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Anaerobic Digestion of Distillery Spent Wash

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ABSTRACT

The present investigation deals with the anaerobic stabilization of distillery spent wash using cow dung as the seed material with varying organic loads. The optimum organic load required for maximum BOD reduction was found to be 0.7 kg BOD/m^3/day. The biokinetic coefficients were determined for the data using modified Monod's equation. The anaerobic digestion of distillery effluent followed a first order kinetics since these are reactions that proceed at a rate directly proportional to the concentration of one reactant that is organic substrate.

Keywords: *Anaerobic digestion, distillery spent wash, Organic load, Biokinetic coefficients*

1. INTRODUCTION

In India, production of alcohol by fermentation from sugarcane molasses has been used for the disposal problem of molasses. The raw material for production of ethyl alcohol is 'molasses' which is the byproduct of the sugarcane industry. In nearly all distilleries, the bath fermentation mode is adopted with about 12–15 liters of spent wash generated per liter of alcohol produced. The untreated distillery effluent (UDE) is a high strength wastewater and can severely affect the environment if not properly treated. The UDE from the distilleries is characterized with a very high organic load with BOD and COD levels in the range of 35000–60000 mg/l and 60000–120000 mg/l, respectively. A routine conventional treatment system reduces the high organic load utilizing anaerobic biological digestion (biomethanation). Distilleries characteristically utilize biomethanation to generate methane (as fuel to compensate for energy needs). This is followed by conventional secondary treatment requiring continued aeration, which is an energy intensive process.

The distillery contains heavily polluting and noxious contaminants in the form liquid, solid and gas. It is expected to generate about 6-15 m^3 of waste water (generally called spent wash) per m^3 of alcohol produced and a large amount of press mud. The COD and BOD values of spent wash appear to be (60-140 kg/ m^3), and BOD (45-70 kg/ m^3),respectively with high inorganic load, low pH and dark brown color. The advantage of the treatment lies in the recovery of energy by biomethanation.

Several methods of waste treatment are in use; but none of them are able to meet the effluent quality standards. The typical odour emanating from distilleries is a major nuisance. The color of the spent wash interferes with its oxygenation and self-purification. The treatment of distillery wastes is a priority area for environmental sustenance and its quality. Recent years have seen many techniques being developed to treat spent wash. Therefore, it is necessary to upgrade the knowledge base of the professionals and functionaries of Pollution Control Boards as also those of distilleries and design and consulting organizations on different aspects of treatment of distillery wastes so as to meet the goals of clean environment.

Anaerobic digestion is a process in which the organic waste is decomposed under anaerobic conditions to a variety of end products including methane and carbon dioxide. The process is carried out by hydrolytic enzymes, acidogenic bacteria and finally by methanogenic bacteria for the conversion into methane and carbondioxide.The treated effluents are expected to be reduced in organic and pathogen content and is non-putrescible.

Phenol degradation was studied by axenic and mixed aerobic bacterial strains isolated from the naturally degrading sludge of an aerobically treated distillery effluent sample and it was noted that It was reported that the Alcaligens eutrophus has highest 74% and 100% phenol degrading efficiency in both pure and mixed culture conditions, respectively after 72 hrs time intervals (Chandra Ram and Rathore Brijesh, 2002). The physico-chemical characteristics of sugar mill effluent, discharged from Tummapala sugar factory, Anakapalli (Andhra Pradesh), and their impact on local fish, *Channa punctatus* were reported. The high concentration of biodegradable organic matter was confirmed from high values of BOD and COD (Avasn Maruthi Y and Ramakrishna Rao,2001). The fermentation kinetics of fuel gas production from the raw distillery effluent in batch-fed culture digester were studied indicated a decrease in very low values correlating the efficient degradation of short chain fatty acids (Gaur Abhishek et al. 2000). The simultaneous determination of some heavy metals, in sugar and final molasses samples using differential pulse anodic stripping voltammetry was investigated (Mahajan Rakesh Kumar and Mahajan,2001).
The treatment of distillery waste with subsequent dilution of the effluent after treatment to make a final discharge was repoted (Malik DS and Malik Amrita,2000). Reports available on the removal of odour from sugar industry waste

by adsorption and chemical oxidation techniques (Raghu Rao A and Gaikwad RW,2001). The biological digestion and the development of a mathematical model for the treatment were reported using synthetic solutions and original wastewater of which the initial chemical oxygen demand (COD) was determined (Ilda Degirmentas and Nuran Deveci, 2004) with winery wastewaters (as for vinasses from distilleries) the removal yield for anaerobic digestion is very high, up to 90–95% COD removal.

The treatment for COD removal was reported after fungal pre-treatment reached 53.3% (Xolisa Melamane et al.2007). The impact of ozonation to investigate on the degradability of wine distillery wastewaters, usually called vinasses, was reported (Fernando J. Beltran et al.1999). Anaerobic-aerobic treatment of distillery wastes (S.K. Billore et al. 2001). The anaerobic treatment results indicated that the distillery waste should be diluted to bring down the COD to about 50000 mgL^{-1} before the same is treated by stationery fixed film anaerobic (S. Shrihari and Vinod Tare,1989).

2. MATERIALS AND METHODS

In the present investigation, the reactor used was a wide mouthed Pyrex glass bottle of 5 liter capacity as shown in figure 1. The reactor has provision for adding wastes, for removing treated effluent and settled solids and for gas transfer. The gas collection apparatus consisted of a glass bottle of 2 liter capacity and another bottle of 1 liter capacity for the water displaced from the gas bottle. Tubes were connected to the digester to facilitate feeding of the waste and removal of the effluent. The digester was kept in water bath at a constant temperature of 35^0C. Cow dung was used as the seed material and fed into the digester to start with. After establishing necessary biota from cow dung sludge, 1.5 liter of the distillery spent wash was fed into the reactor. The BOD load was kept at 0.20kg BOD/m^3/day in the beginning and the same load was continued for five days. After feeding, the contents in the digester were given thorough mixing by manual shaking. After several displacements of the digester contents and after establishing stable conditions of digestion the loading rate was gradually increased. From the digester, about 100 mL was of the effluent was taken out for analysis and the volume was replaced by distilled water. The procedure was continued for 8 days to obtain the stabilization of waste which could be known by the constant BOD and COD values. This means that the BOD kept on reducing until reaching a maximum reduction in accordance with the experimental conditions. The Care was taken to remove the air from the reactor as well as from the gas collection bottle at the beginning of the experiment and the entire set up was checked for gas leaks. The pH of the influent sample was adjusted to pH 7 by adding $CaCO_3$ solution gradually before feeding. Gas measurements were done once a day. The gas was burnt periodically to confirm the presence of methane which formed a major portion of a gas.

The samples of effluents drawn everyday were analyzed for pH, TS, TSS,TDS,VSS, COD, influent BOD (So), effluent BOD (Se), mixed liquor volatile suspended solids (MLVSS) before sludge wasting, initial MLVSS etc. Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), were regularly performed for the untreated and treated effluents according to the Standard Methods (APHA, 1996). Total alkalinity (TA) was measured by titration at pH 3.8. 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 daily gas production, the influent and effluent BOD, 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.

3. RESULTS AND DISCUSSION

The distillery effluent collected from a sugar distillery was analyzed and the results were shown in table 1. The effluent was found to be acidic with a high amount of total solids. The BOD and COD values were observed to be 42500 and 95000 mg/L respectively giving a COD/BOD ratio of 2.2 which indicated that the effluent was highly amenable for biological digestion.

Table 1: Characteristics of Distillery spent wash

Parameter	Value
Volume, L/L Alcohol	14-15
Colour	dark brown
pH	3.7-4.5
COD	80,000-1,10,000
BOD	40,000-45,000
Total Solids	90,000-1,20,000
Total Volatile Solids	60,000-70,000
Total Dissolved Solids	30,000-40,000
Chlorides	5000-6000
Sulphates	4000-8000

Total Nitrogen	1000-8000
Potassium	8000-11000
Phosphorus	200-300
Sodium	400-600
Calcium	2000-3000

All values except pH and colour are expressed in mg/L

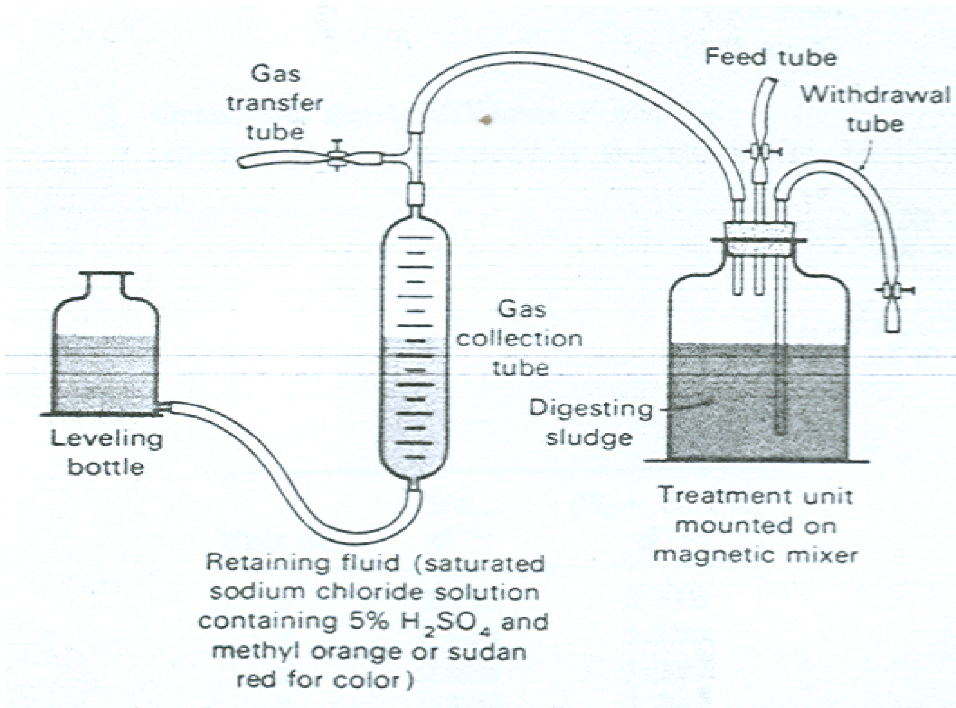

Fig 1: Anaerobic Reactor

Many factors affect the performance of digestion process. Various parameters of importance relating to growth of microorganisms and substrate utilization on which the operation of the reactor is based include mean cell residence time (θ_C) in days, mixed liquor volatile suspended solids (MLVSS) concentration expressed as X in mg/L, hydraulic detention time (θ) , food to microorganism (F:M) ratio in kg BOD_5/kg MLVSS/day, and the dissolved oxygen (DO) in mg/L in the reactor.

The anaerobic digestion of distillery effluent was carried out with varying organic loads rates from 0.2-0.8 kg BOD/m^3/day and the results of the experimental data were shown in table 2.

Table 2

Organic Load (kg BOD/m^3/day	Effluent BOD (mg/L)	MLVSS (mg/L)	Hydraulic Retention time(d)	BOD removal efficiency (%)
0.3	7000	12440	4.5	83.3
0.4	5900	13000	4.8	85.9
0.5	5600	13410	4.8	86.6
0.6	4600	13440	4.6	89.0
0.7	4200	13560	4.8	90.0
0.8	3000	13570	4.8	92.8

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 92.8% . During the digestion, the mean cell residence time θc was varied by operating the reactor at varying food to microorganism ratio(F/M) by varying the MLVSS concentration. Results indicated that the BOD and COD removal efficiency decreases with decrease in mean cell residence time θc and decrease with increase in F/M ratios as represented in tables 3 and 4.

Table 3: Anaerobic Digestion at a BOD load of 0.8 kg BOD/m^3/day

So(mg/L)	Se(mg/L)	θc(d)	X(mg/L)
42000	1600	7.6	13570
42000	2620	5.6	13580
42000	3900	3.3	14210
42000	5400	2.2	13669
42000	6800	1.1	13570

Table 4

So-Se(mg/L)	Xθ(mgVSS/d.L)	Xθ/So-Se(d)	1/θc(d^{-1})	1/Se(mg/L)
40400	63000	1.56	0.131	$6.25x10^{-4}$
39380	46980	1.19	0.178	$3.81x10^{-4}$
38100	37350	0.98	0.303	$2.56x10^{-4}$
36600	22950	0.63	0.454	$1.85x10^{-4}$
35200	16560	0.47	0.909	$1.47x10^{-4}$

The substrate removal constants, namely, half saturation concentration (K_s) and the maximum rate of substrate utilization (k) were determined from the Lawrence and McCarty's modified Monod equation given below:

$$\frac{1}{U} = \left(\frac{Ks}{k}.\frac{1}{S}\right) + \frac{1}{k}$$

S = Substrate (SCOD and NH_4^+-N) concentration at any time in reactor (mg/L), U = Specific substrate utilization rate = $(S_0 - S)/\theta X$ (mg of SCOD or mg of NH_4^+-N/day/mg of MLVSS), θ = Contact time (day), X = MLVSS at any time in the reactor (mg/L), S_0 = Substrate (SCOD and NH_4^+-N) concentration of the influent (mg/L).

The plots made between $1/U$ and $1/S$ develops into a straight line with K_s/k as its slope and $1/k$ as its intercept.

The sludge growth kinetic constants namely the yield coefficient (Y) and the endogenous decay coefficient (K_d), were determined from the Lawrence and McCarty's modified Monod equation given below:

$$\frac{1}{\theta} = \mathrm{YU-Kd}$$

where U = Specific substrate utilization rate (mg of SCOD or mg of NH_4^+-N/day/mg of MLVSS), θ = Contact time (day), k_d = Endogenous decay coefficient (day^{-1}), and Y = Yield coefficient (mg of MLVSS produced/mg of SCOD or NH_4^+-N).

The values of the substrate utilization rate(1/U) were plotted against the reciprocal values of the effluent BOD(1/Se) as shown in the figure 2.

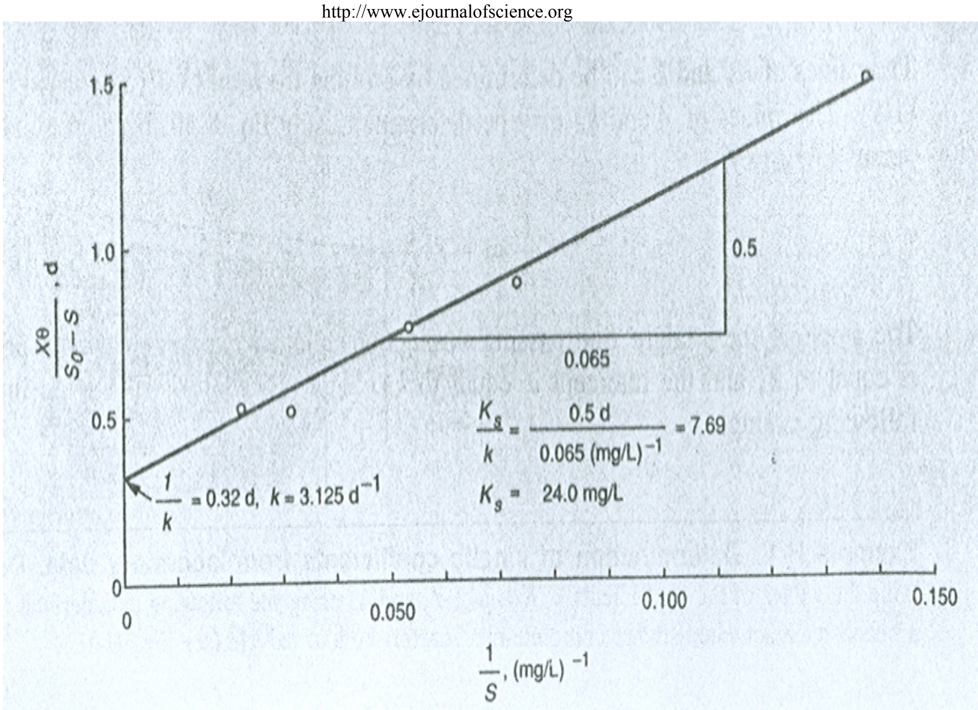

Fig 2: Substrate Removal Kinetics

The substrate removal kinetics, such as the substrate removal rate constant (k) and the 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 θc were plotted against the specific substrate utilization rate (U) as shown in figure 3.

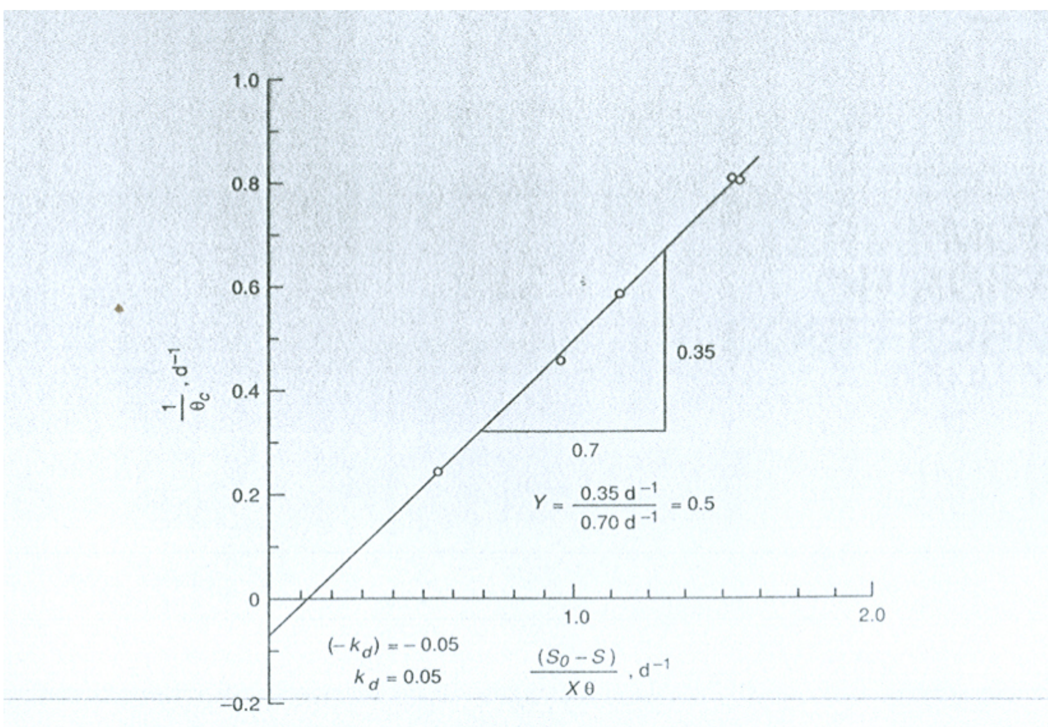

Fig 3: Volatile solids production

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 5. 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 rate may be due to the adsorption of soluble substrate by the bacteria and extra cellular 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 biokinetic coefficients were found to be as follows: Y=0. mg VSS/mg sCOD, Kd=0.05/day, KS=24.0 mg sCOD/L and k=3.215/day. The effect of F/M on the removal efficiency of COD was significant, where COD removal was found to range between 88% and 96.5%.

Table 5: Bio-Kinetic Coefficients

Parameter	Value
Substrate Removal rate constant, k (d-1)	3.125
Half-Velocity coefficient, Ks (mg/L)	24.0
Decay Coefficient, Kd (d^{-1})	0.05
Yield Coefficient, Y	0.5
Maximum specific growth rate of microorganisms, μm(d^{-1})	1.563

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 extra cellular polymers, predator activities and predominance of different microbial species with different energetic characteristics. The yield coefficient obtained in the present investigation 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.

Although, Y, kd, Ks and μmax coefficients for conventional process are within the reported values for conventional processes, they differ quite significantly. The values of Y in conventional process were increasing with the increase in MLSS concentrations, since they represent all the amount of biomass produced by the growth during the removal of the substrate. This clearly shows that the type of substrate and bacterial can have a significant effect on the determination of the biokinetic coefficients. On the other hand, kd was found to decrease with the increase in the MLSS concentration, which could indicate that the amount of sludge produced at higher MLSS values is not reduced. Increasing the MLSS concentration was also found to increase the maximum rate of growth of the biomass and saturation constant.

Studies on the kinetics of BOD reactions have established that they are most practical purposes first order in character as the rate of the reaction is proportional to the amount of oxidizable organic matter remaining at any time, as modified by the population of active organisms. Once the population of organisms has reached a level at which only minor variation occur, the reaction rate is controlled by the amount of food available to the organisms and may be expressed as follows.

$$-dc/dt \propto C \quad \text{or} \quad -dc/dt = kC$$

Where C represents the concentration of oxidizable organic matter at the start of the time t, and k, is the rate constant for the reaction. This means that the rate of reaction gradually decreases as the concentration of C of food or organic matter decreases.

Since the BOD reaction is closely related to a first order type of reaction, a plot of the amount of organic matter remaining versus time yields a parabolic curve. In the present investigation, the anaerobic digestion of distillery effluent followed a first order kinetics since these are reactions that proceed at a rate directly proportional to the concentration of one reactant that is organic substrate. As the rate of the reaction depends on the concentration of the reactant and since the concentration of reactant changes with time, an arithmetic plot of the variation in the concentration with time gives a parabolic curve which confirms that the BOD reactions in the present study followed a first order reaction.

4. ADVANTAGES OF ANAEROBIC TREATMENT

a. Low production of waste biological solids.
b. 2. Low nutrient requirements.
c. Production of methane as an energy source to meet the steam requirement of distillery to the extent of 75-100%.
d. Very high loading rates can be achieved.
e. Active-anaerobic sludge can be preserved unfed for many months

5. LIMITATIONS OF ANAEROBIC TREATMENT

a. Relatively long periods of time are required to start up the process.
b. It is a pre-treatment method. The treated effluent BOD will be in the range of 5000- 8000 ppm and hence an adequate post-treatment is usually required before the effluent can be discharged into receiving water.
c. Dilution water is required ranging from 20-100%

6. CONCLUSION

a. The optimum organic load required for the maximum removal of BOD and COD of the effluent has been determined to be 0.7 kg BOD/m^3/day
b. BOD and COD removal efficiency decreases with decrease in mean cell residence time θc and decrease with increase in F/M ratios
c. BOD and COD removal reached a maximum of 93%
d. The anaerobic digestion of distillery effluent followed a first order kinetics

7. NOMENCLATURE

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

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