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Effects of Refinery Processes on the Quality of Various Water Samples from Kaduna Refinery and Petrochemical Company (KRPC) Limited

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***Abstract*— *Effects of refinery processes on the quality of various water samples from Kaduna Refinery and Petrochemical Company (KRPC) Limited was investigated. Water quality assessment was carried out on samples collected at different water treatment sampling points in the refinery. The physicochemical parameters and other forms of analytical processes used in the work were of the standards of American Standards of Testing Materials (ASTM) and American Public Health Association (APHA) using spectrophotometric and volumetric methods. Results obtained showed that the quality of water samples subjected to treatment at each water treatment section in KRPC during the course of study was acceptable from physico-chemical parameters assessed and may not be injurious to the boiler and its other end uses. Also, result of the pre and post refinery operations on cooling water sample assessed showed the significant effect the refinery operation had on the cooling water.*

Keywords*— *Refinery, water quality, Water treatment, Heavy metals, Kaduna refinery, ASTM and APHA.

I. INTRODUCTION

Water is a liquid without colour, smell or taste that falls as rain, in lakes, rivers and seas and is used for drinking, washing and a host of other industrial processes (Hornby, 1987). Water has a freezing point of 0^0C, boiling point of 100^0C, maximum density of 1g/cm^3 at 4 ^{0}C and it's neutral to litmus paper (Jones and Atkins, 2002).It is chemically composed of hydrogen and oxygen in the ratio of 2:1. An essential and indispensable element/resource in nearly all industrial processes (Lorch, 1987). In industrial sectors such as petroleum refinery, food and beverage or pharmaceutical production, water is either used as a primary product or in the area of cooling, steam generation or boiler feed systems. Using water in the industrial environment requires consistently high water quality with adequate physicochemical parameters which is achieved by treatment at each stage of its usage (Dara, 1995).Water treatment is the process of converting raw water from surface or sub-surface source into a portable form that is suitable for drinking, domestic and industrial uses (Ojo *et al.*, 2012). The water for the production processes and for vital services must be of high quality, equivalent to the drinking water. For the boilers and some production processes, the water must be additionallty demineralized (Aderogba, 2011).

Kaduna Refinery and Petrochemical Company (KRPC) was established for the purpose of refining crude oil into Premium Motor Spirit (PMS) and other petrochemical products with the view of providing fuels for automobile engines and other outputs, without threatening environmental safety (Ahmad, 2014). The process of refining crude oil consumes large amounts of water. It is used in varying quantities and ways in all stages/processes of production in the refinery as its operation is highly dependent on adequate supply of water. Refinery water needs to be treated before being used in different processes and the type of treatment depends on the quality of the source water and its ultimate use in the refinery. Turbidity, sediments and hardness are examples of source water constituents that may require treatment. The raw water comes from River Kaduna but undergoes various purification stages such as coagulation and filtration before usage.Subsequent treatment will depend on the ultimate use for each water system (Aderogba, 2011).

This study therefore seeks to comparatively ascertain the physicochemical and heavy metals characteristics of the various treated refinery water samples, pre and post refinery operations on cooling water.

II. MATERIALS AND METHODS

2.1 Description of study area

The study area is KRPC which is located at Chukun Local Government Area of Kaduna State, Nigeria. It lies between latitudes 10° to 11° North and longitudes 7° to 8° east.

KRPC facility lies between latitudes 10° 24′ 36.18"N and longitudes 7° 29′17.37″E. The facility occupies approximately 1.8 square Kilometers; about 7% of the total area of the region.

The study area was initially characterized by over 80% agricultural land uses. River Romi is one of the tributaries of River Rigasa, it is the largest river in the study area which adds to drain the region into the Kaduna River system. The provision of disposing refinery liquid waste into River Romi was one of the reasons why the refinery was located in the Rido region.

2.2 Samples collection

Water samples from different treatment/sampling units in KRPC stipulated as follows: raw, filtered, demineralized, boiler and cooling were collected with a 2 litre plastic water sampler and transferred to a clean 2 litre polyethylene containers, properly labelled and taken to the refinery quality control laboratory for analysis.The raw, filtered, demineralized and boiler feed water samples were collected for physico-chemical examination while the cooling and water samples were collected for analysis/comparison of pre and post refining operation. All other quality control procedures relevant to samples collection, preservation and analyses were strictly adhered to for the determination of physicochemical parameters and heavy metals content.

2.3 Physico-chemical examination

The physico-chemical parameters were determined according to procedures outlined in the Standard Method for the Examination of Water and Waste Water (APHA, 1998 and 1992) and American Society for Testing Material (1990). The parameters analyzed are those believed to have effects on water quality and referred to by WHO (2008) and FMEnv. (2007). These parameters are Conductivity measured using Conductivity meter (HI 2300), pH and Temperature were measured using HACH pH meter, Turbidity was measured using Turbidimeter (HI 88713-ISO), Silica content and Phosphate were analysed using Spectrophotometer (Hach DR/2010 and Hach DR 2800), Total alkalinity by titration with HCl and Hardness by complexometric titration. A Perkin Elmer model 2380 Atomic Absorption Spectrophotometer was used for the determination of some heavy metals.

III. RESULTS AND DISCUSSION

Table.1: Results of the physico-chemical parameters of treated water samples in Kaduna Refinery and Petrochemical Company

Parameters	Raw	Filtered	Demineralized	Boiler
pH	7.69±0.01	6.61±0.01	8.02±0.006	10.25±0.03
Temp. (^{0}C)	25.33±0.58	26.5±0.36	27.3±0.10	26.07±0.15
Turb. (ntu)	82.27±0.23	0.44±0.03	0.02±0.006	
Cond. (us/cm)	52.43±0.12	59.07±0.32	0.57±0.06	12.13±0.23
Silica (ppm)	8.13±0.12	4.73±0.06	0.07±0.01	1.15±0.13
Alkalinity (ppm)	62.33±0.58	74.0±1.00	24.00±1.00	19.01±0.02
Tot. Hardness (ppm)	46.90±1.01	32.93±1.007	19.53±2.16	27.8±0.20
Ca. Hardness (ppm)	45.07±0.90	25.67±0.58	16.33±0.58	13.37±2.28
Mg. Hardness (ppm)	18.33±1.53	7.27±0.64	3.20±1.59	14.43±2.11
PO_4^{3-} (ppm)	ND	ND	3.76±0.02	2.77±0.12
ND = Not done.				

The physico-chemical parameters of the water samples treated at each water treatment section in Kaduna Refinery and Petrochemical Company were investigated and the level of treatment estimated. The result of the analysis as shown in Table 1 shows that the average pH of the raw water sample is slightly alkaline (7.69). This is in line with the neutral (pH 7) or slightly alkaline (pH 8) permissible levels for pH value for stream water or natural water as set by World Health Organization (WHO). The pH of the filtered water sample was observed to be acidic (6.61). These significant change in pH maybe attributed to the preliminary treatment of the raw water by addition of poly-aluminiumchloride, a coagulant whose dosage is pH dependent (Jowa and Liberty, 2015).The average pH of the assessed demineralized and boiler water were found to be 8.02 and 10.25 respectively. The subsequent increase in pH of the demineralized water to the basic medium is due to the addition of tri-sodium phosphate (a buffer) which help to regulate the pH to meet the requirements of the boiler. The irregular trend and required degree of water pH control depends on the particular use as the pH which measures the acidity or alkalinity (basicity) of any water is one of the most important determination in water chemistry because many of the processes involved in water treatment are pH dependent (Lateef, 2004).

The study also revealed that the average turbidity of the raw water is 82.27 ntu. The high turbidity value obtained might be as a result of dissolution of organic wastes such as faeces and other nitrogenous wastes being discharged by some villagers inhabiting the area of the source water. Another natural primary cause of the turbidity of source water is silt, which consists of suspended minerals particles resulting from land erosion and other dissolved solids.The turbidity of the filtered water is 0.44 ntu. These significant decrease in turbidity from raw to filtered water along the treatment line is due to the addition of poly aluminium chloride (PAC), a coagulant which accounts for 99% turbidity removal (Jowa and Liberty, 2015).Also, the turbidity of the demineralized water is 0.02 ntu. These significant variation in turbidity as compared to the filtered water is attributed to its treatment by Ion exchange which is a reversible chemical reaction where positively or negatively charged ions present in the water are replaced by similarly charged ions present within the resin, thus removes both suspended and dissolved solids. Turbidity level is an important water quality criteria as it makes water cloudy and deposits in water lines and process equipment such as boilers in the refinery. Its complete elimination at the boiler as observed in Table 1 is due to water preliminary treatment by filtration and ion exchange to meet the requirement of the boiler as its presence may be injurious to the boiler (Odigure *et al.*, 2005).The average conductivity value of the raw water is 52.43 us/cm. These value increased slightly to 59.07 us/cm following filtration. Subsequent treatment by demineralization led to a significant decrease in conductivity value to 0.57 us/cm. This is possible as processes such as ion exchange which decreases dissolved solids content will decrease conductivity to a large extent. Conductivity is the measurement of the ability of a solution to carry electric current. Since this ability depends on ions or ionizable solids in solution, a conductivity measurement is an excellent indicator of the total dissolved solids in water (Jernand Wun, 2006). Hence, high conductivity can increase the corrosive characteristics of water in the refinery.

The study also showed that the average silica content of the raw water is 8.13 ppm which reveals the level of suspended solids in the raw water sample. Its presence in the source water maybe attributed to minerals such as sodium feldsparalbite ($NaAlSi_3O_8$) present due to erosion of rocks, atmospheric precipitation and industrial sewage and these maybe harmful to the refining plant. Subsequent treatment by filtration decreased the silica content to 4.73 ppm. This is attributed to the dual media filters which comprised of a layer of anthracite over sand where the larger solid particles are trapped by the anthracite and the finer solids are held up in the sand. Also, the silica content of the demineralized water is 0.07 ppm. These significant decrease is due to treatment by ion exchange following filtration. Silica which if allowed to pass with the water as boiler feed will deposit on boiler tubes which form resistance to efficient heat transfer, scaling on heating, cooling equipment and pipelines (Aderogba, 2011). Hence, silica content assessment is an important water treatment quality criteria.

The alkalinity of the raw water is 62.33 ppm.These value which determine a stream's buffering capacity is within the WHO permissible limit of 32-118 mg/l. Also, a slight increase (74.0 ppm) was recorded upon filtration which fluctuate to 24.00 ppm following demineralization by ion exchange. These irregular trend / fluctuation in alkalinity of water samples along the treatment line maybe due to the chemicals used in water treatment such as poly-aluminium chloride, tri-sodium phosphate and otherswhich causes changes in alkalinity. Determining alkalinity is required when calculating chemical dosages for coagulation (Jowa and Liberty, 2015). It's also an important parameter in water treatment in refinery as it causes foaming in steam systems and attacks boiler steel.

The study also revealed that the average total hardness of the raw water is 46.90 ppm. This is due to the source water coming in contact with limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$), as such picks up calcium ions and magnesium ions which makes it too hard for refinery use. Following subsequent treatment by ion exchange, total hardness of the demineralized water was observed to be 19.53 ppm. These subsequent variation was due to treatment by ion exchange where the mobile hydrated ions of solid are exchanged equivalently with ions of same charge in the water (Walter, 1981). Sodium and Hydrogen cation exchange process are the methods employed in KRPC as hardness is the primary source of scale formation in heat exchangers and pipelines.

Table.2: Heavy metals result of treated water samples in Kaduna Refinery and Petrochemical Company

Parameters	Raw	Filtered	Demineralized	Boiler

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(ppm)				
V	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Pb	0.05±8.49	0.04±0.00	0.01±0.006	0.01±0.00
Zn	0.18±0.01	0.10±0.006	0.01±0.00	0.00±0.00
Fe	0.74±0.01	0.63±0.02	0.23±0.01	0.44±0.02
Cd	0.00±0.00	0.02±0.01	0.01±0.006	0.05±0.02
Cu	0.03±0.006	0.00±0.00	0.00±0.00	0.00±0.00
Ni	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Cr	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00

Table 2 shows that Vanadium, Nickel and chromium were not detected in the source water sample (raw water) and water samples along the water treatment line (Filtered, demineralized and boiler water). The average concentration of K, Fe and Zn in the source water sample were 9.64 ppm, 0.74 ppm and 0.18 ppm respectively. The reason for the high concentration of these metals in the source water maybe attributed to the erosion of minerals from rocks and soil, forest fire runoff, industrial and agricultural sewage (Cohen, 1960). The low concentration of Pb in the source water as shown in table 2 is a plus as the Kaduna River is expected to be polluted with less Pb concentrations and devoid of its associated problems. There was a significant decrease in the concentration of these heavy metal in the source water following filtration and demineralization processes as given in table 2. This is attributed to the use of dual filter media and ion exchange in these treatment processes which effectively removes heavy metals (Marcovecchio,2007).The appearance of Cd in the filtered water which was originally absent in the raw water sample could be as a result of the leaching out of Cd from the sand bed into the water. In summary, there was a significant decrease in the level of the metals originally present in the source water sample and the level at each water treatment section in the plant. These could be attributed to the treatment processes they undergo except for cadmium which was spotted along the water treatment process line and the random trend in Fe and K that both increased at the boiler after initial continual decreasing trend.

Table.3: Results of physico-chemical parameters of the pre and post refinery water sample from KRPC

Parameters	**CBR**	**CAR**
pH	8.41±0.01	7.74±0.005
Temp. (0^c)	21.53±0.31	29.10±0.30
Turb. (ntu)	9.52±0.03	33.67±1.15
Cond. (us/cm)	295.67±0.58	293.67±2.31
Silica (ppm)	7.10±0.10	54.67±1.15
Alkalinity (ppm)	62.13±0.23	203.0±4.36
Tot. Hardness (ppm)	71.10±0.006	134.83±1.04
Ca. Hardness (ppm)	65.72±0.03	95.33±0.58
Mg. Hardness (ppm)	5.39±0.02	39.5±0.50
PO_4^{3-} (ppm)	4.57±0.12	4.57±0.06

CBR= Cooling water before refining. CAR= Cooling water after refining / Cooling effluent. ND= Not done.

In this study, it was also observed from Table 3 that after refining operation, there was a significant increase in temperature (29.10 ^{0}C), turbidity (33.67 ntu), silica content (54.67 ppm), alkalinity (203.0 ppm) and total hardness (134.83 ppm) of the cooling effluent as compared to the temp. (21.53 ^{0}C), turbidity (9.52 ntu), silica content (7.10 ppm), alkalinity (62.13 ppm) and total hardness (71.10 ppm) of the cooling water sample before refining. The sharp increase in the temperature may be as a result of heat from cooling since the water is being used in exchanger units to reduce heat to between 80-90 ^{0}C. Otherwise, the exchanger gets defective during the refining operations. The increase in turbidity could be attributed to the exchange of turbid content alongside heat from petroleum products after its usage. Also, the increase in alkalinity, total hardness, silica content could be attributed to the chemicals such as orthophosphate, silicate, bicarbonate and calcium carbonate which act as inhibitors dosed to the cooling water samples before refining operations/usage. These chemicals are essential for effective scaling, corrosion and fouling control which can hamper the operation of plant equipment or contribute to its deterioration after usage.

Table.4: Results of heavy metal content of the pre and post refinery operations cooling water sample from KRPC

Parameters (ppm)	CBR	CAR
V	0.00±0.00	0.00±0.00
Pb	0.03±0.01	0.12±0.02
Zn	0.19±0.02	0.37±0.01
Fe	0.31±0.20	0.61±0.01
Cd	0.00±0.00	0.00±0.00
Cu	0.01±0.006	0.05±8.50
Ni	0.14±0.006	0.20±0.006
Cr	0.00±0.00	0.01±0.005
K	14.43±0.0	9.62±0.02

CBR = Cooling water before refining. CAR = Cooling water after refining / Cooling effluent. ND = Not done.

From Table 4, the levels of heavy metals in the cooling effluent were in the order of K > Fe > Zn > Ni >Pd> Cu > Cr with V and Cd being absent. These were higher when compared to that of the cooling water samples before refining operation with a trend of K > Fe > Zn > Ni >Pd> Cu with Cr, V and Cd absent. The only exception was the concentration of K which was higher in cooling water sample before refining than the cooling effluent sample. Also, Chromium was originally absent in the cooling water sample before refining but was spotted in the cooling effluent (0.01 ppm). These may be due to chromium dissociation from electroplated materials used in petroleum refining process (Abui,2012). The high level of Pb in the cooling effluent (0.12 ppm) can be attributed to its usage as coolant for lubricating oil fraction and parts of the equipment or machinery used at different stages of crude oil refining. Also, the increase in the concentration of Ni (0.20 ppm), Cu (0.05 ppm), Fe (0.61 ppm) and Zn (0.37 ppm) of the cooling effluent as compared to the cooling water before refining operation maybe attributed to corrosion of pipelines and parts of heat exchangers which the water passes through.

IV. CONCLUSION AND RECOMMENDATION

In conclusion, the result of the study revealed that the refining processes have individual and peculiar influences on the level of physico-chemical parameters of the water leaving each treatment section. The quality of water samples subjected to treatment at each water treatment section in KRPC during the course of study was acceptable from physico-chemical parameters assessed and may not be injurious to the boiler and its other end uses. Also, results of the pre and post refinery operation cooling water sample assessed showed the significant effect the refinery operation had on the cooling water.

Based on the results obtained above, the water treatment before usage in KRPC should be encouraged and continued as poorly treated water used in the boiler for steam production could be manifested through scaling and eventual failure of the boiler.

REFERENCES

[1] Abui, Y.M., (2012). Environmental effect of Kaduna Refinery and Petrochemical Company effluents discharge in the Romi area of Kaduna State, Unpublished PhD Dissertation submitted to the department of Geography and Planning, University of Jos, Nigeria, P. 394.

[2] Ahmad, H.A., (2014). Determination of Effectiveness of Waste Water (Effluent) Treatment process of Kaduna Refinery and Petrochemical Company (KRPC),*American Journal of Environmental Engineering and Science*, 1(1): 6-12.

[3] Aderogba, K.A., (2011). Significance of Kaduna River to Kaduna Refining and Petrochemicals Complex, *International Multidisciplinary Journal*, 5(22): 6-9.

[4] APHA.,(1992). Standard Methods for the Examination of Water and Wastewater, 18th Ed.,American Public Health Association (APHA), inc., Washington D.C., pp. 3-18.

[5] APHA.,(1998). Standard Methods for the Examination of Water and Wastewater, 20th Ed.,American Public Health Association (APHA), Washington D.C., pp. 12-27.
[6] ASTM International, (1990). Annual Book of ASTM Standards, Water and Environmental Technology, West Conshohocken, Pennsylvania, P. 285.
[7] Cohen, J.M., (1960). Taste Threshold Concentration of Heavy Metals in Drinking Water, *Journal of American Water Works Association*, 52(5): 660-663.
[8] Dara, S.S., (1995). A Textbook of Environmental Chemistry and Pollution Control, Chand, S. and Company Limited, P. 65.
[9] Hornby, A.S., (1995). Oxford Advanced Learners Dictionary of Current English, 5th Ed., Oxford University Press, P. 1344.
[10] Jern, N.G. and Wun, J., (2006). Industrial Wastewater Treatment, Imperial College Press, London, pp. 6-8.
[11] Jones, L. and Atkins, P. (2002).Chemistry: molecules, matter and change, 4thEd., New York, Freeman and company. pp. 421-422.
[12] Jowa, T. and Liberty, L.M., (2015). Treatment of Low Turbidity Water Using Poly-Aluminium Chloride (PAC) and Recycled Sludge, *Zimbabwe Journal of Science & Technology*, 10: 1-8.
[13] Lateef,A., (2004). The Microbiology of Pharmaceutical effluent and its public health implications, *World J. Microbiol.Biotechnol*, 20: 167-171.
[14] Lorch, W., (1987). Handbook of Water Pollution, 2ndEd., Ellis Harwood Ltd, London Press Publication, pp. 84-93.
[15] Marcovecchio, J.E., Botte, S.E. and Freije, R.H., (2007). Heavy Metals, Handbook of Water Analysis, Nollet, L.M., 2nd Ed., London: CRC Press, p. 275.
[16] Odigure, J.O., Abdulkareem, A.S. and Asuquo, E.T., (2005). Effect of Water Quality on the Performance of Boiler in Nigerian Petroleum Industry, *Leonardo Electronic Journal of Practices and Technologies,* 7: 41-48.
[17] Ojo, I., Fred, A.O. and Ochieng, G.M., (2012). Groundwater Characteristics, qualities, pollutions and treatments, *International Journal of Water Resources and Environmental Engineering*, 4(6): 162-170.
[18] Pearson, H. W., Mara, D. D., Konig, A., De Oliveira, R., Mills, S. W., Smallman, D. J. and Silva, S.A.,(1987). Water Column Sampling as a Rapid and Efficient Method of Determining Effluent Quality and the Performance of Waste Stabilization Ponds, *Water Science & Technology*, 19(12): 109–113.
[19] Walter, L., (1987). Handbook of water purification, Ellis Horwood, New York, pp. 85-90.