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Assessment of Heavy Metal Persistence Following Conventional Municipal Wastewater Treatment in Nigeria: Implications for Advanced Treatment

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Abstract

Conventional municipal wastewater treatment plants (WWTPs) are primarily designed to remove organic pollutants and nutrients, with limited capacity for eliminating dissolved heavy metals. Consequently, toxic metals may persist in treated effluents and be discharged into receiving water bodies, posing significant risks to aquatic ecosystems and human health. This study evaluated the efficiency of a conventional activated sludge municipal wastewater treatment plant in Nigeria for the removal of physicochemical contaminants and dissolved heavy metals. Wastewater samples were collected from the influent, post-aeration chamber, and final effluent during three sampling campaigns using grab sampling techniques. Standard analytical procedures were employed to determine selected physicochemical parameters, including pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrate, nitrite, and phosphate, alongside the concentrations of selected heavy metals. The activated sludge process demonstrated high treatment efficiency for conventional wastewater quality parameters, achieving substantial reductions in organic pollutants and nutrients, with final effluent concentrations complying with the National Environmental Standards and Regulations Enforcement Agency (NESREA) discharge limits. However, the system exhibited limited effectiveness in removing dissolved heavy metals. Final effluent concentrations of chromium (0.58-1.24 mg/L), iron (1.10-10.21 mg/L), and lead (0.19-0.48 mg/L) remained above the NESREA permissible limits, exceeding the regulatory thresholds by approximately 82-91%, 72-97%, and 47-79%, respectively. These findings demonstrate that compliance with conventional wastewater quality standards does not necessarily guarantee adequate removal of toxic dissolved metals. The study highlights the need to integrate appropriate advanced polishing technologies into conventional activated sludge treatment systems to achieve effective heavy metal removal prior to effluent discharge. Such an approach would enhance environmental protection, minimize ecological and public health risks, and promote sustainable municipal wastewater management.

Keywords

Activated sludge process;
Lead;
Wastewater monitoring; Chromium;
Tertiary treatment;
Effluent quality.



1.0 INTRODUCTION

Municipalities have continued to attract significant influx of people in search for the opportunities available in urban centres. This has led to significant population growth due to urbanisation. In such cities, municipal wastewater treatment plants (WWTPs) are important for the treatment of large quantity of wastewaters generated to protect public health and aquatic ecosystems by reducing the pollutant load discharged into the environment. Conventional treatment systems, particularly those based on activated sludge process, are designed primarily to remove biodegradable organic matter, suspended solids, and nutrients through physical settling and biological degradation. They are not specifically engineered to remove dissolved inorganic contaminants such as heavy metals (Agoro *et al.*, 2020).

Heavy metals are persistent, non-biodegradable contaminants that cannot be degraded through microbial metabolism during biological treatment. Any removal of the metals in conventional WWTPs employing biological processes occurs mainly through indirect physicochemical processes (Hargreaves *et al.*, 2018). The process largely distributes the metals between the aqueous and sludge phases rather than achieving complete removal (Sylwan and Thorin, 2021). This leads to the discharge of appreciable concentrations of heavy metals into receiving water bodies through the final effluent leading to accumulation in sediments and aquatic organisms. This increases the risk of bioaccumulation, and adverse health effects associated with long-term exposure to heavy metals (Sylwan and Thorin, 2021).

In Nigeria, the receiving water bodies are usually used for domestic, agricultural, and recreational purposes, increasing the potential for human exposure to residual contaminants (Amaefule *et al.*, 2023). For example, Ibrahim *et al.* (2025) reported elevated concentrations of heavy metals in the water and sediments of Wupa River, which is downstream of the Wupa Wastewater Treatment Plant, Abuja. Despite increasing recognition of this challenge, there is limited availability of comprehensive wastewater quality data, particularly on heavy metal concentrations throughout the treatment process. Existing monitoring programmes largely emphasise conventional physicochemical parameters, while systematic assessment of residual metals remains limited. This is exacerbated by restricted access to wastewater quality data, inconsistent monitoring practices, limited enforcement of wastewater discharge regulations (Onifade, 2024). Evaluating the persistence of heavy metals throughout treatment process is necessary to identify treatment limitations and informing the selection of appropriate advanced treatment technologies.

This study therefore, assessed the persistence of selected heavy metals across the treatment stages of a Nigerian conventional municipal wastewater treatment plant. It also examined the implications of the observed metal concentrations for advanced wastewater treatment and environmental protection.

2.0 MATERIALS AND METHODS

2.1 Wastewater Sampling

Wastewater samples were collected from a WWTP employing a conventional activated sludge process comprising preliminary

treatment, primary sedimentation, aeration, and clarification before effluent discharge. Grab samples were collected at three treatment stages. These were taken at influent (SP1), post-aeration chamber (SP2), and final treated effluent (SP3). Sampling campaigns were conducted in July 2024, December 2024, and November 2025 to capture temporal variations in wastewater characteristics.

Samples were collected in pre-cleaned plastic containers that were rinsed twice with the wastewater before sampling to minimise contamination and ensure representative collection. Immediately after collection, the samples were transported to the laboratory in insulated ice coolers to minimise physicochemical changes prior to analysis.

2.2 Wastewater Characterisation

2.2.1 pH Measurement

The pH of the wastewater samples was measured using a calibrated digital pH meter (PH-2601, Sinotester, China).

2.2.2 Dissolved Oxygen and Biochemical Oxygen Demand Determination

Dissolved oxygen (DO) and biochemical oxygen demand (BOD₅) were determined using the standard Winkler titrimetric method described by Okezie *et al.* (2020). The BOD₅ was calculated from the difference between the initial and fifth-day dissolved oxygen concentrations after incubation at 20 °C for five days using Equation (1).

$$BOD_5 = \frac{(DO_1 - DO_5)D_f}{V_{ws}} \quad (1)$$

Where DO_1 and DO_5 are the on days 1 and 5 (mg/L), D_f is the dilution factor, and V_{ws} is the volume of wastewater sample used (mL).

2.2.3 Biochemical Oxygen Demand Determination

Chemical oxygen demand (COD) was determined using the dichromate reflux method following Okezie *et al.* (2020). Samples were digested with potassium dichromate in acidic medium containing silver sulphate before titration with ferrous ammonium sulphate. The COD was calculated using Equation (2).

$$COD = \frac{8000M(x_b - x_s)}{V_{ws}} \quad (2)$$

Where x_b and x_s are the blank and sample volumes of titrant used, respectively, M is the molarity of the titrant (mol/L), and V_{ws} is the volume of the wastewater sample used (mL).

2.2.4 Nutrient Concentration Analysis

The nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) concentrations were determined spectrophotometrically as described by Sa'id and Mahmud (2013). The NO_3^- was analysed using brucine-sulphanilic acid method at 410 nm. NO_2^- and PO_4^{3-} were quantified at 520 nm using EDTA with sulphanilic acid and molybdate colour development reagents, respectively. The concentrations were determined from calibration curves prepared using standard solutions.

2.5 Heavy Metal Analysis

Wastewater samples were digested using a mixed acid digestion procedure consisting of HNO_3 , H_2SO_4 , and $HClO_4$ following the method of Ibrahim *et al.* (2024). After digestion, the samples were filtered and diluted to 100 mL with distilled water.

Concentrations of lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), Copper (Cu), and iron (Fe) were determined using atomic absorption spectrophotometer (280FS AA, Agilent

Technologies, USA) based on absorbance values. Calibration standards were freshly prepared for each metal, and the calibration curves ($R^2 \geq 0.999$) were obtained before analysis of samples.

3.0 RESULTS AND DISCUSSION

3.1 Conventional Wastewater Quality Parameters

The physicochemical characteristics of the wastewater are presented in Table 1. Across the monitored treatment stages, progressive improvements in wastewater quality were

observed. The pH remained relatively stable throughout the treatment process, varying between 6.8 and 7.3, with all measured values falling within the NESREA guideline. This signals that the biological system operated under favourable conditions with no process instability. The DO increased from the influent to the final effluent during the first and second sampling periods, respectively, reflecting efficient aeration and oxygen transfer within the biological treatment process of the wastewater.

Table 1: Physicochemical properties of wastewater across the treatment stages compared to NESREA guideline.

	July 2024			December 2024			November 2025			
Parameter	SP1	SP2	SP3	SP1	SP2	SP3	SP1	SP2	SP3	NESREA Guideline
pH	n.d.	n.d.	n.d.	7.30	6.80	7.0	7.32	6.87	7.10	6.0 - 8.0
DO (mg/L)	n.d.	n.d.	n.d.	1.60	4.50	6.20	1.20	5.30	6.20	7.0 - 10.0
BOD ₅ (mg/L)	n.d.	n.d.	n.d.	119	38	15.5	173	21	17.0	50.0
COD (mg/L)	n.d.	n.d.	n.d.	340	120	65.4	369	317	71.0	100.0
NO ₂ ^{-*} (mg/L)	n.d.	n.d.	n.d.	0.47	0.87	0.09	0.35	0.14	0.13	3.0
NO ₃ ^{-*} (mg/L)	n.d.	n.d.	n.d.	1.40	6.50	6.30	2.10	3.50	3.80	10.0
PO ₄ ^{3-*} (mg/L)	n.d.	n.d.	n.d.	2.20	1.70	0.51	2.60	1.90	1.30	-

n.d. stands for "not determined". SP1, SP2, and SP3 stands for influent, post-aeration, and effluent sampling points, respectively.

NO₂^{-*}, NO₃^{-*}, and PO₄^{3-*} values represent ambient surface water quality standards, provided for contextual comparison, NESREA (2009) does not specify their separate effluent discharge limits.

The BOD₅ decreased from 119 and 173 mg/L at the influent to 15.5 and 17.0 mg/L in the final effluent during the December 2024 and November 2025 sampling periods, respectively. Similarly, COD declined from 340 and 369 mg/L to 71.0 mg/L. Both the BOD₅ and COD concentrations in the treated effluent

were well below the NESREA (2009) discharge limits of 50 and 100 mg/L, respectively, indicating effective removal of biodegradable organic matter by the activated sludge systems. Similar trend was observed for the nutrient concentrations. Both NO₃⁻ and PO₄³⁻ over the respective sampling campaigns. Although NO₃⁻ concentrations exhibited some variation between treatment stages, the final effluent values of 6.3 and 3.8 mg/L remained below the ambient surface water quality guideline of 10 mg/L.

The observed reductions in BOD₅, COD, and nutrients demonstrate effective performance of the activated sludge process. Microorganisms oxidise dissolved and suspended biodegradable organic matter during aeration then clarification removes biological flocs and associated suspended solids, thereby reducing the organic load of the treated wastewater. Koul *et al.* (2022) has reported similar performances where

secondary biological oxidation treatment achieved substantial reductions in conventional pollutants.

3.2 Heavy Metal Concentrations

The concentrations of Cr, Pb, Fe, Cd, and Zn are presented in Table 1. The heavy metals exhibited limited removal throughout the treatment process unlike the conventional physicochemical parameters.

Table 3.2: Heavy metal concentrations of wastewater across the treatment stages compared to NESREA guideline.

	July 2024			December 2024			November 2025			
Parameter	SP1	SP2	SP3	SP1	SP2	SP3	SP1	SP2	SP3	NESREA Guideline
Cr (mg/L)	1.07	1.18	1.24	ND	ND	ND	0.86	0.62	0.58	0.10
Cd (mg/L)	0.02	0.01	0.04	0.06	0.06	0.03	0.31	ND	ND	0.10
Pb (mg/L)	0.27	0.31	0.19	0.35	0.24	0.34	0.53	0.51	0.48	0.10
Fe (mg/L)	18.06	16.72	10.21	4.61	3.94	3.86	1.37	1.27	1.10	0.30
Zn (mg/L)	0.35	0.51	0.55	0.67	0.65	0.58	0.17	ND	ND	1.50

ND stands for "not detected".

Cr and Pb exhibited similar pattern with limited reductions observed across the treatment system. The Cr concentrations in the effluent ranged from 0.58 to 1.24 mg/L, which was substantially higher than NESREA (2009) permissible limit (0.10 mg/L). A slight increase in Cr concentrations was observed from the influent to the effluent during the July 2024 sampling, suggesting possible redistribution within the treatment process. The effluent concentration of Pb (0.19-0.48 mg/L) also consistently exceed the 0.1 mg/L limit, with only minor reductions observed across the treatment train. The continued presence of Cr and Pb throughout the treatment process indicates that the conventional biological treatment process was unable to effectively remove them. Sylwan and Thorin (2021) reported similar observation

where substantial fractions of dissolved heavy metals persist after conventional municipal treatment.

In comparison, Cd and Zn displayed comparatively lower concentrations and greater temporal variability. Both Cd and Zn concentrations significantly decreased to below the analytical detection limit in the effluent during the November 2025 sampling campaign. Where detected, their concentrations remained below the limit. These observations suggest that the occurrence and treatment of Cd and Zn was more favourable than that of Cr, Pb, and Fe.

The observed limited removal of heavy metals reflects the main limitation of conventional activated sludge treatment regarding

dissolved inorganic contaminants. Heavy metals cannot be metabolised by microorganisms and remain after biological oxidation processes (Tchounwou *et al.*, 2012) unlike biodegradable organic compounds.

In situations where the metals were partially removed, it is basically as a result of physicochemical mechanisms such as adsorption onto flocs of sludge, precipitation, and suspended solids attachment. This leads to some of the metal transferred from the aqueous phase to the sludge rather than completely removing them from the wastewater stream (Hargreaves *et al.*, 2018). Further, it indicates that clarification following aeration is not sufficient to remove the dissolved or complexed metal species. Heavy metals in soluble form possess high mobility and limited settling characteristics, enabling them pass through secondary

treatment and discharged in effluents (Agoro *et al.*, 2020).

3.3 Implications for Advanced Treatment

It is evident that compliance with conventional wastewater quality parameters does not necessarily ensure adequate removal of toxic inorganic contaminants. The activated sludge process effectively reduced organic matter and nutrient concentrations to permissible limit. But the Cr, Pb, and Fe concentrations remained above their respective permissible limits in the effluent. This highlights a major limitation of conventional secondary treatment. However, Fe is mostly considered as an essential metal, which reduces its toxic environmental significance. Cr exceeded discharge limit by 82 to 91% and Pb by 47 to 79%, depending on the sampling campaign (Figure 1).

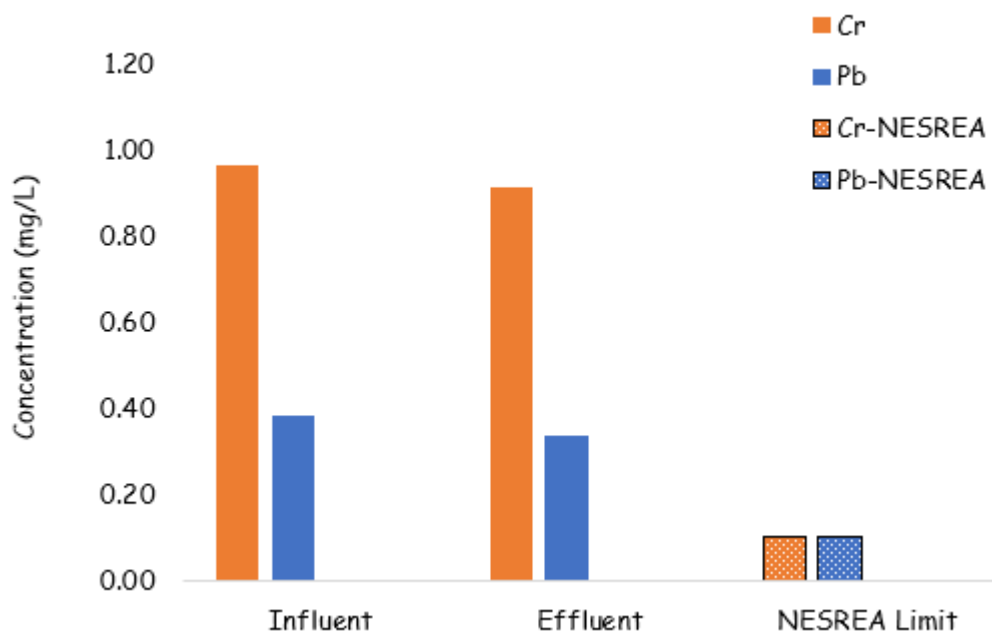


Figure 1: Average Cr and Pb concentrations at influent and effluent stages relative to NESREA discharge limits (2024-2025).

In this context, Ibrahim *et al.* (2025) reported elevated concentrations of heavy metals in both water and sediment of the Wupa River, which is downstream of the Wupa Wastewater Treatment Plant. This suggests the cumulative effects of continuous effluent discharge on the receiving environment. Such observations reinforce the need to consider residual heavy metals in effluents as critical contaminants of concern.

Advanced treatment processes are widely recommended where residual dissolved contaminants persist after biological treatment and sedimentation (Cavalheiro *et al.*, 2017). A variety of technologies for polishing effluents exist such as adsorption, ion exchange, membrane filtration, and chemical precipitation. The choice depends on characteristics of the wastewater, treatment objectives, requirements of the operation, and the economy. Among these technologies, adsorption has received considerable attention for the removal of contaminants especially dissolved heavy metals because of its efficiency, cost effectiveness, simplicity in terms of operation, and variety of adsorbent materials (Fu and Wang, 2011).

4.0 CONCLUSION

The activated sludge process effectively reduced organic pollutants and nutrients, with the final effluent complying with the applicable NESREA discharge limits for conventional wastewater quality parameters. This confirms the satisfactory performance for the treatment of biodegradable contaminants. In contrast, the removal of heavy metals was limited. Although metal concentrations generally declined across the

treatment train, the final effluent contained Cr (0.58-1.24 mg/L), Fe (1.10-10.21 mg/L), and Pb (0.19-0.48 mg/L), all of which exceeded the NESREA permissible limits. Relative to the discharge standards, Cr, Fe, and Pb exceeded the regulatory thresholds by about 82-91%, 72-97%, and 47-79%, respectively.

These findings demonstrate that compliance with conventional wastewater quality parameters does not necessarily ensure adequate removal of toxic inorganic contaminants. Based on practical point of view, the persistence of Cr, Fe, and Pb in the treated effluent highlights the limitations of conventional secondary biological treatment. This provides a justification for incorporating an appropriate advanced polishing process to remove heavy metals effectively for sustainable environmental protection and wastewater management.

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