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Analysis of anaerobic degradation of vegetable wastes and biokinetic constants

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ABSTRACT

The process of anaerobic digestion employs specialized bacteria to break down organic waste, converting it into a stable semi-solid digestate. In the present study, kitchen refuse were collected and digested anaerobically in lab-scale for the analysis of various physico-chemical parameters and biokinetic coefficients. Initial pH and temperature values were 2.3 and 32°C respectively and the final values were 7.2 and 55°C respectively. There were significant percentage reduction in BOD, COD, total solids and volatile solids. In case of kinetic constants, values of the growth yield coefficient Y (mg/mg), the micororganisms decay coefficient k_d (d^{-1}), the substrate removal coefficient k(d^{-1}) and the Half velocity constant i.e., substrate concentration at half of the maximum growth rate k_s, (mg/l) were 0.06, 0.03, 0.004 and 29 respectively.

INTRODUCTION

Anaerobic digestion is a natural process, spontaneously taking place in natural surroundings, such as marshes, bogs, and paddies or in cesspits and dedicated digesters, used for the conversion of organic waste into useful products. The most promising solution for the treatment of kitchen wastes appears to be anaerobic digestion of the source-segregated fraction. Mixture of water and waste products is called wastewater[1]. Domestic sewage is composed of toilet wastewater (black water) and sullage (grey water) from the kitchen and bathroom[2]. Collection of domestic sewage and kitchen wastewater for the treatment began in late 1800's and in India in mid 1900's[3]. Anaerobic treatment is a biological process in which microorganisms convert organic compounds to methane, carbon dioxide, cellular materials and other organic compounds. The process can overcome disadvantages of aerobic and chemical treatment methods, because a high degree of waste stabilization can be accomplished with a relatively low production of biological solids, to a usable byproduct, methane gas is produced in the process[4]. Treatment of domestic wastes with appropriate methods produces useful products. For example, treatment with carbon monoxide and water produces fuel oil; treatment with hydrogen gives substituted natural gas. The digested sludge/digestate (removed at regular intervals) is used as a substitute for chemical fertilizer. An alternative for releasing these kitchen garbage and wastewater into any water sources is to use them as a soil amendment substance on agricultural lands. In the present study, vegetable wastes such as peels, shells, leaves and unused seeds were collected, segregated and grinded well for anaerobic degradation in lab-scale, using an aspirator jar. Various parameters such as pH, COD, temperature, total dissolved solids, volatile solids and the biokinetic

constants were determined.

MATERIALS AND METHODS

Activation of digester and preparation of grey water

The digester used was activated using cowdung slurry and jaggery mixture before the addition of actual kitchen refuse to be analyzed. Kitchen refuse was collected from the canteen of College of Engineering, Gunidy, Chennai-25. It was shredded, grinded well by adding ample amount of water and filtered well. An aspirator jar of 5-L capacity was used for the digestion process.

TABLE 1 : Physico-chemical parameters

Analysis	Methodology
pH, temperature,	APHA-AWWA WEF, 1998
Total solids	APHA-AWWA WEF, 1998
Volatile solids	APHA-AWWA WEF, 1998
COD	Reflux and titration against ferrous ammonium sulphate, APHA-AWWA WEF, 1998

Kinetics to biological treatment

Laboratory studies were undertaken to determine the biokinetic coefficients such as Substrate removal coefficient (k), Growth Yield Coefficient (Y), Decay Coefficient (k_d) and the Substrate Concentration at half of the Maximum Growth Rate (k_s) for anaerobic treatment.

To determine the biokinetic coefficients of wastewater / grey water used, the digester unit was operated at different MLSS concentrations and the temperature was kept constant. The values of the influent BOD_5 (S_0), effluent BOD_5 (S_e), MLSS in the reactor (X_0) and MLVSS in the reactor (X) were plotted against θc. The kinetic coefficients Y, k_d, k_s and k were obtained from the same parameters for different MLSS concentrations.

1. Cell yield

The rate of cell production is proportional to the rate of soluble substrate consumption[6].

$$dX/dt = Y\, dF/dt \qquad (2.1)$$

Where X= Concentration of microorganisms in the reactor, mg/l; t= Time of contact in the reactor, days; F= Soluble substrate, mg/l; Y= Growth yield coefficient, mg/mg

In most of biological reactor designs, concentration of volatile suspended solids in the reactor is taken as the concentration of microbial mass. This assumption is true only when the waste under treatment is soluble in nature. The carbon and energy source (F) are measured in terms of TOC or COD or ultimate BOD (BODu) or 5 day BOD (BOD5). In each case, different numerical value of 'Y' is obtained.

2. Specific growth rate

The microorganisms' growth rate per unit of microorganism is called specific growth rate.

It is given by,

$$\mu = \frac{dX/dt}{X} \qquad (2.2)$$

Where μ= Specific growth rate; X= concentration of microorganisms in the reactor, mg/l

From experimental studies, Monod[6] obserbed that the growth rate, dx/dt was a function not only of organism concentration but also of some limiting nutrient concentration. Monod's empirical function gives the relationship between μ and μ_{max}

$$\mu = \frac{\mu_{max}\,(S)}{k_s + S} \qquad (2.3)$$

Where k_s = Substrate concentration at the utilization rate of $\mu_{max}/2$, mass/unit volume (also called saturation concentration); S = Concentration of rate limiting nutrient or substrate, mg/l; μ_{max} = Maximum rate of specific substrate utilization per day (t^{-1})

3. Net solids production

Combining Eqn.2.2 and Eqn. 2.3,

$$dx/dt = \frac{\mu_{max}\,(S)\,(X)}{k_s + S} \qquad (2.4)$$

Expression for rate of growth must be corrected to account for the energy required for cell maintenance. It is assumed that the decrease in cell mass caused by them is proportional to the concentration of microorganisms present. So, the net growth rate is expressed as,

$$dx/dt = \mu x - k_d X \qquad (2.5)$$

$$dx/dt = \frac{\mu_{max}\,(S)(X)}{k_s + S} - K_d X \qquad (2.6)$$

Where k_d = Cell decay rate ($time^{-1}$) due to endogenous

respiration.

For a finite condition, substituting from Eqn.2.5 and Eqn.2.6,

$$\text{Net solids produced / time} = \Delta x/\Delta t = \frac{S_0 - S}{t} - k_d X \quad (2.7)$$

4. Mean cell residence time

It is the ratio of solids in any system to the solids leaving it per day. Ratio will be same for MLSS or MLVSS or active MLVSS. Hence θ_c tends itself better to process design and control.

$$\frac{1}{\theta_c} = \frac{dx/dt}{X} = \frac{Y(dF/dt)}{X} = \frac{\mu_{max}(S)}{k_s + S} \quad (2.8)$$

5. Food/Microorganism ratio

Another term related to specific utilization rate 'U' is Food-Microorganism ratio (F/M).

$$F/M = S_0/\theta_x \quad (2.9)$$

Where S_0 = Influent substrate concentration; X = Microorganism mass X; θ = Hydraulic detention time, d

Relation between U and F/M:

$$U = \frac{(F/M)E}{100} \quad (2.10)$$

Where E= process efficiency

$$E = \frac{S_0 - S}{S_0} \times 100 \quad (2.11)$$

Where S= effluent substrate concentration

6. Minimum mean cell residence time

The critical value of θ_c below which waste stabilization does not occur is minimum mean cell residence time ($\theta_c M$). It is the time at which the cells are washed out or wasted from the system faster than they can reproduce.

$$\frac{1}{\theta_c M} = \frac{Y\ KS_0}{k_s + S_0} - k_d \quad (2.12)$$

For this condition, influent waste concentration S_0 is equal to effluent waste concentration 'S'.

Since $S_0 > Ks$,

$$\frac{1}{\theta_c M} = Yk - k_d \quad (2.13)$$

To ensure adequate waste treatment, instead of designing with θ_c values equal to $\theta_c M$, they can be designed and operated with $\theta_c d$ values from 2 to 20 times $\theta_c M$. The ratio of $\theta_c d$ to $\theta_c M$ is called as Process Safety Factor.

$$SF = \frac{\theta_c d}{\theta_c M} \quad (2.14)$$

7. Approximation of Substrate Removal

From Eqn. 2.1, substrate removal rate is directly proportional to rate at which the new cells are produced. Substituting Eqn. 2.1 and Eqn. 2.4,

$$Y(dF/dt) = \frac{\mu_{max} S X}{k_s + S} \quad (2.15)$$

Or

$$dF/dt = \frac{\mu_{max} S X}{Y (ks + S)} \quad (2.16)$$

CONDITIONS OF APPROXIMATION

CASE-1:

When $S >> K_s$,

$$dF/dt \approx \frac{\mu_{max}}{Y} X \quad (2.17)$$

$$\text{Or } dF/dt \approx Kx \quad (2.18)$$

Where $K = \mu_{max}/Y$ = Maximum substrate utilization rate per unit time per unit mass of microorganism ($time^{-1}$)

CASE-2:

When $S << K_s$

$$dF/dt \approx \frac{\mu_{max}}{YK_s} X \quad (2.19)$$

$$\text{Or } dF/dt \approx KS\ X \quad (2.20)$$

Where, $K = \mu_{max}/Yks$

Advantage in using this approximation is that only one parameter K is required for design purposes, whereas in Monod case, 3 constants k_s, k_d and μ_{max} are required to be known.

RESULTS AND DISCUSSION

Parameters such as pH, temperature, COD, BOD, TDS, Volatile solids during anaerobic degradation of kitchen refuse were analyzed from 0^{th} day to 60^{th} day of digestion. Initial pH of the slurry was 2.3 and after 55 days of digestion it was at 7.2. Initial temperature was 32°C and at the end of digestion, it was 55°C.

Biokinetic coefficients

The study included determination of BOD_5, volatile

TABLE 2 : Initial and final values of Physico-chemical parameters

Parameters	Initial	Final	Percentage of removal
BOD	2780	445	84
COD	2650	408	85
TS	1500	375	71
TDS	550	175	74

suspended solids, alkalinity and volatile acids of influent and effluent samples and gas production for various MLSS concentrations maintained in the reactor.

pH

Initially the pH values of influent samples were measured for various MLSS concentrations maintained. The optimum pH maintained was 6.8 to 7.4. The pH values for different MLSS concentrations were at 3700 (7.0-7.6) and at 1280 (6.9-7.5).

Determinations of BOD reaction rate constant

Procedure for finding the BOD reaction rate constant is given in calculations. Figure 1 shows the reaction rate constants for wastes were found. Determination of BOD reaction rate constant is presented in calculations.

The values of reaction constants for wastes: (K) (day^{-1}) for influent is around 0.4336 to 0.4655. From the above K values, the detention time required to achieve a desired degree of BOD removal was determined.

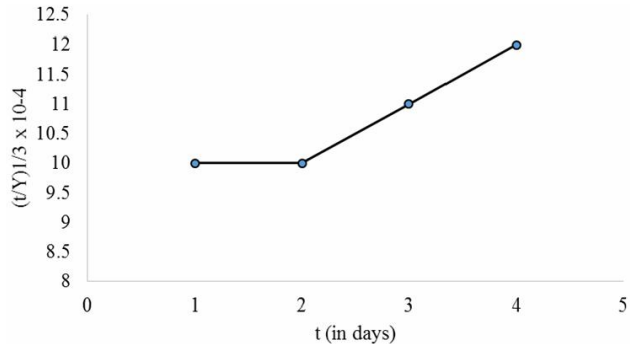

Figure 1 : $(t/Y)_{1/3}$ vs t for waste (influent)

BOD removal efficiency

BOD is the most important parameter in assessing the digester performance.

Reaction rate constant for the waste (influent) = 0.4336 day^{-1}

BOD of effluent after digestion varied from 640 to 650 mg/L. Average removal efficiency % = 84.3.

TABLE 3 : Determination of BOD reaction rate constant for grey water

S. No.	Days t	BOD (mg/L) Y	$(t/Y)^{1/3}$
1.	1	911	0.1055
2.	2	1808	0.1059
3.	3	1921	0.1185

TABLE 4 : Removal of BOD_5 under different mlss concentrations of grey water

S. No.	MLSS maintained in reactor(mg/L)	BOD_5 (mg/L) (Effluent) S_e	% removal
1.	3700	445	89.4
2.	2620	610	85.1
3.	1470	698	82.4
4.	1350	809	80.3

Here e=0.8948 F=0.000955

Relationship between % BOD removal efficiency and MLSS concentration is presented in Figure 2. From this, it was observed that BOD_5 removal increased with increasing MLSS concentration.

Gas production

The daily gas production, at steady state for different MLSS concentrations, room temperature, pressure under which gas was released, volume of methane for that particular pressure and temperature, volume of methane at standard temperature and pressure are presented in the table. The increase in the number of

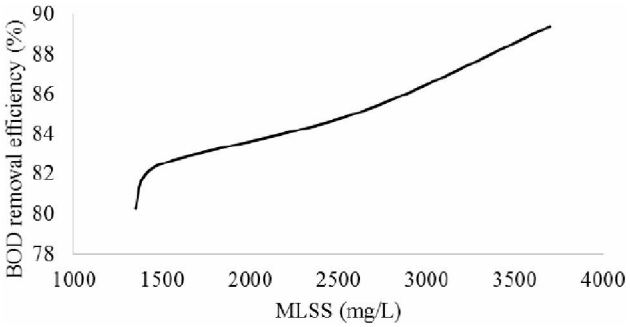

Figure 2 : MLSS vs BOD removal efficiency

TABLE 5 : Gas production Vs MLVSS of wastes

S. No.	MLVSS maintained mg/L X	Absolute pressure mm Hg P_1	Volume of methane C
1.	2760	770	0.1671
2.	2275	773	0.1561
3.	1940	772	0.1451
4.	1520	770	0.1281

TABLE 6 : F/M ratio and mean cell residence time for different MLVSS concentrations

S. No	MLVSS maintained mg/L X	Volume of methane C	Rate of substrate utilization kg/d dF/dT	Net growth of sludge kg/d dX/dT	Mean cell residence time (days) θ_c	F/M ratio d^{-1} U
1.	2760	0.1671	0.000855	0.000266	41.5	0.077
2.	2275	0.1561	0.000790	0.000242	37.6	0.086
3.	1940	0.1451	0.000739	0.000228	34	0.095
4.	1520	0.1281	0.000749	0.000269	22.6	0.123

microorganisms' leads to the destruction of large amount of solids, resulting in gas production.

Gas production from wastes

Methane (61-63%), Carbon dioxide (33-34%) and Hydrogen disulfide (4%).

Effect of mean cell residence time θ_c and food to microorganism ratio 'U'

Values of F/M ratio 'U' – mean cell residence time θ_c values of 1/U, $1/\theta_c$ rate of substrate utilization $\Delta F/\Delta T$, growth of microorganism $\Delta X/\Delta T$, for the wastes are shown in the table.

BOD removal efficiency increased with increase in mean cell residence time. % BOD removal efficiency for waste varied from 65 to 89% with a mean cell residence time ranging from 12-44 days. From the results, maintaining a mean cell residence time around 45 days, upto 90% BOD removal efficiency was achieved.

As the value of mean cell residence time increased, effluent soluble BOD_5 decreased. Minimum effluent BOD_5 values for the wastes were 250-350 mg/l.

Kinetic Coefficients of Sludge Growth

To determine kinetic coefficients of grey water growth, namely growth yield coefficient Y, and the decay coefficient k_d, a plot of $(\Delta X/\Delta T) / (\Delta F/\Delta T)$ was made from the TABLE 7. A straight line was obtained for the wastes as in Figure 3. Intercept of straight line gave 'Y' and the Slope gave 'k_d'.

The growth yield coefficient for the waste was around 0.06 gVSS/mg BOD_5.

The microorganism decay coefficient for the waste was $0.03day^{-1}$.

All the results were plotted for the line of best fit.

TABLE 7 : Values of dF/dT and dX/dT

S. No.	MLVSS maintained mg/L X	Rate of Substrate utilization Kg/d dF/dT	Net growth of Wastewater Kg/d dX/dT
1.	2780	0.000855	0.000266
2.	1940	0.000790	0.000242
3.	1060	0.000739	0.000228
4.	980	0.000749	0.000269

Substrate level coefficients

The substrate removal coefficients namely k_s and k for the wastes were determined by plotting 1/U Vs 1/Se as in Figure 4 and a line of fit was obtained. From the line the intercept 1/k and its slope k_s/k were determined. The values of 1/U and 1/Se were calculated from the values obtained from TABLE 4 and TABLE 6. Substrate removal coefficient for the wastes was found to be $0.004day^{-1}$.

The half velocities constant for the waste was found to be 29 mg/L BOD_5. The values of Y, k_d, k and k_s are

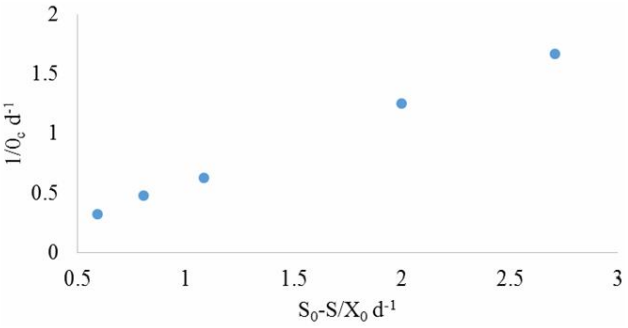

Figure 3 : Plot to determine Y and K_d

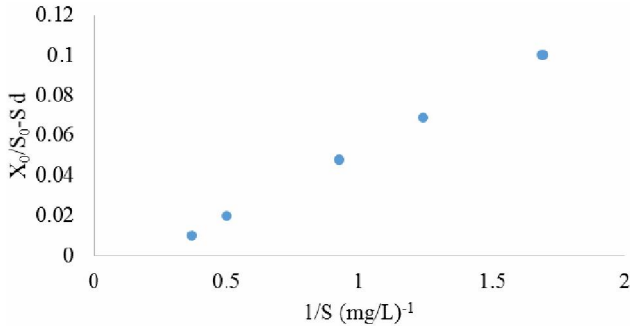

Figure 4 : Plot to determine K_s and k

TABLE 8 : Values of biokinetic coefficients

S. No.	Biokinetic coefficients	Values
1.	Y mgVSS/mg BOD_5	0.06
2.	k_d day^{-1}	0.03
3.	k day^{-1}	0.004
4.	k_s mg/l BOD_5	29

shown in TABLE 8.

Calculation of coefficients

Calculation of BOD reaction rate constant for the waste - influent (grey water)(influent):

TABLE 4.3.

BOD reaction rate constant

k (base 10) = 2.61 X b/a

k (base e) + 2.3 X k (base 10)

From the fig 1, $a=9.8 \times 10^{-2}$, $b=0.76 \times 10^{-2}$

k (base 10) $=2.61 \times (0.76 \times 10^{-2} / 9.8 \times 10^{-2})$

$= 0.2024\ day^{-1}$

$k(base\ e) = 2.3 \times 0.2024 = 0.4655 day^{-1}$

Calculation for determination of first stage ultimate BOD of the waste:

TABLE 4.4

$$\text{First stage Ultimate BOD} = \frac{(BOD_5 \text{ X Quantity of waste added daily})}{(1-e^{-Kt})}$$

From the TABLE 4.7 the value of BOD_5 is taken. The value of t is known as 5 days.

Reaction rate constant for waste (k) = 0.4336 day^{-1}

BOD_5 = 4231 mg/l, $k=0.4336 day^{-1}$, t = 5 days,

Quantity of waste added = 0.2 l/day

$$\text{First stage Ultimate BOD} = \frac{4231 \times 0.200 \times 10^{-6}}{(1-e^{-0.4336 \times 5})}$$

$= 9.55 \times 10^{-4} Kg/d$

Calculation for determination of methane at standard temperature and pressure:

TABLE 5.

Volume of methane at standard temperature and pressure (at 0°C and 760 mm of mercury)

$C= [0.37 \times (P_1 - P_w)\ C_1]/[273.1 + T_1]$

From the TABLE 4.9 the values of P_1, P_w, T_1 and C_1 corresponding to MLVSS concentration of 3670 mg/L are taken.

P_1 = 773 mm Hg, P_w= 31.01mm Hg. At 30°C, C_1= 0.1853 L

$C= [0.37 (773 - 31.01)]/[273.1 + 30] = 0.1671L$

Calculation of dF/dT, dX/dT, $_C$ and U.

$C = 350 [eF - 1.42 (dX/dT)]$

From TABLE 6 eF and C values are taken.

$eF = 8.27 \times 10^{-4}$ kg/d, C=0.1671 L.

$$dX/dT = \frac{[0.1671 - (350 \times 8.55 \times 10^{-4})]}{(350 \times 1.42)}$$

$=2.66 \times 10^{-4} kg/d$

C=MLVSS / (dX/dT)

The values of MLVSS and dX/dT are taken from the TABLE 6.

MLVSS = 2760 mg/l dX/dT = 2.66×10^{-4} Kg/d

$$C = \frac{[4 \times 2760 \times 10^{-6}]}{2.66 \times 10^{-4}} = 41.5 \text{ days.}$$

≈ 42days.

U = (dF/dT) / (MLVSS)

Values of dF/dT and MLVSS are from TABLE.6.

$dF/dT = 8.55 \times 10^{-4} kg/d$

$$U = \frac{8.55 \times 10^{-4}}{2760 \times 4 \times 10^{-6}} = 0.077\ day^{-1}$$

Though the anaerobic treatment of waste is a slow process, different investigators[7-9], used several anaerobic digesters produced to establishing the process as an effective method of pollution control and by product recovery in the form of biogas which could be used as an energy source. A decrease in COD and BOD removal efficiency was observed with decreasing temperature as found in studies by Bodik *et al.*,[10], Varadharajan and Viraraghavan[11]. Balashanmugam[12] studied on the evaluation of biokinetic coefficients for tannery wastes under anaerobic conditions and found its treatability. Also the studies included the evaluation of growth yield coefficient Y (mg/mg), the micororganisms decay coefficient k_d (d^{-1}), the substrate removal coefficient k(d^{-1}) and the Half velocity constant i.e., substrate concentration at half of the maximum growth rate k_s, (mg/l). Likewise, in the present study, the values obtained for the aforementioned kinetics were 0.06, 0.03, 0.004 and 29 respectively. Kitchen waste can be used as a source of energy for the production of biogas in anaerobic reactors. The optimum temperature and pH for the maximum biogas production was between 29°C -33°C and the pH was between 7.2-7.5. The effluent of the reactor was clear and odourless; the present study indicates that kitchen waste can be

digested anaerobically with advantages like odourless effluent, utilization of the digestate as humus, protection of environment and production of biogas etc.

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