissolved in water and diluted to 950 cm³. Then 10 g of sodium azide was dissolved in 40 cm³ of water

Procedure For Dissolved Oxygen (Astm D1589).

Procedure

Two BOD bottles were half-filled with aerated water. Solutions A, B, C and D were added. Then 2 cm³ of the sample was added. The bottles were shaken thoroughly, filled with aerated water without air space and covered. The BOD bottles were kept for incubation for five (5) days at 20 °C. Then 2 cm³ alkaline iodide (sodium azide) solution followed by 2 cm³ of manganous sulphate were apportioned into each BOD bottle, well below the surface of the liquid, stoppered carefully to exclude air bubbles; and the content of each bottle mixed by inverting the bottle several times.

Calculation

$$DO_1 = T_1 \times 0.2 \times 1000/T$$

$$DO_5 = T_5 \times 0.2 \times 1000/T$$

$$BOD_5 = (DO_1 - DO_5) \times T/V$$

and added slowly with constant stirring. The solution will be stored in a dark stoppered bottle.

Concentrated sulphuric acid.

Starch Indicator

A paste of 6 g of soluble iodometric starch was made with cold water. The paste was poured into 1000 cm³ (1 litre) of boiling water. Then 20 g of potassium hydroxide was added, mixed thoroughly and allowed to stand for 2 hours. Then 6 cm³ of glacier acetic acid (99.5%) was added. The solution was mixed thoroughly and then sufficient conc. HCl (SG 1.19) was added to adjust the pH value of the solution to 4.0. The solution was stored in a glass stoppered bottle.

Sodium Thiosulphate Solution.

25 g of sodium thiosulphate crystals was weighed and dissolved in 500 cm³ of previously boiled and cooled water, and made up to 1000 cm³ (1 litre) in a volumetric flask with distilled water. The solution was preserved by adding 1 g of NaOH per dm³ (litre).

The solution was allowed to settle, after which 2 cm³ of conc. H₂SO₄ was added to each. The bottles were then re-stoppered and mixed by inversion until the iodine was uniformly distributed throughout the bottle.

Titration

The prepared sample was poured into a 300 cm³ beaker and titrated continuously with sodium thiosulphate solution until the solution turned to a faint yellow colour.

Then 2 cm³ of starch indicator (solution turns blue-black) was added and the titration continued until the solution turned colourless.

Where DO_1 = Dissolved oxygen before incubation

DO_5 = Dissolved oxygen after incubation

T_1 = titre value before incubation,

T_5 = titre value after incubation,

V = Volume of sample water in incubation bottle, cm^3 .

T = volume of incubation bottle, cm^3

2.2.10 Chemical Oxygen Demand

Preparation of Reagents

Ferrous Ammonium Sulphate Solution (0.25 N)

98 g of ferrous ammonium sulphate solution $[FeSO_4(NH_4)SO_4.6H_2O]$ was dissolved in water. Then 20 cm^3 of sulphuric acid was added and the solution cooled and diluted to 1000 cm^3 (1 litre) with distilled water. Then solution was standardized by diluting 25 cm^3 of 0.25 potassium dichromate ($K_2Cr_2O_7$) to about 250 cm^3 .

After that, 20 cm^3 of sulphuric acid was added and the solution was allowed to cool. Then, the solution was titrated with ferrous ammonium sulphate indicator.

The normality was calculated as follows:

$$N = (A \times B) / C$$

Where; N = Normality of ferrous ammonium sulphate solution.

A = Volume of Potassium dichromate solution (cm^3).

B = Normality of potassium dichromate solution and

Procedure

50 cm^3 of distilled water was measured into a reflux flask as Blank.

Also 10 cm^3 of the sample was measured into another reflux flask and made up to 50 cm^3 with distilled water.

Then the reflux flasks (of sample and blank) were placed in an ice bath and 1 g of powdered mercuric sulphate, 5 cm^3 of conc. Sulphuric acid and several beads or boiling stones were added. The content was mixed to complete dissolution.

C = Volume of Ferrous ammonium sulphate solution (cm^3)

Mercuric Sulphate (Powdered mercuric sulphate)

Phenanthroline Ferrous Sulphate Indicator Solution:

1.48 g of 1, 10-(ortho)-phenanthroline monohydrate and 0.7 g of ferrous sulphate ($FeSO_4.7H_2O$) were dissolved in 100 cm^3 of water.

Potassium dichromate solution, standard (0.25):

12.259 g of potassium dichromate ($K_2Cr_2O_7$) was dissolved in water and diluted to 1000 cm^3 (1 litre) in a volumetric flask.

Sulphuric acid – Silver Sulphate Solution:

15 g of powdered silver sulphate (Ag_2SO_4) was dissolve in 300 cm^3 of concentrated sulphuric acid and diluted to 1000 cm^3 (1litre) with concentrated sulphuric acid.

With the flask still in the ice-bath, 25 cm^3 of 0.25 N standard potassium dichromate solution was slowly added to the sample and the blank. Next, 1 g of silver sulphate was added to the sample and the blank.

Then 70 cm^3 of concentrated H_2SO_4 was added slowly to the sample and the blank. After that, the flasks were attached to the condensers and the flow of cold water was started. Next, heat was applied to the flasks and refluxed for 2 hours. Then the flasks were allowed to cool and were washed down the condenser with about 25

cm³ of water before removing them. Next, the acid solution was diluted to about 300 cm³ with distilled water and the solution was allowed to cool to about room temperature.

Calculation

$$\text{COD} = (A - B) \times N \times 8000/S$$

Where, 8000 = milliequivalence of weight of O₂ x 1000 cm³/L

N = Normality of Ferrous Ammonium Sulphate

A = Titre value of blank

B = Titre value of sample

S = volume of sample used for the test.

Then 8 to 10 drops of phenanthroline ferrous sulphate solution were added and the excess dichromate was titrated with 0.25 N ferrous ammonium solution until a colour change from blue-green to reddish-blue indicated the end point.

Oil And Grease Determination

Procedure

The OCMA-350 analyzer was switched-on and waited for 30 minutes for it to warm up. Then zero and span calibrations of the analyzer were carried out. Next, the mode of measurement (mg/l) was selected. Then the cover of the measuring unit was opened and the cells taken, washed with a clean solvent and air dried. Then the cells were filled with the extract from the effluent sample up to the 6.5 cm³ mark and inserted carefully into the analyzer, making sure that the "V" mark on the cell faces the front of the analyzer. Next the cover was closed, stability check carried out and concentration of the sample read. Finally, the cell was removed from the analyzer and emptied in preparation for the next measurement. Recalibration was done

Determination Of Metals In Water By Atomic Absorption Spectroscopy (AAS).

Sample Digestion

100 cm³ of a well-mixed sample was measured into 125 cm³ beaker. Then 1 cm³ of conc. HNO₃ and 10 cm³ of conc. HCl were added to the beaker. The sample was heated on a hot bath in a well-ventilated hood until the volume was

after every 10 samples (EPA recommendation).

Equipment Calibration

Zero Calibration

The unit of measurement (mg/l) was selected.

The cell was filled with pure solvent, placed in the analyzer and measurement carried out.

The "ZERO CAL" button was pressed to make a zero calibration.

Span Calibration

The unit of measurement (mg/l) was selected.

The cell was filled with B-heavy oil (specific gravity 0.895 at 20°C), placed in the analyzer and measurement carried out.

The "SPAN CAL" button was pressed to make a span calibration.

reduced to 20 cm³ making certain that the sample does not boil. Then the sample was removed and filtered to remove any solids remaining. Next, the sample was quantitatively transferred to a 100 cm³ volumetric flask and made up with distilled water.

After digestion of the sample, the Atomic Absorption Spectrometer was used to determine the amount of each metal in each sample. The measurements were made using a hollow cathode lamp for each of the metals that was determined.

Instrument Used:

Atomic Absorption Spectrometer (Model: Thermoscientific S series. Type: S4 AA System) was used for the analysis. The instrument takes six hollow cathode lamps at a time. The result of each sample was the mean of two sequential readings.

Hollow Cathode lamps were used, while the flame was fueled by nitrous oxide, air and acetylene.

A Hollow Cathode Lamp consisting of the element of interest was selected from the six cathode lamps using the computer attached to the AAS machine. The blank, standard and sample solutions were aspirated and the concentration readings of the samples in mg/l recorded. The procedure was repeated using different lamps, standards and samples. Average concentrations of samples were recorded.

3.0 RESULTS AND DISCUSSION

3.1 Summary Of Results

Table 3.1 Comparison of the Results of the Physico-chemical Properties of Effluent Samples with NESREA Standard.

Property	Unit	Sample A	Sample B	Sample C	Sample D	NESREA Limit
Turbidity	NTU	4.4	4.3	6.5	7.3	100
Conductivity	µS	678	980	542	522	370
Temperature	°C	42	40	30	27	36
pH		5.92	9.17	7.17	7.48	6.5 – 8.5
Oil and Grease	mg/L	19.5	11.3	9.1	1.0	10
Sulphide	mg/L	0.25	0.18	0.04	0.03	0.2
Nitrate	mg/L	1.205	1.080	1.105	0.900	20
Total Hardness	mg/L	59.5	63.5	50.0	44.5	100
BOD	mg/L	82.32	92.61	90.96	77.91	50
COD	mg/L	139.2	115.2	192.0	172.0	100

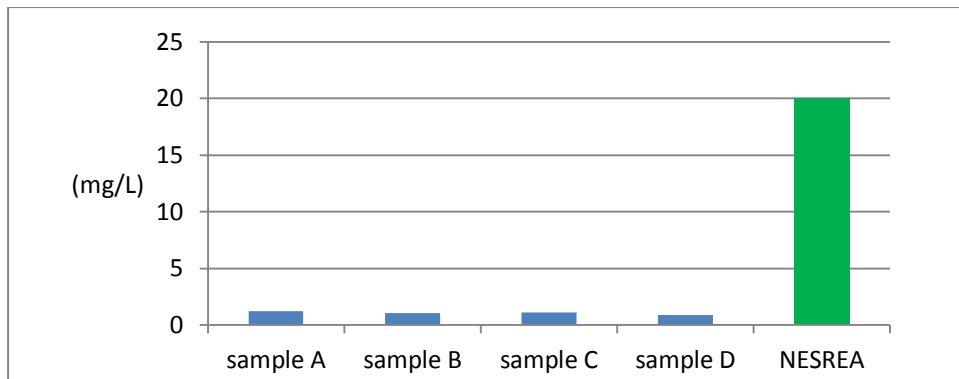


Fig. 3.1 Mean Nitrate in Effluent Samples with NESREA standard.

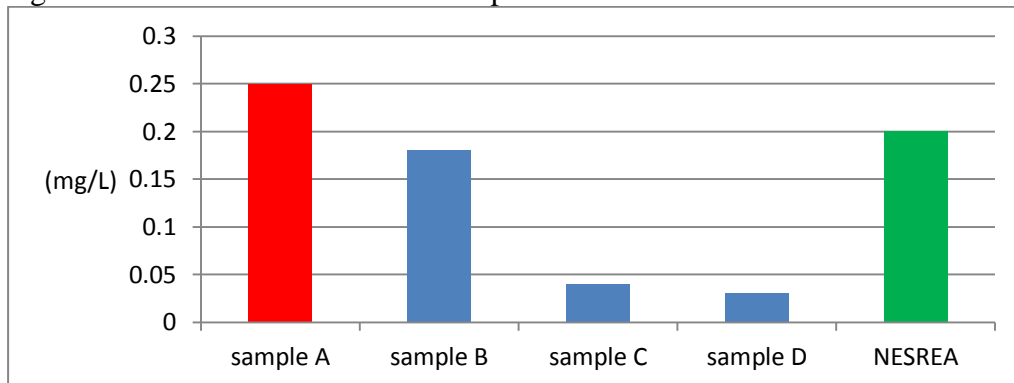


Fig. 3.2 Mean Sulphide in Effluent Samples and NESREA standard

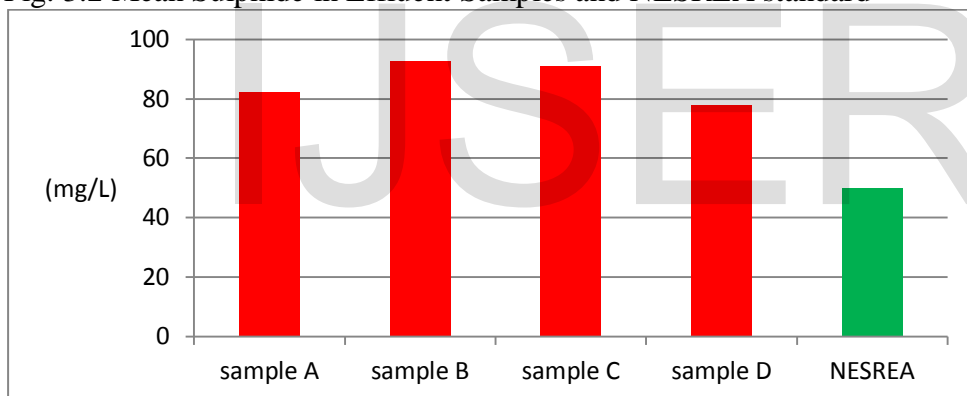


Fig. 3.3 Mean BOD of Effluent Samples and NESREA standard

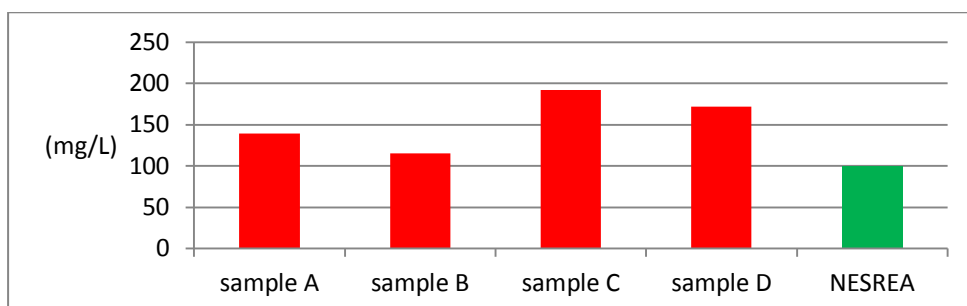


Fig. 3.4 Mean COD of Effluent Samples and NESREA standard

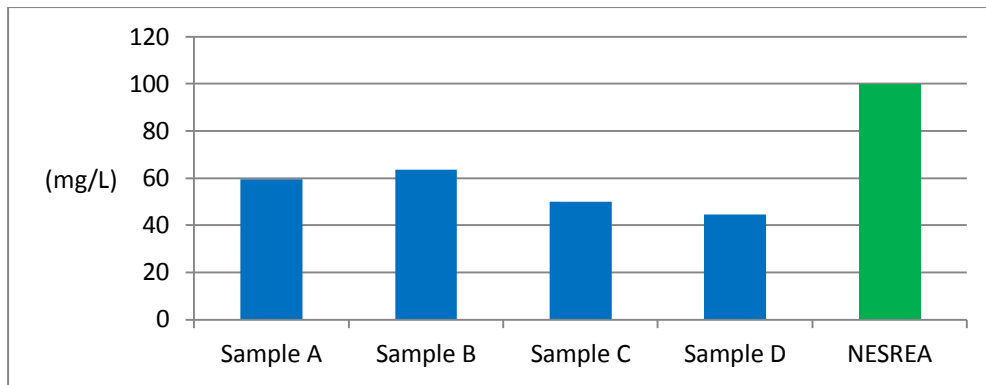


Fig. 3.5 Mean Hardness of Effluent Samples and NESREA standard

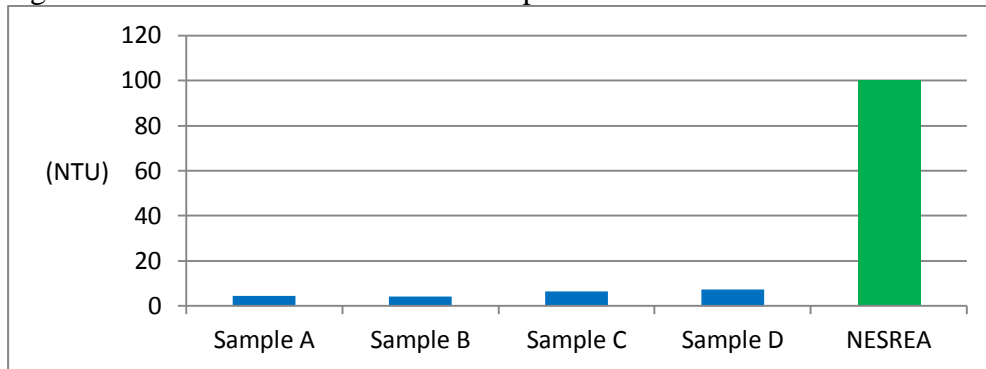


Fig. 3.6 Mean Turbidity of Effluent Samples and NESREA standard

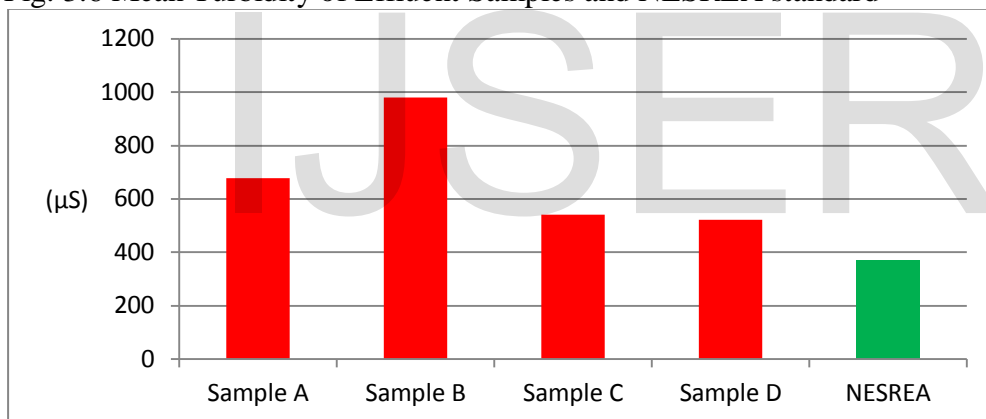


Fig. 3.7 Mean Conductivity of Effluent Samples and NESREA standard

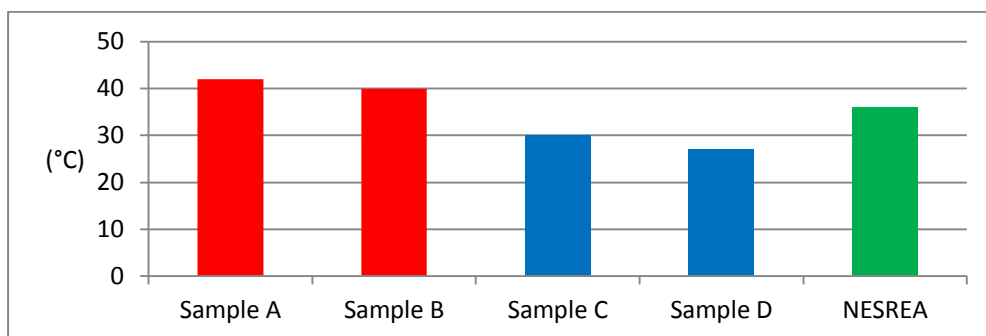


Fig. 3.8 Mean Temperature of Effluent Samples and NESREA standard

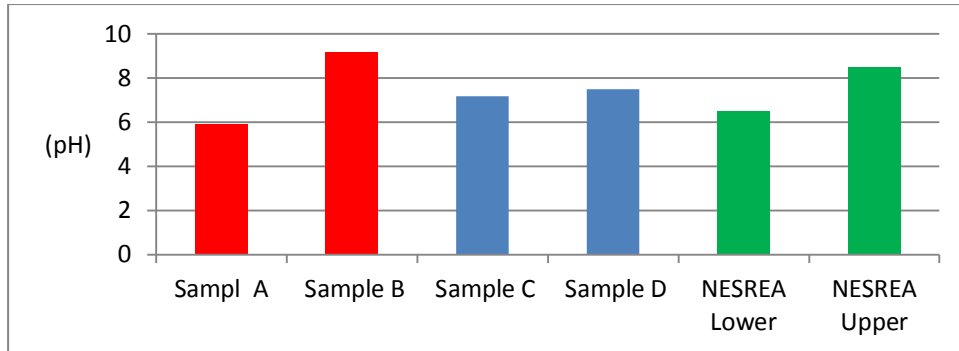


Fig. 3.9 Mean pH of Effluent Samples and NESREA standard

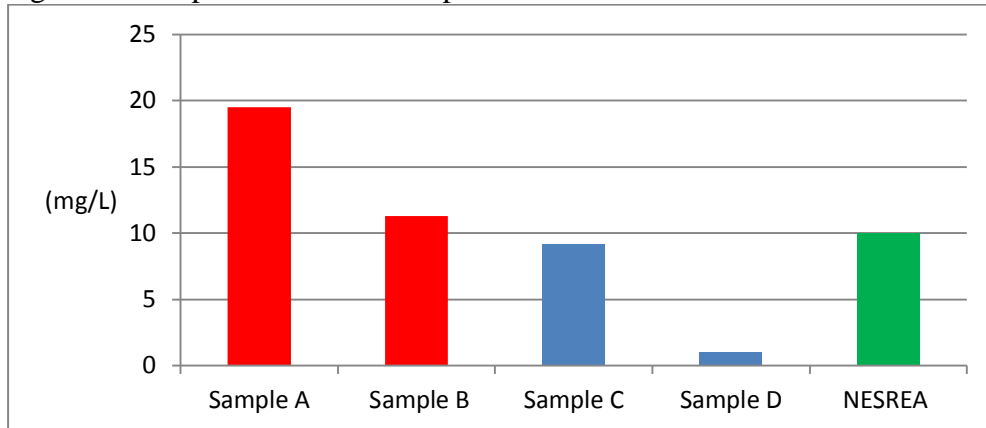


Fig. 3.10 Mean Oil and Grease Concentration in Effluent Samples

Table 3.2 Comparison of the Mean Results of Heavy Metals in Effluent Samples with NESREA Standard.

Metal	Sample A (mg/L)	Sample B (mg/L)	Sample C (mg/L)	Sample D (mg/L)	NESREA (mg/L)
Mercury	0.065	0.044	0.040	0.034	0.05
Cadmium	0.025	0.027	0.012	0.01	0.01
Iron	1.29	0.75	0.82	0.43	20
Lead	0.068	0.021	0.040	0.010	0.05
Zinc	0.056	0.045	0.525	0.354	1.0
Copper	0.970	0.980	0.940	0.920	1.0

Vanadium	<0.01	<0.01	<0.01	<0.01	0.01
Chromium	0.120	0.102	0.08	0.02	0.3

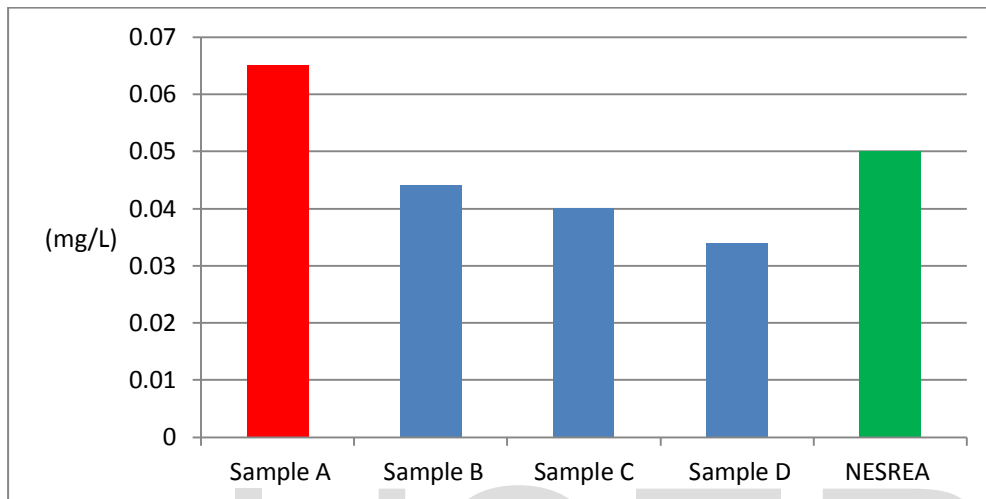


Fig. 3.11 Mean Mercury in Effluent Samples and NESREA standard.

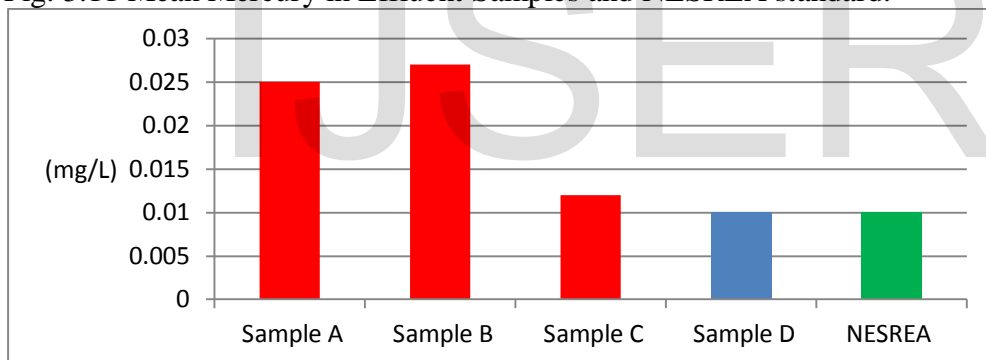


Fig. 3.12 Mean Cadmium in Effluent Samples and NESREA standard

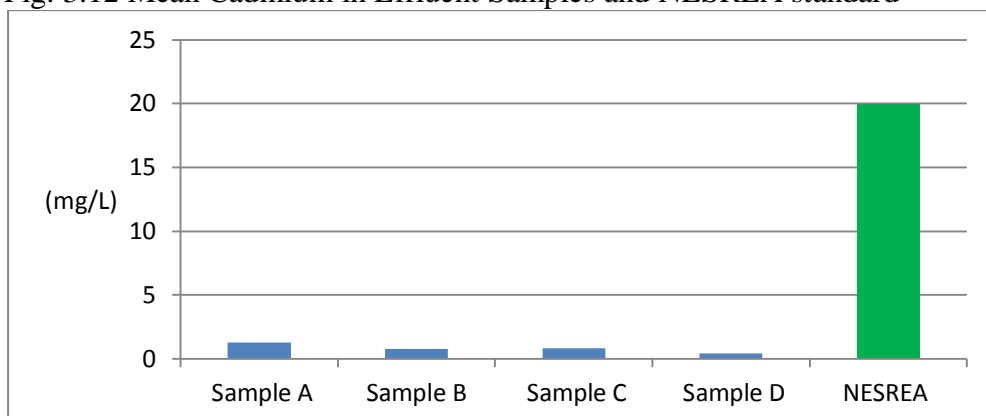


Fig. 3.13 Mean Iron in Effluent Samples and NESREA standard.

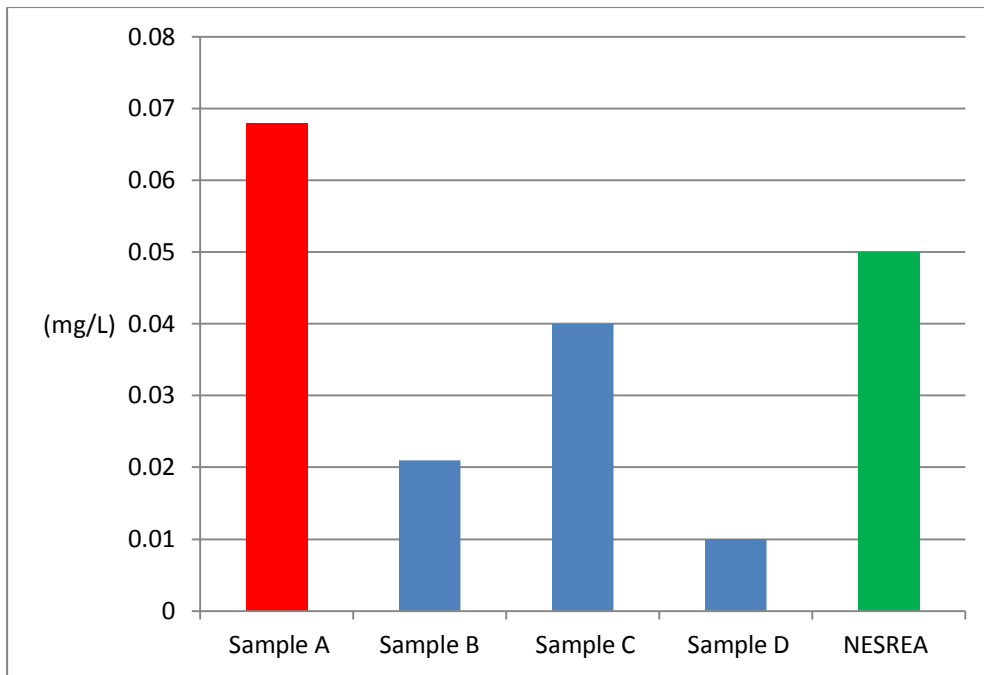


Fig. 3.14 Mean Lead in Effluent Samples and NESREA standard

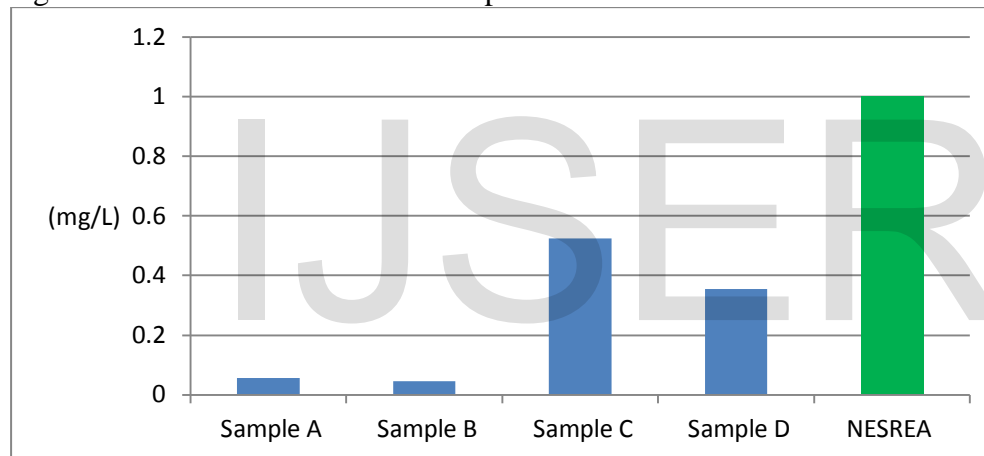


Fig. 3.15 Mean Zinc in Effluent Samples and NESREA standard

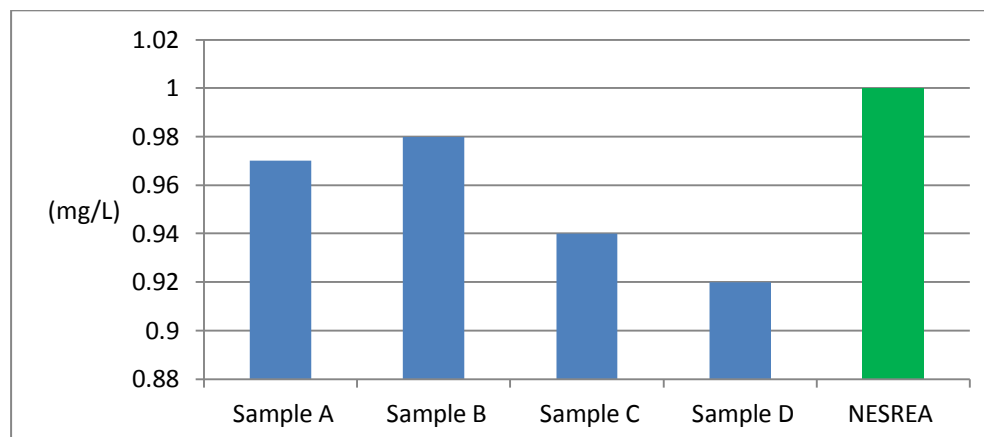


Fig. 3.16 Mean Copper in Effluent Samples and NESREA standard

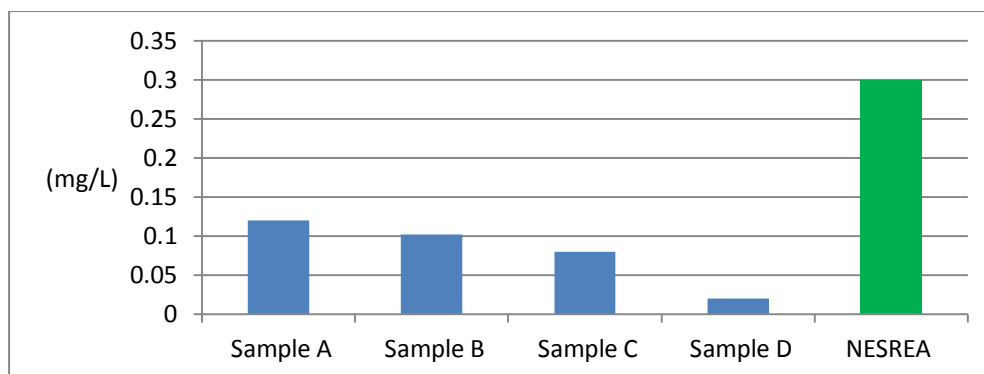


Fig. 3.17 Mean Chromium in Effluent Samples and NESREA standard

3.2 Discussion

Tables 3.1 and 3.2 present the mean values of the physico-chemical characteristics and heavy metals concentration in the effluent samples from the crude distillation unit 1 (Sample A), naphtha hydrotreating unit NHU, and catalytic reforming unit CRU (Sample B), the waste water treatment plant (Sample C) and the outfall (Sample D). The recorded values are replicate of two determinations for each of the effluent samples (Appendix I and II). In Figures 3.1- 3.17, the results are represented in bar chart formats for the physico-chemical properties and the concentrations of heavy metals in order to better visualize the parameters among the investigated effluent samples in comparison with NESREA standard.

In the physico-chemical properties, the range of the values of Turbidity (4.3 NTU – 7.3 NTU), Nitrate (0.900 mg/L – 1.205 mg/L), and Total Hardness (44.5 mg/L – 63.5 mg/L) for all the effluent samples are within the NESREA specifications of 100 NTU, 20 mg/L and 100 mg/L respectively. But the range of the values of Conductivity (522 μ S – 980 μ S), Biochemical Oxygen Demand (77.91 mg/L – 92.61 mg/L) and Chemical Oxygen Demand (115.2 mg/L – 192.0 mg/L) are above the NESREA standards of 370 μ S, 50 mg/L and 100 mg/L respectively. These parameters are observed to be high in the effluent samples from the plants under consideration (CDI-1, NHU and CRU), and still remained high even at the point of discharge to the environment. The pH of the effluent from

CDU-1 (sample A) is slightly acidic (5.92) while that of NHU/CRU is slightly basic (9.17). But the treated effluent at WWT (7.17) and Outfall fall (7.48) within NESREA acceptable pH limit of 6.5 – 8.5. CDU-1 effluent (sample A) temperature (42°C) and NHU/CRU (sample B) effluent temperature (40°C) are above the NESREA standard (36°C). But the treated effluent at WWT (sample C) and Outfall (sample D) had temperatures of 30°C and 27°C respectively, which are within the NESREA acceptable limit.

Sulphide is observed to be high in Samples A (0.25 mg/L) and B (0.18 mg/L) but low in the treated effluents from the Waste Water Treatment plant (sample C) and the Outfall (sample D). The low sulphide concentration in these two samples (C and D) is as a result of the Sour Water Stripper attached to the Crude Distillation Unit, which strips the effluent of Hydrogen sulphide gas and other light poisonous gases.

Oil and Grease concentration in the treated effluent sample (Sample C) and that of the outfall to the environment (Sample D) are both 1.0 mg/L which is far lower than the NESREA limit of 10 mg/L. But the oil and grease concentration in the effluent from the Crude Distillation unit (Sample A) is 19.5 mg/L which is higher than the NESREA limit (10 mg/L). And that of the effluent sample from NHU/CRU (sample B) is also high (9.1), even though it is below the NESREA limit. Therefore, the present treatment for the removal of oil

and grease is good, but there is need to start such treatment at the point of effluent generation (CDU-1, NHU and CRU) before it gets to the treatment plant (WWT), because high water level of the treatment plant, caused by heavy rain, may result in the escape of the oil and grease into the environment.

The result of the concentration of metals also shows that the range of the values of Iron (0.43 mg/L – 1.29 mg/L), Zinc (0.045 mg/L – 0.525 mg/L), Copper (0.920 mg/L – 0.980 mg/L) and Chromium (0.02 mg/L – 0.12 mg/L) for all the effluent samples are within the NESREA specifications of

20 mg/L, 1.0 mg/L, 1.0 mg/L and 0.3 mg/L respectively. Although the concentration of Cadmium in the Outfall effluent is low (0.01 mg/L), it is high in the effluents from CDU-1 (0.025 mg/L), NHU/CRU (0.027 mg/L) and WWT (0.012 mg/L) when compared to the NESREA standards (0.01 mg/L). Mercury and Lead concentrations are also observed to be high in CDU-1 effluent with values of 0.065 mg/L and 0.068 mg/L respectively. Also Vanadium could not be detected in the samples due to either its very low concentration or unavailability.

4.0 CONCLUSION AND RECOMMENDATION

4.2 Conclusion

The effluent from the fuels plants (CDU-1, NHU and CRU), the Waste Water Treatment plant, and the Outfall have been characterized. It was observed that the fuels plants contribute much to the overall effluent characteristics of the refinery. Some physico-chemical properties were determined and it was observed that the Conductivities, the Biochemical Oxygen Demand (BOD), the Chemical Oxygen Demand (COD), the Oil and Grease,

4.3 Recommendation

It is recommended that the treatment of effluent samples for Conductivity, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Oil and grease, pH, Temperature, Sulphide, Mercury, Cadmium and Lead should start at the fuels plants where they are generated. This will reduce contaminants in the effluent at source which will in turn

Sulphide, Temperature and pH of the effluent samples from these fuels plants were higher than the NESREA acceptable standard. This therefore require attention. Heavy metals concentrations in the effluents were also determined. It was observed that mercury, cadmium and lead concentrations were higher than the NESREA limit in the samples from these plants, and therefore contributes heavily to the overall effluent characteristics of the refinery.

result to increase in efficiency and quality of treatment at the waste water treatment plant.

Effluent from other plants in the refinery should be characterized to determine their content so as to determine better handling of such effluent at source. Such characterization should include the Lubes plant, the Petrochemical plant, the Power plant and the Tank farm.

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