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COD and Nutrient Removal Kinetics of Piggery Wastewater in Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Authors NEN and BUO designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author NEN contributed to the literature searches and compilation. Author BUO managed the literature searches, analyses of the study, and managed the experimental process. Both authors read and approved the final manuscript.

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ABSTRACT

Waste stabilisation ponds (WSPs) have been employed in treatment of diverse kinds of wastewater over the years. This system's dynamics have been poorly understood and this has led to diverse problems over time such as reduced efficiency of reactors. This study employed the use of four models in the study of biological reaction in removal of organic matter from the waste stabilisation ponds. Prediction of removal rates of piggery wastewater in the ponds and at different retention times were studied using first order model, Monod, Grau and the Stover Kincannon model by fitting model to experimental data. Adaptability of the Monod model was poor in the anaerobic and part of the facultative pond. Monod model showed extent of substrate utilization by the cell yield coefficient 'Y' while the Stover Kincannon model's maximum utilization rate constant (μ_{max}) increased with increase in retention time. Stover Kincannon model showed a better adaptability (R^2) than first and Monod models. Although the adaptability of first order was very poor, incremental biodegradation with time was noted which agrees with other models. Grau model gives a better system adaptation and agrees with other model substrate degradation prediction and also it best predicts efficiency of removal of substrate.

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1. INTRODUCTION

Urbanization and industrial development is increasing steadily at an alarming rate which implies that the quantity of animal waste generated also increases. These wastes pose a serious threat to public health when they are improperly disposed. Present waste disposal techniques employed by most farms in the country are deep pit dumping (deep pits constructed within farm premises) and open dumping practices; these dumping techniques are very injurious to the ecosystem as there's runoff of waste into nearby water bodies and also infiltration of hazardous chemicals into aquifers. These makes water bodies unsuitable for consumption. Wastewater generated from piggery is usually utilised for agriculture because of the high nutrient content. This water requires a properly planned and engineered system to enable immediate conveyance, storage and application in irrigation schemes.

Piggery waste comprises of feces and urine. Feces include organic carbon (90% of the total discharge), and about 30% of the nitrogen and 80% of the phosphorus are usually discharged [1]. Macro nutrients needed by plants includes carbon, nitrogen and phosphorus. However, the organics in the feces needs to be stabilized before utilization/ application and stabilizing organics in waste can be achieved by composting. A major guide to land application of treated wastewater is Nitrogen load. Phosphorus accumulates in soils and reacts with iron to make a crystal so that the plant does not take up the iron as a nutrient which eventually leads to iron deficiency. It should be noted that these nutrient in the event of a heavy downpour, can be washed into surface water bodies, thereby leading to eutrophication. Nitrogen presence in water can be detrimental; nitrate ion in water has been noted to be a potential risk to children [2].

Chemical oxygen demand (COD), measures the approximate oxygen concentration in a system [3]. Most intensive piggery in Nigeria and beyond are periodically disinfected and cleaned with various disinfectants and water 3-7 times a week depending on management structure and financial strength. This results to high concentration of COD occasioned by a rapid drop in the amount of oxygen in wastewater which makes for difficult life sustenance.

Another method of increasing importance in the globe is the use of ponds, simply called waste stabilization ponds (WSPs). This system of treatment includes a series of flow which also accomplishes stabilization of waste by nitrification. Effluent generated from waste can be utilised in farms. WSPs are robust and operationally simple wastewater technology that provides a considerable degree of economical treatment especially where land is often available at reasonable opportunity costs and skilled labor is in short supply [4–9]. WSP are very efficient in treating wastewater [10]. Pond systems have been shown to achieve a high degree of BOD removal, excreted pathogen removal (bacteria, virus, protozoa and helminths). This enables the WSP effluent to be reused for unrestricted crop irrigation, restricted crop irrigation and fishpond fertilization [11]. WSP are a flexible treatment process. Ponds can support hydraulic and organic shock loads. [12] found that WSP perform satisfactorily when presented with high concentrations of heavy metals (up to 30 mg/l).

Bio-kinetic models have been employed in study of treatment of pollutants in wastewater systems. They can aid the design and optimization of operating conditions of these systems. This research aims at evaluating kinetic constants in the treatment of piggery wastewater using the waste stabilisation pond. Kinetic coefficients of importance are determined; models describing processes in a detailed pattern are selected so as to obtain a more generalized interpretation [13].

2. MATERIALS AND METHODS

2.1 Sample Collection and Analysed

First trial run of reactors was initiated on the 12th of January, 2015 after successful completion of fabrication works. First sample was collected on the 30th of March, 2015. The first two weeks were characterized with sample collection and analysis to check the efficiency of anaerobic digester, and also to ensure system attain a near steady state condition. Sampling continued on consecutive days (Tuesday, Wednesday, Thursday, and Friday) for the weeks following. Samples were collected using a sterilized plastic water bottle with cork. Samples were collected at the outlets and inlets of ponds (Anaerobic, Facultative and Maturation). The overall sampling period lasted a total of thirty five (21) weeks, from which additional ten (10) weeks will be used for data analysis. A total number of 231 samples were collected and analysed in Biochemical laboratory department of the Springboard Laboratory.

Collected samples were placed in a freezer and cooled to 4°C prior to analysis to prevent algae from photosynthesizing and to reduce the metabolic rate of the in-situ bacteria, thus preserving the integrity of the samples. Analysis for the parameters was carried out according to the methods described in Standard Methods for the Examination of Water and Wastewater [14].

2.2 Kinetic Analysis of Substrate Removal

Mathematical and biological models are used to determine the relationship between variables. These relationships can be used to design and assess the results of systems. Models are also used to control and anticipation performance treatment unit and optimize units. In this study, four models i.e. the First-order model pollutant removal, Second order (Grau), Stover-Kincannon model and the Monod model were utilised in studying removal kinetics of reactors.

2.3 First-order Model

A mass balance of organics moving in and out of the anaerobic, facultative and maturation pond can be expressed as:

$$\frac{-dS}{dt} = \frac{Q}{V} \text{ x } S_0 - \frac{Q}{V} \text{ x } S - k_i S \quad (1)$$

Equation 4.1 is a first-order type for pollutants removal:

Where S_i and S_e represents the input and output substrate concentration per mg/L; Q and V represents the wastewater flow rate and the volume of reactor, and K_1 is the first-order kinetic constant [15,13]. Changes in the waste stabilisation pond due to stable conditions in removal of pollutant (dS/dT) is assumed to be zero, this gives rise to Equation 2 which represents the extent of removal of pollutant in the waste stabilisation pond.

$$\frac{S_0 - S}{HRT} = k_i S \quad (2)$$

HRT represents hydraulic retention time. Slope obtained from Equation 2 equals k_1.

2.4 Second-order Model (Grau)

The Grau model, a second-order kinetic model can be expressed as shown in Equation 3:

$$\frac{S_0 \text{ x } HRT}{S_0 - S} = m \text{ x } HRT + n \quad (3)$$

Where n (per day) and m (dimensionless) represents the intercept and slope of line respectively. $S_0 - S/ S_0$ expresses the substrate removal efficiency and is symbolized as E.

2.5 Stover-Kincannon Model

The Stover Kincannon model is shown in Equation 4. The model gives a relationship between efficiency of removal and loading rate.

$$\frac{dS}{dt} = \frac{V}{Q(S_0 - S)} = \frac{K_B}{U_{max}} \cdot \frac{V}{QS_0} + \frac{1}{U_{max}} \quad (4)$$

Where dS/dt represents the pollutant removal rate (g/L.d), μ_{max} is the maximum rate in which pollutant is removed in g/l.day and K_B, saturation constant is g/l.day [13]. A plot of the inverse of the loading removal rate against the inverse of the total loading rate gives an intercept rate and slope as $1/\mu_{max}$ and K_B/μ_{max} respectively.

2.6 Monod Model

Monod model as derived from steady state relationship as defined by Mamais and Jenkins [16] is:

$$\frac{XV}{Q(S_0 - S)} = \frac{K_s}{k} \cdot \frac{1}{S} + \frac{1}{k} \quad (5)$$

Maximum removal rate is depicted as Ks (d^{-1}), k is the half-velocity constant (g/L); X represents the volatile suspended solid (VSS) in various waste stabilisation ponds. VSS was obtained by adopting approximately 80% of the suspended solids in the anaerobic pond (g/L) [17]. Estimation VSS wasn't conducted in the facultative and maturation due to the effects of the algae in the pond which were greatly contributing to the suspended solid in reactors. Plotting Equation 5 gives very useful information regarding Monod kinetic coefficient in the various waste stabilisation ponds.

3. RESULTS AND DISCUSSION

3.1 Chemical oxygen Demand Removal Kinetics

COD removal in the waste stabilisation pond may be attributed to factors such as detention time, temperature e.t.c. Organic matter removal is a major concern/ aim of treating wastewater in

WSPs. Understanding kinetics of pollutants in the system is vital as it aids achieving useful design parameters and improves pond's performance. The Anaerobic pond, the first pond in the waste stabilisation series substantially reduces the concentration of pollutant in the facultative and maturation ponds. Formulated biological and mathematical models are mostly employed in defining relationship between variables which can be utilised in evaluating and validation of system efficiency. Manipulating and/ or altering models can give rise to system design and performance predictions.

3.2 First Order Model

Most biological wastewater treatment processes are described by the first-order kinetics (Mansouri et al., 2014). It was also noted that there may be differences in reaction order when variation exists in the microorganisms, the substrate or environmental conditions and these variation can be measured experimentally. In the first order reaction, the reaction rate (rate of breakdown) is at optimum rate with high organic content and progressively reduces as the organic matter is consumed. Fig. 1 shows the correlated value of the (S_0 -S)/HRT and the substrate concentration (S) for the best retention time of study.

Changes in the waste stabilisation pond due to stable conditions in removal of pollutant (dS/dT) is assumed to be zero, this gives rise to equation (2) which represents the extent of removal of pollutant in the waste stabilisation pond and the slope obtained from Equation (2) equals k_1 (first-order kinetic constant). In the anaerobic pond, the data fitted well as seen from the value of R^2 obtained for 10day HRT (R^2 = 0.72), facultative pond had R^2 = 0.65 while maturation pond was R^2 = 0.95.

From Table 1, the computed values of the first-order kinetic constant (k) were in the range of 1.291 – 107.5 d^{-1} in the anaerobic pond, 0.182 – 37.33d^{-1} in the facultative pond while in the maturation pond kinetic constant range was 1.899 – 15.91d^{-1}. An increase in retention time generally led to an increase in the first-order kinetic constant (k) hence favouring incremental biodegradation of the substrate. Biodegradation of substrate was higher in the anaerobic pond. Similar process kinetics observed in a lab-scale upflow aerobic immobilized biomass (UAIB) reactor treating simulated sugar-manufacturing wastewater [18] reported a k value of 14.549 d^{-1} with correlation coefficient of 0.742.

The high results recorded in values of the determination coefficients (R^2) shows that the waste stabilisation pond (WSPs) was clearly capable of biodegrading the organic matter. High value of R^2 obtained in the maturation pond shows that the first-order kinetics can be applied with a good degree of precision.

3.3 Second-Order Model (Grau Model)

The kinetic coefficients n, m and k_s were determine by plotting Equation (3) and coefficients obtained are shown in Table 2. The kinetic coefficient values n and m were obtained from intersection and slope of graph of the various retention times of ponds. An increase in the kinetic constant (k_s) along the retention time in anaerobic pond was noted, implying a higher degradation. [19] and [18] reported k_s values for synthetic wastewater in the range of 3.58-10.81 d^{-1}, while [20] noted a k_s value for synthetic wastewater being treated in an upflow anaerobic/ anoxic sludge fixed film (UAASFF) bioreactor, to be 5.95 d^{-1} with correlation coefficient (R^2) as 0.99. From Table 2, k_s value obtained ranged between 0.156 – 0.195 d^{-1} in the anaerobic pond, 0.189 – 0.287 d^{-1} in the facultative pond and 0.092 – 0.273 d^{-1} in the maturation pond.

$$\frac{S_0 \text{ x HRT}}{S_0 - S} = n + m\,\text{HRT} \quad (3)$$

$S_0 - S$ / S_0 expresses the substrate removal efficiency and is symbolized as E.

The obtained results conforms with reported values in literature although, a few biodegradation values in anaerobic and facultative pond are slightly higher than reported in literature. The relationship between effluent COD concentration and HRT can be obtained by adopting average value of m and n in all ponds are described by Equations (a):

$$S = S_0\left(1 - \frac{\text{HRT}}{0.4092 + 1.586\,\text{HRT}}\right) \quad (a)$$

Furthermore, the substrate removal efficiency for anaerobic, facultative and maturation ponds are represented by Equation (b):

$$E = \frac{\text{HRT}}{0.4092 + 1.586\,\text{HRT}} \quad (b)$$

Equation (a) and (b) can be used to predict the system's removal efficiency and the effluent concentration. Validation of Equations gave Fcrit>F and significance level '*p*' of 0.9867 (p< 0.05) signifying a non existence of significance difference between the theoretical and experimental substrate removal efficiencies. It was noted that the Grau model best describes the removal efficiency of COD in the waste stabilisation ponds.

Table 1. Kinetic parameters from first order model for COD removal in WSPs

HRT	R^2	k (d^{-1})	R^2	k (d^{-1})	R^2	k (d^{-1})
	Anaerobic pond		Facultative pond		Maturation pond	
5	0.257	1.291	0.552	0.182	0.161	1.899
10	0.720	5.510	0.647	0.540	0.953	1.114
15	0.451	15.270	0.652	2.400	0.463	5.411
20	0.442	52.970	0.476	37.330	0.302	15.910
25	0.289	107.500	*	*	0.281	13.290
30	0.045	46.120	0.461	11.670	0.038	1.184

** – not reported for detention times with two data points or very poor 'R^2'*

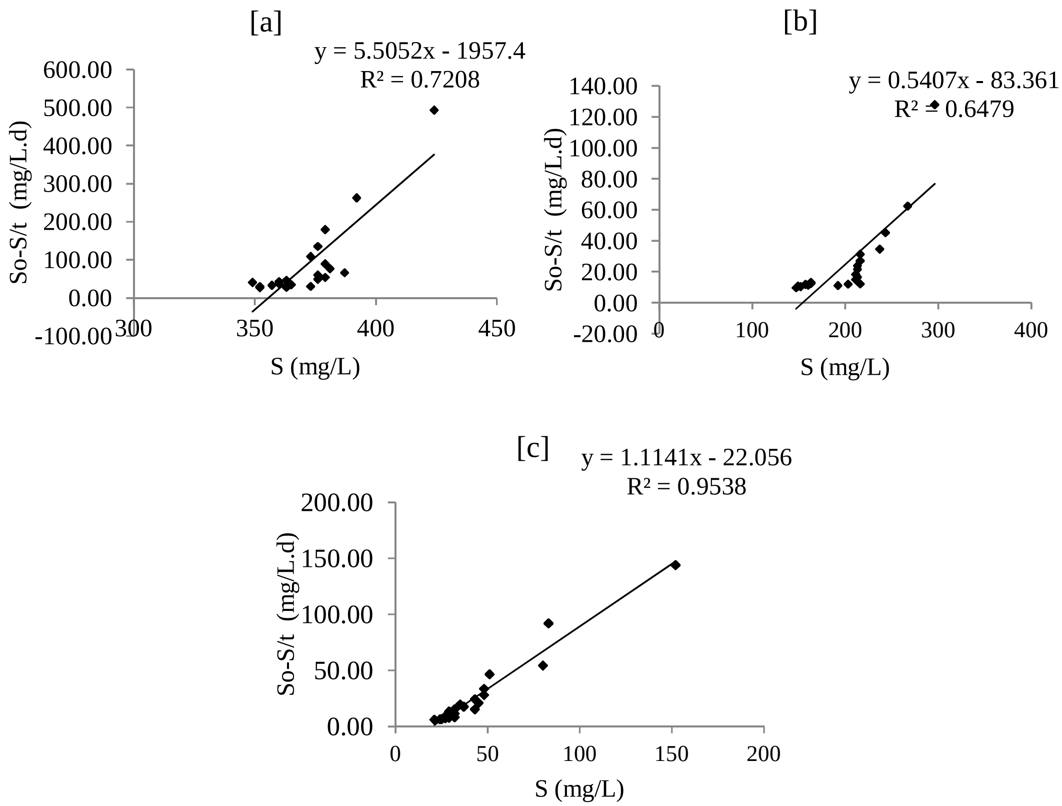

Fig. 1. [a] First order model plot for 10day HRT in anaerobic pond [b] First order model plot for 10day HRT in facultative pond [c] First order model plot for 10day HRT in maturation pond

Table 2. Kinetic parameters from Grau model for COD removal in WSPs

HRT	R^2	n	m (d^{-1})	k_s (d^{-1})	R^2	n	m (d^{-1})	k_s (d^{-1})	R^2	n	m (d^{-1})	k_s (d^{-})
		Anaerobic pond				Facultative pond				Maturation pond		
5	0.989	1.731	1.915	0.156	0.000	95.490	1.041	0.287	0.015	80.910	3.252	0.092
10	0.990	0.429	1.623	0.184	0.941	4.910	1.583	0.189	0.998	0.706	1.155	0.258
15	0.990	0.098	1.537	0.194	0.993	0.693	1.368	0.218	0.997	0.155	1.094	0.273
20	0.999	0.000	1.534	0.195	0.999	0.037	1.405	0.212	0.999	0.066	1.169	0.255
25	0.999	0.010	1.550	0.193	0.999	0.006	1.370	0.218	0.999	0.061	1.136	0.263
30	0.990	0.003	1.543	0.193	0.999	0.113	1.457	0.205	0.995	0.120	1.142	0.261

3.4 Stover-Kincannon Model

Stover-Kincannon model investigates the effect of the influent organic loading rate (OLR) on the removed OLR. The intersection value $1/\mu_{max}$ respectively and slope values K_B/μ_{max} were obtained from least square linear regression plot. The saturation constant (K_B) and the maximum total substrate utilization rate (μ_{max}) calculated are depicted in Table 3.

The Stover Kincannon model is shown in Equation (c). The model gives a relationship between efficiency of removal and loading rate.

$$\frac{dS}{dt} = \frac{Q\,(S_0 - S)}{V} \qquad (c)$$

$$\frac{dS}{dt} = \frac{\mu_{max}\,(QS_0 / V)}{K_B + (QS_0 / V)} \qquad (d)$$

Where dS/dt represents the pollutant removal rate (g/L.d), μ_{max} is the maximum rate in which pollutant is removed in g/l.day and K_B, saturation constant is g/l.day [13]. A plot of the inverse of the loading removal rate against the inverse of the total loading rate gives an intercept rate and slope as $1/\mu_{max}$ and K_B/μ_{max} respectively as shown in Equation (4).

An incremental trend in values of saturation constant and maximum total substrate utilization rate with corresponding increase in retention time were observe while the saturation value constant (K_B), maximum utilization rate (μ_{max}) and regression coefficient were noted as >500 g/L·d, >500 g/L·d and 0.999 for 20 day HRT; 100 g/L.d, 72.90 g/L.d and 0.999 for 25 day; for the anaerobic, and facultative ponds respectively.

The R^2 values for the experimental data were generally found to align with this model. However, the μ_{max} and K_B values obtained in this study were higher than values found by [21], [20] and [22]. [23] obtained 23.81mg/l.d for SCOD in the ponds in Birjand, [15] obtained μ_{max} of 42.735 mg/l.d in Stover - Kincannon Model and [24] obtained μ_{max} of 14.4 mg/l.d. The Stover-Kincannon model showed high compliance in organic matter removal and the maximum utilization rates increases the with retention time and this is highest in the anaerobic pond which may be attributed to the high value of the substrate influent concentration.

3.5 Mass Balance-based (Monod) Model

In order to estimate the cell yield coefficient (Y) and biomass decay coefficient (k_d), the relationship between the inverse SRT (μ =1/SRT) and the specific substrate utilization rate (μ) was utilised for the different hydraulic retention times.

The Kinetic parameters Y and K_d for Monod model can be obtained from equation (e).

$$\frac{S_0 - S}{\theta_H \times X} = \frac{1}{Y} \times \left[\frac{1}{\theta_c}\right] + \frac{1}{Y} \times K_d \qquad (e)$$

The value of μmax and K_d can be obtained from equation (f)

$$\frac{\mu_{max} S}{K_s + S} = \frac{S_0 - S}{\theta X} \qquad (f)$$

The linearised form of equation (f) is gotten by adopting its inverse.

$$\frac{\theta X}{S_0 - S} = \frac{K_s}{\mu_{max}} . \frac{1}{S} \quad \frac{1}{\mu_{max}} \qquad (g)$$

The values of R^2, Y and k_d for Monod model (Fig. 2a, Fig. 2b and Fig. 2c) and the corresponding best HRT with values for the anaerobic, facultative and maturation ponds were 0.783, 0.011 g VSS/ g COD/L and 0.360 per day for 5day HRT; 0.701, 0.026 g VSS/ g COD/L and 0.368 per day for 10 day HRT; 0.946, 0.006 g VSS/ g COD/L and 0.006 per day for 10 day HRT. The decay coefficient value, k_d correlated with values obtained by Pandian et al. [25] of

Table 3. Kinetic parameters from Stover-Kincannon model for COD removal in WSPs

HRT	R^2	μmax (g/L.d)	K_B (g/L.d)	R^2	μmax (g/L.d)	K_B (g/L.d)	R^2	μmax (g/L.d)	K_B (g/L.d)
	Anaerobic pond			Facultative pond			Maturation pond		
5	0.989	1.000	1.915	0.000	0.005	0.002	0.019	0.050	0.001
10	1.000	*	*	0.944	0.200	0.118	0.998	0.500	0.425
15	0.999	14.286	9.286	0.944	1.000	0.724	0.998	1.000	0.909
20	1.000	>500	>500	0.999	12.500	8.888	0.999	*	*
25	1.000	>500	92.143	0.999	100.000	72.900	0.994	*	*
30	1.000	500.000	323.500	0.999	*	*	0.994	*	*

** – not reported for detention times with two data points or very poor 'R^2'*

range 0.0065 – 0.153d^{-1}. High values recorded might be due to substantial decay of cells that occur as a result of endogenous respiration.

The k_d has little significance when the hydraulic retention time is small. However, when the system is operated in the endogenous growth phase, k is important in the calculation of the net amount of microorganisms produced and the oxygen utilization rate [26]. Lower values of k recorded in this study resulted in the short hydraulic retention time as noted by Mansouri et al. [20].

The concentration of biomass in the bioreactor and amount of excess sludge wasted is denoted by Y. The Lower values of Y obtained in this study was because of prolonged HRT which corresponding to lower organic loading rate. From Table 4, an increase in the hydraulic retention time gave a corresponding decrease in Y due to lower sludge production resulting from the low COD consumption rate.

The maximum growth rate (μ_{max}) and substrate saturation constant (K_s), were computed by plotting the experimental data as $\theta X / (S_0 - S)$ vs. 1/S. The value of kinetics coefficients, μ_{max} and K_s in the anaerobic, facultative and maturation ponds are shown in Table 4. K_s determines the speed at which μ approaches μ_{max} [27]. From results obtained, the differences in the kinetic coefficients might be due to significant discrepancy in reactor flow rate, configurations and wastewater composition [21].

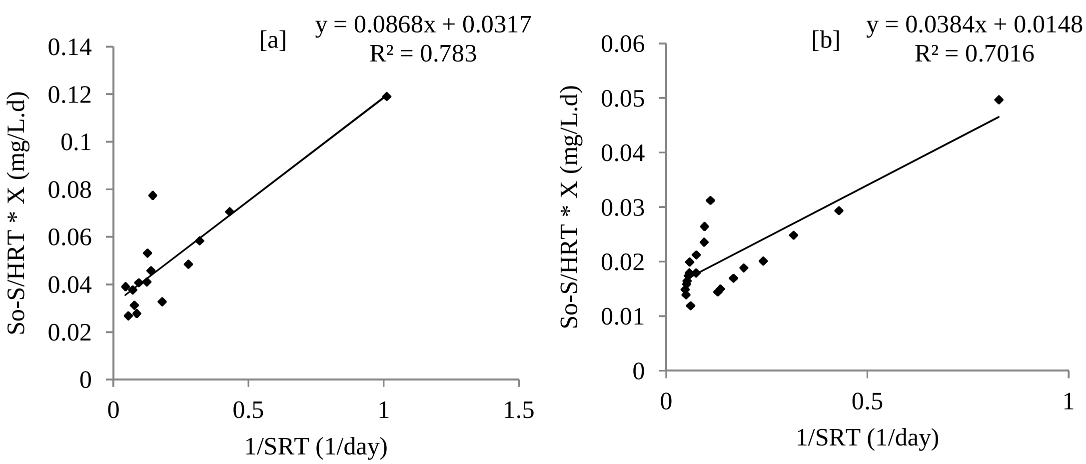

Fig. 2. [a] Monod model plot for 5day HRT in anaerobic pond [b] Monod model plot for 10day HRT in facultative pond

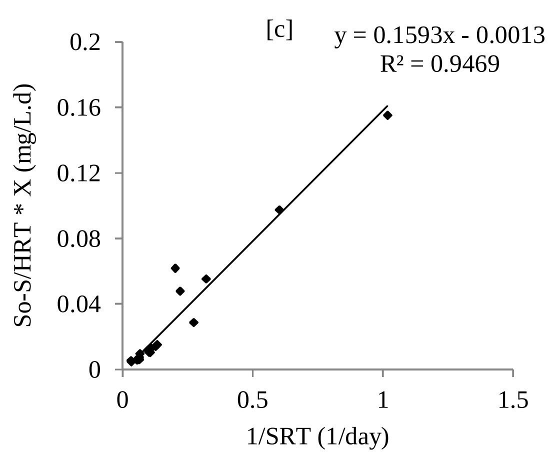

Fig. 2. [c] Monod model plot for 10day HRT in maturation pond

Table 4. Kinetic parameters from Monod model for COD removal in WSPs

HRT	R^2	Y (mg VSS/ mg COD)	k_d (d^{-1})	μmax	K_s (mg COD/L)	K_{max} (mg /COD/ mg VSS/d)
	Anaerobic Pond					
5	0.783	11.628	0.360	0.071	1318.600	0.006
10	0.019	1.626	0.042	0.004	41.095	0.003
15	0.205	0.049	0.047	0.017	355.854	0.342
20	0.121	0.010	0.041	0.000	3.344	0.025
25	0.273	0.006	0.033	0.005	321.005	0.773
30	0.282	0.049	0.010	0.680	736.914	13.773
	Facultative Pond					
5	0.793	17.241	0.155	0.001	20.168	0.000
10	0.701	26.316	0.368	>1000	>1000	276.868
15	0.582	0.000	0.004	0.065	192.503	>1000
20	0.999	1.876	0.019	>1000	>1000	>1000
25	0.999	1.372	0.000	0.167	27.737	0.122
30	0.965	1.883	0.111	0.019	84.984	0.010
	Maturation Pond					
5	0.442	0.000	0.002	0.002	19.894	85.965
10	0.946	6.289	0.006	0.018	97.700	0.003
15	0.998	5.988	0.012	0.435	161.696	0.073
20	0.999	5.181	0.010	0.013	9.561	0.002
25	0.998	5.587	0.045	0.024	16.195	0.004
30	0.949	5.780	0.127	0.065	1.369	0.011

4. CONCLUSION

This research aims at evaluating kinetic constants in the treatment of piggery wastewater using the waste stabilisation pond. Kinetic coefficients of importance are determined; models describing processes in a detailed pattern are selected so as to obtain a more generalized interpretation [13]. An increase in retention time generally led to an increase in first order kinetic constant (k) while increase was recorded in kinetic constant (ks) along the retention time in Grau model with a better adaptability compared to first order, Stover Kincannon and Monod model. Stover Kincannon model showed that μ_{max} value increases with retention time, this agrees with Monod cell yield coefficient 'Y' which reduces with time as concentration reduces.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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