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Kinetic Evaluation of Petroleum Refinery Wastewater Biodegradation in an Activated Sludge Process

O. J. Momoh[1, *], P.C Okonkwo[2] and L.C Edomwonyi-Otu[3]

[1, 2] Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State, NIGERIA
[3]Department of Chemical and Petroleum Engineering, Delta State University, Delta State, NIGERIA

Abstract

Experimental assessment of process kinetic is essential for process modelling and can serve as a useful tool to improve process performance. In this study, kinetic evaluation of petroleum refinery wastewater (PRWW) biodegradation in an activated sludge process (ASP) was carried out in a 25 L ASP reactor which was operated within the conventional aeration mode of 2-10 hours, hydraulic retention time (HRT), effluents from the secondary sedimentation tank were analyzed at various HRT for biochemical oxygen demand (BOD) and biomass growth. The data obtained were analyzed and fitted to different related kinetic models which show that the biodegradation of PRWW in ASP follows the Modified Monod Kinetic Model, amongst the related models evaluated, with 0.9745 correlations with the experimental data. Physicochemical characterization of the PRWW used for the study was carried out using the Standard Methods for the Examination of Water and Wastewater; which gave a biodegradability index of 0.3333.

Keywords: *Kinetic; Petroleum refinery; Wastewater; Activated Sludge; Biodegradation.*

1.0 INTRODUCTION

Petroleum refining processes utilize large quantity of water and generate mostly hydrocarbon-contaminated wastewater streams which have negative impact on the environment, if discharged without proper treatment [1]. Therefore, stringent petroleum refinery wastewater discharge regulations are made in many countries as a way of addressing this problem. Different industries are now making efforts to minimize the quantity of their wastewater generations and to efficiently treat the generated wastewater in order to meet environmental regulatory standards. According to Radelyuk *et al* [2] the discharge of partially treated or untreated industrial wastewaters into the environment is potentially very harmful to human health as they can reach groundwater and create serious harm if consumed. As such, it is important to seek for effective wastewater treatment for industries generating large quantity of wastewater like the refineries and petrochemical industries, for environmental protection and to safeguard human health [3]. Generally, extensive understanding of process kinetic is needed to effectively design, control and to improve on the performance of existing processes [4].

A number of treatment processes exist for industrial wastewater treatment; the activated sludge process is a viable process in the treatment of industrial wastewater like the petroleum refinery wastewater because it is high in organics and bio-degradable compounds. Aerobic process like the activated sludge process is intensively explored for industrial wastewater treatment as a result of its ease of operation, high microorganism growth and organic carbon oxidation rates and resistance to toxic effects [1]. In addition, it is cost effective and environmentally friendly, it does not generate significant amount of secondary pollutants. In the activated sludge process mass of microorganisms (usually bacteria) is used to aerobically treat wastewater, organic contaminants in the wastewater provide carbon and energy required to encourage microbial growth and reproduction; nitrogen and phosphorous are sometimes added to promote this growth [5]. Essentially, the mechanism of the activated sludge process is such that microorganism takes in oxygen and feed on the organic materials in the wastewater which aids reproduction of more microorganisms for the process sustenance [4]. Existing activated sludge process plants still suffers from serious operational problems [1]. This makes it difficult for industries to meet their wastewater standard discharge limit. The determination of appropriate kinetic model for biological wastewater treatment is useful

***Corresponding author **(Tel:** +234 (0) 8035178102**)**

Email addresses: ojamesmomoh@gmail.com (O. J. Momoh), chemstprom@yahoo.com(P.C Okonkwo) and uceclce@ucl.ac.uk(L.C Edomwonyi-Otu)

to understand substrate utilization rate, sludge production and design of activated sludge process for wastewater treatment [6].

In the past, the designs of biological wastewater treatment processes were based on the empirical parameters such as hydraulic loading, organic loading and retention time developed by experience. At present, the design not only requires utilization of empirical data but also biological kinetic equations, which describe the growth of biological solids, substrate utilization rates, food-to-microorganism ratio, and the mean cell residence time [7]. The main objective of chemical kinetics is to enable the prediction of the rate at which given chemical substances react and to produce substances with desirable chemical characteristics in a controllable manner [8]. This study therefore evaluates different related kinetic models to ascertain the one that best describes petroleum refinery wastewater treatment in an activated sludge process.

2.0 MATERIALS AND METHODS

Petroleum refinery wastewater samples were collected from the wastewater treatment plant of Kaduna Refining and Petrochemical Company (KRPC) Kaduna, Nigeria for physical and chemical characterization using the American Public Health Association (APHA) Standard Method for the Examination of Water and Wastewater [9]. Figure 1 shows the components assembly drawing for the study, it includes a primary sedimentation tank for reducing the suspended solids in the influent wastewater to the bioreactor, the bioreactor in which the microorganisms and wastewater are maintained in suspension by aeration at desired hydraulic retention time, a secondary sedimentation tank for liquid-solid separation, an air compressor attached with an airflow meter to control airflow rate into the bioreactor and a sludge recycling system for returning activated sludge back to the bioreactor as shown in Figure 1.

Hydraulic retention time (HRT) of 2-10 hours was maintained in the reactor being the typical HRT for conventional aeration mode activated sludge process [10]. The BOD was monitored for a period of 10 hours HRT, at 2-hour difference in the reactor to provide sufficient oxygen for microbial degradation of the organic pollutant in the wastewater in a continuous flow mode. The air supply was done using an air compressor; an airflow meter was attached to the compressor to control the air flow rate which was kept at 10 L/min.

The petroleum refinery wastewater was collected into 50 L capacity wastewater storage tank. Using the bioreactor working volume of 20 L as a basis, the inlet and outlet valve of the bioreactor were set at various flow rates to achieve the desired HRT of 2,4,6,8 and 10 hours, at the end of each HRT, effluent from the secondary sedimentation tank was taken to measure BOD and biomass concentration using the American Public Health Association (APHA) Standard Method for the Examination of Water and Wastewater [9].

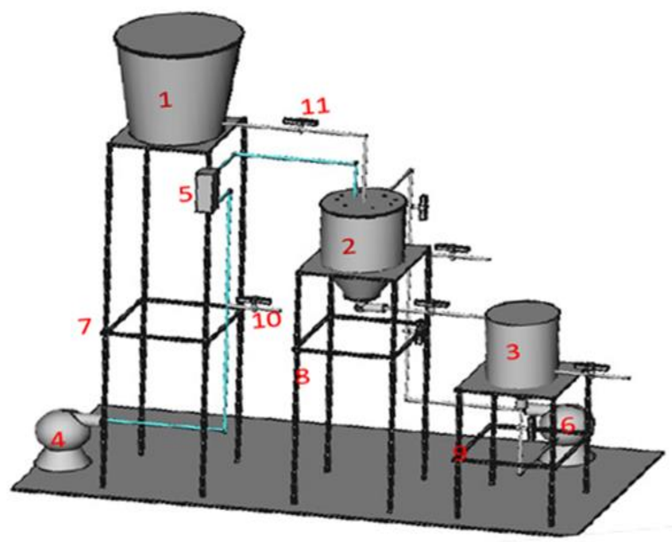

Figure 1: Complete Pilot Plant Assembly

KEY: **1**-Primary Sedimentation Tank, **2**-Bioreactor, **3**-Secondary Sedimentation Tank, **4**-Air Compressor, **5**-Rotameter, 6-Pump, **7**- Waste Water Tank Stand, **8**-Bioreactor Stand, **9**-Secondary Clarifier Stand, **10**- Gauge Valves, **11**- Pneumatic Valve.

Tables 1 show the various kinetic models investigated to ascertain their level of agreement with petroleum refinery wastewater biodegradation in activated sludge process. The model rate equations basically describe the relationship between rate of reaction and concentration of reactants while the order of reaction represents the overall stoichiometry coefficient of reactants in the reaction rate equation. These were determined by measuring the concentration of reactants as the reaction proceeds to completion, the results were compared with the corresponding results obtained from various standard rate equations by which the reaction under study is likely to proceed.

Where Cs represents substrate concentration, Co is initial substrate concentration representing the S and So respectively in the Monod and modified Monod kinetics represented in equation 1 and 2.

$$\mu = \mu_{max}\frac{S}{K_s+S} \quad (1)$$

$$\mu = Y\frac{S}{K_s+S} - K_d \quad (2)$$

Table 1: Reaction Rate Expressions and their Orders

S/N	Rate Expression	Kinetic	Integral Form	Determination Method
1	$r = \frac{dC}{dt} = k$	Zero	$Cs - Co = -kt$	Plot of Cs versus t
2	$r = \frac{dC}{dt} = kC$	First	$ln\frac{Cs}{Co} = kt$	Plot of $ln\frac{Cs}{Co}$ versus t
3	$r = \frac{dc}{dt} = kC^2$	Second	$\frac{1}{Cs} - \frac{1}{Co} = kt$	Plot of $\frac{1}{Cs}$ versus t
4	$r = \frac{dC}{dt} = \frac{kC}{K+C}$	Saturation Reaction	$kt = Kln\frac{Co}{Cs} + (Co - Cs)$	Plot of $\frac{1}{t}ln\frac{Co}{Cs}$ versus $(Co - Cs)/t$
5	$\frac{dc}{dt} = \frac{KsX}{(Ks + Cs)}$	Monod Kinetics	$\frac{X\theta}{Co - Cs} = \frac{Ks}{K}\frac{1}{Cs} + \frac{1}{K}$	Plot of $\frac{X\theta}{Co-Cs}$ versus $\frac{1}{Cs}$
6	$\frac{dX}{dt} = Y\frac{dc}{dt} - K_dX$	Modified Monod	$\frac{1}{\theta} = \frac{Co - Cs}{X\theta}Y - kd$	Plot of $\frac{1}{\theta}$ versus $\frac{Co-Cs}{X\theta}$

K is maximum specific substrate utilization rate, X is biomass (microorganism) concentration, K_s is half saturation coefficient. μ_{max} is maximum specific growth rate, Y is the yield coefficient, μ is specific growth rate, k_d=endogenous decay coefficient which accounts for the loss in cell mass.

3.0 RESULTS AND DISCUSSION

3.1 Physical and Chemical Characteristics

Table 2 is the physicochemical characteristics of the petroleum refinery wastewater used for the study; this was carried out to ascertain its suitability for biodegradation in ASP. This is important, as the composition and inherent biodegradability of the petroleum hydrocarbon pollutant is the first and foremost important consideration when the suitability of a remediation approach is to be assessed [11]. The amount and composition of the refinery wastewater vary considerably depending on crude oil characteristics, plant configuration and process designs [1].

A temperature of 27.4 ℃ which is moderate for aerobic microbial activity was obtained as shown in Table 1. For optimum bacteria activity temperature needs to be maintained slightly below or above room temperature of 25 ℃. Although hydrocarbon biodegradation can occur over a wide range of temperatures, the rate of biodegradation generally decreases with the decreasing temperature [11].

Table 2: Physical and Chemical Characteristics of Kaduna Refinery Wastewater

S/N	*Parameter*	*Average Value*
1	pH	6.8±0.36
2	Temperature (°C)	27.4±0.66
3	Conductivity (μS)	624±4
4	Turbidity (NTU)	145±6.24
5	DO (mg/L)	260±4.36
6	Ammonia Nitrogen (mg/l)	51.53±1.5
7	BOD (mg/l)	90±5
8	COD (mg/l)	270±8
9	TSS (mg/l)	110±4
10	TDS (mg/l)	230±5
11	TS (mg/l)	340±2
12	Phosphate (mg/l)	4.87±0.64
13	Nitrate (mg/l)	79.8±2.62
14	Sulphate (mg/l)	1.7±0.20
15	Cyanide(mg/L)	0.14±0.01
16	Phenol (mg/L)	3.29±0.01

In activated sludge process temperature not only influences the metabolic activities of the microbial population but also has a profound effect on such factors as gas transfer rates and the settling characteristics of the biological solids [12]. A near neutral pH value of 6.8 was obtained; this is habitable for the microorganism to thrive during treatment. Microorganisms have a range of optimum pH for carrying out its vital function in the range 6 to 8 [13].

A Biochemical Oxygen Demand (BOD) of 90 mg/l was obtained. The BOD test gives an indication of the amount of oxygen needed to stabilize or biologically oxidize the waste. A Chemical Oxygen Demand (COD) of 270 mg/l was obtained; the COD is the total measurement of all chemicals in the water that can be oxidized. Ghulam, et al [14] reported 84 mg/L and 175 g/L BOD and COD values respectively. Musa et al [15] reported a BOD and COD of 155 mg/L and 285mg/l for petroleum refinery wastewater respectively. Petroleum refinery wastewater can be high in COD in the range of 500-750 mg/L [16]. This variation may be attributed to the report by Ishak et al [17] that petroleum refinery wastewater streams characteristics are very much dependent on the complexity and number of processes in a refinery plant. A biodegradability index (B.I) of 0.3333 was obtained. It is a measure of the ratio of BOD_5 to COD in the wastewater [18]. Biodegradability index is used to verify the biodegradation capacity of wastewater [12]. There is no specific B.I for a particular wastewater. However, wastewater with biodegradability index less than 0.3 is considered difficult to degrade biologically [19], hence with a value of 0.3333, the characteristics of the wastewater sample shows that it is treatable in an activated sludge process.

3.2 Kinetics Models Evaluation

Figure 2-7 are the plots of the experimental data in accordance with the linearized rate equations in Table 1 to obtain the best quantitative kinetics description of petroleum refinery wastewater biodegradation in activated sludge process. In zero order reaction the rate of reaction is constant and independent of the substrate concentration, typically reaction follows Zero order kinetic at higher concentration. If reaction rate is found to be experimentally proportional to the first power of concentration, it is said to be one, this is usually at low substrate concentration. In second order reaction, rate is proportional to the second power of the reactant been considered [20].

Some wastewater treatments have been associated with zero, first and second order reaction rate [12]. Figure 7 shows that the modified Monod kinetic is the closest in agreement, with the biodegradation petroleum refinery wastewater in activated sludge process with the highest R^2 value of 0.9745

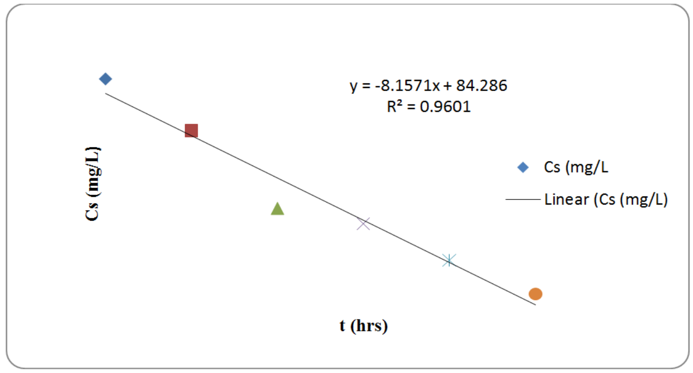

Figure 2: Test of Zero-Order Reaction

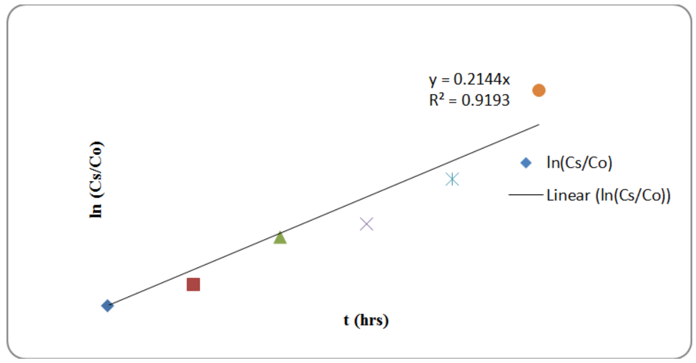

Figure 3: Test of First-Order Reaction

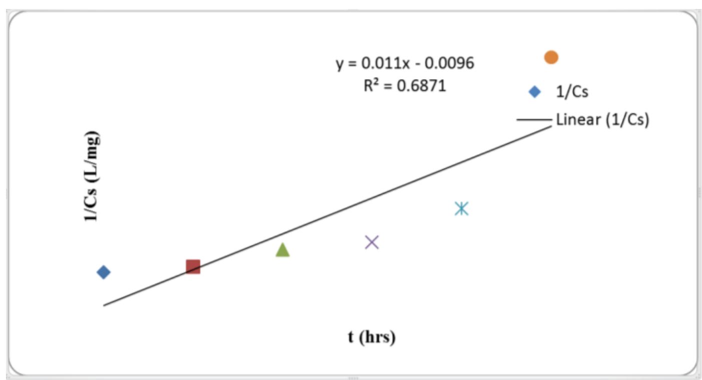

Figure 4: Test of Second-Order Reaction

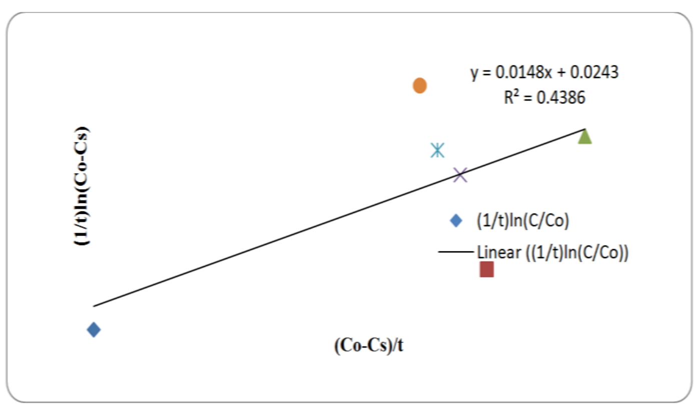

Figure 5: Test of Saturation Reaction

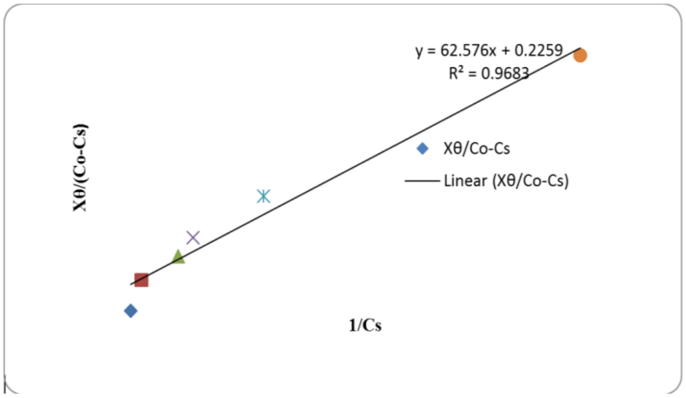

Figure 6: Test of Monod Kinetic Model

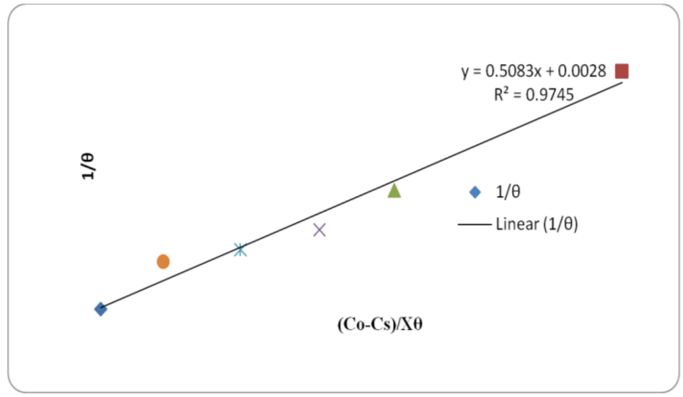

Figure 7: Test of Modified Monod Kinetic Model

***Table 3:** Summary of R^2 values obtained for various Rate Equations*

S/N	*Rate Expression*	*Kinetics*	*Integrated Form*	*R^2*
1	$r = \frac{dC}{dt} = k$	Zero	$Cs - Co = -kt$	0.9601
2	$r = \frac{dC}{dt} = kC$	First	$ln\frac{Cs}{Co} = kt$	0.9193
3	$r = \frac{dC}{dt} = kC^2$	Second	$\frac{1}{Cs} - \frac{1}{Co} = kt$	0.6871
4	$r = \frac{dC}{dt} = \frac{kC}{K + C}$	Saturation Reaction	$kt = Kln\frac{Co}{Cs} + (Co - Ct)$	0.4386
5	$\frac{dC}{dt} = \frac{KsX}{(Ks + Cs)}$	Monod Kinetic	$\frac{X\theta}{Co - Cs} = \frac{Ks}{K}\frac{1}{Cs} + \frac{1}{K}$	0.9683
6	$\frac{dX}{dt} = Y\frac{dC}{dt} - K_dX$	Modified Monod	$\frac{1}{\theta} = \frac{Co - Cs}{X\theta}Y - kd$	0.9745

Table 3 presents the summary of the R^2 values obtained for each reaction kinetic model investigated, the modified Monod Kinetic Model best describe the biodegradation of petroleum refinery wastewater in an ASP with the highest R^2 value of 0.9745.

4.0 CONCLUSION

Physical and chemical characterization of petroleum refinery wastewater shows that it is biodegradable in the activated sludge wastewater treatment process as previously reported. Kinetic evaluation of petroleum refinery wastewater biodegradation in the activated sludge process follows the modified Monod kinetic model among the related kinetic models examined with R^2 value of 0.9745. The agreement with modified Monod kinetic model implies that, the rate of substrate utilization in the biodegradation of petroleum refinery wastewater in the activated sludge process depends on the specific growth rate of the bacteria.

REFERENCES

[1] Kuyukina, M. S., Krivoruchko, A.V. and Ivshina, I.B. "Advanced Bioreactor Treatments of Hydrocarbon-Containing Wastewater", *Applied Science*, 10, (2020),831.

[2] Radelyuk, I., Zhapargazinova, K., Yelubay, M., Tussupova, K. and Persson, M. "Pitfalls of Wastewater Treatment in Oil Refinery Enterprises in Kazakhstan-A System Approach", *Sustainability*, 11, 1618, (2019).

[3] Alyasi, H. S. and Isaifan, R. "A Review on Pollution Emissions and Impact from Waste Treatment and Disposal Facilities", *Journal of Environmental Toxicology Study*, 2(1), 2018.

[4] Momoh, O.J, Okonkwo, P.C and Edomwonyi-Otu, L.C. "Kinetic Coefficients of Substrate Utilization and Biomass Growth in the Bio-degradation of Petroleum Refinery Wastewater in an Activated Sludge Process", *Journal of the Nigerian Society of Chemical Engineers*, 35(1), 2020.

[5] Sustarsic, M. "Wastewater Treatment: Understanding the Activated Sludge Process" *Journal of Chemical Engineering and Processing*", (2009), 26–29.

[6] Haydar, S. and Aziz, J. A. "Kinetic Coefficients for the Biological Treatment of Tannery Wastewater using Activated Sludge Process", *Pakistan Journal of Engineering and Applied Sciences*, 5, (2009), 39-43.

[7] Mardani, S., Mirbagheri, A., Amin, M. M. and Ghasemian, M. "Determination of Bio-kinetic Coefficients for Activated Sludge Processes on Municipal Wastewater". *Iranian Journal of Environmental, Health Science and Engineering*, 1, (2011), 25-34.

[8] Ronald, W.M., Charles, A. M. and Bradley, A.S. "Introduction to Chemical Reaction Engineering and Kinetics", *John Wiley & Sons, Inc., New York*, 1999.

[9] Baird, R and Laura, B. "Standard Methods for the Examination of Water and Wastewater", 23rd Ed. Washington, D.C.: *American Public Health Association*, 2017.

[10] Sperling, M. V. "Activated Sludge and Aerobic Biofilm Reactor" *International Water Association Publication*, Alliance House, London, U.K., 5, 2007.

[11] Niranjana, D. and Preeth, C. "Microbial Degradation of Petroleum Hydrocarbon Contaminants: An Overview", *Biotechnology Research International*, 2012.

[12] Tchobanoglous, G., Burton. F. L., Stensel, H. D., and Metcalf & Eddy. Wastewater Engineering: Treatment and Reuse, *McGraw-Hill*, Boston, 2003.

[13] Herimisa, A. "The Effect of Salinity on Biological Treatment of Wastewater from Oil Industry". *Unpublished Masters in Offshore Technology and Environmental Control Thesis Submitted to the Faculty of Science and Technology, University of Stavanger,* Norway, 2009.

[14] Ghulam, S., Muhammad, A., Razia, T., Samina, I., Qaiser, M. K. and Zafar, M.K. "Treatment of Oil Refinery Wastewater using Pilot Scale Fed Batch Reactor Followed by Coagulation and Sand Filtration", *American Journal of Environmental Protection,* 1(2013), (2015), 10-13.

[15] Musa, N. M., Abdulsalam, S., Suleiman, A. D. I. and Abdullahi, S. "Bioremediation of Petroleum Refinery Wastewater Effluent via Augmented Native Microbes", *Emerging Trends in Engineering and Applied Sciences*, 6(1), (2015), 1-6.

[16] Kutty, S. R. M., Gasim, H. A., Khamaruddin, P. F. and Malakahmad, A. "Biological Treatability study for Refinery Wastewater using Bench Scale Sequencing Batch Reactor Systems", *Water Resources Management*, 145, 2011.

[17] Ishak, S. A. and Isa, H. M. "Biological Treatment of Refinery Wastewater: A review", *Proceeding of International Conference on Sustainable Building and Infrastructure (ICSBI 2010), Kuala Lumpur Malaysia,* 2010.

[18] Dinçer, A. R. "Increasing BOD_5/COD Ratio of Non-Biodegradable Compound (Reactive Black 5) with Ozone and Catalase Enzyme Combination", *SN Applied Sciences*, 2(736), 2020.

[19] Jamil, T. S., Ghaly. M. Y., El-Seesy, I. E., Souya, E. R. and Nasr, R. A. "A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater"*SN Applied Sciences, Hazard Mater*, 2011(185), (2011), 353-358.

[20] Octave, L. "Chemical Reaction Engineering*"*, *John Wiley and Sons*, New York, 1999