ISSN: 2456-8473
International Journal of Chemistry, Pharmacy & Technology
Vol. 2, No.4, pp-154-161, 2017

HEAVY METALS CONTENT OF AN OILY WASTEWATER EFFLUENT FROM AN OIL FIRM AT THE POINT OF DISCHARGE

WOKOMA OAF[1] and EDORI OS[2]*
[1]Department of Biology, Ignatius Ajuru University of Education, PMB 5047 Rumuolumeni, Port Harcourt, Nigeria
[2]Department of Chemistry, Ignatius Ajuru University of Education, PMB 5047 Rumuolumeni, Port Harcourt, Nigeria
Corresponding Author: onisogen.edori@yahoo.com
Received 24-03-17; Revised & Accepted: 20-04-17

ABSTRACT

Wastewater effluent is produced in different industries and these wastes constitute environmental problems because of pollution tendencies. Wastewater effluents from an oil industry were collected for 24 months (January 2014 – December 2015). The effluents were analyzed with atomic absorption spectrophotometer for cadmium (Cd), zinc (Zn), iron (Fe) and lead (Pb). Cd was not detected throughout the period of investigation in any of the samples. Pb was detected in some of the months and some other months were not detected. Zn and Fe were detected in all the months of investigation. The mean value of Zn was 0.266±0.083 mg/L in 2014 and 0.206±0.0957 mg/L in 2015. The mean value for the 24 months was 0.330±0.093 mg/L. The mean value of Fe was 0.275±0.057 mg/L in 2014 and 0.231±0.0988 mg/L in 2015. The mean value for the 24 months was 0.253±0.082 mg/L. The mean value of Pb was 0.0089±0.013 mg/L in 2014 and 0.018±0.0261mg/L in 2015. The mean value for the 24 months was 0.0135±0.021 mg/L. The results obtained from the samples was in the order of Zn > Fe > Pb > Cd. The result obtained showed that Cd and Zn were within the acceptable range or limit by the relevant international regulatory bodies cited. Fe was either higher or lower than the acceptable limits depending on the agency. Pb was within the acceptable limit in 2014 but higher than the acceptable value in 2015. This research therefore showed the need to put adequate legislative, monitoring and implementing measures in place to put the discharge of industrial wastes and effluents under check. This will help to reduce the negative effects of the pollutants transmitted to receiving rivers, since they will be made through these guidelines to treat effluents to the acceptable standard before discharge to the environment.

Keywords: Wastewater, effluents, heavy metals, aquatic pollution, oily

INTRODUCTION

Despite the fact that all over the world countries are putting up both legislative and practical efforts to arrive at a pollution free regime, yet the discharge of industrial effluents into the environment has continued unabated [1]. The role played by industries in the economic growth of any nation cannot be overemphasized. The very high demand on natural resources by man has resulted in the destruction of the ecosystem which has culminated in various ecological and human disasters, subsequently contributing to environmental pollution problems [2]. The increase in industrial development has led increased use of oil and oil related chemicals. Despite the different technical and managerial know how applied in the treatment of oily effluents, yet these methods still show to be imperfect and so still lead to pollution problems. The processes involved in the production of oil which involves oil exploration, exploitation, refining, oil storage, transportation and petrochemical industries give rise to a lot of oily wastewater [3].

Wastewater causes pollution of viable water sources such as groundwater, rivers and streams and consequently affects aquatic plants and animals which dwell in the environment. It endangers human health, since they are the end users of water and or its resources. It affects crops and animal production and destroys the natural environment through alteration of plant and animal diversity and the geographic landscape of the area affected [4].

Since the advent of oil exploration and exploitation in Nigeria, the country has been subjected to different vulnerabilities associated with such activities [5]. Apart from the Refinery and petrochemical plants built by the Nigerian government to refine the crude and also produce other by- products associated with petroleum, other industries have also emanated which depends on them. These industries generate wastes of different compositions of both organic and inorganic chemicals [6]. The unwanted components in the production processes are considered as wastes and so must be discarded.

These wastes in most cases are discharged in form of wastewater into rivers without adequate treatment to required standard, and so become dangerous and toxic to the environment [7]. Moreover, even when the effluents are treated and continuously discharged into the aquatic environment, there is the possibility of bioaccumulation beyond permissible or threshold values. Untreated or partially treated wastes and effluents contains different quantities of heavy metals which possess the capacity to affect aquatic biota and also become components of the food chain, thereby affecting human beings [8], who may use the water directly or indirectly and also use the plants and animals for food.

This study was carried out to determine the concentrations of some heavy metals in effluents discharged by an oil industry in Port Harcourt.

MATERIALS AND METHODS

The wastewater samples were collected at the final effluent discharge point, where the waste water from the premises which is channeled through an oil- water separator empties into the public drainage. Plastic cans of 1.0 L capacity was used for the collection of the water samples. Before the collection of the samples, the cans were thoroughly rinsed with hydrochloric acid, and further washed with de-chlorinated tap water to eliminate any acid that might be left over. At the point of collection, the cans were rinsed with the wastewater sample to be collected and then filled up and sealed with a cover. The sampling was done bi-monthly for two years (January 2014- December 2015). In order to prevent metal precipitation, 1.5 cm^3 of nitric acid was added as a preservative.

The wastewater samples were then transferred to the Jaros Inspection Services Limited for metallic analysis. The concentrations of cadmium (Cd), zinc (Zn), iron (Fe), and lead (Pb) in wastewater effluents were analyzed using an atomic absorption spectrophotometer (UNICAM 929) fitted with solar software. The results obtained from the duplicate samples were expressed as mean ± SD for each of the months. The total annual input of the metals and the mean ± SD concentration values for each of the years were also determined.

RESULTS AND DISCUSSIONS

The result of monthly concentrations of the heavy metals measured in 2014 showed that cadmium (Cd) was not detected. Zinc (Zn) values ranged from 0.112 ± 0.043 - 0.374 ± 0.053 mg/L. The lowest value of Zn concentration was observed in the month of July, while the highest value was observed in the month of June. Iron (Fe) values fluctuated from 0.112 ± 0.081 - 0.339 ± 0.050 mg/L, with the lowest and highest values observed in the months of August and March respectively. Lead values were undetected between the months of January – August. However, a range of 0.021± 0.030 - 0.035 ± 0.049 mg/L was observed in the later months, with the highest value observed in November (Table 1).

Table 1: Mean monthly concentration (± SD) of heavy metal in an oily waste water effluent in 2014

Months	Heavy Metals			
	Cd	Zn	Fe	Pb
January	-	0.337±0.036	0.291±0.019	-
February	-	0.256±0.0622	0.311±0.034	-
March	-	0.279±0.141	0.339±0.050	-
April	-	0.300±0.015	0.306±0.158	-
May	-	0.348±0.037	0.285±0.028	-
June	-	0.374±0.053	0.286±0.021	-
July	-	0.112±0.043	0.249±0.028	-
August	-	0.215±0.006	0.112±0.081	-
September	-	0.148±0.066	0.278±0.001	0.023±0.027
October	-	0.206±0.148	0.247±0.042	0.021±0.030
November	-	0.359±0.054	0.279±0.046	0.035±0.049
December	-	0.263±0.048	0.312±0.012	0.028±0.021

- Undetected

The results of monthly concentrations of the heavy metals measured in 2015 showed that cadmium (Cd) was not detected, zinc (Zn) concentration varied from a low of 0.036±0.010mg/L in July to a higher level of 0.368±0.325mg/L in October. Iron (Fe) fluctuated from 0.071±0.002 mg/L to 0.377±0.148 mg/L obtained in the months of September and May respectively. Lead values were undetected in the months of February – April, and also in September and November. However, the highest and lowest values being 0.087±0.105 and 0.002±0.021 mg/L were observed respectively in the months of October and May (Table 2).

Table 2: Mean monthly concentration (±SD) of heavy metal in an oily waste water effluent in 2015

Months	Heavy Metals			
	Cd	Zn	Fe	Pb
January	-	0.303±0.037	0.299±0.021	0.0158±0.022
February	-	0.199±0.045	0.308±0.051	-
March	-	0.200±0.015	0.250±0.023	-
April	-	0.204±0.021	0.269±0.060	-
May	-	0.185±0.197	0.377±0.148	0.002±0.021
June	-	0.052±0.031	0.308±1.03	0.041±0.001
July	-	0.036±0.010	0.111±0.096	0.031±0.00
August	-	0.177±0.199	0.127±0.156	0.011±0.010
September	-	0.293±0.107	0.071±0.002	-
October	-	0.368±0.325	0.136±0.105	0.087±0.105
November	-	0.265±0.067	0.198±0.007	-
December	-	0.192±0.151	0.315±0.040	0.029±0.017

- Undetected

Data obtained from the analyzed effluents showed that Cd was absent in the effluents throughout the years under investigation. The mean values of Zn were 0.266 ± 0.083 and 0.206 ± 0.0957 mg/L for 2014 and 2015 respectively. The minimum and maximum concentrations of Zn obtained in 2014 were 0.148 ± 0.066 and 0.374 ± 0.053 mg/L respectively. The minimum and maximum values obtained in 2015 were 0.036 ± 0.010 and 0.368 ± 0.325 mg/L. The mean concentrations of Fe in the effluent were 0.266 ± 0.083 and 0.206 ± 0.0957 mg/L in 2014 and 2015 respectively. The minimum and maximum concentrations of Fe in 2014 were 0.112 ± 0.081 and 0.339 ± 0.050 mg/L respectively, and those of 2015 (minimum and maximum) are 0.071 ± 0.002 and 0.339 ± 0.050 mg/L respectively. The mean concentration of Pb in the years (2014 and 2015), were 0.0089±0.013 and 0.018 ± 0.0261 mg/L respectively. The minimum values for the two years were 0.00 ± 0.00 each while the maximum values were 0.035 ± 0.049 and 0.087 ± 0.105 mg/L in 2014 and 2015 respectively (Table 3).

Table 3: The mean, minimum and maximum values of heavy metals in mg/L in effluents

Metal		2014	2015
	Mean	0.00	0.00
Cd	Minimum	0.00	0.00

	Maximum	0.00	0.00
Zn	Mean	0.266±0.083	0.206±0.0957
	Minimum	0.148±0.066	0.036±0.010
	Maximum	0.374±0.053	0.368±0.325
Fe	Mean	0.275±0.057	0.231±0.0988
	Minimum	0.112±0.081	0.071±0.002
	Maximum	0.339±0.050	0.377±0.148
Pb	Mean	0.0089±0.013	0.018±0.0261
	Minimum	0.00±0.00	0.00±0.00
	Maximum	0.035±0.049	0.087±0.105

The results of all the monthly concentration of the heavy metals in each of the investigated years showed that Cd was not detected, while Zn was 3.235 and 2.474 mg/L in 2014 and 2015 respectively. The combined value for the two years was 5.709 mg/L with an average value of 0.330 ± 0.093 mg/L. The concentration of Fe was 3.292 and 2.162 mg/L in 2014 and 2015 respectively. The combined value for the two years was 5.454 mg/L with an average value of 0.253 ± 0.082 mg/L. The concentration of Pb was 0.2503 and 0.2168 mg/L in 2014 and 2015 respectively, and the combined value for the two years was 0.4671 mg/L with an average value of 0.0135 ± 0.021 mg/L (Table 4).

Table 4: Total measured discharge of heavy metal concentrations (mg/L) from the oil firm

Year	Cd	Zn	Fe	Pb
2014	-	3.235	3.292	0.2503
2015	-	2.474	2.162	0.2168
Total	-	5.709	5.454	0.4671
Mean±SD	-	0.330±0.093	0.253±0.082	0.0135±0.021

- Undetected

Table 5: International Drinking Water Guidelines (maximum limit) for the analyzed metals

Metal	WHO	SON	USEPA	EU	Canada	Japan	Omani *
Cd	0.003	0.003	0.005	0.005	0.005	0.1	0.01
Zn	5.5	5.0	1.0	**	5.0	**	**
Fe	3.0	0.3	2.0	**	0.3	**	5
Pb	0.01	0.01	0.015	0.01	0.01	0.05	0.2

* Maximum level for restricted irrigation. ** Not available

Heavy metals are natural constituents of the environment, which in most cases occur at very trace amounts. They are classified into a special group of elements known as transition element or transition metals. At relatively high concentrations, they become hazardous to both plants and animals [1,8].The difference between trace or heavy metals from other pollutants is that they have the tendency to accumulate in the environment unnoticed to the point that consumers of plants and animals contaminated with them become poisoned [9].

Cadmium (Cd) was not detected in the effluents throughout the period of examination probably because the materials used may not have contained it or the little that may have been contained would have been removed during the treatment process. The non-detection of Cd in effluents of industrial wastewater in this work corroborates the findings of [10], who worked on effluents from refinery and petrochemical company. However, other authors [11,12,13] observed the presence of Cd in different wastewater effluents. Sources of Cd contamination of surface water are paints, pigments, glass enamel and corroding pipes. Another source of Cd is burnt tyres on road surfaces which are transported to surface waters through runoffs [1]. Cd when consumed is very toxic and accumulates in the body. Its toxicity lies in the fact that it disrupts calcium homeostasis and metabolism [14].

The observed values for Zn in the effluents were below the recommended standards from all international standards in Table 5. The observed value of Zn in this study was lower than values obtained in similar studies [10,11,13]. Sources of Zn in water include: pesticides, galvanic industries, battery production and paints. Very high concentration of Zn can lead to diseased conditions such as necrosis and chlorosis and further consequence of plant growth inhibition [8]. Other effects of Zn on humans include vomiting (when over 500 mg of Zn is consumed as $ZnSO_4$). Reports showed that mass poisoning by Zn has been associated with drinking of acidic beverages in galvanized containers. Other symptoms of Zn toxicity after ingestion include fever, nausea, vomiting, stomach cramps, and diarrhea [15]. Depending on its concentration, Zn can be a nutrient as well as a poison or environmental contaminant. Zn is mostly absorbed in the small intestine but do not form free radicals and as such exhibits antioxidant characteristics. It is a component of several enzymes such as proteases, anhydrates and super oxides and is involved in the synthesis of proteins, protection against oxidant properties of free radicals and helps in the production of energy [16].

The concentrations of Fe detected in the oily effluents were lower than the standard limits of WHO, USEPA and Omani, but within the range specified by SON and Canada. Fe observed in this study may be from the natural component of the source of the treated effluents. Fe is a natural component of the ecosystem and comes next to oxygen in abundance. Iron exists in two different forms in water, either as ferrous iron, which is soluble or ferric iron, the insoluble form. Fe sources in water come from natural deposits, industrial wastes, refining of iron ores and corrosion of iron containing materials. The presence of Fe in water promotes bacterial growth, which lead to slimy surface on metal works, a result of bacterial deposition on the surface of the metal [17]. Fe adds taste to water at concentrations above 0.3 mg L^{-1}, stains cloths and other wares at concentrations above 0.3 mgL^{-1} and also at concentrations above 0.05 – 0.1 mgL^{-1}, it introduces colour and turbidity to water [18].

Pb was either detected or not detected in the effluents in some of the months in the years of investigation. Similar result was obtained on Pb in pharmaceutical effluent [19]. The values obtained in those months were higher than the standard limits set by relevant international bodies except that of Japan and Omani (for irrigation). The presence of Pb may have resulted from inefficient treatment of the discharge effluents. Pb sources in the environment include wastewater, bio solids, manures, industrial wastes, mining processes, air borne sources which are precipitated by rain, fertilizers, pesticides, lead cell batteries, alloys and solders, pigments and paints, cable sheathing, plastic stabilizers and petrol antiknock (tetra ethyl lead) [20,21]. Pb is a potent poison to children even at very low concentration. The presence of Pb in children causes behavioural and learning problems, low intelligent quotient, retarded growth, anaemia and hearing problems. At higher levels of toxicity, it can lead to coma and death. Pb stored in the body get accumulated or stored in the bones, which results in fetal development problems, abortion or premature birth in pregnant women. Generally in adults, it produces cardiovascular effects, increases blood pressure (hypertension), renal and reproductive disorder in both males and females [20].

CONCLUSION

The results obtained showed the presence of heavy metals Zn, Fe and Pb but Cd was undetected. The concentrations of the metals in the effluents were in the order: Zn> Fe >Pb> Cd. This is an indication that heavy metals were not completely eliminated from the effluents during the treatment processes or that there was complete neglect of duty. Considering the concentration of the metals observed from the samples, it follows that enormous amount or quantity of heavy metals is being discharged into the receiving water body annually, which will constitute threat and danger to the environment in the short and long run. Therefore proper environmental surveillance should be put in place to check the activities of effluents discharging companies and very strong penalties be given to offenders.

REFERENCES

1. Lokhande, R. S., Singare, P. U., and Pimple, D. S. Pollution in water of Kasardi River flowing along Taloja Industrial Area of Mumbai, India. *World Environment*, 2011, 1(1): 6-13.
2. Nkwocha, A. C., Ekeke, I. C., Kamen, F. L. and Oghome, P. I. Quality assessment of effluent discharges from vegetable oil plant. *Ethiopian Journal of Environmental Studies and Management*, 2013, 6: 717-723.
3. Ahmed, A. F., Ahmad, J., Basma, Y., Ramzi, T. *Journal of Hazardous Materials*, 2007, 141: 557–564.
4. Huo, X. B., Xuan, X. M., Jia, J. P. and Wang, Y. L. *Shangai Chemical Industries*, 2003, 9: 11-14.
5. Nduka, J. K. and Orisakwe, E. O. Effect of Effluents from Warri Refinery and Petrochemical Company (WPRC) on water and soil qualities of "Contigious Host" and impact on communities of Delta State, Nigeria. *The Open Environmental Pollution and Toxicology Journal*, 2009, 1:11-17.
6. Suleimanov, R. A. Medicsina Trudai Promy Shlennaia. *Ekologiia*, 1995, 12:31-36.
7. Bay, S., Jones, B.H., Schiff, K. and Washburn, L. *Marine Environmental Research*, 2003, 56:205-223.
8. Tripathi, N. D. and Singh, B. K. Study of toxicity of heavy metal pollutants in wastewater effluent samples. *International Journal of Latest Trends in Engineering and Technology*, 2016, 6(4): 341-345.
9. Kpee, F. and Edori, O. S. Trace metals content in shore crabs (Cardisoma Guanhumi) from coastal area of Port Harcourt City, Rivers State, Nigeria. Archives of Applied Science Research, 2014, 6 (6):16-21

10. Uzoekwe, S. A. and Oghosanine, F. A. The effect of refinery and petrochemical effluent on water quality of Ubeji Creek Warri, Southern Nigeria. *Ethiopian Journal of Environmental Studies and Management*, 2011, 4(2): 107-116.
11. Ahmed, I., Mukhtar, M. D. and Kawo, A. H. Environmental pollution by heavy metals from some industrial effluents at Sharada, Kano, Nigeria. *Journal of Food, Agriculture & Environment*, 2007, 5 (2): 315-317.
12. Oguzie, F. A. and Okhagbuzo, G. A. Concentrations of heavy metals in effluent discharges downstream of Ikpoba River in Benin City, Nigeria. *African Journal of Biotechnology*, 2010, 9(3): 319-325.
13. Joshi, V. J. and Santani, D. D. Physicochemical Characterization and Heavy Metal Concentration in Effluent of Textile Industry. *Universal Journal of Environmental Research and Technology*, 2012, 2(2): 93-96.
14. Emory, E., Pattole, R., Archiobold, E., Bayorn, M. and Sung, F. Neurobehavioral effects of low level exposure in human Neonates. *America Journal of Obstetrics and Gynecology,* 2001, 181: 5-11
15. Elinder, C. G. Zinc. In: Friberg, L., Nordberg, G. F. and Vouk, V. B. eds. Handbook on the toxicology of metals, 2nd ed. Amsterdam, Elsevier Science Publishers, 1986, 664-679.
16. Kaániová, M., Andreji, J., Stráai, I., Ha□ík, P., Ubo, J., and Fel□öciová, S. (2007). Microbiological quality of fish meal and the effect on the heavy metals contents. *Slovak Journal Animal Science*, 2007, 40(4): 185-188.
17. Department of National Health and Welfare (DNHW), Canada. Nutrition recommendations. The report of the Scientific Review Committee. Ottawa. 1990.
18. WHO Guidelines for drinking-water quality, 2nd ed. Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, 1996.
19. James, O. O., Nwaeze, K., Mesagan, E., Agbojo, M.,Saka, L. K. and Olabanji, D. J. Concentration of heavy metals in five pharmaceutical effluents in Ogun State, Nigeria.*Bulletin of Environment*, *Pharmacology and Life Sciences*, 2013, 2(8): 84-90.
20. WHO. Lead in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality World Health Organization, 2011.
21. Sardar, K., Ali, S., Hameed, S., Afzal, S., Fatima, S., Shakoor, M. B., Bharwana, S. A. and Tauqeer, H. H. Heavy metals contamination and what are the impacts on living organisms. *Greener Journal of Environmental Management and Public Safety*, 2013, 2(4): 172-179.