TO STUDY BIOCHEMICAL REACTION KINETICS OF SMALL SCALE AGROBASED PAPER MILLS EFFLUENTS

A DISSERTATION

submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
CHEMICAL ENGINEERING
(INDUSTRIAL POLLUTION ABATEMENT)

By

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I hereby certify that the work which is being presented in this dissertation entitled **'TO STUDY BIOCHEMICAL REACTION KINETICS OF SMALL SCALE AGROBASED PAPER MILLS EFFLUENTS'** in partial fulfilment of the requirements for the award of the degree of **Master of Engineering in Chemical Engineering** with specialization in **Industrial Pollution Abatement**, submitted in the Department of Chemical Engineering, **University of Roorkee, Roorkee**, is an authentic record of my own work carried out for a period of about one year, from June 1989 to May 1990, under the supervision of Dr. P.S. Panesar and Dr. A.K. Agarwal.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

Dated : May 19, 1990

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This is certified that the above statement made by the candidate is correct to the best of our knowledge.

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The small Pulp and Paper Mills using agriculture residue form a large proportion of the paper making capacity in India. These mills do not have chemical recovery system and as a result, large quantity of effluents are discharged into the drains and cause enoromus amount of adverse environmental impact. Bio-oxidation forms the basis of treatment for these effluents.

The BOD exerted at different time intervals were measured for different samples obtained from the agro based paper mills effluents and observed that it follows the first order bio-oxidation kinetics.

Literature reveals that several effluents follow the first order bio-oxidation kinetics and different methods were developed to estimate the kinetic parameters (K, the reaction rate constant and L, the ultimate BOD). These methods were compared using BOD data of Ingram and Orford (1953) and it was observed that the Reed & Therault (1931) was the best followed by method of moments (1950) and Weigand (1954) method. A similar trend was also observed for agro-based small paper mills effluent. A non-linear least square optimizer (Marquardt method) was utilized to estimate the parameters using three parameter modified equation of Reed Therault. The similar results were obtained in all cases. With this finding and present trend of computer facilities, it is recommonded that the non-linear least square optimzer will be the best to use compared to hand calculation in Reed Therault method.

studied in the temperature range 10-30°C. A break was observed in the Arrhenius plot at about 20°C. The activation energy was 24.8 kJ/mole between 10-20°C and 80.5 kJ/mole between 20-30°C.

The effect of pH on the bio-oxidation of effluent was also studied in the pH range of 6.0 to 8.2 and it was observed that activity of micro-orgranism was highest at near neutral pH.

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SYMBOLS

E	Activation Energy (J/mole)
h	Time Difference (days)
K & K'	Reaction Rate Constants (days^{-1})
L	Ultimate BOD (mg/l)
t	Time (days)
Y	BOD Exerted in Time t = 0
θ	Temperature Coefficient

ABBREVIATIONS

BOD	Biochemical Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
gpl	gms/l
IPPTA	Indian Pulp and Paper Technical Association
JWPCF	Journ. of Water Pollution Control Fedration
OD	Oven Dry
TS	Total Solids
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
VDS	Volatile Dissolved Solids

INTRODUCTION

but also for commercial and other social purposes. The per capita consumption of paper is said to be the 'Index of Civilisation' of a country. Unfortunately, in India it is only 2.0 kg, one of the lowest in the world, while this figure stand at 275 kg in USA, 195 kg in Sweden, 190 kg in Canada, 137 kg in UK and 134 kg in Japan (Surendra Nath (1986)).

Pulp and paper industry is highly capital, material and energy intensive. It produces a large volume of gaseous, liquid and solid wastes. Unfortunately as things stand, paper industry has earned a bad name as a major polluting process industry. In India, there are about 305 paper mills and 4 large newsprint mills (above 150 TPD capacity) of these 251 mills belongs to small paper mills category (upto 30 TPD capacity). Fifty two percent of the total paper is produced by small and medium paper mills (upto 60 TPD capacity). Most of the small paper mills use agriculture residues, waste paper and other nonconventional raw materials. About 200 small paper mills are based on waste paper, 47 mills on cereal straws, 20 mills on bagasse and 8 mills are on pulp, while rest 30 mills use conventional raw materials like hard wood, bamboo etc. (Rao (1988), DGTA Report (1989)).

The paper industry is facing a major problem due to the non availability of suitable raw materials to meet the increasing demand for paper and paper products. The forests were the main sources of raw material particularly for larger mills. Unfortunately, the forest cover in India which was about 30% in

(Surendra Nath (1986)).

The forest are undoubtedly denuded drastically over the last 30 years without compensating afforestation. Ecological and environmental imperatives indicate the pulp and paper industry should look for viable alternative raw materials, particularly agriculture residues and waste paper, while agro - residue form an annually replenishable source, recycled secondary fibres (waste paper) could reduce the strain on primary fibre resources.

The government of India is also encouraging enterpreneurs for setting up small mills based on agro-residues. The government is providing fiscal incentives in form of reduced excise for small capacity units, tax exemptions on utilisation of bagasse beyond 75% in furnish.

Basically paper making is a process where natural fibres are separated from raw material by use of chemicals and energy and converted into sheet of paper.

The Fibruos raw material contains lignin and fibres (cellulose) and small amount of other materials such as extractives etc. The fibres are seperated from fibrous raw material with the help of chemicals in the pulping section. These fibres after washing gives cleaner fibres and liquor containing spent cooking chemicals, degraded lignin and other solid material of the raw material. This liquor is called black liquor. The washed pulp (slurry of fibres in water) is subjected to bleaching action to give brighter pulp. The bleached pulp is imparted the desirable properties in the stock preperation section by a sheet of paper in a paper machine.

In large paper mills the black liquor is utilised to recover its chemicals and energy value, while in smill paper mills chemicals are not recovered from the black liquor due to high cost involved in its recovery system.

In general, the black liquor is drained off with the waste water without any treatment and creates pollution.

It is therefore, essential to treat the waste water from the small paper mills. Biological treatment have long formed the basis of treatment of biodegradable organic materials and is one of the cheapest alternative too. Therefore, the understanding of the bio-oxidation kinetics of biodegradable organic materials (waste) is of primary importance in understanding and designing of effluent treatment processes.

PULP AND PAPER MILLS

CONTENT

The installed capacity of pulp and paper industry in India is shown in TABLE A - 1 in Appendix A. The capacity utilisation was 82% in 1974, 72.95 in 1978 and now it is only 60% (Rangan(1986)). The low capacity utilisation at present is possibly due to raw material shortage, nonavailability of fuel, seasonal shortage of fresh water, frequent power cuts, strained labour - management relationship, poor plant machinary maintenance, obselete technology and shortage of financial resources for renovation, modernisation and reconstruction.

The total paper, board and newsprint demand will be 44.31 lakh tons by twenty first century as compared to 28.57 lakh tons in 1991. Subsequently to produce 44.31 lakh tons of paper, the raw material required is estimated to be 115.86 lakh tons (Jain (1986)).

2.2 AGRICULTURE RESIDUE AND THEIR PROPERTIES

Most of paper mills below 30 TPD in India thrive only on agriculture residu~~s~~es like rice and paddy straw, bagasse and locally available other agro - residues. India ranks second in the production of rice and wheat straw, therefore plenty of raw material is availavle for paper manufecturing. In order to understand the working pattern of small mills, it is necessary to know the characterstics of raw material used.

The chemical composition of common agriculture residues is shown in TABLE A-2 of Appendix A. It is evident from the Table that agriculture residue contains almost equal amount of cellulose with additional advantage of lesser lignin content,

content results in good fibre bonding. It is also evident from the TABLE A-2 that the average length of the fibre is in the range of 0.8 mm - 1.5 mm which is less than the conventional raw material.

2.3 PULPING PROCESSES

Soda process is the most common process used for pulping of agriculture residue and is discussed briefly:

NaOH is the principal cooking chemical in soda process. Liquor (aqueous solution of NaOH) and agro-residue are charged to the digester with required ratio. Recycled black liquor from the washer is also added to make up the desired liquor to raw material ratio. The digestor is heated either by direct or indirect steaming to an elevated temperature in the range of 160 to 180 °c and held there untill the desired degree of cooking has been achieved. About 90% of the lignin is usually removed in the digester. In order to complete the cook in a reasonable time, a small excess of chemical is usually used.

2.4 SOURCES AND CHARACTERISATION OF LIQUID EFFLUENTS

Figure 2.1 shows the generalised process flow diagram for small pulp and paper mill using agriculture residues. It also shows various possible waste water generation sources which includes -

(a) black liquor from digestor section,

(b) wash water from washing section,

(c) bleaching section,

(e) paper machine and

(f) fresh water over flow.

The effluent from a paper mill may be characterised according to following scheme -

- suspended solids
- slowly biodegradable compounds
- easily biodegradable compounds
- toxic compounds
- pH changing compounds
- inorganic salts

The major part of **'suspended matter (SS)'** in the mill effluents usually consists of fibres only. Fibres are deterimental because they tend to settle in the receiving water in which fermentation may occur, this may cause oxygen depletion.

The content of **'easily biodegradable compounds'** is usually measured by the BOD test. A considerable part of raw material dissolved in the pulping and bleaching processes is easily biodegradable. Examples of such compounds are low molecular hemicelluloses, methanol, acetic acid, formic acid, sugar etc.

'Slowly biodegradable compounds' in the mill effluent mainly consists of high molecular substances of lignin or carbohydrate origin. The amount of such compounds in a mill effluent can be estimated by measuring of COD (Chemical Oxygen Demand) and substracting the BOD value from it. The lower the ratio BOD/COD the higher is the fraction of slowly biodegradable compounds. Lignin and its derivatives are slowly biodegradable compounds.

agriculture residue alone, with purchased pulp and waste paper & purchaged pulp are shown in the TABLE A - 3 of Appendix A.

2.5 MINIMAL NATIONAL STANDARD (MINAS)

The MINAS for small pulp and paper mill effluent have been evolved after looking into practical difficulties, limitations and economic impact on industry. The Central Water Pollution Control Board has fixed MINAS for small pulp and paper mill effluents.

The tolerence limits are shown in the TABLE 2.1.

TABLE 2.1 : LIMITS FOR WASTE WATER DISCHARGED FROM SMALL PAPER MILLS

Sl.No.	Parameter	Value
1.	pH	6 - 9
2.	SS(mg/l)	100
3.	BOD(mg/l)	50

The standard does not suggest a limit for color and COD as no suitable economical technology is currently available for their reduction. Meeting MINAS level for effluents discharge is a major problem for small paper mills.

BIOOXIDATION OF EFFLUENTS

CONETENT

dissolved oxygen(DO) present in the water. The dissolve oxygen (DO) present in the effluent is utilised during their respiratory and metabolic activities. Micro-organism while using dissolve oxygen (DO) stablise the decomposable organic matter.

Biochemical oxygen demand (BOD) of effluents is usually the most important single criterian used to express pollutional effect. BOD is a measure of reducing properties of effluent, particularly of organic constituents. It is defined as "The quantity of oxygen utilised in the biochemical oxidation of organic matter in a specified time and at a specified temperature" (Gurnhem(1955)).

3.1 IMPORTANCE OF BOD

The BOD test have wide application in effluent treatment. It is a principal test applied to sewage and industrial effluent to determine the strength in terms of oxygen required for stabilization. It is the only test that gives a measure of amount of biologically oxidizable organic matter. BOD, is therefore, the major criterion used in stream pollution control, where organic loading must be restricted to maintain a desired oxygen level.

3.2 STAGES AND PHASES IN BOD EXERTION

The decomposable organic material serve as a source of food and energy for the microbial life present in the effluent. The micro-organism oxidize the organic matters in using them as their food for metabolic activities. The oxygen demand is exerted carbonaceous BOD or first stage BOD.

The waste, rich in nitrogen such as treatment plant effluents, the carbonaceous stage BOD is followed by a second stage, called nitrogenous stage, in which nitrogenous compounds are further broken into simplier compounds by nitrifying bacteria. The oxygen requirement for this stage is caused by a specific group of bacteria which obtain their food and energy from the oxidation of ammonia and nitrite nitrogen.

Buswell et.al. (1950) concluded their studies that nitrification does not occur until about eight days, by which about 80 - 85 percent of the ultimate carbonaceous BOD is already exerted. Many researchers including Counchain (1963), Keswan (1965) and Wild et.al.(1971) also stressed the importance of nitrification in case of effluents from treatment plants and concluded that the second stage BOD exertion may greatly increase the ultimate BOD.

The group of bacteria which exert carbonaceous BOD is known as heterotrophs and the optimum temperature for them ranges from 18 to 25°C. The nitrifying organism, nitrosomans and nitrobector, which use inorganic nitrogenous products for their metabolism are classed as autotrophic bactria and are said to have their optimum temperature for growth in range 25 to 28°C. The two stages of BOD exertion has been shown in Figure 3.1.

Existence of diphasic BOD exertion was first reported by Hoover et.al.(1953). Many researchers have further confirmed it. In waste waters having low substrate concentration there is a upto the end of plateau is called the first phase of BOD exertion. The remaining part of the carbonaceous stage BOD, after plateau is called second phase. It has been observed that at the plateau, the departure between BOD exertion curve and first order equation is maximum.

When the bacteria is unaccustomed to the use of new substrate or its environment, the rate of BOD exertion is very small in the beginning, till such time that the bacteria get acclimated to the substrate and/or its environment. This part of BOD exertion curve having slow rate of BOD progression is varily called **'Zeroth or Lag Phase'** and the duration from the begining of introduction of waste seed to the time when the BOD exertion picks up at a significant increasing rate is called 'Lag time'. Figure 3.3 shows such BOD exertion curve.

3.3 BOD KINETICS AND SOME FORMULATIONS

3.3.1 First Degree Equations

Studies of Sreeter and Phelps(1925) gave the following general expression concering the course of biochemical oxidation of organic matter -

"The rate of biochemical oxidation of organic matter is proportional to the remaining concentration of unoxidised substance, measured in terms of oxidiasibility."

This postulation leads to the formation of following equation for oxygen consumed by a particular point of time t from $t = 0$

or $dY/dt = K (L - Y)$

where, Y is BOD exerted till time t, K is the proportionality constant and is also known as rate constant and L is ultimate carbonaceous BOD. After integration we have :

$$Y = L [1 - \exp (-K t)] \tag{3.2}$$

or

$$Y = L [1 - 10^{-K't}) \tag{3.3}$$

Where, $K' = K/2.303$

Above equation is generally known as 'Monomolecular formula', Phelps model or first degree formula.

3.3.2 Second Degree and Multiorder Approach Equations

Young and Clark (1965) proposed the following second degree equation for BOD exeretion kinetics.

$$(dY/dt) = K (L - Y)^2 \tag{3.4}$$

with initial conditions, that Y = 0 at t = 0, the solution of this differential equation is

$$Y = \frac{L^2 K t}{1 + L K t} \tag{3.5}$$

Hewitt et.al.(1979) while trying to view BOD exertion kinetics in multiorder approach, proposed the generalisation of BOD kinetics as :

$$\frac{dY}{dt} = K (L - Y)^n \tag{3.6}$$

where, n is the degree of equation which on integration with appropriate initial conditions yields

$$Y = L [1 - \{1 + (n - 1)KL^{(n - 1)}.t\}]^{1/(n - 1)} \quad ;n \neq 1 \tag{3.7}$$

limit as $n - 1$. A plot of Y/L vs. $(KL^{(n-1)}.t)$ is shown in Figure 3.4. It is evident from the figure, that there is marked difference between first and higher degree equations.

In this model, the authors found that there is the tendency for the mean square error to decreases as the reaction order increases from 1 to 4. However, reduced error was accompanied by an approximate doubling of ultimate BOD. Ultimate BOD values calculated at the higher reaction order are unrealistically higher (Hewitt et.al (1979)).

Failure of second and multiorder equation of BOD exertion to demonstrate their superiority over first order equation leads to application of first order equation.

3.4 EFFECT OF TEMPERATURE ON BOD EXERTION (Y)

No other ecological parameter has been studied so widely and in detail as the temperature effect on BOD exertion. Gotaas (1948), Bewtra et.al.(1965) and Zonani (1967, 1969) have studied the effect of temperature in detail on different types of waste waters namely domestic sewage, treatment plant effluents and river water samples. Some of their common observations of concern are as follows.

3.4.1 Effect of Temperature on Ultimate BOD (L)

The ultimate BOD(L) is slightly affected, as the oxidizability of substrate increases with temperature.

Phelps (1925) gave the formulation for variation of

20°C, L(20) as

$L(T) = L(20)\ [0.6 + 0.02T]$ ———— 3.8

Gotaas (1948) noted following relation for their observations on sewage samples.

$L(T) = L(20)\ [1 - 0.00066T]$ ———— 3.9

Bewtra et.at (1965) noted following relation for their observations on two sewage samples

$L(T) = [L(20).1.005^{(T - 20)}\ /\ 1.05\ ;\quad 12 < T \le 40$ —— 3.10

$L(T) = L(20)[0.979 + 0.00645(T - 20)]\ ;\ 12 < T \le 40$ —— 3.11

Based on their experiences and observations, Bewtra(1966) noted that the first stage oxygen demand represents indirectly a more readily oxidizable type food material available to bacteria. Although metabolic rate is slower at lower temperature, it is expected that they will use up the food supply if sufficient time is given. Therfore it seems logical that ultimate first stage BOD should not v~~e~~ary greatly with temperature.

3.4.2 Effect of Temperature on Reaction Rate Constant (K)

K is a function of temperature and its relationship is given by Arrhenius experssion as :

$K = A \exp(-E/RT)$ ———— 3.12

where, A is a constant specific to reaction and E is the activation energy.

The common E values for waste treatment processes are in the range of 8.4 k J/mole to 84 k J/mole (Eddy, 1980).

Differentiating the Equation 3.12, we get

$d(\ln K)/dT = E/RT^2$ ———— 3.13

$$\ln K_1/K_2 = E\ (T_2 - T_1)/R\ T_1\ T_2 \qquad \text{———} \quad 3.14$$

where, K_1 & K_2 are rate constants at temperatures T_1 & T_2.

The quantity E/RT_1T_2 may be assumed to a constant and equal to C. The equation 3.14 can be rewritten as :

$$\ln K_2/K_1 = \exp(C\ (T_2 - T_1))$$

$$= \theta^{(T_2 - T_1)} \qquad \text{———} \quad 3.14$$

where, θ is temperature coefficient

Gotaas (1948) observed the effect of temperature ~~of~~ on K. He found the following values of θ for corresponding range of temperature.

TABLE 3.1 : VALUES OF θ FOR DIFFERENT TEMPERATURE RANGES

Temperature Range(°C)	θ
5 - 15	1.108
15 - 30	1.041
30 - 40	0.9657

Schroder(1964) while working on Mississppi river, found the values of θ which are given below -

TABLE 3.2 : VALUES OF θ FOR DIFFERENT TEMPERATURE RANGES

Temperatuer Range (°C)	θ
4 - 20	1.135
20 - 30	1.056

3.5 EFFECT OF pH ON BOD EXERTION

The organism which accomplish the biochemical oxidation of pH range rate of oxidation decreases (Chatterji(1965)).

There is no appreciable change in ultimate BOD in the pH range 6.2 to 7.2 but it definitely falls down in the pH range of 7.2 to 8.0 (Chatterji(1965)).

METHODS FOR DETERMINATION OF THE REACTION RATE PARAMETERS AND ULTIMATE BOD AND THEIR COMPARISON

CONTENT

The first order rate equation for BOD exertion describes the oxygen consumption or BOD as a function of time as follows :

$$Y = L\,(1 - \exp(-Kt))$$

or $$Y = L\,(1 - \exp(-K't))$$

where, $K = 2.30258\,K'$

There are various methods available for evaluating the reaction rate constants, K (or K') and ultimate BOD, L and has been discussed below.

4.1. METHODS OF DETERMINATION OF REACTION RATE CONSTANT AND ULTIMATE BOD

4.1.1 Thomas Method(1950)

This method is developed on the basis of similarity of two functions $(1 - 10^{-K't})$ and $2.3K't(1 + 2.3/6\ K't)^{-3}$.

$$(1-10^{-K't}) = [1-\{1-K't\ \text{Log}_e\ 10)+(K't)^2(\text{Log}_e 10)^2/2!$$

$$-(K't)^3(\log_e 10)^3/3! +(K't)^4(\log_e 10)^4/4!\ \ldots.]$$

$$= 2.3\ K't - (2.3K't)^2\ /2 +(2.3K't)^3\ /6 -$$

$$= 2.3K't[1-(2.3K't)/2+(2.3K't)^2/6-(2.3K'$$

$$2.3K't(1+2.3K't/6)^{-3} = 2.3\ K't\ [1 - 3x2.3K't/6 +3x4$$

$$3x4x5\ (2.3K't/6)^3\ \ \ldots.]$$

$$= 2.3\ K't\ [1 - 2.3K't/2 +(2.3K't)^2/6 -$$

$$(2.3K't)^3/21.6\ \ldots.] \qquad \text{———} \qquad 4.2$$

identical and difference between fourth terms is small. The difference between fourth and onward terms have got a little effect on the calculation. So the rate equation $(1-10^{-K't})$ can be replaced by $2.3K't(1+2.3K't/6)^{-3}$.

$$Y = L\ (1-10^{-K't})$$

$$= L\ [\ 2.3K't\ (1 + 2.3K't/6)^{-3}\ ]$$

Rearranging the terms and taking cube root of both sides.

$$(t/Y)^{1/3} = 1/[2.3K'L]^{1/3} + ((2.3K')^{2/3}/6xL^{1/3})xt \quad \text{———} \quad 4.3$$

This is a linear equation in $(t/Y)^{1/3}$ vs. t with slope $2.3K'^{2/3}/6xL^{1/3}$ and intercept $(1/2.3K'L)^{1/3}$ from which L and K' can be calculated.

4.1.2 Method of Moments (1950)

In this method data are fitted with a first order curve that has its first two moments (ΣY and ΣtY) equal to those of the experimental points. The equation expressing this condition for a series of Y in any specified time sequence in which i denotes the numerical order of the sequence are for the zero moments.

$$\underset{\text{(observed value)}}{\sum_{i=0}^{n} Y_i} = \underset{\text{(calculated value)}}{\sum_{i=0}^{n} L\ [1 - \exp\ (-Kt_i)]}$$

$$= (n+1)L - L\sum_{i=0}^{n}\exp(-Kt_i) \quad \text{———} \quad 4.4$$

Similarly, the first moments of the observed and theoritical values may be equated obtaining the following expersssion

$$\sum_{i=0}^{n} Y_i t_i = \sum_{i=0}^{n} Lt_i\,[1- \exp\ (-Kt_i)]$$

Eliminating L by dividing 4.5 by 4.4.

$$\frac{\sum_{i=0}^{n} Y_i}{\sum_{i=0}^{n} t_i Y_i} = \frac{(n+1) - \sum_{i=0}^{n} \exp(-K t_i)}{\sum_{i=0}^{n} t_i - \sum_{i=0}^{n} t_i \exp(-K t_i)} \qquad \text{———} \; 4.6$$

From equation 4.4

$$\sum_{i=1}^{n} Y_i/L = n - \sum_{i=1}^{n} \exp(-K t_i) \qquad \text{———} \; 4.7$$

In equation (4.6) and (4.7) the magnitude of right hand member can be computed once and for all different values of K and varying time sequence and can be plotted as shown in Figure 4.1.

Now compute the values of $\Sigma Y/\Sigma tY$ from given data. Enter the graph on $\Sigma Y/\Sigma tY$ scale with the value obtained, extend a horizontal line to K scale to get values of K. Extend the same vertical line to curve lebelled $\Sigma Y/L$ and from this point follow a vertical line to $\Sigma Y/L$ scale to get $\Sigma Y/L$ from which value of L can be obtained.

4.1.3 Rapid Ratio Method (1960)

J.P.Sheehy (1960) described a method for solving the monomolecular equation in which graphs are plotted in time vs. BOD_t/BOD_5 (Figure 4.2 to 4.4). Now find out ratio of BOD_t/BOD_5 and enter the graph with value on BOD_t/BOD_5 scale and with values t on t scale. Now extend these lines vertically, mark the point of intersection and get the value of K .

[illegible] ([illegible]) considers that Y is not equal to zero when time is zero. He presented an improved form of the monomolecular formula in the following manner.

$$\frac{d\,(L - Y)}{dt} = K\,(L - Y)$$

Integrating within the limits -

$Y = Y_o$ at $t = 0$

$y = y$ at $t = t$

$$\frac{(L - Y)}{(L - Y_o)} = \exp\,(-Kt)$$

$$= 10^{-K't}$$

$$y = L\,(1 - 10^{-K't}) + Y_o\,10^{-K't} \qquad \text{———— } 4.8$$

differentiation of equation 4.8 gives.

$$\frac{dY}{dt} = K'\,(L - Y_o)\,(\ln 10)\,10^{-K't}$$

$$\log\,(dY/dt) = \log\,[\,K'(L - Y_o)\,\ln 10\,] - K't \qquad \text{———— } 4.9$$

A graph of log (dY/dt) vs. t will be a straight line of slope -K'.

Rearranging equation 4.8

$$Y = L - (L - Y_o) \times 10^{-K't} \qquad \text{———— } 4.10$$

A graph of Y vs. $10^{-K't}$ will be a straight line of slope $(L - Y_o)$ and intercept L.

4.1.5 Method of Fujimoto (1964)

Fujimoto (1964) utilizes the method of finite differences for solving first order equation for first stage BOD as follows.

dt

where, Y_t = BOD exerted in time t days

$$\frac{(L - Y_t)}{(L - Y_0)} = \exp(-Kt)$$

$$= 10^{-K't}$$

$$(L - Y_t) = (L - Y_0)\,10^{-K't}$$

$$Y_t = (L - Y_0)(1 - 10^{-K't}) + Y_0 \qquad \text{———— 4.12}$$

$$Y_{t+h} = (L - Y_0)(1 - 10^{-K'(t+h)}) + Y_0$$

where, h is time difference

$$= L - (L - Y_t)\,10^{-K't}$$

$$Y_{t+h} - 10^{-K'h}\,Y_t - L(1 - 10^{-K'h}) = 0 \qquad \text{———— 4.13}$$

There exists a linear relationship between Y_t and Y_{t+h}. Plot of Y_{t+h} vs. Y_t gives a straight line with slope $10^{-K't}$ and intercept $L(1 - 10^{-K't})$. So if data are available, the parameter L and K' can be obtained. The value of L can also be obtained directly from the intersecting point of straight line and x = Y.

4.1.6 Method of Bagchi and Chaudhary(1965)

In this method the technique used by Fujimoto is modified by plotting Y_t against the difference between Y_{t+h} and Y_t

$$L_t = L_0\,(10^{-K't}) \qquad \text{———— 4.14}$$

$$Y_t = L_0\,(1 - 10^{-K't}) \qquad \text{———— 4.15}$$

$$Y_{t+h} = L_0\,[1 - 10^{-K'(t+h)}] \qquad \text{———— 4.16}$$

where, L_0 = Ultimate BOD at time t=0

L_t = Ultimate BOD at time t=t

Y_t = BOD exerted at time t

h = time difference

$$Y_{t+h} - Y_t = L_o \times 10^{-K't} (1 - 10^{-K'h})$$

Replacing $L_o \times 10^{-K't}$ by L_t

$$Y_{t+h} - Y_t = L_t (1 - 10^{-K'h})$$

$$Y_{t+h} - Y_t = (L_o - Y_t)(1 - 10^{-K'h})$$

$$\frac{Y_{t+h} - Y_t}{L_o(1 - 10^{-K'h})} + \frac{y_t}{L_o} = 1 \qquad \text{———— } 4.17$$

Equation 4.17 is comperable to well known form of the straight line equation described by

$$\frac{x}{a} + \frac{y}{b} = 1 \qquad \text{———— } 4.18$$

If Y_t is plotted against $(Y_{t+h} - Y_t)$ the intercept of the straight line on the ordinate and the abscissa are represented by

$b = L_o(1 - 10^{-K'h})$

$a = L_o$

The graph can be plotted at different values of h. The intercept on abscissa is independent of h and is equal to L, while the intercept on the ordinate changes accordingly to equation (4.18). In this way average value of K can be obtained giving better corelation with experimental values.

4.1.7 Method of Least Square by Reed and Therault (1931)

Reed and Therault (1931) developed a method of least squares to find out values of K and L. He made following assumptions while developed a formula.

(a) If all determinations had been made at any single time the absolute error would have approximated anormal distribution.

degree of precision so that accidental errors in t are negligebly small in relation to corresponding error in Y.

(c) Proper allowance has been made for constant errors.

(d) The equation selected to represent a given process should either be in linear form or it should be possible to place it in linear form without disturbing condition (a) regarding the distribution of error.

Let Y and t are quantities obtained by direct observations and these observations are represented by monomolecular formula

$Y_1 = L_1 (1 - \exp(-Kt_1))$ ———— 4.19

where '1' denotes that true values of Y, L, and t are being considered.

Let the residual constant error in Y is q, and the corresponding error in t is r. Where, q and r are small constant errors. So above eqation takes the form

$(Y - q) = L_1 (1 - \exp(-K(t-r)))$ ———— 4.20

Where, q and t refer to the actual observations uncorrected for constant errors.

$Y = L_1 + q - L_1 \exp(-K(t-r))$

$Y = (L_1 + q)(1 - L_1/(L_1 + q))\exp[-K(t-r)]$

$Y = [L_1 + q)(1 - \exp(K s). \exp\{-K(t-r)\}]$

$Y = L(1-\exp(-K(t+w))$ ———— 4.21

where, $L_1/(L_1 + q) = \exp(K s)$

$s = 1/K \ln(L_1/L_1 + q)$

$w = -(r+s)$

$L = (L_1 + q)$

t may be accounted for by a shift w, in the time axis. It is to be borne in mind, therefore, that w in equation (4.21) refer not necessarily to a time errors but rather to the resultant effect of all constant error on time. Now for the purpose of reducing this expression to a linear form let it be assumed that an approximate value of K has first been obtained by any convnient method so that the most probable value of K is given by relation

$$K = K_1 + Z$$

Where, K_1 is a trial value and Z is a relatively small number.

Let w be represented by the relation.

$$w = w_1 + i$$

Where, w_1 is a first approximation to the value of w and i is a small constant.

$$t + w = t + w_1 + i = t_1 + i$$

Equation 4.21 becomes

$$Y = L\{1 - \exp(-k_1 + Z)(t_1 + i)\}$$

$$= L\{1 - \exp(-K_1 t_1)\ \exp(-Ki - Zt_1)\} \qquad \text{———— } 4.22$$

$[-(Ki + Zt_1)]$ is a small quantity.

$$\exp - (Ki + Zt_1) = 1 - Ki - Zt_1$$

Equation 4.22 becomes

$$Y = L\ [1 - \{\exp(-K_1 t_1)\}x\{1 - Ki - Zt_1\}]$$

$$Y = L[1 - \exp\{-Kt_1\}] + LZ[t_1\ \exp\{-K_1 t_1\}] + LiK\ [\exp\{-Kt_1\}] \qquad \text{———— } 4.23$$

$$Y = af_1 + bf_2 + cf_3 \qquad \text{———— } 4.24$$

Where, $a = L$

$b = LZ$

$C = LiK = Li(K_1 + Z)$

$f_2 = t_1 \exp(-K_1 t_1)$

$f_3 = \exp(-K_1 t_1)$

For equation 4.21 the difference between an observed and a calculated quantity is

$r = Y - af_1 - bf_2 - cf_2$

and sum R of the squares of the residual error is

$R = \Sigma(Y - af_1 - bf_2 - cf_3)^2$

By definition the most probable value of the constants a, b and c will be obtained when R is minimum so from calculus, the equations defining the condition are

$$\frac{\delta R}{\delta a} = \Sigma f_1 Y - a\Sigma f_1^2 - b\Sigma f_1 f_2 - c\Sigma f_1 f_3 = 0 \qquad \text{———— } 4.25$$

$$\frac{\delta R}{\delta b} = \Sigma f_2 Y - a\Sigma f_1 f_2 - b\Sigma f_2^2 - c\Sigma f_2 f_3 = 0 \qquad \text{———— } 4.26$$

$$\frac{\delta R}{\delta c} = \Sigma f_3 Y - a\Sigma f_1 f_3 - b\Sigma f_2 f_3 - c\Sigma f_3^2 = 0 \qquad \text{———— } 4.27$$

Solving equations 4.25 to 4.27 algebrically we can find out values of L, K and w.

4.1.8 Log Difference Method (1936)

The author submits a rapid and simple procedure for approximating the values of K and L. It requires that the BOD be observed at equal intervals of time.

To Find K'

If h equal a uniform interval of time then

$$Y_t = L(1 - 10^{-K't}) \qquad \text{———— } 4.28$$

substracting 4.28 from 4.29 and taking log.

$$\log d = [\log L + \log(1 - 10^{-K'h})] - K't \qquad \text{———} \quad 4.30$$

Where, $d = y_{t+h} - Y_t$

here, $[\log L + \log(1 - 10^{-K'h})]$ is constant, since h is uniform.

hence, $\log d = (c - K't)$ ——— 4.31

This equation is a linear equation for which the value of K may be found by least square procedure.

$$\Sigma R^2 = \Sigma(c - K't - \log d)^2 \qquad \text{———} \quad 4.32$$

For ΣR^2 to be minimum

$$\frac{\delta \Sigma R^2}{\delta K} = \frac{\delta R}{\delta c} = 0$$

From equation 4.32

$$\frac{\delta \Sigma R^2}{\delta c} = 2\,\Sigma(c - K't - \log d) = 0$$

or $nc - K'\Sigma t - \Sigma \log d = 0$ ——— 4.33

$$\frac{\Sigma \delta R^2}{\Sigma K} = 0$$

$$2\,\Sigma\,(c - K't - \log d)\,(-t) = 0$$

$$-\,c\Sigma t + K'\Sigma t^2 + \Sigma t \log d = 0 \qquad \text{———} \quad 4.34$$

Eliminating c from equ. 4.33 and 4.44 by multiplying by t and n respectively and summing

$$nK'\Sigma t^2 + n\Sigma t \log d - K'(\Sigma t)^2 - \Sigma t \Sigma \log d = 0$$

$$K' = \frac{\Sigma t \Sigma \log d - n\Sigma t \log d}{n\Sigma t^2 - (\Sigma t)^2} \qquad \text{———} \quad 4.35$$

since n values of t are equally spaced, we may determine

$$(\Sigma t) = (1 + 2 + 3 + \ldots\ldots.) = n(n+1)/2$$

substituting these quantities in equation 4.35 and simplifying.

$$K' = [6/n(n^2-1)][(n+1)\Sigma \log d - 2\Sigma t \log d] \tag{4.36}$$

To Find L

Applying least square in equation 4.28.

$$\Sigma R^2 = [\Sigma L(1-10^{-K't})-Y_t]^2$$

$$\frac{\delta \Sigma R^2}{\delta L} = 2\Sigma[L(1-10^{-K't})-Y_t][1-10^{-K't}] = 0$$

$$L\Sigma(1-10^{-K't})^2 - \Sigma(1-10^{-K't})Y_t = 0$$

$$L = \frac{\Sigma(1-10^{-K't})Y_t}{\Sigma(1-10^{K't})^2} \tag{4.37}$$

$$\Sigma(1-10^{-K't})^2 = n - 2x\Sigma 10^{K't} + 10^{-2K't}$$

for equal spacing of t

$$\Sigma(1-10^{-K't})^2 = [n-2*10^{-K'}(10^{-nK'}-1)/(10^{-K'}-1) + 10^{-2K'}(10^{-2nK'}-1)/10^{-2K'}-1)]$$

Substituting this value in equation 4.37

$$L = \frac{\Sigma(1-10^{-K't})Y_t}{n-2x10^{-K'}[(1-10^{-nK'})/(1-10^{-K'})]+10^{-2K'}[1-10^{-2nK'})/(1-10^{-2K'})\}} \tag{4.38}$$

4.1.9 Marquardt Non Linear Optimisation Method

All the method described uptil now require the use of graph (except Reed Therault method). Now a days PC's and computer have made the calculation very easy. Non linear optimisers are available which gives very accurate results. Marquard presented a non linear optimiser in 1963. This optimiser is also used to calculate the values of reaction rate parameters.

RATE PARAMETERS

Orford and Ingram (1953) have studied BOD for sewage, their BOD data (Table B-1 of Appendix B) have been used to compare the different available methods.

The estimated values of K and L using different method are listed in table B - 2 of Appendix B. It is evident from Table B-2 that there is wide variation in the estimated values of K and L obtained by different methods. The probable reason of difference in K and L values obtained by different methods is due to poor adherence to kinetics of the oxidation of organic matter in the effluent to first order.

Figure 2.1 to 2.4 show the calculated values of BOD along with observed BOD with time. From these Figures, it is evident that the calculated values obtained by Reed Therault method is most close to the observed BOD followed by method of moments and Weigand. The total absolute deviation of calculated values of BOD from the obsevred values are shown in Table B - 3 of Appendix B. It is evident from the Table B - 3 that the method of Reed Therault is the best method followed by method of moments and Weigand. Similar observations were also observed by Marske et.al.(1972) and Ludzack et.al. (1953).

PAPER MILL UNDER STUDY AND EFFLUENT SAMPLING

CONTENT

India are based on agriculture residue and majority of them do not have any effluent treatment facilities. Due to the economical constrains, these mills were draining their effluent without any treatment, resulting the heavy damage to the ecology. Such paper mills were recently characterised by Go~~a~~yal (1989). The present study was an extension to find the oxidative behaviour of such a paper mill.

5.1 PLANT INFORMATION

Mill produces 80-160 gsm range of unbleached kraft paper and uses non wood fibrous raw material such as rice and paddy straw, bagasse, hessian, and 'Tanta', the locally available agro residue. The fibrous raw material tanta is available in plenty at river banks of western UP. Tanta has proven its importance in paper making as a raw material having qualities comparable to those of straw and bagasse.

The paper mill have installed capacity of 3600 TPA and its reported mill production for the year 1988-89 was 3420 Tons with 95% capacity utilisation.

5.2 PROCESS DESCRIPTION

The block diagram of the mill is shown in Figure 5.1. The brief description of the different processing stages for the manufacture of paper used in the mill are described below.

Raw Material Preparation

The raw material, Tanta, is cut into small pieces with the help of a grass cutter and then taken to digestor floor by a belt any treatment are also taken to digestor floor by a belt conveyor.

Pulping and Washing

The main purpose of pulping is to remove lignin associated with fibres. The raw material is conveyed to the digestor floor and is manually fed into digestors. The raw material is cooked chemically by sodium hydroxide in rotary batch digestors with direct steaming facility. The cooking cycle and its conditions are given in Tables 5.1 & 5.2 respectively. Formed sodium lignate from the pulp is washed in washer which consists of a rotating washing drum. It is a batch operation and takes 3 to 4 hrs. for complete washing. The consistency of pulp is maintained around 5 to 6%, using back water from paper machine and thickner filtrate tank.

TABLE 5.1: DIGESTOR COOKING CYCLE

Operation	Time (hrs.)
Loading Time	1.5
Steaming Time	0.5
Time to Temperature	1.5
Time at Temperature	2.25
Discharging Time	0.25
Total Time	**6.00**

Variable	Digestor 1	Digestor 2
1. Digestor Capacity, ton OD raw Material	3.0	5.0
2. Digestor Volume, m^3	28.0	40.0
3. Chemical Charge (%NaOH)	9-10	9-10
4. Concentration of Liquor, gpl	700.0	700.0
5. Volume of Liquor Charged Per Cook, m^3	0.43	0.71
6. Bath Ratio	1:3-3.5	1:3-3.5
7. Time to Temperature, hrs.	1.5	1.5
8. Time at Temperature, hrs.	2.25	2.25
9. Maxium Temperature, °C	150-160	150-160
10. Cooking Pressurer, kg/cm^2	6-6.5	6-6.5
11. Pulp Yield, %*	35	35

***washed screened unbleached**

Stock Preparation

The washed pulp is taken to a beater and after sufficient defibring for about 2 hrs. at 5 to 6% consistency is collected in chest no.1 at about same consistency. From the chest, pulp is drawn in a chest known as mixing chest where rosin and alum are added in 7 and 40 kg. amount respectively per ton of finished paper and are mixed properly to get a uniform stock for further processing.

Before addition to the machine chest, pulp is refined in a at very low consistency of about 0.5 to 1%. The accept of primary centricleaner is used as feed stock for paper manufacturing, whereas primary rejects are further cleaned in secondary centricleaner. The accept are recycled to the inlet of primary centricleaner, where rejects are drained off.

Paper Making

The accept from primary centricleaner at 0.5 to 1% consistency is fed to the open type head box. About 99.5% water, present in slurry in the head box is reduced to 7-8% at the pope reel.

Major portion of water is removed in wire part section. The water recovered in this section is reused as dilution water for the stock. Machine broke (torn papers) are collected in couch pit, from where they are recycled back to machine chest by a pump. The remaining portion of the water removed form sheet by passing it through a large diameter (3.66 m) steam heated cylinder known as MG cylinder. Steam condensate from cylinder are collected in a small tank and is mixed in feed to the boiler. The paper from the dryer is wrapped on a pope reel and with the help of rewinder and cutter desired size of paper sheets are prepared.

5.3 EFFLUENT SAMPLING

The block diagram of the paper mill, Figure 5.1, shows the different effluent streams of the paper mill and different sampling points are also indicated from where samples are mill section in the mill under study. These two streams meet in a nearby Nullah. The pulp mill section effluent stream is contrbuted by a poucher washer, beater and hydrapulper. The paper machine section stream includes over flows of paper machine, centricleaners rejects, thickner tank overflow and fresh water tank over flow and some water from boiler house. The following points were taken into consideration for collecting the samples.

(1) The sample collected should be homogenous.

(2) Flow of the stream and its temperature should be measured.

The channel flow was measured by using V - notch weirs. The following relationship (Garde(1983)) was used for calculatig the flow rate.

$$Q = (8/15) x C_D x h^{5/2} x (2g)^{0.5} x \tan\theta/2$$

where, Q - flow rate, m^3/sec

h - height of flow, m

g - grvitational constant, m/sec^2

θ - angle of notch=90°

C_D - discharge coefficient=0.58

Samples were collected for a day (24hrs.) at an interval of two hours from the points 1,2 & 3 as indicated in Figure 5.1.

The following parameter were evaluated for each sample collected :

1. BOD
2. COD
3. pH

6. Oil & Grease

7. Total Kjaldhal Nitrogen

The methedology used for estimating these parameter were adopted from prescribed Indian Standards (IS 3025).

In order to supress the exertion of second stage (Nitrogenous) BOD, 4 to 6 ml/l methylene blue of 0.05% concentration in dilution water was added (Young (1973)).

RESULTS AND DISCUSSION

CONTENT

Composite samples were collected six times to cover various seasons of the year. All possible combination of a small mill to include pulp mill, paper mill and total mill effluents were tried. These samples were analysed according prescribed Indian Standards. The results are reported in Appendix C.

Table C-1 to C-3 of Appendix-C shows variation in flow rate and temperature of pulp mill, paper mill and total mill effluents respectively. All streams shows significant fluctation in temperature and flow rate. The flow rate for pulp mill effluent stream ranges 0.18 m^3/hr. to 63 m^3/hr. and 15.6 to 62.04 m^3/hr. for I and II samples respectively, it ranges from 5.88 to 13.92 m^3/hr. and 1.26 to 12.9 m^3/hr. for I and II samples of paper machine, while for I and II samples of total mill effluent the range is 72.6 to 124.8 m^3/hr. and 31.08 to 57.06 m^3/hr respectively.

The flow variation in the pulp mill effluent stream could be due to the batch operation such as pulp washing, beating etc. For paper machine effluents streams, the flow variation could mainly be due to the presence of over flow streams from thickner filterate and fresh water tanks. Besides this, some variation could occur due to paper break down or basis weight change. The total mill stream comprises of pulp mill and paper mill streams, so variation are obvious.

At the time of digestor blowing the temperature of pulp mill effluent stream is maximum and it goes down as washing proceeds, resulting the variation in the temperature of pulp mill effluent stream. The possible reason for variation in the temperature of

---

[illegible]

The effect of ambient temperature on effluent stream is not expected as sampling locations are near to the effluent generation sources.

The characterstics of effluent discharged from pulp mill, paper mill and total mill effluent are shown in Table C-4 to C-6 of Appendix C.

The pH of pulp mill effluent is of the order of 9.6, while that of paper mill effluent it is of the order of 6.4. The total mill effluent pH is close to 7.0.

The COD loads for I and II samples of pulp mill stream is 4800 and 4400 mg/l, for paper mill stream 420 & 380 mg/l and for total mill streams 3200 & 3500 mg/l respectively. Total Kjaldhal Nitrogen is found to be nil in all the cases. Oil & grease are also measured and shown in Table C-4 to C-6 of Appendix C and are 1034, 740, 80, 74, 842, 348 mg/l for I and II samples of pulp mill, paper mill and total mill effluent streams respectively.

6.1 BOD EXERTION WITH TIME

Table C-7 to C-9 of Appendix C shows the BOD exertion with time for all the three streams. Figures 4.1 to 4.3 indicates that BOD exertion with time curve is nearly a first order equation curve. The BOD rate equation parameters are calculated from various methods using these values and are shown in Table C-10 of Appendix C. The total absolute deviation of the calculated values of BOD from the observed values of BOD are shown in Table C-11 of Appendix C. It is evident from Table C 11 that the method significantly influence the the values of parameters. The probable reason of difference in reaction rate constant, K, and ultimate BOD, L, values obtained by different methods are that the BOD exertion curve with time is not excatly the first order equation curve.

It is also evident from the Table C-11 that Reed Therault method gives minimum total absolute deviation followed by Marquardt method and the method of moments. The reason, that the Reed Therault method gives best results, they introduces a third parameter in the rate equation. This third parameter includes the error introduced in the measurement of BOD exertion and time. The introduction of third parameter in BOD rate equation increases the accuracy in the parameter estimations.

Parameters were recalculated using modified Reed Therault equation. Non linear least square optimizer, Marquardt method, was employed. Table C-12 of Appendix C shows the comparison of parameters obtained by Reed Therault method and Marquardt method using modified rate equation. From the Table, it is evident that values of rate constant, K, and ultimate BOD, L, are excatly equal in both the cases. The total absolute deviation is 324.1 and 326.2 for Reed Therault and Marquardt methods respectively.

Reed Therault method and Marquardt methods are same while Reed Therault linearize the function and applied the linear least square to estiamte the parameters and at the same time the method employs the hand calculations while using non linear least square optimizer (Marquardt method) the desk top PC's can be used which are now commonly available. With this comparison all other for different samples Marquardt method is being employed.

6.2 Effect of Temperature on BOD Exertion

Temperature is most sensitive parameter in an ecological system and hence it has been studied in details by many researchers (Gotaas (1948), Bewtra et.al (1965), Zonani (1967, 1969)).

Two grab samples of total mill effluent were collected for measuerment of BOD. One sample was used to measure the BOD in temperature range of 20-30 °C and second sample in the range of 10-20 °C. Table C-13A and C-13B the observed BOD values for temperature 20, 25, 30 °C and 10, 15, 20°C respectively. Table C-14 shows the values of rate constant, K, and ultimate BOD, L, at each of above mentioned temperatures. It is evident from the Table C-14 that the values of rate constant, K, and ultimate BOD, L, increases as temperatures but increase in ultimate BOD, L, is not significantly high.

The increase in the value of rate constant, K, could be due to increase in the activity of bacteria. The activity of bacteria reaches to a optimum at temperature 35°C.

The Arrehinus temperature dependency is shown in Figure 4.4. It is evident from the Figure 4.4 that there is a break in the activation energy curve at 20°C. Similar observation was also observed for other liquid waste (Schroder(1964)).

The values of activation energy, E, and temperature coefficient, θ, for different temperature ranges are shown in Table C-15 of Appendix C. The values of temperature cofficient, respectively. The activation energy, E, are 80.5 kJ/mole and 24.8 kJ/mole for temperature ranges 20-30°C and 10-20°C respectively. These activation energies for the bio-oxidation of agriculture based pulp and paper industries effluent also fall within the range of liquid waste (Eddy(1980)).

6.3 Effect of pH

The pH values of effluent shows its acidic or alkaline nature. This is an important factor for biochemical oxidation.

Table C-16 of Appendix C shows the observed BOD values at different pH from a grab sample of total mill effluent stream. It is evident from the Table C-16 that the the BOD range remain same for pH 6.6 to 7.8 while a drastic decrease in the BOD value beyond this pH range.

Table C-17 shows the values of rate constant, K, and ultimate BOD, L, calculated at different pH. It is evident from the Table C-17 that values for K and L are low at pH 6.0 and 8.2 and a marginal difference for the pH range from 6.6 to 7.8. This behaviour indicates that the bacteria are most active at near neutral pH.

CONCLUSIONS AND RECOMMONDATIONS

7.1 Conclusions

7.2 Recommondations

The present study was divided into two major sections : One was to compare the different method available to estimate the first order kinetic model for the effluent bio-oxidation and the second study was the kinetic study for the agriculture based small paper mills effluents.

In the comparison studies the BOD data for sewage system was taken and the available eight methods were compared based on the total absolute deviation for the observed BOD values. Reed Therault method which is based on linear least square method was come out to be the best method followed by method of moments and Weigand method.

In the kinetic studies, for different samples obtained from the agro-based paper mill effluent. BOD exerted at different time intervals were measured and it was observed that the second phase (Nitrogenous phase) BOD exertion was negligible.

The BOD exerted with time followed the first order kinetic equation. The kinetic model parameters, rate constant, K, and ultimate BOD, L, were estimated by all the eight methods also, Reed Therault method was the best. A non-linear least square method (Marquardt method) was also applied and results were similar to Reed Therault method.

Temperature and pH parameter were also studied to see the variation in the BOD exertion. A break in the Arrhenius plot was observed at about 20°C. The activation energy were within the range of liquid waste. The activity of the bacteria were maximum near neutral.

The following recommondations are made.

1. The mill must segregate the pulp mill section effluent and treat seperately.
2. More reaserch work is required to find out stability of chemical recovery system.
3. For designing the effluent treatment plant, it desired to know the effect of temperature variation excatly i.e. activation energy of BOD kinetics. Therefore, further study is recommended to study the effect of temperature. A wider range of temperature is requested.
4. The effect of pH should studied for wide range.
5. A further study can be recommonded to study and compare different order kinetics for accuracy of designing the effluent treatment plant.
6. It is recommonded to carry out study the effect of toxicants e.g. mercury, cadmium, cyanide etc. on BOD exertion.
7. A non-linear least square method should be employed in estimating the kinetic parameters.

A-1 Installed Capacity of Pulp and Paper Mills in India

A-2 Composition Various Raw Materials

A-3 Characterstics of Waste Water from small Mills

Category	Capacity Range (TPA)	No. of Units	Annual Installed Capacity (Lakh Tons)
1.	Above 20,000	30	14.573
2.	10,000 to 20,000	24	3.971
3.	5,000 to 10,000	87	7.286
4.	2,000 to 5,000	107	3.617
5.	Below 2,000	57	0.875
	Total	305	30.332
News Print Mills		4	3.275

Production During 1988 = 17.20 Lakh Tons

Effective Capacity = 22.42 Lakh Tons

*** DGTA Report Feb 24,1989**

Sl. No.	Resources	Ash %	Legnin %	Pentosens %	Cellulose %	Average Length (mm)
1.	Rice Straw	14–20	12–14	23–25	46–49	1.5
2.	Wheat Straw	6–7	16–17	27–28	52–54	1.5
3.	Bagaasse	2–4	19–21	30–32	59–62	1.7
4.	Jute Sticks	1–2	19–20	34–36	62–65	0.8
5.	Bamboo	1–3	24–29	16–18	60–63	2.7
6.	Hard Wood	1–2	23–30	19–26	54–61	1.25
7.	Soft Wood	1–2	26–34	7–14	53–62	3.0

* Hassan Ibraham (1977) and Rao (1986)

Sl. No.	Prticulars	Agro residue based	Agro residue + Purchased pulp based	Waste paper + Purchased pulp based
1.	Volume, m^3/T	252	170	107
2.	pH	6 - 8.5	6 - 8.5	7 - 7.7
3.	S.S. (mg/l)	615	585	542
	(Kg/T)	155	99.5	58
4.	BOD_5			
	(mg/l)	698	520	187
	(Kg/T)	176	88.4	20
5.	COD (mg/l)	2940	1650	654
	(Kg/T)	741	280	70
6.	Lignin			
	(mg/l)	563	--	--
	(Kg/T)	142	--	--

*** Comorehensive Document for Small Pulp and Paper Industry, NEERI (1985)**

B 1 Data of Orford and Ingram for Sewage

B 2 Estimated Values of K and L from Different Methods

B 3 Total Absolute Deviation of Calculated Values of BOD exertion from Obsered Values

Time, t (days)	BOD (mg/l)
1	45
2	65.4
3	80
4	91.6
5	100
6	108.5
7	114
8	119
9	123
10	125
11	129
12	133
13	136
14	137
16	139
18	140

Sl. No.	Methods	K (day^{-1})	L (mg/1)
1.	Thomas (Thomas (1950)	0.253	132.7
2.	Moments (Moore et.al (1950)	0.288	136
3.	Rapid Ratio (Sheehy(1960))	0.281	129
4.	Weigand (Weigand(1954))	0.230	137
5.	Fujimoto (Fujimoto(1964))	0.235	133.3
6.	Bagchi Chaudhary (Bagchi et.al. (1965))	0.239	138
7.	Reed Therault (Reed et.al. (1931))	0.207	142.4
8.	Log Diffrence (Fair (1936))	0.219	146.4

OBSERVED VALUES

Sl.No.	Methods	Total Absolute deviation
1.	Thomas (Thomas (1950)	98.79
2.	Moments (Moore et.al (1950)	58.8
3.	Rapid Ratio (Sheehy(1960))	95.74
4.	Weigand (Weigand(1954))	69.3
5.	Fujimoto (Fujimoto(1964))	96.89
6.	Bagchi Chaudhary (Bagchi et.al. (1965))	103.90
7.	Reed Therault (Reed et.al. (1931))	16.56
8.	Log Diffrence (Fair (1936))	77.99

APPENDIX C

MILL EFFLUENT

Sl. No.	Time	Sample I		Sample II	
		Flow Rate (m^3/hr.)	Temperature (°C)	Flow Rate (m^3/hr.)	Temperature (°C)
1	8 pm	0.18	22	19.68	27
2	10 pm	63.00	38	35.16	32
3	12 pm	33.00	28	58.74	36
4	2 am	42.60	29	52.32	34
5	4 am	42.60	32	45.00	29
6	6 am	0.90	29	42.90	23
7	8 am	12.00	27	62.04	35
8	10 am	3.00	25	38.28	24
9	12 am	15.60	27.5	26.76	29
10	2 pm	58.80	30.5	15.60	25
11	4 pm	46.88	28	45.00	28
12	6 pm	30.00	34	35.16	31
Average Value		**30.00**	**29.34**	**39.72**	**29.42**

Sl. No.	Time	Sample I		Sample II	
		Flow Rate (m^3/min)	Temperature (°C)	Flow Rate (m^3/min)	Temperature (°C)
1	7 pm	10.38	25	6.06	22
2	9 pm	6.54	27	9.00	27
3	11 pm	13.92	24	5.28	25
4	1 am	9.24	29	1.26	29
5	3 am	9.78	24	6.30	31
6	5 am	11.28	23.5	4.20	23.5
7	7 am	5.88	30	6.54	28
8	9 am	7.68	26	8.46	27
9	11 am	6.30	24.5	11.58	34
10	1 pm	8.46	27	9.00	33
11	3 pm	10.38	23.5	4.20	22
12	5 pm	12.24	30	12.90	25
Average Value		**9.36**	**26.1**	**7.08**	**27.21**

Sl. No.	Time	Total Mill Effluent Sample			
		I		II	
		Flow Rate (m³/hr.)	Temperature (°C)	Flow Rate (m³/hr.)	Temperature (°C)
1	8 pm	72.60	22	27.78	26
2	10 pm	124.80	28	57.06	24
3	12 pm	82.80	27.5	34.56	29
4	2 am	88.20	27	47.82	36
5	4 am	93.60	29	31.08	32
6	6 am	77.40	29	32.82	25
7	8 am	72.60	29.5	53.10	32
8	10 am	72.60	24.5	40.80	34
9	12 am	88.20	28.5	38.94	29
10	2 pm	118.20	29	36.42	25
11	4 pm	105.00	26	44.28	31
12	6 pm	93.60	28	39.60	28
Average Value		**90.60**	**27.25**	**40.32**	**29.25**

Sl.No.	Particulars	Sample I	sample II
1.	pH Range	9.6 ± 0.2	9.4 ± 0.2
2.	Temperature Range (°C)		
	Ambient	10 - 22	14 - 28
	Effluent	22 - 38	23 - 36
3.	Total Solids (mg/l)	7948	6480
4.	Total Suspended Solids (mg/l)	5298	4390
5.	Total Dissolvsd Solids (mg/l)	2650	2090
6.	Volatile Suspended Solids(mg/l)	3246	2364
7.	Fixed Suspended Solids (mg/l)	2052	2026
8.	Volatile Dissolved Solids (mg/l)	1534	1146
9.	Fixed Dissolved Solids (mg/l)	1116	944
10.	Total Kjaldhal N_2 (mg/l)	Nil	Nil
11.	Oil and Grease (mg/l)	1034	740
12.	COD (mg/l)	4800	4400

Sl.No.	Particulars	Sample I	Sample II
1.	pH Range	6.4 ± 0.2	6.5 ± 0.2
2.	Temperature Range (°C)		
	Ambient	11 - 24	14 - 28
	Effluent	23.5 - 30	22 - 34
3.	Total Solids (mg/l)	1420	1380
4.	Total Suspended Solids (mg/l)	606	622
5.	Total Dissolvsd Solids (mg/l)	814	758
6.	Volatile Suspended Solids(mg/l)	392	412
7.	Fixed Suspended Solids (mg/l)	214	210
8.	Volatile Dissolved Solids (mg/l)	304	428
9.	Fixed Dissolved Solids (mg/l)	510	330
10.	Total Kjaldhal N_2 (mg/l)	Nil	Nil
11.	Oil and Grease (mg/l)	80	74
12.	COD (mg/l)	420	380

Sl.No.	Particulars	Sample I	Sample II
1.	pH Range	7.0 ± 0.2	7.0 ± 0.2
2.	Temperature Range (°C)		
	Ambient	10 - 22	11 - 24
	Effluent	22 - 29	24 - 36
3.	Total Solids (mg/l)	6376	5948
4.	Total Suspended Solids (mg/l)	3006	2870
5.	Total Dissolved Solids (mg/l)	3370	3078
6.	Volatile Suspended Solids(mg/l)	1648	1548
7.	Fixed Suspended Solids (mg/l)	1358	1322
8.	Volatile Dissolved Solids (mg/l)	1858	1208
9.	Fixed Dissolved Solids (mg/l)	1512	1870
10.	Total Kjaldhal N_2 (mg/l)	Nil	Nil
11.	Oil and Grease (mg/l)	842	348
12.	COD (mg/l)	3200	3500

Sl. No.	Time (days)	BOD (mg/l)	
		I Sample	II sample
1.	1	590	560
2.	2	1030	970
3.	3	1320	1260
4.	4	1560	1420
5.	5	1660	1540
6.	6	1760	1620
7.	8	1860	1710
8.	9	1900	1730
9.	10	1920	1760
10.	12	1930	1770
11.	15	1950	1780

Sl. No.	Time (days)	BOD (mg/l)	
		I Sample	II Sample
1.	1	65	60
2.	2	130	105
3.	3	175	150
4.	4	200	170
5.	5	220	190
6.	6	235	205
7.	8	255	225
8.	9	260	235
9.	10	270	240
10.	12	275	245
11.	15	280	250

Sl. No.	Time (days)	BOD (mg/l)	
		I Sample	II Sample
1.	1	420	500
2.	2	750	860
3.	3	1000	1110
4.	4	1120	1310
5.	5	1260	1420
6.	6	1350	1510
7.	8	1450	1590
8.	9	1480	1650
9.	10	1510	1670
10.	12	1540	1700
11.	15	1550	1720

Sl. No.	Methods		Effluents Samples					
			Pulp Mill		Paper Mill		Total Mill	
			I	II	I	II	I	II
1.	Thomas Method	K	0.329	0.272	0.290	0.249	0.272	0.302
		L	2166.4	2493.3	307.4	276.8	1754.5	1928.1
2.	Method of Moments	K	0.378	0.389	0.297	0.265	0.320	0.348
		L	1963.8	1789.5	280.9	255.4	1568.5	1717.8
3.	Rapid Ratio Method	K	0.387	0.403	0.300	0.276	0.325	0.366
		L	1892.7	1785.1	286.8	254.9	1555.9	1687.8
4.	Method of Weigand	K	0.387	0.401	0.242	0.274	0.352	0.334
		L	1950	1780	290	255	1540	1720
5.	Method of Fujimoto	K	0.368	0.405	0.322	0.249	0.322	0.350
		L	2015	1770	306.9	251	1581.8	1694.9
6.	Bagchi and Chaudhary Method	K	0.391	0.405	0.380	0.260	0.341	0.362
		L	1965	1798	272	256	1580	1715
7.	Method of Least Square by Reed & Therault	K	0.394	0.410	0.327	0.283	0.332	0.350
		L	1953.8	1781.8	279.0	253.6	1563.4	1721.7
8.	Log Difference	K	0.600	0.592	0.403	0.389	0.553	0.589
		L	1814.6	1774.0	267.8	237.8	1418.2	1668.1
9.	Marquardt Method	K	0.375	0.394	0.306	0.276	0.325	0.348
		L	1962.1	1788	281.6	254.4	1567.3	1723.2

Values of K are in days^{-1} and L are in mg/l

Sl. No.	Methods	Effluents Samples						Total
		Pulp Mill		Paper Mill		Total Mill		
		I	II	I	II	I	II	
1.	Thomas Method	1154.6	4064.8	179.2	108.8	868.2	1102.1	7477.7
2.	Method of Moments	117.1	84.0	38.9	25.0	101.3	91.4	457.7
3.	Rapid Ratio Method	525.3	99.6	44.9	19.8	143.7	203.9	1037.2
4.	Method of Weigand	137.5	81.6	116.7	17.9	202.3	197.2	752.7
5.	Method of Fujimoto	402.7	130.1	253.6	101.1	130.2	214.6	1232.3
6.	Bagchi and Chaudhary Method	221.1	134.1	104.6	35.7	284.2	142.4	922.1
7.	Method ofLeast Square by Reed & Therault	80.2	53.7	30.1	18.0	76.7	65.4	324.1
8.	Log Difference	1208.5	974.1	92.3	122.7	1180.4	1208.4	4786.8
9.	Marquardt Method	107.3	70.7	29.2	19.5	83.9	70.6	381.2

Sample	Reed - Therault			Marquardt Method		
	K	L	Total Absolute Deviation	K	L	Total Absolute Deviation
Pulp Mill Sample I	0.394	1953.7	80.2	0.393	1953.7	80.3
Pulp Mill Sample II	0.41	1781.8	53.7	0.41	1781.8	55.7
Paper Mill Sample I	0.33	279	30.1	0.327	279	30.2
Paper Mill Sample II	0.283	253.6	18.0	0.283	253.6	18
Total Mill Sample I	0.332	1563.4	76.7	0.332	1563.4	76.7
Total Mill Sample II	0.35	1721.7	65.4	0.35	1721.7	65.3
Total			**324.1**			**326.2**

I **TEMPERATURE ≥ 20**

Time (Days)	BOD (mg/l) at		
	20 °C	25 °C	30 °C
1	580	920	1340
2	1000	1420	1790
3	1290	1690	1960
4	1490	1840	2010
5	1640	1920	2025

TABLE C-13B EFFECT OF TEMPERATURE ON BOD

I **TEMPERATURE ≤ 20**

Time (Days)	BOD (mg/l) at		
	10 °C	15 °C	20 °C
1	330	420	530
2	620	760	900
3	840	1000	1160
4	1020	1180	1330
5	1150	1310	1460

I TEMPERATURE ≥ 20°C

Parameter	Tempetature (°C)		
	20 °C	25 °C	30 °C
K	0.356	0.607	1.06
L	1972.5	2016.7	2037.9

I TEMPERATURE ≤ 20°C

Parameter	Tempetature (°C)		
	10 °C	15 °C	20 °C
K'	0.256	0.319	0.366
L	1615.5	1653	1736

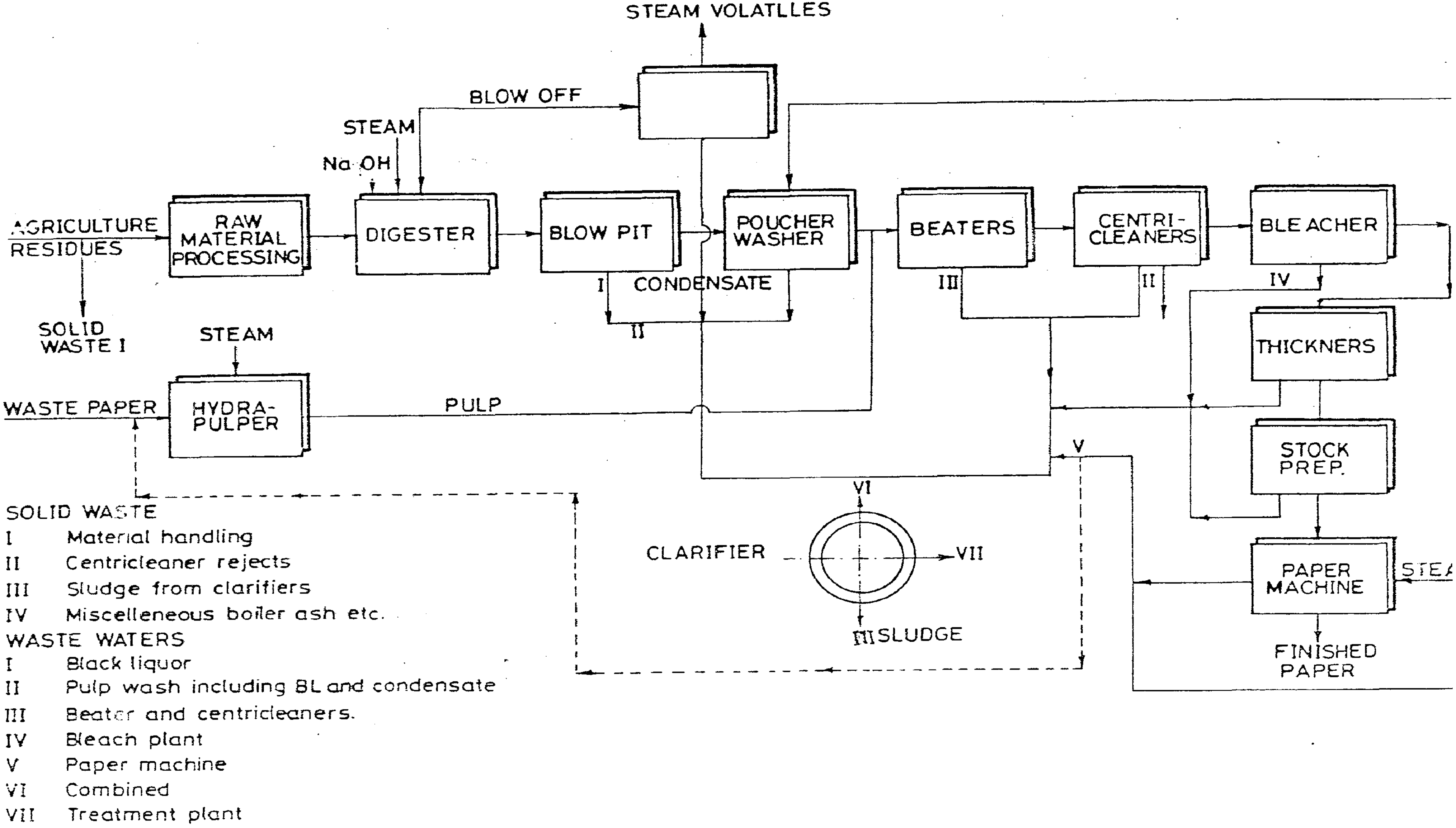
TABLE C-15: VALUES OF E AND θ AT DIFFERENT TEMPERATURE RANGES

Temperature Range (°C)	θ	E J/mole
≥ 20	1.115	80506.8
≤ 20	1.037	24833.4

Time (days)	BOD at pH				
	6.0	6.6	7.0	7.8	8.2
1	320	560	580	570	390
2	580	960	1000	970	690
3	780	1250	1290	1270	910
4	930	1460	1490	1480	1080
5	1050	1600	1640	1620	1210

TABLE C-17: VALUES OF K AND L AT DIFFERENT pH

Parameter	pH				
	6.0	6.6	7.0	7.8	8.2
K (day^{-1})	0.265	0.337	0.356	0.336	0.280
L (mg/l)	1435.8	1968.4	1972.5	1994.1	1604.7



SOLID WASTE
I Material handling
II Centricleaner rejects
III Sludge from clarifiers
IV Miscelleneous boiler ash etc.
WASTE WATERS
I Black liquor
II Pulp wash including BL and condensate
III Beater and centricleaners.
IV Bleach plant
V Paper machine
VI Combined
VII Treatment plant

FIG.21: GENERALISED PROCESS FLOW DIAGRAM FOR SMALL PULP AND PAPER MILL USING AGRICULTURE RESIDUES

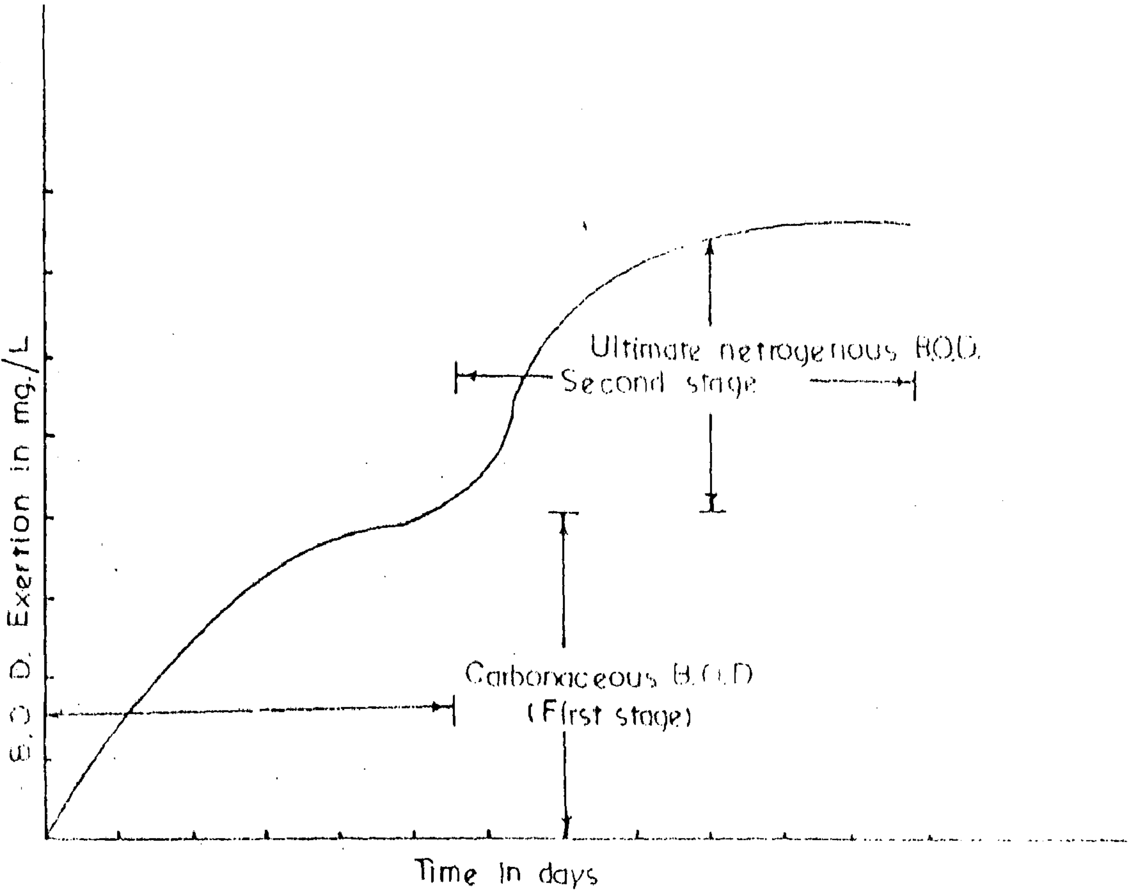


Figure 3·1 Two stage B.O.D. exertion

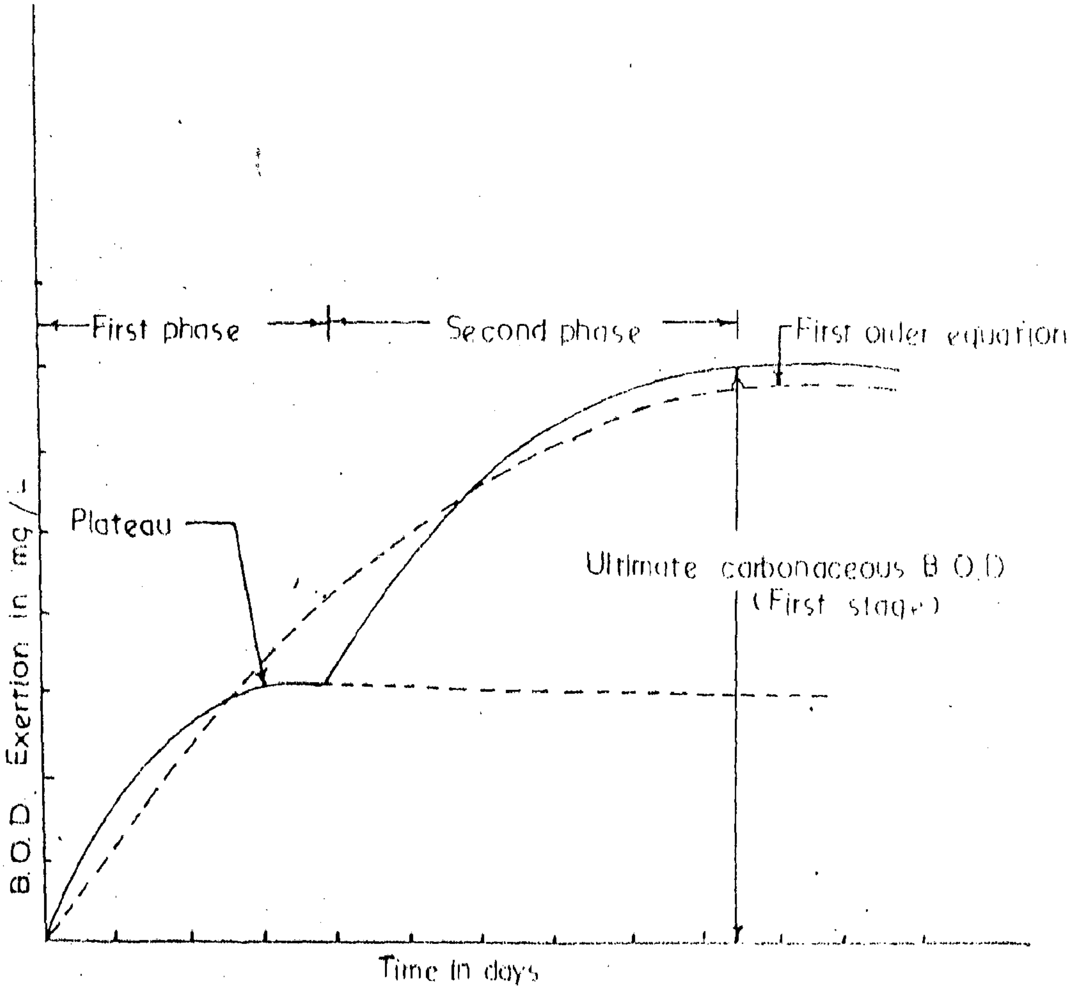


Figure 3·2 Diphasic B.O.D. exertion

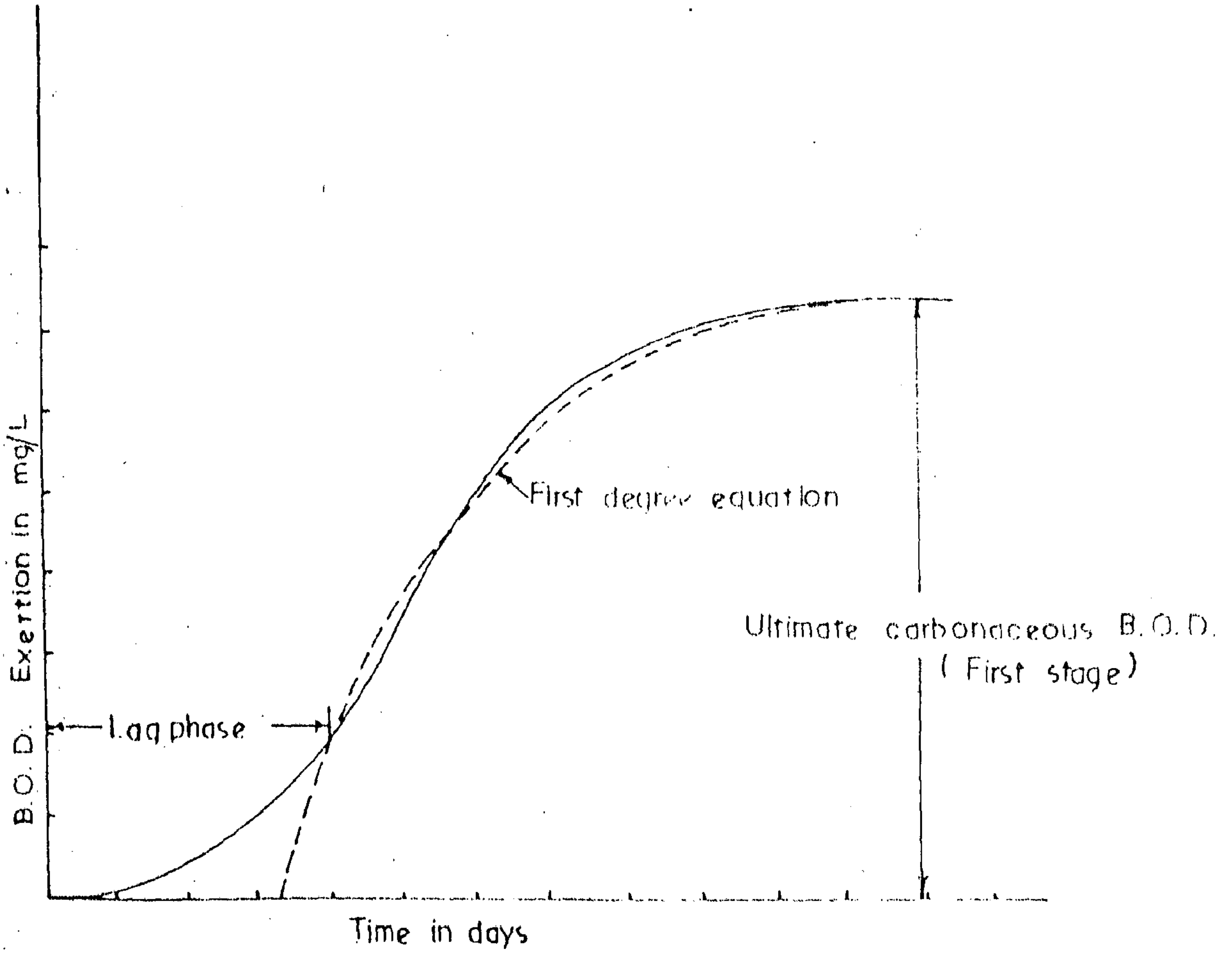


Figure 3·3 B.O.D. exertion curve (with lag)

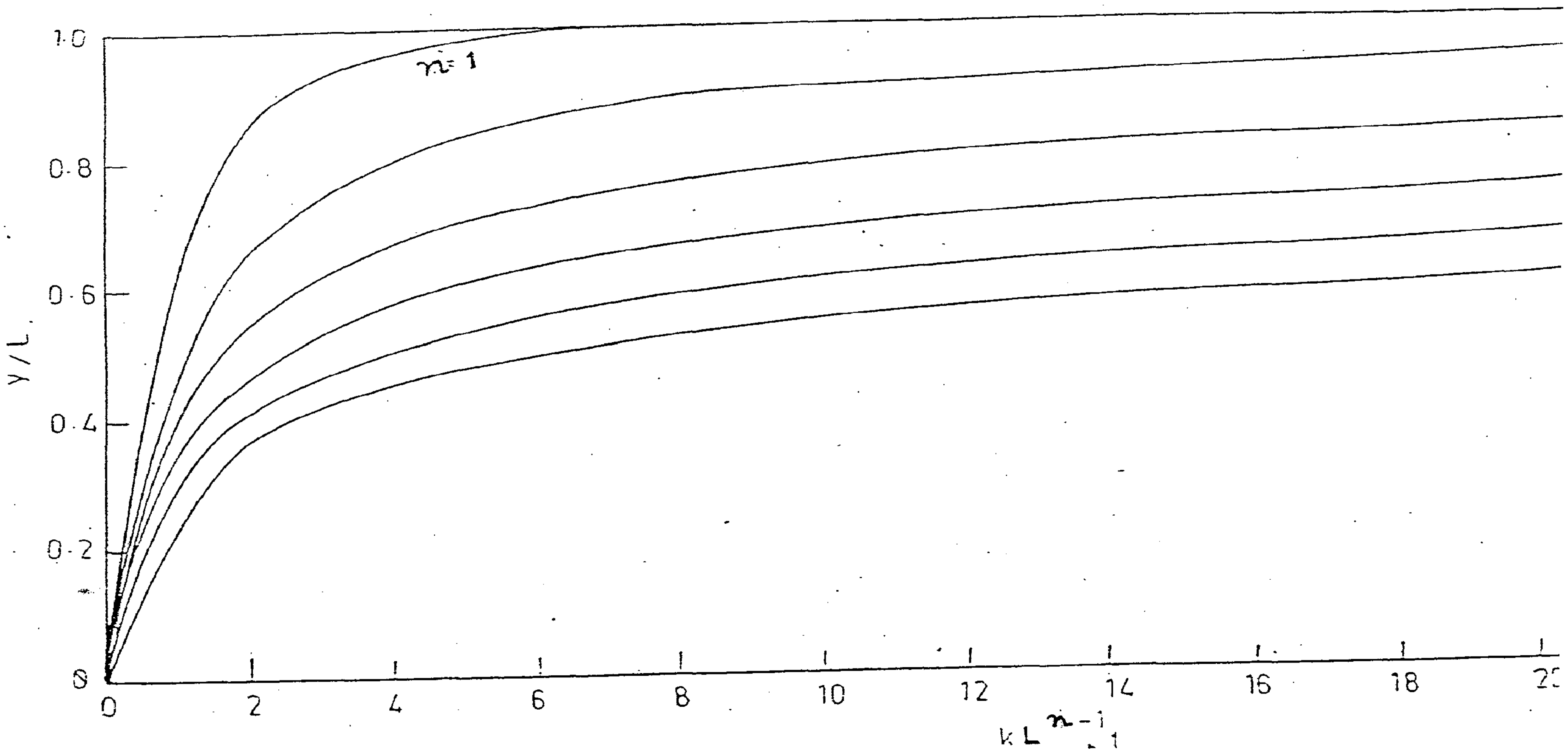


Figure 3-4 Non Dimensional Plots of Higher Degree Equations

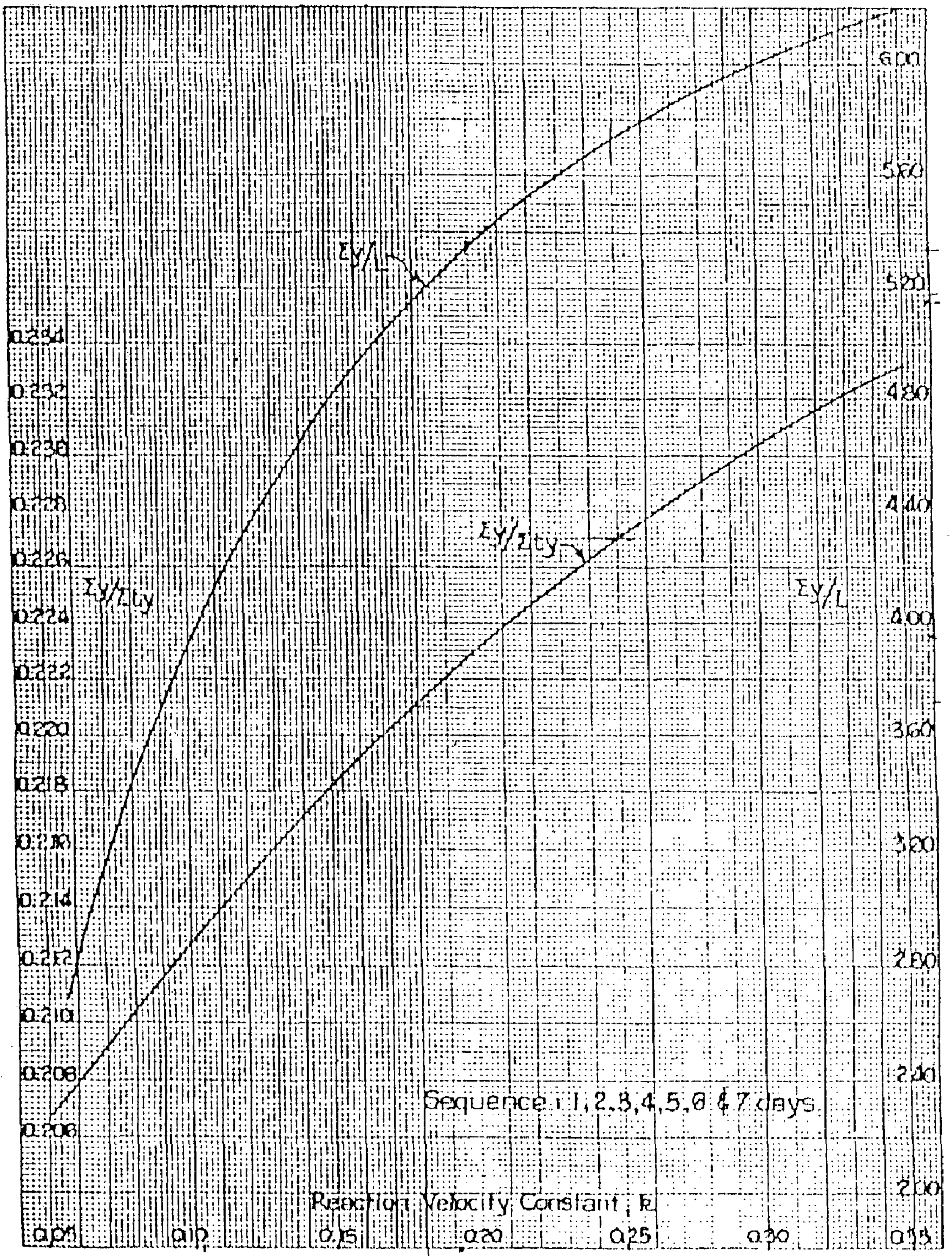


FIGURE 4·1 $\Sigma y \cdot L$ and $\Sigma y/\Sigma(ty)$ for various values of k in 7-day sequence.

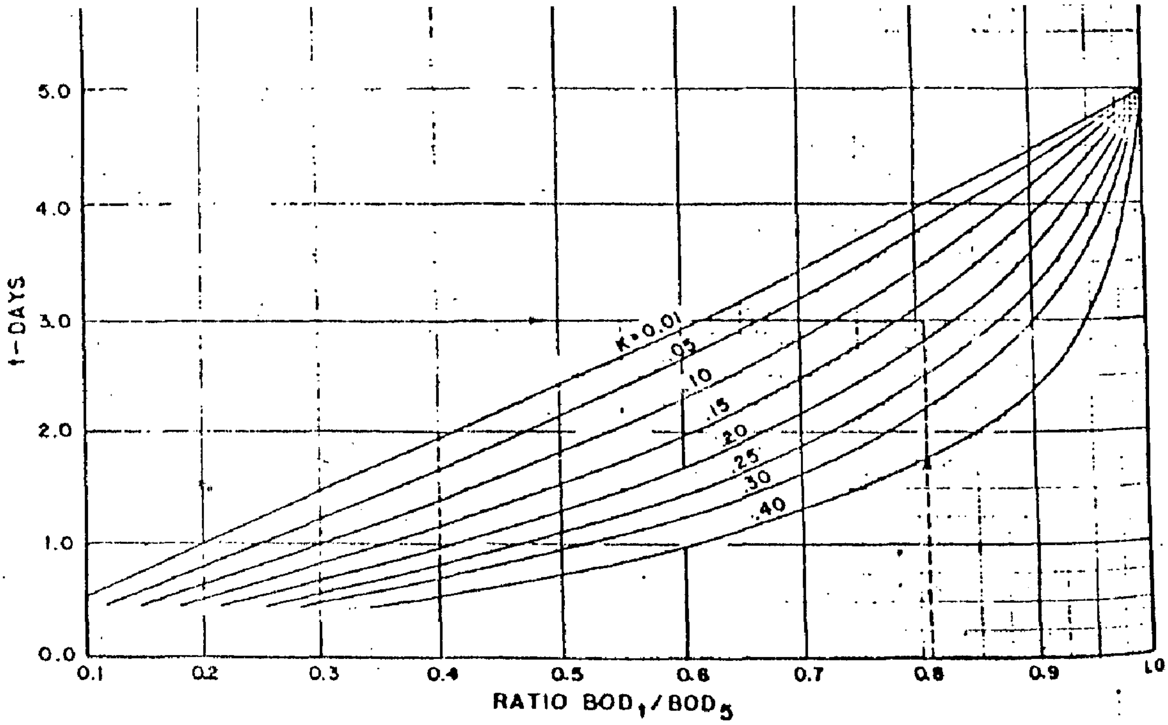


FIGURE 4-2 Values of K for ratios of BOD$_t$ to BOD$_5$ for t less than 5 days.

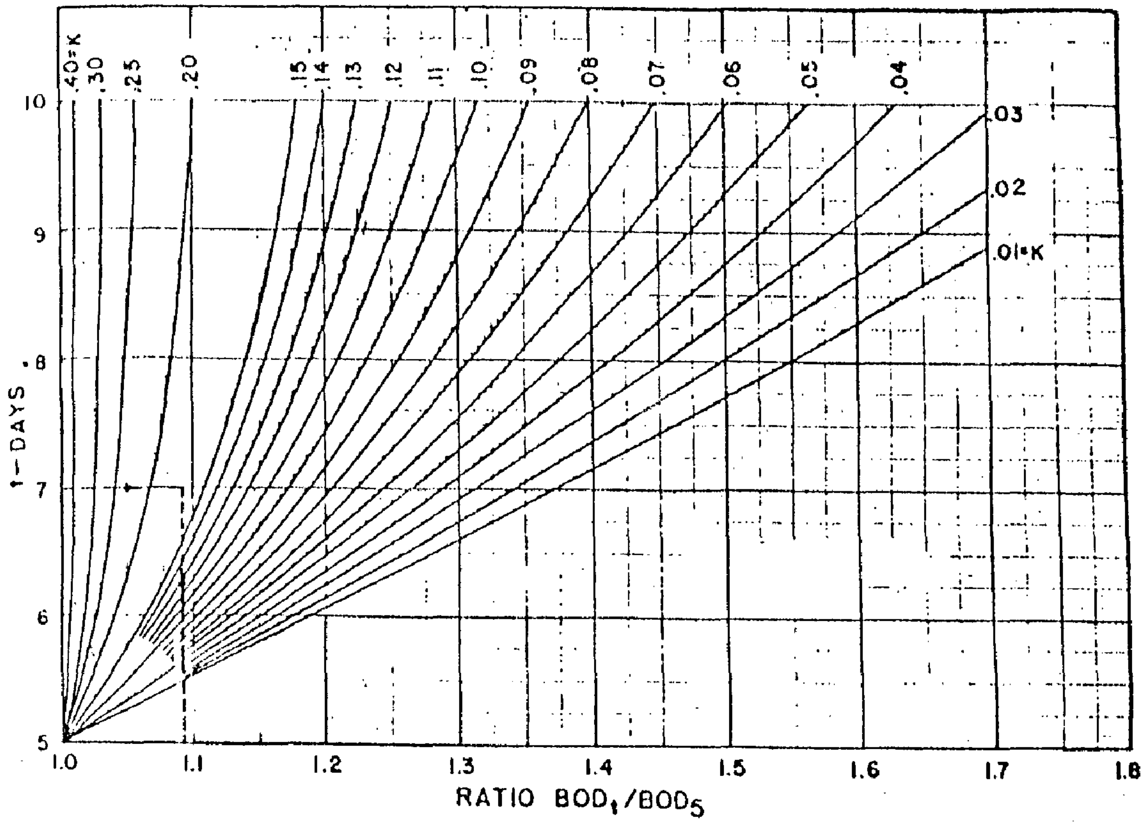


FIGURE 4-3 Values of K for ratios of BOD$_t$ to BOD$_5$ for t greater than 5 days.

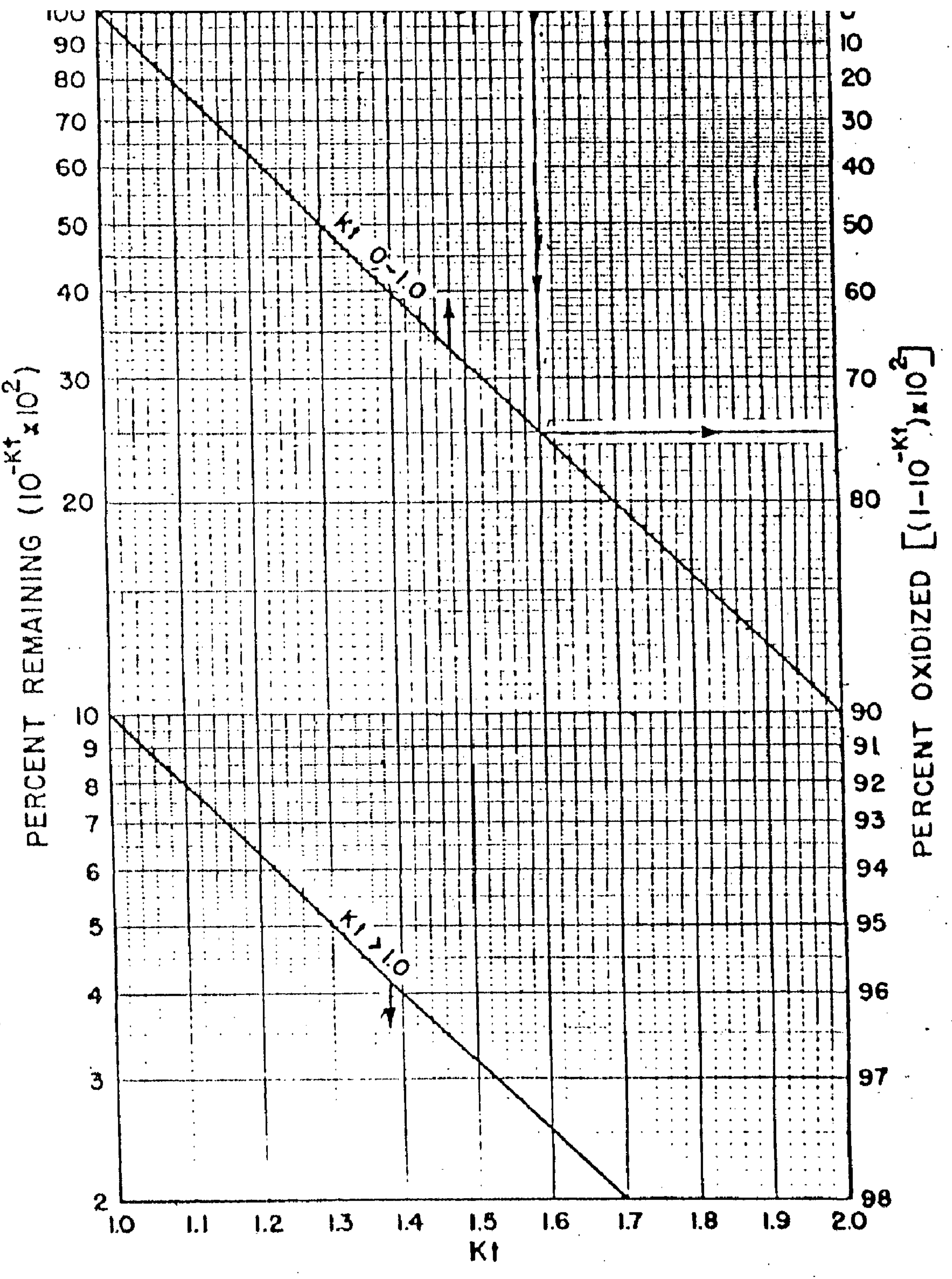


FIGURE 4-4 Amount of ultimate first-stage BOD remaining and oxidized for values of Kt.

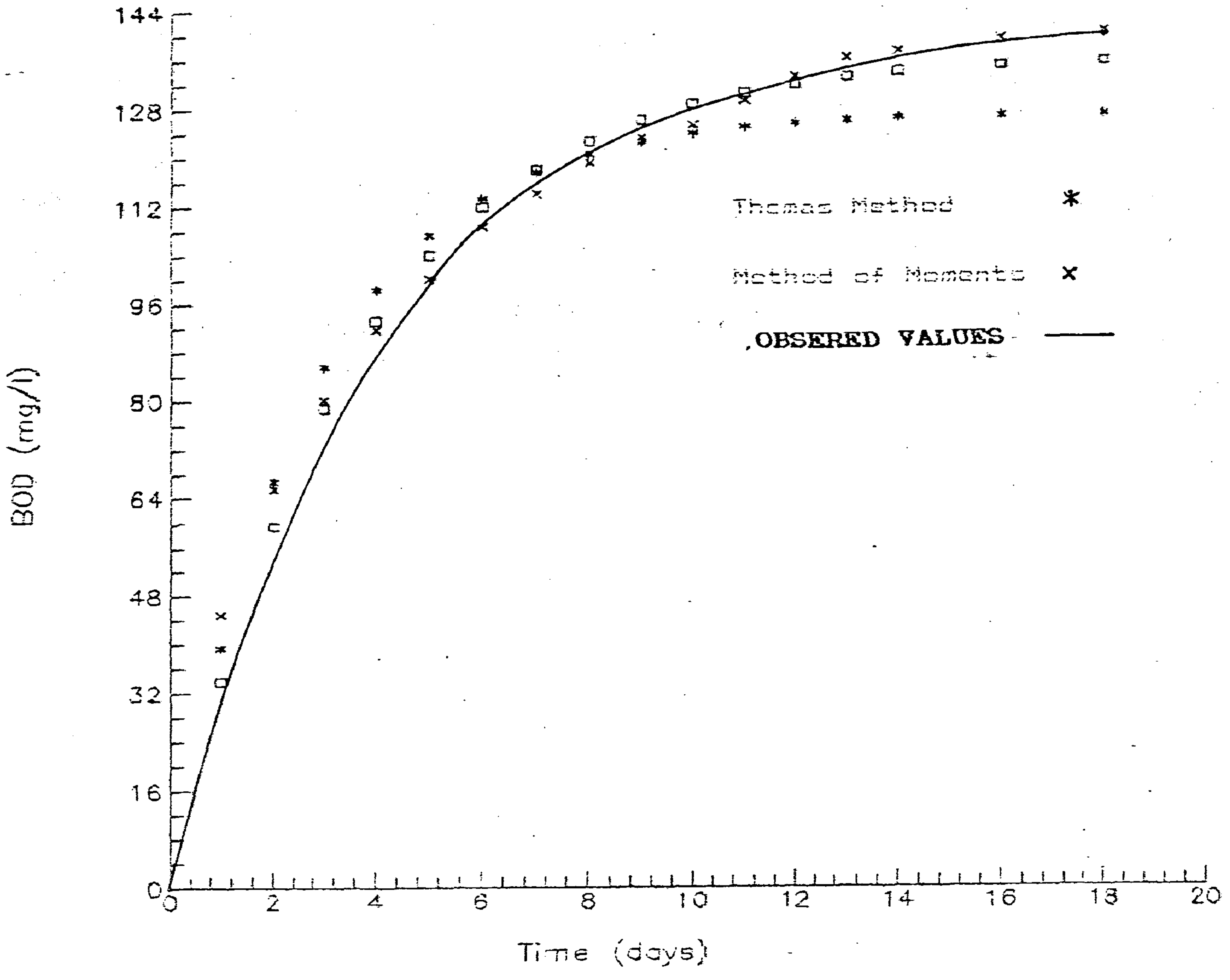


FIGURE 4.5 : PLOT OF BOD Vs. TIME

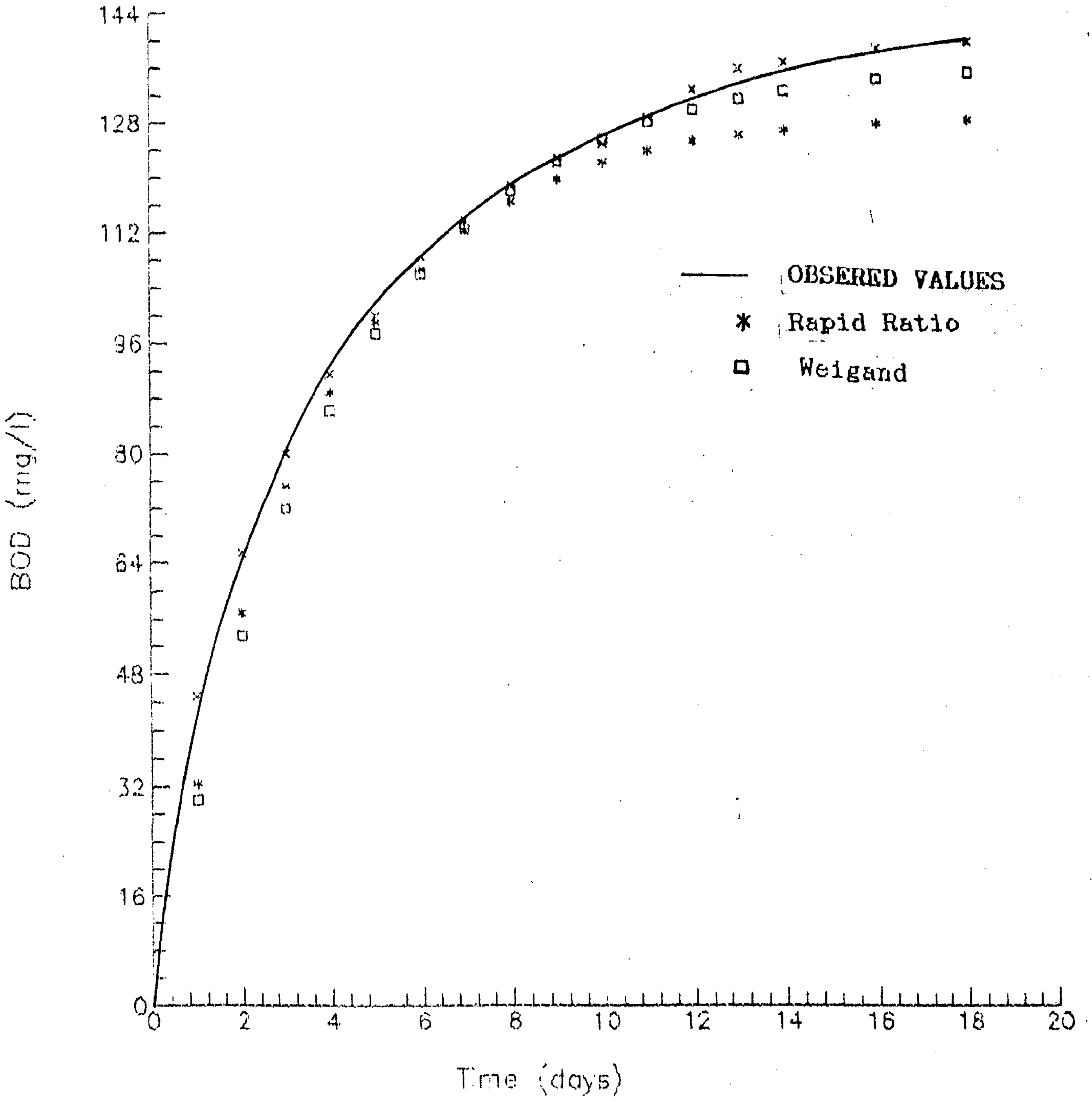


FIGURE 4.6 : PLOT OF BOD Vs. TIME

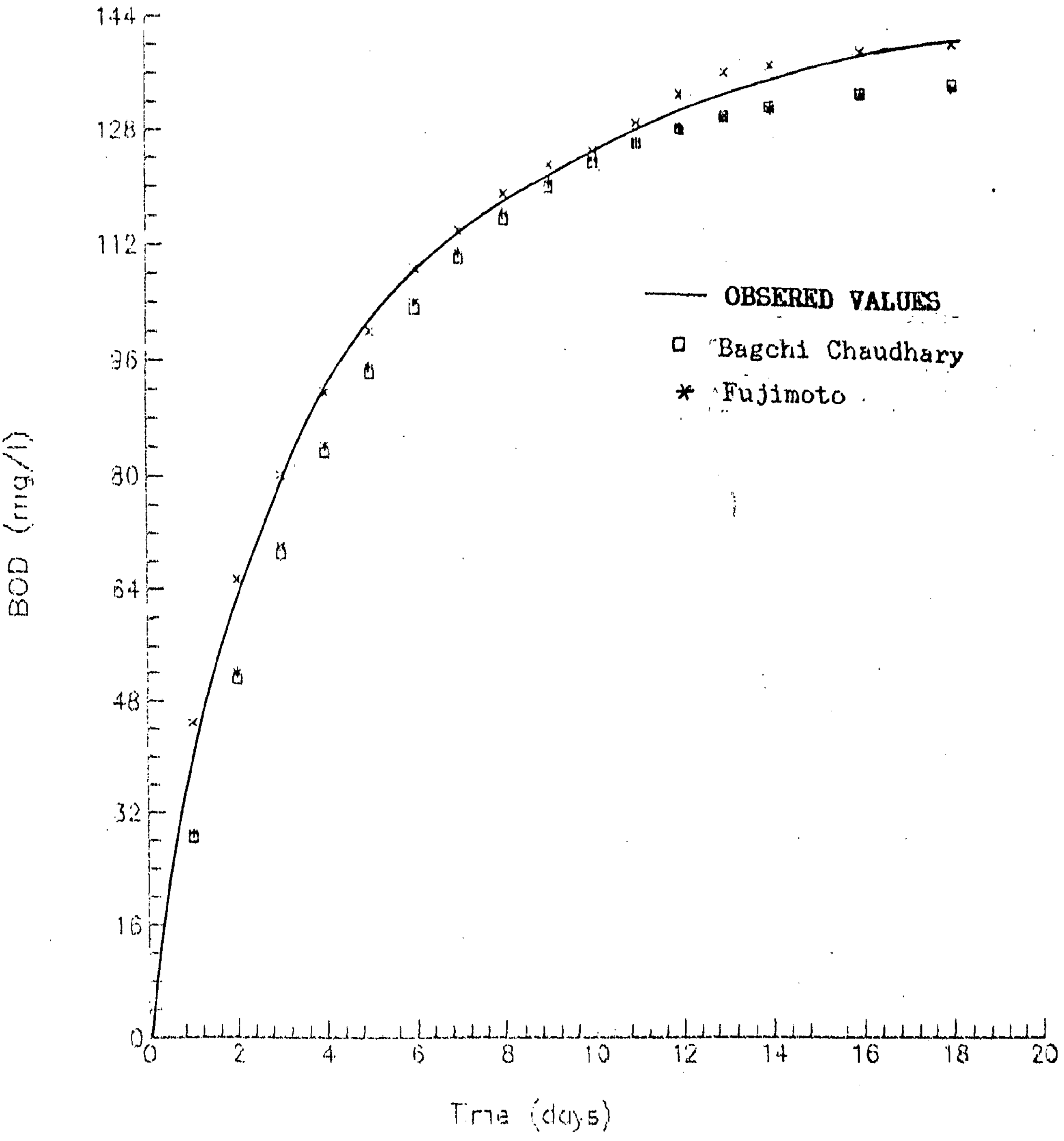


FIGURE 4.7 : PLOT OF BOD Vs. TIME

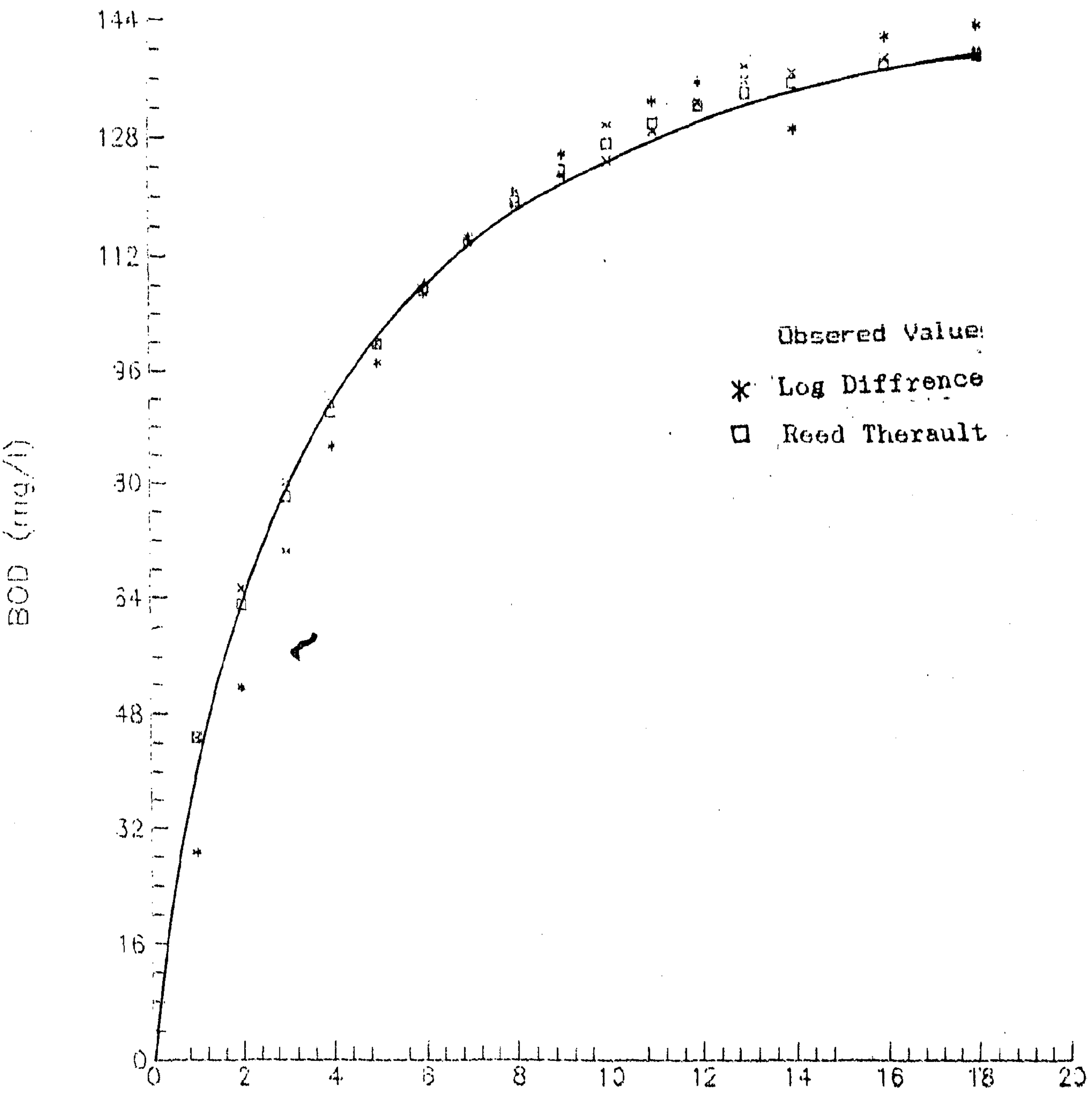


FIGURE 4.8 : PLOT OF BOD Vs. TIME

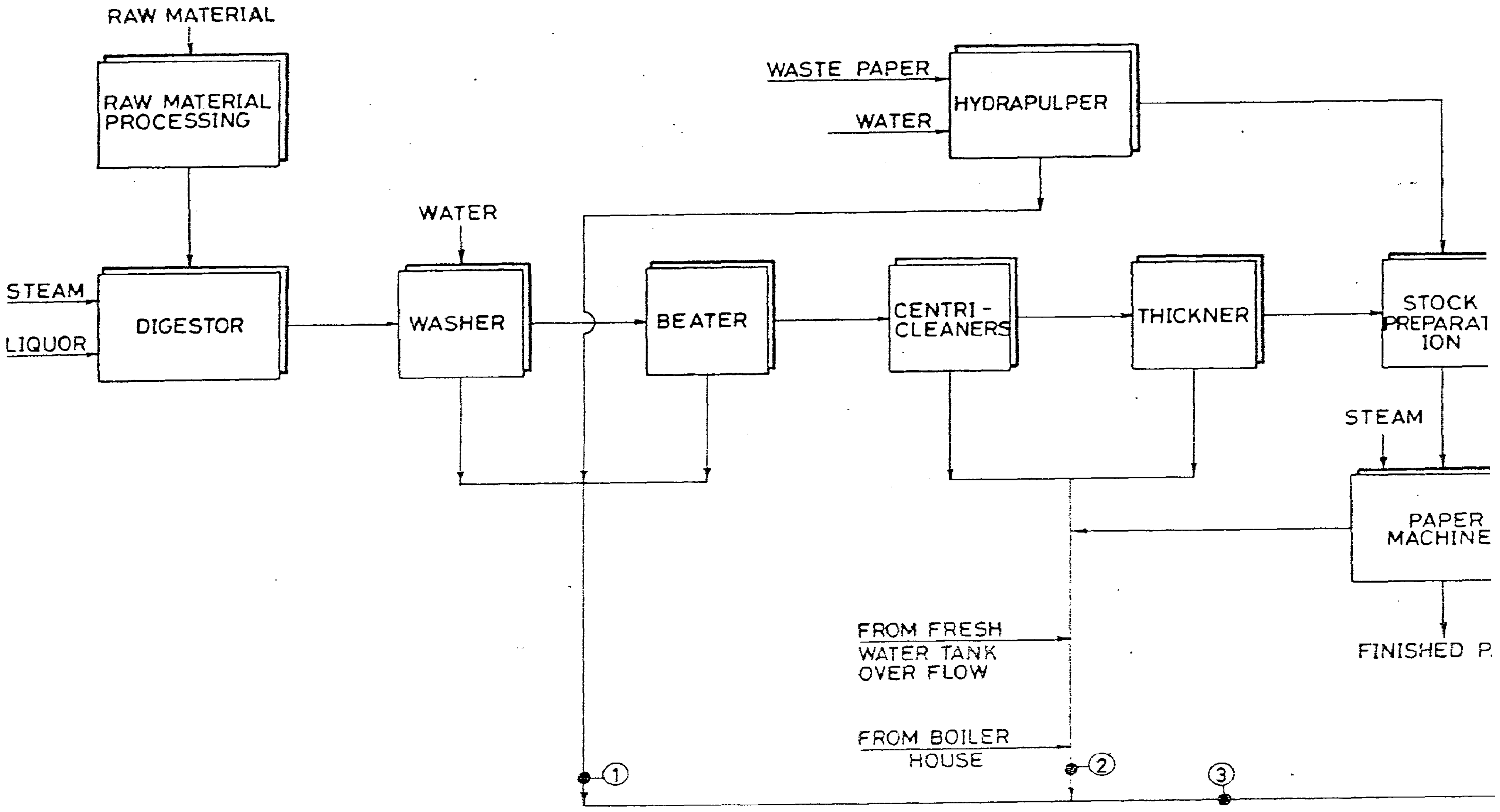


FIG.5·1: BLOCK DIAGRAM SHOWING PROCESS STAGES AND EFFLUENT SAMPLES LOCATIONS IN THE MILL UNDER STUDY

PULP MILL EFFLUENT

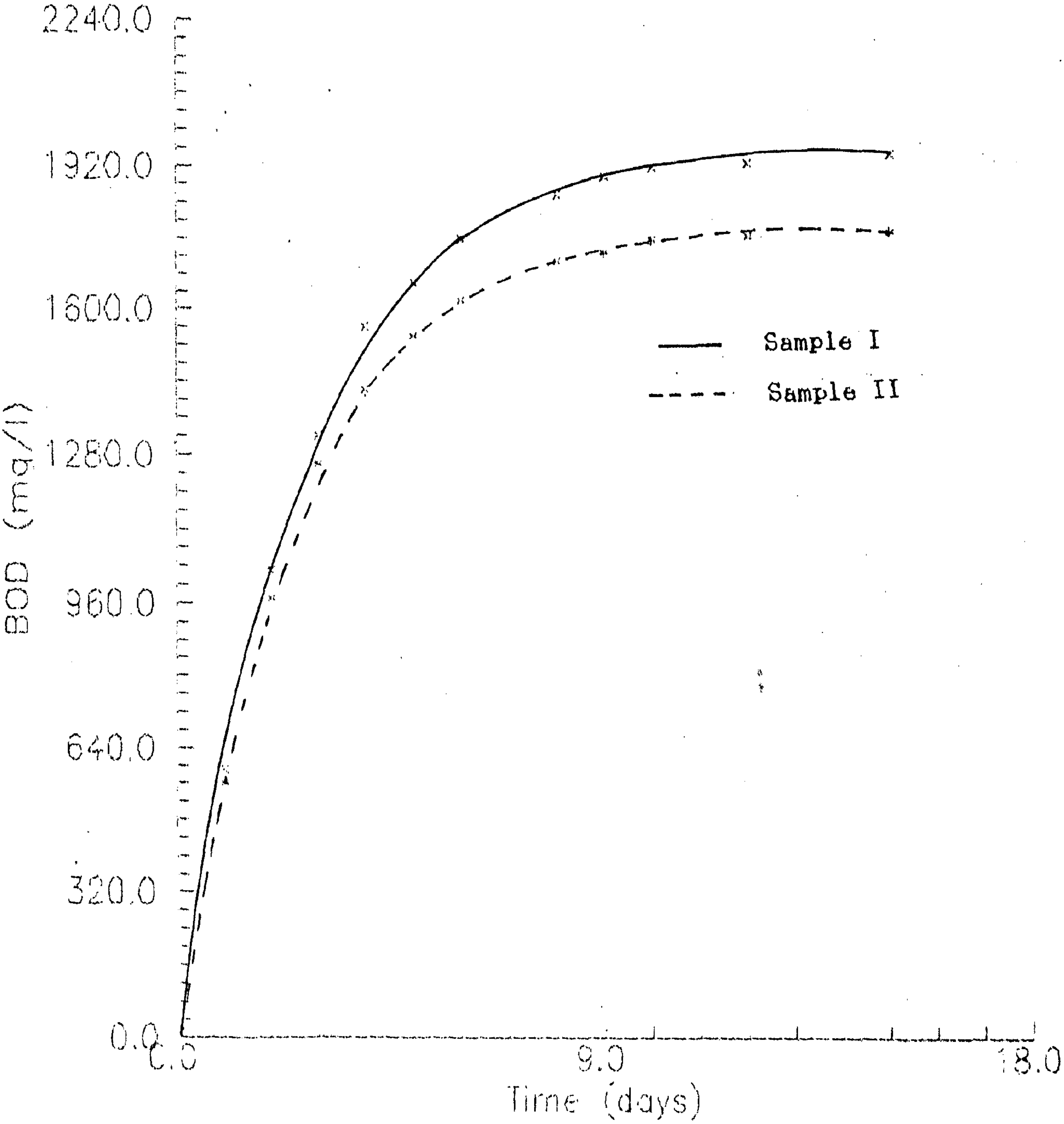


FIGURE 6.1 : PLOT OF BOD Vs. TIME

PAPER MILL EFFLUENT

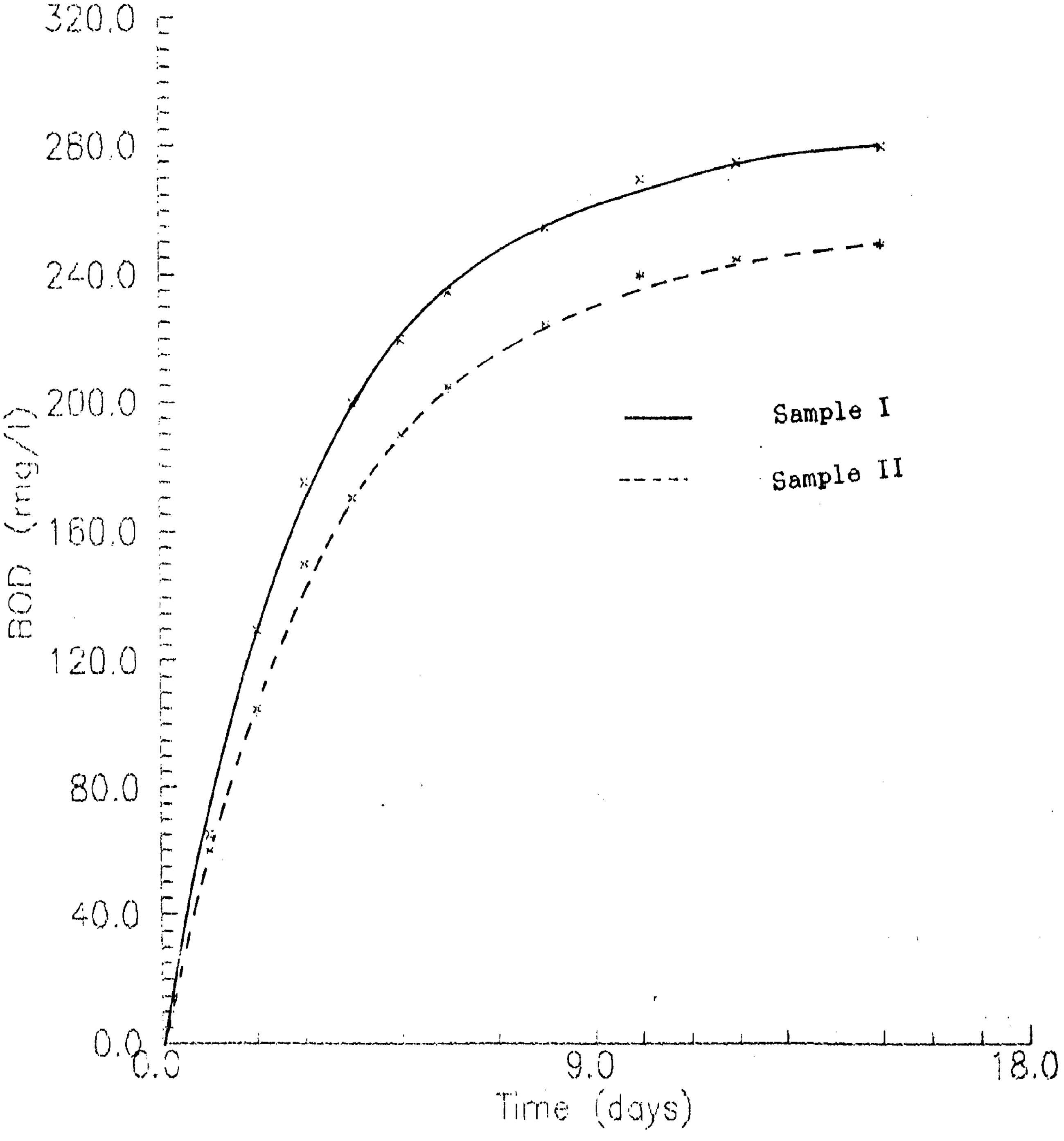


FIGURE 6.2 : PLOT OF BOD Vs. TIME

TOTAL MILL EFFLUENT

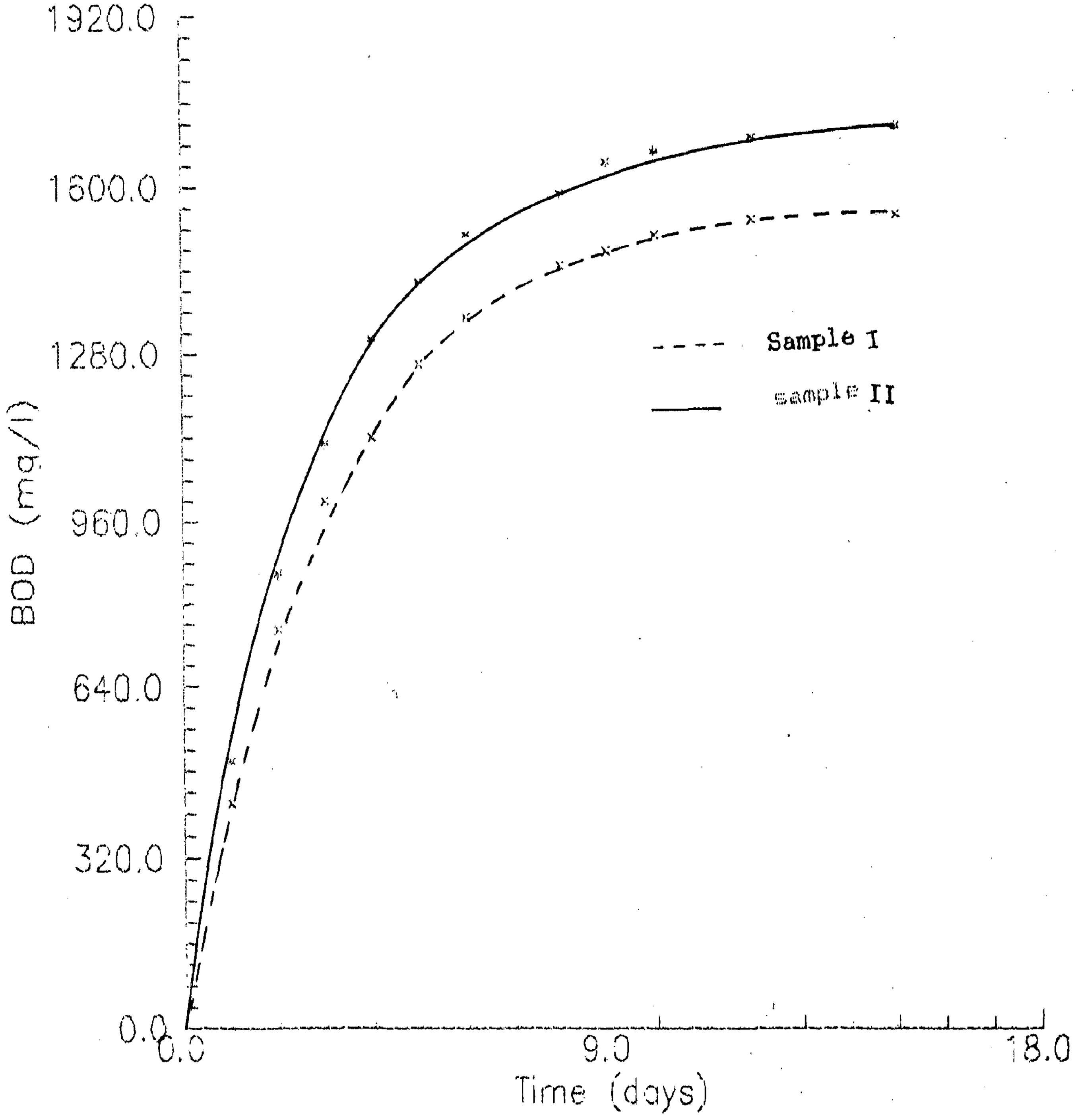


FIGURE 6.3 : PLOT OF BOD Vs. TIME

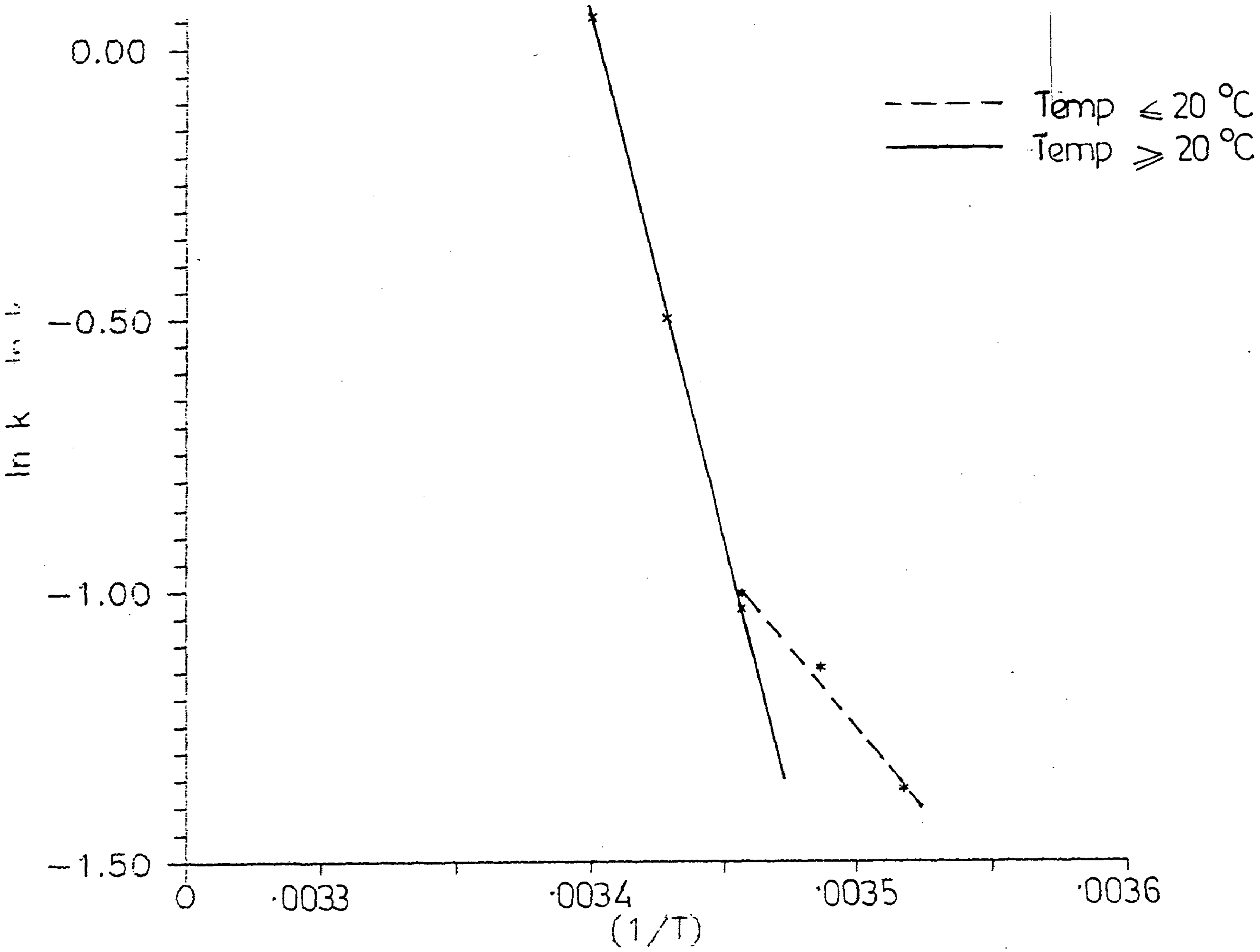


Fig. 6·4 PLOT OF ln k Vs 1/T

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