

Winkler Titration Assessment Of Biochemical Oxygen Demand (BOD₅) In Oka River, Toru-Orua, Bayelsa State

ABSTRACT

Aim:The aim of study was to investigate the Biochemical Oxygen Demand (BOD) levels in water samples from the Oka River.

Study Design: Qualitative Study design.

Place and Duration of Study:Water samples were collected from the Oka River, located in Toru-Orua in Sagbama Local Government Area, Bayelsa State, Nigeria. The study lasted for twenty days.

Methods:Water samples were collected from four different locations and depths in the Oka River, Toru-Orua, Sagbama Local Government Area of Bayelsa State, Nigeria, at various times. Each sample was transferred into 250 ml bottles labeled L1, L2, L3, and L4. The temperatures of the samples were recorded before transporting them to the chemistry laboratory for treatment. Winkler titration method was employed in analyzing the samples.

Results: Location L1 recorded the highest BOD value, 28.38 ppm, measured at sunset (25 °C), from a relatively stagnant region. The high BOD at this location is attributed to minimal photosynthetic activity and significant oxygen consumption by microorganisms. In contrast, L2, collected from the same region at 35 °C during peak sunlight, exhibited a BOD value of 21.76 ppm. The lower BOD at L2 is due to increased photosynthetic activity. These high values suggest significant sludge deposits, domestic sewage and agricultural runoffs, which could lead to oxygen depletion and negatively impact aquatic life. Sample L3, taken from a deeper, stagnant region at sunset (25 °C), recorded a BOD value of 4.50 ppm. This moderate BOD level suggests the presence of moderate sludge deposits and agricultural runoff, but higher water flow speed helped mitigate these effects. Location L4, with the lowest BOD value of 3.74 ppm, was collected during peak sunlight (35 °C). Deeper location and high water flow speed contributed to reduced BOD levels, indicating better water quality and a healthier aquatic environment.

Conclusion: The BOD values at L1 and L2 (28.38 ppm and 21.76 ppm) exceed acceptable limits for fish growth. Conversely, BOD values at L3 and L4 (4.50 ppm and 3.74 ppm) fall within acceptable limits, suggesting healthier aquatic environment, as evidenced by the yearly bountiful fish harvests in these sections of the Oka River.

Keywords: Oxygen, Water, BOD, Factors, Analysis, Oka River

1. INTRODUCTION

Oxygen is the most abundant element on Earth. It exists primarily in two forms: O₂ (molecular oxygen) and O₃ (ozone). Oxygen is the most abundant element in the Earth's crust. It primarily exists in two forms: O₂ (molecular oxygen) and O₃ (ozone). Additionally, oxygen is a component of numerous compounds, including water (H₂O), and can be found dissolved in water as O₂ molecules. Oxygen is also a component of numerous compounds, such as water (H₂O), and can be found dissolved in water as O₂ molecules [1]. The amount of dissolved oxygen (DO) that water can retain is primarily influenced by temperature, salinity, and atmospheric pressure [2].

The stream system both produces and consumes oxygen. It absorbs oxygen from the atmosphere and from plants through photosynthesis [3]. Oxygen consumption in water can result from various sources, including respiration by aquatic animals, decomposition of organic matter, stormwater runoff from farmland or urban streets, feedlots, failing septic systems, and various chemical reactions [4]. The biochemical oxygen demand (BOD) refers to the quantity of oxygen that aerobic bacteria require to decompose organic waste [5].

Surface pollutants have a detrimental impact on aquatic life. Contaminants like heavy metals, pesticides, and industrial chemicals can directly poison aquatic organisms, causing illness, deformities, and even death [6][7].

Hydrocarbons from oil spills coat the water's surface, suffocating fish and disrupting the natural behaviors of aquatic organisms [8]. Certain pollutants can mimic or disrupt the natural hormones of aquatic organisms, causing reproductive and developmental abnormalities. These contaminants may also affect egg viability, resulting in lower hatching success and a decline in population [9]. Excessive nutrient runoff, mainly nitrogen and phosphorus from agricultural and urban sources, often triggers algal blooms. As these algae die and decompose, they consume oxygen, leading to hypoxic or anoxic conditions that can suffocate aquatic life. Additionally, sediment runoff from erosion can bury aquatic habitats, covering spawning grounds and depriving benthic organisms of oxygen [10].

Pollutants can disrupt organisms, causing behavioral changes that impair their ability to locate food, evade predators, or reproduce. Some pollutants also weaken the immune systems of aquatic life, increasing their vulnerability to diseases and infections. This can lead to a decline or even extinction of sensitive species, which reduces biodiversity and weakens ecosystem resilience. Changes in species composition and abundance can upset ecological interactions, resulting in imbalances within the ecosystem. Prolonged exposure to pollutants can cause population declines and degrade ecosystems. Additionally, certain pollutants may induce genetic mutations in aquatic organisms, potentially impacting future generations and reducing genetic diversity within populations.

Maintaining suitable dissolved oxygen (DO) levels is essential for safeguarding aquatic ecosystems and ensuring the well-being of water bodies. It is vital to regularly monitor and manage these levels to prevent issues like eutrophication and pollution, which can lead to dangerously low DO conditions [11]. Biochemical Oxygen Demand (BOD) is a key indicator in water quality management, offering essential insights into organic pollution levels and the health of aquatic ecosystems. Traditional methods for measuring BOD include the Dilution method, Manometric method, Respirometric method, and Electrode method. In the Dilution method, samples are incubated for a set period (5 days at 20°C for BOD₅ in the standard test) in dark bottles. The initial and final oxygen levels are then measured using either an amperometric sensor or iodometric titration.

Uwidia and Ejeomo [12] investigated the correlation between COD and BOD₅ using domestic sewage samples from a sewage treatment plant. Their regression analysis

revealed a robust correlation between these two parameters. Yang [13] employed Near-Infrared Spectrometry to simultaneously measure Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD₅) in wastewater, achieving satisfactory results. Rudaru et al. [14] evaluated the biodegradability of various water types in Romania by analyzing the BOD₅/COD ratio (biodegradability index) and found that this ratio varied depending on the type of water studied.

Al-Sulaiman and Khudai[15] investigated the correlation between BOD₅ and COD in the sewage at the Al-Diwaniyah wastewater treatment plant and reported a high degree of correlation.

Alewi et al. [16] investigated the relationship between BOD₅ and COD in 108 water samples from Iraq's southern region, finding a strong correlation with a coefficient of 0.908 and a determination coefficient (R²) of 0.89. In 2019, Andrio and others [17] demonstrated that ozonation pretreatment improved the BOD₅/COD ratio in co-substrates such as tofu wastewater and cow dung. Additionally, tannery wastewater with elevated BOD₅ levels was effectively treated using a ZnO-Zn/Fe₂O₄ composite photocatalyst supported on activated carbon, which removed 90 % of BOD₅ within two hours [18].

Ayawei and Bennett [19] measured Biochemical Oxygen Demand (BOD) levels in water samples from Ntanwoba Creek, Port Harcourt, Rivers State, Nigeria. They found elevated BOD values, which were linked to runoff wastewater from nearby agricultural activities and automobile workshops. In contrast, Kwak et al. [20] created software sensors using multiple regression analysis, incorporating dissolved organic carbon (DOC) concentration and UV light absorbance to estimate BOD₅ of river water. Their research demonstrated that these software sensors were effective in predicting BOD₅ levels in river water.

Dasgupta and Yildiz [21] investigated three types of wastewater in Morris County, USA, finding that industrial wastewaters exhibited the highest BOD₅ values, while pharmaceutical wastewaters had the lowest. Sha and Wei-Xing [22] used spectrophotometric titration to measure Biochemical Oxygen Demand in 20 waste samples within 40 minutes. Mohammed et al. [23] conducted kinetic studies on BOD₅, COD, and chromium removal in tannery effluent using a ZnO/ZnFe₂O₄ composite photocatalyst supported on activated carbon, reporting that the photodecomposition followed the pseudo first-order Langmuir-Hinshelwood model. Faiza et al. [24] documented BOD₅ values ranging from 5.04 to 6.18 mg/L in the Wupa River, Federal Capital Territory, Abuja, Nigeria, highlighting anthropogenic impacts on water quality. Yang [13] simultaneously determined Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD₅) in wastewater using Near-Infrared Spectrometry.

The aim of my research is to measure the Biochemical Oxygen Demand (BOD) levels of Oka River in the Toru-Orua community of Bayelsa State, Nigeria, using the Winkler method. This river is unique due to its fishing prohibition until the ceremonial four-day fishing festival held annually on February 3rd. During this festival, the community celebrates with plentiful catches, as illustrated in Figure 1, which shows fish caught during the 2024 festival. By analyzing the BOD levels, the research aims to assess the

water quality and its capacity to support aquatic life, especially in the context of the community's fishing practices and the annual festival.



Fig. 1: Fresh fish harvested from Oka River during the 2024 fishing festival

2. MATERIALS AND METHODS

2.1 Materials

All chemicals utilized in the experiments were of analytical reagent grade, sourced from Acros Organics, and were used as received without additional purification.

2.2 Methods

2.2.1 Reagents Preparation

2.2.1.1 0.017 M potassium iodate (KIO_3)

0.89 g of KIO_3 was weighed and dissolved in distilled water in a volumetric flask, and the solution was made up to a total volume of 250 ml.

2.2.1.2 Alkaline Sodium Iodide (NaI)

5.6 g of sodium hydroxide and 16.6 g of potassium iodide were dissolved in distilled water, and the solution was diluted to a final volume of 100 ml with distilled water.

2.2.1.3 0.538 M manganese (II) sulphate tetrahydrate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$)

120 g of manganese (II) sulphate tetrahydrate was dissolved in distilled water, and the solution was brought up to a final volume of 250 ml.

2.2.1.4 Fresh starch solution

To prepare a fresh starch solution using established methods, 2.00 g of soluble starch was dissolved in a 100 ml conical flask. This solution was quickly poured into 250 ml of

boiling water. The resulting mixture was boiled for an additional 5 minutes. After boiling, 0.02 g of sodium iodide was added, and the mixture was allowed to cool [25].

2.2.1.5 1:1 H₂SO₄ solution

30 ml of concentrated sulfuric acid was transferred into a 100 ml flask, followed by the addition of 30 ml of distilled water.

2.2.1.6 0.1 M solution of sodium thiosulphate

12.60 g of sodium thiosulfate was weighed and dissolved in distilled water. The solution was then made up to a total volume of 500 ml with distilled water.

2.2.1.7 Standardization of sodium thiosulfate (Na₂S₂O₃) using potassium iodate (KIO₃)

Standardization of Na₂S₂O₃ was calculated using equation (1) and (2).

$$\frac{MS_2O_3^{2-} \cdot VS_2O_3^{2-}}{MIO_3^- \cdot VIO_3^-} = \frac{nS_3O_3^{2-}}{nIO_3^-} \quad (1)$$

$$MS_2O_3^{2-} = \frac{MIO_3^- \cdot VIO_3^- \cdot nS_3O_3^{2-}}{VS_2O_3^{2-} \cdot nIO_3^-} \quad (2)$$

Where MS₂O₃²⁻ is the molarity of sodium thiosulphate

MIO₃⁻ is the molarity of the iodate

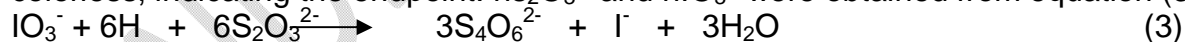
VIO₃⁻ is the volume of the iodate

VS₂O₃²⁻ is the volume of thiosulphate

nIO₃⁻ is the number of moles of iodate and s the number of moles of thiosulphate

nS₃O₃²⁻ is the number of moles of thiosulphate

To get VS₂O₃²⁻, 25 ml of potassium iodate solution was transferred into a 250 ml volumetric flask. 5 ml of 1:1 H₂SO₄ and 15 ml of potassium iodide solution were added to the flask to liberate iodine (I₂). The liberated iodine was then titrated with sodium thiosulphate until a pale yellow solution was obtained. Three drops of freshly prepared starch solution were added, causing the solution to change to a dark greenish-blue color. The titration with sodium thiosulphate was continued until the solution turned colorless, indicating the endpoint. ns₂O₃²⁻ and nIO₃⁻ were obtained from equation (3).



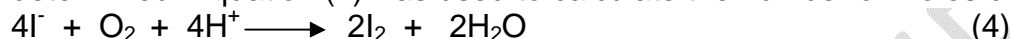
2.2 Collection of Water Samples

Water samples were collected from four different locations and depths in Oka River, Toru-Orua, Sagbama Local Government Area, Bayelsa State, Nigeria, at various times. Each sample was transferred into 250 ml bottles labeled L1, L2, L3, and L4. The temperatures of the samples were recorded before transporting them to the laboratory for treatment and analysis. To minimize experimental errors, the time between sample collection and treatment was kept between 30 minutes and 2 hours [26].

2.3 Treatment of Water Samples

The Winkler titration method was used to determine the Biochemical Oxygen Demand (BOD) values of the water samples. Each sample was treated with 2 ml of alkaline NaOH solution, and the bottles were tightly sealed to eliminate air bubbles. The samples were manually equilibrated for 20 minutes, and inverted for 5 minutes. Following this, 2 ml of 1:1 H₂SO₄ was added, and the bottles were agitated and inverted again for 5 minutes. A clear yellow solution was achieved as the precipitates dissolved. The procedure was repeated three times, and the average BOD value was calculated.

25 mL of the treated water (first fraction) was titrated with a 0.0975 M Na₂S₂O₃ solution. The solution initially appeared pale yellow. Following this, 3 drops of freshly prepared starch solution were added, and the titration was continued with the Na₂S₂O₃ solution [27][28][29][30]. The method was performed in triplicate, and the average value was determined. Equation (4) was used to calculate the number of moles of S₂O₃²⁻.



The second fraction of the treated samples were stoppered to avoid air penetration (oxidation) and incubated in a dark cupboard for five (5) days at 20 °C. The samples were incubated to stall further photosynthesis process in the samples. At the end of day 5, the samples were analyzed to determine the final Dissolved Oxygen (DO). The difference between the initial dissolved oxygen and the final dissolved oxygen gave the investigated Biochemical Oxygen Demand (BOD) of the water samples [19].

The value of dissolved oxygen in the four locations was calculated using the formula:

$$BOD_5 = D_1 - D_2$$

Where BOD₅ = biochemical oxygen demand after incubation

D₁ = initial dissolved oxygen

D₂ = final dissolved oxygen.

3. RESULTS AND DISCUSSION

Biochemical Oxygen Demand (BOD) levels were measured in water samples from Oka River, in Toru-Orua, Bayelsa State, Nigeria, using the Winkler titration method. All titrations were performed in triplicate and the results are as presented in Table 1.

Table 1: BOD₅ values in Oka Creek

S/N	Location	Depth(ft)	Time of sample collection (Central African Time)	D ₁ (ppm) Mean ± S.D	D ₂ (ppm) Mean ± S.D	BOD ₅ (ppm) Mean ± S.D
1.	L1	1.8	8:00 am	64.10 ± 0.03	35.72 ± 0.02	28.38 ± 0.01
2.	L2	1.8	3:45 PM	59.20 ± 0.02	37.44 ± 0.01	21.76 ± 0.01
3.	L3	2.5	8:00 am	25:30 ± 0.03	21:50 ± 0.01	4:50 ± 0.01
4.	L4	2.5	3:53 PM	19 34 ± 0.03	15.60 ± 0.02	3.74 ± 0.01

Results reveal the impact of location, depth, water flow rate, time, and temperature on BOD values. Location L1 had the highest BOD value of 28.38 ppm. This sample was taken from a relatively stagnant area at sunset with a temperature of 25 °C. The absence of sunlight at this time limited photosynthetic activity, leading to higher oxygen consumption by microorganisms and thus a higher BOD. The elevated BOD suggests significant organic pollution due to high levels of sludge, domestic sewage, and

agricultural runoff. Such levels can deplete oxygen, harming aquatic organisms that depend on dissolved oxygen.

Location L2 recorded a BOD value of 21.76 ppm. This sample, collected during midday at 35°C, benefited from higher sunlight, which enhanced photosynthesis and slightly reduced the BOD. Despite this, the BOD still indicates substantial organic pollution, though slightly less severe than at L1.

Sample L3, taken from a deeper, stagnant area at sunset and 25 °C, showed a lower BOD value of 4.50 ppm. This moderate BOD suggests a reduced impact of domestic sewage and sludge, aided by moderate water flow that dispersed pollutants and reduced bacterial load.

Location L4 had the lowest BOD value of 3.74 ppm. It was collected during midday at 35 °C. The increased sunlight further reduced BOD by promoting photosynthesis. The combination of deeper water and moderate flow rate also minimized sludge and bacterial presence, indicating better water quality and a healthier aquatic environment compared to L1 and L2.

Overall, BOD values at L1 and L2 (28.38 ppm and 21.76 ppm) exceed acceptable limits for aquatic life, suggesting severe organic pollution and potential harm to fish and other organisms. In contrast, BOD values at L3 and L4 (4.50 ppm and 3.74 ppm) are within acceptable limits, indicating a less adverse impact on aquatic life and a more suitable environment for fish [31]. The yearly bountiful fish harvest in these locations could be attributed to these favorable conditions.

4. CONCLUSION

The Biochemical Oxygen Demand (BOD) levels in water samples from the Oka River in Toru-Orua, Bayelsa State, Nigeria, were assessed at four distinct locations (L1, L2, L3, and L4) using the Winkler titration method. The findings revealed significant variation in BOD values influenced by factors such as location, depth, water flow rate, time, and temperature.

Location L1 recorded the highest BOD value of 28.38 ppm. This sample, collected from a relatively stagnant area at sunset with a temperature of 25 °C, had elevated BOD levels due to minimal sunlight, which restricted photosynthetic activity and led to a higher consumption of dissolved oxygen by microorganisms. The high BOD value indicates significant organic pollution, likely attributed to sludge deposits, domestic sewage discharges, and agricultural runoff.

Location L2 had a slightly lower BOD value of 21.76 ppm, taken from the same region as L1 but at midday and a higher temperature of 35 °C. The increased sunlight during midday promoted photosynthesis, which reduced the BOD value compared to L1. Despite the reduction, the BOD levels still suggest notable organic pollution in this area. In contrast, Location L3 exhibited a BOD value of 4.50 ppm, sampled at sunset from a deeper, stagnant area with a temperature of 25 °C. This moderate BOD level suggests a lower concentration of domestic sewage and sludge deposits, likely due to a higher water flow rate that dispersed organic matter and reduced bacterial load. Location L4 had the lowest BOD value of 3.74 ppm, collected at midday at 35 °C. The combination of high sunlight and increased water flow facilitated photosynthesis and minimized sludge deposits, resulting in better water quality.

The high BOD values at L1 and L2 (28.38 ppm and 21.76 ppm) exceed acceptable limits for fish growth, indicating severe organic pollution that can negatively impact aquatic life. Conversely, the BOD values at L3 and L4 (4.50 ppm and 3.74 ppm) are within acceptable limits, reflecting improved water quality and a healthier aquatic environment. These favorable conditions in L3 and L4 likely contribute to the abundant yearly fish harvests reported in these sections of the Oka River.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

RECOMMENDATION

To improve water quality in the Oka River, reduce pollution by improving waste management and enforcing discharge regulations, enhance flow by increasing water circulation in stagnant areas, promote vegetation by establishing buffer zones to absorb runoff, monitor regularly by tracking BOD and water quality, and engage the community through education and involvement.

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