



MATHEMATICAL PREDICTION OF NITROGEN AND PHOSPHORUS REMOVAL FROM PIGGERY WASTEWATER BY HORIZONTAL SUB-SURFACE FLOW CONSTRUCTED WETLAND

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ABSTRACT

Mathematical equations were derived for estimation of nitrogen and phosphorus removal from piggery wastewater in horizontal subsurface flow constructed wetlands. The model inputs included wastewater inflow, retention, plant uptake and nutrient loss to the atmosphere by volatilization of nitrogen. Plant die off, precipitation and exchange with subsurface were considered negligible. The calibration and validation of the model was carried using different sets of experimental data generated from a pilot constructed wetland monitored over a period of seven months. The results show that the amount of nitrogen and phosphorus concentrations decreased exponentially within three days of retention in the wetland and, thereafter, the reduction appeared constant over higher retention time subject to the decay coefficient. There was high correlation between the simulated and observed parameters with $R^2 = 0.9537$ for nitrogen and 0.9912 for phosphorus respectively. The low values of the mean bias error (ME) of 0.211 and 0.139 , root mean square error (RMSE) of 0.32 and 0.18 , and relative error of RE of 24 and 12% , demonstrated the ability of the model to predict nutrient removal accurately. The models efficiencies of 84 and 77% and index of agreements of 0.6527 and 0.8676 for nitrogen and phosphorus respectively, indicate an acceptable level of the models predictive capacities. The linear regression coefficients appear reasonable given that the system was a natural system located in the field, where uncontrolled influencing factors could weaken optimal performance. Because of challenges associated with Scaling-up this result. longer field studies are recommended. The models developed in this study considered the features of horizontal-subsurface-flow constructed-wetlands for removal of nitrogen and phosphorus from piggery wastewater. The high correlation between the developed models and the calibrated parameters showed that they are rational. The models can be used to simulate nitrogen and phosphorus removal in horizontal-subsurface-flow constructed-wetlands. The performance of these models meets the water quality discharge or reuse standards of Nigeria for wastewater discharge to land and surface water.

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1.0 Introduction

Pigs provide a significant amount of meat for human consumption. Currently, pig meat provides over 30% of world-wide meat consumption. According to official statistics by the Organization for Economic Cooperation and Development (OECD), as reported by Soare and Chiurciu (2017), the highest meat consumption per capita in the world in 2016, was 39.8% pork (of the total meat consumed per capita). Nigeria's pig industry is an important part of the livestock sub-sector in the overall agricultural sector (Uddin and Osasogie, 2016).

The major problem associated with industrial pig production is pollution of the environment by nutrients from pig waste. Piggery waste has high nutrient content because only 15 per cent of the nutrients contained in their feed material is retained and transformed into animal product.

The remaining 85 percent are eliminated as waste (Kiely, 1998; Ogbuewu et al., 2012) mainly urine and faeces comprising water (90%). Additionally, complex carbohydrates and nutrients constitutes between 40 – 70% of the total fertilizer value of piggery manure). However, this includes 75% of nitrogen, 80% of phosphorus (as P_2O_5) and 85% potassium (as K_2O). This high nutrient content may result in degradation of land, inland water quality and marine ecosystems through eutrophication, and direct toxicity to organisms (Mason, 2002). It can also contribute to ground water pollution which causes mucosal irritation, respiratory ailment, increased stress and also high blood pressure (Horton et al., 2009, Wendee, 2017).

Additionally, the high doses of copper and zinc fed to pigs to promote growth eventually accumulate and degrade the soil. Zamani, (2016) reports that improper application of raw pig manure can cause degradation of the soil such. Proper management is, therefore, required to sustain the standards for protection of the environment, reduce the effect of effluent addition to land and avoid off-site impairment of water quality safety (ECC, 1999; EPA, 2000). It is important to recycle or treat the waste before releasing into the environment. However, this is not done properly in Nigeria where waste is stored in ditches and lagoons and left to decompose and integrate with the soil (Kadurumba and Kadurumber. 2019). A study by Ewuziem et al., (2009) showed that 80% of the pig farms in Imo State in the tropical South Eastern Nigeria managed their waste by dumping on open land (75%) and on streams (5%).

Nitrogen and phosphorus are the main pollutants of worry from piggery wastewater. Nitrogen is regulated in drinking water to protect the health of children and may be regulated in surface waters to check eutrophication.

Phosphorus is the main factor regulating the growth of plant and algae in freshwater systems (EPA, 2000) and can ensure significant effects on downstream receiving waters (Wallace and Knight, 2006). Its surplus triggers eutrophication which changes ecosystem productivity, reduces biodiversity, upsets water clearness, light dispersion and photosynthesis and causes blooms of algae and cyanobacteria which produce toxins affecting organisms and producing health problems (Gouriveau, (2009).

Commonly, inadequate wastewater treatment in developing countries is essentially financial (Muga and Mihelcic, 2008), due to the vast investments needed to construct, maintain and improve wastewater treatment facilities, but it is also due to lack of data on progresses in wastewater treatment technologies and the use of low cost wastewater treatment technologies (Mburu et al., 2012).

Constructed Wetlands (CWs) are engineered systems designed to remove pollutants from contaminated water. CWs have been shown to collect, hold and process nutrients in wastewater through a combination of physical, chemical, and biological processes (Abbasi et al., 2019; Nandakumar et al., 2019) as water progressively flows through the wetland. These processes are responsible for a variety of treatment mechanisms, which has been found to vary with time and locality due to poor understanding of the removal mechanisms and how they are affected by environmental conditions and system design (Kadlec and Wallace 2009).

Proper design and use of CWs and improving their benefits require a measureable understanding of how these systems function and their response to different management conditions. Design standards and analysis methods for CWs have progressed from relations based on empirical equations derived only from the relationship between input and output nutrient levels to advanced models that can explain the complexity in pollutant removal (Kadlec and Wallace, 2009). Mathematical models are increasingly being used for the design of CWs (Kadaverugu, [2016). Mathematical models describe the relationship between the model

components and link them together using specific mathematical expressions and equations that correctly describe the processes (Jorgensen and Bendoricchio, (2001). FITOVERT (Giraldi et al., 2010), HYDRUS 2D/3D (Simunek et al. 2008), PHWAT (Brovelli et al., 2009) are complete CW models which accounts for the variably saturated hydrodynamics of filter media and also include sub models for determining the fate of pollutants. However, these models are not available as open source software. According to Allen (2019), the commercial version of STELLA software package, widely used in biological, ecological and environmental sciences and in CW modelling, sold for \$2299 as at May, 2019. Therefore, there is the need to develop simple, realistic and readily available model that can be used for planning and designing of new systems as well as investigating the dynamics of nutrients and performance assessment of constructed wetlands. The objective of this paper is to develop a simple mathematical model for prediction of nutrient removal from piggery wastewater by a Horizontal Subsurface Flow (HSF) CW. This will provide a tool for CW design and management to enable piggery farmers, environmental practitioners and designers to model their own nutrient removal from piggery wastewater.

2.0 Materials and Methods

2.1 Study Area and Project Location

The pilot HSFCW was located near the effluent source behind the piggery facility at the Obio Akpa campus of Akwa Ibom State University (AKSU), Figure 1. Obio Akpa is located in the humid tropics between longitudes 07° 3" E and 07° 3" E and latitude 04° 45" N and 04° 55" N.

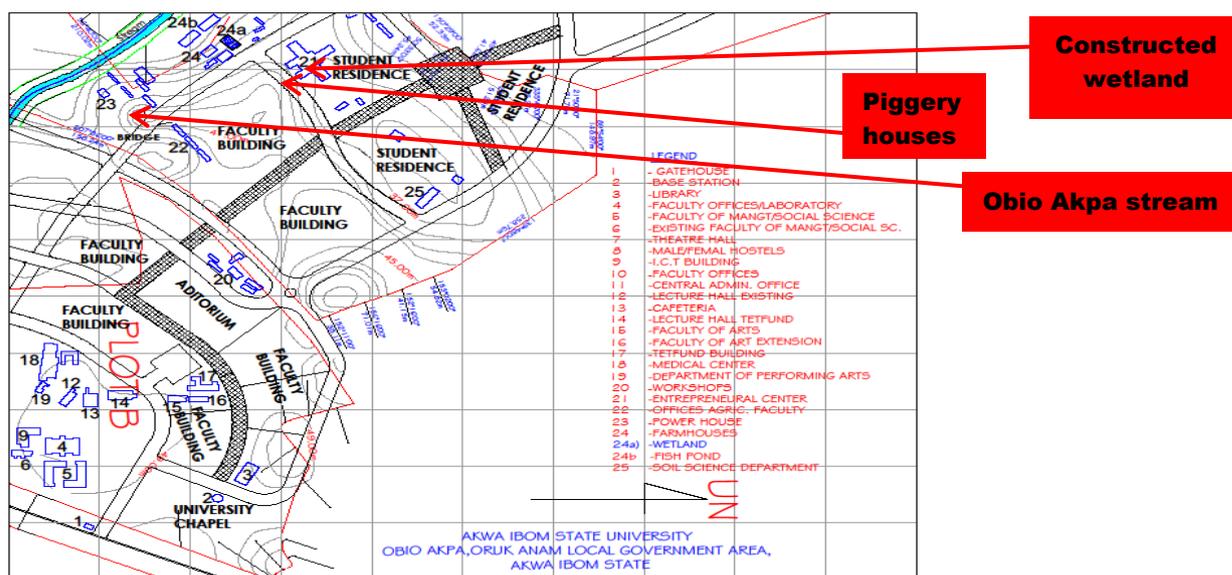


Figure 1: Map of AKSU showing location of piggery and constructed wetlands (Udom et al., 2018)

The average minimum and maximum temperatures range between 18 °C - 27°C and 24°C - 36°C. Relative humidity ranges between 55-86%. Rainfall has a bimodal distribution lasting from April to October with a short break in August. Average rainfall values range from 2050 to 2450mm. The piggery produces an estimated 9.46m³/day wastewater and releases it without treatment onto the floodplain of Obio Akpa stream; a perennial stream which serves as a major source of water to over 150,000 people (NPC, 2006) in three villages which the stream traverses before emptying into the Qua Iboe River at Ekpene Obo in Oruk Anam L. G. A. of Akwa Ibom State (Udom et al., 2018)

2.2 Experimental Setup

The research was conducted at the Akwa Ibom State University. A constructed wetland (Udom et al., 2018) having three wetland cells (7 m x 1.75 m x 0.60 m) enclosed with five courses of 127 mm sandcrete blocks and 75 mm thick floor slab on a concrete foundation were created. A 2.5 mm thick Texclear soil liner was laid to cover the entire wetland floor. Both the wastewater inlet and outlet regions of the wetland basin were filled up to 0.60 m depth of 30 mm crushed granite rock extending one meter from the walls into the treatment area. The wetland basin was filled up to 0.60 m depth with coarse sand medium as substrate. Two of the wetland cells were then planted with *Pennisetum clandestinum* (PC) collected from the Obio Akpa floodplain and the third cell was the control. Thereafter, the wetland was left for about three months to consolidate before being fed with wastewater.

2.3 Sample Collection and Monitoring

Seven months' grab samples data collected before and after the wetland detention time of three days were analyzed for total nitrogen (TN) and total phosphorus (TP) concentrations according to Standard Methods (AOAC, 2007). Destructive and systematic sampling techniques for plant and soil respectively were adopted. Nutrient mass balances were evaluated by changes in concentration. The treatment efficiency was determined using the average influent and effluent concentrations of the water quality parameters.

2.4 Conceptual Model

The conceptual model for complete biogeochemical paths of mineralization of organic matter to ammonia and phosphate and subsequent transport, retention, uptake and removal (denitrification, volatilization, and burial) in the CW is shown in Figure 2.

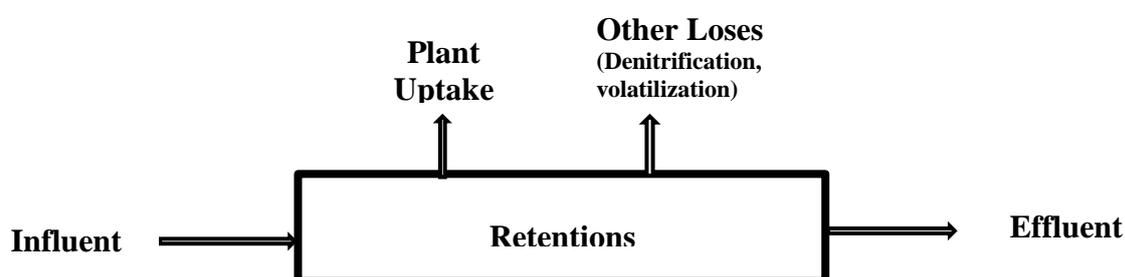


Figure 2: Conceptual model of nutrient removal in the constructed wetland (Udom et al., 2018)

The model partitions the wetland into three basic compartments: (1) water column (2) wetland media, and (3) plant biomass. Sources of nutrient to the wetland water column include piggery runoff, mineralization of suspended organic nitrogen and phosphorus, sediment diffusion and resuspension. Atmospheric depositions play a minor role in constructed wetlands. Nitrification of ammonium nitrogen occurs in the aerobic part of the soil and the water column, whereas nitrate removal by denitrification is confined to the underlying anaerobic zone of the active soil layer and near roots in the rhizosphere of wetland plants. Volatilization to the atmosphere is a significant loss pathway for nitrogen under conditions of high alkalinity (Reddy and Delaune, 2008). In addition to influent concentrations, nitrate is produced by oxidation of ammonium ion in the water column and oxidized soil layer.

Phosphorus removal follows the sediment pathways of sedimentation and resuspension with no gaseous losses. The physical processes of advection (inflow, outflow), settling, resuspension, and diffusion similarly apply to inorganic phosphorus transport and fate in the wetland water. Only the biologically available inorganic phosphorus (typically orthophosphate) is available for uptake by plants. Imported phosphorus (runoff, sediment, ground water) and decomposition of organic matter are primary sources of inorganic phosphorus in wetland soil and water.

Excluding plant harvesting, burial is about the only mechanisms for the removal of phosphorus in wetlands (Kadlec and Wallace, 2009).

2.5 Model Assumptions

The following assumptions were made in the derivation of necessary first order dynamic equations describing the rate of the nutrients removal from the CW:

- (a) zero initial concentration of the nutrient in the CW system $N(0) = N_0$
- (b) nutrient is periodically introduced into the wetland system at the rate $f(t)$.
- (c) the concentration of nutrient in the wetland at time $t > 0$ is $N(t)$
- (d) plant uptake, retention in the media, biogeochemical process constitutes the nutrient reduction pathways from the wetland system at the rate ρ proportional to the quantity present.
- (e) rate of nitrogen input into the wetland from rainfall is negligible,
- (f) there is no percolation by groundwater (because the wetland is lined).

2.6 Model Derivation

In wastewater treatment, a first order degradation model is often used to simulate the chemical and biological degradation of the residual mass of a chemical compound. All constructed wetland systems are considered to be an attached-growth first-order biological reactors which show an exponential decay of pollutant concentration level with the distance through the wetland from inlet to outlet. Degradation in constructed wetlands follow the first order degradation model (Sperling, 2007; Adelegan, 2012; Dotro *et al.*, 2017), and can be represented by first order plug flow reaction kinetics expressed as:

$$\frac{dC}{dt} = -KC \quad (1)$$

Where,

C = concentration of the product of interest.

k = first order rate constant.

t = time

With the above assumptions, the following mathematical model equations were derived for:

(i) Nitrogen

$$\frac{dN}{dt} = -\rho N(t) + f(t) \quad (2)$$

$N(0) = N_0$ Where,

N = nitrogen concentration (mg/l)

ρ = rate of nitrogen removal from the wetland system (mgd^{-1})

$$\frac{dN}{dt} + \rho N(t) = f(t) \quad (3)$$

By using integrating factor, I.F

$$I.F = P(t) = \rho$$

$$e^{\int P(t)dt} = e^{\int \rho dt} = e^{\rho t}$$

Multiplying both sides of (2.2) by the integrating factor, we have

$$e^{\rho t} \left(\frac{dN}{dt} + \rho N(t) \right) = e^{\rho t} f(t)$$

$$\frac{d}{dt} (N e^{\rho t}) = e^{\rho t} f(t)$$

$$d(N e^{\rho t}) = e^{\rho t} f(t) dt$$

$$\int_0^t d(Ne^{\rho s}) = \int_0^t e^{\rho s} f(s) ds$$

$$N(t)e^{\rho t} - N_0 = \int_0^t e^{\rho s} f(s) ds$$

$$N(t)e^{\rho t} = N_0 + \int_0^t e^{\rho s} f(s) ds$$

Dividing through by $e^{\rho t}$

$$N(t) = N_0 e^{-\rho t} + e^{-\rho t} \int_0^t e^{\rho s} f(s) ds \quad (4)$$

Suppose $f(t) \equiv 0$, where $f(t)$ is the influent, then

$$N(t) = N_0 e^{-\rho t} \quad (5)$$

Our model, results in a first order differential equation with the initial condition

$$N(0) = N_0$$

The initial condition represents the background concentration.

The quantity of N nutrient in the wetland system is represented by

$$N(t) = N_0 e^{-\rho t} + e^{-\rho t} \int_0^t e^{\rho s} f(s) ds, \quad \text{at } t > 0 \quad (6)$$

This is a decay exponential function which tells us that as $t \rightarrow \infty$, the quantity of $N(t)$ decreases to zero (0) but, not rapidly because of the presence of the influent $f(t)$.

Suppose $f(t) \equiv 0$, then the decay of nitrogen will be rapid. From experimental observation, the above assumption and explanation does not represent reality. Hence, we assume further that the introduction of nitrogen $f(t) = D$ into the system is at a constant quantity over a period of time, and then the model equation becomes

$$\frac{dN}{dt} = -\rho N(t) + D \quad (7)$$

$$N(0) = N_0$$

$$\frac{dN}{dt} + \rho N(t) = D \quad (8)$$

$$N(0) = N_0$$

By still using the method of integrating factor to find the solution of the above problem,

$$I.F = e^{\int \rho dt} = e^{\rho t}$$

Multiplying both sides of Equation (2.7) by the integrating factor, we have

$$e^{\rho t} \left(\frac{dN}{dt} + \rho N(t) \right) = e^{\rho t} D$$

$$\frac{d}{dt} (N e^{\rho t}) = e^{\rho t} D$$

$$d(N e^{\rho t}) = e^{\rho t} D dt$$

$$\int_0^t d(N e^{\rho s}) = D \int_0^t e^{\rho s} ds$$

$$N(t) e^{\rho t} - N_0 = \frac{D}{\rho} [e^{\rho t} - e^0]$$

$$N(t) e^{\rho t} = N_0 + \frac{D}{\rho} [e^{\rho t} - 1]$$

Dividing through by $e^{\rho t}$

$$N(t) = N_0 e^{-\rho t} + \frac{D}{\rho} [1 - e^{-\rho t}] \quad (9)$$

The quantity of nitrogen that will remain in the system at $t > 0$ after a constant quantity D has been introduced into the system is represented by,

$$N(t) = N_0 e^{-\rho t} + \frac{D}{\rho} [1 - e^{-\rho t}] \quad (10)$$

This shows that though the quantity of nitrogen will decay in the system it will not be totally eliminated from the system. Complete removal of nitrogen in the CW is not feasible and there will still be some background concentration within the wetland system.

In practice, piggery effluent is introduced into the system at a prescribed period of time, T. Suppose, the first influent is at a time $t = 0^+$ then the initial concentration is $N(0^+) = D$.

And we have the model to be

$$\frac{dN}{dt} = -\rho N(t), \quad 0 < t < T, \text{ that is, } t \in (0, T) \quad (11)$$

$$N(0^+) = D$$

Then solving this, we have,

$$N(t) = D e^{-\rho t} \quad (12)$$

Which means that, the concentration before the second influent is,

$$N(T^-) = D e^{-\rho T} \quad (13)$$

The model for next influent, that is, $T \leq t \leq 2T$ is

$$\frac{dN}{dt} = -\rho N(t), \quad (14)$$

$$N(0^+) = N(T^-) + D = D + D e^{-\rho T},$$

where,

$$r = t - T, t = T + r$$

T = loading interval (d)

t = wetland retention time (d)

Solving the above equation, we have

$$N(t) = (D + D e^{-\rho T}) e^{-\rho(t-T)} \quad (15)$$

$$N(2T^-) = D(1 + e^{-\rho T}) e^{-\rho T}$$

The concentration before the third influent is

$$N(2T^-) = D(1 + e^{-\rho T}) e^{-\rho T}$$

The model for next influent, that is, $2T \leq t \leq 3T$ is

$$\frac{dN}{dt} = -\rho N(t), \quad (16)$$

$$N(0^+) = N(2T^-) + D$$

$$= D(1 + e^{-\rho T} + e^{-2\rho T}),$$

Where,

$$r = t - 2T$$

$$t = 2T + r$$

Solving, we have

$$N(t) = D(1 + e^{-\rho T} + e^{-2\rho T}) e^{-\rho(t-2T)} \quad (17)$$

The concentration before the 4th influent is

$$N(3T^-) = D(1 + e^{-\rho T} + e^{-2\rho T}) e^{-\rho T}$$

The general concentration before the nth influent is

$$N((n-1)T) = D(1 + e^{-\rho T} + e^{-2\rho T} + e^{-3\rho T} + \dots + e^{-(n-1)\rho T}) e^{-\rho T} \quad (18)$$

When making the nth influent,

$$N(nT^+) = N((n-1)T) + D \quad (19)$$

$$= D(1 + e^{-\rho T} + e^{-2\rho T} + e^{-3\rho T} + \dots + e^{-(n-1)\rho T})$$

$$e^{-\rho T} N(nT^+) = D(e^{-\rho T} + e^{-2\rho T} + e^{-3\rho T} + \dots + e^{-(n-1)\rho T} + e^{-n\rho T})$$

$$N(nT^+) - e^{-\rho T} N(nT^+) = D(1 - e^{-\rho T})$$

$$(1 - e^{-\rho T}) N(nT^+) = D(1 - e^{-\rho T})$$

$$N(nT^+) = \frac{D(1 - e^{-\rho T})}{1 - e^{-\rho T}}$$

$$\lim_{n \rightarrow \infty} N(nT +) = \frac{D}{1 - e^{-\rho T}} \quad (20)$$

2.7 Summation of Nutrient Removal Sites

The above model, Equation 2.19, does not take into consideration the partitioning of nitrogen into different sinks in the wetland ecosystem. To include these sinks into the model, further assumptions made and conceptualized below include,

- (i) rate of nitrogen input into the wetland from rainfall is negligible,
- (ii) rate of nitrogen uptake by plant is δ_2 ,
- (iii) rate of nitrogen outflow (effluent) from the system is α ,
- (iv) the rate of nitrogen input into the wetland is D
- (v) the rate of retention of nitrogen in the wetland water column is δ_1
- (vi) the rate of retention of nitrogen in the wetland medium is ε
- (vii) the rate of volatilization of nitrogen from the wetland is β

By introducing the above symbols representing the various wetland sinks into the conceptual model in Figure 2 above, the flowchart of nitrogen distribution in the wetland ecosystem is obtained in Figure 3 below

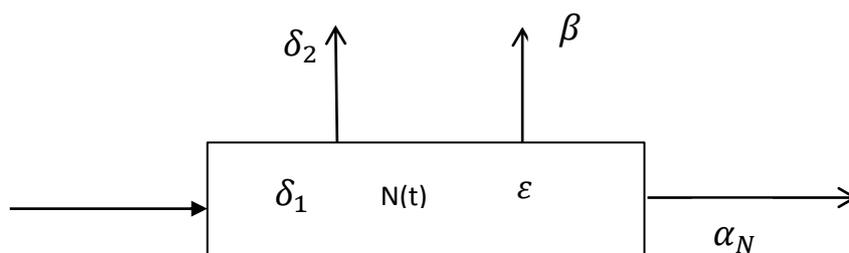


Figure 3: Flowchart of Nitrogen distribution in constructed wetland ecosystem

Using the above assumption and symbols, we obtain the following mass balance equation

$$\frac{dN}{dt} = D - \delta_2 N(t) - \delta_1 N(t) - \alpha N(t) - \beta N(t) - \varepsilon N(t) \quad (21)$$

From Equation (2.15), we collate all the constants together

$$\frac{dN}{dt} = D - (\delta_2 + \delta_1 + \alpha + \beta + \varepsilon)N(t) \quad (22)$$

$$\text{Let } \gamma = \delta_2 + \delta_1 + \alpha + \beta + \varepsilon$$

Then

$$\frac{dN}{dt} + \gamma N(t) = D \quad (23)$$

$$N(0) = N_0$$

Solving, we have the nitrogen removal model as,

$$N(t) = N_0 e^{-\gamma t} + \frac{D}{\gamma} [1 - e^{-\gamma t}] \quad (24)$$

(ii) Phosphorus

Phosphorus removal model was also derived based on the first order degradation model principle as nitrogen. The only difference is in the partitioning of phosphorus which does not include loss to the atmosphere as shown in Figure 4 below.

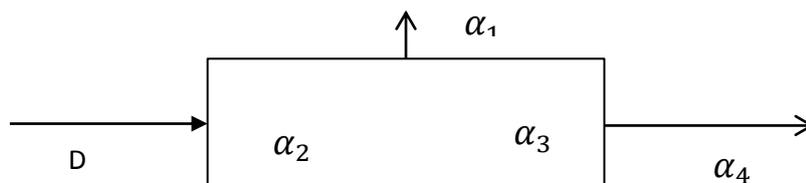


Figure 4: Flowchart of Phosphorus distribution in wetland ecosystem

From the assumptions and the parameters above, the model equation becomes

$$\frac{dP}{dt} = D - kP$$

$$P(0) = P_0$$

Where $k = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$

D = Influent phosphorus concentration (mg/l)

α_1 = Plant uptake (mg/l)

α_2 = amount accumulated in wetland soil and sediment (mg/l)

α_3 = retention in wetland water column (mg/l)

α_4 = effluent phosphorus concentration (mg/l)

Other parameters are as defined for nitrogen.

Hence,

$$\frac{dP}{dt} + kP = D \quad (25)$$

$$P(0) = P_0$$

Solving, we have the phosphorus removal model as

$$P(t) = P_0 e^{-kt} + \frac{D}{k} [1 - e^{-kt}] \quad (26)$$

2.8 Model Solutions

Solutions to first order equations relating the nutrients removal from the CW were provided by using MATLAB version 9.2 of 2017 approach. Subsequently, calibration of model constants and verification of the model were carried out using data acquired from the experiment. Lastly, the model was validated by comparing observed values with model predictions.

2.9 Evaluation of Model Performance

The ability of the model to predict nutrient removal was evaluated quantitatively using the following statistics to indicate overall model performance (Fox, 1981).

2.9.1 Bias or Mean Bias

$$ME = \frac{1}{N} \sum_{i=1}^N (P_i - O_i) \quad (27)$$

Where P and O are the predicted and observed values and N is the number of observations.

2.9.2 Root Mean Square Error (RMSE)

It quantifies the dispersion between simulated and measured data.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (P_i - O_i)^2} \quad (28)$$

2.9.3 Relative Error (RE):

$$RE = \frac{RMSE}{\bar{y}} \times 100 \quad (29)$$

Where,
y is the mean of observed values.

2.9.4 Model Efficiency

Model efficiency (EF) was calculated as:

$$EF = \frac{\sum(\text{Observed} - \text{Observed means})^2 - \sum(\text{Predicted} - \text{Predicted means})^2}{\sum(\text{Observed} - \text{Observed means})^2} \quad (30)$$

2.9.5 Index of Agreement (IA):

$$d = 1 - \frac{\sum_{i=1}^N (O_i - P_i)^2}{\sum_{i=1}^N (O'_i + P'_i)^2} \quad 0 \leq d \leq 1 \quad (31)$$

Where $O'_i = |O_i - \bar{P}|$, $P'_i = |P_i - \bar{P}|$, O_i is the observed value, P_i is the simulated value and \bar{P} is the mean of the simulated mean. $d = 1$ corresponds to a perfect match of predicted to observed data.

2.10 Model Calibration

Model calibration parameters for nitrogen and phosphorus removal respectively, are presented in Table I

Table I: Model calibration parameters for nitrogen and phosphorus removal

Symbols	Description	N	P	Unit
N_0	Initial concentration of Nitrogen	6.00		mg/l
P_0	Initial concentration of Phosphorus		2.23	mg/l
t	Retention time	3	3	Days
ρ	Rate of Nutrient removal from the wetland system.	0.122	0.078	m ³ /day
D	Input rate (mean)	29.2	11.52	m ³ /day
T	Period time of introducing nutrient.	3	3	Days
δ_1	Nutrient retention in wetland water column	1.48		mg/l
δ_2	Plant Nutrient uptake	8.90		mg/l
β	Denitrification (52% of net N input)	15.2		mg/l
ε	Nutrient retention in wetland sediment	5.05		mg/l
α_N	Effluent rate or output	2.07		m ³ /day
α_1	Plant uptake		2.08	mg/l
α_2	Nutrient retention in wetland sediment		2.87	mg/l
α_3	Retention in wetland water column		2.01	mg/l
α_4	Effluent rate		1.24	mg/l

Model calibration was carried out using experimental data obtained between February – April, 2018. The process involved adjustment of the model parameters and forcing within the margins of the uncertainties to obtain a model representation of the processes of interest that satisfies pre-agreed criteria.

2.11 Model Validation

Parameters used as input to calibrate the model are as presented in Table 2.

Table 2: Model simulation parameters for nitrogen and phosphorus removal

Symbols	Description	N	P	Unit
N_0	Initial concentration of Nitrogen	6.06		mg/l
P_0	Initial concentration of Phosphorus		2.23	mg/l
t	Retention time	3	3	Days
ρ	Rate of Nutrient removal from the wetland system.	0.125	0.082	md ⁻¹
D	Input rate (mean)	27.40	10.21	m ³ /day
T	Period time of introducing nutrient.	3	3	Days
δ_1	Nutrient retention in wetland water column	1.28		mg/l
δ_2	Plant Nutrient uptake	8.76		mg/l
β	Denitrification (52% of net N input)	5.82		mg/l
ε	Nutrient retention in wetland sediment	5.65		mg/l
α_N	Effluent rate or output	1.28		m ³ /day
α_1	Plant uptake		2.43	mg/l
α_2	Nutrient retention in wetland sediment		2.81	mg/l
α_3	Retention in wetland water column		1.71	mg/l
α_4	Effluent rate		0.96	mg/l

The validation of the model was carried out by comparison of the experimental data against the model prediction. This was done by plotting the simulated and measured graphs against time after running a calibrated model with a new set of data (independent data set) with physical parameters and the derived functions to mirror new conditions and to detect how well the model simulations fit the new data set.

3.0 Results and Discussion

3.1 Model Simulation Results

Simulations were performed with the parameters presented in Table 2 above to determine the general relationships and interactions which affect the removal of nitrogen and phosphorus in HSFCW. The model simulations after introducing mathematical equations, parameters and initial values in the state variables are shown in Figures 5 and 6.

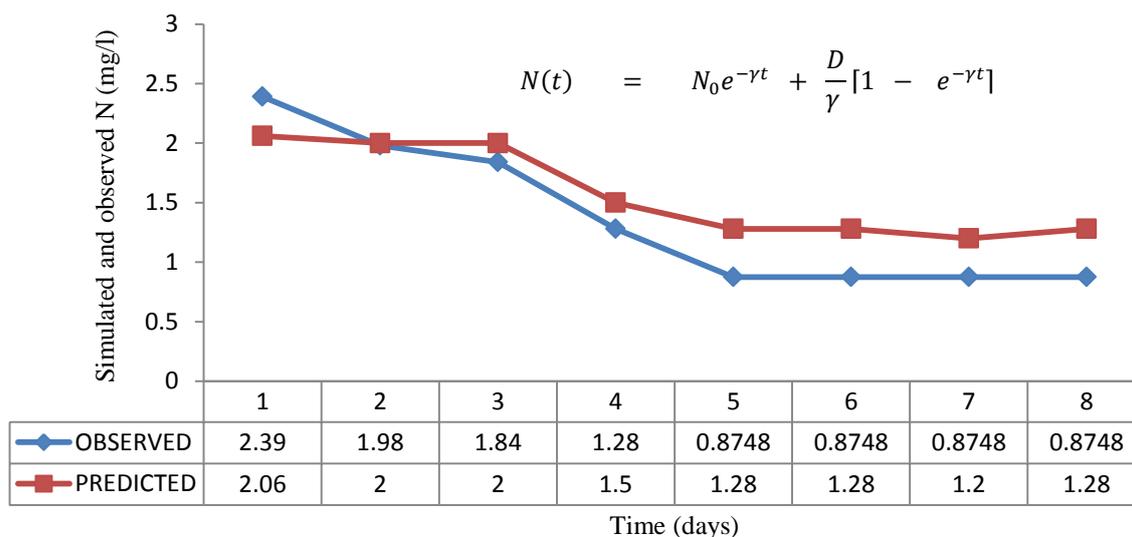


Figure 5: Simulated and observed variations for nitrogen removal in constructed wetland. ($N(t)$ = nitrogen concentration in wetland system (mg/l); N_0 = initial concentration of nitrogen (mg/l); γ = sum of nitrogen in wetland sinks (mg/l); D = rate of nitrogen input into the wetland (m^3/day ; t = wetland retention time (d))

The correlation between the simulated and observed reduction of nitrogen pollutant in the wetland is shown in Figures 6. There was high correlation between the simulated and observed parameters.

Based on Table 2 also, the relationship and correlation between simulated and observed reduction in phosphorus pollutant in the CW is shown in Figures 7 and 8 respectively. The high correlation coefficient observed in the removal of nitrogen was also noticed in the case of phosphorus removal from the CW.

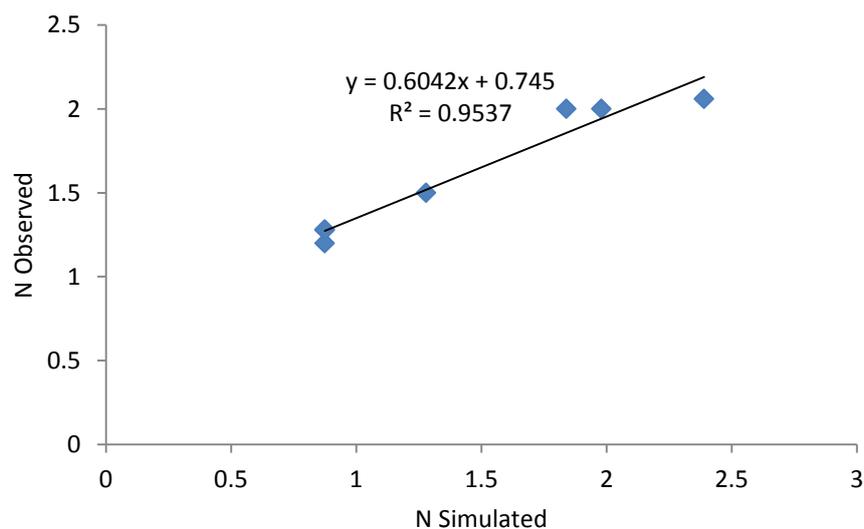


Figure 6: Correlation of observed and simulated removal of nitrogen in constructed wetland.

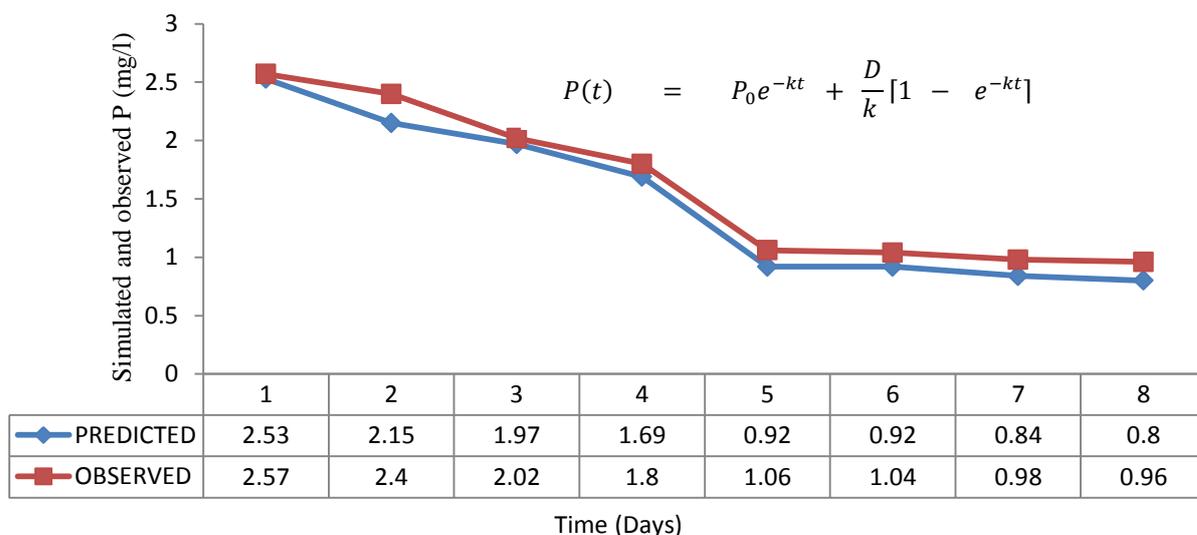


Figure 7: Simulated and observed variations for phosphorus removal in CW
 $P(t)$ = phosphorus concentration in wetland system (mg/l); P_0 = initial concentration of phosphorus (mg/l); K = sum of phosphorus in wetland sinks (mg/l); D = rate of phosphorus input into the wetland (m^3/day); t = wetland retention time (d)

The correlation between the simulated and observed reduction of phosphorus in the wetland is shown in Figure 8. There was high correlation between the simulated and observed parameters.

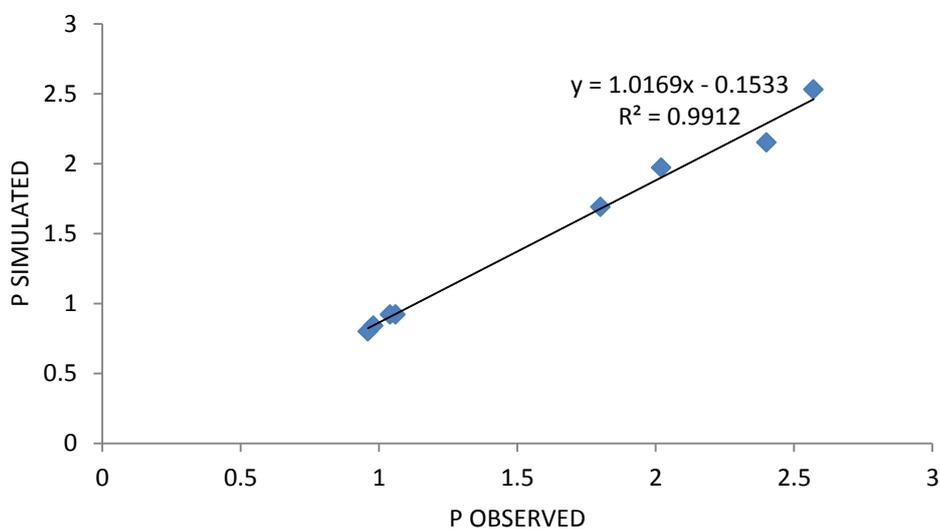


Figure 8: Correlation of observed and simulated removal of phosphorus in CW
 $(Y = \text{predicted values}; X = \text{observed values})$

3.2 Process Model Assumptions and Development

Nutrients stored within plant tissues can potentially be returned to water or enter components of the wetland upon senescence. Many aquatic plants undergo complete senescence before dormancy potentially releasing soluble nutrients to the water.

In this model, nutrient release owing to plant die off was not considered to have an input into the wetland since the macrophytes are expected to be harvested young for feeding the pigs.

Denitrification of nitrogen is predominantly the source of nutrient loss to the atmosphere by wetlands that receive high nitrate loadings from agricultural runoff or wastewater treatment plant discharge. This is because of the presence of anoxic conditions in wetlands, which makes microbial denitrification of nitrates to gaseous forms of nitrogen in wetlands and their subsequent release to the atmosphere remain one of the more significant ways in which nitrogen is lost from the soil and water to the atmosphere. Denitrification is primarily performed by bacteria that are heterotrophic, meaning they require a carbon source for growth and energy. Wetland plants are a key source of this carbon. Since denitrification is facilitated by microbes, the process is temperature-dependent. Higher rates of denitrification occur during higher temperatures when the bacteria are more active.

Thereby, successful application of SFWs largely depends on the effectiveness of this process. The process ensures permanent removal of N. Quantifying denitrification in constructed wetlands is critical because it is often cited as the dominant mechanism of N removal (Casey et al., 2001). Pollutant fluxes due to precipitation and exchange with subsurface are negligible compared to other mechanisms. This is because the wetland was sealed to avoid possible contamination of groundwater and also to prevent groundwater from infiltrating into the wetland.

In this study, the amount of nitrogen and phosphorus concentrations decreased exponentially within three days of retention in the wetland, and thereafter, the reduction appeared constant over higher retention time subject to the decay coefficient. The wetland design was based on first order plug flow reaction which is characterized by decay reaction that estimates a decline in pollutant concentrations through the wetland provided the incoming concentration levels exceed that of the wetland. The observed variation in wetland nitrogen concentration could be attributed to residence time. This observation is consistent with that of Kadlec and Wallace (2009) for horizontal subsurface flow wetlands who reported an exponential reduction in nitrogen with increase in residence time.

The correlation between the observed and simulated removal rates for N and P in Figures 6 and 8 showed good agreement for N ($R^2 = 0.9537$) and for P ($R^2 = 0.9912$) respectively. The linear regression coefficients are very good since the system was a natural system located in the field, where uncontrolled influencing factors could weaken optimal performance according to Jørgensen and Bendoricchio, (2001).

3.3 Statistical Indicators of Model Performance

Statistical indicators of model performance are presented in Table 3.

Table 3: Statistical Indicators of Model Performance

Nutrient	R^2	R	Mean bias error (mm)	Root Mean Square Error (mm)	Relative Error (%)	Model efficiency (%)	Index of Agreement
Nitrogen	0.9537	0.9766	0.211	0.32	24	84	0.6527
Phosphorus	0.9912	0.9956	0.139	0.18	12	77	0.8676

Various procedures for evaluating model predictive accuracy have been recommended for numerical data. Of these measures, besides r and r^2 , MBE and root MSE (RMSE) are among the

most commonly used or recommended measures (Liu *et al.*, 2011; Bennett *et al.*, 2013). These statistical pointers of simulation performance are summarized in Table 3. The rate of coefficient of determination (R^2 , 0.9537, 0.9912) shows that a good inter-relation occurs amongst observed and simulated values for both nitrogen and phosphorus respectively. Tiffany *et al.*, (2017) observed R^2 values between 0.70 and 0.99 with an average of 0.95 in first order decay models in subsurface-flow constructed wetland mesocosms. The lower R^2 values were detected during the cold months when average water temperature was below 12 °C. But, all estimates throughout the growing season had R^2 values above 0.90. Similarly, Kadlec (2000), obtained an R^2 of 0.95 when some variations of the plug flow models were fitted to data from practically all kinds of treatment wetlands. It is expected that with the high temperature in the tropics, R^2 are likely to be higher than reported above since many individual wetland processes, such as microbial mediated reactions, are affected by temperature (Kadlec and Reddy, 2001). The values of R^2 , 0.9537 and 0.9912 for nitrogen and phosphorus respectively shows that the first order decay model provided stronger statistical agreement between their predicted and measured removal rates. Generally, a higher coefficient indicates a better fit for the model.

The MBE provides information on the long-term performance of a model. The smaller the absolute value, the better the model performance. The rate of MBE is equal to 0.21 and 0.14 mm for both nitrogen and phosphorus respectively. A positive value of MBE indicates overestimation and vice-versa.

The RMSE provides information on the short-term performance of a model by allowing a term by term comparison of the actual difference between the estimated value and the measured value. The smaller the value, the better the model's performance. The root mean square errors are 0.32 and 0.18 mm for both nitrogen and phosphorus. The extent of root mean square error (RMSE) is a convenient parameter of model performance. In a perfect condition, the values of relative error (RE) and the model efficiency (EF) will be 0% and 100%, respectively. So the recorded RE value of about 24% and 12 % and EF value of about 84% and 77% indicate that the performance of model in simulating actual removal of the nutrients was good for nitrogen and phosphorus.

The limit of index of agreement (d) value is from 0 to 1. A higher value indicates a better agreement between the simulated and observed values. In this study, the value of d (0.6527 and 0.8676) shows a good performance of the model in removing the nutrients. However, much deviation from the ideal value for the model may be due to inherent assumptions in the model principle, and also in the field data. For example, the model assumes the steady-state condition but in reality, this may not be true (as the flux varies with the change in moisture level and atmospheric demand). Saturation of phosphorus in the wetland bed and /or low bed permeability of the parent material used for bed construction could impair phosphorus removal efficiency as observed by Karczmarczyk (2004).

3.2.3 Model Applications and Limitations

The models developed in this study are appropriate for performance analysis of HSFCW receiving secondary piggery wastewater. Their application needs the knowledge of inflow concentrations (mg/l) of organic nitrogen and phosphorus in the wetland and the inflow rate. The initial values of nitrogen and phosphorus in the soil and in the wastewater are also required.

4.0 Conclusion

This study developed mathematical models for prediction of nitrogen and phosphorus removal from secondary piggery wastewater treated in HSFCW. The model partitions the wetland into three basic compartments: (1) water column (2) wetland media, and (3) plant biomass. Major

processes considered were wastewater influent, retention, plant uptake and effluent in nitrogen and phosphorus respectively and volatilization to the atmosphere in nitrogen only. Mathematical equations created from the conceptual model were developed from first principles based on input-output variables of mass balance principles. A series of field experiments were continuously carried out over a period of seven months. The water quality of influent and effluent wastewater was analyzed and mass balance changes in the wetland sediment and plants were observed and balanced with the influent. The observed deficit was accounted for by losses such as volatilization in the case of nitrogen. Simulation results from the model agreed well with the results from the experiments. The difference between computed and measured removal rate was less than 20% and 30% for nitrogen and phosphorus respectively. This shows that the model and the calibrated parameters were rational. The model can be considered suitable for simulation of nitrogen and phosphorus removal in HSSF CWs operating under similar conditions (climatic conditions, wastewater composition, porous filter material and plant species). But, scaling-up results from this study can be challenging as physical processes can show temporal and spatial variation, which can affect the assumptions on which the derivation of this model was based. The model efficiencies are good but can be improved by extensive data. Therefore, longer field studies must be conducted to complement the results of this study for constructed wetland design. Although the models developed in this study offered a good prediction of nitrogen and phosphorus removal from HSSFCW, the most important consideration however, is whether the resulting effluent meets the water quality discharge or reuse standards of the area with regards to intended use. For this study, the effluent met Nigerian water quality standards for discharge to land and surface water.

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