Bio-decomposition and Bio-kinetic Characterization of Tannery Effluent Treatment

N. B. Prakash

Vimala Sockan

Salalah College of Technology
Salalah, Sultanate of Oman

Abstract

The paper mainly deals with the kinetic behavior of anaerobic organisms, bacterial growth kinetics, substrate utilization, kinetic models describing the biotransformation of reactions during anaerobic digestion of composite tannery effluent under varying organic loads. The studies showed that an optimum BOD influent load of. 0.8 Kg BOD/m^3/day with 3 days retention time could be adopted to yield about 97 percent BOD reduction. The Bio-kinetic coefficients were evaluated using modified Monod's equations to study the metabolic performance of the digestion process. The role of magnesium carbonate during anaerobic digestion has been studied for the enhancement of methane generation.

Keywords: Anaerobic digestion, Tan liquor, Biokinetic coefficents

Introduction

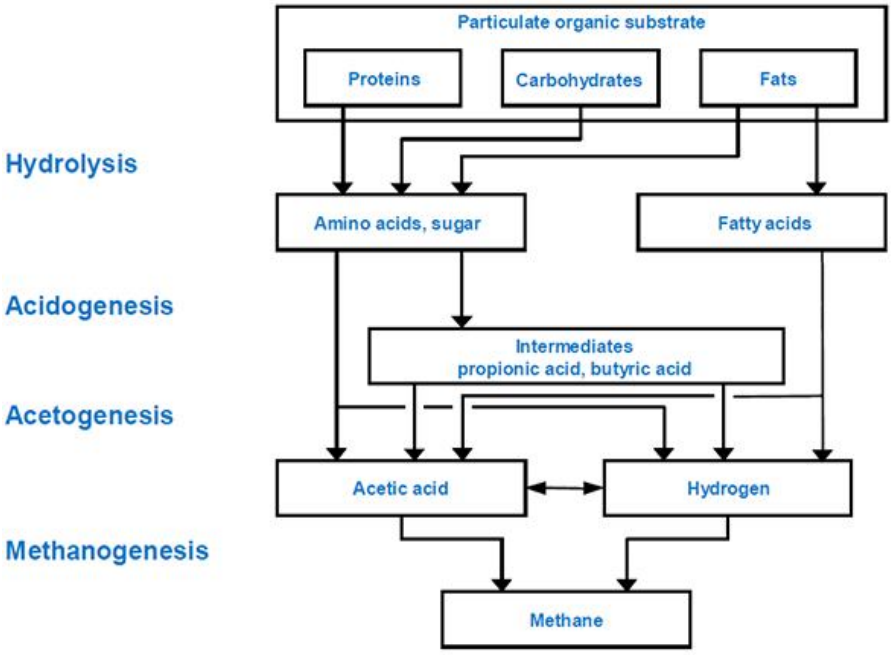
Environmental pollution has become major concern in developing countries in the last few decades. Major sources of water pollution are the untreated or partially treated industrial effluents. Tanning industry is reputed globally as major industry which contributes to water pollution. The quality of discharged water from tanneries is far from the desired level of acceptance into water ways.

A tannery discharges from 21,500-21,950 liters a day, corresponding to 86-88 liters per kg of leather processed. Chromium is known to be highly toxic to the living aquatic organism in the hexavalent state and somewhat less toxic in the trivalent form. The effluents from chrome tanning industry shall meet with the specific tolerance limits for chloride with 1000 mg/L, BOD (5 day at 20^0C)with 30 mg/L ,hexavalent chromium with 0.1mg/L and pH between 5.5 to 9.0.

Tanning of animal hides to convert them into leather is an important industrial activity. 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.

The decomposition of bio-waste occurs in four stages:



Kinetics

The kinetics of biodegradation are a set of empirically derived rate laws. Three equations are shown below to describe most biological reactions:

$dC_A/dt = -k_0$ Zero order
$dC_B/dt = -k_1C_A$ First order
$dC_B/dt = -k_2C_AC_B$ Second order
k_0, k_1, k_2 = rate constants mol/L-sec, /sec, L/mol-sec, respectively
C_A, C_B = some reacting species

This can be applied to the reaction of the compounds with a surface such as a metal catalyst, a soil surface or an enzyme. Two extremes of concentration can be delineated; the first is when there are few molecules of reactant (CA) and many of the surfaces. In this case, few of the available sites will be covered, so the reaction rate dC_A/dt is proportional to the concentration of A (first order reaction above). Secondly, when C_A is so large that every site is saturated with A, the rate is constant (zero order reaction above).

The combined function of these reactions can be written;

$$\frac{dC_A}{dt} = \frac{k_0 C_A}{k^1 + C_A}$$

Where $k' = k_o/k_1$

This is the very common biological form of the equation for growth on a substrate as the concentration of the substrate is increased. It leads to Michaelis-Menton (or Monod-) type kinetics. The saturation coefficient (K_s) is the concentration of substrate equal to half that causing saturation of the enzyme sites (zero order). It is that same as adsorption onto a surface-area-limited substrate. The enzyme sites or the adsorbing sites are "saturated". The enzyme cannot operate faster, and the adsorbing substrate cannot adsorb any more material. Bacterial growth kinetics are slightly more complex and follow the classical "Monod-type" kinetics.

In this case, the rate of substrate utilisation is proportional to the concentration of the microorganisms present [X] and is a function of the substrate concentration.

The Monod bacterial growth kinetics is traditionally written as:

$$\frac{d[S]}{dt} = \frac{k[X][S]}{y[K_S][S]}$$

Where:

[S] = substrate concentration
k = maximum utilisation rate for the substrate per unit mass of bacteria
[X] = concentration of bacteria
[Ks] = half-velocity coefficient for the substrate
y = yield coefficient = d[X]/d[S]

K_s (or K_m in graph above) typically ranges from 0.1 to 10.0 mg/L. Wastewater systems therefore usually operate in the range where Ks is more than [S]. In this particular case, the equation reduces to second order kinetics;

$$- \frac{d[S]}{dt} = \frac{k[X][S]}{yK_S} = K^1[X][S]$$

Where K' = k/yKs

If substrate concentrations are low, the reaction becomes first order with respect to both substrate and bacterial population size. This has been confirmed experimentally in many sites and with many systems.

There are really three kinds of kinetic models used in describing biotransformation in waste water systems. The first, Batch model kinetics, deal with the utilization and biotransformation of the substrate and the growth of bacteria over time in a closed system. The second, Continuous model kinetics deal with a more-or-less constant flow of the substrate through or into a known volume system. These models are useful for predicting results of slow but continuous processes. The third is that of Biofilm model kinetics. It is based on the theory that the bacteria are attached to solid particles in the subsurface environment and behave accordingly. This last model still uses Monod-type kinetics but extends the model to include the effects' of biofilm thickness and diffusion of substrate into and out of the biofilm. More than likely the actual "biofilms" in the field situation are so sparse as to simply constitute a random distribution of individual cells attached to mineral or organic matter particles.

The model below shows a series of simplified Monod-type kinetic models developed to describe some simple systems with a single type of organism and a single substrate using only substrate concentration and cell density as the variables. To generate these models, a mass balance equation is substituted into the Monod equation. The population density is B and is expressed as equivalent biomass [X], which is the amount of substrate required to produce a population density B and has units of concentration;

X = B = Y

Where Y is the yield and is assumed to be independent of biomass and substrate concentrations. Since it is based on a closed batch system, the sum of the substrate and equivalent biomass at any time must equal the initial substrate concentration [S_0] added to the initial equivalent biomass [X_0];

$X + S = X_0 + S_0$

Then, by combining the Monod equation and the equation above, the Monod equation with growth can be derived. Another five equations can be derived depending on the initial substrate concentration and initial equivalent biomass. Three of the models are based on the initial substrate concentration being much smaller than the initial equivalent biomass (Zero order, Monod with no growth, and first order). For zero order and logarithmic growth, the initial substrate concentration far exceeds the half saturation constant while for logistic growth the reverse is true.

The study on Hexavalent Chromium removal from Industrial waste water by chemical precipitation method was reported[1]. The characterization, kinetics and thermodynamics studies were carried out for the removal of hexavalent chromium from wastewater by FeO-nanoparticles-chitosan composite beads[2]. The separation of the chromium(III) dissolved in a tanning wastewater was studied by means of precipitation with calcium carbonate, reverse osmosis with polyamide membrane and adsorption on activated carbon[3]. The Electrochemical precipitation of chromium (Cr^{6+}) from an electroplating wastewater was reported[4].

The Chromium removal from Tannery waste water using chemical and biological Techniques for zero discharge pollution was reported by Hesham et al.,[5] Tanning process using chromium compounds is the most common methods for processing of hides (Sreeram, and Ramasami, 2003)[6]. In this process about 60% - 70% of chromium reacts with the hides.

Although actinomycetes constitute a significant component of the microbial population in most environments, their metabolic diversity and genomic characteristics indicate them as well suited agents for bioremoval of metal and organic compounds (Polti*et al*., 2007)[7]. Recent studies showed chromium bioremoval by *Streptomyces rimosus*generated from the antibiotic industry (Sahmoune and Louhab, 2008) and biological reduction of chromate by *Streptomyces griseus*(Poopal and Laxman, 2009)[8].

Arumugam has reported on the recovery of chromium from spent chrome tan liquor by chemical precipitation using lime[9]. Pathe et al. have studied the properties of chromium sludge from chrome tan liquor and related the sludge volume, sludge settling rate, surface loading rate etc[10].ArchanaShukla and Shukla have studied the treatment of tannery and electroplating effluents by using lime, NaOH and their mixture in the temperature range of 25 to 100^0C[11].Guruswamyet al. conducted study on a laboratory scale completely mixed continuous flow activated sludge system to treat settled chrome tannery wastewater and observed that the BOD and COD removal ranged from 84 to 96%.[12]. Elangovan et al. have conducted experiments on the activated sludge treatment of vegetable tanning waste admixtured with 10, 25, and 50% settled sanitary sewage and obtained BOD removal from 87 to 96%.[13]

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 this objective, experiments were conducted using chrome tanning wastewaters for the treatment.

A comprehensive review of the methods for handling tannery effluent showed that the effluents from such plants are generally high in both dissolved organic and inorganic materials, posing particular treatment difficulties. Although a number of treatment procedures are being used or have been proposed, there is no widespread agreement on the most suitable methods. Also information on the design of treatment plants based on biokinetic parameters for tannery effluent is very limited, the prime objective of the present study is to determine the biokinetic parameters which enable us to describe the metabolic performance of the microorganisms when fed with the substrate and other components in the tannery treatment processes.

Experimental

The experiment was designed and operated on the principle of an anaerobic digestion process to evaluate the bio-kinetic parameters, which could be used in the rational design and operation of large-scale anaerobic installations. The Reactor used for anaerobic digestion is shown in figure 1. The reactor was a wide mouthed Pyrex glass bottle of 5 liter capacity. 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 I liter capacity for the water displaced from the gas bottle. 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. Tubes were connected to the digester to facilitate feeding of the west 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, the chromium free composite liquor is fed into the digester daily. The pH of the influent sample was adjusted to pH 7 by adding alkali before feeding. After feeding, the contents in the digester were given thorough mixing by manual shaking. The BOD load was kept at 0.25kg BOD/m^3/day in the beginning. After several displacements of the digester contents and after establishing stable conditions of digestion the loading rate was gradually increased. 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 at various stages were analyzed 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 up to 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/m^3/day. 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.

Results and Discussion

The general characteristic properties of composite tannery effluent are presented in table 1. The result indicates that the liquor is basic with pH 7.8. Optimization of pH for Chrome reduction is shown in figure 2. The chromium content has been found to 120 mg/Land the BOD and COD of the effluent have been estimated to be1360 and 2510mg/L respectively. The results indicate that the effluent has to be treated for an effective removal of chromium before being subjected to biological treatment. Lime was used as the precipitating agent for chromium removal and effect of lime on chrome precipitation is presented in table 2. It was observed that the chromium removal increased with increase in pH and the maximum chromium removal of 99.7% was observed at pH at 11.9 with a lime dose of 7.0 g/lt. Further increase in lime has resulted in the decrease of chromium removal due to redissolution of the mixture under such experimental conditions. The results of the anaerobic digestion of the chrome free composite liquor are presented in table 3. The data consists of varying BOD loading rate changes in pH alkalinity, volatile acid, and percentage BOD reduction. It was observed that a maximum BOD reduction of 96.9% was obtained at the BOD loading rate of 0.80kg BOD/m^3/day and throughout different loading rates, The BOD reduction was more than 94% which could be due to the proper maintenance of alkalinity and volatile acids in the digester. In the beginning of the process, the pH of the effluent was 6.9. As the loading increased gradually the pH increased to 7.6 up to the optimum loading and dropped down slightly to 7.4 at the maximum loading. The increase in alkalinity was steady as the loading increased gradually. Side by side there was a production of volatile acids but was not considerable. With the initial pH correction and with proper seeding of the waste, the process of digestion was taken place unhindered, without undue accumulation of intermediate products. There was no possibility for the formation of free volatile acids. BOD Removal Efficiency with varying organic load is represented in Figure.3.

Due to initial pH correction the alkalinity level in the waste was boosted up and this gradually increased at every increase in loading. This helped in maintaining adequate buffer capacity in the digester to neutralize the volatile acid. Much of the alkalinity build up the digester may also be due to the release of ammonia from nitrogenous organic matter in the waste undergoing digestion. The volatile acids also react with the alkalinity formed and form an acid salt with release of carbon dioxide. The salt in turns reacts with acid and appears as part of the alkalinity.Methane organisms are extremely sensitive to pH values. They are most reactive in the pH range 6.6 to 7.2.

In the present study, the influent pH was adjusted to 7.0 using Magnesium carbonate which apart from raising the pH also useful for methane organisms as a source supply of CO_2 in producing additional quantities of methane. The reaction may be represented as follows;

$MgCO_3 + 2H_2O \rightleftharpoons Mg(OH)_2 + H_2CO_3$

$H_2CO_3 \longrightarrow H_2O + CO_2$

This is a reversible reaction. Initially there was certain amount of $Mg(OH)_2$ produced which helped to neutralize the acidity in the raw waste. It was possible that during anaerobic digestion of the waste, the methane organisms might utilize the CO_2 gradually for forming methane since CO_2 is a hydrogen acceptor.

$4\ H_3A + CO_2 \longrightarrow 4\ A + CH_4 + 2\ H_2O$

Where A is any oxidized substrate.

The presence of traces of H_2S in the gas may be due to the reduction of sulphates present in the waste. Although the presence of higher sulphide concentrations affect volatile acid production and methane fermentation during an aerobic digestion the presence of less amount of volatile acids in the experiment seemed to indicate that methane fermentation has in no way been affected. The variation of Alkalinity with organic load is shown in Figure.4. The volatile acid production was kept under control and this may be due to the high level of alkalinity maintained in the digester. The optimum and the maximum values of the treated liquor is shown in table 4. The biokinetic coefficients were evaluated using modified Monod's equations and were represented in table 5. The rate of substrate utilization was found to be higher at the early stages of digestion throughout the processes and the reason for the initial high substrate utilization rate may be due to the adsorption of soluble substrates 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 be cell growth. Adsorption and metabolism occur concurrently.

The kinetic rate constants for the anaerobic digestion of tannery effluent at an optimum organic load of 0.8 kg BOD/m^3/day are represented in table 6. It was observed that the concentration of the reactant decreases and that of the product increases exponentially with time. The constancy values of rate constants confirm a first order reaction.

Conclusion

The results of the study lead to the following conclusions

(A) By proper maintenance of required alkalinity, the BOD reduction can be increased.
(B) The maximum BOD reduction was obtained at an applied organic load of 0.80Kg BOD/m^3/ day.
(C) The BOD reduction was more than 94% which could be due to the proper maintenance of alkalinity and volatile acids in the digester.
(D) Due to pH correction, the alkalinity level in the waste was boosted up and this helped in maintaining adequate buffer capacity in the digester to neutralize the volatile acid.
(E) Compared to other alkalis, it appears to be an increase in biogas production during anaerobic digestion by the use of $MgCO_3$ in the system.
(F) The substrate utilization rate increase may be attributed to continued increase in metabolic activities caused be cell growth.
(G) The rate constant values confirm a first order reaction.

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Table 1: General characteristics of Composite Tan liquor

Parameter	Value
pH	7.8
Alkalinity (as $CaCO_3$)	1100
Total solids	22400
Total dissolved solids	20890
Total suspended solids	1510
Volatile suspended solids	810
Chlorides	7600
Sulphates	2840
BOD	1360
COD	2510
Chromium	120
Sulphide	90

All Values except pH are expressed in mg/L.

Table 2: Effect of Lime on Chromium Precipitation

Weight of lime added(g/Lt)	pH	Chromium in filtrate (mg/L)
4.0	9.6	3.64
4.5	9.9	2.89
5.0	10.3	2.66
5.5	10.9	2.00
6.0	11.4	1.64
6.5	11.6	0.90
7.0	11.9	0.40
7.3	12.0	0.54
7.8	12.3	0.66
8.5	12.4	0.68

Table 3: Anaerobic Digestion of Composite Liquor

BOD load (Kg BOD/m^3/day	pH	Alkalinity (as$CaCO_3$)	Volatile acids	% BOD reduction
0.25	6.9	340	40	94.6
0.30	7.0	410	60	95.0
0.35	7.2	560	76	95.2
0.40	7.4	950	110	95.4
0.50	7.4	980	144	96.0
0.60	7.6	1460	168	96.2
0.70	7.6	1880	190	96.8
0.80	7.6	1920	236	96.9

Table 4: Results of the Treated Liquor

Parameter	Maximum	Optimum
BOD load,Kg BOD/m^3/day	0.80	0.60
pH	7.6	7.4
BOD reduction %	96.9	95.4
Volatile matter reduced (%)	80	76
Alkalinity (as $CaCO_3$)	1920	980
Volatile acids (mg/L)	236	168
Methane production (%)	34	28

Table 5: Bio-Kinetic Coefficients

Parameter	Value
Substrate Removal Rate Constant, k/day	1.66
Half Velocity Constant, Ks, mg/L	1132
Decay constant, Kd, day^{-1}	0.05
Yield Coefficient, Y	0.22
Maximum Specific growth rate of Microorganisms, μ_m/day	0.368

Table 6: First Order Rate Constant Values

Time (Hours)	Rate constant, k
24	0.0301
48	0.0208
72	0.0204
96	0.0253
120	0.0260
144	0.0245

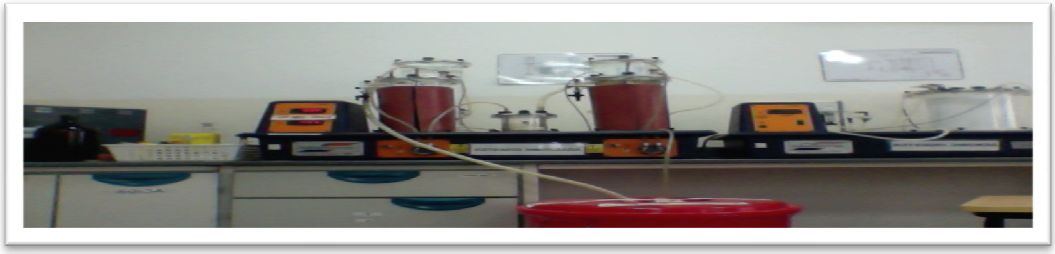

Figure 1. Anaerobic Reactor

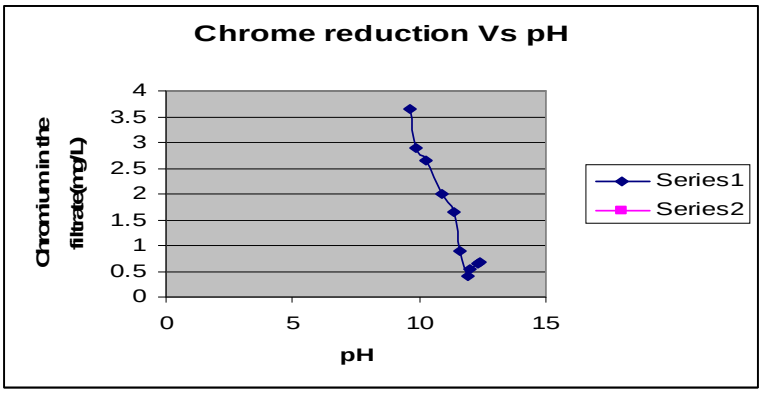

Figure.2. Optimization of pH for Chrome Reduction

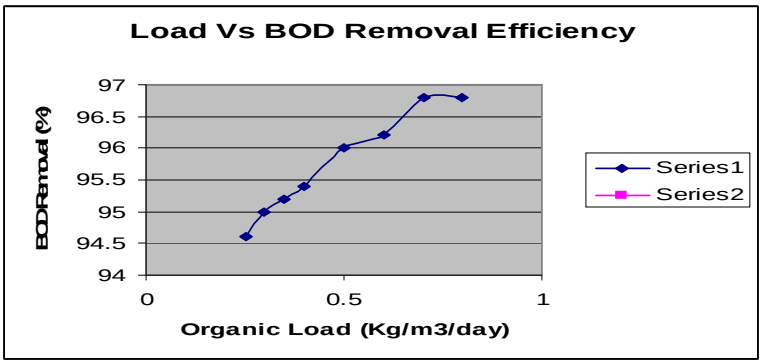

Figure.3: BOD Removal Efficiency with Load

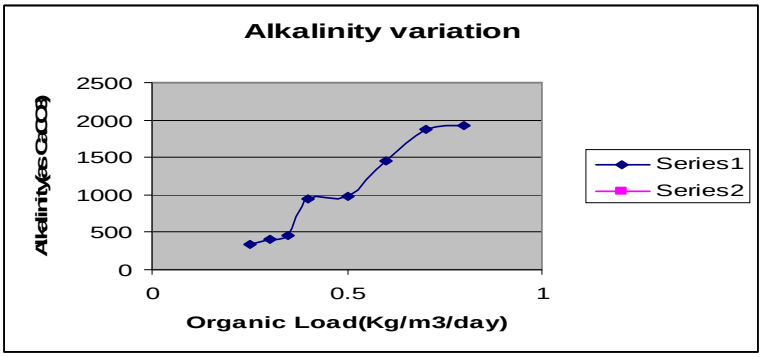

Figure.4: Alkalinity Variation with Load

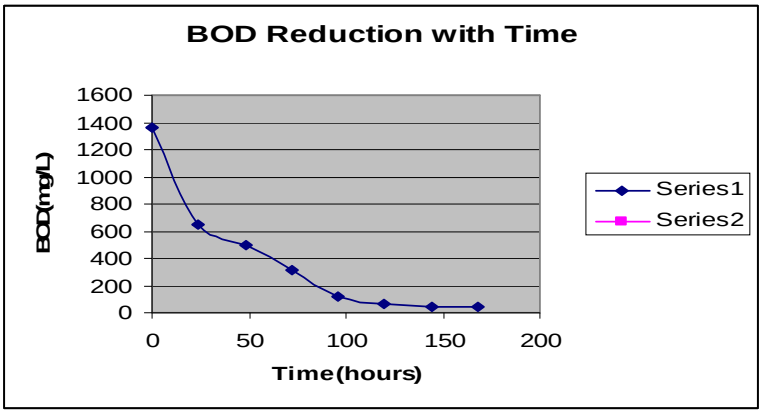

Figure.5: BOD Reduction with Time

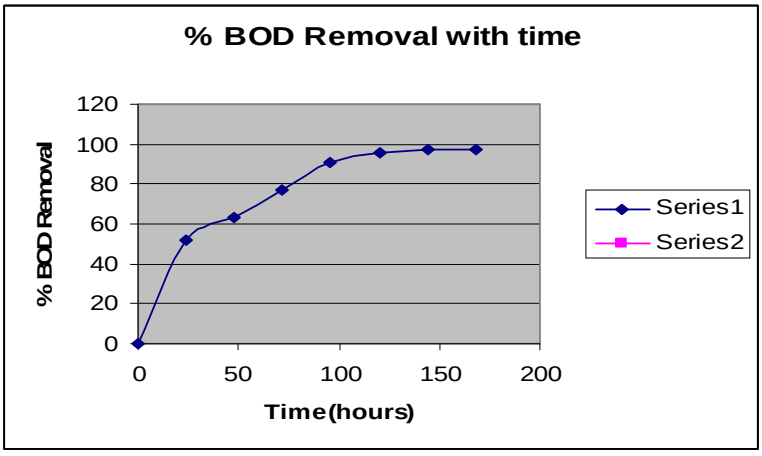

Figure.6: % BOD Reduction