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Research Article

Modelling Nitrogen Removal in the Kibendera Wastewater Stabilization Ponds in Ruiru, Kenya

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Abstract

Application of waste stabilization ponds (WSP) in wastewater treatment in the tropical regions is primarily due to their affordability and relatively high treatment performance. Monitoring of 2-year nitrogen removal behavior in Kibendera WSP in Ruiru, Kenya, was undertaken between January 2021 and December 2022. The experimental work determined the concentrations and removal efficiencies of Ammonia, Nitrate, Nitrite, Organic Nitrogen and Total Nitrogen. Standard Methods for the examination of water and wastewater determined Nitrogen and Dissolved Oxygen (DO) concentrations. Based on the experimental data obtained, mass balance reaction rate models characterized the nitrogen transformation and removal behavior in the WSP. Whereas model calibration was achieved using observed data from January to December 2021, model validation was achieved using observed data from January to December 2022. Ammonia volatilization, sedimentation, mineralization, nitrification, denitrification and microbial ammonia uptake were the possible transformation and removal pathways. Whereas ammonia volatilization contributed the least to the overall nitrogen removal (0.01-0.02 mg/L.d), denitrification contributed the most (2.12-14.67 mg/L.d). Low DO levels and high ammonia concentrations were responsible for low nitrification rates and high microbial ammonia uptake respectively. Comparison between experimental and modelled effluent concentrations yielded correlation coefficients (r) of 0.77 and 0.69 for ammonia and organic nitrogen respectively during the calibration period. The corresponding model validation r values were 0.74 and 0.93 respectively. The good agreement between the model output and observed effluent concentrations implies that nitrogen removal prediction and optimization is possible. External aeration to spike DO concentration levels is necessary to enhance the long-term nitrification rates.

Keywords

Modeling, Nitrification-Denitrification, Nitrogen Removal, Shock Load, Waste Stabilization Pond

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1. Introduction

Application of biological wastewater treatment technologies such as septic tanks, aerated lagoons, trickling filters and waste stabilization ponds (WSP) in tropical developing countries owes to the fact that they are affordable. In addition, their high sewage treatment performance attributed to relatively high temperatures experienced throughout the year renders them appropriate in wastewater management [1, 2]. Temperature enhanced biological processes include nitrification-denitrification, biological phosphorus removal and breakdown of organic matter. The preference and subsequent adoption of WSP as reliable wastewater treatment technology in Kenya is obvious as 55% of the available wastewater treatment plants are WSP [3]. Nevertheless, the performance of these systems in conformity with local effluent guideline values remains unsatisfactory. This is attributed to the fact that some of the WSP are either operating beyond their hydraulic design capacities or are non-resilient and incapable of withstanding shock loadings introduced at their intake points by privately owned sewage exhausters [4]. Devastating concentration variations caused by shock loadings have not only been responsible for overwhelming and upsetting the microbial populations in the ponds but have also resulted in non-compliant effluent based on the National Environmental Management Authority Standards [4, 5]. The consequence has been deteriorating wastewater treatment performance, posing a threat to their long-term sustainability in wastewater treatment.

The deteriorating performance has been responsible for discharge of nitrogen containing wastewater into natural waters as optimization of nitrification and denitrification processes is not achieved [6-8]. Whereas nitrification is responsible for transformation of ammonia to nitrate, denitrification is an anaerobic process where nitrate transforms to nitrogen gas. Nitrification is characterized by two stepwise reactions namely ammonia oxidation and nitrite oxidation [9]. The effectiveness of biological nitrification and denitrification in nitrogen removal has been questionable due to the high oxygen and external carbon source requirements [10-12]. In addition to nitrification-denitrification, other nitrogen removal pathways are sedimentation of organic nitrogen, uptake by algae and ammonia volatilization [13-16]. Whereas some studies have revealed that nitrification denitrification is the major nitrogen removal pathway [16, 17], others have asserted that sedimentation of organic nitrogen is the main nitrogen removal pathway [14, 15].

Modeling achieves complete evaluation of WSP performance in terms of nitrogen removal prediction under varying operating and shock loading conditions. Mathematical modeling methods have been found suitable for the analysis of nitrogen removal (Mayo 2013; Mukhtar et. al., 2017). Although studies have been conducted to investigate sewage treatment performance of WSP in Kenya [4, 19, 20], their ability to withstand hydraulic shocks and daily influent concentration variations remains unaddressed in available literature. Therefore, modeling nitrogen removal using available data would guarantee short term and long-term WSP performance.

The Kibendera Waste Stabilization Ponds have been in operation for the last six years. Although, several system performance studies have been carried out previously [4, 21], modeling studies to analyze nitrogen removal behavior are yet to be conducted and scientifically documented. In this regard, conducting such a study would not only form the basis for nitrogen removal optimization but also a scientific blueprint for possible replication in other WSP in Kenya. This study therefore aimed to:

1. Determine the concentrations and removal efficiencies of different nitrogen fractions (Total Nitrogen, Ammonia, Nitrate, Nitrite and Organic Nitrogen) in the Kibendera WSP over the 2021-2022 period.
2. Model nitrogen transformation and removal using various mass balance reaction rate models.

2. Materials and Methods

2.1. Description of Waste Stabilization Ponds

The Kibendera WSP commissioned in 2017 and serving the entire Ruiru sub-county's population, covers a net area of 12.6 ha. Its 4-train design configuration is characterized by four (4) Anaerobic, four (4) Primary Facultative, four (4) Secondary Facultative, two (2) First Maturation and two (2) Second Maturation ponds as shown in Figure 1. Sewage from secondary facultative ponds A and B drains into First Maturation A. On the other hand, that from secondary facultative ponds C and D drains into First Maturation B. Whereas the dry weather flow design flow capacity for each train is 2,625m^3 per day, that of the entire system is 10,500m^3/day. In addition, the system is characterized by an average hydraulic retention time (HRT) of 20 days (Table 1).

Table 1. *Design parameters for the Kibendera WSP.*

Ponds Depth (m)		HRT (Days)	Surface Area (m^2)	Volume (m^3)
Anaerobic	4	1	5,500	22,000
Facultative	1.75	9	55,600	97,300

Ponds Depth (m)		HRT (Days)	Surface Area (m^2)	Volume (m^3)
First Maturation	1.50	5	32,300	48,450
Second Maturation	1.50	5	32,300	48,450
TOTAL		20		216,200

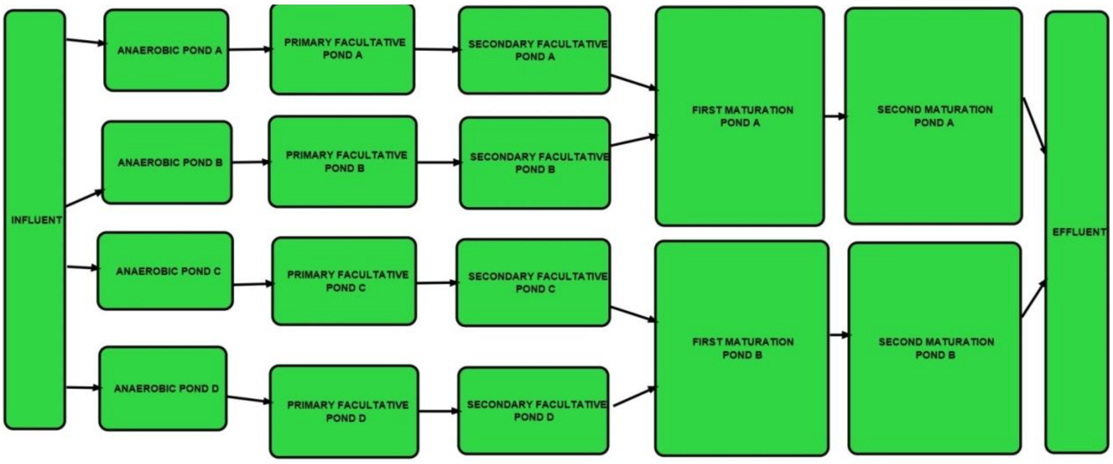


Figure 1*. Schematic of the Kibendera WSP.*

2.2. Flow Data

The average inflow and outflow data over the period of study was obtained by reading the Parshall flume head readings both at the intake and effluent points and computing the discharge using Equation 1

$$Q = C(H)^n \quad (1)$$

Where; Q = Discharge (m^3/day); H = Head (m); C = 1.612; n =1.578 (C is the free-flow coefficient and n is the exponent coefficient of the Parshall flume)

2.3. Sampling and Analytical Methods

Daily influent and effluent grab samples collected at 8.00 a.m., and 4 p.m. were analyzed in the wastewater laboratory within the treatment plant. Standard Methods for the Examination of Water and Wastewater procedures [22] were applied for the analysis of total nitrogen and all the inorganic nitrogen fractions (ammonia, nitrate and nitrite). Organic Nitrogen was empirically derived using Equation 2. Dissolved oxygen (DO) concentrations were obtained in situ using a portable HACH dissolved oxygen/ pH meter.

$$Organic\ Nitrogen\ (ON) = Total\ Nitrogen - (Ammonia + Nitrate + Nitrite) \quad (2)$$

2.4. System's Treatment Efficiency

The overall system efficiency was obtained using Equation 3 calculated as:

$$System\ Treatment\ Efficiency\ (\%) = \frac{Influent(Ci) - Effluent\ (Ce)}{Influent\ (Ci)} x100 \quad (3)$$

Where;
Influent (C_i) = Influent concentration
Effluent (C_e) = Effluent concentration

2.5. Modeling Nitrogen Transformation and Removal

The conceptual model represented by Figure 2 summarizes the various nitrogen fractions modeled in the study as well as their corresponding transformation and removal pathways. Model calibration and validation were achieved by splitting the data set into two sets. Model calibration was realized from January-December 2021 data while model validation was realized from January-December 2022 data.

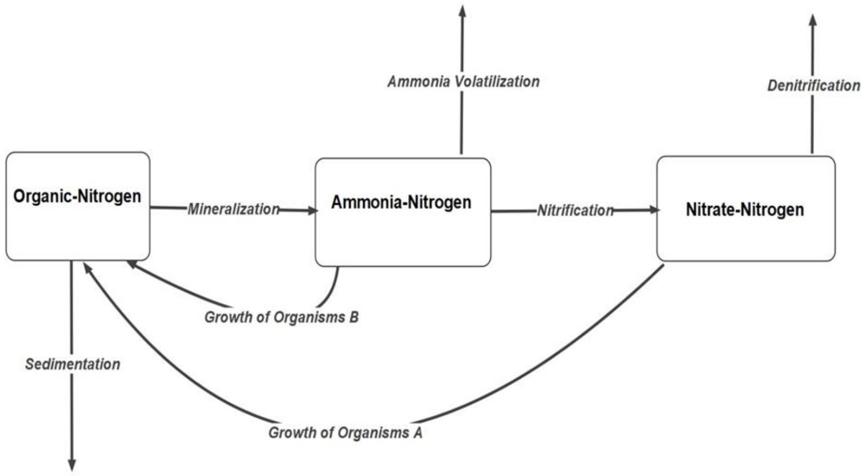


Figure 2. *Nitrogen transformation and removal pathways [23].*

Nitrogen removal model was developed and calibrated using the following set of equations

$$\frac{d(Org-N)}{dt} = \frac{Q_{in}}{V}(Org-N)_{in} - \frac{Q_{out}}{V}(Org-N)_{out} - r_m - r_s + r_A + r_B \tag{4}$$

$$\frac{d(NH_3-N)}{dt} = \frac{Q_{in}}{V}(NH_3-N)_{in} - \frac{Q_{out}}{V}(NH_3-N)_{out} - r_B + r_m - r_V - r_n \tag{5}$$

$$\frac{d(NO_3-N)}{dt} = \frac{Q_{in}}{V}(NO_3-N)_{in} - \frac{Q_{out}}{V}(NO_3-N)_{out} + r_n - r_A - r_d \tag{6}$$

Where, Q_{in} = Influent flow rate in m^3/day; Q_{out}= Effluent flow rate in m^3/day. r_n = Nitrification rate, (mg/L.d); r_d = De-nitrification rate, (mg/L.d); r_m= Mineralization rate, (mg/L.day); r_s = Net loss of organic nitrogen through sediments, (mg/L.d); r_v = Volatilization rate, (mg/L.d); r_B = Uptake rate of NH_3-N by micro-organisms, (mg /L.d); r_A = Uptake rate of NO_3-N by micro-organisms (mg/L.d), d=depth of the pond (m).

The rates for mineralization, nitrification, denitrification, ammonia volatilization, sedimentation of organic nitrogen and growth of microorganisms A and B are summarized in equations 7, 8, 12, 13, 14, 15 and 16. The process rates were later used to estimate the organic nitrogen and ammonia effluent concentrations based on Equations 4 and 5.

$$r_m = 0.002T * Org - N \tag{7}$$

$$r_n = \frac{U_n}{Y_n}\left(\frac{NH_3-N}{K_1 + NH_3-N}\right) x \left(\frac{DO}{K_2 + \mathrm{DO}}\right) \mathrm{x} C_T \mathrm{x} C_{PH} \tag{8}$$

Where, U_n, Y_n, DO, K_2 represent the nitrosomonas maximum growth rate (0.008 day^{-1}), nitrosomonas yield coefficient (0.13), dissolved oxygen concentrations and oxygen nitrosomonas half saturation (assumed to be 1.3 mg/l) respectively. In cases where pH ≥ 7.2, $C_{PH} = 1$ while where pH < 7.2, the existence of free ammonia inhibits the growth of nitrifying bacteria. Hence the correction for the nitrification rate is expressed as

$$C_{pH} = 1 - 0.833(7.2 - pH) \tag{9}$$

$$K_1 = 10^{(0.051(T-1.58))} \tag{10}$$

$$C_T = e^{\propto(T-T_0)} \tag{11}$$

Where, T_o is the reference temperature and α is an empirical constant. The assumed respective values for T_o and α were 15 ℃ and 0.098/ ℃ [17]. Denitrification rate, r_d was obtained using Equation 12.

$$r_d = R2_{20}\theta^{(T-20)} NO_3 - N \tag{12}$$

Where, θ and $R2_{20}$ are the Arrhenius constant (1.02< θ<1.09) and denitrification constant (0 <$R2_{20}$ <1) respectively.

Whereas the rate of ammonia (NH_3-N) volatilization was estimated using Equation 13, that of net loss of nitrogen to the sediments was represented by Equation 14.

$$r_v = 0.0566 * Exp(0.13(T-20)) \left(\frac{NH_3-N}{10^{(10.05-0.032T-pH)}}\right) \tag{13}$$

$$r_s = Rs * Org - N \tag{14}$$

Growth of organisms A and B representing the uptake of nitrate and ammonia fractions respectively by microbial populations was modeled using the Monod Kinetics as summarized by Equations 16 and 17. However, considering the high abundance of ammonia over nitrate in the sewage, preferential uptake of ammonia was considered over that of nitrate. This was due to the high ammonia abundance as well as the high preference of ammonia over nitrate for cell synthesis [15]. Consequently, the uptake of nitrate by microorganisms was not considered further.

$$r_A = \mu_{max20}\theta^{(T-20)} \left(\frac{NO_3-N}{K_4+NO_3-N}\right) Org - N * P_1 \quad (15)$$

$$r_B = \mu_{max20}\theta^{(T-20)} \left(\frac{NH_3-N}{K_3+NH_3-N}\right) Org - N * P_2 \quad (16)$$

3. Results and Discussion

3.1. Effect of Flow Rate on Nitrogen Removal

The mean monthly flow rates over the study period are shown in Figure 3. A previous study on the WSP revealed that the removal efficiency for nitrate and nitrite decreased with increased flow rate [4].

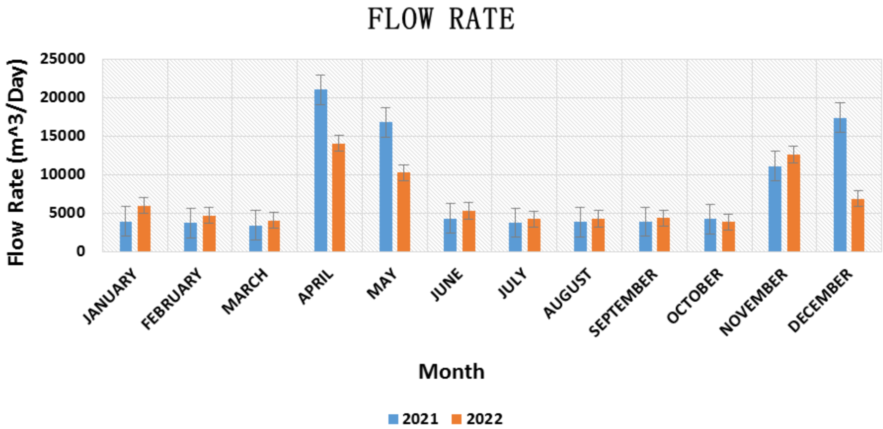


Figure 3. *Mean monthly sewage influent flow rate.*

From Figure 3, highest flow rates of 21,054 m^3/day and 14,065 m^3/day were observed in April 2021 and 2022 respectively. The high flow rates were attributed to storm water intrusion of the ponds caused by long rains experienced during the period. Relatively higher flow rates were also observed during the short rainy months of November (11,091 and 12,602 m^3/day) and December (17,383 and 6,879 m^3/day). The results were consistent with previous studies that showed high flow rates in wastewater treatment plants during the wet seasons [4, 24, 25]. The relationship between flow rate and the removal of various nitrogen fractions investigated by regression analysis, revealed no correlation between the flow rate and nitrogen removal rates ($0.048<R^2<0.126$).

3.2. Dissolved Oxygen Concentrations

The dissolved oxygen (DO) concentration levels in the influent, Anaerobic (AP), Primary Facultative (PF), Secondary Facultative (SF), First Maturation (FM) and Second Maturation (SM) ponds are as shown in Figure 4.

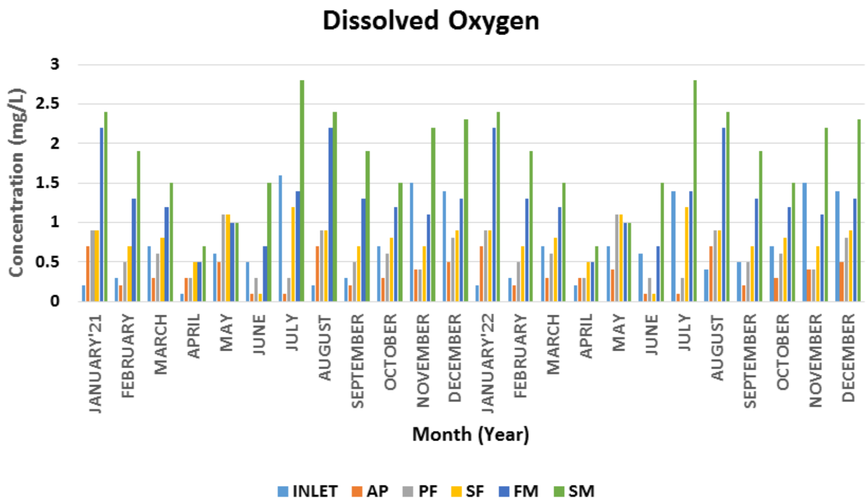


Figure 4. *Mean monthly DO levels in the various ponds within the system.*

From Figure 4, least and highest DO concentrations were observed in the anaerobic (AP) and secondary maturation (SM) ponds. Anaerobic ponds receive sewage with very high organic loading compared to the oxygen entering the ponds. In addition, the high organic loading is responsible for depleting the available dissolved oxygen. Based on this fact, low DO concentrations (0.1-0.7 mg/L) observed in the anaerobic ponds were expected [26, 27]. On the other hand, the shallow maturation ponds permitted surface transfer of atmospheric oxygen into the sewage to realize higher DO levels (0.7- 2.8 mg/L). However, the DO values were relatively lower to those observed in the Dandora Waste Stabilization Ponds, where the range was from 2.66 to 19.77 mg/L [5]. Based on Figure 4, moderate DO concentrations (0.1-1.2 mg/L) observed in the primary and secondary facultative ponds were relatively lower to those observed in the Dandora WSP (0.79-14.05 mg/L). DO in the facultative ponds was a result of symbiotic consumption of carbon dioxide and release of oxygen by the algal population within the ponds, that developed and produced oxygen in excess of their own requirements. This played a crucial role in breaking down organic matter in the sewage. Wind effect also contributed to the marginal increase of oxygen levels in the P.F. and S.F ponds [28]. Considering that bacteria uses oxygen to break down the organic matter in the sewage, the DO values observed were low to guarantee significant nitrogen transformation and removal [28].

3.3. Nitrogen Concentrations and Removal

The concentrations and removal rates for various nitrogen fractions are represented in Figures 5, 6, 7, 8 and 9.

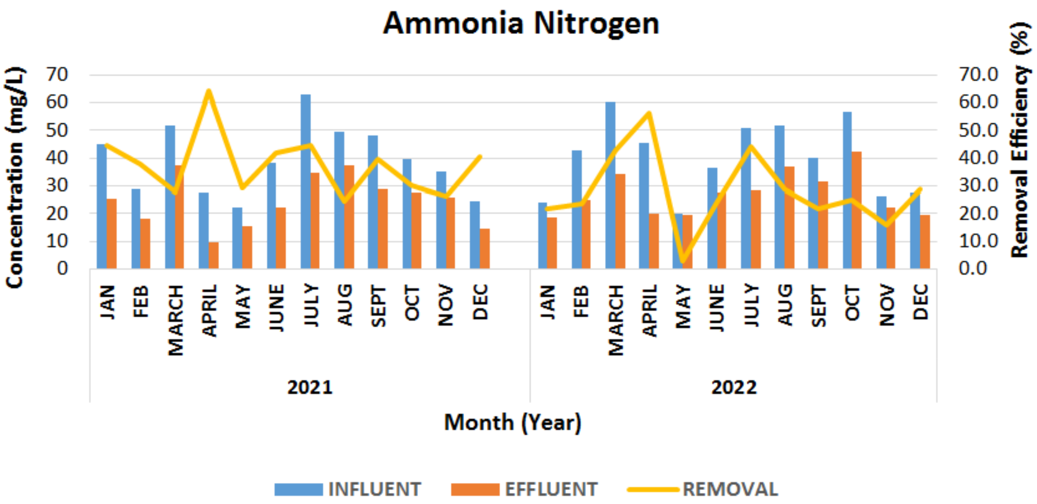


Figure 5. *Ammonia concentrations and removal rates.*

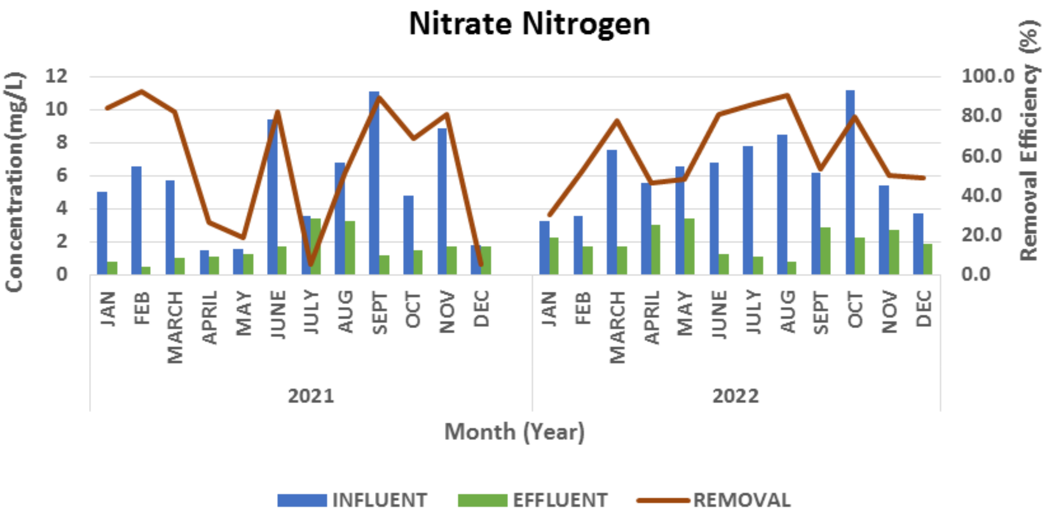


Figure 6. *Nitrate concentration and removal rates.*

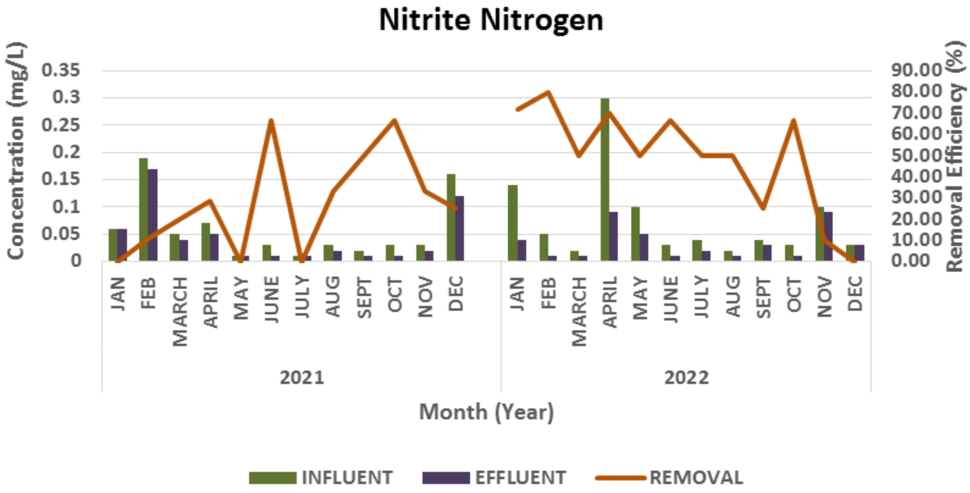


Figure 7. Nitrite concentrations and removal rates.

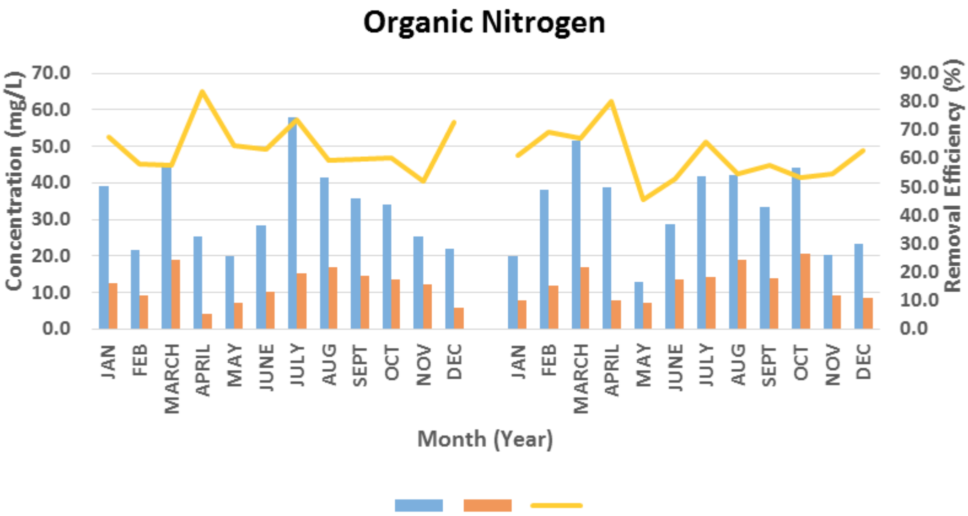


Figure 8. Organic Nitrogen concentrations and removal rates.

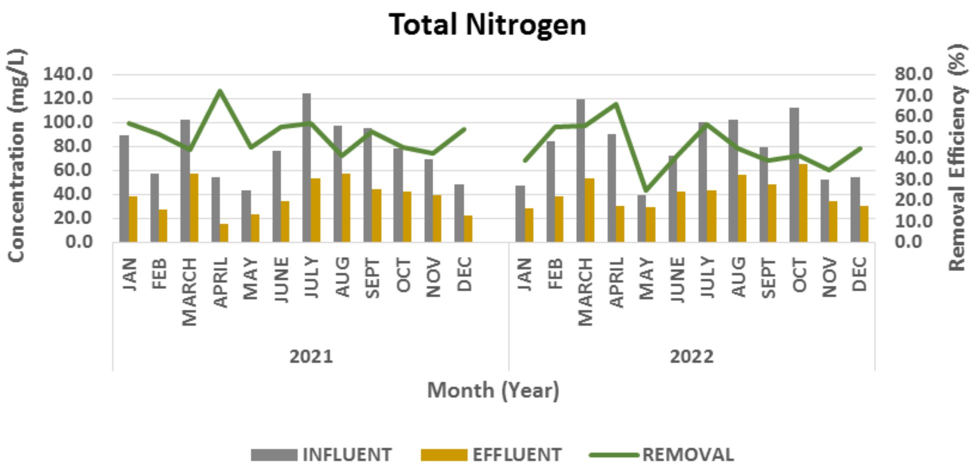


Figure 9. Total Nitrogen concentrations and removal rates.

From Figure 5, highest and least ammonia influent concentrations of 62.8 mg/L and 20 mg/L respectively were observed in July 2021 and May 2022 respectively. Least Organic Nitrogen and Total Nitrogen concentrations of 12.9

mg/L and 39.6 mg/L respectively (Figures 8 & 9) also characterized the latter period. The observed concentrations were as a result of dilution effect caused by the increased flow rate recorded during the period (Figure 3). Similarly, storm water dilution was responsible for the least nitrate influent concentration of 1.5 mg/L observed in April 2021. The effect of dilution on sewage concentration was previously studied [24, 25]. Nitrite influent concentration values remained low throughout the study period (0.01-0.19 mg/L). Previous studies were also characterized with very low NO_2^- concentrations (0.001<Nitrite< 1 mg/L) [29, 30].

From Figures 5, 8 & 9 least effluent concentrations of 9.8, 4.1 and 15.1 mg/L were observed for ammonia, organic nitrogen and total nitrogen respectively in April 2021. Sewage dilution was responsible for the low effluent concentrations observed during the period [25, 31, 32]. On the other hand, highest ammonia, organic nitrogen and total nitrogen effluent concentrations of 47.3, 22.2 and 72.8 mg/L respectively were observed in August 2021. The high concentrations observed during the dry month of August reveals the system's non-resilience to high variations in influent concentrations. Shock loads resulting in highest influent concentrations in July 2021 (Ammonia- 62.8, Organic Nitrogen- 57.9 and Total Nitrogen-124.3 mg/L) were responsible for the high effluent values in July and August 2021.The shock loads were as a result of external discharges from the privately owned sewage exhausters [4]. Preferential oxidation of ammonia that hindered denitrification was responsible for the highest nitrate effluent concentration of 3.4 mg/L observed in July 2021 and May 2022. In July 2021, an influent ammonia concentration of 62.8mg/L observed favored the activity of ammonia oxidizing bacteria (AOB) hence limiting the activity of denitrifying bacteria [33].

Based on Equation 3, the mean monthly removal efficiencies were obtained and summarized in Figures 5, 6, 7, 8 and 9. Highest removal efficiencies of 64.3%, 83.7% and 72.3% for Ammonia, Organic Nitrogen and Total Nitrogen respectively were observed in April 2021 under a flow rate of 21,054 m^3/day (Figure 3). High dilution of the sewage due to storm water intrusion was responsible for this observation. Highest nitrate and nitrite removal efficiencies of 92.4% and 80% respectively were observed in February 2021 and February 2022. This was indicative of the fact that the denitrification process was optimal under dry weather flow conditions. The highest removal efficiencies observed were a result of low dilution effect, reduced storm water intrusion into the WSP and long retention time that favored the denitrification processes. The relationship between influent concentrations, effluent concentrations and removal efficiencies was conducted to determine the R^2 values. The relationship between influent and effluent concentrations yielded R^2 values of 0.709, 0.022, 0.628, 0.601 and 0.709 for ammonia, nitrate, nitrite, organic nitrogen and total nitrogen respectively. Increased influent concentrations translated to increased effluent concentrations, an indication of the system's non-resilience in attenuating spiked influent concentrations hence the spiked effluent concentrations. The corresponding R^2 values between influent concentrations and removal rates were 0.077, 0.598, 0.013, 0.065 and 0.085 respectively. The high R^2 value observed for nitrate (0.598) was consistent with a previous study [34], where high influent nitrate concentrations under long HRT contributed to high nitrate removal rates and reduced nitrite concentrations. This was due to dissimilatory nitrate-to-ammonia process, explaining the low R^2 values for nitrite and ammonia.

3.4. Modeling Nitrogen Removal

The major nitrogen removal pathways; volatilization, mineralization, sedimentation of organic nitrogen, denitrification, nitrification and ammonium uptake as well as their corresponding rates are shown in Figure 10. The contribution of each process in the overall nitrogen removal is summarized in Table 2.

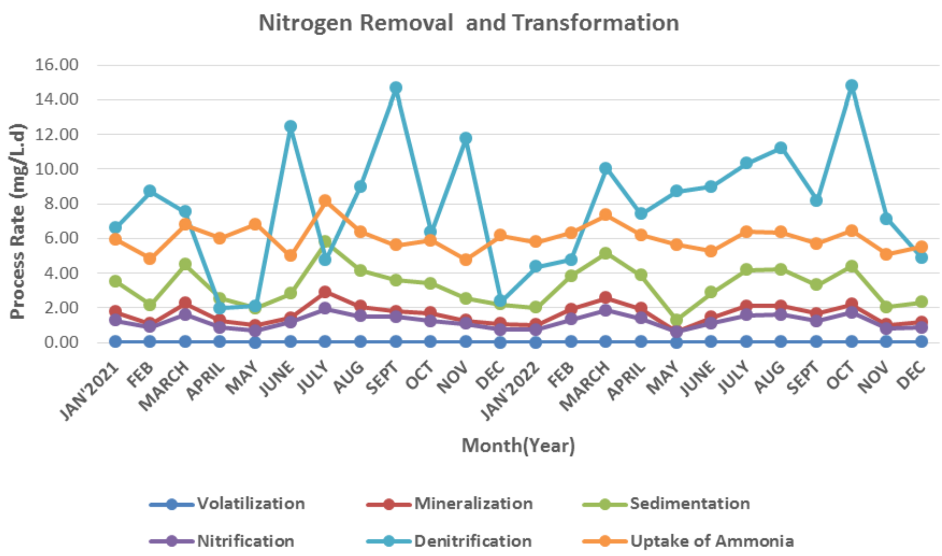


Figure 10. *Nitrogen removal and transformation process rates.*

Table 2. *Percent Contribution for nitrogen removal and transformation processes.*

Process	% Removal Contribution
Volatilization	0%
Mineralization	4– 12%
Sedimentation	12– 25%
Nitrification	4– 8%
Denitrification	16– 55%
Microbial ammonia uptake	21–54%

From Figure 10, ammonia volatilization was the lowest compared to the other processes (0.01-0.02 mg/L.d) with a very insignificant contribution to the overall nitrogen removal (Table 2). This was consistent with previous studies that observed very low ammonia volatilization rates [17, 35]. The studies observed that loss by volatilization is more likely at higher pH (pH>12) since all the ammonia present in the sewage is converted into ammonia gas. The observed pH values (6.5 - 8.5) in Kibendera WSP were inadequate to realize high volatilization rates.

The corresponding rates of mineralization, sedimentation, nitrification, denitrification and microbial ammonia uptake were 0.65-2.9, 1.29-5.79, 0.62-1.93, 0.31-2.33, 1.98-14.67 and 4.77-8.16 mg/L.d respectively. Whereas mineralization realized the transformation of organic nitrogen to ammonia, nitrification realized the biological oxidation of ammonia to nitrate. The sedimentation of non-biodegradable organic nitrogen was also another pathway through which organic nitrogen was removed from the WSP. Previous studies have reported sedimentation coefficient values ranging between 0.001 to 0.1 [36, 37].The higher sedimentation values observed in the Kibendera WSP are attributed to high settling velocities of suspended solids observed in a previous study conducted on the same system [21]. In addition, the long retention time (Table 1) enhanced the sedimentation of non-biodegradable organic nitrogen. Previous research observed that settling of biodegradable organic nitrogen into sediments in the ponds is a permanent organic nitrogen removal pathway [38, 39]. Denitrification and microbial ammonia uptake contributed the highest nitrogen removal as summarized in Table 2. The contribution of algae in ammonia uptake in WSP is available in previous research [36, 40]. Low nitrification rates observed were attributed to very low DO concentrations observed over the study period (0.1-2.8 mg/L). Complete nitrification is possible under high DO conditions as 1 milligram (mg) of ammonia requires 4.57 mg of dissolved oxygen to be fully oxidized to nitrate [28]. In cases where the dissolved oxygen of sewage is low, nitrate becomes the electron acceptor thus enhancing the oxidation of ammonia. However, in this study, high ammonia influent concentrations (20-62.8 mg/L) compared to nitrate influent concentrations (1.5-11.2 mg/L) failed to realize significant ammonia oxidation. Hence the high ammonia presence resulted in a high ammonia preference for cell synthesis [15]. The calibration parameter values are summarized in Table 3.

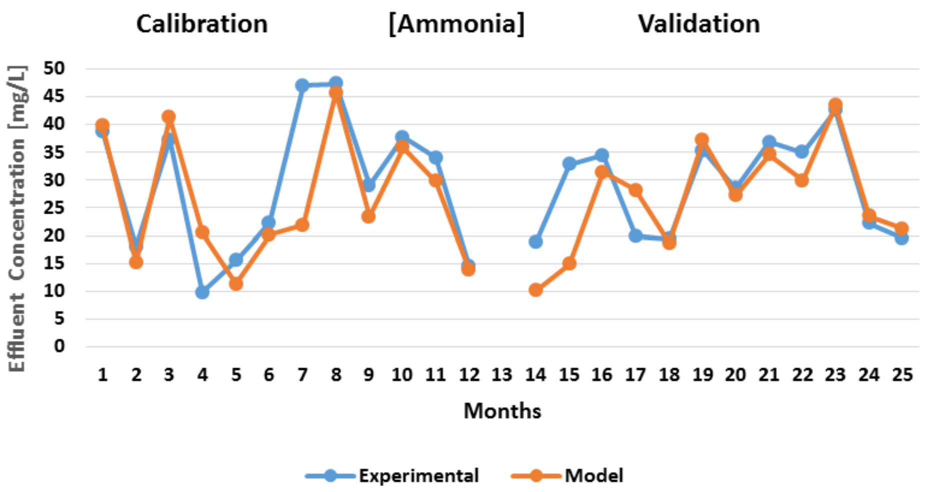
Table 3. *Model calibration parameter values.*

Parameter	Description	Literature Value	Calibrated Value	Reference
θ	Arrhenius constant	1.01 to 1.09	1.08	[41]
R_s constant (d^{-1})	ON. Sedimentation	0.001-0.1	0.1	[42]
K_1	Nitrosom. half sat. const. (mg/L)	0.3-1.3	1.17	[43]
K_2 half sat. const. (mg/L)	Oxygen. Nitrosom.	1.3	1.3	[17]
K_3	Ammonia. half sat. const. (mg/L)	18	9.1	[44]
R_{20}	denitrification constant (d^{-1})	0.0-1.0	0.9	[42]
Y_n	Yield coeff. Nitrosom. (VSS/mg N)	0.03-0.13	0.13	[45]
μ_n	Nitrosom. growth rate (d^{-1})	0-0.008	0.008	[17]

Parameter	Description	Literature Value	Calibrated Value	Reference
μ_{max} at 20˚C (d^{-1})	maximum growth rate	0.1 to 0.77	0.77	[17]

Table 4. Calibration and validation results for measured and estimated concentrations.

Nitrogen Fraction		Correlation Coefficient (*r*)
	Calibration	Validation
Ammonia	0.78	0.74
Organic Nitrogen	0.69	0.93



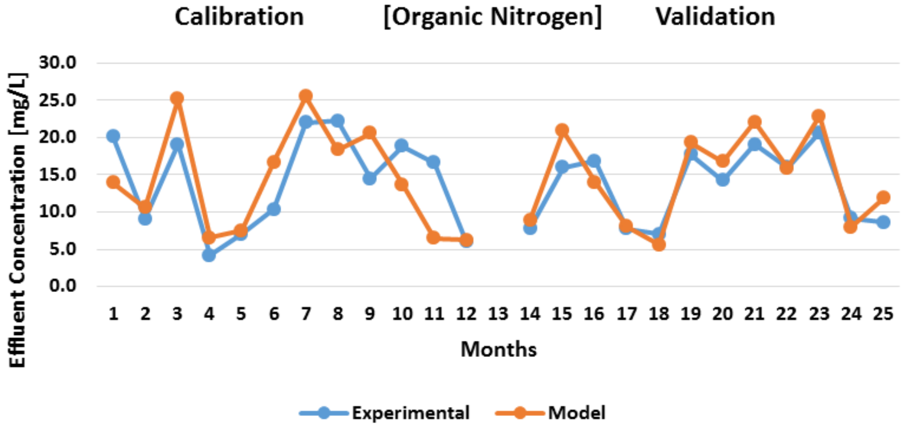


Figure 11. Experimental and Model Effluent Concentrations.

From Table 3, observations made show that many of the parameters resembled or were within the range of values obtained by other researchers. The high preference for ammonia for cell synthesis and dissimilatory nitrate-to-ammonia process may be responsible for the lower K_3 value observed. Based on Equations 4 and 5, estimated ammonia and organic nitrogen effluent concentrations were compared with experimental data (Figure 11). The estimated values for the modeled organic nitrogen and ammonia nitrogen agreed well with the experimental values. Table 4 shows the calibration and validation results for estimated concentrations with measured ammonia and organic nitrogen concentrations. The high *r* values indicate that modelled concentrations were close to their corresponding observed concentrations for both calibration and validation periods. The values were consistent with those observed in previous studies [17, 18]. Considering that experimental data was collected under uncontrolled environmental, chemical and physical conditions, the agreement between the model output and the observed effluent concentrations is reasonably good.

4. Conclusion

Nitrogen transformation and removal characteristics in Kibendera WSP were investigated in 2021 and 2022. The study involved both experimental and modeling work to determine effluent characteristics and removal rates for Ammonia, Nitrate, Organic Nitrogen, Nitrite and Total Nitrogen. The experimental data obtained modeled the nitrogen transformation and removal through ammonia volatilization, sedimentation of non-biodegradable organic nitrogen, mineralization, nitrification denitrification as well as microbial ammonia uptake. Mass balance reaction rate models estimated process removal rates. The experimental data revealed highest removal efficiencies of 64.3%, 83.7%, 92.4%, 80% and 72.3% for Ammonia, Organic Nitrogen, Nitrate, Nitrite and Total Nitrogen respectively. Dilution effect due to storm water intrusion into the ponds as evidenced by lower influent and effluent concentrations was observed during the rainy months of April, May, November and December. Ammonia volatilization (0.01mg/L.d) and denitrification (14.67 mg/L.d) contributed to the least and highest nitrogen removal respectively. High ammonia presence over nitrate favored preferential microbial ammonia uptake over nitrate uptake. In addition, low DO levels (0.1-2.8 mg/L) were insufficient to fully oxidize the ammonia present in the sewage, hence very low nitrification rates (0.62-1.93 mg/L.d). Model calibration results yielded correlation coefficients (*r*) of 0.77 and 0.69 for ammonia and organic nitrogen respectively. The corresponding correlation coefficients during model validation were 0.69 and 0.93 respectively. The good agreement between experimental and modelled effluent concentrations renders the model useful to predict and optimize nitrogen removal from the Kibendera WSP. Providing external aeration to spike DO levels in the ponds is urgent to enhance nitrification process.

Abbreviations

WSP: Waste Stabilization Ponds
DO: Dissolved Oxygen
AP: Anaerobic Pond
PF: Primary Facultative
SF: Secondary Facultative
FM: First Maturation
SM: Second Maturation
AOB: Ammonia Oxidizing Bacteria

Conflicts of Interest

The authors declare no conflicts of interests.

References

[1] Ho, L. T., Van Echelpoel, W., & Goethals, P. L. (2017). Design of waste stabilization pond systems: A review. *Water research*, 123, 236-248. https://doi.org/10.1016/j.watres.2017.06.071

[2] Mburu, N., Tebitendwa, S. M., Van Bruggen, J. J., Rousseau, D. P., & Lens, P. N. (2013). Performance comparison and economics analysis of waste stabilization ponds and horizontal subsurface flow constructed wetlands treating domestic wastewater: A case study of the Juja sewage treatment works. *Journal of environmental management*, 128, 220-225 https://doi.org/10.1016/j.jenvman.2013.05.031

[3] Bundi, L. K., & Njeru, C. W. (2018). Use of vegetative wastewater treatment systems for counties' effluent management in Kenya. *Rwanda Journal of Engineering, Science, Technology and Environment*, 1(1). https://doi.org/10.4314/rjeste.v1i1.1S

[4] Kirumba, G., Thumbi, G., Mwangi, J., & Mbugua, J. (2022) Evaluation of Sewage Treatment Efficiency of the Kibendera Waste Stabilization Ponds in Ruiru, Kenya. *Journal of International Academic Research for Multidisciplinary*, 10 (8), 6-23 https://www.jiarm.com/Oct2022.html

[5] Sewe, H. A. (2013). A study on the Efficiency of Dandora Domestic and Industrial Wastewater Treatment Plant in Nairobi (Doctoral dissertation). http://ir.jkuat.ac.ke/handle/123456789/995

[6] Canfield, D. E., Glazer, A. N., & Falkowski, P. G. (2010). The evolution and future of Earth's nitrogen cycle. *Science*, *330*(6001), 192-196. https://doi.org/10.1126/science.1186120

[7] Kuypers, M. M., Marchant, H. K., & Kartal, B. (2018). The microbial nitrogen-cycling network. *Nature Reviews Microbiology*, *16*(5), 263-276. https://doi.org/10.1038/nrmicro.2018.9

[8] Wang, B., & Lan, C. Q. (2011). Biomass production and nitrogen and phosphorus removal by the green algae *Neochloris oleoabundans* in simulated wastewater and secondary municipal wastewater effluent. *Bioresource technology*, 102(10), 5639-5644. https://doi.org/10.1016/j.biortech.2011.02.054

[9] Fujitani, H., Kumagai, A., Ushiki, N., Momiuchi, K., & Tsuneda, S. (2015). Selective isolation of ammonia-oxidizing bacteria from autotrophic nitrifying granules by applying cell-sorting and sub-culturing of microcolonies. *Frontiers in microbiology*, 6, 1159. https://doi.org/10.3389/fmicb.2015.01159

[10] Shalini, S. S., & Joseph, K. (2012). Nitrogen management in landfill leachate: Application of SHARON, ANAMMOX and combined SHARON–ANAMMOX process. Waste Management, 32(12), 2385-2400. https://doi.org/10.1016/j.wasman.2012.06.006

[11] Wang, H., Song, Q., Wang, J., Zhang, H., He, Q., Zhang, W.,... & Li, H. (2018). Simultaneous nitrification, denitrification and phosphorus removal in an aerobic granular sludge sequencing batch reactor with high dissolved oxygen: effects of carbon to nitrogen ratios. *Science of the Total Environment*, 642, 1145-1152 https://doi.org/10.1016/j.scitotenv.2018.06.081

[12] Zhou, X., Song, J., Wang, G., Yin, Z., Cao, X., & Gao, J. (2020). Unravelling nitrogen removal and nitrous oxide emission from mainstream integrated nitrification-partial denitrification-anammox for low carbon/nitrogen domestic wastewater. *Journal of environmental management*, 270, 110872. https://doi.org/10.1016/j.jenvman.2020.110872

[13] Valero, C., Read, L. F., Mara, D. D., Newton, R. J., Curtis, T. P., & Davenport, R. J. (2010). Nitrification-denitrification in waste stabilisation ponds: a mechanism for permanent nitrogen removal in maturation ponds. *Water Science and Technology*, 61(5), 1137-1146. http://dx.doi.org/10.2166/wst.2010.963

[14] Bastos, R. K. X., Rios, E. N., & Sánchez, I. A. (2018). Further contributions to the understanding of nitrogen removal in waste stabilization ponds. *Water Science and Technology*, 77(11), 2635-2641. https://doi.org/10.2166/wst.2018.218

[15] Mayo, A. W., & Abbas, M. (2014). Removal mechanisms of nitrogen in waste stabilization ponds. *Physics and Chemistry of the Earth*, Parts A/B/C, 72, 77-82. https://doi.org/10.1016/j.pce.2014.09.011

[16] Ghneim, N. (2003). Quantification of Nitrification and Denitrification Rates in Algae Based and Duckweed Based Waste Stabilization Ponds (Doctoral dissertation). http://hdl.handle.net/20.500.11889/5337

[17] Mayo, A. W. (2013). Nitrogen mass balance in waste stabilization ponds at the University of Dar es Salaam, Tanzania. African Journal of Environmental Science and Technology, 7(8), 836-845. https://doi.org/10.5897/AJEST2013.1495

[18] Mukhtar, H., Lin, Y. P., Shipin, O. V., & Petway, J. R. (2017). Modeling nitrogen dynamics in a waste stabilization pond system using flexible modeling environment with MCMC. *International Journal of Environmental Research and Public Health*, *14*(7), 765. https://doi.org/10.3390/ijerph14070765

[19] Wanjohi, L., Mwasi, S., Mwamburi, L., & Isaboke, J. (2020). The efficiency of University of Eldoret Wastewater Treatment Plant, Kenya. Africa, *Environmental Review Journal*, 3(2), 99109. https://doi.org/10.2200/aerj.v3i2.174

[20] K'oreje, K. O., Kandie, F. J., Vergeynst, L., Abira, M. A., Van Langenhove, H., Okoth, M., & Demeestere, K. (2018). Occurrence, fate and removal of pharmaceuticals, personal care products and pesticides in wastewater stabilization ponds and receiving rivers in the Nzoia Basin, Kenya. *Science of the Total Environment*, 637, 336-348. https://doi.org/10.1016/j.scitotenv.2018.04.331

[21] Kirumba, G., Thumbi, G., Mwangi, J., & Mbugua, J.(2023) Analysis of the Sludge Settling Behavior of the Kibendera Waste Stabilization Ponds in Ruiru, Kenya. Journal of Energy, Environmental & Chemical Engineering, 8(1), 18-25. https://doi.org/10.11648/j.jeece.20230801.13

[22] American Public Health Association (APHA) (2005), American Water Works Association (AWWA) & Water Environment Federation (WEF): Standard Methods for the Examination of Water and Wastewater, 21st Edition.

[23] Mayo, A. W., & Hanai, E. E. (2014). Dynamics of nitrogen transformation and removal in a pilot high rate pond. *Journal of Water Resource and Protection*, *6*(05), 433. https://doi.org/10.4236/jwarp.2014.65043

[24] Rashid, S. S., & Liu, Y. Q. (2020). Assessing environmental impacts of large centralized wastewater treatment plants with combined or separate sewer systems in dry/wet seasons by using LCA. Environmental Science and Pollution Research, 27(13), 15674-15690. https://doi.org/10.1007/s11356-020-08038-2

[25] Li Y, Hou X, Zhang W, Xiong W, Wang L, Zhang S, Wang P, Wang C (2017) Integration of life cycle assessment and statistical analysis to understand the influence of rainfall on WWTPs with combined sewer systems. *J Clean Prod* 172: 2521–2530. https://doi.org/10.1016/j.jclepro.2017.11.158

[26] Kayombo, S., Mbwette, T. S. A., Mayo, A. W., Katima, J. H. Y., & Jorgensen, S. E. (2000). Modelling diurnal variation of dissolved oxygen in waste stabilization ponds. *Ecological modelling*, *127*(1), 21-31. https://doi.org/10.1016/S0304-3800(99)00196-9

[27] Pescod, M. B. (1996). The role and limitations of anaerobic pond systems. *Water science and Technology*, *33*(7), 11-21. https://doi.org/10.1016/0273-1223(96)00335-6

[28] Tchobanoglous, G., Stensel, H. D., Tsuchihashi, R., and Burton, F. L. (2014). Wastewater Engineering: Treatment and Resource Recovery, 5th Edn. Metcalf and Eddy I AECOM. New York, NY: McGraw-Hill Book Company.

[29] Rodda, J. C. and Ubartini, L. (2004). The Basis of Civilization. Water Science and Technology, 161. International Association of Hydrological Sciences (International Association of Hydrological Sciences Press 2004).

[30] Abagale, F. K., Osei, R. A., &Kranjac-Berisavljevic, G. (2020). Occurrence dynamics of nitrogen compounds in faecal sludge stabilisation ponds in the Tamale Metropolis, Ghana. *African Journal of Environmental Science and Technology*, 14(10), 329-335. https://doi.org/10.5897/AJEST2020.2885

[31] Xu, Z., Xiong, L., Li, H., Liao, Z., Yin, H., Wu, J.,... & Chen, H. (2017). Influences of rainfall variables and antecedent discharge on urban effluent concentrations and loads in wet weather. Water Science and Technology, 75(7), 1584-1598 https://doi.org/10.2166/wst.2017.020

[32] Stephenson, T., Brindle, K., Judd, S., & Jefferson, B. (2000). Membrane bioreactors for wastewater treatment. IWA publishing.

[33] Kim, D. J., & Kim, S. H. (2006). Effect of nitrite concentration on the distribution and competition of nitrite-oxidizing bacteria in nitratation reactor systems and their kinetic characteristics. *Water research*, 40(5), 887-894. https://doi.org/10.1016/j.watres.2005.12.023

[34] Zhao, Y., Li, Q., Cui, Q., & Ni, S. Q. (2022). Nitrogen recovery through fermentative dissimilatory nitrate reduction to ammonium (DNRA): Carbon source comparison and metabolic pathway. *Chemical Engineering Journal*, *441*, 135938. https://doi.org/10.1016/j.cej.2022.135938

[35] Picot, B., Andrianarison, T., Olijnyk, D. P., Wang, X., Qiu, J. P., & Brissaud, F. (2009). Nitrogen removal in wastewater stabilisation ponds. *Desalination and Water Treatment*, *4*(1-3), 103-110. https://doi.org/10.5004/dwt.2009.363

[36] Senzia, M. A.; Mayo, A. W.; Mbwette, T. S. A.; Katima, J. H. Y.; Jørgensen, S. E (2002). Modelling nitrogen transformation and removal in primary facultative ponds. Ecol. Model., 154, 207–215. https://doi.org/10.1016/S0304-3800(02)00018-2

[37] Ferrara R. A., Avci C. B. (1982). Nitrogen dynamics in waste stabilization ponds. *J. Water Pollut. Control Fed*. 54: 361–369. https://www.jstor.org/stable/25041314

[38] Trang, N. T. D.; Konnerup, D.; Schierup, H.-H.; Chiem, N. H.; Brix, H. (2010). Kinetics of pollutant removal from domestic wastewater in a tropical horizontal subsurface flow constructed wetland system: Effects of hydraulic loading rate. *Ecol. Eng*., 36, 527–535. https://doi.org/10.1016/j.ecoleng.2009.11.022

[39] Merino-Solís, M. L.; Villegas, E.; de Anda, J.; López-López, A. (2015). The effect of the hydraulic retention time on the performance of an ecological wastewater treatment system: An anaerobic filter with a constructed wetland. Water, 7, 1149–1163. https://doi.org/10.3390/w7031149

[40] Faleschini, M., Esteves, J. L., & Camargo Valero, M. A. (2012). The effects of hydraulic and organic loadings on the performance of a full-scale facultative pond in a temperate climate region (Argentine Patagonia). *Water, Air, & Soil Pollution*, *223*, 2483-2493. https://doi.org/10.1007/s11270-011-1041-0

[41] Baca, R. G., & Arnett, R. C. (1976). A limnological model for eutrophic lakes and impoundments. In *Proceedings of the Conference on Environmental Modeling and Simulation, EPA 600/9-76* (Vol. 16, pp. 768-772).

[42] Jørgensen, S. E. (1994) Fundamentals of Ecological Modelling: Development in Environmental Modelling. Elsevier Science B. V., Amsterdam.

[43] Mayo, A. W., & Mutamba, J. (2005). Modelling nitrogen removal in a coupled HRP and unplanted horizontal flow subsurface gravel bed constructed wetland. *Physics and Chemistry of the Earth, Parts A/B/C*, *30*(11-16), 673-679. https://doi.org/10.1016/j.pce.2005.08.007

[44] Ferrara, R. A., & Harleman, D. R. (1980). Dynamic nutrient cycle for waste stabilization ponds. *Journal of the Environmental Engineering Division*, *106*(1), 37-54. https://doi.org/10.1061/JEEGAV.0001010

[45] Charley, R. C., Hoper, D. G. and McLee, A. G. (1980) Nitrification Kinetics in Activated Sludge at Various Temperatures and Dissolved Oxygen Concentrations. *Water Research*, 14, 1387-1396 https://doi.org/10.1016/0043-1354(80)90002-0