Treatment Of Composite Tan Liquor

by
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Abstract

Detailed laboratory studies were carried out to determine the optimum conditions of operation under which anaerobic digestion of tannery effluent could be done. The studies showed that an optimum BOD influent load of 0.3 Kg BOD/m^3/day with 3 days retention time could be adopted to yield about 97.1 percent BOD reduction. The role of magnesium carbonate during anaerobic digestion has been studied for methane generation.

Introduction

Tanning of animal hides to convert them into leather is an important industrial activity in our country. But the pollution from tanneries has a long-term negative impact on the environmental resources. The liquid waste from tanneries is a dangerous pollutant because it contains organic matter and inorganic pollutants in the solution, in suspension as well as in colloidal dispersion. Hence, there is a need to remove these pollutants before they are released to render them harmless. In the past ten years, a number of different anaerobic processes have been developed for the treatment of industrial wastes.

Anaerobic digestion is one of the oldest processes used for the stabilization of sludges. It involves the decomposition of organic and inorganic matter in the absence of molecular oxygen. In this process, the organic matter in the mixture of primary settled and biological sludges is converted biologically, under anaerobic conditions, to a variety of end products including methane and carbondioxide. The process is carried out in an airtight reactor. Sludge, introduced continuously or intermittently, is retained in the reactor for varying periods of time. The stabilized sludge, withdrawn continuously or intermittently from the reactor, is reduced in organic and pathogen content and is non-putrescible.

Anaerobic biotechnology, with recent development of innovative high efficiency reactors, categorized as immobilized cell reactors, has now been recognized as an appropriate method for rapid treatment of low and medium strength industrial and domestic waste waters with the advantage of energy recovery.[1] Many alternatives have been proposed for immobilized cell reactor which have different modes of sludge retention.[2] The upflow anaerobic sludge blanket reactor, developed during the seventies, has a unique feature of sludge accumulation without supporting media.[3] Studies on the properties of chromium sludge from chrome tan liquor and related sludge volume, sludge settling rate, surface loading rate etc. have been reported.[4] Experiments on the treatment of tannery and electroplating effluents by using lime, have been studied.[5] Experiments conducted on a laboratory scale completely mixed continuous flow activated sludge system to treat settled chrome tannery waste water[6] and observed that the BOD and COD removal ranged from 84 to 96%. Studies on the activated sludge treatment of vegetable tanning waste admixtured with 10, 25 and 50 settled sanitary sewage were reported[7] which showed BOD removal from 87 to 96%.

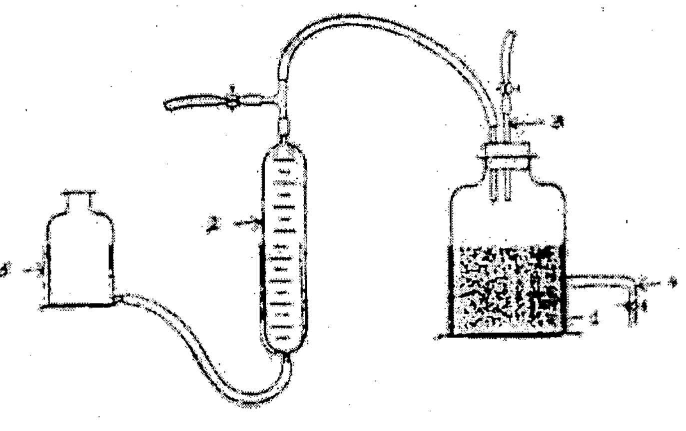
The design of any biological wastewater treatment system must depend on the proper relationships between the organic matter in the wastes and the microorganisms which can metabolize the organic matter, the generation time of the microorganisms, the temperature of the treatment system, pH, the nutrient elements in the waste, the wastewater retention period in the system and other environmental factors. Bio-kinetics is based on the actual environment and the biological metabolic activities in the system. Hence, the design of biological wastewater treatment based on biokinetics will have a better control over environment and biological community in the system. For a specific waste, a biological community and proper set of environmental conditions, the biokinetic coefficients are fixed. Hence, design of biological treatment system based on the bio-kinetic parameters will be more rational than many of the modern designs.

Several quantitative mathematical models have been developed over the period to describe the kinetics of tannery waste treatment processes. However, successful application of these models to design is contingent on the use of a number of kinetic parameters, which in turn, depend on the nature of the wastewater. The values of biokinetic parameters for tannery wastewaters are not widely available for the biological treatment systems. Hence there is a need to evaluate these parameters for anaerobic systems. To accomplish is objective, experiments were conducted using chrome inning wastewaters and vegetable tanning wastewaters.

. comprehensive review of the methods for handling tan-ery effluent showed that the effluents from such plants are enerally high in both dissolved organic and inorganic iaterials, posing particular treatment difficulties. Although number of treatment procedures are being used or have een proposed, there is no widespread agreement on the iost suitable methods. Also information on the design of eatment plants based on biokinetic parameters for tannery ffluent is very limited, the prime objective of the present udy is to determine the biokinetic parameters which nable us to describe the metabolic performance of the iicroorganisms when fed with the substrate and other com-onents in the tannery treatment processes.

EXPERIMENTAL

'he experiment was designed and operated on the principle f an anaerobic activated sludge process to evaluate the bio-inetic parameters, which could be used in the rational esign and operation of large-scale anaerobic installations. 'he reactor was a wide mouthed pyrex glass bottle of 5 litre apacity. The reactor has provision for adding wastes, for emoving treated effluent and settled solids and for gas ansfer. The gas collection apparatus consisted of a glass ottle of 2 litre capacity and another bottle of 1 litre capac-y for the water displaced from the gas bottle. Care was iken to remove the air from the reactor as well as from the as collection bottle at the beginning of the experiment and ie entire set up was checked for gas leaks. The digestion



/as conducted at room temperature as shown below.
. Digested Sludge, 2. Gas Collection tube, 3. Feed tube
. Withdrawal tube, 5. Levelling bottle

ixperiments were conducted under anaerobic conditions for ight different types of wastes such as settled chrome tan-ning waste, settled vegetable tanning waste, in admixture with 10%, 25% and 50% settled cowdung seed, vegetable tanning waste in admixture with 10%, 25% and 50% settled cow dung seed. The samples of effluents drawn at various stages were analysed for pH, influent BOD (So), effluent BOD (Se), mixed liquor volatile suspended solids (MLVSS) before sludge wasting, initial MLVSS and the net growth rate of microorganisms $\Delta X/\Delta t$ which was obtained from the difference of MLVSS before sludge wasting and initial MLVSS values. The pH was maintained within the optimum range of 6.8 to 7.4 which is favorable for anaerobic bacterial growth. Calculated amount of diammonium phosphate and urea were added to the feed solution as and when required in order to maintain the BOD : N : P ratio at 100 : 2.5 : 0.5 which is effective for anaerobic digestion. In anaerobic digestion, biomass is formed having a molecular formula $C_5H_7O_2N$. Cell synthesis requires Nitrogen (amino acid formation) for which Nitrogen (in the form of Urea) rich nutrient is supplied. During cell synthesis, energy in the form of ATP is released for which phosphorus acts sink. The contents in the reactor were continuously mixed with the help of magnetic stirrer. The tannery wastewater was filled upto a volume of 2 litres in the anaerobic reactor and the mixture was mixed daily at frequent intervals. Neither waste feeding nor withdrawal of mixed liquor was done until gas production was noticed. Regular wasting and feeding were continued until a steady state condition was reached. The daily BOD loading rate was kept constant at around 0.3 kg/m3/day. The daily gas production, the influent and effluent Biochemical Oxygen Demand (BOD) which is defined as the oxygen required for the biological decomposition of organic matter at 20°C for period of 5 days, Mixed Liquor Volatile Suspended Solids (MLVSS) which indicates the concentration of microorganisms in the reactor, pH, volatile acids and alkalinity were recorded at the steady state condition at which the sludge growth and gas production remained constant. The mean cell residence time was varied by operating the reactor at several MLVSS concentrations.

RESULT AND DISCUSSION

The general characteristic properties of composite chrome tan liquor and composite vegetable tan liquor are shown in table I. It was observed that both liquors are alkaline with a high solids content. Both have a high BOD content indicating that they are amenable for anaerobic treatment. Table II and III indicate the results for chrome tanning effluent, vegetable tanning effluent and their admixture with 10%, 25% and 50% of cowdung seed. It has been observed that a maximum of 97.1% BOD was removed in the present study.

For each waste, studies were carried out at different mean

TABLE I
Characteristics of Settled Composite Chrome Tanning and Vegetable Tanning Waste

Parameter	Composite chrome tan liquor	Composite vegetable tan liquor
pH	8.2	8.5
Alkalinity	1960	4200
Total solids	16850	31600
Total dissolved solids	15900	30790
Total suspended solids	950	810
BOD	1460	3150
COD	2920	6400
Chlorides	3180	2940
Total nitrogen	580	1060
Phosphate	6.8	3
Sulphate	1070	1100
Sulphide	30	10
Chromium	8.4	-

All values except pH are expressed in mg/L.

TABLE II
Anaerobic Digestion of Composite Chrome Tanning Waste

S. No.	Parameter	Chrome tanning waste	90% chrome tanning waste + 10% cow dung	75% chrome tanning waste + 25% cow dung	50% chrome tanning waste + 50% cow dung
1	MLVSS before sludge wasting (mg/L)	4260	4100	4320	4390
2	Initial MLVSS (mg/L)	3920	3800	4000	4080
3	Net growth rate of micro-organisms $\Delta X/\Delta t$ (mg/lt/day)	340	300	320	310
4	Influent BOD, So (mg/L)	1160	1050	1200	980
5	Effluent BOD, Se (mg/L)	42	40	54	28
6	BOD removal (%)	96.4	96.2	95.5	97.1

TABLE III
Anaerobic Digestion of Composite Vegetable Tanning Waste

S. No.	Parameter	Vegetable tanning waste	90% vegetable tanning waste +10% cow dung	75% vegetable tanning waste + 25% cow dung	50% vegetable tanning waste + 50% cow dung
1	MLVSS before sludge wasting (mg/L)	4290	4200	4400	4160
2	Initial MLVSS (mg/L)	3910	3980	4160	3890
3	Net growth rate of micro-organisms $\Delta X/\Delta t$ (mg/lt/day)	380	220	240	270
4	Influent BOD, So (mg/L)	2800	2650	2400	1400
5	Effluent BOD, Se (mg/L)	150	170	80	56
6	BOD removal (%)	94.6	93.6	96.7	96.0

residence times by varying the MLVSS concentrations he reactor. The observed experimental data on the influ- and effluent BOD (So and Se), MLVSS in the reactor, growth rate of microorganisms were analysed to obtain strate removal rate constant (k), half velocity coefficient), endogenous decay coefficient (Kd), yield coefficient and maximum specific growth rate of microorganisms n) for both chrome and vegetable tanning wastes.

modified Monod's equation expressing the biological wth and substrate utilization rates has been used to esti- te the bio-kinetic coefficients for the anaerobic process. both batch and continuous culture systems, the rate of wth of bacterial cells can be defined as

$$r_g = \mu X$$

ere r_g = rate of bacterial growth, mass/unit volume.time.
μ = specific growth rate, time^{-1}
X = concentration of microorganism, mass/unit volume

ce $dX/dt = r_g$,

$$\frac{dX}{dt} = \mu X$$

nod has proposed an expression for μ in terms of limit- substrate concentration as

$$\mu = \mu_m \frac{Se}{Ks+Se}$$

ere μ_m = maximum specific growth rate, time^{-1}
Se = Concentration of growth limiting substrate in solution, mass / unit volume
Ks = half-velocity constant, mass/unit volume

bacterial growth rate, r_g thus becomes

$$r_g = \frac{\mu_m X\, Se}{Ks + Se}$$

both batch and continuous culture systems, a portion of substrate is converted into new cells and a portion is oxi- ed to inorganic and organic end products. Since the antity of new cells produced has been observed to be producible for a given substrate, the following relation- p has been developed between the rate of substrate uti- ation and the rate of growth

$$r_g = - y r_{su}$$

here y = maximum yield coefficient
r_{su} = substrate utilization rate, mass/unit volume time

or

$$r_{su} = -\frac{r_g}{y}$$

$$\therefore \quad r_{su} = -\frac{\mu_m X\, Se}{YKs + Se}$$

or $$r_{su} = -\frac{k\, X\, Se}{Ks + Se} \quad (\text{since } \mu_m / Y = k)$$

But r_{su} is related to the influent and effluent substrate concentration as

$$r_{su} = \frac{So - Se}{\theta}$$

therefore, $$r_{su} = -\frac{k\, X\, Se}{Ks + Se} = -\frac{So - Se}{\theta}$$

Dividing by X yields

$$\frac{kSe}{Ks + Se} = -\frac{So - Se}{X\theta}$$

The linearized form of the equation obtained by taking its inverse is

$$\frac{X\theta}{So - Se} = \left[\frac{Ks}{k}\right]\left[\frac{1}{Se}\right] + \left[\frac{1}{k}\right]$$

The endogeneous decay term is given by:

$$r_d = - KdX$$

The net bacterial growth is:

$$r_g' = r_{su} + r_d$$

or $$r_g' = \frac{\mu_m\, SeX}{Ks + Se}\ KdX$$

An unsteady state mass balance for the mass of microorganisms is:

$$\frac{dX}{dt} V_r = Qxo - QX - v_r \cdot r_g'$$

substituting the value of r_g',

$$\frac{dX}{dt} V_r = Qxo - QX + V_r \left[\frac{\mu_m XSe}{Ks + Se} - KdX\right]$$

It is assumed that the concentration of microorganisms in the influent can be neglected and that steady state conditions prevail ($dX/dt = 0$), therefore

$$\frac{Q}{V_r} = \frac{1}{\theta} = \frac{\mu_m Se}{Ks + Se} - Kd$$

The term $1/\theta$ corresponds to the net specific growth rate is also related to $1/\theta_c$:

$$\therefore \frac{1}{\theta_c} = \frac{Q}{V_r} = \frac{\mu_m Se}{Ks + Se} - Kd$$

or $$\frac{1}{\theta_c} = \frac{\mu_m Se}{Ks + Se} - Kd$$

or $$\frac{1}{\theta_c} = YU - Kd$$

In the present study, the modified Monod's equations were used to develop biokinetic parameters

$$\frac{X\theta}{So - Se} = \frac{Ks}{k} \times \frac{1}{Se} + \frac{1}{k} \qquad \ldots (1)$$

and $$\frac{1}{\theta_c} = YU - Kd \qquad \ldots (2)$$

The optimum organic load required for the maximum removal of BOD and COD of the effluent has been determined and it was observed that the BOD and COD removal reached a maximum of 97% and during the digestion the mean cell residence time θ_c was varied by operating the reactor at varying food to microorganism ratio (U) by varying the MLVSS concentration. Results indicated that the BOD and COD removal efficiency decreases with decrease in mean cell residence time qc and decrease with increase in food to microorganism ratio (U) which is defined as the relationship between the quantity of BOD to be treated each day and the mass of sludge contained in the reactor.

The values of the food to micro organism ratios (1/U) were plotted against the reciprocal values of the effluent BOD (1/Se). The substrate removal kinetics, such as the substrate removal rate constant (k) and half velocity constant (Ks) could be evaluated from the intercept and slope of the straight line. The values of the reciprocal of the mean cell residence time, qc were plotted against the food to microorganism ratios (U). The yield coefficient (Y) was determined from the slope of the straight line and the endogenous decay coefficient was obtained from the intercept. The biokinetic coefficients were evaluated using modified Monod's equations and were given in Table IV. The rate of substrate utilization was found to be higher at the early stages of digestion throughout the process and the reason for the initial high substrate utilization rate may be due to adsorption of soluble substrates by the bacteria and extracellular slime. The subsequent drop in rate following the initial high rate may be interpreted as saturation of adsorption sites. The subsequent rate increase may be attributed to continued increase in metabolic activities caused by cell growth. Adsorption and metabolism occur concurrently.

The value of the substrate removal rate indicates the hydraulic retention period actually required for complete waste stabilization to occur. The half velocity constant, Ks which signifies the substrate concentration at one half of the maximum specific utilization rate was found to be significant. The decay coefficient, Kd was found to be slightly higher which might be due to the substantial decay of cells because of endogenous respiration. The yield coefficient value indicated that a relatively large proportion of biodegradable organic waste has been synthesized into new cells. Factors which contribute to the decrease in observed yield as mean cell residence changes are maintenance energy, cell death and lysis, cryptic growth, formation of extracellular polymers, predator activities and predominance of different microbial species with different energetic characteristics. The yield coefficient obtained in the present inves-

TABLE IV
Biokinetic Coefficients

S. No.	Type of waste	k(day^{-1})	Ks(mg/L)	Kd(day^{-1})	Y	μ_m(day^{-1})
1	Chrome tanning waste	1.20	580	0.068	0.682	0.818
2	90% chrome tanning waste + 10% cowdung	1.88	720	0.062	0.514	0.966
3	75% chrome tanning waste + 25% cowdung	2.0	530	0.070	0.620	1.240
4	50% chrome tanning waste + 50% cowdung	2.12	400	0.076	0.740	1.569
5	Vegetable tanning waste	1.14	640	0.088	0.588	0.670
6	90% vegetable tanning waste + 10% cowdung	0.86	390	0.066	0.626	0.540
7	75% vegetable tanning waste + 25% cowdung	0.66	280	0.080	0.734	0.484
8	50% vegetable tanning waste + 50% cowdung	0.50	240	0.092	0.594	0.297

gation was found to be higher than the value reported in the literature which might be attributed to the higher concentration of hydrolysable carbohydrates in the effluent.

Development of Mathematical Model

While many formulae can be used to ascertain the relationships among more than two variables, the most frequently used method is that of linear equations. The multiple linear regression takes the following form,

$$Y = a + b_1X_1 + b_2X_2 + b_3X_3 + ... + b_xX_x \quad ...(3)$$

In the present investigation, the multiple linear regression technique has been used to predict the BOD removal efficiency using the biokinetic parameters.

If X_1 and X_2 are substituted with biokinetic constants, then,

$$X_1 = \frac{k}{Ks} \times \frac{V}{Q} \times X \quad ...(4)$$

and

$$X_2 = \frac{BOD_{influent}}{BOD_{effluent}} \quad ...(5)$$

Where,

k = Substrate removal rate constant, day^{-1}
Ks = Half-velocity constant, mg/L
V/Q = Hydraulic retention period, day
X = Mixed Liquor volatile suspended solids, mg/L

Substituting X_1 and X_2 in equation 3, the Y, BOD removal efficiency, takes the form:

$$Y = a + b_1 \frac{k}{Ks} \times \frac{V}{Q} \times X + b_2 \times \frac{BOD_{influent}}{BOD_{effluent}} \quad ...(6)$$

The constants a, b_1, and b_2 are determined by the methods of least squares by solving the systems of equations. The values of influent BOD, effluent BOD, k/Ks, V/Q and X are shown in Table V.

$$\Sigma Y = na + b_1\Sigma X_1 + b_2\Sigma X_2$$
$$\Sigma X_1Y = a\Sigma X_1 + b_1\Sigma X_1^2 + b_2\Sigma X_1X_2$$
$$\Sigma X_2Y = a\Sigma X_2 + b_2\Sigma X_1X_2 + b_2\Sigma X_2^2$$

The constants a, b_1, and b_2 are evaluated by taking data of the present study under varying organic loads. The data used for the estimation of the multiple regression coefficients are present in Table VI. The regression coefficients a, b_1, and b_2 evaluated are given below.

a = 91.27
$b_1 = 6.126 \times 10^{-4}$
$b_2 = 0.273$

TABLE V
Substituents of the Mathematical Model

S. No.	Type of waste	Influent BOD (mg/L)	Effluent BOD (mg/L)	k/Ks	V/Q (day)	X (mg/L)
1	Chrome tanning waste	1160	42	0.0020	3.0	4090
2	90% chrome tanning waste + 10% cowdung	1050	40	0.0026	3.0	3950
3	75% chrome tanning waste + 25% cowdung	1200	54	0.0038	3.2	4160
4	50% chrome tanning waste + 50% cowdung	980	28	0.0053	3.2	4235
5	Vegetable tanning waste	2800	150	0.0018	3.6	4100
6	90% vegetable tanning waste + 10% cowdung	2650	170	0.0022	3.6	4090
7	75% vegetable tanning waste + 25% cowdung	2400	80	0.0024	3.6	4280
8	50% vegetable tanning waste + 50% cowdung	1400	56	0.0021	3.8	4025

TABLE VI
Application of Data in the Mathematical Model

X_1	X_2	Y_{expt}	X_1^2	X_2^2	X_1Y	X_2Y	X_1X_2
24.54	27.62	96.4	602.21	762.86	2365.66	2662.57	677.80
30.81	26.25	96.2	949.26	689.06	2963.92	2525.25	808.76
50.58	22.22	95.5	2558.33	493.73	4830.39	2122.01	1123.90
71.82	35.00	97.1	5158.11	1225.00	6973.72	3398.50	2513.70
26.57	18.67	94.6	705.96	348.57	2513.52	1766.18	496.06
32.39	15.59	93.6	1049.11	243.05	3031.70	1459.22	504.96
36.98	30.00	96.7	1367.52	900.00	3575.97	2901.00	1109.40
32.12	25.00	96.0	1031.69	625.00	3083.52	2400.00	803.00

TABLE VII
Results of the Mathematical Model

X_1	X_2	Y_{cal}	Y_{expt}	Deviation
24.54	27.62	98.8	96.4	2.4
30.81	26.25	98.4	96.2	2.2
50.58	22.22	97.3	95.5	1.8
71.82	35.00	100.00	97.1	2.9
26.57	18.67	96.3	94.6	1.7
32.39	15.59	95.5	93.6	1.9
36.98	30.00	99.4	96.7	2.7
32.12	25.00	98.11	96.0	2.1

Hence, the proposed equation for the prediction of BOD removal efficiency is:

$$Y_{cal} = 91.27 + 6.126 \times 10^{-4} + \frac{k}{Ks} \times \frac{V}{Q} \times X + 0.273 \times \frac{BOD_{influent}}{BOD_{effluent}} \quad (7)$$

The analysis of the data on anaerobic digestion of tannery effluent according to equation 7 is shown in Table VII which gave a maximum deviation of ± 2.7. Thus the results of the present study on the prediction of BOD removal efficiency using multiple linear regression technique has successfully arrived at a model for anaerobic digestion process of tannery effluent.

Conclusions

The results from this study lead me to conclude that:

1. The composite waste is highly suitable for stabilization of anaerobic digestion.
2. Cowdung can be employed as an effective seed in starting the process.
3. The optimum BOD load was found to 0.3 kg BOD/m^3/day.
4. The sludge with rich nutrients obtained in the present study has the potential to be used as fertilizer.

Definition of Symbols

K = Substrate removal rate constant, $days^{-1}$, Ks = Half velocity constant, mg/L, Y = yield coefficient, Kd = Decay coefficient, $days^{-1}$, (μ_{max}) = Maximum specific growth rate of microorganisms, $days^{-1}$, θ = Hydraulic retention time/day, θ_c = Mean cell residence time, mg/L/d, So = Influent BOD, mg/L, Se = Effluent BOD, mg/L, X = Concentration of microorganisms in reactor, mg/L.

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