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Full Length Research Article

STUDIES ON THE PHYSICOCHEMICAL CHARACTERISTICS AND BIOREMEDIATION POTENTIALS OF SURFACE WATER AND EFFLUENT IN KADUNA REFINERY ENVIRONMENT

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ABSTRACT

Petroleum operations are potential sources of environmental pollution capable of contaminating rivers which pass through the industrial areas and consequently affect human health. Hence there is need for bioremediation interventions. The aim of this study was to provide data on the physical and chemical characteristics of surface water and effluent in the study area which could be used for bioremediation strategy in the area. Surface water and effluent samples were analysed for physicochemical parameters using standard methods. The surface water and effluent were acidic. Temperature was found to be within the range favourable for bioremediation. The dissolved oxygen (DO) is not limiting for bioremediation. Electrical conductivity and chloride were high. Low levels of nitrate nitrogen (0.30 – 2.42mg/L) observed are limiting for bioremediation. The effluent and Romi River downstream had BOD greater than the allowable limit (10mg/L). Biostimulation is recommended as bioremediation strategy in the site.

Keywords: Bioremediation, Surface Water, Effluent, Characteristics, Kaduna Refinery.

INTRODUCTION

There has been a vast increase in environmental pollution, in particular, pollution by petrochemical industries contaminants (Al – Amin 2013; Damau *et al*., 2020) It has become a very serious environmental problem. Pollution can cause harmful damage to the environment and human health (Amadi *et al.,* 2014). Pollutants from petrochemical industries are introduced into the environment through intentional or accidental spillage, biological waste treatment units, during cleaning of processing equipment, waste dump site among others. In KRPC there are four potential sources through which crude and petroleum product are spilled into the environment. A pipeline from Warri brings crude oil into the KRPC facilities. The pipelines are buried underground coming closer to the surface in the vicinity of the factory. Two pipelines carry away refined petroleum products from the refinery to Jos and Kano respectively. These pipes are located below the ground level. There are also storage tanks for refined petroleum products. The storage tanks are all located above the ground and they all constitute potential spill points.

There are several hazards associated with petroleum hydrocarbon contamination. Among them are several pathologies including encephalopathy, arrhythmia, acidosis and dermatitis (Tormoehlem *et al.,* 2014). Aspiration which results in pneumonitis is the most dangerous consequences of acute hydrocarbon ingestion (Mickiewicz and Gomez, 2006). Polyaromatic hydrocarbons are toxic, mutagenic and carcinogenic (Yu 2002; Rengarajan *et al.,* 2015; Abdel-Shafy and Mansour 2016). Hence there is need to remediate contaminated environment (Mahjoubi *et al.,* 2018).

Among the options to remediate contaminated water, bioremediation stands out (Obukohwo *et al.,* 2020). Bioremediation is based on the metabolic capabilities of micro-organisms. It is regarded as the most basic and reliable way to remove contaminants, in particular petroleum and recalcitrant compounds. Moreover, it is cost effective and environmental friendly. There are two general approaches to bioremediation; environmental modification such as through nutrient application and aeration, and the addition of special assemblage of naturally occurring oil degrading microorganisms, or introduction of genetically engineered microorganisms (GEM), with special oil degrading properties (seeding). The second approach is known as bioaugmentation while the first is referred to as biostimulation (Prince and Atlas 2005). There had been recommendations from research works that the contaminated effluent and water in KRPC should be subjected to bioremediation (Al - Amin, 2013; Buggy, 2020). A very vital approach to bioremediation is site characterization. Hence this study will provide data that will assist in bioremediation strategy for the environment.

MATERIALS AND METHODS

The study site was KRPC, a subsidiary of Nigeria National Petroleum Corporation (NNPC), which is located at kilometre 16 along Kaduna-Kachia highway, Kaduna, Nigeria. (Fig. 1).

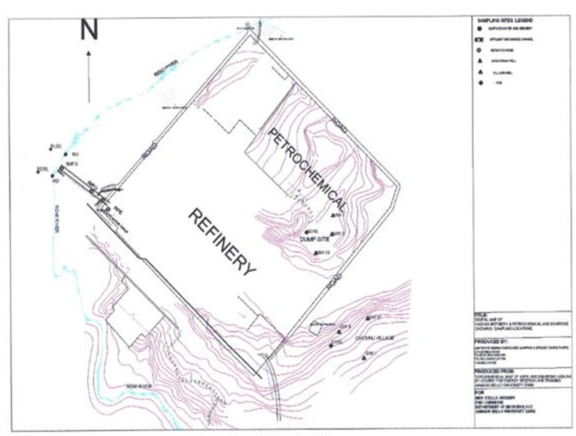

Fig. 1: Map of Kaduna Refinery and Petrochemical Company
Source: Adapted from Topographical map of KRPC by Centre for Energy Research and Training, Ahmadu Bello University, Zaria.

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Sampling sites
Samples were obtained from the following sites.
Wastewater treatment facility and effluent discharge channel. The stations were designated RPE (Retention pond effluent), ORE (Outlet of retention pond effluent), IMFO (100 meters from outlet of retention pond,) and 5MFO (500 meters from outlet of retention pond.
Wastewater receiving water body (Romi River). The surface water sampling stations were coded RU (100m upstream of effluent discharge point on Romi River), and RD (100m downstream of effluent discharge point on Romi River).

Collection of Samples
Surface water samples were collected at a depth of 10cm in the direction of water flow, with 250 mL transparent plastic containers. Sterile wide mouth, screw-capped bottles were used. Samples were stored in a cool box and taken to the laboratory for analysis at KRPC.

Physicochemical Analysis of Water Sample
The pH and temperature of the samples were measured using a pH meter (Horiba m-13) and Horiba m-13 temperature instrument respectively. A microprocessor conductivity metre (Harma instruments 419932) was used to determine the electrical conductivity. Turbidity was determined with automated turbidity meter (Hanna L. P. 2000). Total solids and total dissolved solids were determined gravimetrically. Suspended solid was calculated by subtracting total dissolved solids from total solids. Phosphate, sulphate, sulphide, ammonia-nitrogen and nitrate concentrations were determined using spectrophotometer (HSCH DR/2010). Chloride was determined by silver nitrate method of chloride analysis using a digital titrator (HACH model 16900). BOD was determined using titrimetric method. Dissolved oxygen was measured before and after incubation. BOD was computed based on the difference between the initial and final dissolved oxygen (APHA 2002).

RESULTS AND DISCUSSION
In surface water and effluent samples, a site variation in pH was observed (Fig.2).The results indicated that the pH of the effluent and downstream surface water were acidic (2.92 – 4.87), while the upstream surface water was slightly acidic (6.59). In another study by Al-Amin (2013), surface water samples from the area had average acidity of pH 5.7. Low pH of the effluent samples may be attributed to inadequate effluent treatment or microbial degradation activity. According to Nwachukwu *and* Ugoji (1995), microbial utilization of hydrocarbons usually lead to formation of organic acids. Since this pH can influence the process of bioremediation, pH adjustment may be needed for bioremediation exercise in the site. Most bacteria and fungi capable of degrading hydrocarbon require a neutral pH (Leahy and Colwell, 1991*;* Margesin and Schinner, 2001).

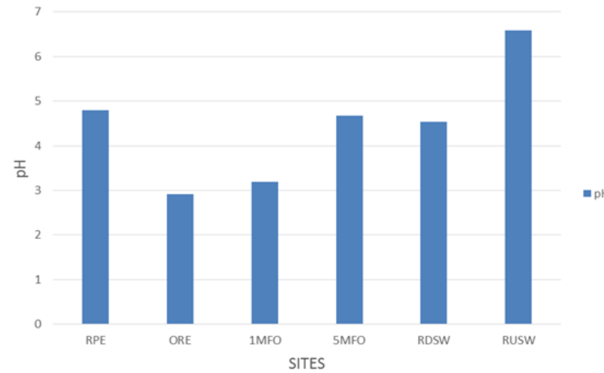

Fig. 2: Mean pH of the effluent and surface water from Kaduna Refinery environment.

The temperature of the sites (Fig. 3) fell within the mesophilic range, which according to the report of Nwachukwu and Ugoji (1995), favour microbial growth during bioremediation. Also, Boopathy (2000) confirmed that the degradation of pollutant in mesophilic temperatures is better and more efficient than the degradation at very low or high temperatures.

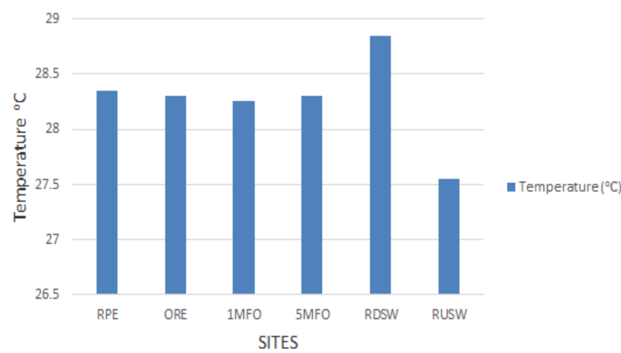

Fig. 3. Mean Temperature (°C) of the effluent and surface water from Kaduna Refinery environment.

Electrical conductivity (EC) is a reflection of the status of inorganic pollutants and is a measure of total solids and ions species in water (WHO 1996). The electrical conductivity values (Fig.4) ranged between 105.50 to 1057.00 µs/cm. The least value 105.50µs/cm was recorded in Romi River upstream. The highest (1057.00µs/cm) was found in effluent from the outlet of retention pond (ORE). Higher EC values observed at the effluent sites and Romi River downstream surface water is probably indicative of the presence of possible pollutants. Obukohwo *et al.,* (2020) reported that the effluent from the refinery contained heavy metals and other toxicants. It is important to note that in the refinery during the process of refining crude oil, the desalted water which is rich in organic waste, trace metals, inorganic salt, and other waste matters generated are channelled to waste water treatment plant, for treatment before the effluent is discharged into Romi River (Adeniyi *et al.,* 2017*).* Therefore, high concentrations of electrical conductivity and chlorides are not surprising. Lekwot *et al.* (2012) also observed that the electrical conductivity, pH, total suspended solids (TSS), total dissolved solids (TDS) of Romi River were quite high and exceeded the maximum permissible limit given by the National Standard Nigeria and World Health Organization (WHO). Al-Amin (2013) also observed high concentration of heavy metals

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in both water and soil samples from Kaduna refinery area. Buggu (2020) reported that the values of arsenic, cadmium, iron, manganese, nickel and lead in the river were greater than the maximum tolerable limits set by Standard Organization of Nigeria (SON) and WHO.

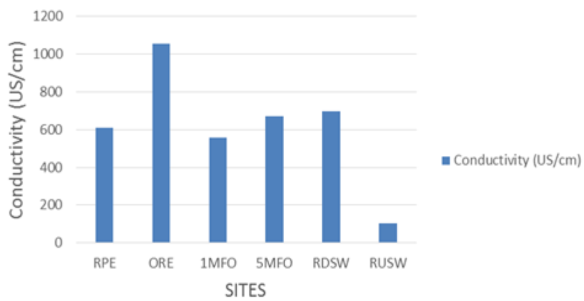

Fig. 4. Average conductivity (us/cm) of effluent and surface water from Kaduna Refinery environment.

The values for turbidity (Fig.5) ranged between 10.21 and 23.25 NTU. Highest turbidity (23.25 NTU) was recorded in outlet of retention pond site (ORE). This may be due to the fall of effluent at the site, which does not allow suspended solids to settle. High level of total solids (Fig.6) observed in water from Romi River is not unexpected and reflects the pollutant burden of the water. Rivers are exposed to surface runoffs from residential, commercial, industrial and farming areas.

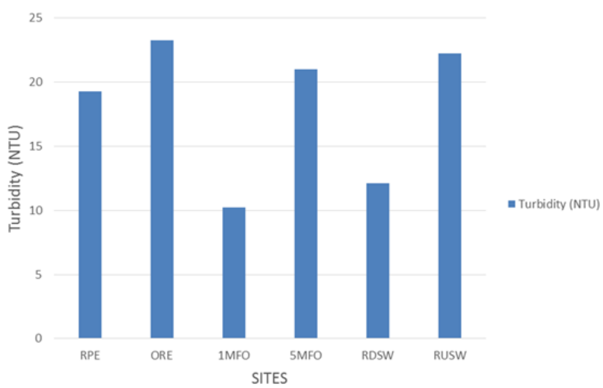

Fig. 5. Average (NTU) of effluent and surface water from Kaduna Refinery environment.

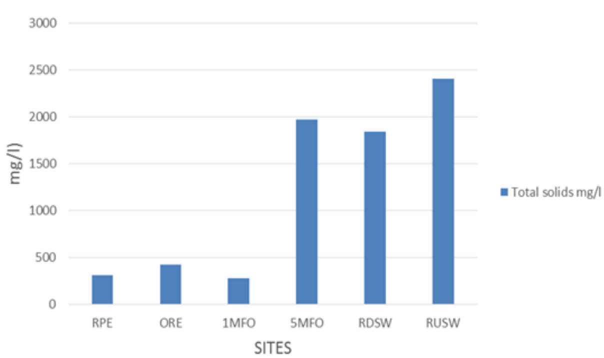

Fig. 6. Average total solids (mg/L) of effluent and surface water from Kaduna Refinery environment.

Low levels of phosphate (Fig.7) observed at all sites except Romi River downstream is limiting for microbial hydrocarbon degradation. Microorganisms require phosphorus as phospholipids in synthesizing cell membranes, as nucleotides to replicate nucleic acids, and as pyrophosphates for sugar phosphorylation during metabolism (Nwachukwu *et al.,* (2001). Higher phosphate level noted in Romi River downstream (46.10mg/l) could be due to phosphate runoff from fertilizer application in farmlands at the banks of the River.

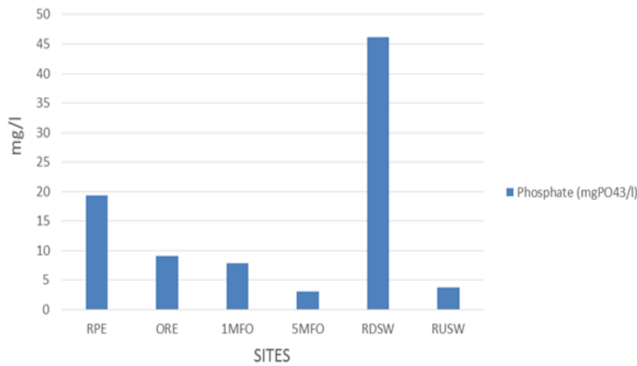

Fig. 7. Average Phosphate (PO_4^{3-}/L) mg/L of effluent and surface water from Kaduna Refinery environment.

High sulphate concentrations (Fig. 8) observed in the effluent samples and Romi River downstream surface water (88.00 – 171.70mg/L) are suitable for sulphate reducing bacteria activity (Leethem *et al.,* 1995; Thi *et al.,* 2021). However, low concentration of sulphide observed in these sites, indicated probably lack of reduction of sulphate to sulphide. The fact that sulphate was not detected in Romi River upstream surface water, suggests that the refinery effluent is probably the source of the sulphate in Romi River downstream surface water. It is a known fact that all crude oil contains sulphur compounds in varying degrees (Van Hamme *et al.,* 2003). In addition, in the refinery waste water treatment system, sulphuric acid is used as a pH controller in the biofilters and aluminium sulphate is used as a coagulant for the removal of suspended solids in the biofilters.
The significance of sulphate in water are possible reduction of sulphate to hydrogen sulphide, corrosion of concrete and possible gastrointestinal irritation. It is important to note that the refinery effluent discharge channel is concrete lined; therefore, the concrete channel may also be exposed to possible concrete corrosion.

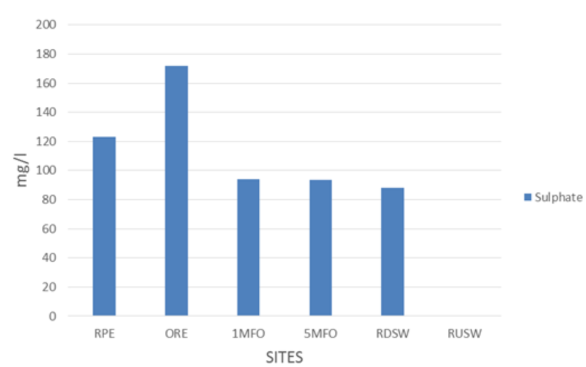

Fig. 8. Mean sulphate ($mgS04^{2}$) mg/L of effluent and surface water from Kaduna Refinery environment.

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The relatively higher concentration of Ammonia nitrogen (27.06 – 46.08 mg/l) (Fig.9) in three effluent sites including the retention pond is indicative of the presence of nitrogenous organic matter in the effluent samples. It also indicates that nitrifying bacteria may be present at these sites. Ammonia nitrogen is toxic. The maximum concentration of ammonia allowed for discharge into inland waters by petroleum refinery is 0.21 mg/l (FEPA, 1991). Low levels of nitrate-nitrogen (Fig.10.) observed in the sites (0.30 -2.42 mg/l) is limiting for bioremediation. Many investigators have reported that concentrations of available nitrogen in water is severely limiting to hydrocarbon biodegradation (Atlas and Bartha, 1992*;* Prince and Atlas 2005*;* Vyas and Dave, 2010).

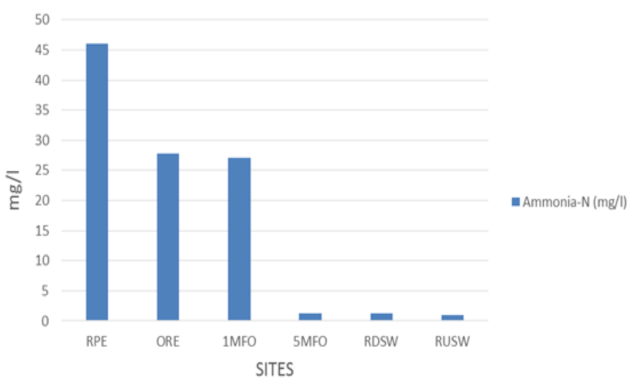

Fig. 9. Mean Ammonia Nitrogen (mg/L) of effluent and surface water from Kaduna Refinery environment.

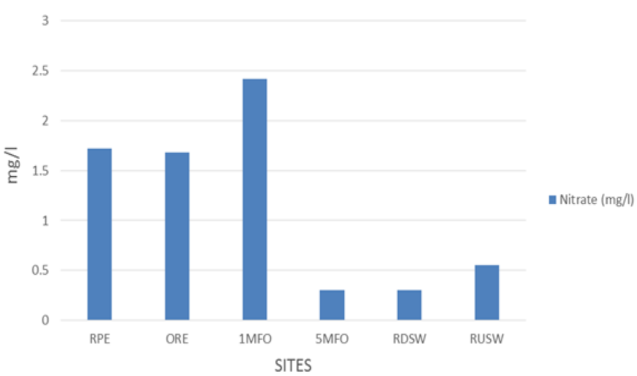

Fig. 10. Mean Nitrate (mg/l) of effluent and surface water from Kaduna Refinery environment.

In unpolluted water the chloride levels are often below 10mg/L Tebbutt (1990). High chloride level in the effluent samples (50.75 - 70 mg/L) (Fig.11) is probably indicative of pollution, and sewage contamination. This may lead to corrosion problems in the system, and retardation of the rate of microbial degradation of hydrocarbons. Higher chloride concentration found in the effluent sites could probably be from metal contamination and domestic waste from the plant toilets that go into the waste water treatment area. It is a proven fact that sodium chloride, a common component of diet passes unchanged through the digestive system (WHO 1996). Chikere and Okpokwasili (2004) reported that domestic waste contributes copious amounts to petrochemical effluent. However, salt tolerant organisms would be expected to thrive in the environment.

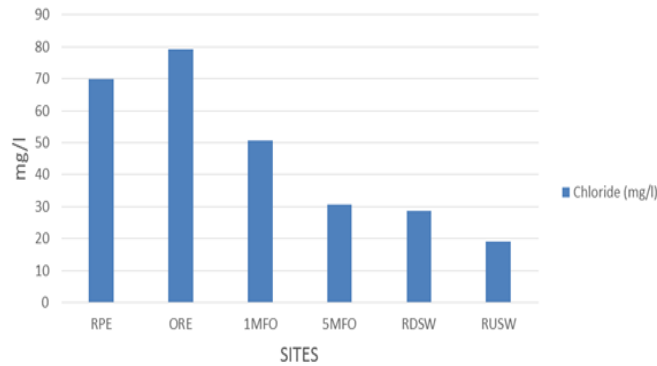

Fig. 11. Mean chloride (mg/L) of effluent and surface water from Kaduna Refinery environment.

Dissolved Oxygen (DO) levels (Fig.12) observed in the sites (6.94 – 7.82 mg/L) are not limiting for bioremediation, rather the DO levels are indicative of potentials for oxidation of organic matter in the sites. Aerobic degradation is the most attractive of the microbial processes for degradation of gasoline component in groundwater, because it proceeds at a more rapid rate and does not produce the noxious by products associated with anaerobic decomposition (Mohammed *et al*., 1996; Geng, 2016).

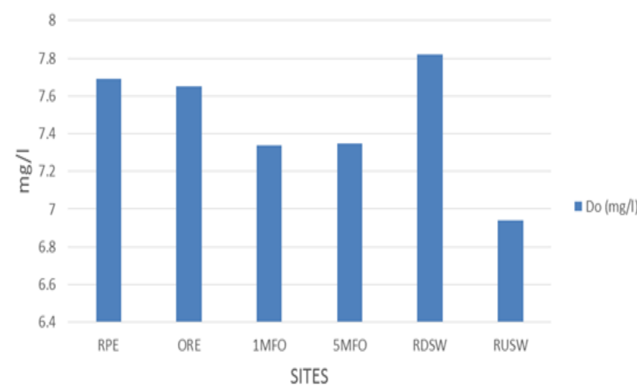

Fig. 12. Mean DO (mg/L) of effluent and surface water from Kaduna Refinery environment.

The maximum concentration of biochemical oxygen demand (BOD) allowed for petroleum refinery effluent discharge into inland water is 10mg/l. In this study the effluent samples and Romi River downstream surface water had BOD greater than 10mg/l, while Romi River upstream surface water had BOD (4.41mg/l). This is also not surprising, since desalted water rich in trace metals and inorganic salt are channelled to the waste water (effluent) treatment plant in the refinery. The high BOD of Romi River downstream could be due to the influence of the effluent discharged into it, since Romi River upstream had less BOD value. Since BOD levels signify the extent of biodegradable organic matters, the effluent retention pond had the highest amount of biodegradable organic matter, and should be bioremediated.

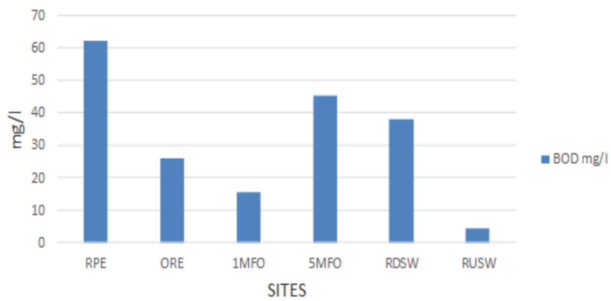

Fig. 13. Average BOD (mg/L) of effluent and surface water from Kaduna Refinery environment.

Conclusion

The pH of the effluent and downstream surface water was acidic. The pH is not suitable for bioremediation strategy. The temperature and DO level were found to be favourable for bioremediation strategy. The electrical conductivity values, chloride concentration, BOD level and the level of turbidity observed are indicative of pollution. Low levels of phosphate and nitrate are limiting for bioremediation. High sulphate levels observed is indicative of corrosion problems.

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