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Mathematical Modelling Of Cyanide Inhibition on Cassava Wastewater Treatment

E. Onukwugha[1] and A.O. Ibeje[*]
Department of Civil Engineering, Federal Polytechnic, Nekede, Owerri, Nigeria Department of Civil Engineering, Imo State University, P.M.B. 2000, Owerri, Nigeria.

Abstract: - Anaerobic Baffled Reactors (ABR) is used to evaluate the extent of cyanide inhibition of cassava wastewater treatment. The reactor has aspect ratio of 4:1:1. Kinetic analyses of specific growth rate $\boldsymbol{\mu_{max}}$ and half saturation constant $\boldsymbol{k_s}$ are evaluated for the reactor. For non-inhibited cassava wastewater treatment, Monod model yields $\boldsymbol{\mu_{max}}$ **= 10.87 day^{-1}; and** $\boldsymbol{k_s = 0.87\, mgCODL^{-1}}$. Coefficient of determination R^2 is used to verify the model to yield value of $\mathbf{0.917}$ for Monod model. For inhibited cassava wastewater treatment, the inhibition constant $\boldsymbol{k_i}$ is evaluated from the reactor as $\boldsymbol{1.172 * 10^{-5} mgCyanide/L^{-1}}$. This clearly indicates that the extent of cyanide inhibition of cassava waste water treatment is minimal.

Key Words: - *Cyanide inhibited, Treatment, Cassava Wastewater, Monod model and Reactor*

I. INTRODUCTION

Cassava (Manihot esculenta crantz, also known as manioc or yucca) is one of the leading food and feed plants in the world: it ranks fourth among staple crops with a global production of about 160 milllion tons per year (1). Most of these are grown in three regions, West Africa, and the Congo basin, tropical South America, and South East Asia (2), while in Western countries it is not commonly used, because of the presence of cyanoglucosides (linamarin and lotaustralin). Cassava roots contain cyanogenic glucosides (the precursors of HCN) in various concentrations depending on the variety and growing conditions (3). This cyanide is released during peeling, slicing and crushing. The bound cyanide is converted to free cyanide during the milling operation. About 40% to 70% of the total cyanide appears in the water used to wash the starch from the disintegrated tissue (4). The press water, although produced in relatively low volumes (250 – 300 litres per tonne of roots), is the main problem because of its high biological oxygen demand (BOD) of 25,000 – 50,000 mg/l with a typical cyanide concentration in excess of 400 mg/l (5). Cyanide, being an acidic component will naturally have an inhibiting action on the biological degradation of cassava wastewater. This effect on the environment is yet to be addressed properly in developing countries due to inadequate equipment and lack of research materials. The objectives of this study are to formulate an improved mathematical model to describe cassava wastewater treatment taking into account its inhibition characteristic and to determine the extent of inhibition caused by cyanide, on the degradation of cassava wastewater.

II. MATERIALS AND METHODOLOGY

The Reactor

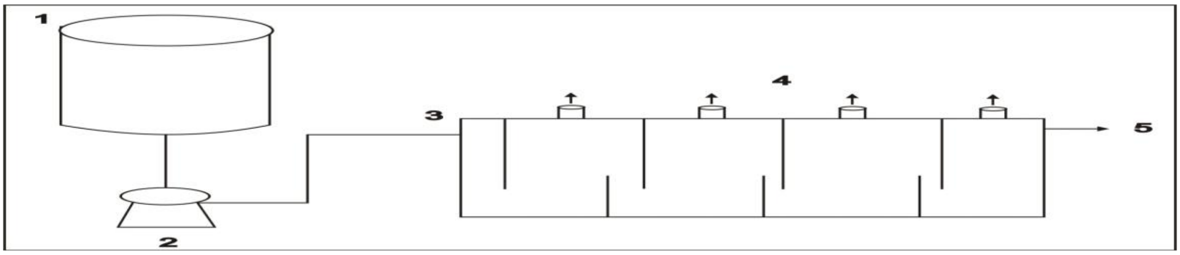

Figure 1: Scheme of the ABR. 1. Feed Tank; 2. Peristaltic Pump; 3. Influent; 4. Sampling Ports; 5. Effluent.

The laboratory scale ABR was constructed from 6mm thick stainless steel, with external dimensions of lengths, widths, depths and working volumes as shown in table 1. Figure 1 shows a schematic diagram of the reactor. The reactor was divided into different number of equal compartments by vertical baffles with each compartment of the reactor having downcomer and riser regions created by a further vertical baffle. The widths of upcomers were multiples of the widths of downcomer. The lower parts of the downcomer baffles were angled at 45^0 in order to direct the flow evenly through the upcomer. This produced effective mixing and contact between the wastewater and anaerobic sludge at the base of each riser. Each compartment was equipped with sampling ports that allowed biological solids and liquid samples to be withdrawn. The operating temperature was maintained constant at 35 ± 0.5°C by putting the reactor in a water bath equipped with a temperature regulator. The influent feed was pumped using variable speed peristaltic pump. The outlet was connected to a glass U-tube for level control and to trap solids.

Start-up of ABR

Start-up without seed sludge was rather difficult and time consuming for suspended growth anaerobic reactors. The following 3 steps were taken: (i) the reactor was filled with cassava wastewater and allowed to rest for 15 days (ii) the sludge bed was allowed through a process of sludge accumulation by settling and sludge improvement and (iii) after 15 days, feeding of the wastewater was resumed at a flow rate of 5.33litres per day and HRT of 6days with a very low organic loading rate (OLR) of $0.067 kgCOD/m^3.day$. The resumed wastewater feeding helped the development of sludge bed at the bottom of individual chambers of the ABR. This process of feeding the system followed by two weeks rest is based on the experiment made in Kanpur (India) for the start-up of a UASB plant without inoculum (6).

Characterization of Wastewater

The cassava wastewater from a cassava processing factory at Imo Polytechnic Umuagwo in eastern Nigeria was used as feed. The supernatant of the wastewater after the simple gravity settling, used in the investigation, had low TSS, as approximately 90% of the solids were removed. The supernatant wastewater was diluted to achieve the COD concentration required for each loading rate with water. In order to achieve pH and alkalinity adjustment, the supernatant was neutralized by NaOH and $NaHCO_3$. A COD:N:P ratio of 300:5: 1 was kept during operation using NH_4C1 and K_2HPO_4. The micro-nutrient deficiency was added occasionally to correct growth conditions according to (7).

Procedure for Experiment 1 (Non-Cyanide Inhibited Treatment)

The wastewater was collected twice a day from the cassava processing plant, and it was intermittently mixed to feed the reactor with a consistent quality. The wastewater came from processing cassava specie (bogot) that had no cyanide content (Table 2). The wastewater was fed to the reactor with the help of a variable speed peristaltic pump. The ABR was operated at various hydraulic retention times (HRTs) by varying the flow rate of influent wastewater (Q_{inf}), thereby varying the organic loading rate (OLR). The wastewater flowed from the downcomer to the upcomer within an individual chamber through the sludge bed formed at the bottom of the individual chambers. After receiving treatment in the particular chamber, wastewater entered the next chamber from the top. Due to the specific design and positioning of the baffle, the wastewater is evenly distributed in the upcomer and the vertical upflow velocity (V_{up}) could be significantly reduced. The treated effluent was collected from the outlet of the 3rd compartment (C3). The reactor was kept in a temperature controlled chamber maintained at 35 ^{O}C.

Procedure for Experiment 2 (Cyanide Inhibited Treatment)

After the start-up stage has been completed; the steady-state operation was conducted. The ABR was operated at various cyanide concentrations by using influent wastewater from different cassava species as listed in table 1. The steady-state performance was evaluated under hydraulic retention time of 3 to 10 days. (Organic loading rate of 1.60 to 5.33 g-COD (l day). At any given loading rate, the bioreactor was continuously operated until steady-state condition is achieved, when effluent COD, VSS and gas production rate in bioreactor become constant. Then samples were collected and subjected to the analysis of the following parameters, i.e. influent and effluent COD, suspended solids and volatile suspended solids, according to standard methods.

Model Formulation

Nomenclature

S_i = Substrate concentration in the influent (mgl^{-1}); S_e= Substrate concentration in the effluent (mgl^{-1}); k_s= Half saturation constant (mgl^{-1}); μ = Specific growth rate of organism (per day); μ_{max} = Maximum specific growth rate of organism (per day); X = concentration of active biomass (mg/L); r_A = Rate of utilization of substrate (mg/l.day) ; K_i = the inhibition constant and I = the noncompetitive (Cyanide) inhibitor concentration (mgl^{-1}).

Monod Model for ABR

The Monod model is described as

$$r_A = \frac{ds}{dt} = \frac{Q}{V}(S_i - S_e) = \mu.X \qquad (1)$$

$$= \frac{\mu_{max} S_e}{K_s + S_e} X$$

$$\frac{XV}{Q(S_i - S_e)} = \frac{K_s}{\mu_{max}} \frac{1}{S_e} + \frac{1}{\mu_{max}} \qquad (2)$$

Applying experimental results to Equations (2), graph will be plotted. In this, graph $XV/(S_i-S_e)$ is plotted against $1/S_e$

Cyanide-inhibited Monod Model for ABR

Monod kinetics with substrate inhibition are assumed (Andrews, 1969), i.e.

$$\mu_g = \frac{\mu_{max}}{1 + \frac{K_s}{S_e} + \frac{I}{K_i}} \qquad (3)$$

Substituting Equation 3 into Equation 1, by replacing μand μ_g gives

$$\frac{ds}{dt} = \frac{Q}{V}(S_i - S_e) = x.\mu \qquad (4)$$

$$= x\left[\frac{\mu_{max}}{1+\frac{K_s}{S_e}+\frac{I}{K_i}}\right] \qquad (5)$$

$$= \frac{x\mu_{max}}{1+\frac{K_s}{S_e}+\frac{I}{K_i}} \qquad (6)$$

$$\text{i.e.} \qquad \frac{Q}{V}(S_i - S_e) = \frac{x\mu_{max}}{1+\frac{K_s}{Se}+\frac{I}{K_i}} \qquad (7)$$

Taking inverse of both sides of the Equation;

$$\frac{1}{\frac{Q}{V}(S_i - S_e)} = \left[\frac{x\mu_{max}}{1+\frac{K_s}{Se}+\frac{I}{K_i}}\right]^{-1} \qquad (8)$$

$$\frac{V}{Q(S_i - S_e)} = \frac{1+\frac{K_s}{Se}+\frac{I}{K_i}}{x\mu_{max}} \qquad (9)$$

$$xV\mu_{max} = Q(S_i - S_e)\left[1 + \frac{K_s}{Se} + \frac{I}{K_i}\right] \qquad (10)$$

$$\frac{xV}{Q(S_i - S_e)} = \frac{1+\frac{K_s}{Se}+\frac{I}{K_i}}{\mu_{max}} \qquad (11)$$

Linearising equation 11 gives:

$$\frac{xV}{Q(S_i - S_e)} = \frac{1}{\mu_{max}} + \frac{K_s}{\mu_{max}}.\frac{1}{S_e} + \frac{1}{\mu_{max} K_i}(I) \equiv y = c + mx \qquad (12)$$

$$\frac{xV}{Q(S_i - S_e)} = \text{plot on y} - \text{axis}; \quad I = \text{plot on x axis}; \quad \frac{1}{\mu_{max} K_i} = \text{slope}$$

And: $\frac{1}{\mu_{max}} + \frac{K_s}{\mu_{max}}.\frac{1}{S_e} = \text{intercept}$

Table 1: Cassava Species of Varying Cyanide Concentrations

Variety	**Total Leaves Cyanide (µg/g)**	**Free Leaves Cyanide (µg/g)**	**Total Roots Cyanide (µg/g)**	**Free Roots Cyanide (µg/g)**	**Total Cyanide Content Ratio in Leaves and Roots**
Java Brown	490	33(6.7)	185	9(4.9)	2.6
Datu	541	19(3.5)	120	9(7.5)	4.5
Bogot	456	21(4.6)	n.d.	n.d.	n.d.
Lakan	189	13(6.9)	45	0.4(1.0)	4.2

n.d. = not detected; Source: (8).

III. RESULTS AND DISCUSSION

Model Calibration

From linear regression (Figure 2);

$$y = mx + c$$

$$\mathbf{y = 0.078x + 0.092}$$

By comparison with equation 2;

$$\frac{1}{\mu_{max}} = c = \text{intercept; i.e.}\ \mu_{max} = \frac{1}{c} = \frac{1}{0.092} = \mathbf{10.87/day}$$

and;

$$\frac{K_s}{\mu_{max}} = m = \text{slope; i.e.}\ K_s = \ \mu_{max} * m$$

$$\therefore K_s = 10.87 * 0.078 = \mathbf{0.87mgCOD/L}$$

Substituting μ_{max} and k_s into equation 1 gives;

$$r_A = \frac{ds}{dt} = \frac{Q}{V}(S_i - S_e) = \frac{\mu_{max} * S_e}{K_s + S_e} = \frac{\mathbf{10.87 * S_e}}{\mathbf{0.87 + S_e}}$$

From linear regression equation (Figure 3);

$$y = mI + c$$

$$\mathbf{y = 96909I + 6.267}$$

By comparison with equation 12 and substituting μ_{max} from experiment 1 gives;

$$\text{slope} = m = \frac{1}{\mu_{max} K_i};\ K_i = \frac{1}{m\mu_{max}} = \frac{1}{96909 * 21.74}$$

$$= \frac{1}{85308.993} = \mathbf{1.172} * \mathbf{10^{-5}}$$

Substituting k_s from experiment 1 into equation (12) gives;

$$\frac{xV}{Q(S_i - S_e)} = \frac{1 + \frac{K_s}{S_e} + \frac{I}{K_i}}{\mu_{max}} \equiv \frac{xV}{Q(S_i - S_e)} = \frac{1 + \frac{\mathbf{2.37}}{S_e} + \frac{I}{\mathbf{1.172 * 10^{-5}}}}{21.74}$$

Thus, the new kinetic model for cassava wastewater ABR is

$$\frac{V}{Q(S_i - S_e)} = 3{,}924.80 + 0.109S_e^{-1}$$

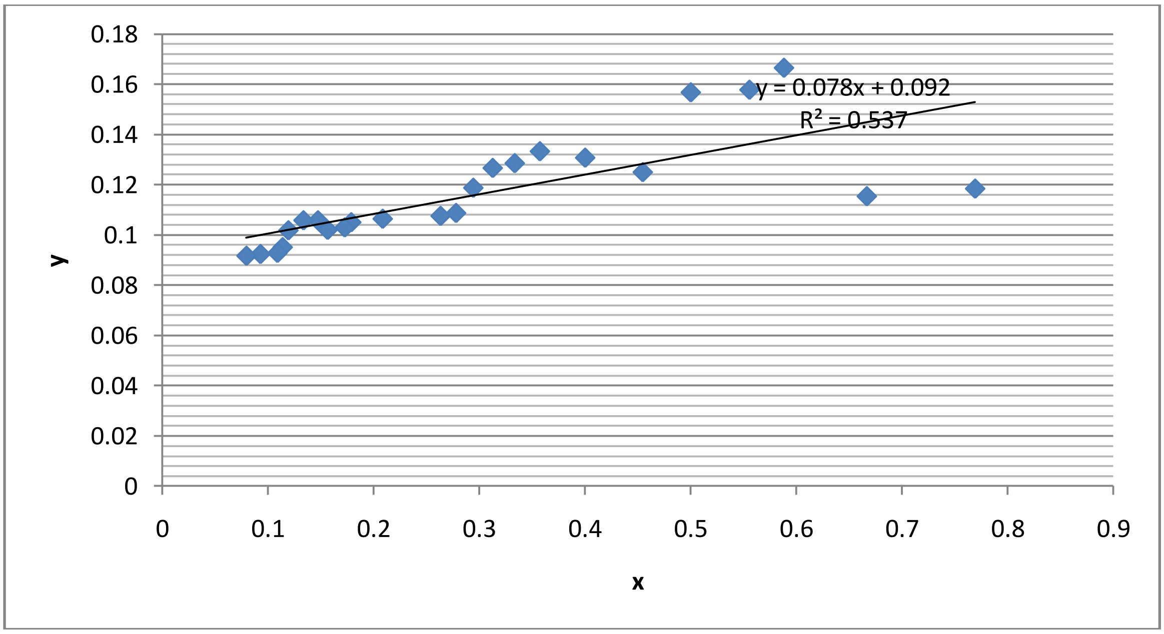

Figure 2: A Plot of $y = \frac{xV}{Q\,(S_i - S_e)}$ (L.d/mg) Versus $x = \frac{1}{S_e}$(L/ mg)

Table 2: Computations for Monod Model (Experiment 1)

S/N	$x_i = SV_i - SV_e$ (mg/ L.d)	$\frac{Q\,(S_i - S_e)}{V}$ (mg/ L.d)	$\frac{V}{Q\,(S_i - S_e)}$ (mg/ L.d)	$y = \frac{x.V}{Q\,(S_i - S_e)}$ (mg/ L.d)	S_e (mg/L	$x = \frac{1}{S_e}$ (L/ mg)
1	0.9	7.6	0.1315789	0.1184211	1.3	0.7692308
2	0.9	7.8	0.1282051	0.1153846	1.5	0.6666667
3	1.5	9	0.1111111	0.1666667	1.7	0.5882353
4	1.5	9.5	0.1052632	0.1578947	1.8	0.5555556
5	1.6	10.2	0.0980392	0.1568627	2	0.5
6	1.6	12.8	0.078125	0.125	2.2	0.4545455
7	1.7	13	0.0769231	0.1307692	2.5	0.4
8	1.8	13.5	0.0740741	0.1333333	2.8	0.3571429
9	1.8	14	0.0714286	0.1285714	3	0.3333333
10	1.9	15	0.0666667	0.1266667	3.2	0.3125
11	1.9	16	0.0625	0.11875	3.4	0.2941176
12	2	18.4	0.0543478	0.1086957	3.6	0.2777778
13	2	18.6	0.0537634	0.1075269	3.8	0.2631579
14	2	18.8	0.0531915	0.106383	4.8	0.2083333
15	2.1	20	0.05	0.105	5.6	0.1785714
16	2.1	20.4	0.0490196	0.1029412	5.8	0.1724138
17	2.1	20.6	0.0485437	0.1019417	6.4	0.15625
18	2.2	20.8	0.0480769	0.1057692	6.8	0.1470588
19	2.2	20.8	0.0480769	0.1057692	7.5	0.1333333
20	2.3	22.6	0.0442478	0.1017699	8.4	0.1190476
21	2.3	24.2	0.0413223	0.0950413	8.8	0.1136364
22	2.3	24.8	0.0403226	0.0927419	9.2	0.1086957
23	2.4	26	0.0384615	0.0923077	10.8	0.0925926
24	2.4	26.2	0.0381679	0.0916031	12.6	0.0793651

Table 3: Computations for Cyanide-Inhibited Monod Model (Experiment 2)

S/N	$\frac{Q(S_i - S_e)}{V}$ **(mg/ L.d)**	$\frac{V}{Q(S_i - S_e)}$ **(mg/ L.d)**	x_i	$y = \frac{x.V}{Q(S_i - S_e)}$ **(mg/ L.d)**	**I (mg/L)**
1	250	0.004	2.2	0.0088	8500
2	400	0.0025	1.4	0.0035	3600
3	500	0.002	0.6	0.0012	1250
4	782.17	0.0013	0.2	0.0002557	250
5	800	0.0013	0.6	0.00075	750
6	849.98	0.0012	1	0.0011765	1100
7	849.98	0.0012	1.4	0.0016471	1550
8	899.95	0.0011	1.7	0.001889	1800
9	900.01	0.0011	2	0.0022222	2100
10	900.02	0.0011	2.2	0.0024444	2350
11	899.99	0.0011	2.4	0.0026667	2550

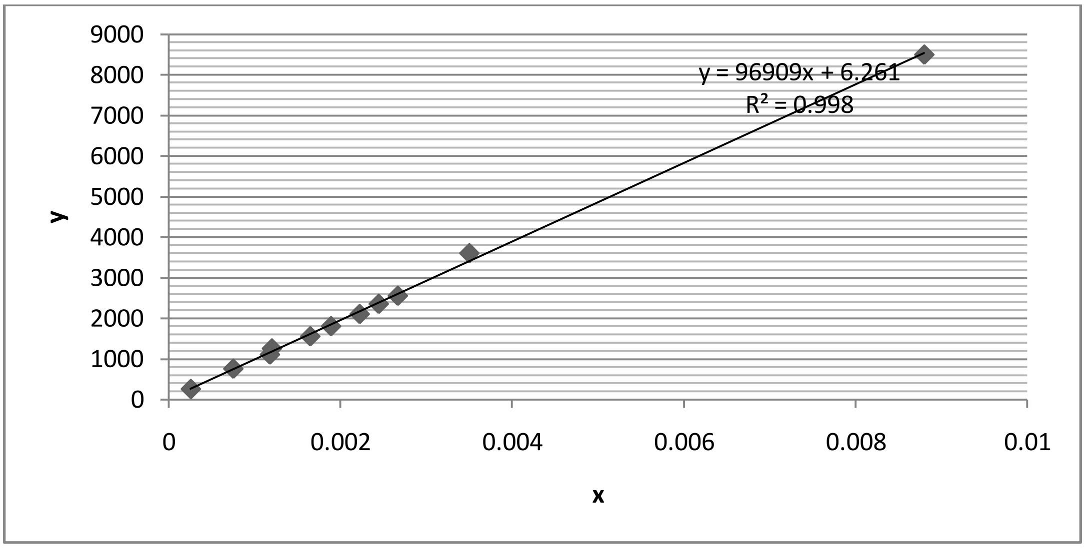

Figure 3: A Plot of $y = \frac{XV}{Q(S_i - S_e)}$ **(L.d/mg) Versus I(L/ mg) for Cyanide Inhibited Monod Model**

Model Verification

Table 4: Simulation for Monod Model

Observed y $\frac{x_i.V}{Q\ (S_i - S_e)}$ (mg/L.d)	Simulated y’ $\frac{x_i.V}{Q\ (S_i - S_e)}$ (mg/L.d)
0.1184211	0.11456
0.1153846	0.114208
0.1666667	0.137882
0.1578947	0.135333
0.1568627	0.131
0.125	0.127455
0.1307692	0.1232
0.1333333	0.119857
0.1285714	0.125214
0.1266667	0.116375
0.11875	0.114941
0.1086957	0.113667
0.1075269	0.112526
0.106383	0.10825
0.105	0.105929
0.1029412	0.105448
0.1019417	0.104188
0.1057692	0.103471
0.1057692	0.1024
0.1017699	0.101286
0.0950413	0.100864
0.0927419	0.100478
0.0923077	0.099222
0.0916031	0.09819

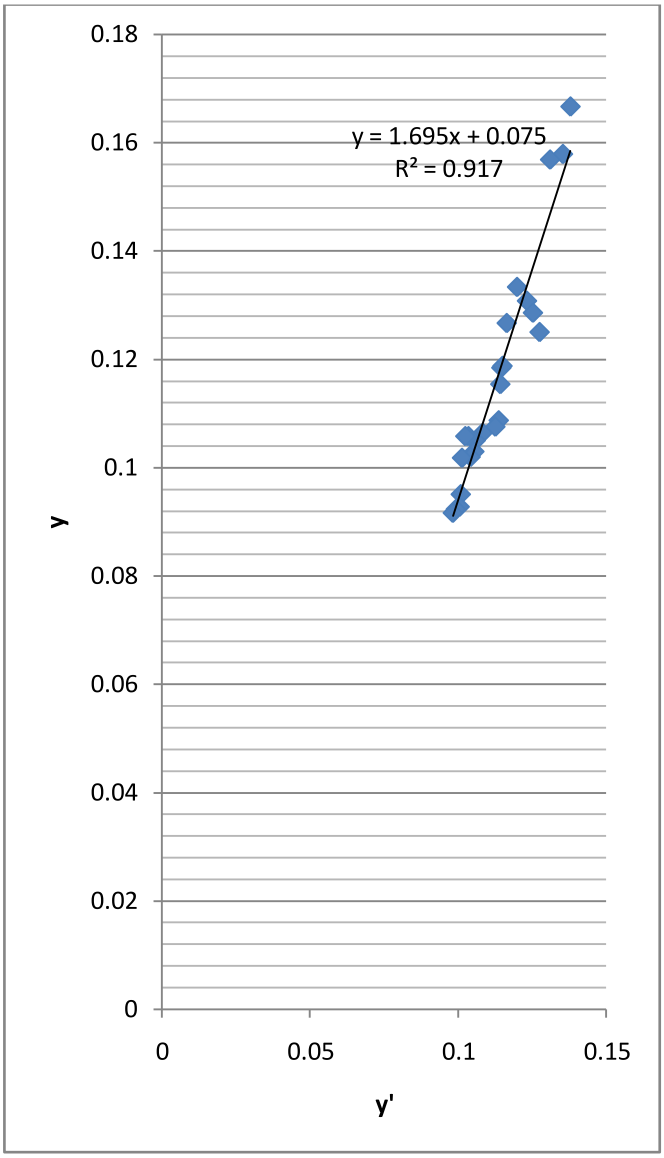

Figure 4: A Scatter plot of Observed y versus Simulated y’ for Monod Model

The coefficient of determination, R^2 for reactor 1 in Monod Model yielded 0.916, suggesting a satisfactory fitting of the developed model.

IV. CONCLUSIONS

For inhibited cassava wastewater treatment, the inhibition constant $\mathbf{k_i}$ was evaluated from reactor as $\mathbf{1.172 * 10^{-5} mgCyanide/L^{-1}}$. This clearly indicates that the extent of cyanide inhibition of cassava wastewater treatment is minimal. Despite the fact that the mathematical model proposed for design purposes was found to be suitable though some deviations between experimental and theoretical data were observed, there is an urgent need to generate models for larger scale reactors and to model reactor behaviour when hydrolysis is at the rate-limiting step. The improvement of the model, without it becoming too complicated and impracticable for practical applications, is a challenge to be confronted in future researches.

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