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Modelling Phytoremediation Rates of Aquatic Macrophytes in Aquaculture Effluent

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***Abstract*—**Pollutants from aquacultural practices constitute environmental problems and phytoremediation could offer cheaper environmentally sustainable alternative since equipment using advanced treatment for fish tank effluent is expensive to import, install, operate and maintain, especially in developing countries. The main objective of this research was, therefore, to develop a mathematical model for phytoremediation by aquatic plants in aquaculture wastewater. Other objectives were to evaluate the retention times on phytoremediation rates using the model and to measure the nutrient level of the aquaculture effluent and phytoremediation rates of three aquatic macrophytes, namely; water hyacinth (*Eichornia crassippes*), water lettuce (*Pistial stratoites*) and morning glory (*Ipomea asarifolia*). A completely randomized experimental design was used in the study. Approximately 100 g of each macrophyte were introduced into the hydroponic units and phytoremediation indices monitored at 8 different intervals from the first to the 28th day. The water quality parameters measured were pH and electrical conductivity (EC). Others were concentration of ammonium–nitrogen ($NH4^+$ -N), nitrite-nitrogen (NO_2^- -N), nitrate- nitrogen (NO_3^- -N), phosphate – phosphorus (PO_4^{3-} -P), and biomass value. The biomass produced by water hyacinth was 438.2 g, 600.7 g, 688.2 g and 725.7 g at four 7–day intervals. The corresponding values for water lettuce were 361.2 g, 498.7 g, 561.2 g and 623.7 g and for morning glory were 417.0 g, 567.0 g, 642.0 g and 679.5g. Coefficient of determination was greater than 80% for EC, TDS, NO_2^- -N, NO_3^- -N and 70% for NH_4^+ -N using any of the macrophytes and the predicted values were within the 95% confidence interval of measured values. Therefore, the model is valuable in the design and operation of phytoremediation systems for aquaculture effluent.

***Keywords*—**Phytoremediation, macrophytes, hydroponic unit, aquaculture effluent, mathematical model.

I. INTRODUCTION

IN closed aquaculture systems, the accumulation of some nitrogenous compounds such as un-ionized ammonia (NH_3), ionized ammonia (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) is of interest. The main sources of these nitrogenous compounds are from fish feeds and the metabolic wastes of the fish which causes water quality degradation. These wastes are basically ammonia, urea, CO_2, organic faecal material etc. The organic faecal material is further degraded to produce additional ammonia, nitrites (NO_2^-) and nitrates (NO_3^-), which depresses water pH, deplete dissolve oxygen, increase turbidity and make the water more toxic to aquatic species. Therefore, the more intensive the culture practice, the greater the impact and rate of waste production in an aquaculture system [1]

Commercial aquacultures in Nigeria are done more in semi-closed concrete or plastic tanks, dug-out ponds, etc. Effluents from semi-closed systems are usually discharged in the open or dug-out pits thereby polluting the surface and groundwater.

A. Toxin Kinetics

Nitrification is the oxidation of ammonia to nitrate with nitrite formed as an intermediate product. The conversion of ammonia to nitrate is an aerobic process. If anaerobic conditions develop, denitrification occurs, and nitrate is converted back to ammonia.

The chemical reaction is shown by (1):

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2 \quad (1)$$

The oxidation of nitrite is a single-step process that uses oxygen from water to form nitrate. The chemical reaction is shown in (2):

$$NO_2 + 0.5O_2 \rightarrow NO_3 \quad (2)$$

Conventional wastewater treatment plants of activated carbon, electrodialysis, ion exchange, reverse osmosis etc. are expensive to install, operate and maintain especially in developing countries, therefore, the use of macrophytes (aquatic floating or rooted plants growing in wetland) for wastewater purification is a viable alternative. Common examples of these aquatic macrophytes in Nigeria include; water hyacinth, water lettuce, water lily, duckweed, ferns etc.

In their work, [2] developed and analyzed a mathematical model for studying the phytoremediation potential of water hyacinth against pulp and paper industry effluent at three retention times of 15, 30 and 45 days. They propounded that if P is the phytoremediation potential of water hyacinth in pulp and paper industry wastewater at time, t from initial day of the experiment, then the rate of change of P with respect to t from the initial day of the experiment up to the time when the plants attain equilibrium is directly proportional to P, at that time i.e.

$$\frac{dp}{dt} \alpha P = \mu P \quad (3)$$

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TABLE I
CHEMICAL CONSTITUENTS OF THE AQUACULTURE WASTEWATER

Parameter ($mg\ L^{-1}$)	Value
pH	6.40
EC ($\mu s\ cm^{-1}$)	4020
Total Dissolved Solids (TDS)	2010
Total Suspended Solids (TSS)	12.60
Ammonium-Nitrogen (NH_4^+-N)	0.054
Nitrite-Nitrogen (NO_2^--N)	0.338
Nitrate-Nitrogen (NO_3^--N)	0.56
Ortophosphate (PO_4^{3-}-P)	0.40
Chemical oxygen demand (COD)	108.0

Note: Concentrations are in mg/l except pH and EC

where μ is a constant. Integrating (3) and substituting the value of the constant of integration gives;

$$P = P_0 \exp(\mu t) \quad (4)$$

where P is the pollutant concentration at time, t (mg/l); P_0 is the pollutant concentration at start of the experiment, (mg/l); μ is the phytoremediation constant, and t the time interval of phytoremediation, (day). The model was then applied to some important physicochemical parameter of the effluent which were pH, EC, BOD, COD, TSS, Na and K. Results show that the phytoremediation potential increased for a short time and then level off, resulting in pollutant removal which enables the calculation of differential equation for developing uninhibited growth model. The model was a cost effective in phytoremediation technology. Some phytoremediation models have been developed and have been successfully used for treatment of contaminated sites [3]-[7].

The world percentage of freshwater is about 3% and its depletion by continued population growth, contamination of both surface and groundwater by human activities, uneven distribution of water resources have necessitated the search for new sources of water supply, while ensuring water conservation and an efficient re-use of the existing water supplies [8].

The method of controlling ammonia and its by-product is a limiting factor for a successful commercial aquaculture in a developing country like Nigeria. The technology for an advanced biological treatment of fish tank effluent is uneconomical and also the complex nature of the nitrogen cycle to local fish farmers has caused the disposal of aquaculture wastewater indiscriminately or unprofessionally, thereby increasing the concentrations of ammonia, nitrites, nitrates and other contaminants in surface and groundwater above the permissible level. The ineffectiveness of relevant regulatory agencies contributes to the non-compliance of the approved standards for wastewater disposal and so the attendant effect as a result of these could cause an epidemic [9]. The objectives of this research will be therefore to develop a mathematical model which describes the phytoremediation of aquatic plants in aquaculture wastewater, evaluate the effects of retention times on phytoremediation rates using the model and to validate the model by comparing the predicted values of the model with the observed values from the experiment.

II. MATERIALS AND METHODS

The experimental site was an open space in front of the Agricultural and Environmental Engineering Laboratory, Niger Delta University, Amassoma, Wilberforce Island, Bayelsa State, Nigeria. Located in the mangrove swamp vegetative zone in Nigeria, Amassoma Town (longitude 6^0 6’35 E and latitude 4^0 58'9 N) has a tropical climate with two seasons: the wet season from March to October and the dry season between November and April.

On the day of the experiment, adequate quantities of the selected aquatic macrophytes in their natural habitats were randomly and carefully obtained from nearby streams, lakes and ponds within and around Yenagoa metropolis in Bayelsa State. This was expected to take care, to a large extent, the age and varietal differences. Aquatic macrophytes were then placed in non-flow hydroponic units containing the aquaculture effluent in order to obtain data on the effect of their retention time on nutrient depletion rates within the effluent. The chemical constituents of the aquaculture effluent are presented in Table I. The study was a 4 × 4 completely randomized design with control. The experiments were conducted using 16 hydroponic units each containing 12 liters of the effluent weighing 12274 g out of which 4 units contained effluent only and were used as control.

Following studies [2], [10] the plants were first washed thoroughly with clean water to avoid pre-contamination carry-over effects and allowed to dry in the open air for 1 hour. The plants were then weighed using a 0.1 g precision digital weighing balance (Model HL 122, Avery Berkel) and the hydroponic units labeled accordingly before the commencement of the experiment. Each hydroponic unit was then stocked with plants of approximately 100 g accordingly.

In order to maintain dissolved oxygen (DO) in the hydroponic units, mechanical aeration using air pump and air stone was applied every three days for 10 minutes, throughout the experimental period. On the first day of the experiment, the effluent level of each hydroponic unit after the introduction of the aquatic plant was marked on the inside of the trough, and was topped with clean water to the same level on each day of aeration and observation, in other to compensate for evaporation loses. The mass of each hydroponic unit containing a plant was also recorded.

During the experimental period, water samples were collected on days 3, 7, 11, 14, 18, 21, 24 and 28 from each unit and refrigerated in 75cl labeled plastic bottles until needed for chemical analyses. The plant biomass yield was also recorded on each day of observation by weighing the hydroponic unit.

A. The Mathematical Model Assumptions

It was assumed that the nutrient concentration of the aquaculture wastewater for the experiment was homogeneous. The age and varietal differences of the aquatic macrophytes are subsumed and negligible. There exists a symbiotic relationship between the aquatic macrophytes and the aquaculture wastewater i.e. the aquatic macrophytes will phytoremediate the wastewater by using some of the pollutant as nutrient for its growth. The concentration of the pollutant decreases with time as a result of the introduction of aquatic macrophytes and is inversely proportional to the quantity (weight) of the macrophyte. The decrease in pollutant concentration will continue until the macrophyte attain equilibrium i.e. no change in concentration with respect to time.

B. Formulation of the Phytoremediation Model

If P is the concentration of a pollutant in an aquaculture wastewater at time, t on day 1 of an experiment and a macrophyte with mass, M is introduced, then the rate of change of P with respect to t from day one of the experiment until the time the macrophyte attains equilibrium (ceases to absorb the pollutant) is inversely proportional to the quantity (mass) of the macrophyte in the polluted module.

$$\frac{dP}{dt} \propto \frac{1}{M}$$

$$\frac{dP}{dt} = \frac{k}{M} \quad (5)$$

where k is the constant of proportionality for the macrophyte after time t of the exposure.

$$dP = \frac{k}{M}\,dt$$

Integrating both sides of (5) gives

$$P = \frac{kt}{M} + C \quad (6)$$

where C is the constant of integration. In order to get the value of C, put the initial condition in (6) as at day 1 of the experiment. i.e. t = 0; P will be maximum, and is P_0

$$P_0 = \frac{k}{M}.(0) + C$$

$$P_0 = C$$

Putting the value of C in (6)

$$P = \frac{kt}{M} + P_0 \quad (7)$$

$$k = \frac{(P - P_0)M}{t} \quad (8)$$

The rate of absorption of a nutrient by the root of a plant is directly proportional to the volume of the plant [11].

If M is the mass of the macrophyte and V is the volume. Then,

$$\frac{dM}{dt} \propto V$$

$$\frac{dM}{dt} = \beta V \quad (9)$$

where β is a constant of proportionality. But

$$V = \frac{M}{\rho}$$

where ρ is the density of the macrophyte, then (9) becomes

$$\frac{dM}{dt} = \beta\frac{M}{\rho} \quad (10)$$

$$\frac{dM}{M} = \beta\frac{dt}{\rho}$$

Integrating both sides gives

$$\ln M = \beta\frac{t}{\rho} + C \quad (11)$$

where C is the constant of integration. Similarly, to get the value of C, put the initial condition in (11) as at day 1 of the experiment. i.e. t = 0; M will be maximum, and is M_0

$$\ln M_0 = \beta\frac{(0)}{\rho} + C$$

$$\ln M_0 = C$$

Substituting for C in (11)

$$\ln M = \frac{\beta t}{\rho} + \ln M_0$$

$$\ln M - \ln M_0 = \frac{\beta t}{\rho}$$

$$\ln\left(\frac{M}{M_0}\right) = \frac{\beta t}{\rho} \quad (12)$$

$$\frac{M}{M_0} = \exp\left(\frac{\beta t}{\rho}\right)$$

$$M = M\exp\left(\frac{\beta t}{\rho}\right) \quad (13)$$

Substituting (13) in (7) gives

$$P = P_0 + \frac{kt}{M_0\exp\left(\frac{\beta t}{\rho}\right)} \quad (14)$$

Equation (13) implies that the growth pattern of the macrophyte is exponential in nature and will therefore grow indefinitely. This will mean that modelling macrophyte growth with (13) cannot be realistic since macrophyte will not grow indefinitely, hence predictions made with (14) will not be accurate [11]. Equation (13) will then be modified to assume that macrophyte growth is approximately in arithmetic progression for the period before equilibrium state is attained.

Recall sum of an arithmetic series;

$$T_n = a + (n-1)d$$

where T_n = nth term; a = first term, n = 1, 2,3; d = common difference. Therefore, the mass M of the macrophyte at any given time t before equilibrium is attained is given by;

$$\mathrm{M} = \mathrm{M}_0 + (\mathrm{t} - 1)d \quad (15)$$

This will mean that (7) becomes

$$\mathrm{P} = \mathrm{P}_0 + \frac{kt}{\mathrm{M}_0 + (\mathrm{t}-1)\,d} \quad (16)$$

and

$$k = \frac{(\mathrm{P} - \mathrm{P}_0)[\mathrm{M}_0 + (\mathrm{t}-1)d]}{\mathrm{t}} \quad (17)$$

$$d = \frac{\mathrm{M} - \mathrm{M}_0}{\mathrm{t}-1} \quad (18)$$

where P = Pollutant concentration at time, t (mg/l); P_0 = Pollutant concentration at day 1 of the experiment, (mg/l); k = Phytoremediation constant, g(mg/l)day^{-1}; t = Time of phytoremediation, (day); M_0 = Initial mass of the macrophyte, (g); d = Mean difference in mass per day (g/day).

By substituting the values of k and d in (16), the pollutant concentration at the various time intervals can then be predicted.

C. Properties of the Model

The model will be valid for t > 0 days. From (17)

$$k = \frac{(\mathrm{P} - \mathrm{P}_0)[\mathrm{M}_0 + (\mathrm{t}-1)\mathrm{d}]}{\mathrm{t}} \; k = \frac{(\mathrm{P} - \mathrm{P}_0)[\mathrm{M}_0 + (\mathrm{t}-1)d]}{\mathrm{t}}$$

Now take t at equal interval, let these be $t_1, t_2, t_3 \ldots \ldots \ldots \ldots . t_n$. Then,

$$\mathrm{k}_\mathrm{i} = \frac{(\mathrm{P}_\mathrm{i} - \mathrm{P}_0)[\mathrm{M}_0 + (\mathrm{t}_\mathrm{i}-1)\mathrm{d}_\mathrm{i}]}{\mathrm{t}_\mathrm{i}} \; k_i = \frac{(\mathrm{P}_\mathrm{i} - \mathrm{P}_0)[\mathrm{M}_0 + (\mathrm{t}_\mathrm{i}-1)d_i]}{\mathrm{t}_\mathrm{i}}$$

where i = 1, 2, 3 ……n

$$k = \frac{\sum_1^n k_\mathrm{i}}{\mathrm{n}}$$

Similarly, in (18)

$$d_i = \frac{\mathrm{M}_\mathrm{i} - \mathrm{M}_0}{\mathrm{t}_\mathrm{i} - 1}$$

where i = 1, 2, 3 ……n

$$d = \frac{\sum_1^n d_\mathrm{i}}{\mathrm{n}}$$

D. Calibration of the Model Results

The calibrated mean difference d for water hyacinth, water lettuce and morning glory and with their corresponding k is shown in Table II. By substituting these values in (16), the pollutant concentration at any given time were predicted.

E. Validation of the Model Using the Macrophytes

The experimental data of each macrophyte sample were splitted into two sets; set 1 and set 2. Set 1 was used to calibrate the model and then used to predict (validate) set 2. Paired sample t-test was performed on the experimentally obtained and the predicted values in set 2 for variations using Microsoft Excel Stat software and was further tested by an analysis of variance. R squared was also determined so as to ascertain if the model can predict the phytoremediation trend.

TABLE II
CALIBRATED MEAN DIFFERENCE *D* FOR WATER HYACINTH, WATER LETTUCE AND MORNING GLORY AND WITH THEIR CORRESPONDING *K*

Macrophyte Sample		Water Hyacinth	Water Lettuce	Morning Glory
d (g/day)		46.92	29.36	24.37
k g(mg/l)day^{-1}	pH	-35.0	-12.28	-15.84
	EC (μs cm^{-1})	-1.8 x 10^5	-1.05 x10^5	-9.08 x 10^4
	NH_4^+-N	-2.03	-1.44	-1.21
	NO_2^-N	-12.32	-6.99	-5.70
	NO_3^-N	-26.16	-16.11	-14.25
	PO_4^{3-}P	-22.52	-12.34	-7.03

III. RESULTS AND DISCUSSION

The macrophytes in all the hydroponic units initially looked stressed especially Morning glory, but grew well and later looked healthy with lush green colours as the phytoremediation days increased. The mean effects of each macrophyte on the aquaculture effluent and the mass gained are shown in Tables III-V. Pollutant concentrations were reduced gradually as the phytoremediation days increase with few exceptions.

TABLE III
MEAN EFFECTS OF THE WATER HYACINTH ON SOME PHYSICOCHEMICAL CHARACTERISTICS OF THE AQUACULTURE EFFLUENT AND ITS WEIGHT FOR THE 7 DAYS TIME INTERVALS

Effluent Parameter (mg L^{-1})	Phytoremediation Period (Days)				
	0	7	14	21	28
pH	6.40	5.82	5.66	5.50	5.46
EC (μs cm^{-1})	4020.0	1276.5	397.4	189.1	122.5
TDS	2010.0	499.8	102.5	49.1	54.4
TSS	12.60	5.80	5.75	2.73	4.58
NH_4^+-N	0.054	0.023	0.010	0.008	0.008
NO_2^-N	0.338	0.120	0.079	0.075	0.052
NO_3^-N	0.560	0.079	0.029	0.007	0.008
PO_4^{3-}P	0.400	0.180	0.125	0.078	0.048
COD	108.00	161.95	143.25	114.00	104.13
Weight (g)	103	438.2	600.7	688.2	725.7

TABLE IV
MEAN EFFECTS OF THE WATER LETTUCE ON SOME PHYSICOCHEMICAL CHARACTERISTICS OF THE AQUACULTURE EFFLUENT AND ITS MASS FOR THE 7 DAYS TIME INTERVALS

Effluent Parameter (mg L^{-1})	Phytoremediation Period (Days)				
	0	7	14	21	28
pH	6.40	6.15	5.85	5.98	5.48
EC (μs cm^{-1})	4020.0	1703.0	466.8	152.9	445.2
TDS	2010.0	851.5	232.0	76.5	222.6
TSS	12.60	3.93	7.78	2.30	5.30
NH_4^+-N	0.054	0.020	0.010	0.005	0.005
NO_2^-N	0.338	0.189	0.099	0.089	0.085
NO_3^-N	0.56	0.203	0.051	0.035	0.023
PO_4^{3-}P	0.400	0.300	0.195	0.195	0.095
COD	108.0	140.0	74.8	58.5	65.0
Mass (g)	99.2	361.2	498.7	561.2	623.7

TABLE V
MEAN EFFECTS OF THE MORNING GLORY ON SOME PHYSICOCHEMICAL CHARACTERISTICS OF THE AQUACULTURE EFFLUENT AND ITS MASS FOR THE 7 DAYS TIME INTERVALS

Effluent Parameter (mg L^{-1})	Phytoremediation Period (Days)				
	0	7	14	21	28
pH	6.40	6.11	5.68	6.19	5.66
EC (µs cm^{-1})	4020.0	1957.3	625.0	304.5	229.8
TDS	2010.0	978.8	312.8	152.3	114.8
TSS	12.60	4.74	3.36	4.31	7.42
NH_4^+-N	0.054	0.035	0.013	0.008	0.013
NO_2^-N	0.338	0.206	0.123	0.079	0.087
NO_3^-N	0.560	0.120	0.091	0.054	0.070
PO_4^{3-}P	0.40	0.53	0.35	0.20	0.19
COD	108.00	140.3	88.8	44.5	33.6
Mass (g)	100.8	417.0	567.0	642.0	679.5

Figs. 1-6 show minimum variations between predicted and observed values of the selected parameters, with respect to the macrophytes phytoremediation period, when compared. These variations could be attributed to minor experimental error that may have occurred during laboratory analysis of the water samples, overestimation or underestimation of the model. At 95% confidence level the t-test shows that the t (stat) is less than t (critical) Similarly, ANOVA also shows that F (cal) is less than F (critical) and $p > 0.05$ therefore it can be concluded that the inequality between the observed and predicted values level is not significant. Regression analysis gave more than 80% for EC, TDS, NO_2^- -N, NO_3^- -N and 70% for NH_4^+ -N using any of the macrophytes.

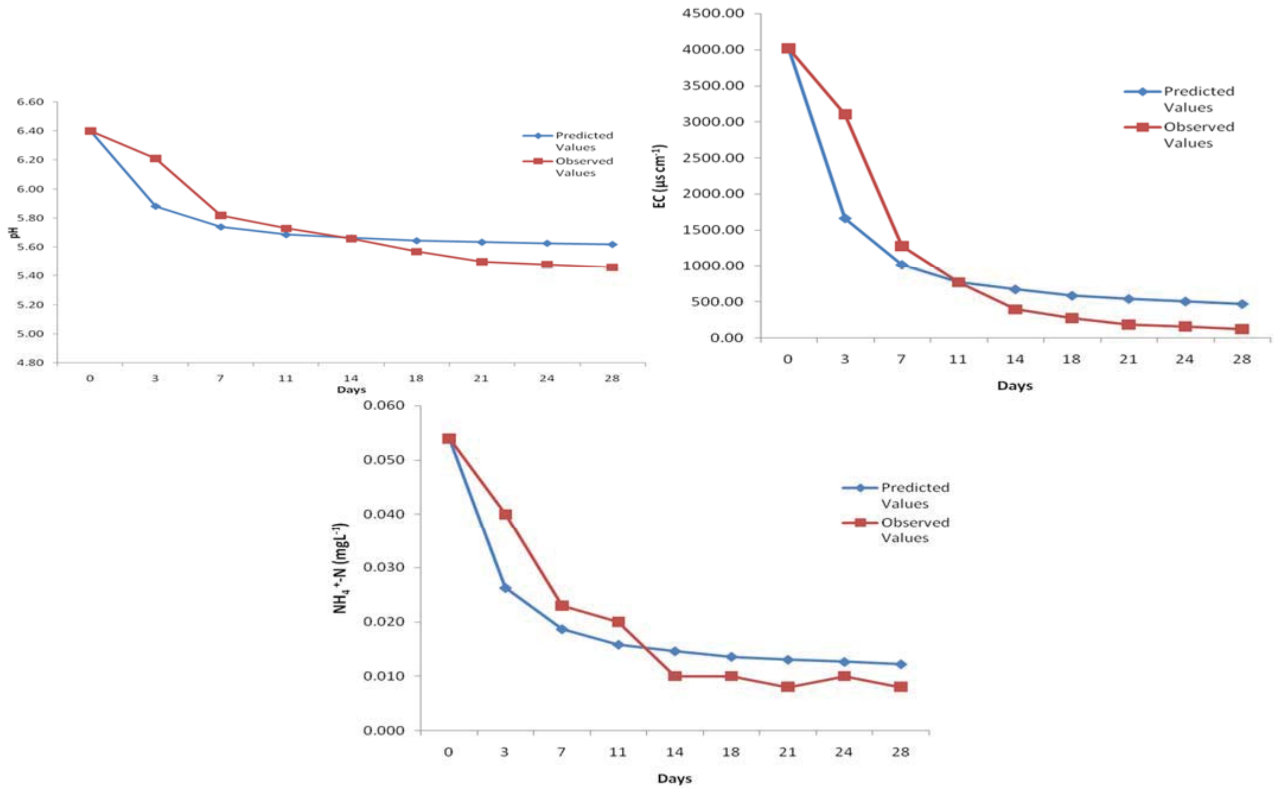

Fig. 1 Comparison between observed values and predicted values of pH, EC and NH_4^+-N with respect to the Water hyacinth phytoremediation period (day)

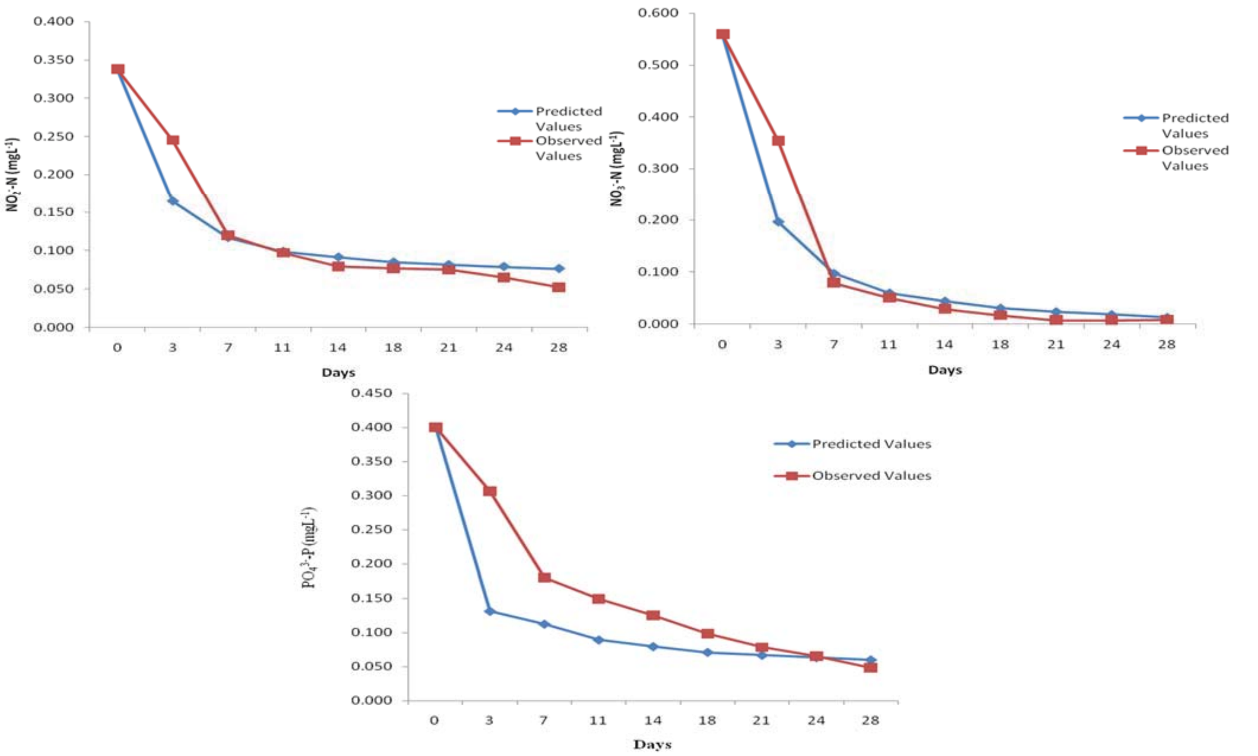

Fig. 2 Comparison between predicted values and observed values of NO_2^- -N, NO_3^--N and PO_4^{3-}-P with respect to Water hyacinth phytoremediation period (day)

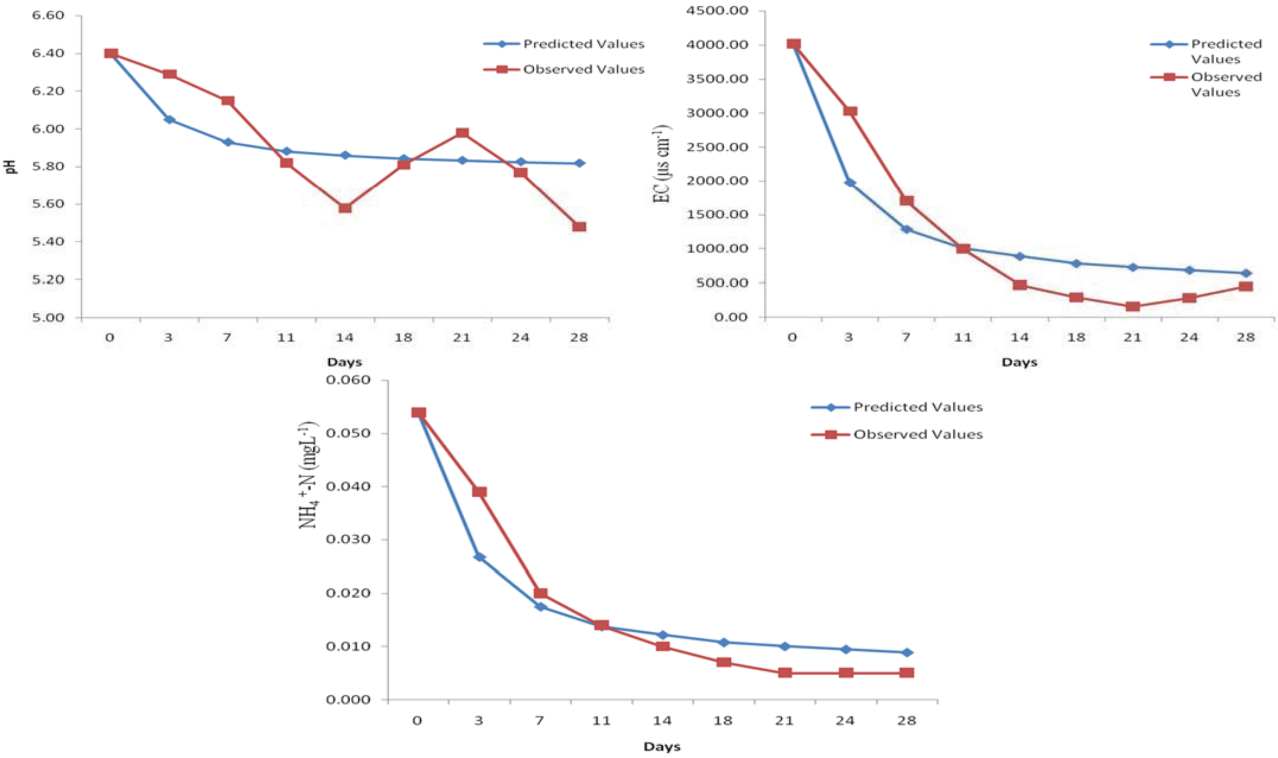

Fig. 3 Comparison between observed values and predicted values of pH, EC and NH_4^+-N with respect to the Water lettuce phytoremediation period (day)

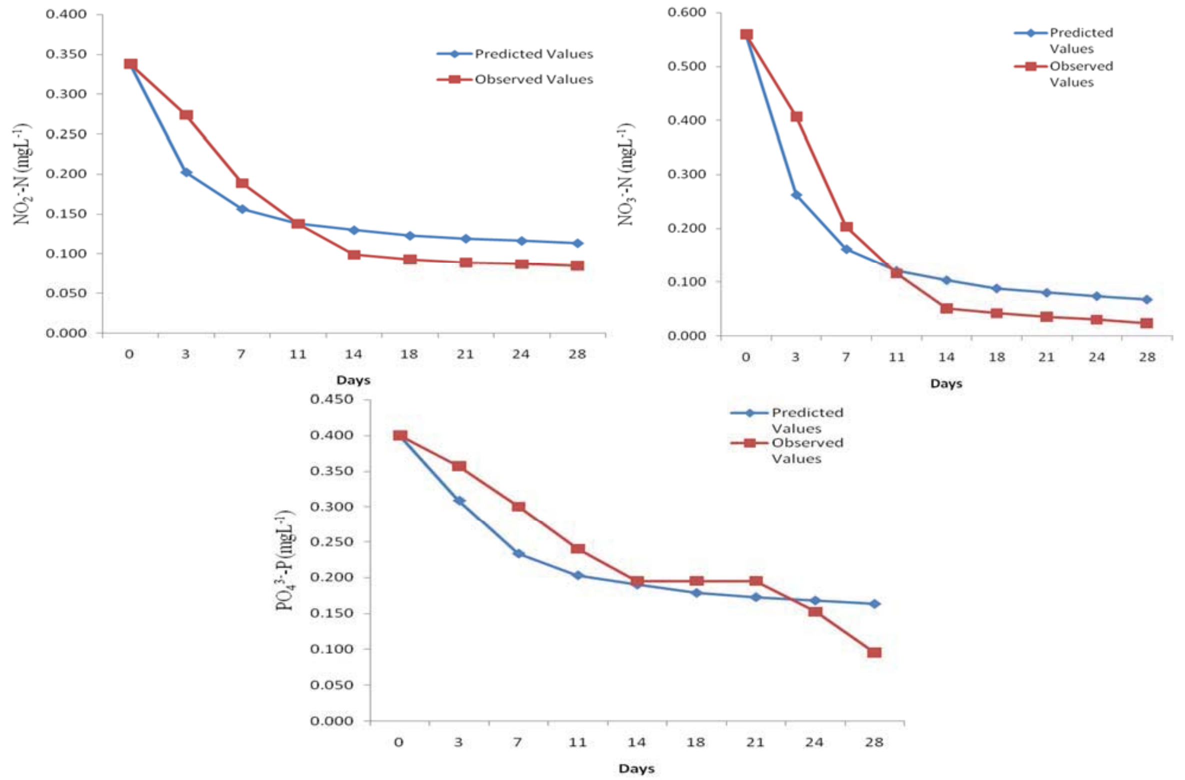

Fig. 4 Comparison between predicted values and observed values of NO_2^--N, NO_3^--N and PO_4^{3-}-P with respect to Water lettuce phytoremediation period (days)

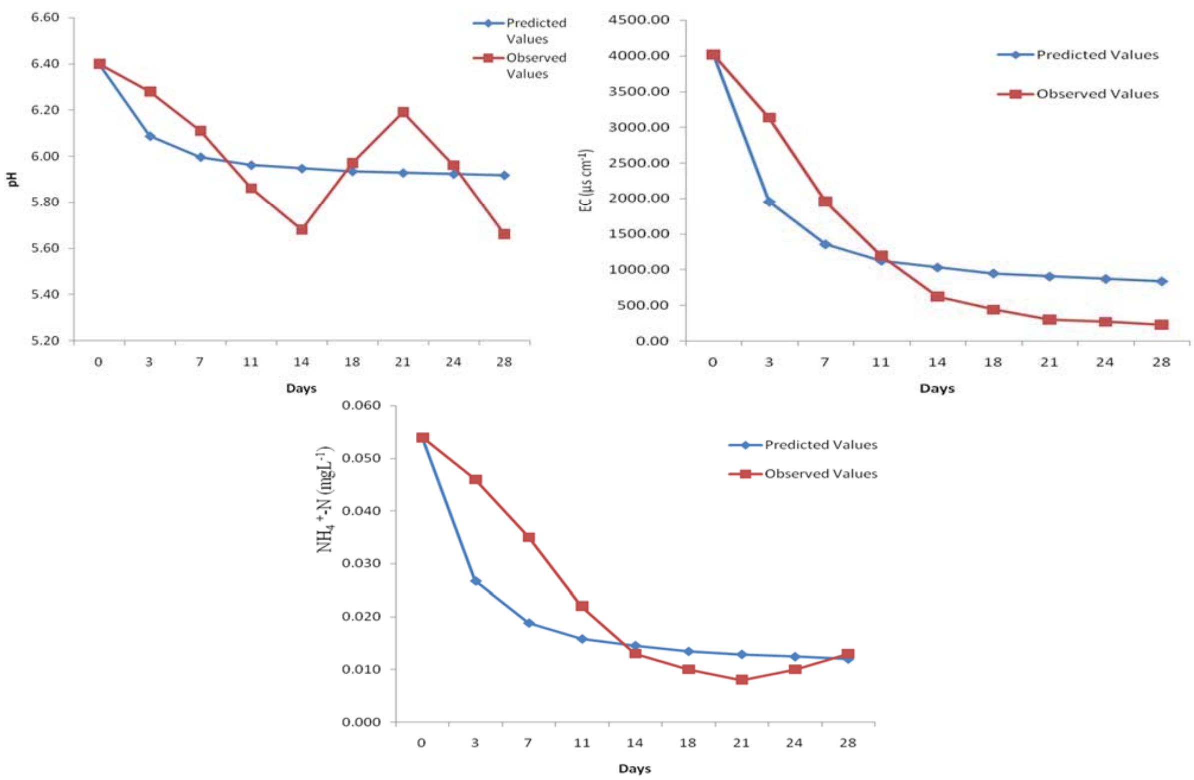

Fig. 5 Comparison between observed values and predicted values of pH, EC and NH_4^+-N with respect to the Morning glory phytoremediation period (day)

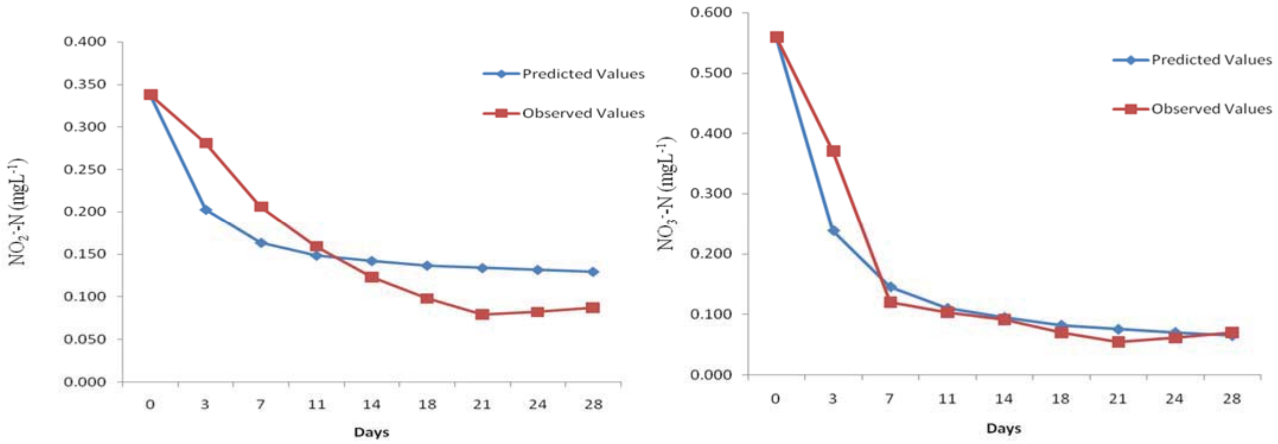

Fig. 6 Comparison between predicted values and observed values of NO_2^--N, and NO_3^--N with respect to Morning glory phytoremediation period (days)

IV. Conclusions and Recommendations

The mathematical description of nature's phytoremediation rates by some tropical aquatic macrophytes in aquaculture effluent is what this work focuses on, and the results demonstrate that:

1. The selected macrophytes which were water hyacinth, water lettuce and Morning glory, were able to phytoremediate the aquaculture effluent containing pollutants which were ammonium-nitrogen (NH_4^+ -N), nitrite-nitrogen (NO_2^- -N), nitrate-nitrogen (NO_3^- -N), phosphate-phosphorus (PO_4^{3-} -P), pH, and electrical conductivity (EC) to permissible levels.
2. The phytoremediation in the hydroponic unit containing water hyacinth was the best.
3. The pollutant reduction increased with increase in phytoremediation period.
4. The concentration of the pollutant decreases with time as a result of the introduction of aquatic macrophytes and is inversely proportional to the quantity (mass) of the macrophyte.
5. The decrease in pollutant concentration will continue until the macrophyte attain equilibrium i.e. no change in concentration with respect to time.
6. The treated effluent can be used for a recirculating aquaculture system since the quality is within the permissible level. This optimizes the use of water especially in areas with limited water supply.
7. The mathematical model when used with the selected macrophytes was able to make reasonable predictions on the selected parameters of the aquaculture effluent except for COD and alsoPO_4^{3-} -P using Morning Glory.

This research is multidisciplinary and its findings will help aquaculturists, wastewater managers, environmentalists etc. in economic design, construction and management of water systems for commercial aquaculture, farms, domestic and municipal supplies. It is therefore recommended that this model be adopted by environmental engineers and wastewater managers to predict the phytoremediation pattern of the specified macrophytes in aquaculture effluent.

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