

Treatability Studies of Pulp and Paper mill waste water at different pH

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Abstract - The study of Biokinetic constants gives the complete pattern of the biological activities in the waste water. The various parameter related to microbial growth are useful in design of treatment plants for batter efficiency. This paper study Biokinetic constant of pulp and paper mill waste water at different pH value and suggest that the acidic range is more harmful comparing to the alkaline pH. The acidic range has shown 29% of growth while alkaline range has shown 59% of increment in active microorganism at the end of 1.2 day. The maximum growth in all ranges of pH was found to be at 7 pH.

IndexTerms - BOD, COD, pH, Microorganism, Growth-kinetic, Substrate

I.INTRODUCTION

The pulp & paper industry is one of the oldest industries in our county. But there has been a tremendous expansion in this industry during last twenty-five years. The paper industry, as it stands now, is one of the largest industries in our county. And also this is one of the major industries, which contributes a lot towards the pollution of our water environment. The indispensability of paper & its importance in the present society is beyond doubt. The pulp & paper industry caters to this requirement. On one hand we have a growing demand of paper, which is necessary for the overall growth of our society; & other hand we have a need to preserve the forest, which are the main raw materials for this industry. By introducing eco friendly technology; waste minimization; chemical recovery & by efficient design of biological treatment with the help of biokinetic constants.

Paper mill use the 'pulp' as the raw material, which is again produced utilizing different cellulosic materials like wood; bamboo, Rice straw and Bagasse. Pulp & paper industry is among 20 highly polluting industries in India. The pulp & paper mill waste characteristically contain very high BOD so that the biological treatment must be required in pulp & paper mill. During the digestion process of bamboo chips black liquor is produced. This black liquor contain a high amount of lignin is not easily biodegradable & unutilized chemical. This black liquor cannot be directly disposed into the stream. Thus the chemical recovery & reuses unutilized chemicals are must be required. Chemical recovery is the heart portion of the pulp & paper mill without it paper mill cannot run. The paper mill industry is water intensive industry. Most of the paper industry is situated at the bank of river. Biodegradable organic substances are always in soluble colloidal or suspended form. These substance are removed through many stages like mass transfer, adsorption, enzymic reactions, etc. to optimize the biodegradation, a rational design based on microbial growth kinetics is necessary for a particular type of waste. Thus, prior information and knowledge of microbial metabolism & growth kinetics are necessary in the design of biological treatment units.

In order to understand the growth, decay and substrate utilization a batch reactor example can be taken, where there is no inflow or outflow.

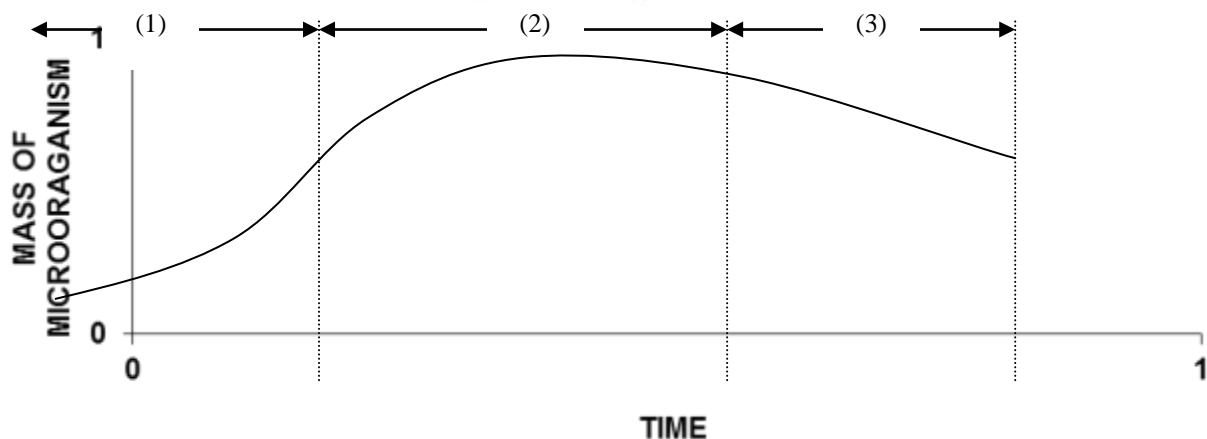


FIG-1 MICRO ORGANISAM GROWTH PATTERN IN BATCH REACTION LOG GROWTH PHASE (2) STATIONARY GROWTH PHASE (3) ENDOGENUOS GROWTH PHASE

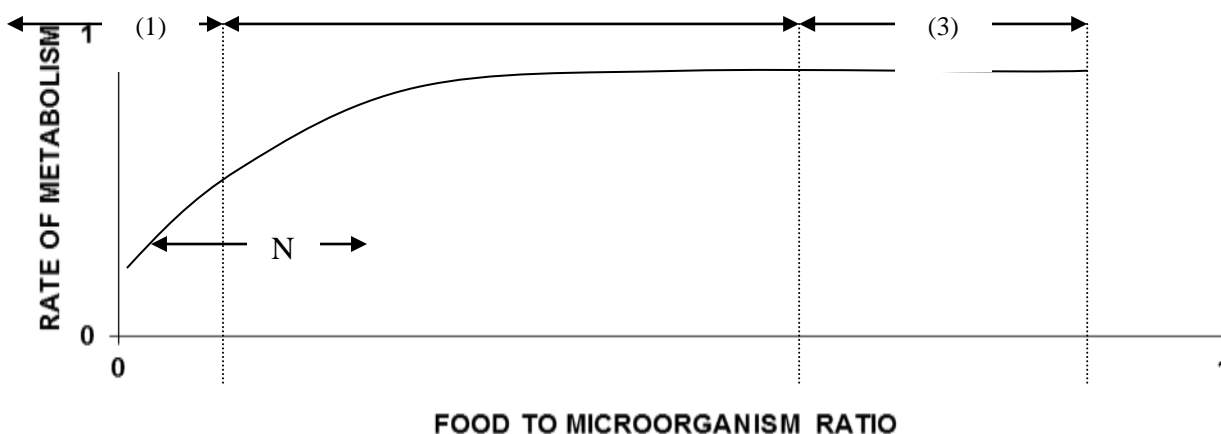


FIG-2 RATE OF MICROBIOLOGICAL METABOLISM IN CONTINUOUS BIOLOGICAL REACTION
 (1) ENDOGENOUS GROWTH PHASE (2) STATIONARY GROWTH PHASE (3) LOG GROWTH PHASE (N) NORMAL RANGE OF OPERATIONS IN MOST OF THE BIOLOGICAL REACTIONS

Whenever a bacterium is inoculated, in a batch reactor contained by substrate, it starts oxidation the substrate. As the substrate is exhausted, microbial growth also takes place. A typical growth pattern is shown in fig -1. The growth pattern can be plotted in terms of mass of microorganism versus time. The figure shown three distinct phases: (1) Log or exponential growth phase (2) Declining or retarded growth phase (3) Endogenous growth phase or death phase.

In the first phase, microbes try to acclimatize themselves to the environment. After this, the substrate is utilized rapidly and growth also starts rapidly. Secondly stationary phase comes when the substrate is exhausted. Lastly the declining phase comes, where microbes are forced to metabolize their own protoplasm. This represented as endogenous respiration. The growth pattern-taking place in a batch reactor cannot be applied to a continuous flow reactor. In a continuous flow reactor the metabolism is controlled by the rate of substrate supply and the mass of active microorganism. In other words ‘food –to – microorganism ‘ratio, controls the rate of metabolism in a continuous biological reactor. Low F/M ratio results in to endogenous growth phase, and its high values results into log growth phase. Now the sludge produced in the endogenous phase is of good settling characteristic. Moreover, the same is stable in nature. That is why the biological units are designed, in endogenous phase only. Fig-2 shown, that biological process can be formulated, in terms of changes in substrates concentration or in term of microbiological growth. On the availability of relevant data biological treatment can be designed. However, the microbiological growth kinetics offers a more rational method of its design. The growth rate depends upon environmental factors like pH, temperature, nutrients, present state of oxygen, etc. if, these parameters are controlled, then it will provide ideal conditions for biological growth. To allow the microorganism to grow, they must remain in the system for a specific and enough time periods. Now this period depends upon their growth rate, which is related directly to the rate at which they metabolize the waste. If, growth rate of the microorganism is controlled, then waste can be stabilized effectively. On the basis of this researcher has designed the following objectives

Objectives

The lignin in pulp and paper mill waste water is not easily degradable and it makes COD/BOD ratio of the wastewater is very high. The basis of this study was to determine the biokinetic constants associated with wastewater which will help in design biological treatment process for such waste. So the objective of the study that we include in this paper are: (1) To evaluate the biokinetic constants of pulp and paper mill wastewater (2) To find the influence of flow on performance of setup(3) To find effect of pH on biodegradability (4) To assess the performance of the system. The biokinetic constants described in this study is a function of the environmental condition of this particular mixture of raw material & ambient temperature. Any variation in the above mentioned factor is liable to give erroneous results. This study was conducted on small scale, which gives more efficiency, but same study on large scale can reduce the efficiency

Components of waste water and Permissible limits: Important components of Liquid Effluents from Large pulp and paper industry include: PH value, Colour, Odour, Temperature, Suspended solids, Biochemical Oxygen Demand, Chemical Oxygen Demand, Sulfides, Residual chlorine, Lignin Emission loads form the Mills are regulated by almost all of the pulp and paper industry in our country. Permissible limits of the pollutants to be complied with by large pulp and paper Industry effluents as per ISI – 2490 are given in below Table-1.

Sr NO.	Characteristics	Units	Maximum Tolerance Limit
1	pH	-	5.5-9.0
2	Temperature	C	40
3	Suspended Solids	mg/l	100
4	BOD (5 days at 20 C)	mg/l	30
5	COD	mg/l	250
6	Dissolved Oxygen	mg/l	4
7	Oil and Grease	mg/l	10
8	Sulphide	mg/l	2.0

9	Sulphate as SO ₄	mg/l	1000
10	Total Dissolved Solid	mg/l	2100
11	Residual Chlorine	mg/l	1.0
12	Per cent Sodium	mg/l	60

Table-1: Permissible Limit of different parameter of waste water

Effluent standards should be strict enough to protect the quality of the receiving waters and should treat all discharges fairly but in so far as possible should be tailored to the character and volume of wastes at each point of discharge. Country to country review of the effluent standards to be studied.

II. LITERATURE REVIEW

The study of the biokinetic Constant is important because it gives us a view of the treatment plant design & the nature of the effluent. By studying the biokinetic constants, we are able to predicate the biodegradability & the efficiency of the treatment plant as such. Several studies have been conducted on the biokinetic studies of different effluent from different industries. The pulp & paper mill industry with its unique set of the raw material, high BOD, COD, color provides a challenge to environmental engineers. Several studies were conducted on the biokinetic constants of pulp & paper industry. Some of the relevant studies are reported here with

Biokinetic constants

S. Raghuvver & C.A. Sastry [1], studies were conducted on treatment of combined pulp & paper mill wastewater by activated sludge using laboratory model units by varying aeration time from 4 – 24 hours & MLSS concentration from 1000 – 4000 mg/l. During the usage of bamboo, eucalyptus, subabul plus hardwood & bamboo & hardwoods as raw materials for pulp & paper making, combined wastewater samples are collected and experiments were carried out to determine biokinetic constants in laboratory bench scale continuous activated sludge unit. Monod's kinetic equations were used to determine the biokinetic constants. The values of biokinetic constants of wastewater of (60% Bamboo + 40% MHW) raw materials were obtained by using lab study specific substrate utilization (K) – 1.33, Half velocity constant (K_S) – 72.5, yield coefficient (Y) – 2.28; Decay coefficient (K_d) – 0.14

M.N Rao & A.K. Dutta [11] have described the principle of biological treatment experimental methodology to determine the biokinetic constants with Aerobic continuous reactor & Basic Kinetic equation. He has suggested that, for effective biological treatment of industrial waste nutrient are added to reactor in the form of Nitrogen & Phosphorus & BOD: N: P ratio of 100:5:1 in aerobic systems is to be maintenance. He has also suggested that if BOD/COD ratio is greater than 0.6 the wastes are biologically treatable without acclimatization, if the ratio ranges from 0.3 to 0.6 the waste needs acclimatization for biological treatment. Met - Calf & Eddy, [12] have described that the performance of biological process used for wastewater treatment depend on the dynamics of substrate utilization & microbial growth. The environment constants are effect the substrate utilization & microbial growth rate so that, it may be necessary to control such conditions as PH, Nutrient, temperature, dissolved. They have also determine the K, K_S, Y, K_d & mean cell residence time θ_c & F/M ratio. Graphical method to evaluate the Biokinetic constants. Benfield & Randle [14], has described that the microbial activity is become faster between 6.5 to 8.5 PH & lower at acidic PH & alkaline PH. Oliver J. Hao, [7], Measurement of both soluble COD & BOD on activated sludge effluent reveals that effluent organic matter contain a significant quantity of slowly biodegradable organics. These slowly degradable organics exhibit a significant effect on the determination of kinetic coefficient, e.g. the specific substrate removal rate for the multiple substrate models and the first – order rate constant. The use of effluent soluble COD for estimating the yield coefficients & decay rate, however is valid under many practical conditions. Since concentration of the influent substrate is much greater than that of the effluent substrate concentration. Without knowledge of wastewater and its features designing of treatment is like groping in the dark. S. Raghuvver & C.A. Sastry [2], has reported on the wastewater characteristic of pulp & paper mill. The abstract of the study is as under. Wastewater generated when different raw materials, like bamboo, eucalyptus, 50% Subabul + 50 % mixed hardwoods were used for pulp & papermaking were treated in a full-scale activated sludge process wastewater treatment plant to study the performance of the plant. The treatment plant could satisfactorily treat wastewater obtained when different raw materials were used for making pulp & paper except for colour, complying with the standard fixed for other parameters. The treatment efficiency achieved for BOD₅ removal 86%. The performance of a plant is one of the key features in effluent treatment plant designing. S. Raghuvver & C.A. Sastry [3], have done so & reported the following findings. Wastewaters generated when different raw materials; like bamboo, eucalyptus, 50% subabul + 50% mixed hardwood and 60% bamboo + 40% mixed hardwoods were used for pulp & papermaking were collected & characteristics were studied. Maximum quantity of wastewater was generated then eucalyptus was used as raw material, colour in the wastewater was highest when eucalyptus was used as raw materials. Mark K. Knudson; Kenneth J. Williamson, peter O. Nelson [6], A laboratory study was carried out to find the influence of dissolved oxygen on substrate utilization kinetics of activated sludge. In this study two reactor A & B was operated with low & high DO levels to determine the Monod kinetic coefficients by varying θ_c . Maximum substrate utilization rates of activated sludge based on TVSS increased with increasing DO concentration over the range of 1.5 to 15 mg/l. This effect can allow the operation of oxygen systems at higher specific utilization rates than air system & is used to obtain equal removals.

Effluent management

Management of the effluent in E.T. plant is one of the most important factor, which effect the performance of the E.T. plant. The human angle evolved in this segment is one of the most important and paradoxically most confusing aspects. A proper design of effluent management helps in controlling accident and negating the human error associate with the process.

Effect of temperature

The effect of temperature was studied and reported by Dr. J.E.M.Macwan [25] is reviewed here under. A pulp & paper board effluent was taken & biokinetic constants was derived at 29° C it was later compared to () by correcting the temperature to 20°C

$$\frac{r_T}{r_{20}} = \theta^{(T-20)}$$

temperature by Arthenius equation

Where, r_T = reaction rate at T° C, r_{20} = reaction rate at 20°C, θ = temperature activity coefficient, T = temperature °C Richard E. Muck & C.P. Leslie Grady; [5], Experiments were carried out to find out the effect of temperature upon the biokinetic constants required to characterize microbial growth. This experiment was carried out in Stirred tank reactors. The maximum specific growth rate constant & the bacterial decay rate constant were found to increase with increases in temperature in accordance with the Arthenius equation over the temperature range of 10°C - 30°C. The rate of increases of the decay rate constant was slightly larger so that the ratio of the temperature characteristics for decay to that for growth was 1.11. The chemical recovery aspect of pulp & paper mill pays a very important role in the overall economics & pollution control. The necessity of this process was described by Gerald W. Hough [29], A.K. Tripathi, A.K. Srivastava & S.N. Pandey [18], have descried about sources of waste from pulp & paper mill & existing pollution control technique in India.R.D. Ross [33], has descried the operating principle of ESP as a Air pollution control technology.Gerald W. Hough [29], has described the principles and of Kraft liquor recovery process of pulp & paper mill.

III. MATERIAL AND METHODOLOGY

Under proper environmental conditions, the soluble organic substance of the soluble organic substances of the waste are completely destroyed by biological oxidation, part of it is oxidized while rest are converted into biological mass, in the biological reactors. The end products of the metabolism are either gas or liquid: on the other hand, the synthesize biological mass can flocculate easily, particularly with increasing mean age of the cells, and are separated out in a clarifier. Therefore, the biological treatment system usually consists of (1) a biological reactor, and (2) a settling tank to remove the produced biomass or sludge.

The objectives in any biological waste treatment studies in the laboratory are usually twofold: (1) to examine whether the waste is amenable to biological treatment or not, and (2) To determine the kinetic growth coefficient that may be used in the design and operation of pilot or prototype plants. The experimental studies may be carried out either in a continuous flow reactor. However a continuous flow reactor should be employed wherever possible, as it's simulates of prototype closely. Depending on the characteristics of the raw waste, and the expected response to the particular type of biological treatment, the tests are to be conducted to assess the treat ability under aerobic condition. Tests are to be conducted at a constant room temperature. The feed is to be pretreated for the removal of heavy suspended solids and floating oil or grease. The pH of the feed is to be adjusted for the optimum metabolism of the microorganism.

IV.EXPERIMENTAL MODEL

To determine biokinetic constants for a particular waste, a bench scale continuous flow reactor was used. The laboratory model was fabricated by transparent acrylic sheet. Fig-5 shows the schematic diagram of model arrangement. Table shows the dimensions and other details of the model.

Experimental process

The laboratory model was operated on continuous daily feed basis, in which pre calculated quantity of wastewater was fed. During the experimental period the reactor was running under atmospheric pressure and room temperature, which ranged from 24°C to 34° c. The wastewater, for which biokinetic constants were to be determined, was analyzed, for different parameters as show below. The laboratory tests were conducted as per the standard methods.

<u>Parameters</u>	<u>Units</u>
PH	-
TEMPERATURE	°C
TOTAL SOLIDS	MG/LITER
DISSOLVED SOLIDS	MG/LITER
SUSPENDE SOLIDS	MG/LITER
VOLATILE SUSPENDE SOLIDS	MG/LITER
CHLORIDE	MG/LITER
TURBIDITY	PPM
BOD ₅ (So)	MG/LITER
COD	MG/LITER

1. It may be noted that the pulp & paper mill wastewater does not contain necessary nutrients for the bacterial growth, and hence Nitrogen & Phosphorous were added to maintain BOD: N: P ratio of the 100: 5: 1 in the feed, throughout the study.
2. The reactor was filled fully and aeration was started. Initial seeding of 200 ml active bio mass sludge was provided, wherever the same was needed. Aquarium aerator was used to build the desired MLSS @ 1000 to 3000.
3. The MLSS was measured periodically. If the same was not built within 24 hours of continuous aeration, then the sludge was allowed to settle and supernatant was decanted. After decanting a fresh batch of feeding was done in the reactor.
4. After the desired level of MLSS was built, adjusting flow started continuous feeding.
5. The flow was adjusted in such a way, that the same should remain consistent for particular period.
6. Five different mean cell residence times, for a particular waste was varied.
7. Wasting of sludge was done at the end of every mean cell residence type.
8. Samples were collected at the end of every mean cell residence time for testing of BOD₅ and V.S.S
9. The laboratory model was operated without recycling of solid sludge.
10. The influent and effluent substrate was measured in terms of BOD₅ the biomass measured as volatile suspended solids.

	Particulars		Dimensions
A	Feeding tank:		80 Liters
B	Reactor:		
	Aeration chamber		
		Length (cm)	49.5
		Breadth (cm)	21.2
		Depth (cm)	15
	Setting chamber		
		Length (cm)	14.5
		Breadth (cm)	21.2
		Depth (cm)	15
C	Baffle:		
		Length (cm)	17
		Depth (cm)	12
D	Outlet:		
		Depth (cm)	12

Table-2: Detail of laboratory model

Aeration

In the presents study the size of aeration tank was $49.5 \times 21.2 \times 15 \text{ cm}^3$ and constants head flow was maintain. The purpose of the tank was to maintain a optimum biomass and to maintain a particular pH and flow rate. In the aeration chamber the organic material is degraded with the help of microorganism in the presence of oxygen.

Settling

In this study the size of settling tank was $14.5 \times 21.2 \times 15 \text{ cm}^3$ and the purpose of this tank was to settle the biomass.

Parameter significances

BOD: is indicates the amount of biodegradable organic matter which is to be treated from the waste water. it also gives an idea of the amount of oxygen to be supplied in to system which can be consume by the micro organism to stabilizes the organic matters MLVSS in the biological reactor, the concentration of volatile suspended solid (VSS) in the reactor is taken as the concentration of microbial mass. This assumption is true only when the waste under treatment is soluble in nature. Mean cell residence time (θ_c): the parameter θ_c is easily controllable, hence it can fixed. In a continuous flow reactor, the effluent concentration and treatment efficiency, E are related directly to $\theta_c = \theta$. Here, the mean microorganism retention time and the liquid retention time is same. That is why separate control to the microorganism is not required. So, it can be stated that longer θ_c results into higher efficiency of treatment. Shorter the θ_c lesser is the efficiency as microorganism are not getting enough time for reproduction.

Substrate: the smount of biodegradable substance present in wastewater is called substrate. This substrate can be measured in wastewater by BOD test. F/M ratio: food to microorganism is the ratio of the effluent substrate concentration to the product of cell concentration and mean cell residence time

$$F/M = S_0 / \theta_c X$$

Where, X= biomass concentration mg/lit

S_0 = influent substrate concentration mg/lit

θ_c = mean cell residence time, day

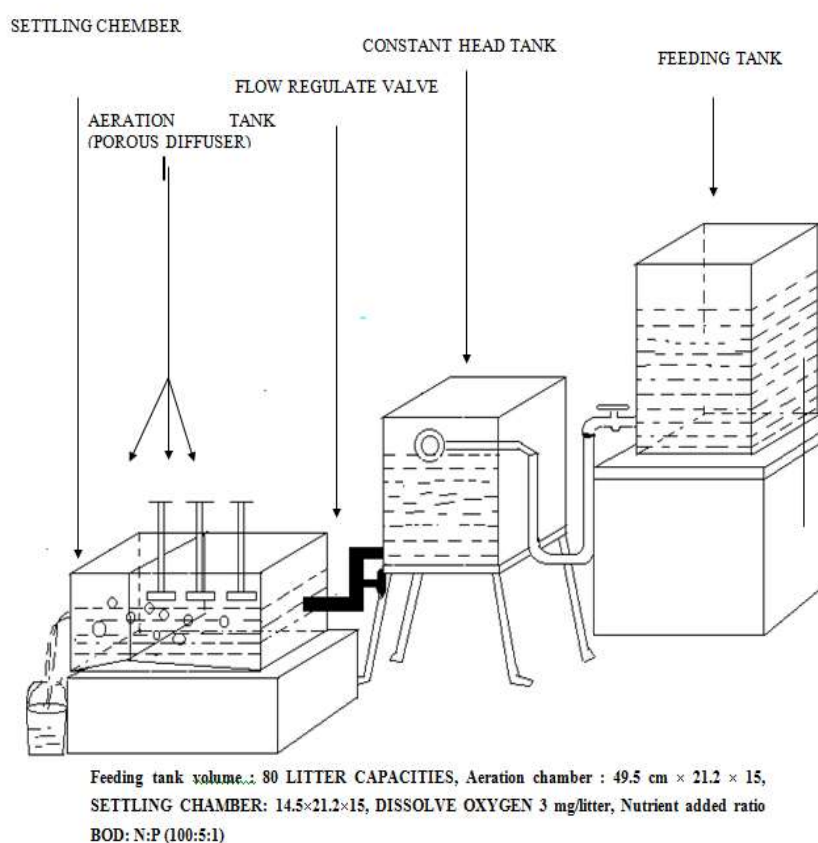
The product of food to microorganism and process efficiency gives the specific substrate utilization rate U

$$U = (F/M)/100$$

Raw wastewater was collected from the inlet of the effluent treatment plant. The various characteristics of the wastewater were found out before transferring to the feed tank of the bench scale continuous flow reactor. The characteristics are tabulated as below.

Parameters	Values
pH	7
Temperature	30°C
Total Solids	2200 mg/liter
Total Suspended Solid (TSS)	800mg/liter
Total Dissolved Solid (TDS)	1400 mg/liter
BOD	300 mg/liter
Colour (light honey)	Light honey colour
W.W/Flow/day	20000m ³ /day
COD	1000 mg/liter
Chlorides	500 mg/liter
BOD/COD	0.3

Table -3:- characteristic of pulp & paper mill waste water under study



The study of Biokinetic assumes signification it gives the complete patten of the biological activity in the wastewater. The biokinetic constants evaluated by laboratories study is a function of the environmental conditions of this particular mixture of raw material and ambient temperature. Any variation in the above mentioned factor is liable to give variation in results. The objective of this laboratory studies to evaluate the biokinetic constant, by which Biological treatment units can be more rationally designed to increase the efficiency of the system.

V. TREATABILITY STUDIES AT DIFFERENT PH VAULES.

In this laboratory experiment, raw wastewater was collected from the inlet of the effluent treatment plant. The various characteristics of the wastewater were found out before transferring to the feed tank of the bench scale continuous flow reactor. Characteristics are tabulated below.

Parameters	At 6 PH		At 7 PH		At 8 PH		Literature Value
	Sample-I	Sample-II	Sample-I	Sample-I	Sample-I	Sample-II	
PH	6	6	7	7	8	8	6-10
BOD	300	303	300	315	300	315	240-380
COD	1000	1010	1000	1050	1000	1050	840-1660
BOD/COD	0.3	0.3	0.3	0.3	0.3	0.3	2.95-4.37
T.S	2320	2366	2335	2455	2325	2440	2000-3500
T.S.S	620	635	630	655	625	650	620-1120
T.D.S	1700	1731	1705	1800	1700	1790	1380-2380
Colour	LIGHT HONEY COLOUR						
Chlorides	565	555	522	512	540	530	500-600
Temperature	30 0C	30 0C	30 0C	30 0C	30 0C	30 0C	30 0C -400C

Table-4: Characteristics of waste water

On comparing the parameters of the influent wastewater of the pulp & paper mill. It was found that the paper mill influent has same characteristics parameters as that of a typical pulp and paper mill wastewater. Thus the result obtain from this study can be applied to any of the pulp and paper industry. The experiment was conducted at room temperature of 30° with three different sets of sample having 6,7,8 PH values reswpectively. The experiment was done with varying values of mean cell residence time of 6, 13.2, 18, 28.8,34.8,42 hours. After each mean cell residence time BOD and MLVSS of effluent were measured following results is obtain during this laboratory experiment.

Biokinetic Constance	Evaluated value at 30°C temp.						Literature Value at 30°C temp and at 8 pH	Range of evaluated biokinetic constants
	Set-I At 6 PH		Set-II At 7 PH		Set-III At 8 PH			
	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II		
K	1.0	1.052	1.66	1.72	1.33	1.36	1.33	1.0 to 1.72
KS	53.33	57.38	150	156.2	100	110	72.5	53.33 to 156.2
Y	2.72	2.85	3	3.15	2.77	2.80	2.28	2.72 to 3.15
Kd	0.34	0.32	0.20	0.18	0.26	0.24	0.14	0.20 to 0.34

Table-5: Evaluated values of biokinetic constants of pulp & paper mill waste water

Where,

K = Specific substrate utilization rate (day-1)

Ks = Half velocity constants (mg/litre)

Kd = Decay coefficient (day-1)

The values of biokinetic Constants K, Ks and Y at PH value 7 is higher as compare to values observed at pH value 6 and PH value 8. Also decay coefficient Kd is lower for PH value 7. From this it can be concluded that pH 7 is the optimum pH for the wastewater treatment. Any alteration in the PH values has a negative impact of the treatment. Efficiency as K, Ks and Y values tends to become lower as compared with pH value 7. Also the decay constant (Kd) is higher. It is also observed that acidic wastewater to the microbial activity more adversely affected. Therefore to optimize the biological treatment neutralized is desired.

VI.CONCLUSION

The present study was aimed at evaluation of biokinetic constants of pulp & paper mill wastewaters at a different pH values, by a laboratory model of bench scale continuous flow reactor. During the study on pulp & paper mill wastewater, various parameters were observed and by graphHical method the constants were evaluated. From the observations the following conclusion can be drawn. (1) The evaluated values of biokinetic constants at 8 pH (from experiment) varied with the reported values of literature at 7.9 pH. This might be due to the influence of pH and chloride concentration, which are due to varying composition of wastewater and environmental conditions. (2) The value of constants Y, K & Ks are found to be maximum at pH 7. This indicates there is a higher Treatability at neutral pH.

Neutral pH is the optimum pH for treatment. Acidic and basic wastes reduce the efficiency of treatment. (1) The values of decay constant K_d is almost similar for the three pH values of wastewaters. This indicates that the rate of metabolism, in endogenous pHase, may be remaining constant, for mixed culture in different pH wastewaters. However at a neutral pH, K_d is lowest and hence most suitable. (2) It can be stated that the relationship between substrate concentration and rate of specific substrate utilization, is continuous over the entire range of substrate concentration, as the graphs for the same follow the same pattern for all the wastewaters. (3) The bioactivity in the initial stage of mean cell residence time was observed to be faster i.e. up to 12 hrs. If, the same is confirmed by further studies, then wasting the degraded substrate may increase the efficiency of the treatment.

From this study, it can be stated that, biokinetic constant vary with the composition of wastewaters. Efficiency of the treatment unit as well as Microbial activity is higher at Neutral pH (7.0) value than acidic and basic wastewater. it is recommended that if, a similar lab scale study is carried out for different ranges of biodegradable pollutants, then a definite co relationship can be established between the biodegradable pollutants and the values of biokinetic constants for a particular set of environmental conditions.

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