CHARACTERIZATION AND BIO-KINETIC STUDY-SUGAR MILL EFFLUENT

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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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this dissertation entitled **"CHARACTERIZATION AND BIO-KINETIC STUDY SUGAR MILL EFFLUENT"**, 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 under the supervision of Dr. P.S. Panesar, Professor and Dr. A.K. Agarwal, Lecturer in Department of Chemical Engineering, University of Roorkee, Roorkee.

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

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SUMMARY

Most of the sugar mills in India do not have the adequate effluent treatment facilities and as a result, large quantity of effluents are discharged into the drains and cause enormous amount of adverse environmental impact. Characterization and bio-oxidation forms the basis of treatment for these effluents.

The waste streams from different sections of a sugar factory were characterized according to the prescribed standard methods and found that the pollution load exerted by the combined mill effluent is significantly high and therefore, cannot be discharged into the water bodies without doing proper pretreatment.

The BOD exertion with time were measured for different samples and observed that it follows the first order bio-oxidation kinetics. Different methods were also used for estimating the kinetic parameters (k' the reaction rate constant and L_0 the ultimate BOD). With the present trend of available computer facilities, it is recommended that the non-linear least square optimizer (Marquardt method) is the best method for representation of BOD exertion data for sugar mill effluents.

The temperature effect on the effluent bio-oxidation was studied in the temperature range 10-40^{o}C. A break was

observed in the Arrhenius plot at about 20°C. The activation energy was 9.614 MJ/mole between 10-20°C and 25.50 MJ/mole between 20-40°C.

The effect of pH on the BOD_5, 20°C was also studied in the pH range of 6.0 to 8.5 and it was observed that the activity of micro organism is highest at near neutral pH.

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SYMBOLS AND ABBREVIATIONS

SYMBOLS

E	Activation energy (J/mole)
k & k'	Reaction Rate Constants (day^{-1})
L_o	Ultimate BOD (mg/l)
t	Time (days)
Y_t	BOD exerted in time $t = 0$
θ	Temperature Coefficient

ABBREVIATIONS

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
TDS	Total Dissolved solids
TSS	Total Suspended solids
VDS	Volatile Dissolved solids

CHAPTER — I

CHAPTER - I

INTRODUCTION

The sugar industry ranks second amongst the agro-industries in India and is, therefore, vital for India's economy. There are about 400 sugar factories in operation in India. About 55 percent are located in Maharashtra and Uttar Pradesh (U.P.) and around 25 percent of total sugar factories in U.P. are located in West Uttar Pradesh (TABLE 1.1)(1). Also, these two states produce about 60% of the total sugar produced in India. Considering its annual production, India is one amongst the leading sugar producing countries in the world and ranks fourth.

In India, about 3.1 million hectares of land is utilized for sugarcane harvesting which yields 180 million tonnes of sugarcane per year. TABLE 1.2(1) shows that over the last 2 decades, there has been a continuous increase in the land under sugarcane crop, and the sugar production also shows a corresponding increase. It is also evident from TABLE 1.2 that there is an increase in cane production and corresponding increase in the number of factories, working capacity, cane crushed, recovery, sugar production, molasses production and duration of working season in a year.

The sugar industry is of a seasonal nature and remains in operation from November to May or June in a year. On a world wide basis, about 10 percent of the weight of cane is recovered as sugar. However, in India, yield of sugar fluctuates from 6 to 12 percent depending upon the quality of sugarcane and efficiency

TABLE 1.1 State wise - growth of Sugar Industry (1)

	1986-87				1987-88				1988-89				1989-90				1990-91			
	No. of factories	Cane crushed	Sugar prod.	% recovery	No. of factories	Cane crushed	Sugar prod.	% recovery	No. of factories	Cane crushed	Sugar prod	% recovery	No. of factories	Cane crushed	Sugar prod.	% recovery	No. of factories	Cane crushed	Sugar prod.	% recovery
		000 Tonnes				000 Tonnes				000 Tonnes				000 Tonnes				000 Tonnes		
A.P.	31	4,225	406	9.60	31	5,657	530	9.36	31	5,934	544	9.17	33	5,666	565	8.99	33	7,295	701	9.61
Assam	1	27	2	7.82	2	67	5	7.45	2	133	10	7.47	2	130	10	8.10	2	100	8	8.35
Bihar	23	2,633	250	9.48	26	3,244	299	9.22	27	3,478	312	8.97	28	3,720	334	8.99	28	4,576	415	9.07
Goa	1	67	6	8.89	1	93	8	8.83	1	111	9	8.23	1	101	9	876	1	97	8	8.44
Gujarat	13	5,086	558	10.97	12	5,279	576	10.91	11	5,661	578	10.22	14	6,083	666	10.86	14	7,619	831	10.91
Haryana	8	1,699	161	9.48	8	2,916	289	9.91	8	2,739	272	9.94	8	3,435	335	9.77	10	3,980	375	9.44
Karnataka	22	4,868	509	10.44	24	6,023	611	10.23	25	7,357	745	10.13	27	7,665	796	10.38	27	9,190	942	10.25
Kerala	2	82	7	8.98	2	122	10	8.10	2	90	7	7.64	2	157	14	8.92	2	110	9	8.48
Madhya Pradesh	8	472	42	8.97	8	772	71	9.20	8	909	85	9.30	8	732	72	9.78	8	1,033	103	10.01
Maharashtra	88	21,328	2388	11.21	91	21,752	2,388	10.98	90	25,837	2,795	10.83	86	36,617	3,923	10.71	97	38,284	4,118	10.76
Nagaland	1	26	2	8.58	1	42	4	8.54	1	68	6	8.15	1	59	5	8.30	1	52	4	7.80
Orissa	3	545	13	9.34	3	245	21	8.93	3	360	28	7.70	5	162	15	9.17	5	258	23	8.90
Punjab	10	1,502	146	9.78	11	2,415	234	9.69	13	2,075	210	10.18	13	3,235	295	9.13	17	3,102	275	8.95
Pondicherry	2	160	51	9.16	2	663	59	8.91	2	594	50	8.47	2	391	36	9.29	2	540	48	8.89
Rajasthan	3	145	13	9.32	3	251	25	8.99	2	76	6	8.35	2	134	12	9.24	3	278	23	8.44
Tamilnadu	24	8,491	811	9.56	25	8,520	814	9.55	25	8,505	785	9.23	30	9,557	889	9.37	31	9,007	1,183	9.11
East U.P.	41	4,888	456	9.33	41	6,550	617	9.42	41	7,281	656	9.01	41	7,726	703	9.09	42	8,556	768	8.98
West U.P.	23	4,647	448	9.63	23	8,390	811	9.66	23	9,385	830	8.91	23	11,275	1,041	9.24	23	11,156	1,030	9.23
Central U.P.	36	7,677	746	9.74	37	12,170	1,129	9.28	39	13,299	1,173	8.84	40	12,637	715	8.84	40	11,763	647	9.02
West Bengal	1	9	1	6.45	2	58	3	6.97	2	51	3	6.40	1	34	1	4.17	1	38	3	7.62
Total	341	68,576	7016	10.23	353	85,224	8501	9.98	356	93,943	9110	9.70	377	109,516	10436	9.89	387	117,034	11,514	9.85

TABLE 1.2 Statistics of Sugar Production in India (1)

Year	Area under Sugarcane ('000 Hectare)	Yield of Cane per Hectare (Tonnes)	Production of Sugarcane ('000 Tonnes)	No. of Factories in Operation	Average Actual Capacity (Tonnes Per 24 hrs.	Total Cane Crushed ('000 Tonnes)	Recovery of Sugar % Cane	Total Sugar Produced ('000 Tonnes)	Average Duration (days)	Mol asses Production ('000 Tonnes)
1970-71	2617.1	48.3	126,368	215	1394	38,205	9.79	3740	139	1611
1980-81	2667.0	57.8	154,248	314	1707	87,356	9.98	5147	105	2126
1984-85	2953.0	57.7	170,319	338	1813	60,092	10.24	6144	107	2463
1985-86	2862.0	60.0	171,681	341	1891	68,576	10.23	7016	116	2849
1986-87	3055.0	59.7	182,480	353	1868	85,224	9.98	8501	141	3663
1987-88	3279.0	60.0	179,800	356	-	93,943	9.70	9110	153	4206
1988-89	3329.0	61.0	203,000	366	-	85,693	10.21	8752	133	3606
1989-90	3438.0	65.6	225,600	377	-	11,1149	9.89	10,988	158	4880
1990-91	3682.0	65.3	240,300	385	-	122,319	9.85	12,047	166	5444

of the mill.

Sugar is primarily sucrose, (a disaccharide) extracted from sugarcane. The sugarcane is a weight losing raw-material and therefore, cannot be stored for a long period as the loss of sucrose content is inevitable. Besides, it cannot be transported to long distances because the transportation cost adds to the cost of production and on the other hand the sugarcane may dry on the way. This requires the sugar factory to be in close proximity to the regions of sugarcane cultivation.

The impurities from sugarcane remaining after the extraction of the sugar which flow down the drain are mainly carbohydrate and hence easily biodegradable. The wastes from sugar industry being highly putrid and tend to deplete the dissolved oxygen from receiving water bodies when discharged into them. Also, sugar mills located in rural areas, have no large water resources for disposal of effluents by dilution and the rainfall during sugar season being very low. The extreme pollution of small rivers and foul smell in the vicinity of running sugar mills is commonly experienced. It has been a common practice to dispose off the effluents into nearby streams, without its proper treatment in most cases. This has created considerable localized problems in the sugar producing states of India. With the enforcement of water pollution (Prevention and control) Act, 1974 and minimal national standards set by the Central Board for prevention and control of pollution, it has become mandatory to treat effluents from cane sugar industries, so as to conform to the requirements of the act.

Inspite of the cane sugar manufacturing processes having been standardized long ago and the sugar industry practising them fairly uniformly, the volume of the effluent and its pollution load vary considerably from factory to factory, even with the same crushing and production capacity. It is, therefore, intended that each sugar factory must select the effluent treatment process best suited to its local conditions. This warrants an indepth study before designing the treatment facilities, and selecting an appropriate and practicable technology. The prerequisite task in this field is the analysis of the effluent characteristics and determination of the total pollution load, evaluation of the methods for estimating biochemical oxygen demand parameters, so as to assess the waste assimilative capacity of the water streams and to design the plant of suitable capacity. Keeping this in mind the following objectives have been envisaged for the present work :

1) Identification of all pollution generating sources in a sugar factory ,

2) To carryout the waste water sampling and analysis, so as to ascertain the pollution load from the factory , and

3) Study of the bio-oxidation kinetics to form the basis of treatment for these effluents.

CHAPTER - II

CHAPTER - II

SUGAR MANUFACTURING PROCESS AND WASTE PRODUCTION

This chapter deals with the compilation of available data and information on the sources, nature, volumes and pollution effects of effluent generated from the sugar mill. The brief description about the sugar manufacturing process is also discussed in the begining of the chapter.

2.1 Description of the sugar manufacturing process

Table 2.1 shows the statistics of operation in sugar industry. The various processes involved in cane sugar manufacturing are described under different sub headings :

2.1.1 cane Procurement :

The sugarcane is harvested manually in the field by cutting the stalk with a knife or a machete, stripping off the adhering leaves and removing the topmost green parts, which contain little or no sugar. The harvested cane is brought to the factory, weighed and sent to the milling plant.

2.1.2. crushing :

The cane is cut into short lengths in a shredder and then crushed in a series of roller mills, where the juice is squeezed out. The partially crushed cane is wetted with water in the later stages of crushing operation to aid maximum extraction.

Table 2.1 Sugar Industry-Statistics of Operation (2)

Particulars	* Range%	*Average %
Sugar Recovery	7.5-12.28	9.48
Bagasse	26.22-45.72	33.29
Molasses	3.27-7.78	4.45
Press Mud:		
a. Double Sulphitation	2.25-4.99	3.43
b. Double Carbonation	8.09-9.9	9.31

(* Expressed as % of cane Crushed)

This operation is known as maceration. The extracted juice flows into a trough screens to remove any particles of cane fiber and the juice is then ready for clarification. The fibre left after extracting the juice is the bagasse, which is generally used in boilers as a fuel and is also useful raw-material for the pulp and paper industry.

2.1.3 Clarification of Juice :

The extracted juice is treated by either double sulphitation process or double carbonation with double sulphitation process. Till recent years, most of the plant uses double carbonation double sulphitation process. But now the recent trend is towards using the double sulphitation process. In double sulphitation proces, after the extracted juice is weighed, ~~for [illegible]~~ lime is added to raise its pH to 7.6 to 8.4, to prevent the inversion of the sucrose molecule to glucose and fructose, and to help in the clarification of the juice. The mixture is then passed to a heat exchanger to raise its temperature to 105^{o}C. This heating is necessary to promote the clarifying action of the lime, and is also essential to check all biological processes which would otherwise rapidly occur in freshly clarified juices and cause deterioration. By raising the temperature to the boiling point, coagulation of colloidal and other suspended impurities takes place. Bulk of the colour of juice is also removed by treatment with SO_2. The flocs formed in this process are settled and removed by passing the juice through a clarifier. The clarifier sludge or sediment is sent to rotary vacuum filters. In vacuum filters the juice mud is removed as solid waste.

In double carbonation double sulphitation process juice is heated to 50°C to 55°C and the hot juice is mixed with lime and concentrated simultaneously, such that the pH of the system remains at 10.5. During the process, a thick precipitate of calcium carbonate is obtained. By the process of absorption, it removes inorganic and organic impurities of the juice. Then the juice is filtered through large filter presses. The treated juice which has pH of 9.8, is again carbonated with CO_2 till the pH falls down to 8.2 to 8.5. During this process also, a thin precipitate is obtained which is filtered off. The clear juice at pH of 8.2 to 8.5 is heated to about 70°C and sulphitation is done after which it is sent to evaporators for further process.

2.1.4. Evaporation :

The thin juices from the clarification is now evaporated in order to produce crystal sugar. This operation must not be delayed since the thin juice rapidly decomposes with loss of sugar. The clarified juice from the clarifier is preheated by passing it through heat exchangers and then evaporated in multiple effect evaporators. The clarified juice is concentrated to about 65% solids from about 15% solids. The vapour from the last effect is condensed in barometric condenser, from where the water and condensate go to spray pond and are cooled and reused. The concentrated syrup from the evaporator is again bleached by passing SO_2 through it and the pH of the syrup drops down to about 5.4. It is then sent to the vacuumpan, where the thickened syrup is boiled three to four times as per purity.

2.1.5. Crystallization & Centrifugation

The concentrated syrup known as massecuite is then taken to crystallizers to deposit additional sucrose content in liquid on the crystals. The massecuite is then fed to centrifugal baskets where the sugar crystals are separated from mother liqour which drains away as molasses. During the process of centrifugation small amount of water is sprayed on the surface of sugar crystals to remove the adhering molasses. The weak molasses thus obtained is recycled to the process. From the centrifugal baskets, sugar is taken out and dried in a drier and bagged.

The schematic flow diagram of the double sulphitation process and double sulphitation-double carbonation process is shown in Figure - 2.1 & 2.2 respectively.

2.2 Raw - materials requirements

Table 2.2 shows the consumption of major raw-materials in the Indian sugar industry based on the purification process used. Both lime and sulphur are used for purification of sugar.

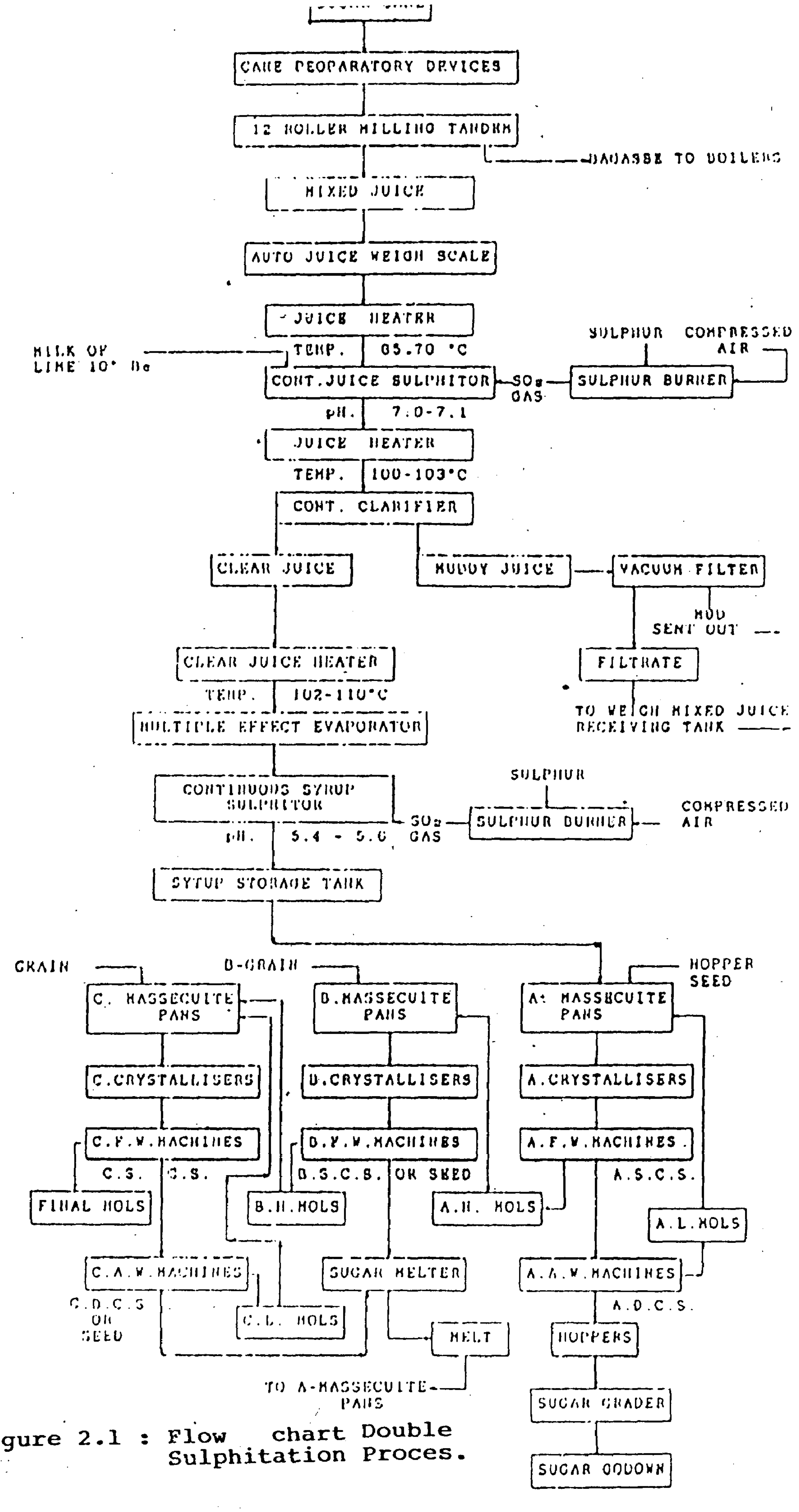

Figure 2.1 : Flow chart Double Sulphitation Proces.

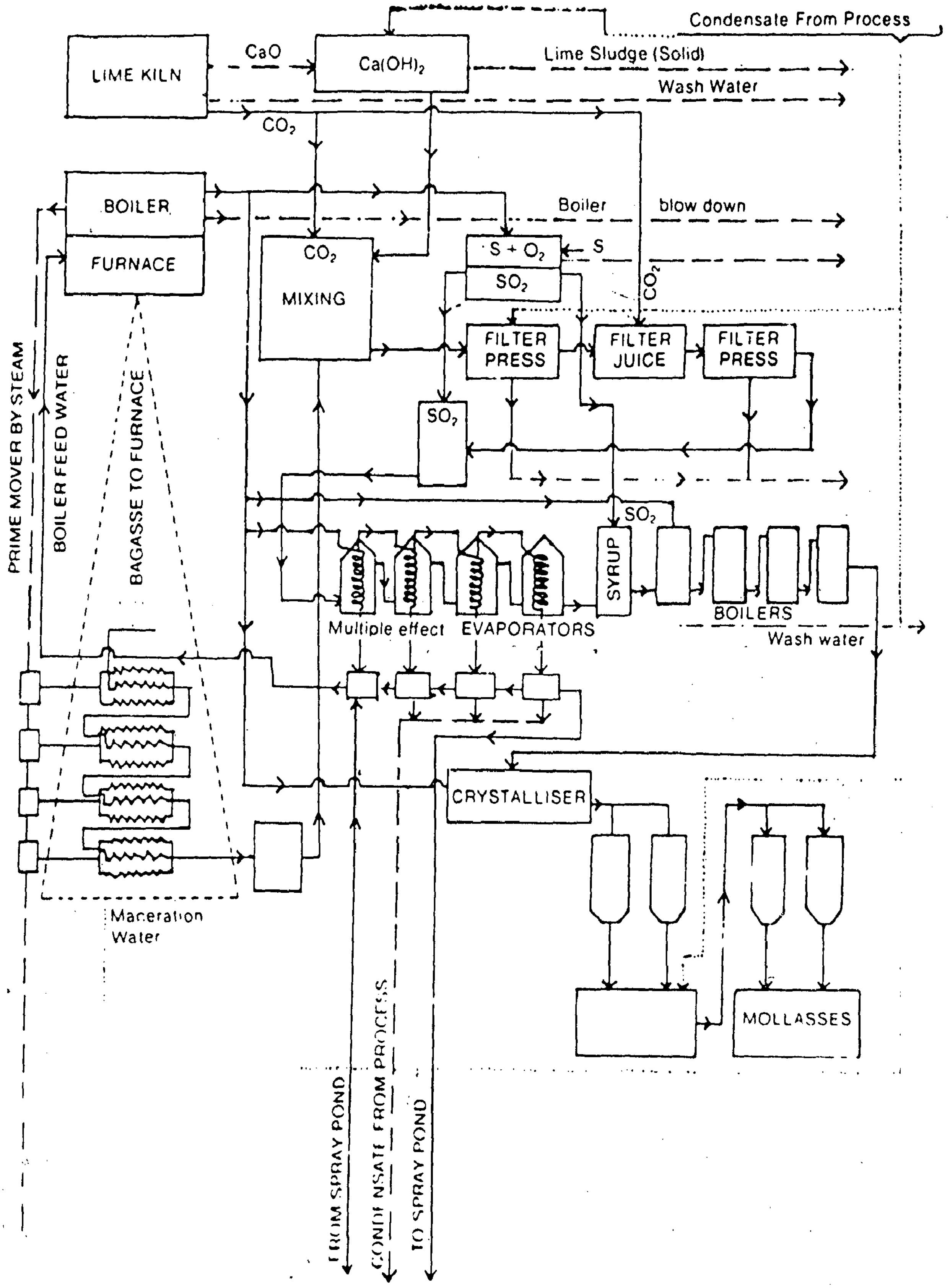

Figure 2.2. : Flow chart of double sulphitation - double carbonation Process.

TABLE 2.2 : Raw - materials Consumption (2)

Sugar Purfication Processes	% Cane Crushed		Kg/Tonne of cane Crushed	
	Lime	Sulphur	Caustic Soda	Bearing Oil & Grease
(a) Double Carbonation-Double Sulphitation Process	3.840	0.056	0.037	0.092
(b) Double Sulphitation Process	0.187	0.056	0.037	0.092

nd grease are used as lubricants and caustic soda is used for cleaning purposes. Average consumption of these materials per TCD depends upon the plant crushing capacity and purification processes. Lime is the only raw - material which is consumed more in double carbonation- double sulphitation process as compared to double sulphitation process.

The requirement of raw water is also large in quantity. In India, average requirement is 1300 to 4360 liters per TCD.(4) However, the present trend is to reduce this figure by 500 to 750 liters per TCD.

2.3 Sources of Wastewater Generation :

The sugar mills generate large volumes of wasteswater during the manufacturing operations and these contain high amount of pollution load, particularly, in terms of BOD and suspended solids. The volume of the effluent and its pollution load vary considerably from factory to factory, even with the same crushing and production capacity, and more or less the same manufacturing process. These variations are due to various causes, principal among which are housekeeping, condition of plant and machinery, mode of their operation and water use. Table 2.3 shows the effluent generated by plants of different crushing capacities.

Various possible waste water generating sources in a sugar mill are :

TABLE 2.3 : Volume of effluent generation from different capacity plants (2)

Crushing capacity in Tonnes per day	Effluent generated in cubic meters per day
Upto 1500	300 - 500
1500 to 3000	800 - 1200
3000 and above	2000 - 2500

Note : Above Figures exclude spray-pond overflow & cooling water overflows

2.3.1 Mill House :

The mill bearings are cooled by a flow of water which picks up grease and oil, as well as juice from the spill-over and leakages. The cane wash water also carries solids in suspension and dissolved organic and inorganic materials. The mill house waste water is large in volume and has high grease and organic content.

2.3.2 Excess condensate :

The condensate does not normally contain any pollutant but the entrained sugar and is used as boiler feed water and in the washing operations. It may so happen sometimes that it gets contaminated with juice due to entrainment or carry-over of solids with the vapour being condensed, in which case it goes into wastewater drain. The treatment required in this case is almost negligible and water can directly be used for irrigation.

2.3.3 Cooling and condenser waters :

Spent steam from the 2nd and 3rd evaporator and the vapours from the last evaporator are condensed in barometic condenser, from where the water and condensate go to spray pond and are cooled and reused. The vapours from the vacuum pans are also condensed in barometric condenser and go to the spray pond. From spray pond, a large quantity of this water overflows and is mixed with the wastewater. The pollution load in this water is the result of entrainment of sugar-syrup through the barometric condenser of the evaporators. Over-loading the evaporators and vacuum pans, boiling at excessive rate, operating them at incorrect liquid level and variation of vacuum, lead to loss of sugar through the condenser water. Improper design of these units, and particularly the entrainment separator , may also result in irregular boiling and splashing in the units.

Although the organic concentration of the cooling and condenser waters in terms of BOD is not too much, but the total organic load contributed by these waters is high, as the waters are generally high in volume.

2.3.4 Boiling house and floor washings :

The effluents from boiling house results from leakage from pumps, pipes, evaporators, crystallizers and specially from centrifuges together with periodic washings of floor. Waste water from floor washing contains grease, oils and spill-overs of the juice etc. The BOD conc. of the waste may vary in the range of 500 to 1000 mg/l. Although the discharge is intermittent and not large in volume, it represents the most polluting fraction of effluents because of its extremely high BOD, due to a large concentration of sugar.

Also during cleaning of the units, in particular, when the clarifiers are cleaned the wastes are very strong, attaining a BOD in the range of 35,000 to 75,000 mg/l. But this is generally effected twice or thrice in the curshing season.(3)

2.3.5 Boiler Blow - down :

The waste water from boiler blow - down is of intermittent nature, but contains relatively high solids and alkalinity.

2.3.6. Improper handling of molasses :

This as well as leakage and overflow from molasses storage tanks may seriously increase the pollution load of sugar factory effluents.

2.3.7 Sulphur and Lime Houses :

The washings of sulphur and lime house is intermittent in nature and contain a considerable amount of inorganic solids which include carbonates and sulphates. The effluents from these two units, when combined, would give neutral pH value of waste. This combined waste can be characterised as inorganic waste and does not contribute to organic pollution.

2.3.8 Soda and Acid wastes :

The juice heaters usually foul very quickly, so it is necessary to clean heating surfaces throughout the plant to remove accumulation of scales. This is accomplished by boiling with dilute caustic soda solution and inhibited with dilute Hydrochloric acid followed by rinsing with water.

Even though the rinsings from soda and acid wastes contain a very little organic pollution, the inorganic pollution is more in content and poses a shock load to wastewater treatment plants, since the discharge of the waste is occasional, once in a fortnight or so.

2.4 CHARACTERISTICS OF LIQUID EFFLUENTS FROM VARIOUS POINTS :

Table 2.4 shows the quantities of various effluent streams for 1,250 tonnes daily crushing capacity plant. Table 2.5 shows the characteristics of the major fractions of the effluent

Since the data varies widely among the different mills, actual survey of the conditions and analysis of wastes are necessary to determine the quantity and quality of the waste to be handled in a particular factory.

Tables 2.6 & 2.7 show the figures given in **IS :4903-1979** for volumes of wastewater from different sections and characteristics of major fractions.

2.5 CHARACTERISTICS OF COMBINED WASTEWATER :

Table 2.8 shows the characteristics of the combined waste emanating from a typical sugar factory.

Table 2.9 shows the figures given by **IS :4903-1979**.

The final effluent from a sugar mill, as it leaves the plant, does not appear to be very bad, because of its relatively clear appearance. The organic pollutants present in the waste remain in solution, being mainly, sugar and other carbohydrates. When the effuent stagnates in an area for a few hours, biological

TABLE 2.4 : PROCESS WISE EFFLUENT FLOW FROM SUGAR FACTORY OF 1,250 TONNES DAILY CRUSHING CAPACITY (2)

S.No.	Process	Flow(m^3 /day)
1.	Milling plant	50-80
2.	Cooling water of pumps	80-100
3.	Boiler blow-down	40-50
4.	Boiling house	150-200
5.	Excess condensate	20-30
6.	Sulphur house	14-20
7.	Lime house	14-16
8.	Final effluent	400-500
9.	Spray pond overflow	400-500

TABLE 2.5 CHARACTERISTICS OF WASTE STREAMS (2)

Plant/House	Temp.	PH	Dissolved Solids, (mg/l)	SS, (mg/l)	Oil& Grease (mg/l)	COD (mg/l)	BOD (mg/l)
Milling Plant	25-30	5-5.5	350-400	500-550	30-50	1000-1500	700-1000
Pump cooling at milling plant & at boiler house	30-50	6-6.5	400-500	30-50	-	200-300	50-80
Boiler blow down	85-90	5.8-6	450-500	50-100	-	500-550	30-40
boiling house	40-60	4.5-5	400-450	400-600	5-10	2000-3000	1500-2000
Excess Condensate	60-70	6-6.2	80-1000	5-10	-	250-300	100-150
Sulphur House	30-35	-	-	-	-	-	-
Lime House	25-30	9-10	1400-1500	3500-4000	4-6	200-250	100-150

TABLE 2.6 Volume of different type of effuents from Sugar Industry(4)

Sr.no.	Source of effuent	Average Quantity (litre/day/tonne cane)
1.	Mill House	730
2.	Boiling House and floor washing	230
3.	Filter cloth washing	360
4.	Condenser Water	1640

TABLE 2.7 Characterstics of Sugar Factory effluents(4)

Sr.no.	Source of Effluents	pH	Total Solids (mg/l)	SS (mg/l)	BOD (mg/l)
1.	Mill House	6.7	1760	910	210
2.	Filter cloth Washing	9.5	6970	4000	1765
3.	Boiling House	7.2	5130	120	5150

TABLE 2.8 Characterstics of Combined Waste(2)

Parameter	Range
Temp(^{0}C)	30-40
pH	4.6-6.0
Dissolved Solids,mg/l	1000-1200
Suspended solids,mg/l	250-300
Oil & Grease,mg/l	5-10
COD,mg/l	2000-3000
BOD, mg/l	1000-1500

TABLE 2.9 Characteristics of Combined effluents(excluding Condenser Water)of Sugar Factory

Sr.no.	Characterstics	Analysis
1.	pH	4.6 to 7.1
2.	Solids,mg/l	
	a) Total	870 to 3500
	b) Suspended	220 to 800
	c) Volatile	400 to 2200
3.	Biochemical oxygen demand (5 days at $20^{o}C$),mg/l	300 to 2000
4.	Chemical Oxygen demand,mg/l	600 to 4380
5.	Total Nitrogen,mg/l	10 to 40

action starts and septic condition soon developes in the region. The septic condition results in production of hydrogen-sulphide gas, imparting black colour to the waste. If the waste is discharged in a small stream its oxygen reserve is rapidly exhausted resulting in death of fish and other aquatic life (5).

Banerjee and Motwani(6) investigated the fish kills downstream from a sugar factory, which occured during the low water season. The BOD of the waste was 800 to 920 mg/l. Bioassay showed that the waste did not contain substances directly toxic to fish, but the high demand of the waste for dissolved oxygen resulted in anaerobic conditions, producing hydrogen sulphide which was lethal at low concentrations.

2.6 POLLUTION PROBLEM DUE TO BY-PRODUCTS

2.6.1 **Bagasse** – Generally, bagasse does not pose a problem of disposal of waste as it can be used as a fuel or as a raw material for manufacturers of paper, pulp, newsprint and insulation board. However, sometimes fibres from the bagasse find their way into waste stream via surface drain during a rainy season, but this can be controlled by proper house keeping .

2.6.2 **Press Mud** –Press mud originates from the settled sludge in the juice clarification process. The mud separated from the juice in vacuum filters, generally is transported to the sugar fields near the factory, as it has a high fertilizer value and the same is used as fertilizers after composting. Table 2.10 shows the characteristics of the press mud.

2.6.3. **Molasses** – The concentrated boiled juice is converted into the consistency of syrup,sugar is separated by crystallisation and centrifuging and the bottom liquor is molasses or mother liquor. Molasses is the basic raw material for the production of alcohol and many other organic compounds.

However,improper handling of molasses can drastically increase the pollution load of the mill effluent and the pollutional potential of molasses is evident from Table 2.11.

The production of molasses exceeds the amount required by all the distilleries of the country. About 70 percent of the molasses produced in the country is utilized by the distilleries (4). Besides this, molasses is also used as-cattle feed and tobacco curing. There is a good demand of molasses abroad and some quantity is exported.

2.7 MINIMAL NATIONAL STANDARDS (7) (MINAS)

The minimal National Standards (MINAS) for the sugar industry are the effluent standards achievable by the industry by installing Pollution Control measures which are within the techno-economic capability of the industry. MINAS may be attained in one stroke or in phases.

The Central ~~Water~~ Pollution Control Board has fixed Minimal National Standards (MINAS) for the sugar industry and

TABLE 2.10 : Press Mud Characteristics(2)

Nutrients	mg/kg
Phosphorous as (P_2O_5)	4470
Potassium as (K_2O)	4500
Calcium as (CaO)	10500
Magnesium as (MgO)	9450
Available Nitrogen	50
Moisture	76%
Wax	9%

TABLE 2.11 : Pollutional Potential of Molasses (2)

Parameters	Molasses
pH	3.5 to 4.1
Colour	Dark Brown
Total Dissolved Solids (mg/l)	200,000 to 320,000
BOD (mg/l)	440,000
COD (mg/l)	960,000
Chlorides (mg/l)	32,000
Sulphates (mg/l)	15,000
DO (mg/l)	Nil

Table 2.12 shows the tolerance limits.

Maximum tolerance limits indicated in Table 2.12 are acceptable both to the industry and to the states boards for pollution control and govt. is adoptingg the policies that under no circumstamces these standards are to be relaxed.

TABLE 2.12 Minimal National Standards

S.NO.	Parameter	Value
1.	pH	6.5 to 8
2.	$BOD_{5,20^{\circ}C}$ (mg/l)	100
3.	SS (mg/l)	100
4.	Oil & Grease (mg/l)	10

CHAPTER — III

CHAPTER III

BIO-OXIDATION KINETICS

Analysis of the organic content of waste waters is essential to determine their treatability, to design its pollution control plants and monitor their performance, and to evaluate the impact of waste water discharges on lakes and streams. The cumbersome task of identifying and measuring each compound has led to the general use of nonspecific or indirect tests to indicate the gross amount of organic material in waste waters. Under non specific tests, biochemical oxygen demand is the most widely used test and finds extensive application in design and operation of biological treatment.

Therefore, in this chapter, the basic concept of BOD is discussed. The mathematical models of BOD reaction, the effects of environmental parameters on BOD reaction and the methods for determination of BOD reaction constants are reviewed.

3.1 BIOCHEMICAL OXYGEN DEMAND

Biochemical oxygen demand(BOD) is the amount of oxygen required by aerobic microorganisms to degrade the organic material present in the wastewater effluent. The BOD is usually proportional to the amount of organic matter present and, therefore, is a measure of the pollutional strength of the waste.

The microorganisms, generally bacteria present in wastewaters remove organic matter by synthesis into new protoplasm. The degradable organic matter is used for food by the microorganisms to synthesize new cell mass and obtain energy for metabolic functions by oxidation of the organic matter to carbon dioxide and water.

The common standard test for BOD consists of determining the amount of oxygen used in a sample during 5 days of incubation at 20°C. To satisfy the oxygen requirement of the active microorganisms, most samples must be diluted with BOD free water containing essential salts and buffers that will not inhibit growth. The BOD test may also measure the oxygen used to oxidize reduced forms of nitrogen (Nitrogenous demand) unless their oxidation is prevented by an inhibitor.

Many factors can cause variation in BOD test data and affect the reliability of BOD measurements. Sampling procedure,sample storage, varying characteristics of the sample, lack of stirring, dilution,seeding,method of dissolved oxygen measurement and nitrification can contribute significant variation to BOD test measurements.

3.2 CARBONACEOUS VS NITROGENOUS BOD

The BOD reaction consists of two major phases as shown in Figure - 3.1. The first is a carbonaceous phase in which organic material is oxidized.

$$\text{Organic material} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{microbiological solids}$$

The accumulated first stage oxygen consumption after a 20 to 30 day(thoretically infinite) period of incubation represents the ultimate BOD. Because some organic material remains as nonbiodegradable cell residue, it is not possible biologically to oxidize all the organic material originally present in a sample.

In the second phase, ammonia and nitrite are converted to nitrate as follows :

$$NH_4^+ + 3/2\ O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + 1/2\ O_2 \xrightarrow{\text{Nitrobacter}} NO_3^-$$

$$\text{Net :}\quad NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

These reactions collectively are defined as nitrification. Nitrifying organisms, especially Nitrosomonas, exhibit a lower maximum growth rate than the carbon decomposing organisms,often causing nitrification to be delayed until much of the organic material has been oxidized.

A plateau often is observed in the carbonaceous BOD reaction within 24 hr. of incubation as shown in Figure - 3.2. The plateau generally represents the effect of a change between major phases of the carbonaceous metabolic reaction.(8,9)

The first phase involves the uptake of soluble organic substrate initially present in the sample; part is oxidized and

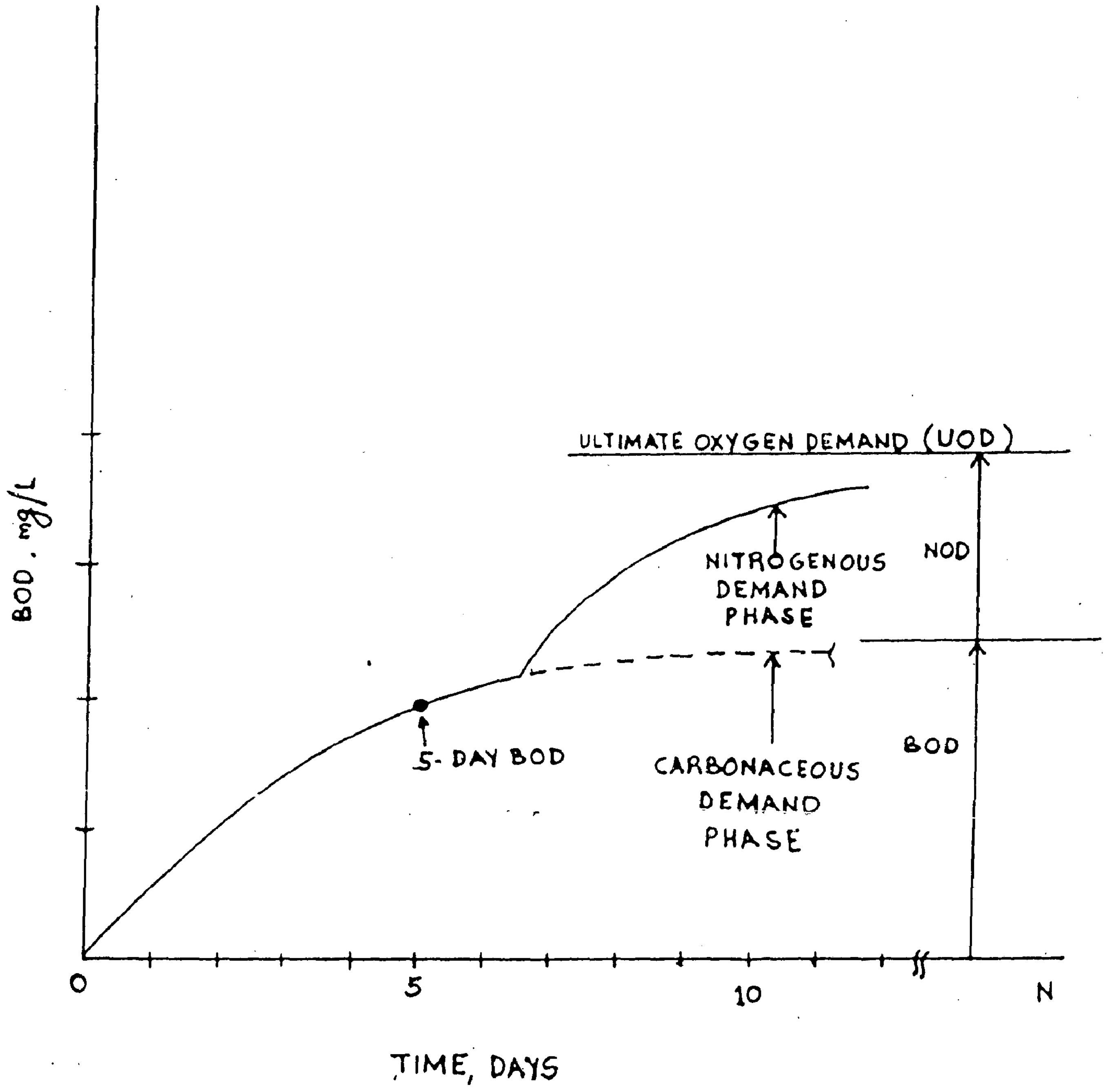

Fig. 3.1: BOD Curve showing Carbonaceous and Nitrogenous BOD Reactions.

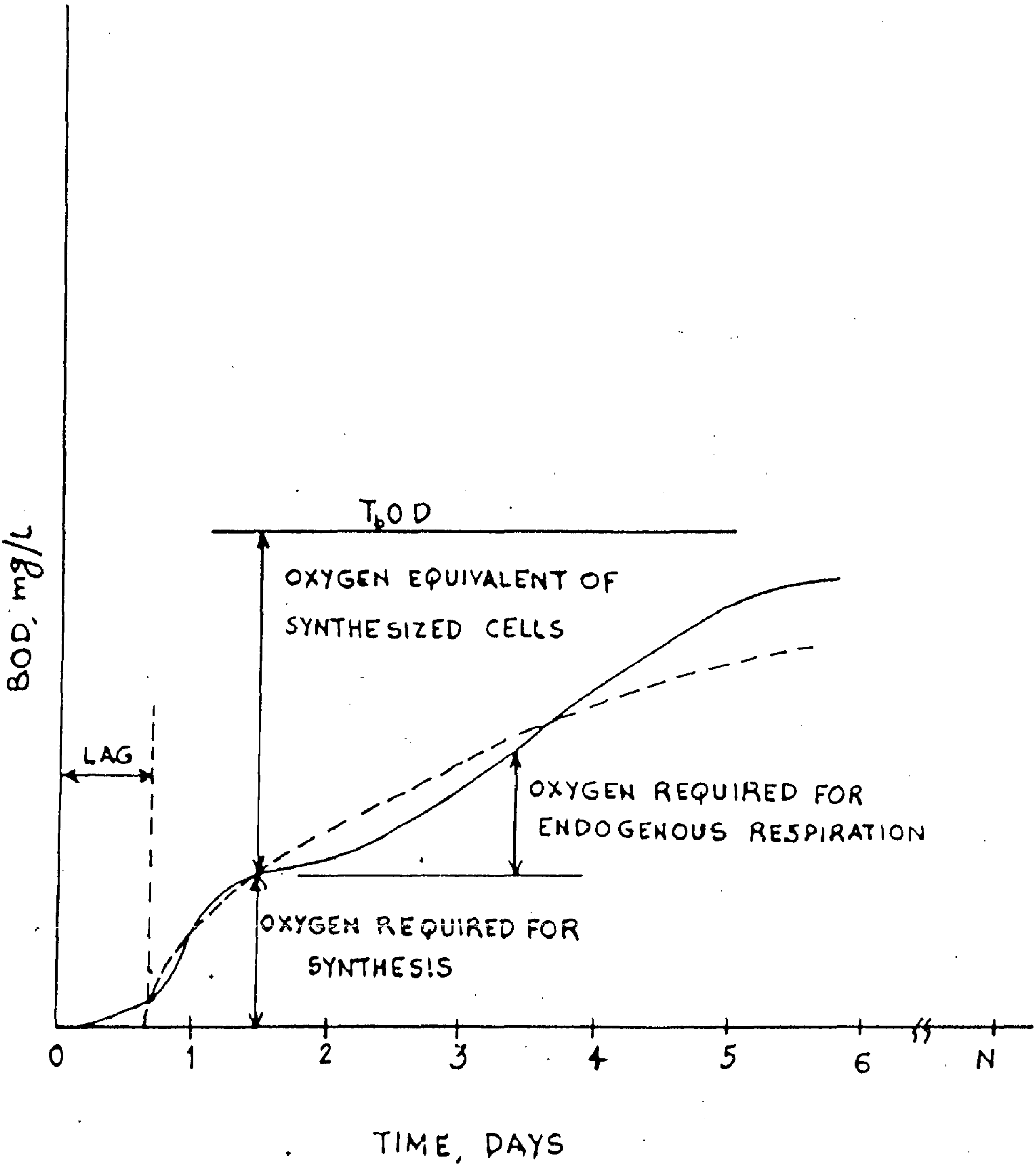

Figure 3.2 : Curve showing plateau in the BOD reaction.

part is synthesized into bacterial cell solids. The second phase is associated primarily with endogenous respiration of bacterial cells, growth of predator organisms that graze on bacterial cells produced during the first growth phase, lysis of microbial cells, and regrowth of bacteria on the soluble products released.

A lag occurs in the BOD reaction when an insufficient number of acclimated microorganisms is present, (Figure - 3.2). This lag can be reduced by adding seed microorganims to the test sample. In some instances organisms must acclimate to new environmental conditions, such as a change in temperature, pH, or waste concentration. Such acclimation usually occures within a few hours after seeding a sample.

3.3 Mathematical modelling of the BOD reaction

The mathematical formulation of the BOD progression curves has been widely attempted but the exact nature of the process is open to conjecture. However, the most frequent mathematical models in use are :

3.3.1 The First - order or monomolecular equation

The first order BOD model (10) defines the rate of disappearance of organic matter from polluted waters by means of microbial oxidation as proportional to the concentration of the remaining organic matter L, or

$$-dL/dt = K'L \qquad (3.1)$$

which on integration over suitable limits and the substitution of $(L_o - Y_t)$ for L gives ;

$$Y_t = L_o(1 - e^{-k't}) \quad \text{or} \quad Y_t = L_o(1 - 10^{-kt}) \qquad (3.2)$$

Where, Y_t = amt. of BOD that has been exerted at any time t (mg/l) or organic material at time t

= $L_o - L$

L_o = BOD remaining at time t = 0, i.e. the total or ultimate first stage BOD initially present (mg/l)

t = time in days

K' = rate constant of the BOD reaction in days^{-1} (base

K = K'/2.303

From Equation - 3.2 it follows that for a vary long oxidation period (that is time tending to infinite) the BOD exerted at timet equals to the ultimate BOD. Therefore, k' (ork) and L_o measure, respectively, the rate of biochemical stabilization and the total amount of putrescible (or organic) matter present.

3.3.2 The Second order equation

The model that too has gained some acceptance is a second order reaction equation in the form of a transposed, rotated hyperbola. This model (11) describes the rate of disappearance of organic matter as being proportional to the square of the concentration of remaining organic matter, or

$$-dL/dt = k' L^2 \qquad (3.3)$$

Which on integration over a suitable limits and substitution of $(L_o - Y_t)$ for L gives :

$$Y_t = (L_o k't) / [(1 + L_o k't)] \qquad (3.4)$$

Where, k' = rate constant in $(mg/l)^{-1}$ day^{-1} and other bears the same as described in first order equations.

Evaluation of second order equation has produced conflicting results. Certain investigators have found that the second order equation fits BOD data as well as the first order (12) or that it gives a better fit than the first order (13) Also, it has been observed that the first order equation gave the better fit when the rate constant was below 0.2 per day and the second order equation gave a better fit when the rate constant was above this value (14). Such conflicting reports suggest that if the first and second order equations do not adequately describe BOD kinetics, then perhaps some other order kinetic equation could be superior to both.

3.3.3 The multiorder equations

If n is defined as the order of the reaction, then a generalized form of equation (1) would be :

$$-dL/dt = K' L^{n} \qquad (3.5)$$

Where, k' is rate constant in $(mg/l)^{-1(1-n)}/t$ upon integration and introduction of Y_t , this equation becomes :

$$Y_t = L_o - [(n-1)K't + Lo^{(1-n)}]^{1/(1-n)} \qquad (3.6)$$

This equation is valid for any reaction order except the first where 1 /(1-n) becomes indeterminate.

Despite all the discrepancies, the first order equation still remains the most widely employed BOD mathematical model. Although the first order or second order equations may be fit for data from tests lasting < 10 days, the second order equation provides a better fit for data collected from long-term oxidation tests. The first- order equation has a covariant property of giving satisfactory fit to most data because of a compensating relationship between k' (or k) and Lo, that is, an increase in one coefficient compensates for a decrease in the other coefficient, producing a number of coefficient pairs that describe a given set of data with equal precision **(15,16)**.

Another reasons for the use of first order equations may be the ease with which it can be combined with atmospheric reaeration (later other factors) to form the oxygen sag equation **(17)** and the failure to demonstrate the unquestionable superiority of alternative models.

3.4 Effects of Environmental parameters on BOD reaction

The BOD exertion phenomenon in an effluent is a complex biochemical reaction. Several factors affect the process and one has to incorporate their effects before it can be used in design, operation and control of treatment plants. Some of the important factors include temperature, pH , presence of toxicants, seed and substrate concentration.

3.4.1 Effect of Temperature

Several authors have studied the effect of temperature in detail on different types of waste waters namely domestic sewage, treatment plant effluents and river water samples. It has been confirmed that both L_o and K'(or k) are dependent on temperature and the nature of samples tested.

(a) Effect of Temperature on Ultimate BOD (Lo)

Many empirical relation has been proposed in the literature relating the ultimate BOD at any temperature and BOD at temperature 20°C. Using different effluents (18,19,20) and base, the general observation is that the ultimate BOD does not vary greatly with temperature. This could be due to the fact that the BOD (1st stage) represents indirectly the concentration of oxidizable organic matter available for the bacteria. While the metabolic rate of bacteria is slower at the lower temperatures, it might be expected that if given sufficient time they will use up the food supply.

At higher temperatures, there could be considerable nitrification taking place during the apparent first stage of oxidation. (21)

(b) Effect of Temperature on reaction rate Constant (k)

The parameter k appears in the BOD expression is temperature dependent and has been defined either by Arrhenius expression as :

$$K_T = A \exp(-E/RT) \qquad (3.7)$$

or by Vant Hoff - Arrhenius relation as :

$$K_T = k_{20} \theta^{(T-20)} \qquad (3.8)$$

Where, K_T - the rate constant at Temperature T

A - Arrhenius specific rate constant

E - activation energy

R - gas constant

K_{20} - rate constant at 20^{o}C temperature

θ - is contant in most cases, however it often vary with temperature.

The activation energy (E) found to vary in between 8 to 9.0 kJ/mole (22) for different waste treatment processes. While the value of θ has been found to vary from 1.056 in the temperature range between 20 and 30^{o}C to 1.135 in temperature range between 4 and 20^{o}C (23).

3.4.2 Effect of pH on BOD exertion

The organisms which accomplish the biochemical oxidation of organic matter are acclimated to a narrow pH range. A normal range of pH values for such organism is 6.5 to 8.3 Outside this range, the rate of oxidation decreases.

Information about the effect of pH on the ultimate BOD is limited in the literature, however, it is observed that there is no appreciable change in the ultimate BOD in the pH range of 6.2 to 7.2 and beyond 7.2 pH value, a decreasing trend is observed .(24)

3.5 METHODS FOR DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND PARAMETERS

The determination of the constants Lo and K in Eq (3.2) is manadatory if a water quality model is to be used for finding the solution of the wastewater problems. It seems a simple task to find out the constants but the problem has been compounded due to the non-liner nature of the equation.

Therefore, as an aid to the solution of finding out these constants, many ingenious mathematical and graphical procedures have been developed and are listed in Table 3.1. All these methods are based on the assumption that the BOD progression is a first - order reaction.

Hewitt etal (25) while comparing different methods have concluded that the results obtained from different methods are strikingly different. Certain methods tended to give higher K and/or Lo values and others to give low K and /or Lo values. The cause of these deviations was not due to deficiencies in the calculation methods but probably due to poor adherence to first order kinetics.

Available method to estimate the BOD kinetic parameter requires either laborious hand calculations or uses graphical techniques. On the other hand, Gupta (26) has used the non-linear least square optimiser (Marquardt Method) in estimating the first order BOD equation parameters for the small scale agro-based paper mill effluent. He concluded in his finding that the non-linear least square optimiser is the best to use compare to hand calculations in Reed-Theriault method, which gave the best result among the all other methods reported in the literature.

TABLE 3.1 Different methods for the estimation of K and Lo

S.NO.	Method Description	Equation Type	Reference
1.	Least square method	Integral	Reed & Theriault, 1931 (27)
2.	Two-point method	Integral	Rhame, 1956 (28)
3.	Slope method	Differential	Thomas, 1937 (29)
4.	Log difference method	Integral	Fair, 1936 (30)
5.	Moments	Integral	Moore etal, 1960 (31)
6.	Simplified slope	Differential	Navone, 1960 (32)
7.	Graphical method	Differential	Fuji moto, 1964 (33)

CHAPTER - IV

CHAPTER - IV

SAMPLING AND ANALYSIS

The aim of the present work is to obtaine the field data by actual survey of the plant and to determine the bio-oxidation behaviour and nature of the effluents. Generally, Pollution Control measures being adopted by various sugar industries are arbitrary in nature and there is no common basis or guidelines for adopting a particular treatment process. Also, the volume of the effluent and its pollution load vary significantly from factory to factory, inspite of using the same manufacturing process. Therefore, an indepth study of a sugar unit by actual survey of the plant is a must before selecting an appropriate and practicable technology. The following points were taken into consideration for selecting a mill :

1. Effluent samples collected sould be considered as representative samples of the sugar industry as a whole of that particular size,
2. Management willingness to share the informations, and
3. Proximity of the mill with easy accessibility.

Accordingly, a sugar plant in North - Western U.P. around Roorkee was selected. This mill do not have at present the external treatment facility but have already taken up the work and are expecting to commission their treatment plant in the next crushing season. It is expected that the results of the present work will find the utility during the operation of their treatment plant.

4.1 Description of the mill under study

Table 4.1 gives detail of the plant under study.

The schematic process flow diagram alongwith sources of waste generation are shown in Figure - 4.1. The processing stages are described below :

4.1 Milling

The sugarcane is usually procured from the nearby fields. After initial preparation of the sugarcane, juice extration by crushing the cane between massive rollers is the first step in raw sugar processing. Mills consist of 5 units through which the crushed cane or bagasse successively passes, as shown in Figure - 4.1. To aid in the extraction of the juice, sprays of water or thin juice directed on the blanket of bagasse as it emerges from 1st, 2nd, 3rd, and 4th mill unit further helps to leach out sugar. Nearly 95% of the sugar in the cane goes into the juice and this percentage being called the sucrose extraction. The water spray on the bagasse is the main source of effluent produced in the milling plant. Alongwith the sugarcane juice, it carries solids in suspension. The final bagasse from the 5th mill contains the unextracted sugar, the woody fiber, and 40 to 50 percent of water. This goes to boilers as fuel for production of process steam.

4.1.2 Clarification

The juice from the mills is acidic, turbid and dark-green coloured. The clarification (or defaction) process designed to remove both soluble and insoluble impurities , employs lime

Table 4.1 PLANT DETAILS

Plant set-up	:	Private
Installed Capacity	:	3500 TCD
Actual Crushing Capacity	:	3200 TCD
Sugar manufacturing Process	:	Double Sulphitation
Statistics of Operation	:	
a) Sugar Recovery	:	9.48%
b) Bagasse Produced	:	33 to 34%
c) Molasses Produced	:	4.3 to 4.5%
d) Press Mud	:	3.80 to 4.0%
Effluent treatment Facility	:	Nil(in an erection stage)
Mode of effluent discharge	:	To a Nullah nearby and mixing alongwith municipal sewage.

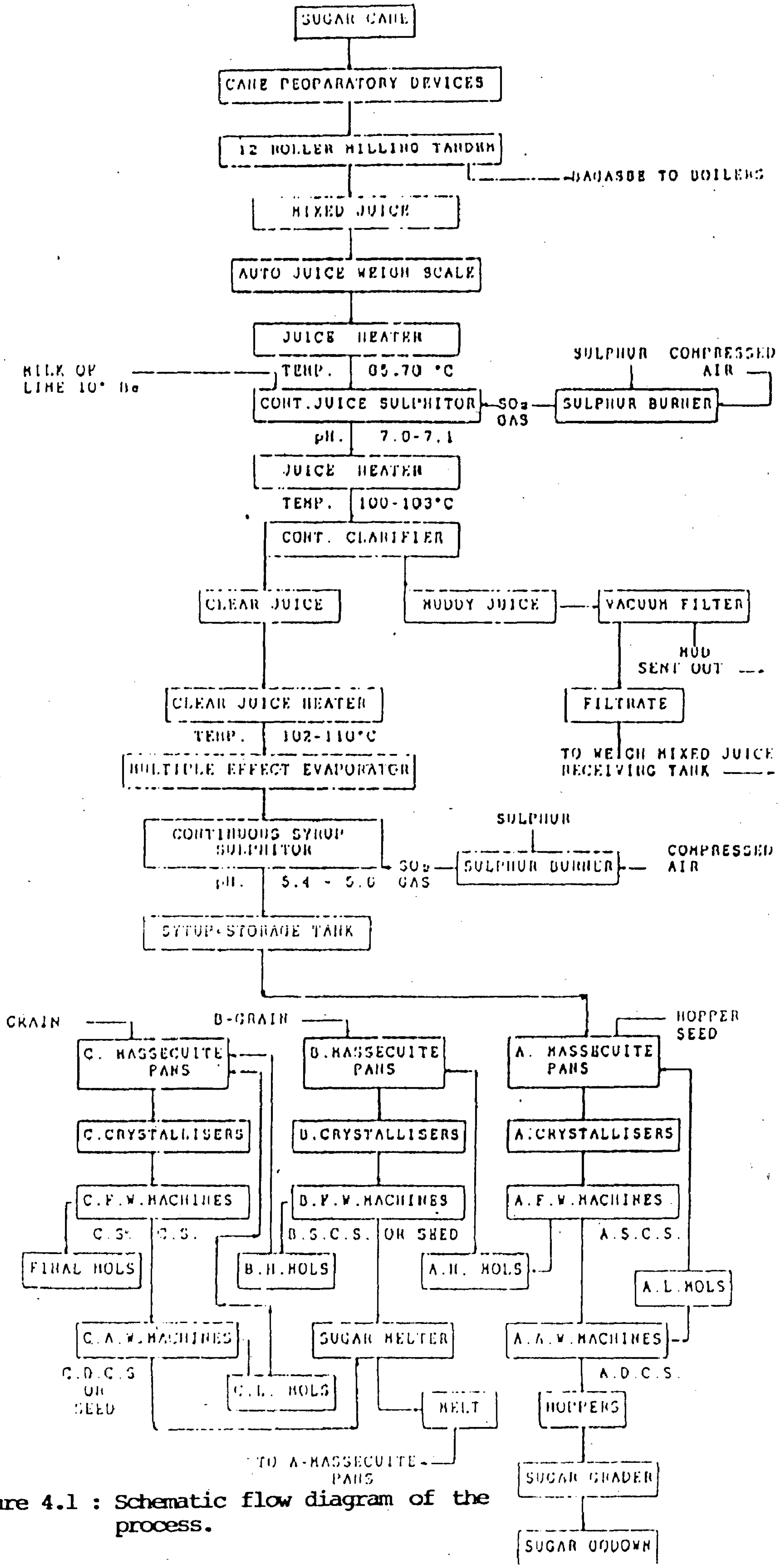

Figure 4.1 : Schematic flow diagram of the process.

and sulphur dioxide in the Juice sulphitation tank. The mud separate from the clear juice by sedimentation. The muds are filtered on Dorr - rotary vacuum filter. The filter press juice returns to sulphitation tank and the press mud is sell to farmers for manure purpose and therefore, does not pose a disposal problem. The clear dark-brown clarified juice goes to the evaporators without further treatment.

4.1.3 Evaporation

The clarified juice contains about 85% of water. Two thirds of this water is evaporated in vacuum multiple effects evaporators. The syrup leaves the last body continuously with about 65% solids and 35% water. The vapour from the last effect is condensed in barometric condenser and appear as liquid effluent stream. The concentrated syrup is again bleached by passing sulphur dioxide through it and the pH of the syrup drops down to about 5.4.

4.1.4 Crystallization

Crystallization takes place in single effect vacuum pans, where the syrup is evaporated until saturated with sugar. At this point, seed grain is added to serve as a nuclei for the sugar crystals and more syrup is added as the water evaporates. The growth of the crystals continues until they are of a predetermined size when the pan is full. The mixture of crystals and syrup is concentrated to a dense mass called massecuite.

4.1.5 Centrifugation

The massecuite from mixer or crystallizer is drawn into automatic operated centrifugals. The perforated lining retains the sugar crystals, which may be washed with water, if desired. The mother liquor 'molasses' passes through the lining because of the centrifugal force exerted. The molasses is stored in masonary pits or steel storage tank and ultimatly sold to distilleries.

4.2 Effluent sampling

The sampling method used should be one that presents a representative picture of the quality of the waste stream. Generally, composite sampling is preferred over grab sampling, as these provide more meaningful data because they represent average plant conditions over a relatively long period of time and are invaluable in determining treatability and equipment design.

Selection of sample points is of prime importance.For choosing appropriate sampling locations, the following points were taken into consideration :

- Flow rate measurement facility
- To ensure the sample to be representative and the effluent must be homogeneous
- The total mill discharge should be monitored at a minimum of one check point location having high degree of reliability.
- The block discharges should be monitored at locations that give the maximum information about the function of the block.

For the mill under study, there are two outlet streams of waste water, representing boiling house and mill house. The effluent through two different channels meet in a Nullah nearby alongwith municipal sewer, since the mill do not have the treatment facility. The mill house effluent stream consists of water used for cooling the mill bearing, water used for maceration of sugarcane which gets contaminated with sugarcane juice and the washings of the mill house floor (which is intermittant). The leakages from the pipes and spill-overs of the sugarcane juice also increase significantly the organic load of the effluent stream.

The boiling house effluent stream includes the condensate water from the vacuum pans, excess condensate from the evaporators, leakages from pumps, pipes, evaporators, crystallizers and centrifuges together with periodic washings of the floor. The organic load in this stream is mainly due to the entrainment of sugar syrup with the vapours from the vacuum pans and the evaporators. These vapours are condensed in the surface condenser and therefore, appears as a liquid effluent. The washings of the Dorr-rotary filter also increases the suspended solids and, organic load. But, this is generally effected once in 3 hours or 2 to 3 times in a shift.

After selecting the sampling point , flow measurements were made using V-notch weirs. The flow rate is calculated by measuring the height of the flow. The flow rate is calculated as:

$$Q = 8/15\ [C_D]\ [2gh^5]^{0.5}\ \tan\theta/2$$

Where, Q – flow rate , m^3/s

h – height of flow , m

g – gravitational constant , m/sec^2

θ – angle of notch , 90°

C_D – discharge coefficient (=0.58)

In addition to the selection of sample points and the methods of sampling , following point were taken into consideration for sampling the effluent.

- volume of sample
- analysis and handling
- preservation of samples.

The volume of sample required depends on the analyses to be performed. When samples have been collected , proper handling is often of paramount importance to obtain valid test results. Many parameters require that samples be specially preserved immediately after collection. This prevents change in characteristics of particular constituents during storage. The maximum limits of storage of wastewater are :

Unpolluted water = 72 hrs.
Slightly Polluted water = 48 hrs.
Grossly Polluted water = 12 hrs.

During sampling of liquid effluents from three points representing boiling house effluent, mill house effluent and combined mill effluent, the samples were kept at $4^{o}C$ by placing the sample bottles in an ice-box. Since, composite sampling was done every 2 hrs. for 24 hrs. the volume taken each time was 500 ml. After obtaining the total volume of 6 liters for each effluent stream at the end of one day, 300 ml. was taken out for

BOD and stored in an air-tight BOD bottles. The remaining amount was utilized for determining the other parameters.

4.3 Characterization of the parameters

The samples collected should be analysed as quickly as possible so that the sample characteristics do not get distorted. All the parameters have to be evaluated in accordance with well established standard analytical methods.(As per IS specifications)

The parameters important for sugar mill effluents as discussed in Chapter - II are :

- BOD
- COD
- pH
- Suspended solids
- Dissolved solides
- Temperature
- Oil & grease
- Dissolved oxygen (D.O.)

These parameters were evaluated for each effluent stream. Three of the parameters i.e. D.O., temperature and pH were measured at the sampling point and at each time , the samples were collected. Samples collected for chemical oxygen demand (COD) were preserved by concentrated sulfuric acid to bring the $pH<2$.

Biochemical oxyggen demand (BOD) test was carried out after the 4 hr. interval period between collection and analysis, therefore, no preservative was used. However, all the samples were kept in the ice-box both during the collection and transportation to maintain the temperature at or around $4^{o}C$.

CHAPTER — V

CHAPTER - V

RESULTS AND DISCUSSIONS

The composite and grab samples collected from three different streams of the plant , viz boiling House , Mill House and combined mill were analysed according to the prescribed standard methods. The following section of the chapter discusses the results of composite samples collected. Also,the results of grab samples collected at different stages are also taken into consideration and have been incorporated in the results.

5.1. Characterization of sugar mill effluents

Figure 5.1 (also see Table A1) shows the variation in flow rates with time for boiling house, mill house and combined mill effluents. Significant fluctuations are observed with time for these streams. The reason for flow rate fluctuation in mill house streams is the intermittant mixing of water used for floor washing and therefore , peaks are observed two to three times in a eight hour shift. In the case of boiling house effluent stream, the flow - rate variation is mainly due to the presence of excess condensate which is disposed off as the liquid effluent. The vapours from the evaporators and vacuum pans are condensed in the condenser and therefore, leaves the house as a liquid effluent stream. Depending on the amount of steam required in the process, the condensate from the evaporators is sent to the boiling house and the excess one get mixed with the condensate water and results in the increase of flow rate. The flow rate for mill house effluent stream ranges between 19 to 36 (avg. 29.0) m^3/hr , whereas it ranges between 42 to 60 (avg. 50) m^3/hr for the boiling house effluent stream. The figure also shows the combined mill effluent flow rate variation at a particular time. The flow rate ranges 68-90 m^3/hr. with avg. flow rate of 80.0 m^3/hr.

Figure 5.2 (also see table A-2) shows the variation in temperature of effluent from mill house, boiling house and combined mill sections. The temp varies between 41.0 to 46.0°C, 22.0°C to 27.0°C and 35.0 to 37.0°C respectively for boiling house, mill house and combined mill streams. The mill house waste is more or less at the ambient temperature. However, the temperature of the effluent from boiling house is significantly high. This is due to the presence of condensate water in the liquid effluent stream. The temperature of combined mill effluent has a marginal variation. The effect of ambient temperature on effluent stream is not expected as sampling locations are near to the effluent generating sources. The ambient temperature varied between 19 to 27°C.

Table 5.1 represent the characteristics of effluents discharged from mill house. It is apparent from Table 5.1 that the mill house wastewater is low in pH. The low pH is mainly due to the contamination of sugarcane juice. The oil and grease content is high, since the water which is used for cooling the mill bearings picks up oil & grease and carries along with it. The zero dissolved oxygen (DO) level indicates the extent of organic load exerted by the mill house effluent. This severity of

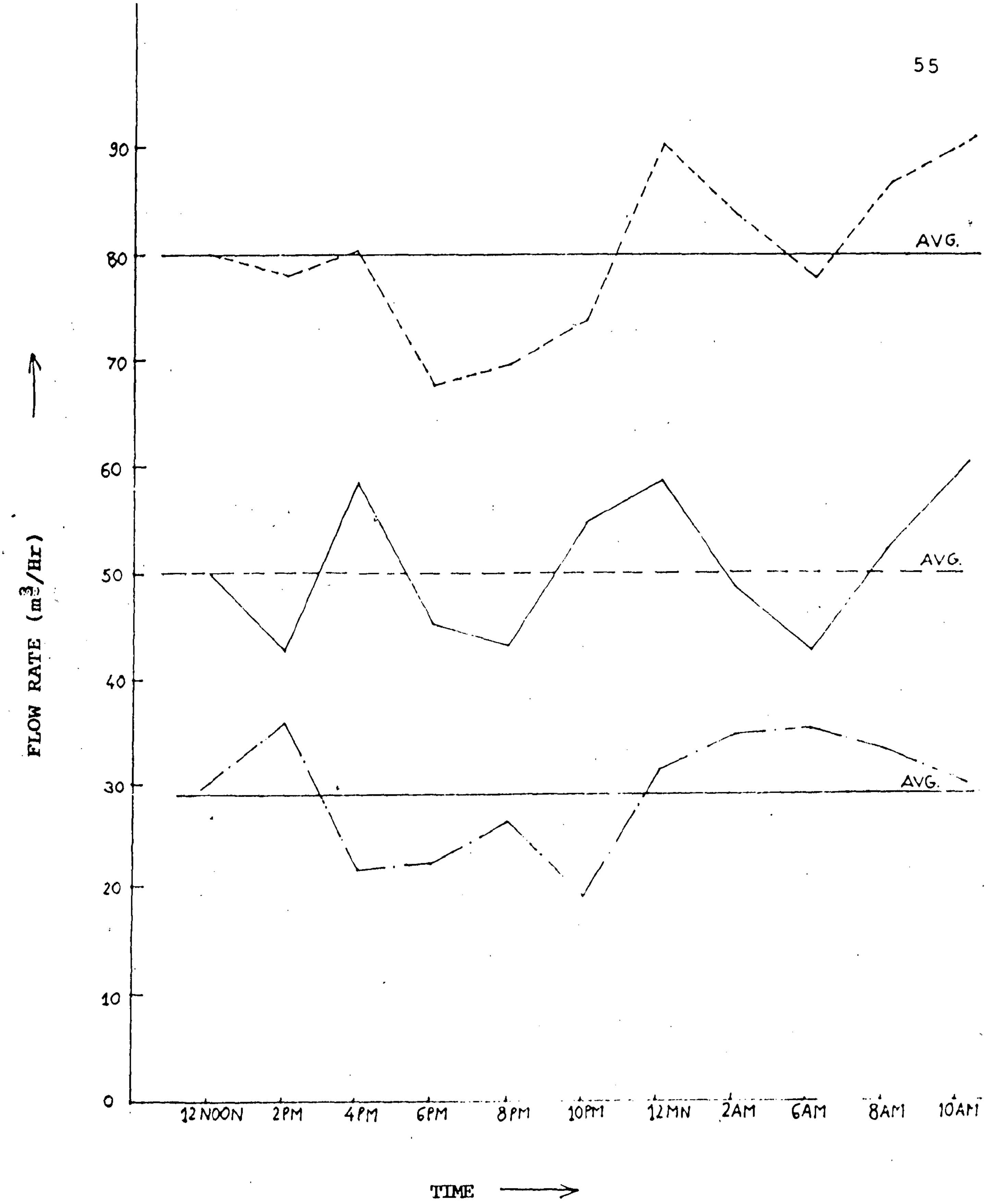

Figure 5.1 : Variation of effluents flow-rate with time.

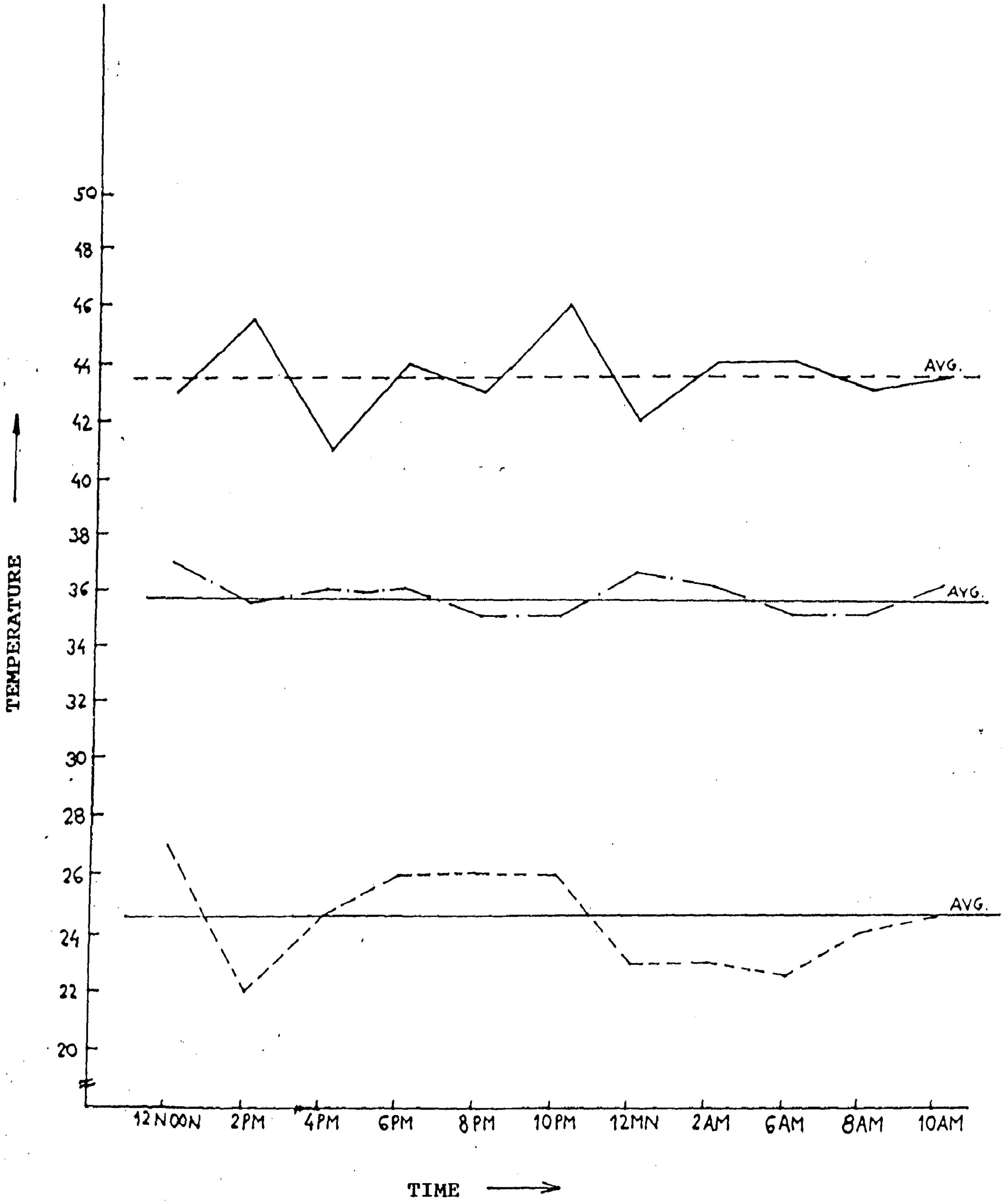

Figure 5.2 : Variation in effluent temperature with time.

the pollution load is further supplemented by high values observed for BOD and COD. In the mill house section, the water is sprayed on the bagasse as it emerges from first and second mill unit. Alongwith sugarcane juice, it carries bagasse fibers and leave the mill house as a waste stream. The biodegradable nature of the extracted juice is the main reason for the high BOD_5 and COD values . The total suspended and total dissolved solids are 510 mg/l and 340 mg/l respectively. Though the dissolved solids content is not too high, the total suspended solids is much above the permissible limits. This is mainly due to the presence of suspended impurities present in the freshly extracted juice as well as the bagasse fiber present in the waste stream. It can be concluded that the pollution load exerted by the mill house waste stream is significantly high and therefore, cannot be left as such without treatment.

Table 5.2 represents the characteristics of effluents discharged from boiling house. The boiling house section includes evaporators, vacuum pans , crystallizer , centrifuges. The washings of the Dorr - rotary filter also leaves with the same waste stream. The boiling house effluent has high temperature (41 °C-46 °C) which is mainly due to the mixing of condensate water with the waste stream. The pH and oil & grease level is within the permissible limits. The BOD and COD are less compared to values obtained for the mill house effluent (see table 5.1). However, the organic load exertion is still high. The entrainment of sugar syrup with the exit vapours from the evaporators and

TABLE 5.1

Characteristics of Mill House effluent

S.NO.	Parameters	Values
1.	pH range	5.5 ± 0.2
2.	Temperature (^{o}C)	22 - 27
3.	Total solids (mg/l)	850
4.	Total Suspended solids (mg/l)	510
a.	Volatile Suspended solids (mg/l)	325
b.	Fixed suspended solids (mg/l)	185
5.	Total dissolved solids (mg/l)	340
a.	Volatile dissolved solids (mg/l)	215
b.	Fixed dissolved solids (mg/l)	125
6.	Oil and grease (mg/l)	35
7.	$BOD_{5,20\ C}$ mg/l)	730
8.	COD (mg/l)	1150
9.	D.O. (mg/l)	NIL

TABLE 5.2

CHARACTERISTICS OF BOILING HOUSE EFFLUENT

S.No.	Parameter	Values
1.	pH range	7.3 ± 0.2
2.	Temperature (^{o}C)	41-46
3.	Total solids(mg/l)	1100
4.	Total suspended solids(mg/l)	725
(a)	Volatile suspended solids(mg/l)	450
(b)	Fixed suspended solids(mg/l)	275
5.	Total dissolved solids(mg/l)	375
(a)	Volatile dissolved solids(mg/l)	225
(b)	Fixed dissolved solids(mg/l)	150
6.	Oil & Grease (mg/l)	10
7.	$BOD_{5, 20 C}$ (mg/l)	550
8.	COD (mg/l)	950
9.	D.O.(mg/l)	Nil

vacuum pans is the main reason for the large BOD exertion. These vapours are condensed in the surface condenser and therefore, appears as a liquid waste stream. The total suspended and total dissolved solids in the boiling house waste stream is 725 mg/l and 375 mg/l respectively. The absence of dissolved oxygen (DO) in the waste stream indicate the extent of pollution load exerted by the boiling house effluent.

Table 5.3 shows the characteristics of the combined mill effluent. The dissolved oxygen is practically nil in this final discharged effluent stream. BOD and COD values are 1050 mg/l and 2100 mg/l. This shows the extent of water pollution problem posed by the sugar mill under study. Since the mill does not have the treatment facility,the combined mill effluent is discharged alongwith the sewer to the nearly nullah. The total volume of effluent generated is 1800 m3/day. The total suspended and dissolved solids are 650 mg/l & 1100 mg/l respectively.

5.2 BOD EXERTION WITH TIME

Table 5.4 shows the BOD exertion with time at $20^{\circ}C$ for all the three effluent streams. The generation of such type of long term BOD data is useful in calculating k' and L_0.

Figures 5.3, 5.4, 5.5 indicate that BOD exertion with time for all the three streams is nearly a first order reaction. To arrive at this decision, the two widely used mathematical models, viz. first order and second order equations are compared using the observed BOD data. After determining the values of the constants in the two equations, Y_t values are calculated at

TABLE 5.3

CHARACTERISTICS OF COMBINED MILL EFFLUENT

S.No.	Parameters	Values
1.	pH range	6.9± 0.3
2.	Temperature(^{o}C)	35-37
3.	Total solids(mg/l)	1750
4.	Total suspended solids(mg/l)	650
(a)	Volatile suspended solids(mg/l)	360
(b)	Fixed suspended solids(mg/l)	290
5.	Total dissolved solids(mg/l)	1100
(a)	Volatile dissolved solids(mg/l)	710
(b)	Fixed dissolved solids(mg/l)	390
6.	Oil & Grease (mg/l)	10
7.	BOD_5, 20 C$^{(mg/l)}$	1050
8.	COD (mg/l)	2100
9.	Volume(m^3/day)	1800
10.	D.O(mg/l)	Nil

different time period and thereafter plot is made. The observed data has also been plotted to know the deviation of the observed data points from the respective curves. The statistical parameter the standard error of estimate is also used for determining the precision obtained in fitting the curves to the observed data. The standard error of estimate is defined as :

$$Syx = \left(\frac{(Y_o - Y_e)^2}{n-2} \right)^{1/2}$$

Where Syx = Standard error of estimate.

Y_o = Observed Y-axis values

Y_e = Y-axis values computed using the regression equation.

n = No. of observed values.

The smaller standard error of estimates found in case of first order equation for all the three streams and also more closely found the observed data points to the first order curve line, have confirmed that the first order equation fits BOD curves for sugar mill effluents much better than does the second order equation.

Table 5.5 shows the values of K' and L_o calculated from various mathematical methods(see table 3.1) using the observed long term BOD data. (Table 5.4) The total absolute deviation of the calculated values of BOD from the observed values of BOD are shown in Table 5.6 . It is evident from Table 5.6 that the method employed in the calculation of parameters significantly influence the values of parameters.

TABLE 5.4 : BOD exertion with time

Time (in days)	Average BOD(in mg/l) at 20°C		
	Boiling House effluent	Mill house effluent	Combined Mill effluent
1.	180	300	400
2.	260	420	500
3.	360	580	720
4.	450	640	840
5.	520	750	1040
6.	580	810	1080
7.	660	860	1150
8.	700	900	1200
9.	730	930	1230
10.	760	950	1270

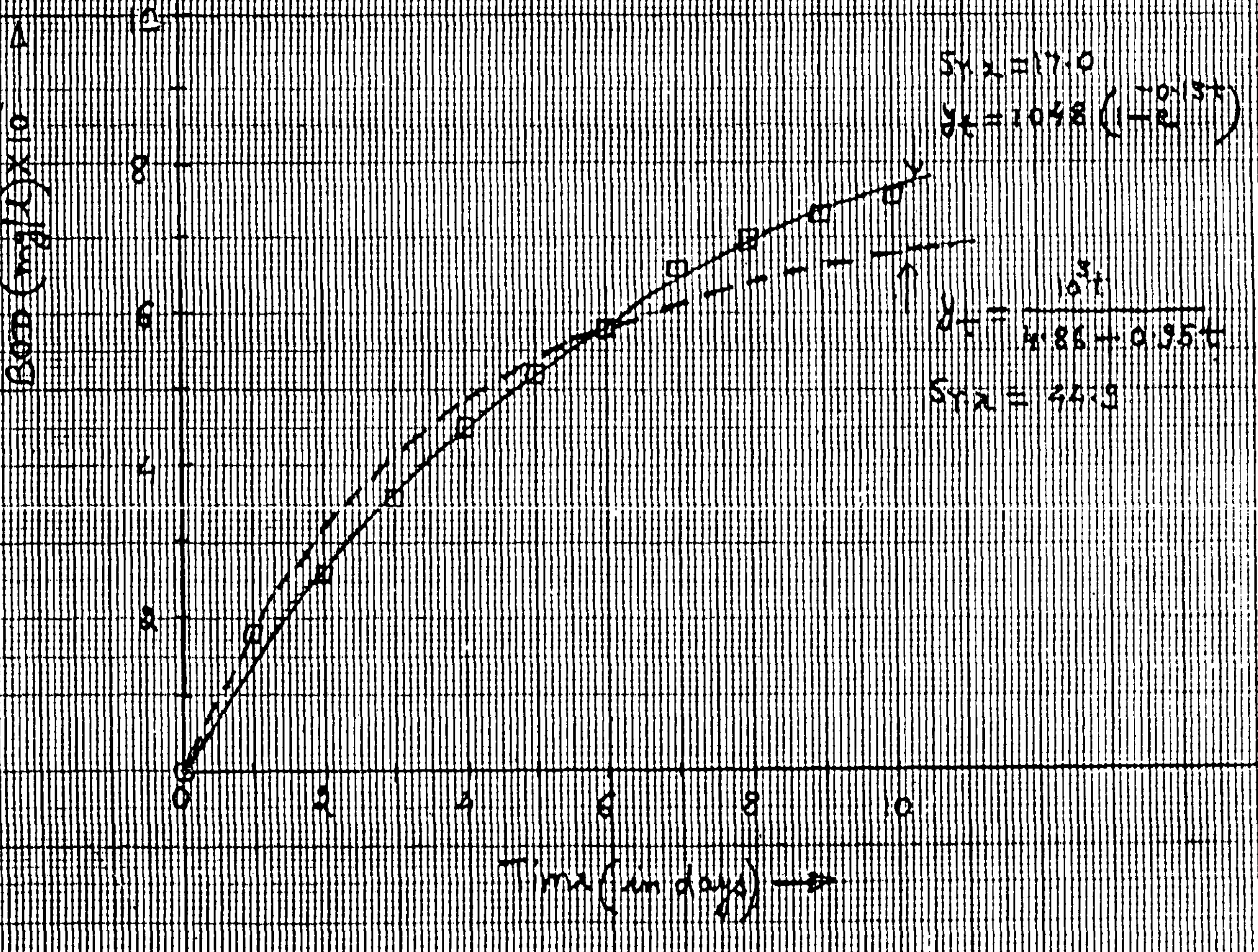

Figure 58 BOD progression curve fitting first and second order equations (for Boiling House effluent)

⊡ Observed value

— Calculated value fitting first order equation

- - - Calculated value fitting second order equation

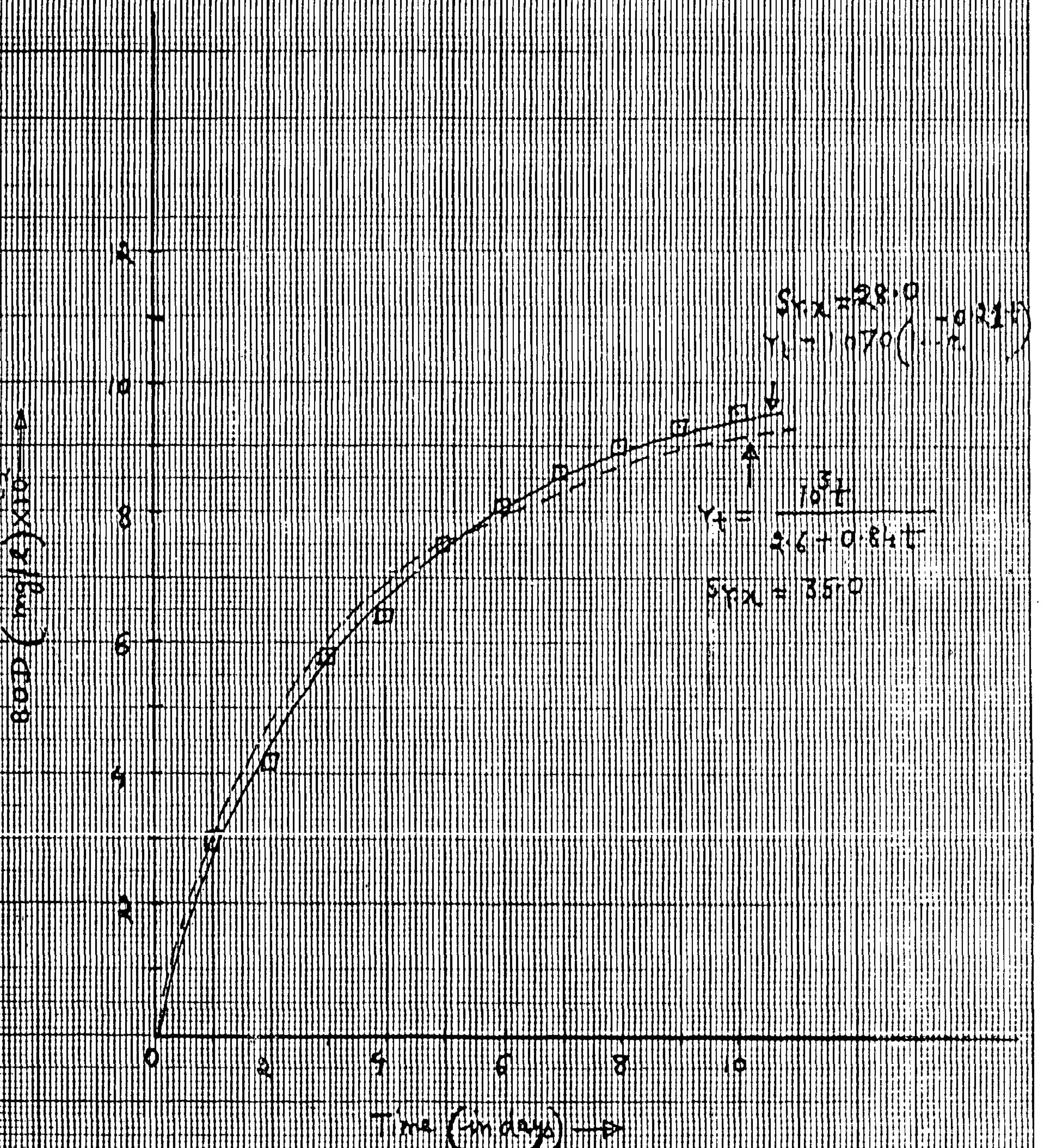

Figure 5.4. BOD progression curve fitting first and second order equations (for [illegible] effluent)

□ Observed value
— Calculated value fitting first order eqn
-- Calculated value fitting second order eqn

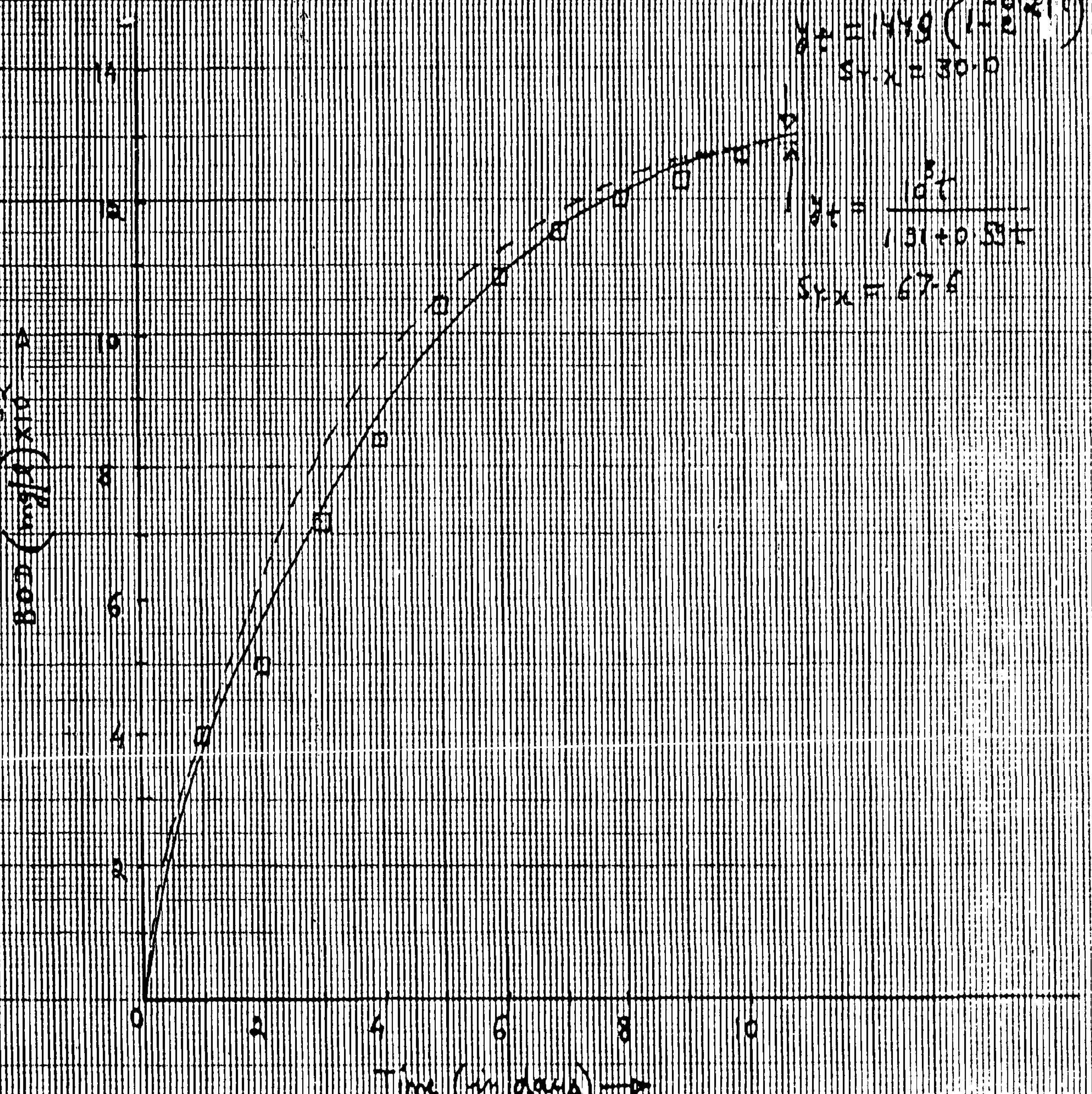

Figure 5.5 : BOD progression curve fitting first and second order equations (for [illegible] mill effluent)

□ observed value
— Calculated value fitting first order equation
--- Calculated value fitting second order equation

TABLE 5.5 : VALUES OF K'(in day^{-1}) AND L_o (in mg/l) USING DIFFERENT METHODS

S.No.	Method	Source of effluent		
		Boiling House	Mill House	Combined Mill
1.	Least square method	K'=0.15 Lo=1000	K'=0.25 Lo=1050	K'=0.23 Lo=1440
2.	Fair's Log-difference method	K'=0.17 Lo=930	K'=0.25 Lo=990	K'=0.25 Lo=1370
3.	Thomas slope method	K'=0.16 Lo=950	K'=0.23 Lo=1080	K'=0.23 Lo=1400
4.	Moor'smethod moments	K'=0.18 Lo=920	K'=0.29 Lo=980	K'=0.28 Lo=1340
5.	Navone simplified slope method	K'=014 Lo=1010	K'=0.255 Lo=1030	K'=0.28 Lo=1340
6.	Yoshinori Fujimoto Graphical method	K'=015 Lo=990	K'=0.21 Lo=1070	K'=0.22 Lo=1350
7.	Rhame's Two-point Method	K'=0.14 Lo=1010	K'=0.23 Lo=1080	K'=0.23 Lo=1470
8.	Marquardt method	K'=0.13 Lo=1048	K'=0.21 Lo=1070	K'=0.21 Lo=1449
9.	Reed - Theriault leat square method	K'=0.13 Lo=1042	K'=0.215 Lo=1074	K'=0.21 Lo=1450

TABLE 5.6 Total Absolute deviation of calculated values of Yt from observed values

S.NO.	Method	Source of effluent			Total
		Boiling House	Mill House	Combined Mill	
1.	Least Square Method	104.92	169.44	289.09	563.45
2.	Fair's log-difference method	113.31	439.49	303.41	856.21
3.	Thomas slope method	119.16	212.92	337.53	669.61
4.	Moore's method of moments	165.02	181.07	412.04	758.13
5.	Navone Simplified slope method	165.53	178.03	412.04	755.60
6.	Yoshinori Fujimoto Graphical method	128.83	426.40	342.86	898.09
7.	Rhame's Two-point method	165.53	212.92	315.04	693.49
8.	Marquardt method	84.38	100.34	263.62	448.34
9.	Reed Theriault least square method	85.68	103.92	263.53	453.13

It is also evident from Table 5.6 that Reed-Theriault Least square method gives minimum total absolute deviation follwed by Marquardt method and Thomas slope method. The reason of Reed- Theriault Method giving best result is that it introduces a third parameter in the rate equation. The third parameter includes the error introduced in the measurement of BOD exertion with time. The introduction of third parameter in BOD rate equation increases the accuracy in the parameter estimations.

5.3 Effect of Temperature on biochemical - Oxidation

The composite samples for the three different effluent streams was used to measure BOD exertion with time at temperatures 10°C, 15°C, 20°C,25°C, 30°C, 35°C and 40°C. Tables - 5.7, 5.8 & 5.9 give the magnitude of the BOD exertion with time at these temperature ranges for the three effluent streams.

It is apparent from the tables that as temp. increases from 10°C to 40°C, BOD exertion at any particular time period also increases. The increase is observed to be exponential. The increase is, however, not uniform at different temperatures, but follow a relatively varied pattern, e.g. BOD increase is from 840mg/l at 10°C to 1300 mg/l at 40°C for combined will effluent (i.e. nearly 55% increase), whereas for mill house effluent, BOD increase is from 600 mg/l at 10°C to 1020 mg/l at 40°C (i.e.nearly 70% increase). The difference in the pattern is due to the different bio-oxidation rates. Therefore, the values of BOD at different temperatures have to be found only through

TABLE 5.7

Effect of Temperature on BOD exertion in Boiling House effluent

Time (in days)	BOD (in mg/l) at 10°C	15°C	20°C	25°C	30°C	35°C	40°C
1	60	120	180	190	190	240	300
2	150	200	260	300	340	380	440
3	240	280	360	420	480	500	560
4	310	390	450	500	570	610	620
5	380	440	520	610	620	740	780
6	460	510	580	660	750	780	850
7	510	570	660	720	800	840	900

TABLE 5.8

Effect of Temperature on BOD exertion in Mill House effluent

Time (in days)	BOD (in mg/l) at 10°C	15°C	20°C	25°C	30°C	35°C	40°C
1	140	220	300	310	340	400	480
2	300	340	420	440	500	550	610
3	400	480	580	600	640	700	780
4	510	580	640	720	750	800	900
5	600	650	750	800	840	880	1020
6	680	720	810	900	960	980	1100
7	800	810	860	920	990	1050	1160

TABLE 5.9

Effect of Temperature on BOD exertion in Combined Mill Effluent

Time (in days)	BOD (in mg/l) at 10°C	15°C	20°C	25°C	30°C	35°C	40°C
1	240	320	400	410	430	560	680
2	400	460	500	610	720	730	800
3	580	650	720	780	880	960	1040
4	760	780	840	910	1000	1100	1170
5	840	900	1040	1100	1110	1180	1300
6	950	990	1080	1140	1200	1240	1320
7	1000	1040	1150	1220	1240	1280	1360

experimentation.

Table - 5.10 shows the values of rate constant k' and ultimate BOD, Lo at each of the above mentioned temperatures. It is evident from the table- 5.10 that the values of rate constant (k') and ultimate BOD (L_o) increases as temperature increases but the increase in ultimate BOD(L_o) is not significantly high. The value of k' is nearly doubled for 20°C rise. The increase in the values of k' could be due to the increase in the activity of bacteria.

The Arrhenius temperature dependency is shown in figure - 5.6 . It is evident from the figure that there is a break in the activation energy curve at 20°C. The values of activation energy, E(MJ/mole) and temperature coefficient (0) for different temperature ranges are shown in the table - 5.11. The values of 0 in the temp. range 10-20°C & 20-40°C are 1.014 and 1.034 respectively. The activation energies in these ranges are 9.614 MJ and 25.50 MJ respectively.

5.4 Effect of pH on BOD values

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

TABLE 5.12 shows the BOD values observed at different pH in the range 6.0 to 8.5 for the three effluent streams. It is evident from this table that BOD values changes at different pH. The decrease in the BOD values is observed when the pH is either acidic or alkaline. However, the BOD5 values shows its maxima at near neutral pH.

Between pH 6.5 to 7.5, the decrease is however, not very significant, but between pH < 6.5 and >7.5 , the change becomes more pronounced . e.g. BOD at pH 6.0 is 93% of BOD5 at pH 7.0 and BOD5 at pH 8.5 is 91% of BOD5 at pH 7.0. This behaviour indicates that the bacteria are most active at near neutral pH.

Table : 5.10 Values of K' and Lo at different Temperature

Temperature (°C)	Parameters	
	K'(perday)	Lo (mg/l)
10	0.20	1360
15	0.22	1380
20	0.23	1440
25	0.29	1450
30	0.36	1465
35	0.39	1480
40	0.45	1435

Table : 5.11 Values of E and θ at different temperature ranges

Temperature range (°C)	θ	E(MJ/mole)
10-20	1.014	9.614
20-40	1.034	25.50

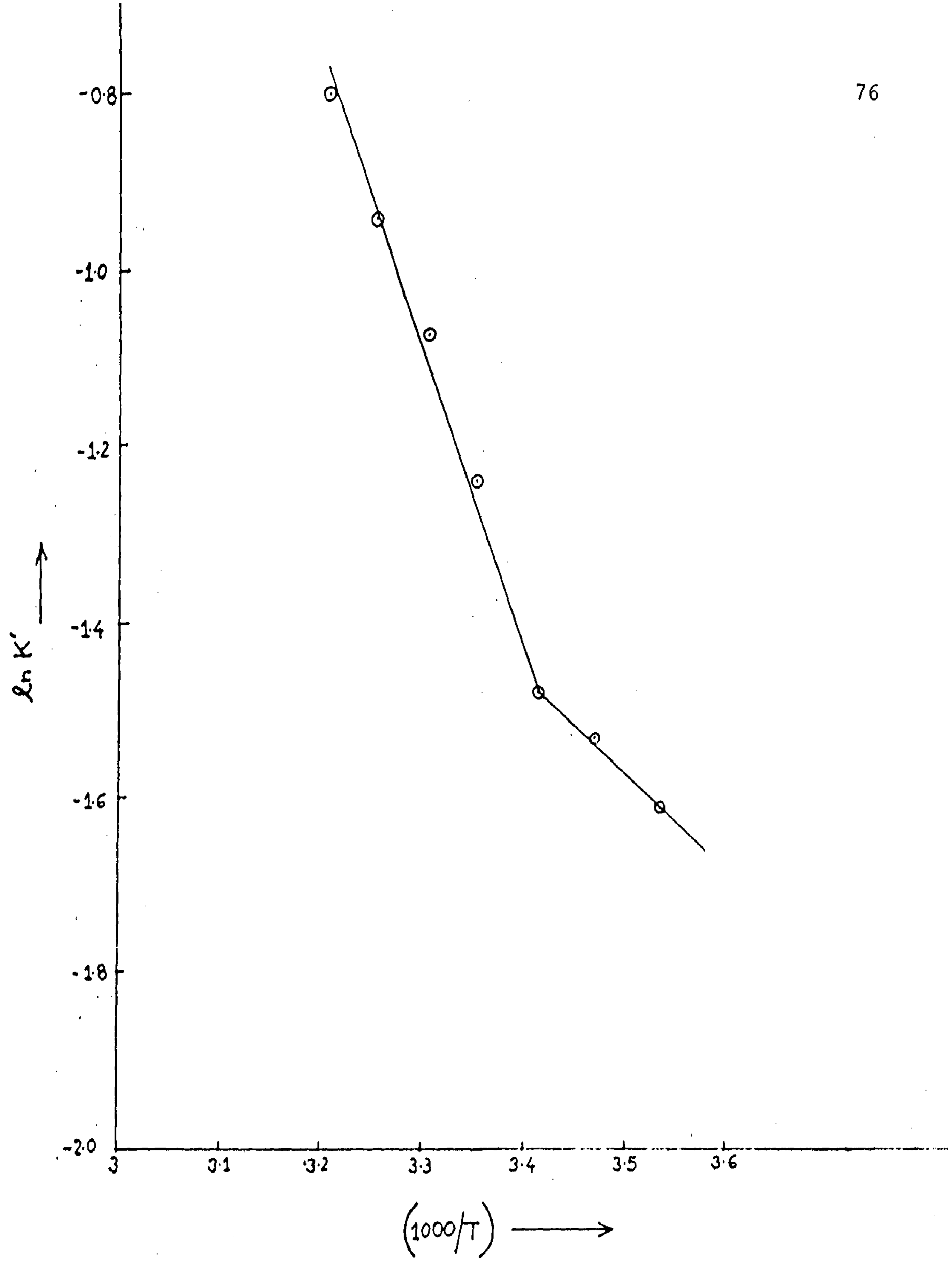

Figure 5.6 : Plot of lnk' Vs 1/T

TABLE 5.12 Effect of pH on $BOD_{5,20^{\circ}C}$ values

Source of effluent	$BOD_{5,20 C}$ at pH					
	6.0	6.5	7.0	7.5	8.0	8.5
Boiling House effluent	410	510	520	510	500	435
Mill House effluent	660	735	750	740	715	680
Combined mill effluent	980	1020	1040	1010	1000	950

CHAPTER — VI

CHAPTER - VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The following conclusions are drawn from the prese study :

1. The flow-rate of the liquid effluent generated from boiling house and mill house vary significantly with time.

2. The pollution load exerted by both mill house and boiling house waste streams is significantly high.

3. The BOD exertion with time follow the first order kinetics. The kinetic model parameters, K' and L_o are estimated by different methods and it is established that the sugar wastewater BOD exertion is best expresed by non linear least square method (Marquardt method).

4. BOD exertion with time increases as the temperature increases. Also k' and L_o increases with increase in temperature.

   A break in the Arrhenius plot is observed at about 20°C. The activation energy are within the range of liquid waste.

5. The activity of the bacteria is maximum near neutral pH.

6.2 RECOMMENDATIONS

1. The flow equalization tank is necessary before treating the effluent for BOD removal.
2. The mill house waste be treated for physical removal of oil and grease in grease and oil trap.
3. Before Designing the effluent treatment plant, the effect of temperature is to be studied thoroughly and activation energy of the effluents determined.
4. The effect of pH is to be studied for a wider range.
5. A non-linear least square method should be employed in estimating the kinetic parameters.

APPENDIX — A

TABLE : A-1

Variation in flow rates with time

S.no.	Times	Boiling House effluent	Mill House effluent	Combined Mill effluent
1	12 Noon	50.0	30.0	80.0
2	2 PM	42.5	35.7	78.2
3	4 PM	58.7	21.5	80.3
4	6 PM	45.2	22.3	67.6
5	8 PM	42.9	26.4	69.4
6	10 PM	54.5	19.0	73.5
7	12 Midnight	58.7	31.1	89.9
8	2 AM	48.7	34.6	83.3
9	6 AM	42.5	34.8	77.3
10	8 AM	52.3	33.4	85.8
11	10 AM	60.3	30.0	90.3
Average Value		**50.1**	**29.0**	**80.0**

* All the values are in m^3/hr

TABLE : A-2

Variation in effluents temperature with time

S.no.	Times	Boiling House effluent	Mill House effluent	Combined Mill effluent
1	12 Noon	43.0	27.0	37.0
2	2 PM	45.5	22.0	35.5
3	4 PM	41.0	24.5	36.0
4	6 PM	44.0	26.0	36.0
5	8 PM	43.0	26.0	35.0
6	10 PM	46.0	26.0	35.0
7	12 Midnight	42.0	23.0	36.5
8	2 AM	44.0	23.0	36.0
9	6 AM	44.0	22.5	35.0
10	8 AM	43.0	24.0	35.0
11	10 AM	43.5	24.5	36.0
Average Value		**43.5**	**24.4**	**35.7**

* All the values are in ^{o}C.

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