# Determination of Kinetic Coefficients for Secondary Aerobic Treatment of Digested Spentwash based on COD Analysis

Shrenik T Patil

*Asst Prof, FCivil, College of Military Engineering, Pune, India,411031*

**Abstract- Liquid waste generated in distillery after extracting alcohol from sugarcane molasses is called Spentwash. Due to its high COD, BOD, TDS and low pH , it is a potential source of pollution if it is disposed off in streams or on land without proper treatments. Present practice of spentwash treatments is limited mainly to economical methods such as anaerobic digestion which is made compulsory primary treatment by the pollution control boards due to its high efficiency of BOD removal and energy recovery. Some distilleries treat their spentwash by composting only or by anaerobic digestion followed by composting . Composting can be done only if good filler material like pressmud is adequately available. The effluent of anaerobic digestion also has high BOD. Though not as economical as above two methods, secondary aerobic treatment of digested spentwash is necessary for its safe disposal. The kinetic coefficients and the design parameters for aerobic treatment of digested spentwash are not well established like in case of domestic waste. Experimental study for the aerobic treatment of digested spentwash , on the principles of extended aeration, done on a laboratory model , aims at determination of the kinetic coefficients of the treatment. Due to time constraints many researchers prefer to use COD analysis instead of BOD analysis to determine the kinetic coefficients. This paper presents the determination of kinetic coefficients of the secondary aerobic treatment of digested spentwash based on COD analysis .**

**Key Words - Spent wash, COD, F/M ratio, MLVSS, Kinetic coefficients**

## I. INTRODUCTION

Distillery is an industry in which molasses , a by-product/ waste of sugar industry, is fermented and alcohol is extracted . The liquid waste generated in the process called spentwash, has dark brown colour, low pH, extremely high COD, BOD and TDS values . The volume of spentwash is as high as 15 times the volume of alcohol extracted [1]. It needs a number of treatments for its safe disposal in the environment.

Due to very high organic content in the spent wash, it is a potential source of renewable energy. Anaerobic digestion with methane gas recovery is, therefore, a compulsory primary treatment of spent wash. However , though it has BOD reduction efficiency of about 80 to 90% , the digested spentwash still has BOD of 6000 to 10000mg/L. The standard laid down by the pollution control boards for disposal of treated industrial waste water, either in streams or on land for irrigation, is 100 mg/L for 5 days BOD at $20^0$ C temperature ( or 3 days BOD @ $37^0$ C temperature) [2]. The average characteristics of the anaerobically digested spentwash are shown in table 1. Huge quantity of fresh water may be required for dilution of the digested spentwash to comply with the standards for disposal. Composting of spentwash or / and digested spentwash with filler materials like pressmud, bagasse, rice husk is a very good treatment as it gives almost zero liquid discharge and produces a very good manure rich in N, P and K. However, composting is not possible for distilleries which do not have adequate filler materials. It is ineffective in rainy days , needs more land and may cause pollution of groundwater in the adjacent environment due to seepage. One more option for treatment of spentwash is Concentration of the spentwash to higher brix followed by Incineration. The advantages of this method are savings in consumption of fuels in boilers and possible recovery of potassium salts from the ash. However, very high initial investments and problems in maintenance of the machinery are the major limitations of this method.

The methods of treatments for any particular distillery depends on site conditions and techno economical feasibility of the treatments. As anaerobic digestion of spentwash is techno economically feasible and a mandatory primary treatment, a rational approach towards spentwash treatment should be anaerobic digestion with biogas recovery followed by secondary aerobic treatment and further use of the effluent as irrigation aid with appropriate dilution. In secondary aerobic treatment, the growth rate of micro organisms is directly related to the rate at which they utilize the organic matter in the waste. The determination of kinetic coefficients ($k, K_s$, Y and $k_d$) of the secondary aerobic treatment helps in evaluating design parameters of the treatment. These kinetic coefficients and design parameters are well established for domestic waste, but not for spentwash which has very high pollution strength. As BOD analysis is time consuming and many researchers prefer to use COD analysis which is quick and more reliable, an effort has been made to determine the kinetic coefficients based on COD analysis after conducting laboratory experiments on a on bench scale aeration tank reactor.

Table 1- Average characteristics of Anaerobically Digested Spent Wash from RPSSK Sakharale Dist Sangli

| Sr No | Important Characteristic | Value |
|---|---|---|
| 1. | pH | 7.2 to 7.6 |
| 2. | COD | 20000 to 28000 |
| 3. | BOD | 5600 to 7000 |
| 4. | Total Solids | 30000 to 350000 |
| 5. | Chlorides | 4000 to 5000 |
| 6. | Sulphates | 436 |
| 7. | Alkalinity | 7675 |
| 8. | Volatile Acids | 3000 |

Note: All values are in mg/L except pH

## II. Secondary Aerobic Treatment – Activated Sludge Process.

It is a biological treatment process that occurs in presence of oxygen. In this process, the microorganisms responsible for conversion of organic matter in the waste to gases and cell tissues are kept in suspension in the reactor. Of many suspended growth aerobic treatments, Activated Sludge Process is the most commonly used method for secondary treatment of waste water. Arden and Locket [3,4] were the first to work with a biomass resembling what is presently known as activated sludge. They found that a well oxidised effluent could be obtained with aeration time of 6 to 9 hours. It was noted that a higher strength waste required a longer time than lower strength waste and an increase in the concentration of biomass decreased the aeration tank required to produce the desired effluent quality. The microorganisms carry out the conversion of organic matter in general accordance with the equation (1)

$$\underset{\text{(Organic matter)}}{COHNS + O_2} + \text{nutrients} \xrightarrow{\text{Bacteria}} CO_2 + NH_3 + \underset{\text{(New bacterial cells)}}{C_5H_7NO_2} + \text{other end products} \quad (1)$$

### A. *Various design parameters of Activated Sludge Process*

Aeration Time was the only parameter considered in the design of aeration tank till 1940. Text books of waste water treatment and research papers had presented a direct relationships between the aeration time and BOD removal and had recommended an aeration time of 4 to 10 hours for domestic waste treatment [3,4]. But the use of aeration time as a design parameter fails to consider organic loading and amount of biomass present in the reactor.

Another parameter **,** Organic Loading per unit volume, had originated in Germany around 1930 by Karl Imhoff [3] In 1943 , Greeley presented a relationship between organic loading ( gm BOD/ $m^3$ d ) and BOD removal [3]. As the organic loading increased from 0.640 Kg BOD/ $m^3$ d to 3.8 Kg BOD/ $m^3$ d, the % BOD removal decreased from 90 to 40. This parameter did not consider the amount of biomass in the reactor.

The most important parameter, Organic loading per unit Biomass, is expressed as gm BOD/ gm MLSS per day. Some references use MLVSS ( Mixed Liquor Volatile Suspended Solids ) in place of MLSS. This parameter attempts to relate the organic loading to the number of micro organisms available for the stabilization of the waste and is often referred to as food to micro organism ratio ( F/M) . In 1940 Sawyer [3] found that increasing MLSS concentration from 800 to 3200 mg/L caused BOD removal to increase from 84 to 97 % at a constant aeration time. In 1944 Okun [3]noted that the use of MLVSS data provided a better correlation between F/M ratio and BOD removal than the MLSS data. This parameter is generally considered to be more representative of the actual conditions in the reactor than other parameters. There are several references to present different recommendations of F/M ratios for various modifications of Activated Sludge Process, but the most commonly used recommendations are from a text book by Metcalf and Eddy [4] which are given in table 2

Table 2 - Recommendations of F/M for modifications Activated Sludge Process

| Sr No | Modification of Activated Sludge Process | F/ M Ratio |
|---|---|---|
| 1 | Conventional | 0.2 to 0.4 |
| 2 | Complete Mix | 0.2 to 0.6 |
| 3 | Step Aeration | 0.2 to 0.4 |
| 4 | High Rate | 1.5 to 5.0 |
| 5 | Contact Stabilization | 0.2 to 0.6 |
| 6 | Extended Aeration | 0.05 to 0.15 |

*B. Extended Aeration*

In this process, the organic matter which is converted into new cells is also oxidised. The auto oxidation of these cells shown in equation (2) is called ‘Endogenous Respiration’. [4]

$$\underset{\text{(Cells)}}{C_5H_7NO_2} + 5\,O_2 \xrightarrow{\text{Bacteria}} 5\,CO_2 + 2H_2O + NH_3 + \text{energy} \qquad (2)$$

This process is used for certain industrial wastes having high organic strength like spentwash which otherwise may remain partially treated due to less aeration. The advantages are better quality effluent, less sludge production and no requirement of sludge treatment. Typical values of the design parameters for Extended Aeration are shown in table 3.

Table 3 - Typical values of Design Parameters for Extended Aeration

| Sr No | Design Parameter | Value |
|---|---|---|
| 1 | Mean Cell Residence Time □c in days | 20 to 30 |
| 2 | F/M ratio Kg BOD/ Kg MLVSS . d | 0.05 to 0.15 |
| 3 | Organic Loading in Kg BOD / $m^3$ d | 0.16 to 0.4 |
| 4 | MLSS in mg/L | 1500 to 5000 |
| 5 | Recycle ratio Q r / Q | 0.5 to 1.5 |

*C. Determination of Kinetic Coefficients using COD Analysis*

From the equations of mass balance of microorganisms and substrate for completely mixed activated sludge process [4] , following equations can be written

$$r_{su} = -kXS/(Ks+S) = -(So-S)/\square \qquad (3)$$

Dividing equation (1)by X,

$$kS/(K_s+S) = (So-S)/(X\square) \qquad (4)$$

The linear form of equation (2),obtained by taking its inverse, is

$$X\square/(So-S) = (Ks/K)(1/S) + 1/K \qquad (5)$$

$$1/\square c = [Y(So-S)/X\square] - k_d \qquad (6)$$

Where,

$r_{su}$ = Substrate Utilization Rate

X = Concentration of microorganisms in the reactor MLVSS

$\theta$ = Hydraulic Retention Time (HRT)

$\theta_c$ = Solids Retention Time ( S R T)

So and S = Substrate concentration of influent and effluent respectively, mg / L

$K_s$ = Substrate concentration at half the maximum growth rate

k = Maximum rate of substrate utilization, per unit mass of microorganisms

Y = Maximum yield coefficient, Mass of cell formed per mass of substrate consumed.

$K_d$ = Endogenous decay coefficient, per day

From equation (5), the values of $K_s$ and k can be determined by plotting the term $X\theta$ / (So – S) versus 1/S . The values of Y and kd may be determined from equation (6), by plotting 1/ $\theta_c$ versus ( So – S ) / $X\theta$.

For determination of kinetic coefficients based on BOD analysis, 5 days BOD @ $20^0$ C or 3 day BOD @$37^0$ C are converted to ultimate BOD prior to making a plot. However, due to time constraints, researchers prefer to use COD analysis instead of BOD analysis in calculating substrate utilization rate. In such case, usable substrate concentration Δ COD as proposed by Gaudi and Gaudi [ 5,6] is used. Before determining the kinetic coefficients k and $K_s$, a plot of Specific Substrate Utilization Rate versus effluent COD concentration is made. The abscissa intercept in this plot represents the non- degradable portion of the substrate. This value must be subtracted from the influent and effluent substrate values before calculating Substrate Utilization Rate used in determination of k and $K_s$ [5].

## III. Experimental Work

### *A. Materials and Methods*

The experiments were carried out in a laboratory scale aeration tank model of 6.5 L capacity. The effluent from digester, which was brought from RPSSK (Rajarambapu Patil Sahakari Sakhar Karkhana) Ltd Sakhrale Dist Sangli, was used as feed. The aeration was achieved by two diffused aerators used in aquarium. The rate of oxygen transfer of the two aerators was experimentally determined and was found out to be 40.75 mg/hr. The photograph of experimental set up is as shown in figure 1.

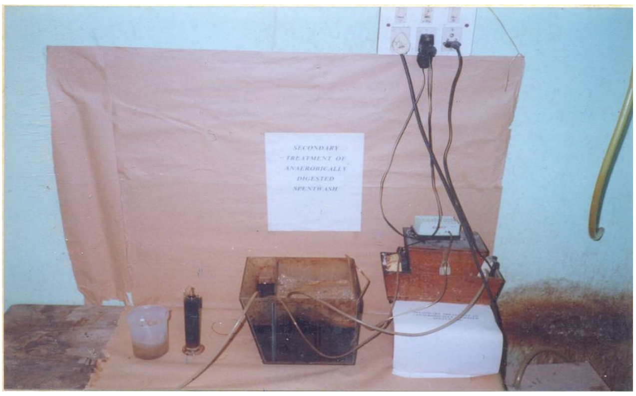

Fig 1. Photograph of Bench Scale Experimental Set Up

Initially the reactor was filled with 5 L of domestic sewage and was aerated for 24 hrs. Then 2.5 L of the sewage was replaced by 2.5 L of the feed. After 5 days of aeration, 50 ml loading of the feed was started for 15 days keeping constant volume of 5 L in the reactor. After achieving adequate growth of biomass acclimatised to the digested spentwash, the reactor was operated over a range of organic loadings and F/M ratios to study COD and BOD reduction. The programme of operation of the reactor is shown in table 4 . The sludge removal and recycling was done only to maintain a constant MLSS in the reactor. The COD, pH of the influent and effluent was determined every day. The BOD of influent & effluent and MLSS of the reactor were analysed at a regular interval of 5 to 6 days.

Table 4 : Programme of operation of the reactor

| Sr No. | F/M | Hyd Loading ml | HRT (□) days | Organic Loading $KgBOD/m^3$. d | No of days of operation |
|---|---|---|---|---|---|
| 1 | 0.15 | 250 | 20 | 0.3 | 40 |
| 2. | 0.15 | 300 | 16.66 | 0.42 | 17 |
| 3. | 0.3 | 750 | 6.66 | 1.05 | 7 |
| 4. | 0.3 | 625 | 8 | 1.05 | 24 |
| 5. | 0.3 | 833 | 6 | 1 | 18 |
| 6. | 0.3 | 625 | 8 | 0.937 | 22 |
| 7. | 0.15 | 300 | 16.66 | 0.51 | 51 |
| 8. | 0.15 | 350 | 14.28 | 0.42 | 33 |
| 9. | 0.2 | 500 | 10 | 0.7 | 19 |
| 10. | 0.15 | 375 | 13.33 | 0.525 | 28 |

*B. Results and Discussions*

The average reactor monitoring data is presented in table 5.

Table 5 : Average reactor monitoring data in the descending order of HRT.

| Sr No | HRT | Influent Characteristics. | | | | Reactor Characteristics | | | | Effluent Characteristics | | | % Removal | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (□) | pH | COD | BOD | Organic Loading | MLSS | MLVSS (X) | SVI | F/M | pH | COD | BOD | COD | BOD |
| | d | | mg/L | mg/L | $Kg/m^3$.d | mg/L | mg/L | | | | mg/L | mg/L | | |
| 1 | 20 | 7.3 | 22070 | 6250 | 0.3 | 6380 | 3509 | 29 | 0.15 | 7.7 | 9570 | 438 | 56.6 | 93 |
| 2 | 16.66 | 7.4 | 30353 | 6950 | 0.42 | 8120 | 4466 | 30 | 0.15 | 8.5 | 11548 | 520 | 62 | 92.5 |
| 3 | 14.28 | 7.3 | 24818 | 5600 | 0.42 | 5156 | 3094 | 23 | 0.15 | 8.5 | 12918 | 356 | 47.9 | 93.6 |
| 4 | 13.33 | 7.6 | 29407 | 6600 | 0.525 | 6243 | 3746 | 23 | 0.15 | 8.6 | 13754 | 603 | 53.2 | 90.9 |
| 5 | 10 | 7.6 | 28295 | 7300 | 0.7 | 6263 | 3758 | 13 | 0.2 | 8.8 | 15284 | 1103 | 46 | 84.9 |
| 6 | 6.66 | 7.4 | 28000 | 6800 | 1.05 | 7917 | 4354 | 25 | 0.3 | 8.4 | 15400 | 1100 | 45 | 83.8 |
| 7 | 6 | 7.2 | 19756 | 5950 | 1 | 7287 | 4008 | 11 | 0.3 | 8.5 | 11533 | 1183 | 41.6 | 80.1 |

The computations for Kinetic Coefficients k , $K_s$ , Y and $K_d$ based on COD analysis are tabulated in table 6.

Table 6 : Computation table to determine non-degradable portion of COD and Kinetic Coefficients on COD Basis

| Sr No | Influent COD | Effluent COD | | | | Corrected Effluent COD | | |
|---|---|---|---|---|---|---|---|---|
| | So | S | So - S | X□ | X□ /( So-S) | $S_1$= S-5000 | $1/S_1$ | 1/□c |
| | mg/L | mg/L | mg/L | mg d /L | d | mg/L | $(mg/L)^{-1}$ | $d^{-1}$ |
| 1 | 22070 | 9570 | 12500 | 70180 | 5.61 | 4570 | 0.000219 | 0.0500 |
| 2 | 30353 | 11548 | 18805 | 74404 | 3.96 | 6548 | 0.000153 | 0.0600 |
| 3 | 24818 | 12918 | 11900 | 44182 | 3.71 | 7918 | 0.000126 | 0.0700 |
| 4 | 29407 | 13754 | 15653 | 49934 | 3.19 | 8754 | 0.000114 | 0.0750 |
| 5 | 28295 | 15284 | 13011 | 37580 | 2.89 | 10284 | 0.000097 | 0.1000 |
| 6 | 28000 | 15400 | 12600 | 28998 | 2.30 | 10400 | 0.000096 | 0.1502 |
| 7 | 19756 | 11533 | 8223 | 24048 | 2.92 | 6533 | 0.000153 | 0.1667 |

The terms Substrate (COD)utilization rate (So-S)/X□ and Effluent Substrate (COD) Concentration S are plotted as shown in figure 2. The abscissa intercept represents the non-degradable portion of COD which is found out to be 5000 mg/L.

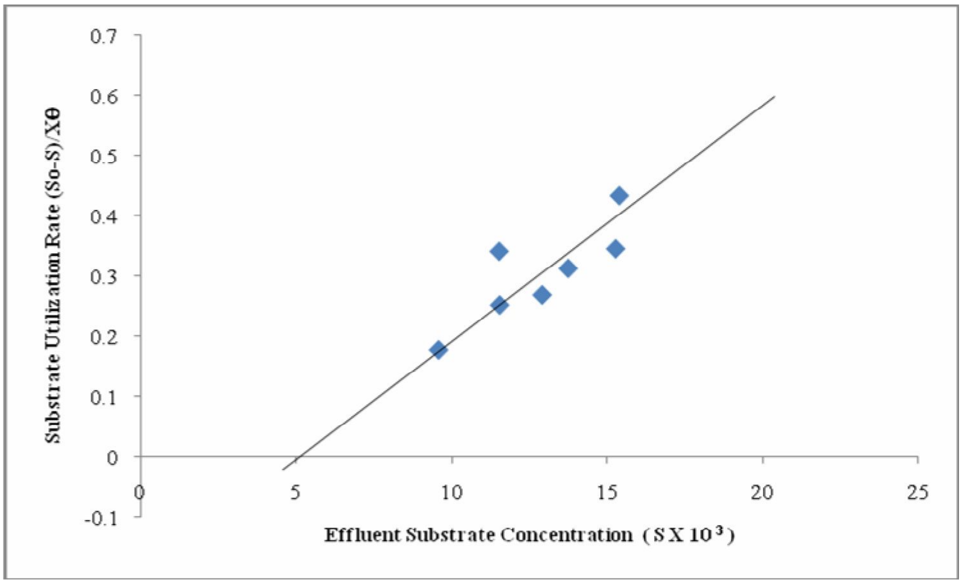


Fig 2- Plot between Substrate (COD)utilization rate and Effluent Substrate (COD) Concentration

Before determining the kinetic coefficients k and $K_s$, the effluent substrate concentration ie effluent COD was corrected by subtracting the non-degradable portion of COD from the actual effluent COD as denoted by $S_1$ in the table 6. From equation (5), the term X□ / (So – S) is plotted versus $1/S_1$ as shown in the figure 3 to determine k and $K_s$. The slope of this plot represents $K_s$/ k and the ordinate intercept equals 1/k

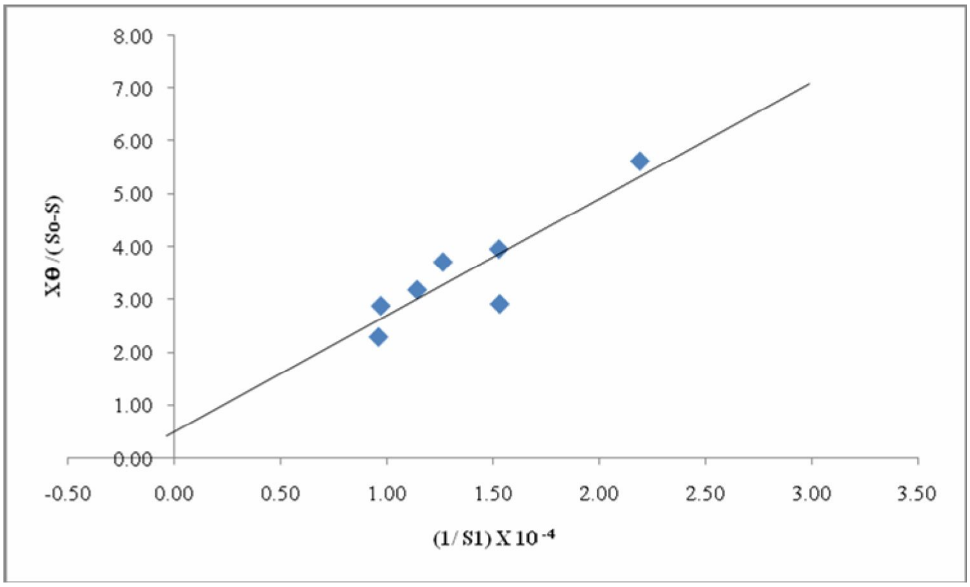


Fig 3- Plot between X□ / (So – S) and 1/S to determine kinetic coefficients k and Ks

From fig 3, 1/ k = 0.5 and $K_s$/k = 25000

Therefore, k = 2 per day and $K_s$ = 50000 mg/L

From equation (6), the term 1/ □c is plotted versus ( So – S ) / X□ and is shown in figure 4. The slope of this plot represents Y and ordinate intercept equals $k_d$ .

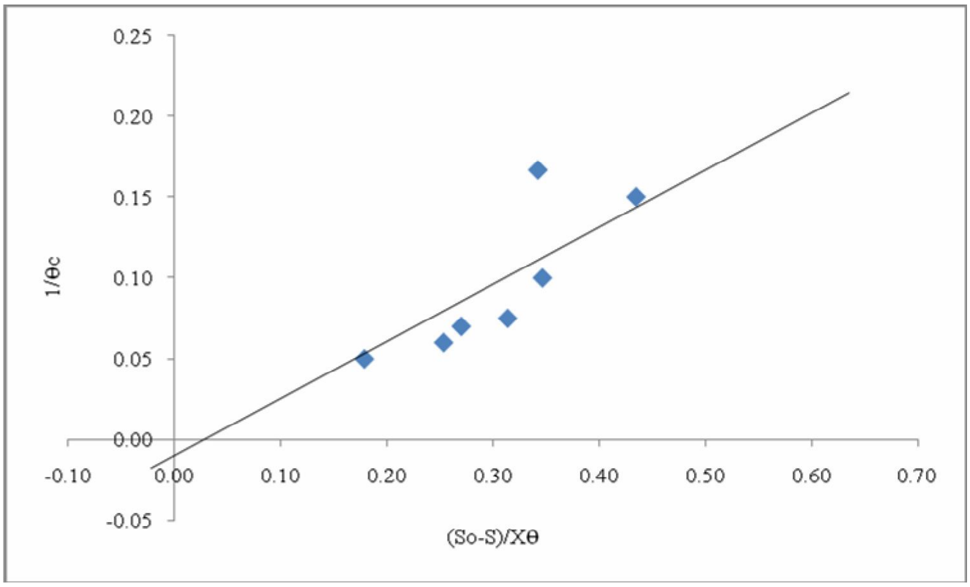


Fig 4- Plot between 1/□c and (So-S)/X□ to determine kinetic coefficients Y and $K_d$

From fig 4, slope = 0.25 and Ordinate intercept = -0.01

Therefore, Y= 0.25 and $k_d$ = 0.01 (negative sign indicates that it is decay)

## IV. CONCLUSIONS

1. The anaerobically digested spentwash can be treated on the principles of extended aeration in secondary aerobic treatment. The BOD removal efficiency varies between 93 % to 80 % and COD removal efficiency varies between 41.6 % to 56.6% at F/M ratio of 0.15 to 0.3 respectively. Though the BOD of the effluent after the secondary aerobic treatment is still slightly higher than the disposal standards for BOD, it can be used for irrigation with dilution.
2. The kinetic coefficients for anaerobically digested spentwash can be determined by using COD analysis also. The non degradable substrate (COD ) concentration was found out to be 5000mg/L. The values of the kinetic coefficients obtained from the experiments by using COD analysis are
   k = 2 per day , $K_s$ = 50000 mg/L COD , Y = 0.25 and Kd = 0.01 per day
3. Design parameters for treatment of anaerobically digested spentwash can be evaluated from these coefficients and comparison between these parameters can be done with the actual reactor monitoring data. Similar studies can be done on BOD basis as well using the same reactor data to determine kinetic coefficients for secondary treatment of digested spentwash .
4. For better efficiency of BOD and COD removal, the reactor may be operated in a continuous flow in a pilot scale with separate settling facility.

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