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Effect of Black Liquor on the Activated Sludge Process

An experimental investigation of the effect of black liquor on the activated sludge treatment of bleached kraft mill effluents

Sanjay N. Vadodaria

Department of Chemical Engineering
McGill University, Montreal

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ABSTRACT

The Activated Sludge Process is the most widely used wastewater treatment process in the pulp and paper industry. Black liquor from the Kraft Pulping Process is characterized by high inorganic and organic load; it also contains toxic compounds. Upsets in the plant operation lead to disturbances in the activated sludge process and the process fails to produce effluents that meet regulatory standards. In this project, the effect of black liquor on the activated sludge was studied.

Experiments were carried out in batch reactors and growth kinetics for the activated sludge were studied for each condition. In addition, the removal of chemical oxygen demand (COD), total organic carbon (TOC) and soluble lignin was studied with respect to time. Results from initial rate were compared. Characterization of activated sludge was done using the 'Biolog' technique. An attempt was made to correlate the results of the kinetic study and the activated sludge population.

Results from the specific rates indicate that for 0% black liquor, initial specific rates of COD (or TOC) removal (or the activity of microorganisms) were different for different initial biomass concentration. This trend however was not clear for the black liquor concentrations. For all conditions of biomass concentration, the specific rate was nearly the same. Due to the toxicity of black liquor, microorganisms that can survive the toxicity shock or those that can adapt to black liquor, may lead to a similar population in the system resulting in the same specific rate or the activity of the microorganisms. This was confirmed by the sludge characterization technique.

RÉSUMÉ

Le procédé par boues activées est le procédé de traitement biologique d'eaux usées le plus largement utilisé dans l'industrie papetière. La liqueur noire provenant du procédé Kraft Pulping est characterisée par une charge organique et inorganique élevée. Cette liqueur contient également des composés toxiques. Des bouleversements à l'usine d'opération entraîne des perturbations dans le procédé des boues activées et le procédé ne réussit pas à produire des effluents qui rencontrent les normes réglementaires. Ce projet de recherche a pour but d'étudier l'effet de la liqueur noire sur les boues activées.

Des expériences ont été effectuées avec des réacteurs "batch" et la cinétique de croissance des boues activées a été étudiée pour chacune des conditions. De plus, la dégradation de la demande chimique en oxygène (DCO), du carbone organique total (COT) et la lignine soluble ont été analysés en fonction du temps. Les résultats des taux initiaux ont été comparés. La caractérisation des boues activées a été faite selon la technique du Biolog. Une corrélation entre les résultats de l'étude sur la cinétique et ceux de la population des boues activées a été étudiée.

Les résultats des taux spécifiques indiquent que pour une concentration de 0% de liqueur noire, les taux spécifiques initiaux de la dégradation de la DCO (ou COT) (ou de l'activité des microorganismes) étaient différents pour différentes concentrations initiales de la biomasse. Toutefois, cette tendance n'était pas claire pour les autres concentrations de liqueur noire. Pour toutes les conditions de concentration de la biomasse, le taux spécifique est semblable. Du à la toxicité de la liqueur noire, les microorganismes qui survivent au choc toxique ou s'y adaptent, résultent en à une population homogène dans le systéme. La conséquence en est un même taux spécifique ou une même activité des microorganismes. Ceci a été confirmé par la technique de caractérisation des boues activées.

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Nomenclature

A	absorbance
BKME	bleached kraft mill effluent
BOD	biological oxygen demand (mg/l)
COD	chemical oxygen demand (mg/l)
D	dilution factor
DO	dissolved oxygen (mg/l)
FSS	fixed suspended solids (mg/l)
MLSS	mixed liquor suspended solids (mg/l)
N	nitrogen
P	phosphorous
PCA	principal component analysis
SL	soluble lignin
t	time
TME	total mill effluent
TOC	total organic carbon (mg/l)
TSS	total suspended solids (mg/l)
VSS	volatile suspended solids (mg/l)
X	biomass concentration (mg/l)

Greek letters

μ	specific growth rate (sec^{-1})

CHAPTER 1
INTRODUCTION

All industrial activities are associated with generation of waste either in the solid, liquid or gaseous form. These wastes are eventually released in the environment. This addition of wastes has brought unfavorable changes in the environment. In this study, consideration is given to the liquid form of waste, mainly the wastewater from pulp and paper mills. Addition of liquid wastes has led to deterioration of water quality and has affected aquatic life. The pollutants in the liquid waste can be broadly classified into three groups:

1. Chemical Pollutants (heavy metals, organic and inorganic wastes)
2. Physical Pollutants (hot water, suspended solids)
3. Biological Pollutants (bacteria, viruses)

The chemical pollutants have both direct and indirect effects. An indirect effect is the oxygen depletion of the receiving body by the high oxygen demand of the pollutants causing the asphyxiation of the aquatic life that require oxygen for their respiration. Another indirect effect is the introduction of excess nutrients causing the proliferation of one or two species, thus upsetting the ecological balance. The direct effect of the chemical pollutants is the toxicity itself, which is the adverse action of chemicals on the aquatic organisms. Groups of toxicants include substances such as heavy metal salts, cyanides and various compounds.

One of the most important industries producing chemical pollutants, is the pulp and paper industry. Water is one of the most important raw materials. An average quantity of water, for the kraft pulp production is 34,650 gallons per ton of unbleached kraft pulp (Freeman, 1995). Since, water does not appear in the final product, it comes out as a waste effluent. In a typical pulping operation, water insoluble cellulose fibers of the wood are isolated by solubilizing substances binding these fibers together by

mechanical or chemical action. It is these organic and inorganic solubilized chemicals produced during pulping operations that find their way into the receiving streams and contribute to the detrimental effects to the environment disturbing normal ecological cycles (Allan et al, 1972). These effluents have high chemical oxygen demand (COD), biochemical oxygen demand (BOD) and toxicity. Hence, they cannot be directly discharged into the environment without any treatment.

Generally, facilities provided to treat the process wastewater fulfill mainly two functions:

1. Remove contaminants so that wastewater is suitable for discharge, and / or
2. Improve the water quality so that it is satisfactory for reuse in the plant.

The major pollutants of concern to the paper industry are BOD, COD, color, dissolved solids, suspended solids, and bacteria (coliform). There is no treatment process that can remove these contaminants in one step. Hence, a sequence of treatment processes is needed. This uses various physical, chemical and biological methods for treatment. These treatment processes can be grouped into four categories:

1. Pretreatment (fine screening, sedimentation etc.)
2. Primary treatment (flocculation, air floatation etc.)
3. Secondary treatment (activated sludge process, aerated lagoons etc.)
4. Tertiary treatment (chlorine contact or chlorination)

Figure 1.1 shows one of such sequence of operations. This sequence and the steps vary depending on effluents from industry to industry.

1.1 Activated Sludge Process

Activated sludge process is extensively used wastewater treatment process because it can effectively reduce the organic content and toxicity of various wastewaters. Activated sludge is a complex microbial population, which contains bacteria, protozoa,

rotifers and many other types of organisms. The activated sludge process consists of two steps. The first step occurs in a reactor (aerator) where the activated sludge is contacted with the effluent. The activated sludge metabolizes the soluble organic compounds present in the wastewater. The second step is the setting tank or a clarifier where flocs (biomass) are allowed to settle (Klopping et al, 1995 and Gray, 1990).

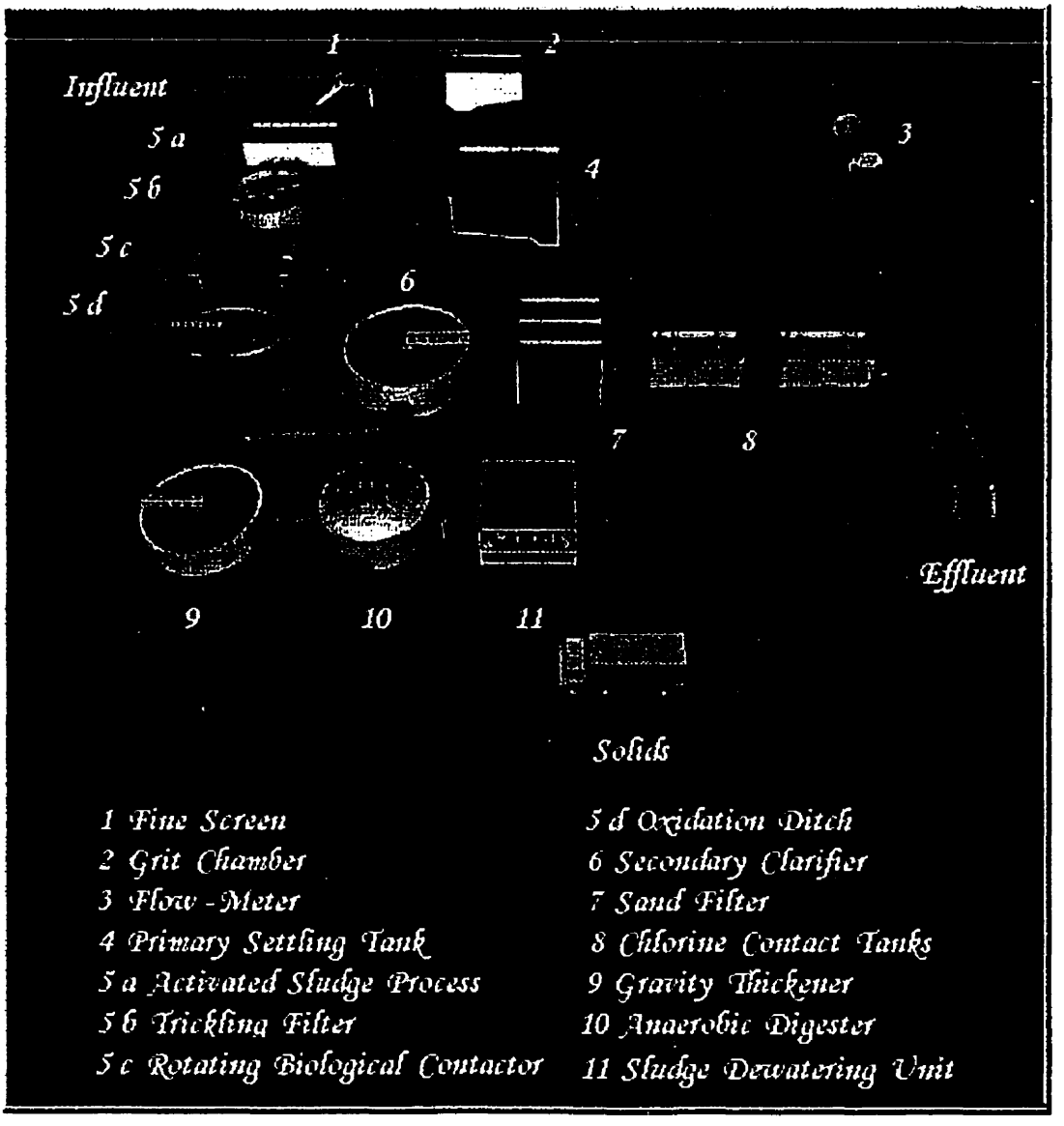


Figure 1.1 Sequence of steps in wastewater treatment (image obtained from reference no. 30)

The performance of the activated sludge process is affected by various parameters such as pH, reactor temperature, hydraulic retention time, nutrients, dissolved oxygen and the nature and composition of the microbial population. Changes in these parameters may lead to growth of unwanted organisms affecting the quality of wastewater treatment. Activated sludge population consists of a mixed culture, and the more diverse the culture is, more adaptable is the sludge to different effluent streams. Hence, to control the process, information about the effect of changes is required.

1.2 Foam Fractionation

Biological treatment of kraft mill effluent is currently the only practical method for removing BOD and toxicity of the highly concentrated effluents from the bleached kraft mill or other pulp and paper mill in one step. This is mainly carried out by either of two aerobic biological methods namely the activated sludge process and aerated lagoons. Upsets in plant operations may lead to toxicity shocks to the biological systems. This shock can adversely affect the sludge. Consequently, BOD and toxicity removals are poor. Some of the toxic chemicals present in the kraft mill effluents are surface active and cause effluents to produce foam. Therefore, foam fractionation, as a pretreatment step to biological systems, has a potential of protecting them against toxicity shocks.

Foams have high surface energy due to large surface area and surface tension. Surface active agents (surfactants) are adsorbed at the gas liquid interface and cause reduction in the surface tension. Thus, they reduce the surface energy and stabilize the foam. The differential concentration of surfactants on the gas-liquid interface is the basis of a separation technique called Foam Fractionation. In foam fractionation, gas is bubbled through a liquid head. This generates large gas-liquid interfacial area. Surface active toxicants such as resin acids and unsaturated fatty acids present in the liquid migrate to the gas-liquid interface. They are adsorbed on the interface and are carried to the top of the liquid and concentrate in the foam thus leading to their separation.

Foam fractionation offers various advantages over other separation methods:

1. It is a physical separation process.
2. It is faster and less expensive.
3. Many of the toxicants present in the kraft mill effluent can be removed without undue sophistication.
4. It concentrates toxic organic compounds in small liquid volume, which may be economically incinerated due to high COD.
5. Foam fractionation results in a liquid, which has lower foaming tendency and lower toxicity.

1.3 Scope and Objectives

In pulp and paper mills, total mill effluent (TME) is fed to the treatment facilities. TME is a combination of streams originating from various sections of plant such as the wood chips and pulp washing stages, bleaching plant and spills from digesters. Changes in the effluent composition can affect both the performance and efficiency of wastewater treatment. Black liquor is one of the important wastewater streams in the kraft mill operation. It is characterized by very high organic and inorganic load. The main objective of the project was to study the effect of black liquor on the performance of activated sludge process which is affected by how the sludge grows and utilizes the organic waste material under different conditions. Therefore, to study the effect of black liquor batch growth curves for various initial concentrations of activated sludge and for various black liquor concentrations in TME were established. In addition, one of the major objectives of this study was to observe the effect of black liquor on the sludge population and correlate the activated sludge kinetics results to sludge population using a population characterization technique Biolog.

The experimental investigation could be carried out in continuous mode or batch mode. In the continuous mode, the study could be performed with or without sludge recycle. Continuous mode experiments without sludge recycle lead to wash out of reactor hence it was decided not to use that type of system. In addition, continuous system with

sludge recycle requires very long time to reach steady state and a similar study was carried out by Peters (1998). Hence, it was decided to carry out study in batch mode.

As described earlier, black liquor has surfactants and there is a potential for using the foam fractionation. Therefore, feasibility of foam fractionation as a pretreatment step to activated sludge process was evaluated. In this study, foam fractionation operation was not optimized and only the feasibility of foam fractionation operation as a pretreatment step was evaluated. Hence, many of the parameters used in the experiments were directly taken from the literature.

1.3.1 Objectives

The major objectives for the present work are outlined below.

1. To study the effect of black liquor on the kinetics of the activated sludge process
2. To characterize the activated sludge population and relate it with the activated sludge kinetics results
3. To evaluate feasibility of foam fractionation for the given effluent samples

To achieve these objectives, it was decided to use effluent samples and activated sludge obtained from an actual pulp and paper mill. The other alternative was to prepare the simulated effluent samples. To include the effect of variability in the samples due to the plant operation, the alternative of using simulated effluent was ruled out. Therefore, effluent samples and activated sludge were obtained on regular intervals from a kraft paper mill located in Quebec.

1.4 Thesis Outline

This thesis consists of seven chapters. After this Introductory Chapter, the Second Chapter presents a review of pulp and paper mill operations, the activated sludge process and the foam fractionation operation. Chapter 3 provides a summary of experimental methods and procedures used in the examination of the activated sludge and effluent samples. Results from the activated sludge kinetics experiments are discussed in the

Chapter 4 and Chapter 5 discusses the feasibility study of foam fractionation operation. Conclusions from the experimental study are summarized in the Chapter 6 and references are presented in Chapter 7.

CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

2.1 Background

Pulp and paper products play a significant role in nearly every aspect of our lives. We use paper for communicating, recording, and storing variety of information. Paper manufacturing is an old industry. It is one of the important industries for Canada. Together Canada and United States produce about 36% of the world's paper (Noyes, 1993).

2.1.1 Pulp and Paper Mill Operation

Pulp and paper mills use wood as their primary source of fibers. Constituents of wood can be divided into four major groups: cellulose, hemicellulose, lignin and extractives. Cellulose consists of complex polymeric carbohydrate chains, with the basic molecular unit being glucose (a sugar). Hemicelluloses are also polymers, but consist of five different sugars. Extractives are the substances in wood that can be extracted from wood by neutral solvents such as cold water, benzene, ether and acetal. This fraction has a variety of compounds. It includes low molecular weight carbohydrates, terpene, aromatic and aliphatic acids, alcohols, tannins, proteins, alkaloids and soluble lignins. There are other non-cell wall substances present in wood such as pectins, starch and proteins that are not extractable. These together with the extractives form extraneous materials. Despite their relatively small concentration, the extraneous compounds are very important since they inhibit pulping and bleaching and in many cases, they are found to be the prime cause of toxicity of mill effluents (Noyes, 1993).

The production of pulp and paper can be divided into three major steps namely pulping, bleaching and paper production (Biermann, 1996).

Pulping

Depending on the desired qualities of the paper required, various types of pulping operations are used. The main objective of the pulping process is to isolate the cellulose fibers in as free form as possible. The pulping process ruptures the bonds between the wood structure and reduces the wood to fibers composed of cellulose and hemicellulose. Lignin and extractives are the components removed from the wood fibers during pulping (Freeman, 1995). Pulping operation is carried out either chemically, thermally, mechanically or by a combination of these methods. The mechanical pulping includes groundwood pulping, refiner mechanical pulping (RMP), and thermomechanical pulping (TMP). Chemical pulping processes include the Kraft and the Sulfite process. Semi-chemical pulping incorporates both chemical and mechanical pulping techniques. The pulping process includes washing, screening, and deknotting of the pulp.

The purpose of chemical pulping is the dissolution of lignin network by chemical reactions and obtaining the cellulose fiber in relatively pure form. The kraft process and the sulfite process are two primary chemical pulping methods. In chemical pulping, wood chips are processed at elevated pressures and temperatures in aqueous solutions (Freeman, 1995). The lignin is dissolved out of the wood during cooking, leaving most of the cellulose and hemicellulose fibers intact. Chemical pulping typically produces lower yields than mechanical or TMP pulping. The sulfite process uses an acidic mixture of sulfurous acid and bisulfite ions to dissolve lignin. Samples for the present study were obtained from a kraft mill. The kraft mill operation is described in the next section.

Bleaching

The next step in the process of papermaking is the bleaching of pulp. The purpose of bleaching is to enhance the physical and optical properties of pulp. Bleaching continues the delignification process that began during the pulping and whitens the pulp. The bleaching process typically consists of series of stages where chemical reactions remove lignin and bleach the pulp to the desired brightness. After each stage, pulp is washed to remove chemicals before entering the next stage. The lignin content of the

pulp determines the degree of bleaching required to achieve the desired quality of the end product. A common measurement of the lignin content is the Kappa number (or K number). The K number can be used to determine the degree of delignification during the cooking and digestion process or the amount of bleaching chemicals required to achieve a specific level of delignification or brightness in the pulp (Biermann, 1996).

Paper production

One of the biggest uses of pulp is the paper manufacturing. Pulp obtained after processing is prepared into paper stock. Chemical additives, including dyes, clays and thickeners may be mixed into paper stock to form desired characteristics. Basic components to the papermaking machine include the stock inlet, the press section, the dryer section, the calendar section, and the reel. After this, the paper is sent either to market, or for further processing.

2.1.2 Kraft Process

The kraft process involves cooking wood chips in an alkaline solution of sodium hydroxide (NaOH) and sodium sulfite (Na_2S). Under heat and pressure, the alkaline solution breaks down lignin molecules. A high degree of chemical recovery is achieved in the kraft process by recycling cooking chemicals, extracting useful by-products, and recovering energy from the digestion liquor. The kraft process produces a strong, dark-brown pulp (Freeman, 1995).

In the kraft process, a mixture of wood chips and cooking liquor is heated in a large pressure vessel called a digester. The cooking temperature is usually in the range of 170 - 173 °C, with a cooking time about 90 min. Salts present in the cooking liquor are in the ratio 5/2 ($NaOH/Na_2S$). Other salts present have little effect on pulping reactions. Cooked chips are then discharged from the digester under pressure. As the chips are blown from the digesters, the mechanical force of ejection breaks up wood into fibers producing the pulp. The cooking liquor coming out from digester is very dark in color and it contains dissolved and degraded wood components. This liquor is called as the

black liquor. The pulp then goes to a washing stage and then the washed pulp is screened to remove uncooked wood. The pulp is sent for bleaching if white pulp is desired or directly to paper machine if unbleached grades of paper are produced (Alkaline pulping vol.5, 1983).

There are various sources of wastewater in the sulfate (kraft) pulping with a chemical recovery system. These include the digester blowdown, black liquor leaks, spills, overflows, circulating pump cooling and sealing, multiple effect evaporator, dregs washing, lime mud washing, white liquor backwashing, and lime kiln scrubbing.

2.1.3 Kraft Mill Effluents

Kraft mill effluents are toxic to fish and other aquatic life. Sulfides, mercaptans, unsaturated fatty acids, resin acids are some of the toxic substances present in the bleached kraft mill effluents [2]. The most important effluent in the kraft mill is black liquor. In addition to the inorganic material that enters with the white liquor, black liquor contains both organic and inorganic material removed from the wood during the cooking process. The composition of inorganic compounds typically present in black liquor from the cooking of the softwood is shown in the Table 2.1 (Alkaline pulping, 1983).

Table 2.1 Chemical composition of inorganic compounds present in black liquor

Compound	Median*	Range*	% of total
NaOH	1.4	1.0 - 4.5	6 - 7
Na_2S	4.2	1.6 - 5.6	19
Na_2CO_3	7.8	5.0 -1.2	36
Na_2SO_3	2.0	0.4 - 3.8	9
Na_2SO_4	2.8	0.5 - 1.2	13
$Na_2S_2O_3$	3.4	1.8 - 5.1	16
			100

* g/l as Na_2O

Most of the toxicity in pulp and paper effluents and process streams is attributed to resin and fatty acids, chlorinated phenols and to a lesser extent a broad group of neutral compounds. Both unbleached and bleached kraft mill effluents contain wide range of these compounds.

2.2 Wastewater Treatment

Generally, a sequence of various treatment processes is used to treat industrial wastewaters including those from pulp and paper mills. Biological treatment processes form an integral part of this sequence where in BOD and COD of paper mill effluents are reduced. Many studies have been done on wastewater treatment systems for pulp mill using biological treatment processes like activated sludge process. It is a common practice to study the performance of laboratory reactors in activated sludge treatment by analysis of COD and BOD removals. The following section presents the background information on the activated sludge process. The next section to it, presents a review on the treatment of kraft mill effluents and on the treatment of other types of pulp and paper wastewaters for the purpose of introducing typical process conditions and the quality of treatment obtained.

2.2.1 Activated Sludge Process

The activated sludge process is the most widely used biological treatment process. It can effectively reduce the organic content and toxicity of various wastewaters. The activated sludge is a complex microbial population, which contains bacteria, protozoa, rotifers and many other types of organisms. These microorganisms are mixed in suspension with the wastewater under aerobic conditions, and they metabolize the soluble organic compounds present. Bacteria form aggregates or flocs that are easily separated from the treated wastewater in a settling tank. Protozoa and other grazers feed on the edges of the flocs. Thus, the activated sludge process is a two step process. First the reactor (aerator) where the activated sludge is well mixed with the effluent and then the setting tank or a settler where flocs (biomass) is allowed to settle. Figure 2.1 shows the schematic diagram of the activated sludge process.

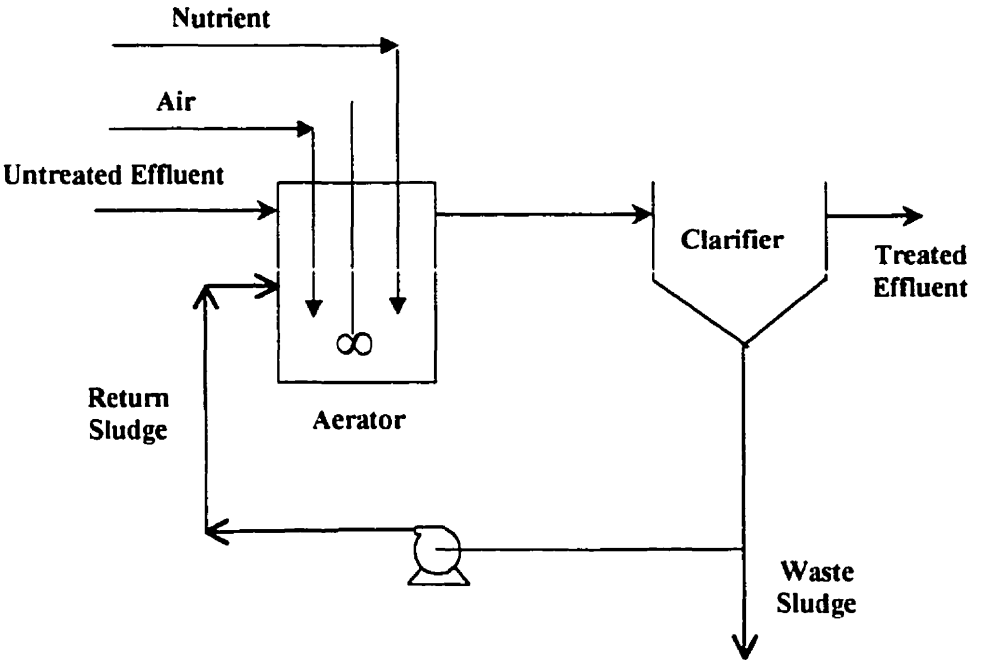


Figure 2.1 Schematic diagram of activated sludge process

The reactor contents are referred to as mixed liquor suspended solids (MLSS). In the reactor, the bacteria culture consumes the dissolved organic compounds (substrate) from the incoming wastewater and produces water, carbon dioxide and new cells as by-products. The aerobic environment is maintained by use of mechanical aeration. After leaving the reactor, the sludge and treated wastewater flows into a settling tank where the cells are separated from the treated wastewater. A portion of the settled cells is recycled to maintain the desired concentration of organisms in the reactor and rest of is wasted. The concentration of biomass in the reactor depends on the desired treatment efficiency, limitations of the settling tank and other factors related to the growth kinetics. Because of its complex nature, the activated sludge process is difficult to control. The performance of the activated sludge process is affected by various parameters like pH, reactor temperature, hydraulic retention time, nutrients, dissolved oxygen and the nature and composition of the microbial population. (Klopping et al, 1995 and Gray 1990)

Activated sludge contains fungi, algae, bacteria and protozoa. Bacteria are the main group present in the activated sludge followed by protozoa. Bacteria are single-celled organisms that use soluble food and generally reproduce by binary fission. The optimal range of pH for bacterial growth is 6.5 to 7.5. Heterotrophic bacteria are the most important types of bacteria present in activated sludge. Heterotrophs are those organisms, which derive their energy from organic oxidation-reduction reactions. Protozoa are single-celled, motile organisms that include amoebas, flagellates, free-swimming and stalked ciliates. They feed on the bacteria and help maintain a balance within the population. Most protozoa are aerobic heterotrophs. Another groups of microorganisms present in healthy sludge are rotifers. Rotifers are aerobic, heterotrophic and multicellular organisms. They consume dispersed and flocculated bacteria as well as some organic matter. They help improve the efficiency of the treatment process. Aerobic organisms grow best in non-limiting dissolved oxygen conditions (dissolved oxygen greater than 6 mg/l) but a dissolved oxygen concentration between 1-2 mg/l is sufficient for most active aerobic heterotrophic microbial activity.

2.2.2 *Studies on Treatment of Kraft Mill Effluents Using Activated Sludge Process*

In a study involving molecular weight fractions, Bullock et al (1996) fractionated bleached kraft mill effluents (BKME) into high and low molecular fractions (HMW and LMW) and found that HMW was the main contributor to absorbable organic halides (AOX) and COD in treated effluent. The authors carried out series of batch experiments at room temperatures with hydraulic residence time (HRT) 48hr and sludge retention time (SRT) 10days, with VSS concentrations 1000 and 1500mg/l. The system was observed to achieve BOD and COD removals greater than 90 and 60% respectively. The author found that HMW accounted for 75-85% of AOX, 60% NO_X and contained three times as much total Kjeldahl nitrogen than LMW. They observed good microbial growth in the unfractionated effluent but LMW and HMW fractions both had poor growth.

Barr et al (1996) considered the effect of HRT, SRT and temperature on the performance of the activated sludge reactor for BKME. The authors studied high operating temperature 45-47°C. In a series of experiments operated at 35°C with HRT 12hr, SRT 15days and food to mass ratio 0.37 and 045, authors observed removal efficiencies of 87.9% for BOD and 32.4% for COD. The specific oxygen uptake ratio (SOUR) was 16.5 mgO_2/g MLVSS/hr (where MLVSS is the mixed liquor volatile suspended solids) and the acute toxicity removal of 97.7% was observed. By changing HRT and SRT, they observed that HRT affected BOD removal more strongly than SRT. As HRT decreased BOD, COD, AOX and toxicity removal all decreased while SOUR increased.

Kemeny and Banerjee (1997) investigated relationship between AOX and COD in an aerated lagoon system for bleached kraft mill. They observed that residual COD and AOX were due to lignin residuals not degraded during treatment. After treatment, color increased across the lagoon and exceeded inlet color by 22%. Color and COD correlated well at the exit of the lagoon indicating color was derived from carbon that was not removed during treatment. The authors also concluded that conductivity was a good indicator of the presence of black liquor in the effluent.

2.2.3 *Studies on Treatment of Other Pulp Mill Wastewaters Using Activated Sludge Process*

Schnell et al (1990) presented work on aerobic and anaerobic biological treatment systems. The authors considered combinations of stone groundwood and thermo-mechanical pulping (TMP) wastewater and magnetite condensates. Aerobic treatment achieved consistent and high BOD and COD removal. Detoxification was achieved with a longer HRT being required for complete detoxification. Anaerobic treatment provided insufficient BOD and toxicity removal and required aerobic treatment.

Liver et al (1993) presented a study on bench-scale batch and continuous treatment of TMP effluent. Batch studies showed that biodegradation and detoxification were possible and acclimation did improve the rate of biodegradation. Continuous

experiments were performed with acclimated biomass at various HRT (8-22hr) and operating conditions over a time period which allowed steady state to be achieved. BOD removal of 94-98% and COD removal of 64-84% were achieved and detoxification was found in all cases except for the case of short HRT.

Franta and Wilderer (1997) studied the reduction of residual organics using sequencing batch reactors by modifying the sludge age, react period (batch phase) and fill period (time to fill the reactor). In terms of biodegradability, they achieved a reduction in COD between 85-93% and 98% reduction of BOD. Low molecular weight compounds such as alkenes, resin acids, aromatics and aliphatics were significantly reduced in the effluent. Higher molecular weight fractions required high sludge ages to achieve significant degradation ratios.

Lo et al (1994) characterized the effluents of two TMP mills to determine the variation and contribution of process elements on BOD and toxicity to trout. They collected TME samples and samples from various operations to determine which streams contributed the most to BOD and toxicity. They examined the effect of HRT and sludge age on BOD reduction and toxicity removal. They observed 93% BOD removal for HRT between 8 and 24hr and varying sludge age from 10-20days had no effect. In another paper, the same authors (1994) derived the biokinetic parameters using their results. They used first order reaction model to determine BOD removal rate, oxygen use and biomass yield.

The short review given above indicates that all the studies have been mainly done on continuous systems. The kinetics of the activated sludge process have been studied using various methods such as studying a particular type of substrate or fractionating effluents according to their molecular weight. So far, no studies have been reported that considers the effect of black liquor on the activated sludge population.

2.2.4 *Batch Growth*

Most of organisms follow a general growth pattern. Figure 2.2 shows a typical growth curve. It can be divided into several growth phases. These include lag phase, acceleration phase, exponential (log) growth phase, declining growth phase, stationary phase and finally endogenous or death phase (Metcalf and Eddy, 1991).

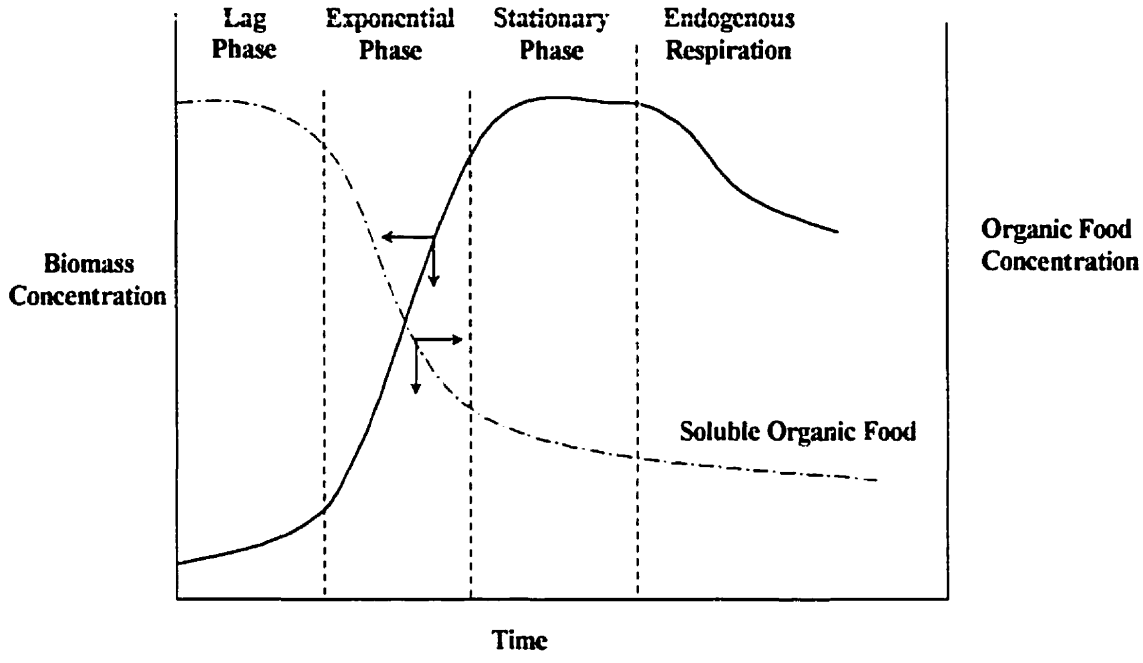


Figure 2.2 Growth curve in a batch reactor

The lag phase represents the acclimation period for the cells and it is characterized by long generation times. The acceleration phase occurs when the generation time decreases and the growth rate begins to increase. This is followed by the exponential growth phase, which involves a constant and maximal specific growth rate. The rate of metabolism is only limited by microbial generation and its ability to process the substrate. This phase continues until the substrate becomes limiting. Then the microbes enter the declining growth phase where the growth rate slows down as the substrate concentration gradually diminishes and generation time increases once again. When the cells have exhausted the nutrients and substrate, the microbes enter the stationary phase. At this stage, growth is offset by death. Finally, when the substrate is used up the microbes enter the endogenous (log-death) phase. During this phase the

microbes metabolize their own protoplasm without replacement since the food supply is limiting and lysis occurs causing the release of nutrients within the dead cells which may be used by the remaining cells. The concentration of toxic metabolites becomes unfavorable to the population and the cell death rate exceeds the growth rate (Gray 1990).

The wastewater industry uses the batch reactor assay to estimate maximum rates of substrate oxidation and growth for both heterotrophic and autotrophic bacteria (Ekama et al, 1986). To determine the kinetic parameter in batch assays, relationship between substrate uptake and bacterial growth must be determined. The standard approach is to assume that the relationship between substrate and specific growth rate (μ) follows simple Monod kinetics which is derived for a single substrate system (Pollard et al, 1998). It is used for activated sludge system mainly because of simplicity and its fit to experimental data. There are other models also available, which are developed for multi-component substrate systems.

During the growth and decline phases, rate of growth is described by the first order auto-catalytic rate equation:

$$r_X = \mu X \quad \text{.....(2.1)}$$

where; r_X = rate of growth ((mg/l)/sec)

X = cell concentration (mg/l)

μ = specific growth rate (sec^{-1})

In the above equation specific growth rate (μ) is expressed by Monod equation:

$$\mu = \mu_{max} \frac{S}{k_s + S} \quad \text{.....(2.2)}$$

where; S = concentration of growth limiting substrate (mg/l)

μ_{max} = maximum specific growth rate (sec^{-1})

k_s = half saturation constant (mg/l)

Using this system model, it can be expected that the microbial population grow at their maximum ($\mu = \mu_{max}$) when supplied with excess substrate ($S >> k_s$) and this is the basis of using batch assay. The growth curve can be described based on the specific growth rate as shown in Table 2.2.

Table 2.2 Summary of batch growth

Growth phase	Description	Specific growth rate
Lag	Cells adept to the new environment; no or very little growth	μ almost zero
Acceleration	Growth starts	$\mu < \mu_{max}$
Exponential	Growth achieves its maximum rate	$\mu \approx \mu_{max}$
Decline	Growth slows down due to nutrient exhaustion or build-up of inhibitory products	$\mu < \mu_{max}$
Stationary	Growth ceases	μ almost zero
Endogenous	Cells lose viability and lyse	$\mu <$ zero

In the batch experimental systems, a portion of the substrate is converted to new cells and a portion is oxidized to inorganic and organic end products. The yield coefficient (Y) is defined as the ratio of the mass of cells formed to the mass of substrate consumed. It is measured during any finite period of the exponential growth.

The yield coefficient depends on various factors like the oxidation state of carbon source, nutrient elements, the degree of polymerization of the substrate, pathways to metabolism. The degradation of substrate is thus related to the growth of cells by the equation 2.3.

$$r_X = -Yr_S \quad \text{.....(2.3)}$$

where; r_X = rate of growth ((mg/l)/sec)

X = cell concentration (mg/l)

r_S = rate of substrate utilization ((mg/l)/sec)

S = substrate concentration (mg/l)

Y = yield coefficient

Combining equation 2.1, 2.2 and 2.3 for a batch system, we get:

$$\frac{dS}{dt} = -\frac{\mu_{max} XS}{Y(k_s + S)} \quad \text{.....(2.4)}$$

$$\therefore \frac{dS}{dt} = -\frac{kXS}{k_s + S} \text{.....} where \cdot k = \frac{\mu_{max}}{Y} \quad \text{.....(2.5)}$$

Equation 2.5 describes the maximum rate of substrate utilization per unit mass of microorganism.

2.2.5 Foam Fractionation

Foam fractionation is a separation technique based on adsorptive bubble separation. It is the partial separation of dissolved (or sometimes colloidal) substances from liquid by adsorption on the surface of bubbles, which ascend through the liquid to form foam. Foam fractionation can also be used for substances, which are not surface active by themselves such as various inorganic salts and organic salts. This can be achieved through deliberate addition of suitable surfactant (termed as a collector) which combines with the substance in question (termed as colligend) by chelatation or other mechanism. These complexes migrate to the foam phase and thus it can be adsorbed and separated (Lemlich R., 1966).

Figure 2.3 shows a typical foam fractionation operation. Foam fractionation operation can be explained by counter-current flow of foam and liquid (Grieves, 1963). According to this mechanism, rising bubbles tend to carry some of the bulk liquid with them while surfactants are being adsorbed on the bubble surfaces. As they cross the surface of the liquid into the foam layer, they form spherical bubbles with the interstitial liquid having essentially the same bulk concentration as the liquid pool, whereas the surface contains some adsorbed surfactants. The main transfer operation then starts from this point. As more bubbles are added from the bottom, the liquid in the interstitial starts trickling down due to gravity and pressure differences. The films separating the bubbles get thinner, and consequently more adsorption of the surfactants on the gas-liquid interface takes place. The bubbles, which have changed from spherical shape to

polyhedral, rise to encounter richer liquid draining down causing further migration and transfer of the surfactants to the surface. Thus, two counter-current streams are observed:

1. rising lean films with relatively few adsorbed surfactants
2. draining rich liquid from the top of the column

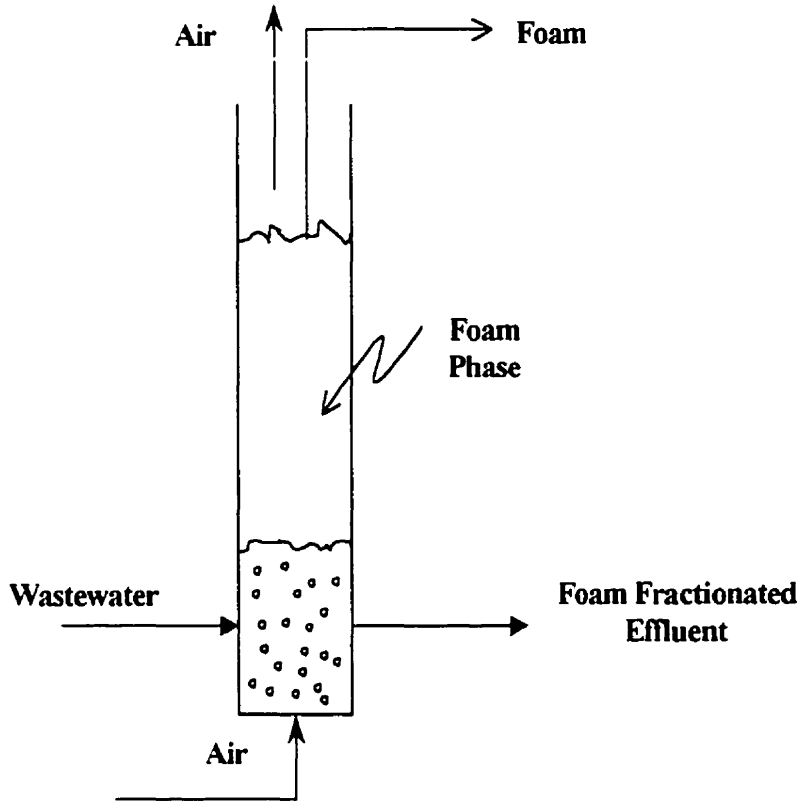


Figure 2.3 Foam fractionation operation

As the first stream rises, it gets richer and richer and as the second stream trickles down it gets leaner and leaner with surfactants. Drainage is not the only cause of the enrichment of the rising stream. Bubbles bursting constantly spray the oncoming foam below with enriched liquid. This counter-current separation mechanism is similar to distillation operation Rubin and Gaden (1962). Foam fractionation is affected by any parameter that affects the surface properties. These factors include pH, concentration of surfactants. Other parameters that affect the foam fractionation operation include gas flow rate, temperature and other chemicals present in the system.

2.2.6 *Studies on Foam Fractionation*

Earlier experiments done with kraft mill effluents during 1972-73 (Walden et al.) established that detoxification by foam fractionation is the most readily applicable to whole mill effluents and caustic extraction effluents. However, combined condensates, unbleached white water and acid bleach effluent alone could not be detoxified, partly because of poor foaming characteristics. This observation has been verified for a number of mills, on a large number of samples. It was also found that pH was an important factor in controlling the efficiency of the foam fractionation process. Laboratory investigations indicated that typical wholemill effluent, with median survival time (MST) values for fish of 6 to 12 hr, could be detoxified using about 15 min retention time at pH 7 to 8, at approximately 20 °C, and at gas/liquid ratios of less than 2. Detoxification of wholemill effluents by foam fractionation was found to produce some beneficial side effects. Under continuous operating conditions, the foaming tendency of the effluent could be reduced by 80-87 % and the fibrous, suspended solids, content by about 50 %. Conceivably, detoxification by foam separation may be combined with removal of fibrous suspended solids in a primary treatment process. This approach would be useful to mills that require reduction in toxicity and suspended matter only, but not in BOD_5 (CPAR Progress report, 1974).

Foam Fractionation decreased the concentration of toxicants in Spent Sulfite Liquor (SSL) by 40 % under the best conditions for the separation. The optimum pH was 10, no toxicity removal was found at pH values less than 8. The rate of toxicant removal was found to depend on the flow rate of the gas used for generating foam (Berk, 1977).

CHAPTER 3
MATERIALS AND METHODS

3.1 Materials

3.1.1 Effluent Samples

Effluent samples were obtained from a kraft mill located in western Quebec. They were received approximately once a week in shipments of about 16 or 32 liters. Samples were transported in coolers with ice packs to keep samples cooled and thus minimizing the changes in the sample properties. Similarly, activated sludge was shipped about 2-4 liters per week depending on the need. Both sludge and effluent samples were refrigerated immediately upon receipt and stored at 2-4°C until needed. Sludge was used as soon as possible to ensure that it was fresh and cells were viable. Prior to use, the activated sludge was allowed to settle at room temperature and then the supernatant was decanted to get concentrated sludge. It was important to bring sludge at room temperature before using to avoid any thermal shocks to sludge. Total mill effluent (TME) is a combination of all the wastewater streams in the mill. TME was taken after primary settling tank, which removes most of the large fibers and particles. Activated sludge samples were taken directly from the return activated sludge line. Black liquor samples were taken from their respective points prior to joining the total mill effluent.

3.1.2 Nutrient Addition

For the growth of activated sludge, nutrients like nitrogen and phosphorous were added to effluent samples. Nitrogen was added in the form of urea (NH_2-CO-NH_2) and phosphorous was added in the form of ortho-phosphoric acid (H_3PO_4). Nutrients were added in the ratio COD:N:P of 100:3:1 (Peters, 1998). For both N and P, solutions of urea and o-phosphoric acid were prepared at lower concentrations. These prepared solutions were stored at 2-4°C. Solutions were added to effluents. Equivalent amount of urea and phosphoric acid were calculated using stoichiometry as shown in Appendix A.

3.2 Analytical Procedures

Total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC), soluble lignin concentration and carbohydrate concentration analyses were performed. TSS, VSS, TOC, COD and BOD were measured according to the procedures outlined in Standard Methods for the Examination of Waste and Wastewater (17^{th} Ed., APHA, 1989).

3.2.1 Total Suspended Solids (TSS), Volatile Suspended Solids (VSS) and Fixed Suspended Solids (FSS)

Total suspended solids represent the total amount of suspended solids present in the effluent sample. TSS refers to the portion of total solids retained by a filter after drying. Volatile suspended solid is the portion of TSS, which can be oxidized and it represents the organic matter in the sludge while fixed suspended solid represents the portion of TSS, which can not be oxidized. TSS and VSS were determined using vacuum filtration of a known volume of sample using the Millipore® filtration apparatus. Glass fiber filter papers (Millipore® AP40) were used for the filtration. Before use, filter papers were washed, dried and ignited in a muffle furnace. The filtrate was collected and stored at 2-4°C for later analyses while the filter paper was dried in an oven at 103-105°C to constant weight. The increase in weight of filter paper gives the TSS. To determine VSS, filter paper was ignited in a muffle furnace at 550 ± 50°C to combust all volatile matter. The difference in weight before and after ignition represents the VSS and the difference between TSS and VSS represents FSS.

3.2.2 Chemical Oxygen Demand (COD)

The chemical oxygen demand is the measure of oxygen equivalent of the organic matter content of a sample that can be oxidized by a strong chemical oxidant. The closed reflux, titrimetric method was used for COD measurements. This method uses the principle that most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. Sample is refluxed in strongly acid solution with a known access of

potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate (FAS) to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent. Samples were filtered and stored at 2-4°C for their analyses. Care was taken to analyze samples as soon as possible. Reagents used for COD test were prepared a day or two before the assay to allow time for the solids to dissolve and solutions to cool. Reagents were prepared as described in the standard methods (APHA, 1989).

Standard 10 ml ampules and caps were pre-washed with 20% H_2SO_4 to prevent any contamination. The ampules were prepared by combining 2.5 ml of sample, 1.5 ml of dichromate digestion solution and 3.5 ml of sulfuric acid reagent. It was necessary to dilute samples (the filtrate collected during the tests for TSS and VSS) so that the resulting COD would be within the range of 100-300 mg/l. This range was acceptable for this test and it avoided the necessity of using small volumes of titrant. Four blanks ampules containing distilled water instead of sample were also prepared. Two of these were digested to provide a blank reading and two were set aside to determine the molarity of FAS. The ampules were digested on a heating block preheated to 150°C for 2 hr. Ampules were cooled to room temperature before titration. Ferroin was used as the indicator for titration. 1-2 drops of ferroin were added and then samples were titrated against FAS with stirring. The end-point was change of color from blue-green to reddish brown. COD was then determined using the equation 3.1.

$$COD(mg/l) = \frac{(FAS_{blank} - FAS_{sample}) \times M_{FAS} \times 8000}{V_{sample}} \quad \text{.....(3.1)}$$

where, FAS_{blank} = volume of FAS titrated for blank (ml)

FAS_{sample} = volume of FAS titrated for sample (ml)

M_{FAS} = Molarity of FAS

V_{sample} = volume of sample in ampule (ml)

The molarity of FAS was obtained from the following:

$$M_{FAS} = \frac{V_{dig}}{V_{FAS}} \times 0.1 \quad \text{.....(3.2)}$$

where, M_{FAS} = Molarity of FAS

V_{dig} = volume of 0.0167M $K_2Cr_2O_7$ solution titrated (ml)

V_{FAS} = volume of FAS used in titration (ml)

There are some possible interferences in COD test. Silver sulfate, added as catalyst, reacts with halides to produce precipitates that are only partially oxidized. Standard Methods suggests use of mercuric sulfate to overcome complications due to the presence of halides but in the present study, it was assumed that the halides were present in insignificant amounts. In addition, interferences due to nitrite (NO_2^-) were neglected.

3.2.3 Total Organic Carbon (TOC)

Total organic carbon (TOC) is the total organic content of the wastewater. The method involves the oxidation of organic molecules to carbon dioxide (CO_2) by persulphate in the presence of ultraviolet light. CO_2 is measured by a nondispersive infrared analyzer producing quantitative results. Samples were pre-filtered and then 40 or 200 µl, depending on the expected TOC concentration, were injected into a DC-80 Total Organic Carbon Analyzer (Dohrmann® Division, Rousemount® Analytical Inc.). The detection range for 200 µl was between 10 to 400 mg/l while for 40 µl, it was between 200 to 2000 mg/l. The instrument was calibrated using either a 400 ppm standard (potassium hydrogen phthalate) in the case of 200 µl samples and 2000 ppm standard in case of 40 µl sample volume.

3.2.4 Biological oxygen demand (BOD)

The 5-day biological oxygen demand measures the oxygen utilized via biological degradation during five days of incubation at room temperature. The samples were diluted with dilution water. The dilution water was prepared as described in standard methods (APHA, 1989). Reagents used for dilution water were bought already prepared

to the correct molarities for the BOD_5 assay. A nitrification inhibitor (2-chloro-6-(trichloro-methyl) pyridine) was added at the rate of 1 mg/l of dilution water to ensure that only carbonaceous demand was measured. The dilution water was aerated for several hours to allow the nitrification inhibitor to dissolve and to ensure that the dilution water was saturated with air. Polyseed® capsules were used as source for seed. Polyseed® is a uniform preparation of a range of bacteria responsible for the degradation of municipal and industrial wastes and allows for more reproducible measurements of BOD_5.

Standard methods suggest doing several controls to ensure the quality of the dilution water and seed. One such control is the seed control. A seed control was performed by plotting the dissolved oxygen depletion vs. seed volume. This plot should be a straight line with y-intercept less than 0.1 mg/l. In addition, standard glucose-glutamic acid check was done to see the quality of dilution water. All samples were filtered as described in the TSS analysis (section 3.2.1) and stored in a freezer. Samples were brought to room temperature before doing BOD_5 assay. 300 ml bottles were used for the BOD_5 assay. Depending on the estimated BOD value, appropriate amount of sample was taken in bottle and 3 ml of seed were added. Bottles were then filled with dilution water. The initial dissolve oxygen (DO) was measured by inserting DO probe. After DO measurement, bottles were topped off with more dilution water, stoppered and covered with parafilm to create a water seal and prevent evaporation. Samples were then incubated in darkness at room temperature for 5 days before measuring the final DO. The BOD_5 was calculated using the equation 3.3.

$$BOD_5(mg/l) = \frac{(D_1 - D_2) - (B_1 - B_2) \times f}{P} \quad \text{.....(3.3)}$$

where; D_1 = DO of diluted sample immediately after preparation (mg/l)

D_2 = DO of diluted sample after 5 day incubation at 20°C (mg/l)

B_1 = DO of seed control before incubation (mg/l)

B_2 = DO of seed control after incubation (mg/l)

f = ratio of seed in diluted sample to seed in seed control

P = decimal volumetric fraction of sample used

3.2.5 Soluble Lignin Concentration

Soluble lignin represents lignin present in the samples. Pre-filtered samples were used for this analysis. Analysis was performed according to the methods suggested by the PAPRICAN. For the black liquor samples, absorbance was measured at 280 nm. Samples were suitably diluted with pH 13 sodium hydroxide solution to get the absorbance in the range of 0.1 to 0.7. For TME effluent samples absorbance was measured at 205 nm. Samples were acidified with concentrated sulfuric acid (2-3 drops) before making measurements. Soluble lignin were calculated using the following equations:

For black liquor samples:

$$lignin(gm/l) = \frac{A \times D}{23.7} at 280nm \quad \text{.....(3.4)}$$

For total mill effluent samples:

$$lignin(gm/l) = \frac{A \times D}{100} at 205nm \quad \text{.....(3.5)}$$

where; A = absorbance

D = dilution factor

3.2.6 Carbohydrate Concentration

Samples were shipped to the Pulp and Paper Research Institute of Canada (PAPRICAN) for the carbohydrate analysis. Carbohydrate analysis was done using gas chromatograph equipped with flame ionization and a DB225-30N fused silica column. Samples were first hydrolyzed with 72% sulfuric acid in autoclave for an hour at 121°C (15 psi). Samples were then neutralized using ammonium hydroxide to pH 5.6-6.1. Acetylation of samples was carried out before injecting the extract into gas chromatograph. Soluble lignins are then calculated using the response factor.

3.2.7 *pH, Temperature, Dissolved Oxygen (DO), Conductivity and Surface Tension*

pH was measured using a Fisher Accumet® pH meter, which was calibrated using two points (using buffer solutions of pH 7 and 10) calibration. Temperature was measured by a standard mercury thermometer. DO was measured using an Orion DO probe. DO meter was calibrated in air saturated water at room temperature with a correction for atmospheric pressure. Depending on the temperature and pressure, instrument read the dissolved oxygen value in ppm.

Conductivity was measured using a Cole-Parmer conductivity meter. Surface tension measurements were carried out using Fisher Autotensiomat® (model 215). It employed du Nouy ring method. It used a platinum-iridium ring. Results were directly obtained in dynes/cm.

3.2.8 *Biolog Technique*

Biolog analytical technique was used to characterize the activated sludge population. This analytical technique used a microplate, image analysis and statistical analysis. Each step of analysis is described in short below.

Microplate Preparation

The biolog technique relies on the irreversible reduction of a tetrazolium dye as an indicator of carbon source utilization. Since the activated sludge consists mainly of gram-negative species (Gray, 1990), GN microplates were used in the biolog analysis. Each microplate consists of 96 wells. Out of 96 wells, 95 wells have a specific carbon source (substrate) while the remaining one is the control well (without any carbon source). Each well also has dye and nutrients in a dried-film form, which is reconstituted upon inoculation of the cell suspension. The microplates were stored at 2-4°C. Prior to use, microplates were brought to room temperature. For preparing the cell culture, method described by Victorio et al (1996) was followed. Fresh samples of sludge were

collected from the reactor. Deflocculating agents like sodium pyrophosphate and Tween 80, were added to the sample to the ratio of 0.01%. Samples were homogenized by vigorous shaking and solids were removed from the suspension by centrifugation at 5000 rpm for 5 min. Recovered solids were washed three times with 0.1M phosphate buffer by centrifugation at 10000 rpm for 10 min. Cells were then resuspended in 2 ml of 0.85% saline.

The turbidimeter was calibrated using the turbidity standards and an uninoculated saline tube. The cell suspension was added to a saline tube and its turbidity was set in the range to obtain cell density of 3×10^8 cells/ml. All microplate wells were filled with 150µl of suspension. The plates were incubated in a closed box for 48 hr. If the cells utilized the substrate in the well, the tetrazolium redox dye turned purple. Pattern of violet colors was thus developed and this pattern was read using imaging software and then analyzed statistically to determine the response.

Image Analysis

After 48 hr of incubation period, picture of microplate was taken using a Sony Hi-Resolution CCD-IRIS monochrome digital camera. Picture was directly transferred to a computer. Visilog 5.1 image analysis software was used to convert color intensity values of microplate wells to numbers between 0 to 256. Color intensity in each well was determined using a macro that computed the average pixel value of a 5 x 5 matrix taken from the center of each well. Raw difference data were then calculated by subtracting the color intensity for the response well from the color intensity for the control well. Then raw difference data were divided by the average well color to get normalized data. These normalized data were used to do principal component analysis.

Statistical Analysis

Simca-P statistical analysis software was used to do the statistical analysis on the normalized data obtained from the image analysis. It used principal component analysis (PCA). PCA is a multivariate method that essentially rotates a swarm of data points about

their centroid to reveal any intrinsic patterns. It follows the nonlinear iterative partial least squares (NIPALS) method of calculating the principal components. The method consists of rewriting a data matrix as a sum of linearly independent matrices. These can in turn be expressed as products of two vectors, a score (column) vector t and a loading (row) vector p^T. Once vectors t and p^T are calculated, they can be plotted to reveal any intrinsic patterns. Generally, plot of t[1] and t[2] were plotted to demonstrate differences among plates.

3.3 Experimental Design

3.3.1 Shake Flask Experiments

Preliminary experiments were carried out in shake flasks using 500ml Erlenmeyer flasks on a rotary shaker operating at 180-200 rpm. In preparation of shake flask, first the TSS of inoculum sludge was determined. Knowing the TSS needed for the experiment required amount of sludge was calculated. Nutrients (nitrogen and phosphorous) were added to the effluent samples. See appendix A for calculations. Required amount of sludge was then added to the effluent samples. This sludge-effluent mixture was prepared as one large batch. 100-150 ml of this mixture was then transferred to 500 ml flasks. An initial sample was immediately filtered. Flasks were then placed on shaker at 180-200 rpm and at room temperature. Samples were taken at various times to study the kinetics of activated sludge.

3.3.2 Batch Reactor Experiments

Figure 3.1 shows the schematic diagram of the experimental setup for the batch experiments. Two such similar setups were used to carry out batch experiments. Reactors of volume 4 and 7 lit were used. Working volume for liquid was 1.5 and 3 l. Dissolved oxygen was maintained at 6-7 mg/l using aeration.

Effluent samples were prepared in the same way as with shake flask experiments (calculations are shown in appendix A). Initial TSS of activated sludge was measured and

required amount of sludge was calculated depending on sludge concentration needed. After adding nutrients, effluent samples were poured in the reactor. Aeration and agitation were started and activated sludge was added to the reactor. Complete mixing was assumed to be achieved in 5 min. Then the initial sample for various analyses was taken. Reactors were operated for several days with sampling at given time intervals.

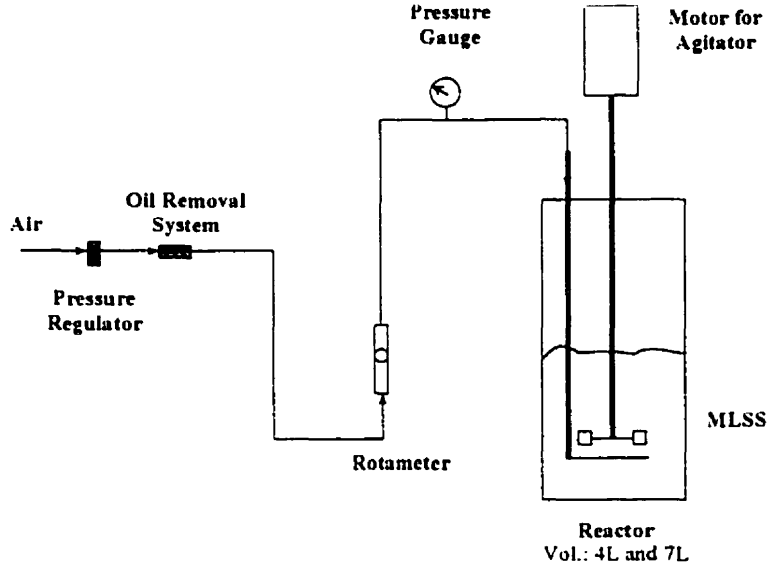


Figure 3.1 Batch experiment setup

3.3.3 Foam Fractionation Experiments

Figure 3.2 shows the foam fractionation setup. The foam fractionation column was made of Plexiglas and had diameter of 8.89cm and height 60 cm. The foam fractionation column had a conical head. Oil-free air was introduced in the column from bottom through a ceramic porous plate. Porous plate had pore size of 40 μm. Sparger plate was cleaned ultrasonically. To carry out experiments, effluents were brought to room temperature. Then required concentration of black liquor was prepared. The pH of samples was measured and it was brought to desired values using either sodium hydroxide or diluted nitric acid. While starting the experiment, air flow rate was first started and then 500 ml of prepared effluent was poured in the column. All the foam fractionation experiments were carried out in batch mode. Samples were taken at various

times to study the operation. Experiments were carried out for 3-6 hr. Samples were analyzed immediately after the experiment.

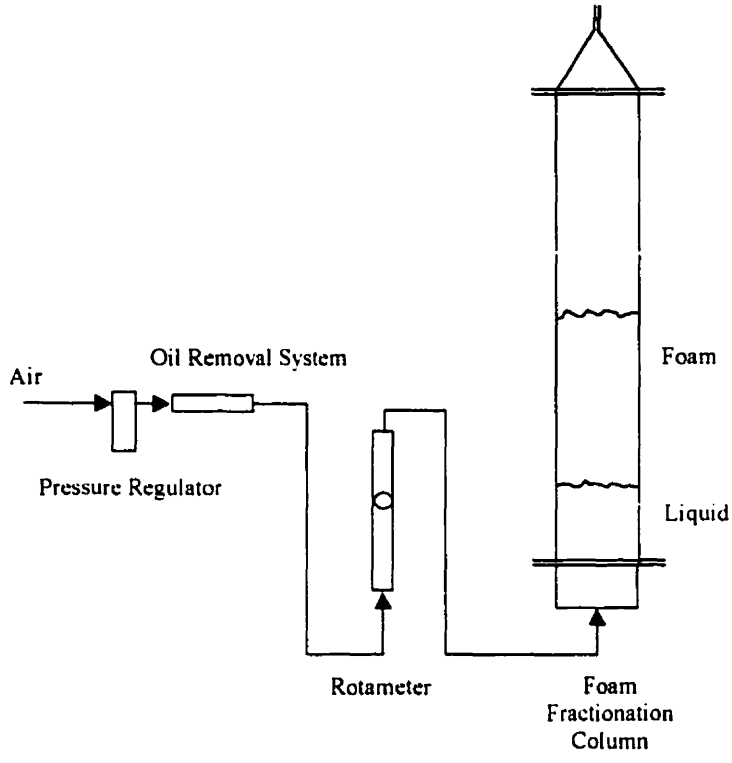


Figure 3.2 Foam fractionation setup

CHAPTER 4

RESULTS AND DISCUSSION

(ACTIVATED SLUDGE KINETICS)

In this chapter, results from the activated sludge kinetics experiments, studying the effect of black liquor are presented. Two parameters, namely the initial sludge concentration based on total suspended solids (TSS) and the black liquor concentration were studied. The black liquor concentrations were in total mill effluent. First the results from the preliminary experiments are presented and then results from the black liquor experiments are presented for a given initial sludge concentration. Combined results, which include results of initial rates, are then presented to see the effect black liquor and the initial sludge concentration.

4.1 Initial Experiments

4.1.1 Effect of Anti-foam

Experiments for studying the activated sludge kinetics were carried out in batch reactors of volume 4 and 7 lit. Due to addition of Black Liquor, problems of foaming were observed. To prevent foaming, anti-foam A (obtained from Sigma Chemicals) was used. Anti-foam was added to the reactor as and when foaming was observed. Preliminary shake flask experiment was carried out to study the effect of anti-foam on the growth kinetics of the activated sludge and on biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) removal.

Two different concentrations of anti-foam in Total Mill Effluent (TME) were studied. Three sets of shake flasks were prepared. First with 0.26% (0.66 ml of anti-foam in 250 ml), second with 0.53% (1.25 ml in 250 ml) and third without anti-foam were prepared. The third set was used as a control. Samples were taken at various time

intervals and various parameters like TSS, volatile suspended solids (VSS), BOD, COD, TOC were measured.

Effect on the growth kinetics

In all three sets, 2 ml of activated sludge was added to get initial TSS of 250 mg/l. Samples were taken from the flasks immediately to get samples at time zero. It was observed that anti-foam increased the suspended solids of the solution. Figure 4.1 shows the growth behavior for different concentrations of anti-foam while Figure 4.2 shows normalized TSS and normalized VSS with time. Normalization of TSS and VSS was done using the initial TSS and VSS values respectively. In the present study, results of initial rates were calculated and compared. For the comparison purpose, it is important that all the curves start at the same point. To have that normalization of various parameters were carried out.

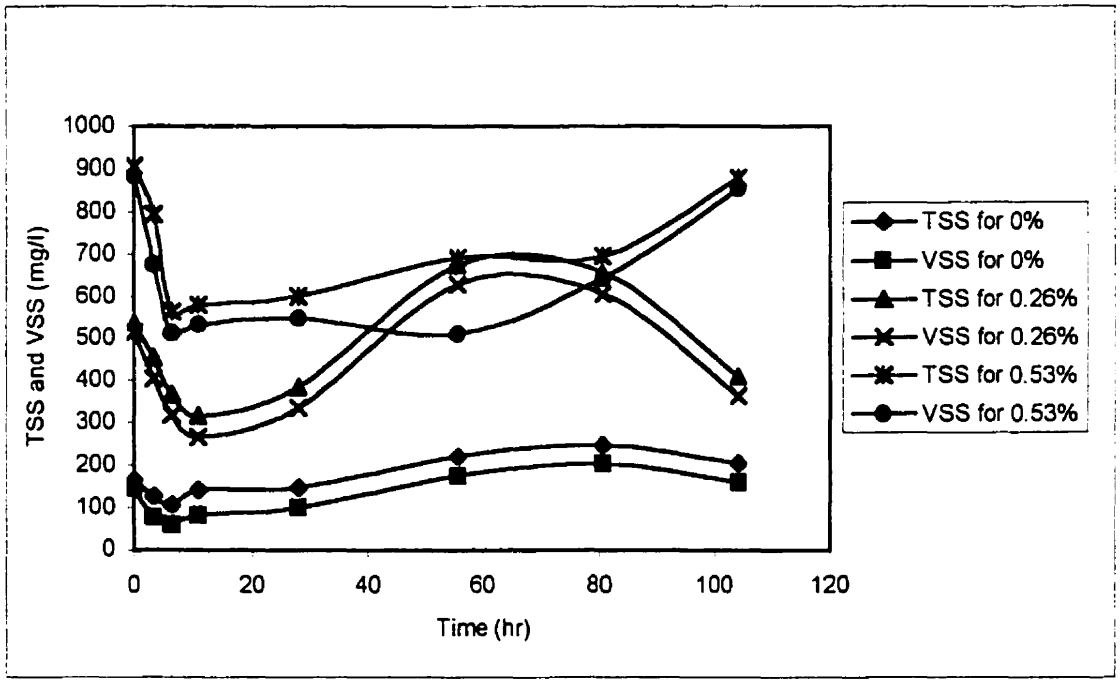


Figure 4.1 Effect of anti-foam on the growth kinetics

Figure 4.1 shows that for 0.53% anti-foam, there was a longer lag phase which was absent for other concentrations. Curves for 0% anti-foam and 0.26% anti-foam were nearly the same on normalized scale. However, for 0.53% anti-foam, similar growth was not observed. Therefore, it was concluded that for lower concentrations of anti-foam, its

effect on the growth could be neglected. However, for higher concentrations effect was significant and could not be neglected. In experiments, care was taken not to exceed anti-foam concentration above 0.25% while adding anti-foam.

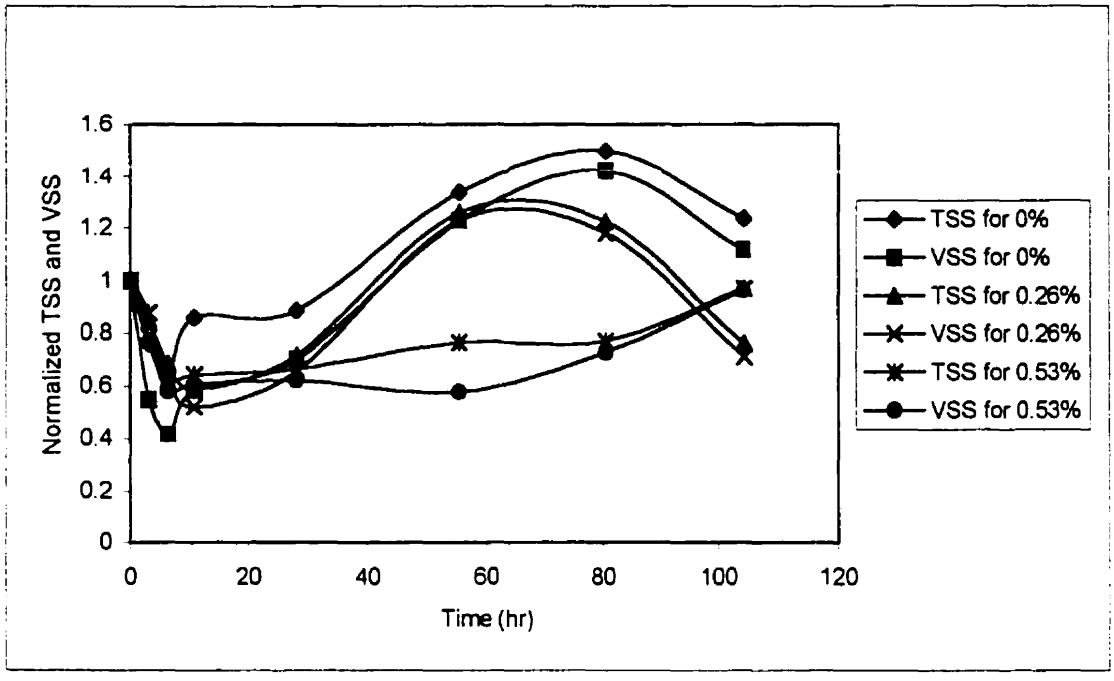


Figure 4.2 Normalized TSS and VSS values for different concentration of anti-foam

Effect on BOD, COD and TOC removal

Due to large volume of sample needed for BOD test, BOD was measured only in the beginning and at the end. Figure 4.3 shows the graph for the BOD. It was observed that the anti-foam increased BOD of samples linearly. The final value of BOD was unaffected by the anti-foam concentration. Hence, it was concluded that BOD removal was unaffected by the anti-foam.

COD was measured for all time intervals. It was observed that anti-foam increased COD of sample. However, at the lower concentration of anti-foam, final values of COD were same as that for samples without anti-foam but for the higher concentration of anti-foam, final value for COD was higher than that for samples without anti-foam. Figure 4.4 shows the comparison of absolute values of COD for various time intervals.

COD removal behavior was nearly the same for 0% and 0.26%. Therefore, it was concluded that COD removal was unaffected for lower concentrations of anti-foam.

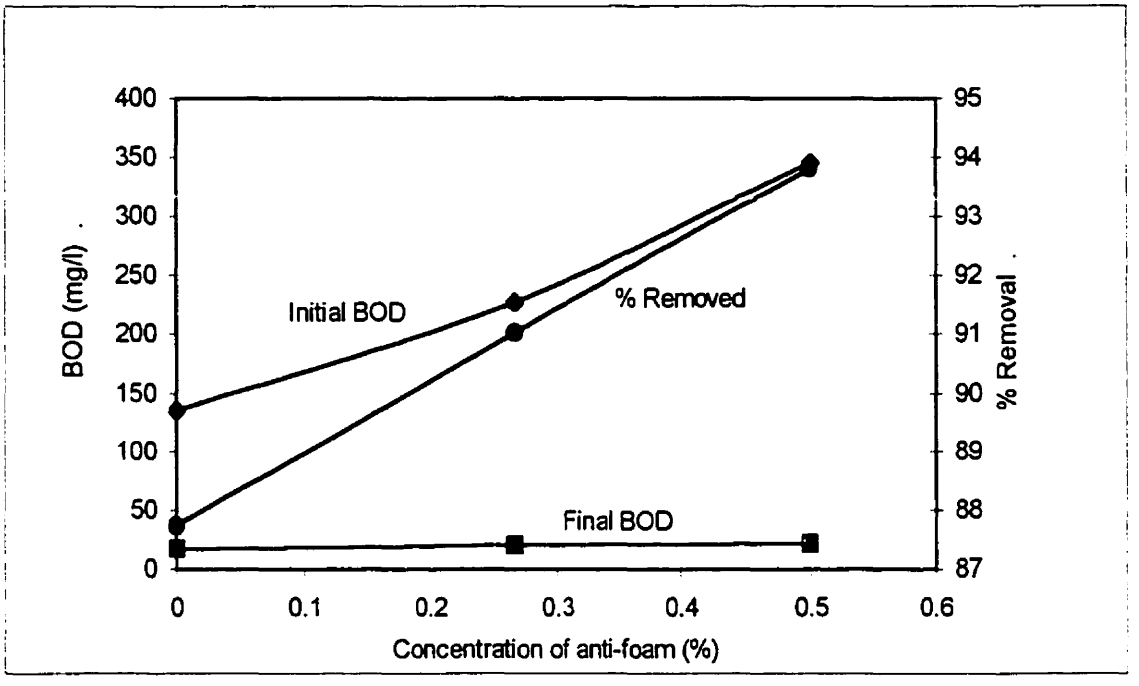


Figure 4.3 Effect of anti-foam on BOD removal after 150hr

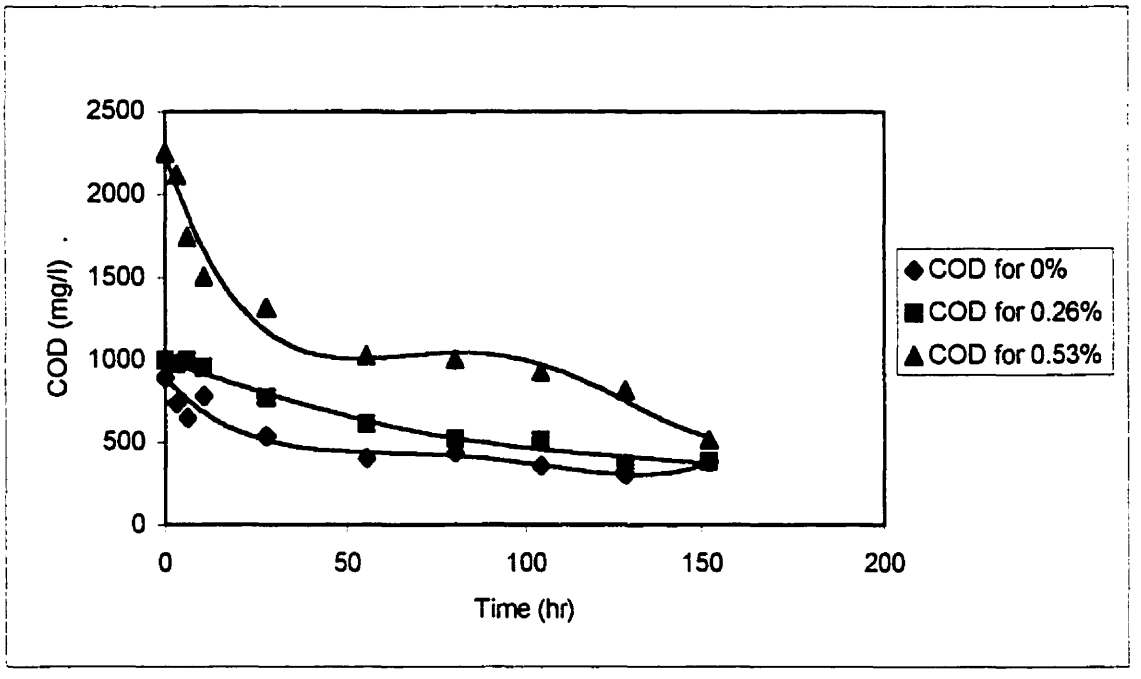


Figure 4.4 Effect of anti-foam on the COD reduction

Total organic carbon (TOC) was also measured for all time intervals. TOC removal behavior was similar to that for COD. The anti-foam increased TOC of samples. Again, at lower concentration of anti-foam, final values were same for 0% and 0.26% anti-foam but for higher concentration of anti-foam, final value was higher than that for 0% anti-foam. Therefore, it was concluded that at lower concentrations of anti-foam, TOC removal was unaffected by anti-foam. Table 4.1 shows for TOC for different concentrations of anti-foam.

Table 4.1 Effect of anti-foam on TOC (mg/l)

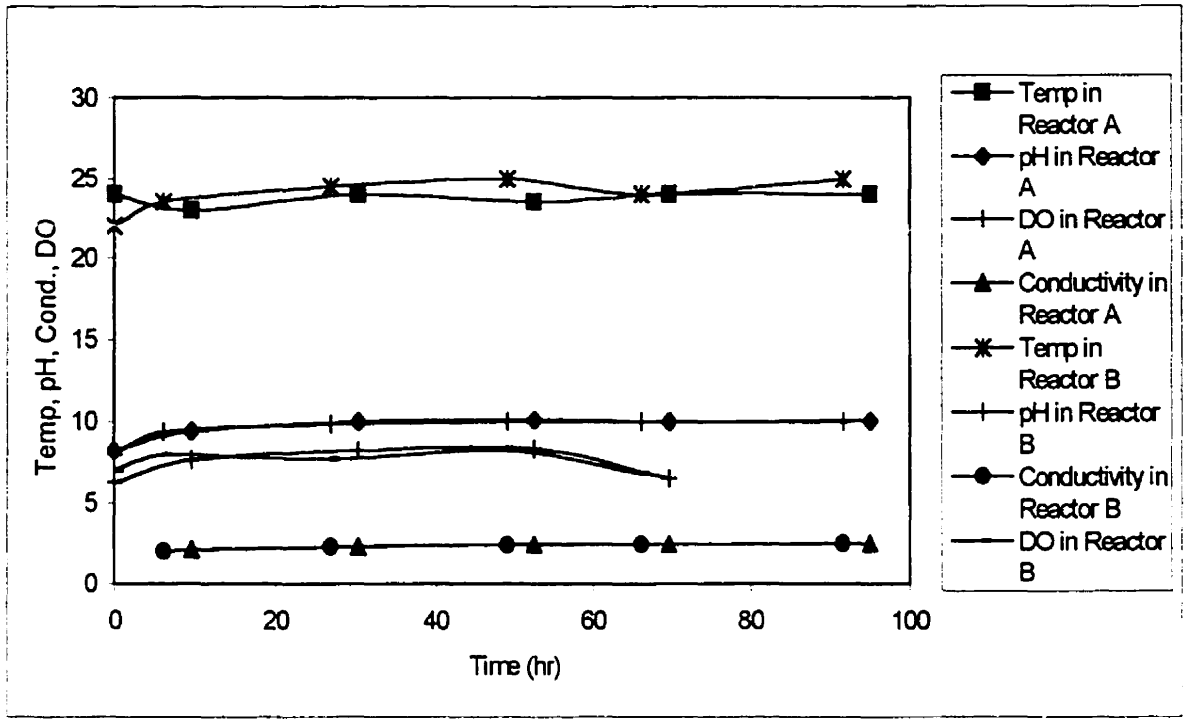
Anti-foam conc. (%)	Initial TOC (mg/l)	Final TOC (mg/l)	% Removed
0	275.4	146.7	47
0.26	402.4	141.8	65
0.53	611.6	214.8	65

Hence, it can be concluded that anti-foam changes the parameters of effluent and affects the growth of activated sludge, however at lower concentrations, effect of anti-foam can be neglected. In experiments, care was taken not to exceed anti-foam concentration above 0.25% while adding anti-foam.

4.1.2 Effect of Reactor Volume

Two different reactors of volume 4 lit and 7 lit were used for the activated sludge kinetics experiments. For making comparison of results, it was important that both the reactors gave the same results under same conditions. This could be achieved only if the critical parameters like pH, Dissolved Oxygen (DO), conductivity, temperature and speed of agitator were same. To check this, preliminary experiments were carried out to study these parameters for both the reactors. Speed of agitator was kept at 400-450 rpm. Experiments were carried out for 1% black liquor in total mill effluent. Results are summarized in Figure 4.5. Values of parameters were same for both reactors and the growth behavior was also same. Therefore, results from these reactors could be compared

directly because the most important parameters for the activated sludge process showed the same values and trend.



Temperatures in °C Conductivity in mS DO in mg/l
Reactor A: volume = 4 lit Reactor B: volume = 7 lit

Figure 4.5 Effect of reactor volume

4.1.3 Effect of Black Liquor

Black liquor is characterized by high organic and inorganic load. To find the effect of black liquor, calibration curves for various parameters were established for different concentrations of black liquor in total mill effluent (TME). Figure 4.6 shows the graph for conductivity, COD, BOD and pH vs. concentration of black liquor in TME and Table 4.2 shows the ratio of COD to TOC for different black liquor concentrations. Black liquor affects all parameters of TME. Addition of black liquor from 0% to 5% in TME increases COD from 1000 to 7000 mg/l but BOD increases from 250 to 1000 mg/l. Thus, black liquor increases COD seven times but increases BOD only four times.

In addition, values from the Table 4.2 show that the ratio of COD to TOC increases as the black liquor concentration increases. This indicates that black liquor

contains large amount of inorganic compounds as compared to organic compounds. As shown in Table 2.1 (page 11), black liquor contains many oxidizable inorganic compounds (sodium salts) which contribute to COD but are not biodegradable.

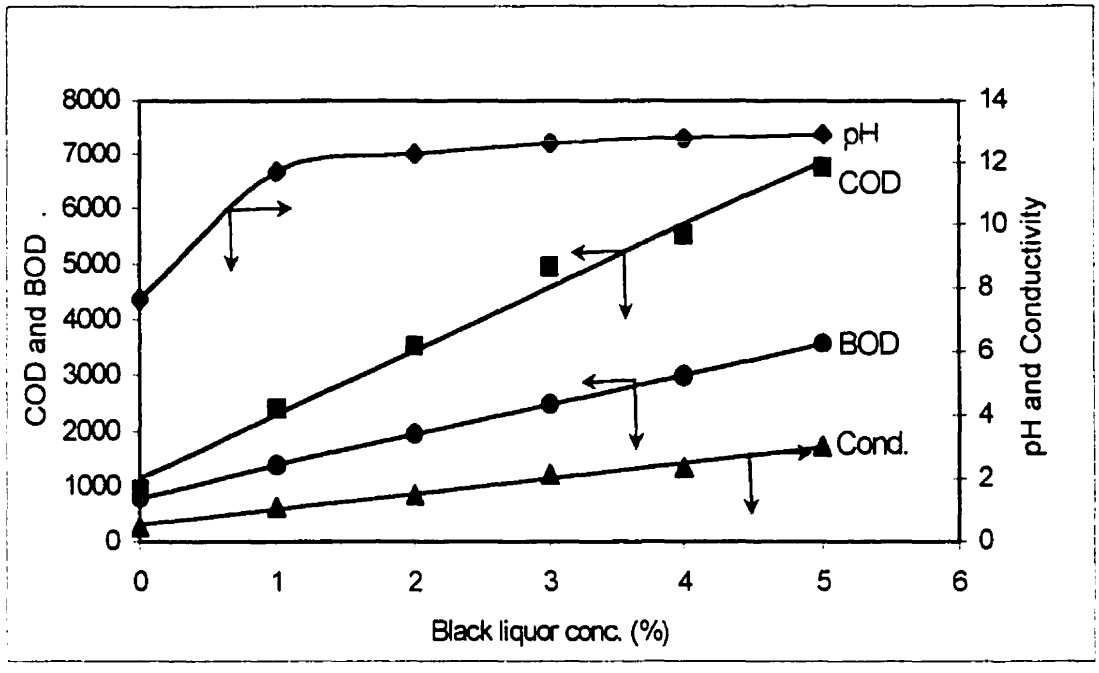


Figure 4.6 Effect of black liquor

Table 4.2 Effect of black liquor on the ratio of COD (mg/l) and TOC (mg/l)

Black liquor conc. in TME (%)	COD (mg/l)	TOC (mg/l)	COD/TOC
0	626.1	217.5	2.86
0.5	1001.1	352.9	2.84
1	1671.3	477.8	3.50
2	2787.5	671.1	4.16

4.1.4 Shake Flask Experiments

Initial shake flask experiments were performed to study the growth behavior of the activated sludge and time needed to complete the entire growth cycle. These

experiments served in establishing some of the operating parameters that were used in main reactor experiments.

Activated sludge kinetics experiments

Initial shake flask experiments were carried out with TME only. Experiments were carried out to study the effect of initial sludge concentration on the growth curve and TOC removal. Figure 4.7 shows TSS curves for TME for two different initial concentrations of 700 and 1200 mg/l based on TSS and Figure 4.8 shows results on normalized TSS scale. As is evident from Figure 4.7, for both the initial TSS concentrations, no increase in TSS was observed. Figure 4.8 shows that as compared to the case of 1200 mg/l, there was a small increase in TSS in case of lower initial TSS 700mg/l between 20 to 60hr. Hence, it can be concluded that for lower initial sludge concentration, TSS showed higher increase as compared to higher initial sludge concentration.

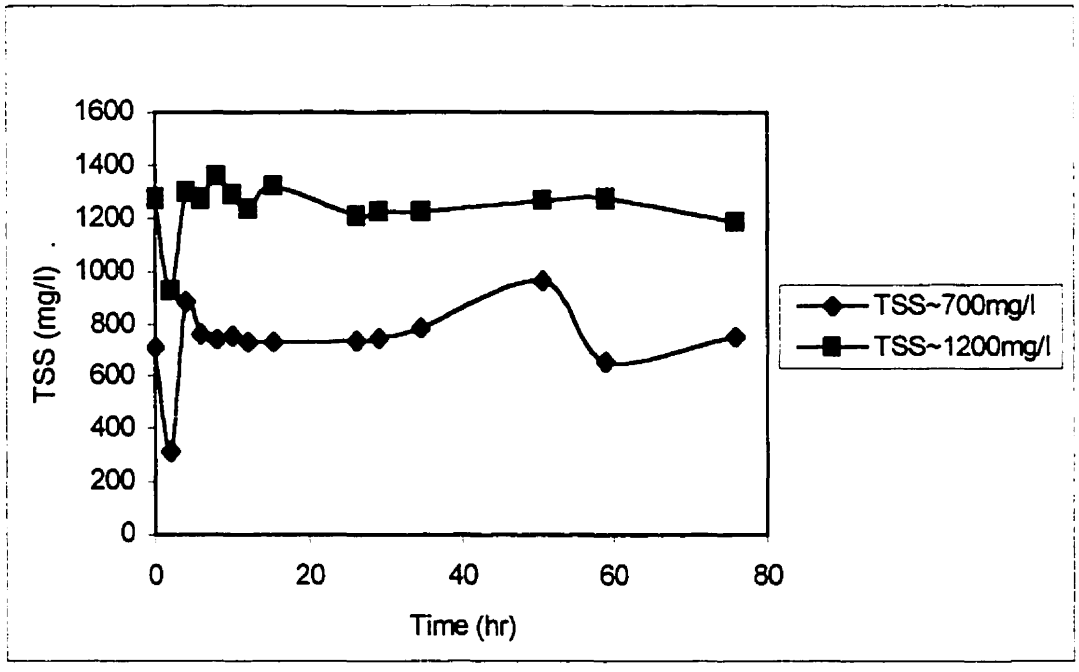


Figure 4.7 Growth Curve for TME for different initial sludge concentrations

It was observed that TSS results did not show any expected trend. In addition, the duplicate samples for each time interval had large variations. This was attributed to the

poor sampling method. Micropipette (1-5 ml) was used for taking samples. It led to incorrect suspended solids values. From results of shake flask experiments, it was decided, not to use micropipette but to use another sampling method based on the weight of sample taken.

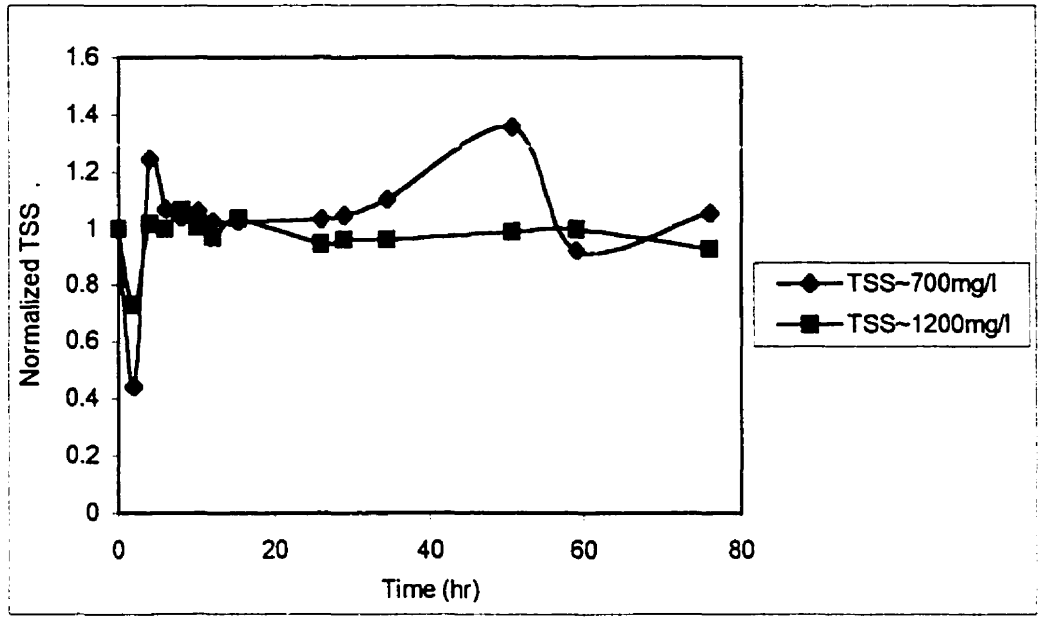


Figure 4.8 Growth curves on normalized TSS scale

Figure 4.9 shows the graph of TOC removal for two different initial sludge concentrations. It was observed that initial concentration had little effect on the initial rate of TOC removal. However, this was not observed when activated sludge kinetics experiments were carried out in the reactor. In those cases, it was observed that the initial sludge concentration had a strong effect on the initial rate of TOC removal.

4.2 Activated Sludge Kinetics Experiments (Effect of Black Liquor)

To study the effect of black liquor, experiments were performed with different black liquor concentrations and different initial sludge concentrations. Black liquor concentrations of 0, 0.5, 1 and 2% in TME were considered and initial sludge concentrations of 250, 500, 800, 1400 mg/l based on TSS were studied. For a given initial sludge concentration, results are presented for different black liquor concentrations.

Results are then combined to see the overall effect of the black liquor and the initial sludge concentration.

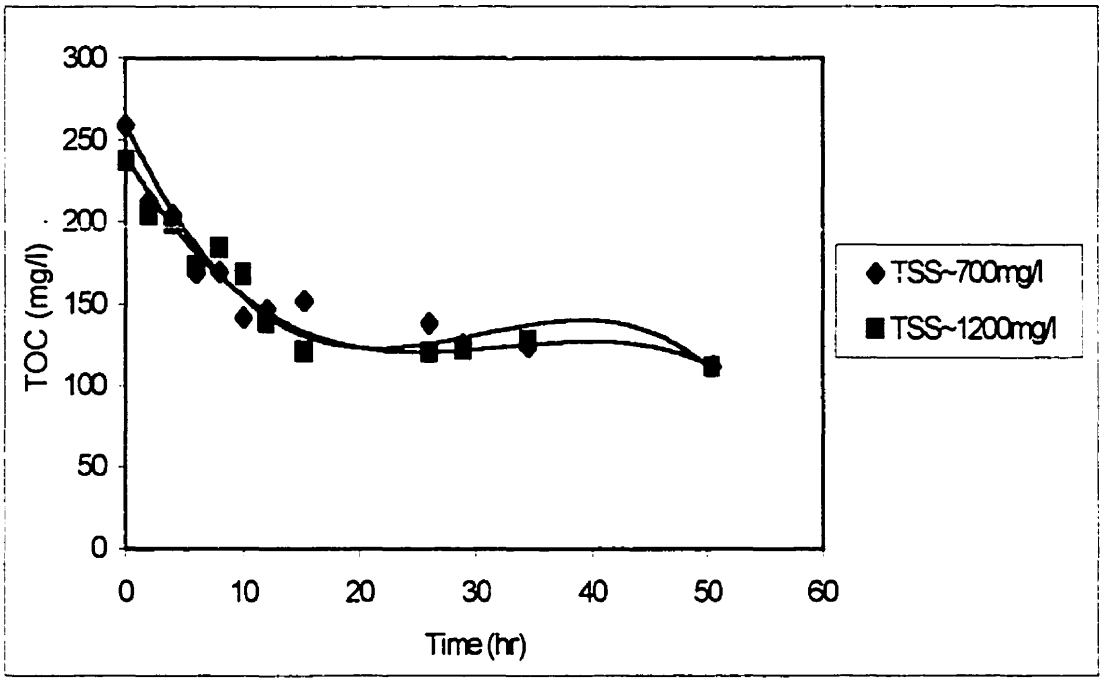


Figure 4.9 Comparison of TOC for Shake flask experiments

4.2.1 Initial Sludge Concentration of 250, 500 and 800 mg/l

Experiments were carried out for TME and three different concentrations of black liquor in TME. Experiments were run for 160-180hr. Growth curves were established for each black liquor condition to see all the phases of growth. For all experiments, pH was in the range 7-9 depending on black liquor concentration. Temperature and dissolved oxygen were 24°C and 6-7 mg/l respectively. Biolog microplates were prepared in duplicates for the starting sludge population and the final population. Results of the experiments with initial sludge concentrations 250, 500 and 800 mg/l were grouped together as they showed the same trends.

For all experiments, TSS and VSS started increasing right from the time zero and no lag phase was observed. Table 4.3, 4.4 and 4.5 show the starting and final values for TSS and VSS for all conditions and average value for the VSS/TSS ratio.

Table 4.3 TSS and VSS values (in mg/l) for initial sludge concentration 250 mg/l

BL conc. (%)	Initial TSS (mg/l)	Final TSS (mg/l)	Initial VSS (mg/l)	Final VSS (mg/l)	Average VSS/TSS
0	235	367	222	296	0.81
0.5	258	395	233	331	0.81
1	306	383	230	278	0.73
2	358	548	286	403	0.77
Average	289	-	243	-	0.78

Table 4.4 TSS and VSS values (in mg/l) for initial sludge concentration 500 mg/l

BL conc. (%)	Initial TSS (mg/l)	Final TSS (mg/l)	Initial VSS (mg/l)	Final VSS (mg/l)	Average VSS/TSS
0	471	612	364	467	0.76
0.5	520	651	409	497	0.78
1	554	1099	475	850	0.81
2	444	629	289	397	0.64
Average	497	-	385	-	0.75

Table 4.5 TSS and VSS values (in mg/l) for initial sludge concentration 800 mg/l

BL conc. (%)	Initial TSS (mg/l)	Final TSS (mg/l)	Initial VSS (mg/l)	Final VSS (mg/l)	Average VSS/TSS
0	987	895	853	754	0.86
0.5	866	1001	741	762	0.80
1	766	961	578	651	0.72
2	856	1364	695	976	0.76
Average	869	-	717	-	0.79

Average value of VSS/TSS was in the range 0.75-0.78 and it remained nearly the same irrespective of black liquor conditions. This showed that the black liquor did not affect the VSS/TSS ratio. This indicates that the increase in TSS was due to the increase in VSS only.

Figure 4.10 shows growth curves based on TSS and Figure 4.11 shows growth curves based on VSS for initial sludge concentrations of 250mg/l. Similarly, Figure 4.12 to 4.15 show growth curves based on TSS and VSS for initial sludge concentrations 500 and 800 mg/l. The nature of TSS and VSS curves were similar for a given initial TSS. This was because the increase in TSS was due to increase in VSS.

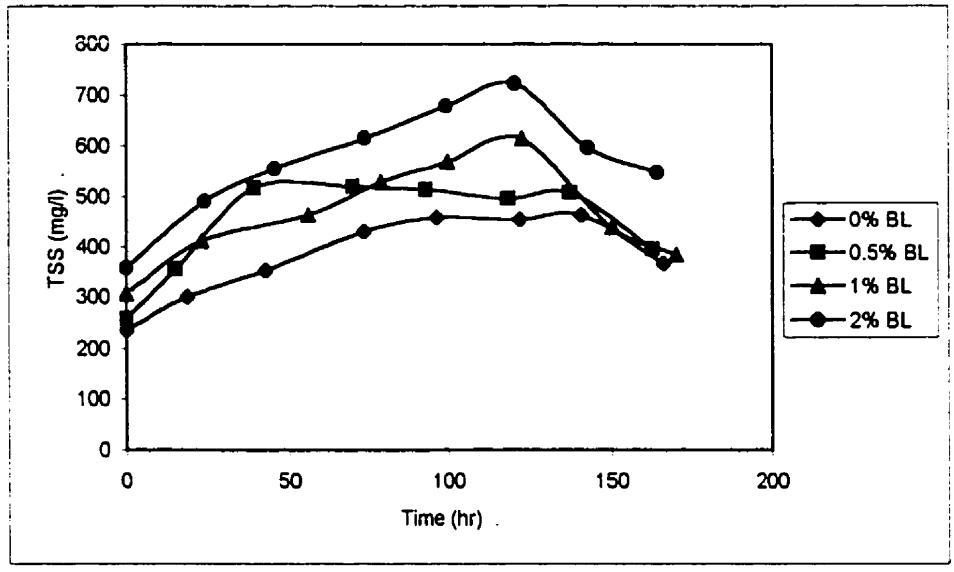


Figure 4.10 TSS Comparison for initial TSS ~ 250 mg/l

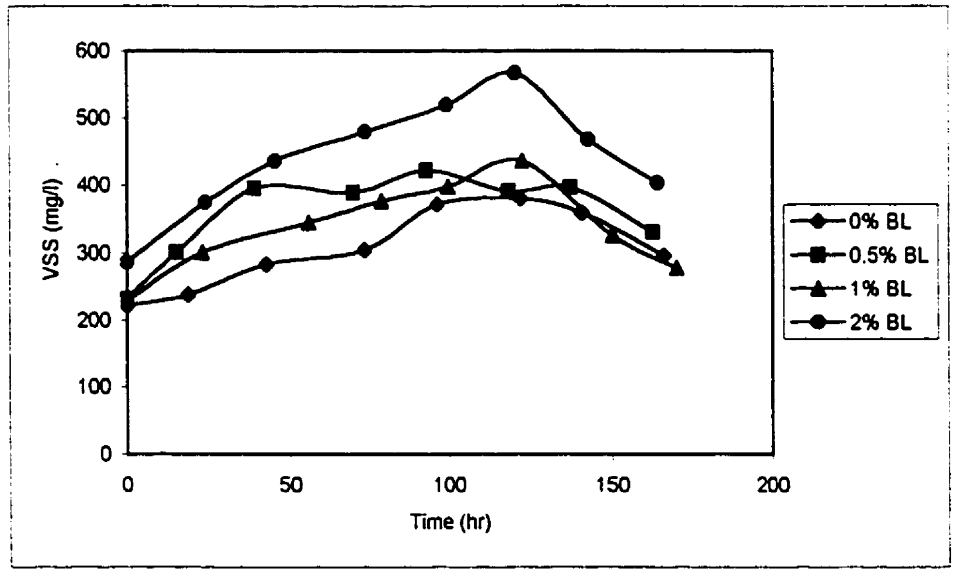


Figure 4.11 VSS Comparison for initial TSS ~ 250 mg/l

Figure 4.12 and 4.13 show the variation of TSS and VSS for initial sludge concentration 500 mg/l. In comparison to initial sludge concentration 250 mg/l, lower growth in TSS and VSS was observed. This can be explained based on the food to microorganism ratio. For initial TSS 500 mg/l, food to microorganism ratio is lower as compared to that for initial TSS 250 mg/l; therefore lower growth was observed. TSS and VSS showed a lag phase for 0%. The lag phase in 0% black liquor was due to a slightly older sludge. For 0%, rate values were calculated at 70 hr.

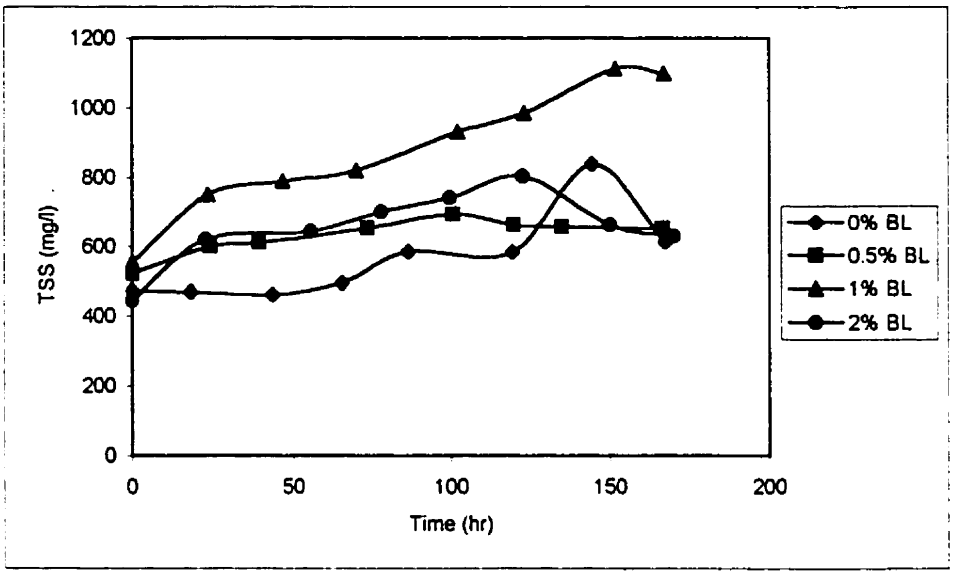


Figure 4.12 TSS Comparison for initial TSS ~ 500 mg/l

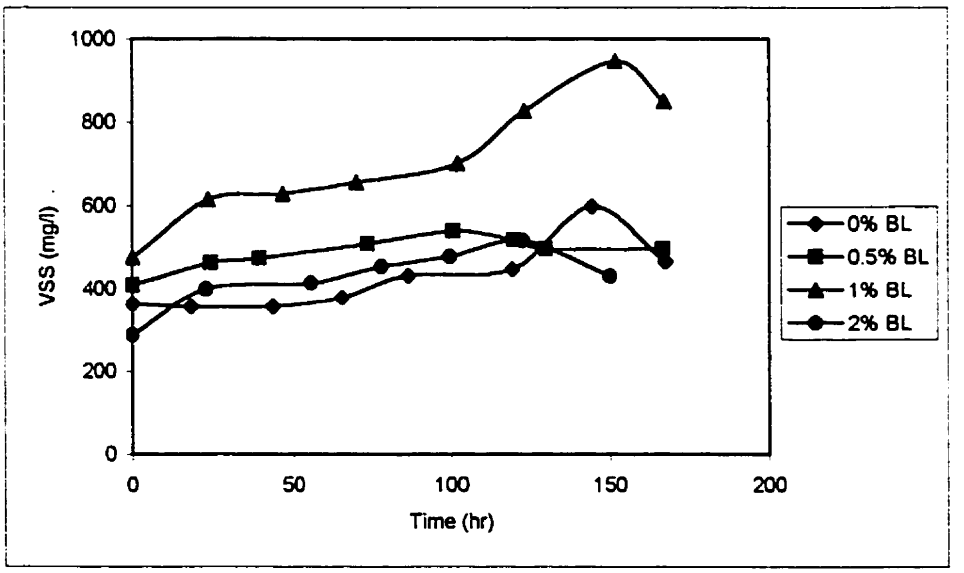


Figure 4.13 VSS Comparison for initial TSS ~ 500 mg/l

Figure 4.14 and 4.15 show growth curves based on TSS and VSS for initial TSS 800 mg/l. Increase in TSS and VSS were lesser than that observed for cases of initial TSS 250 and 500 mg/l.

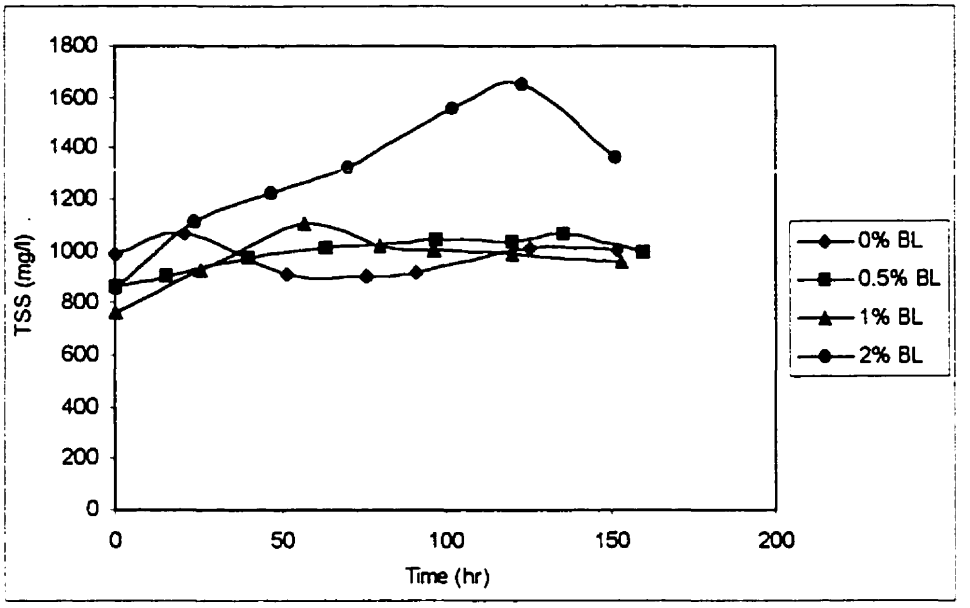


Figure 4.14 TSS Comparison for initial TSS~ 800 mg/l

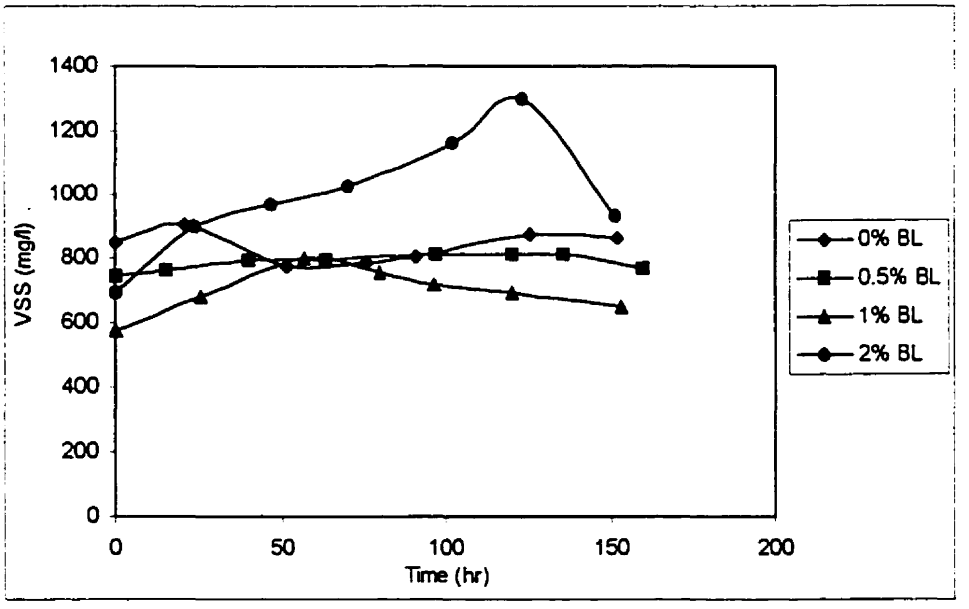


Figure 4.15 VSS comparison for initial TSS ~ 800 mg/l

Results from Figures 4.10 to 4.15 show that the black liquor increases the initial slope of both TSS and VSS curves. This can be explained by considering the increase in

the organic content of the effluent as reflected by the increase in BOD, COD and TOC values for the increase in black liquor concentration. Thus, black liquor increases the amount of food available to microorganisms for their growth and therefore, the initial slope increases with increase in the black liquor concentration.

Variation of COD, TOC, Soluble Lignin concentration with time

COD, TOC and soluble lignin (SL) showed the same behavior with time. These parameters showed a decrease in the first 60 hr and then they remained constant. Table 4.6 to 4.8 shows the initial and final values and percentage decrease for these parameters for initial TSS of 250, 500 and 800 mg/l respectively. For 0% black liquor, the percentage changes in the parameters were higher as compared to those for other black liquor concentrations for all cases of initial TSS. This indicated that the activated sludge was not able to degrade all compounds present in black liquor and black liquor had an adverse effect on the sludge capability to treat effluents. In addition, the percentage changes in these parameters for black liquor concentrations 0.5%, 1% and 2%, were nearly the same for a given initial TSS.

Table 4.6 COD, TOC and Soluble lignin values (in mg/l) for initial TSS ~ 250 mg/l

Parameter	Black Liquor Concentration			
	0%	0.5%	1%	2%
Initial COD (mg/l)	728	987	1696	2948
Final COD (mg/l)	530	886	1476	2551
% decrease in COD	34	14	14	15
Initial TOC (mg/l)	252	382	494	696
Final TOC (mg/l)	168	328	425	592
% decrease in TOC	27	12	13	13
Avg. COD/TOC	3.05	2.64	3.48	4.31
Initial SL conc. (mg/l)	250	386	507	908
Final SL conc. (mg/l)	188	348	450	813
% decrease in SL conc.	24	10	11	11

Table 4.7 COD, TOC and Soluble lignin values (in mg/l) for initial TSS ~ 500 mg/l

Parameter	Black Liquor Concentration			
	0%	0.5%	1%	2%
Initial COD (mg/l)	749	1046	1755	2899
Final COD (mg/l)	343	847	1397	2337
% decrease in COD	50	19	20	19
Initial TOC (mg/l)	247	348	487	680
Final TOC (mg/l)	111	291	394	549
% decrease in TOC	56	15	17	18
Avg. COD/TOC	3.03	3.01	3.62	4.26
Initial SL conc. (mg/l)	276	357	567	893
Final SL conc. (mg/l)	134	301	476	744
% decrease in SL conc.	50	16	18	17

Table 4.8 COD, TOC and Soluble lignin values (in mg/l) for initial TSS ~ 800 mg/l

Parameter	Black Liquor Concentration			
	0%	0.5%	1%	2%
Initial COD (mg/l)	525	1041	1723	2989
Final COD (mg/l)	193	794	1314	2337
% decrease in COD	63	23	24	22
Initial TOC (mg/l)	187	341	459	662
Final TOC (mg/l)	89	267	354	477
% decrease in TOC	53	22	23	26
Avg. COD/TOC	2.81	3.06	3.76	4.52
Initial SL conc. (mg/l)	276	385	548	897
Final SL conc. (mg/l)	113	305	415	679
% decrease in SL conc.	60	21	24	24

For initial TSS of 250 mg/l, Figure 4.16 shows variation of COD with time and Figure 4.17 shows percentage change in COD for various time intervals. Figure 4.17 shows that as the black liquor concentration increases, initial slope of COD decrease curve decreases. This was due to the toxic effects of black liquor on the activated sludge.

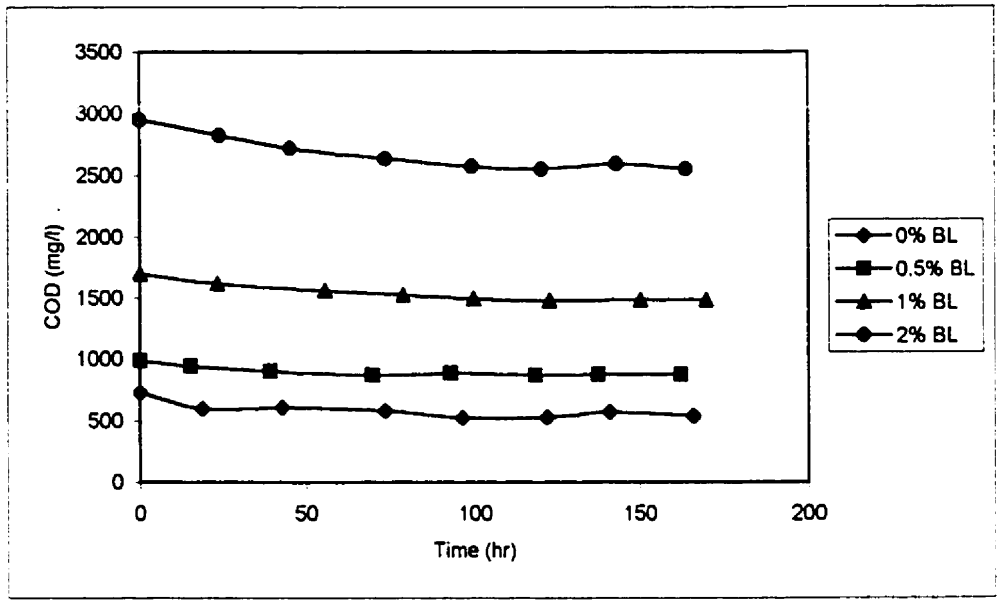


Figure 4.16 Variation of COD with time for initial TSS ~ 250 mg/l

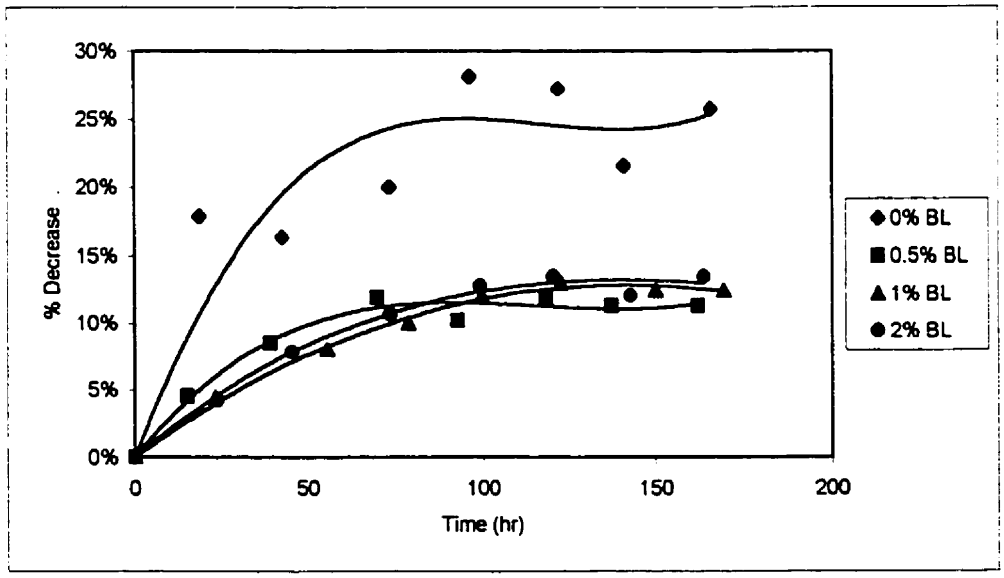


Figure 4.17 Variation of percentage decrease in COD with time for initial TSS ~ 250 mg/l

Figure 4.18 and 4.19 shows the variation of COD and percentage decrease in COD with time for initial TSS of 500 mg/l and Figure 4.20 and 4.21 shows the similar curves for the initial TSS of 800 mg/l.

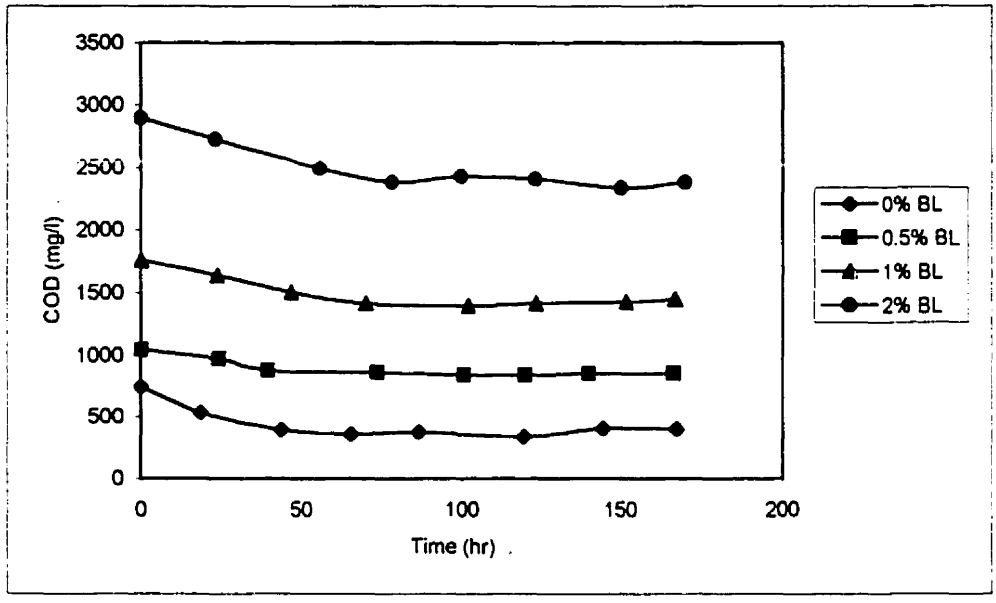


Figure 4.18 Variation of COD with time for initial TSS ~ 500 mg/l

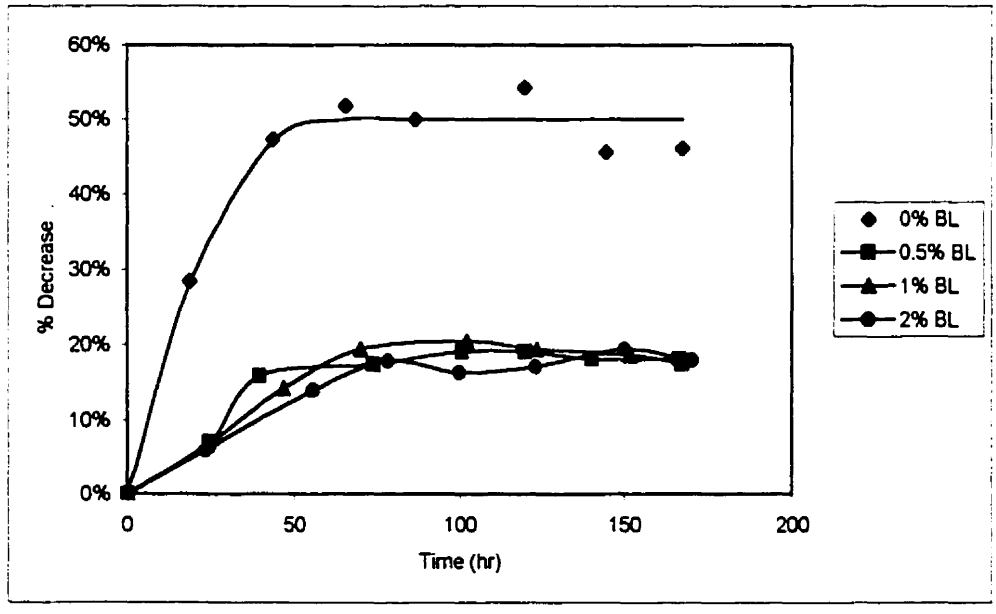


Figure 4.19 Variation of percentage decrease in COD with time for initial TSS ~ 500 mg/l

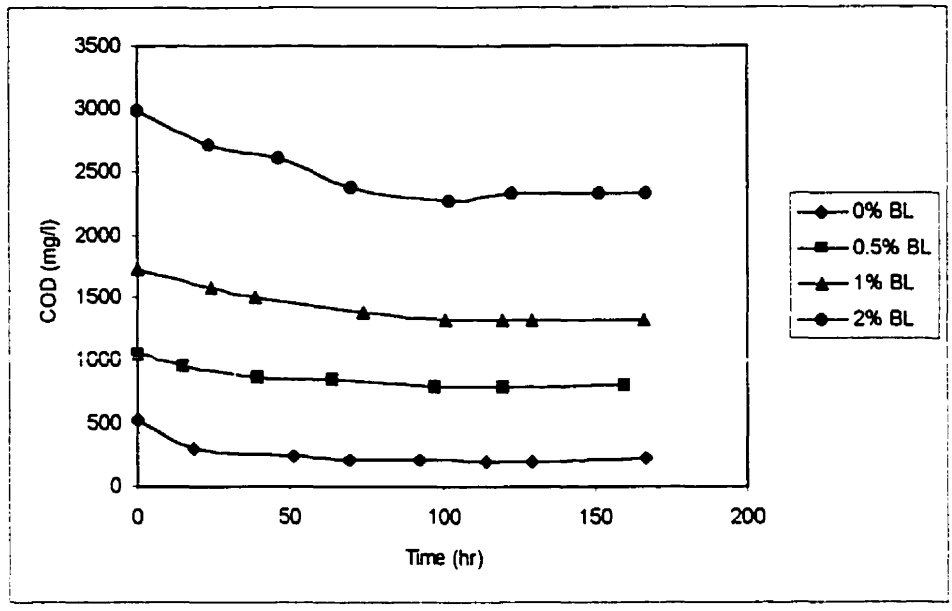


Figure 4.20 Variation of COD with time for initial TSS ~ 800 mg/l

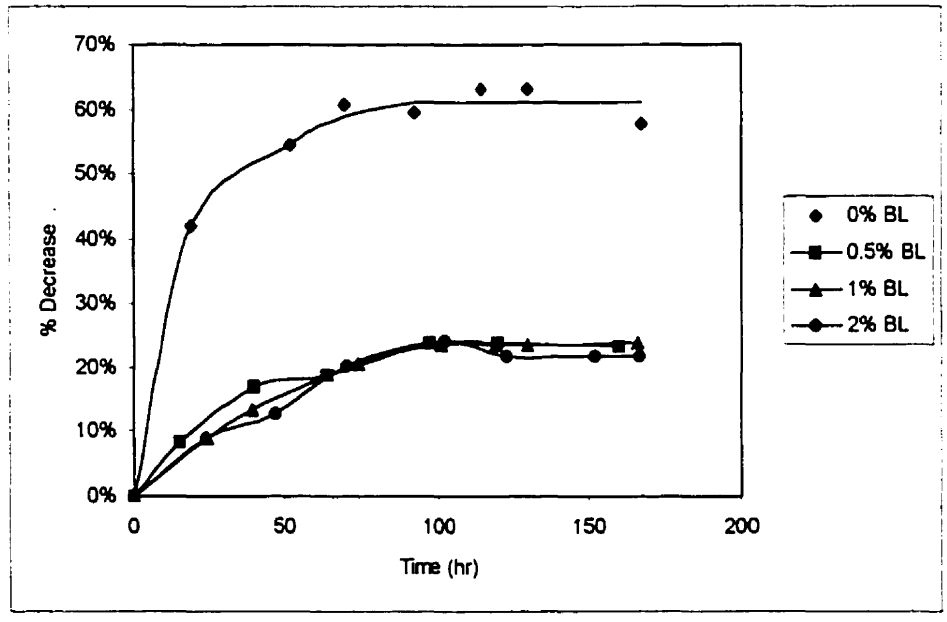


Figure 4.21 Variation of percentage decrease in COD with time for initial TSS ~ 800 mg/l

As the initial concentration of TSS increases for a given black liquor concentration, the percentage decrease in COD increases. For example, for 0% black liquor, final percentage decrease in COD was 34% for initial TSS of 250 mg/l. But for 0%, the percentage decrease in COD was 50 and 63% for initial TSS 500 and 800 mg/l

respectively. This can be explained based on the number of organisms consuming the available substrate.

Variation of TOC and Soluble lignin concentrations with time

Figure 4.22 and Figure 4.23 show the variation of TOC and soluble lignin concentration with time respectively for the initial TSS of 250 mg/l. Both show the behavior similar to COD. Again, as the black liquor concentration increases, initial rates of TOC and soluble lignin removal decrease showing the adverse effect of the black liquor.

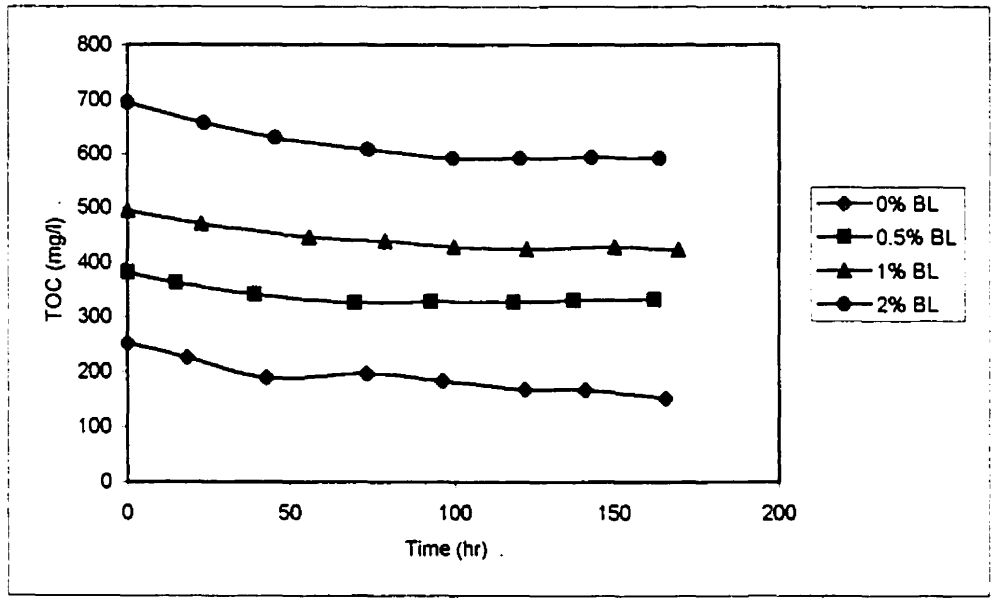


Figure 4.22 Variation of TOC with time for initial TSS ~ 250 mg/l

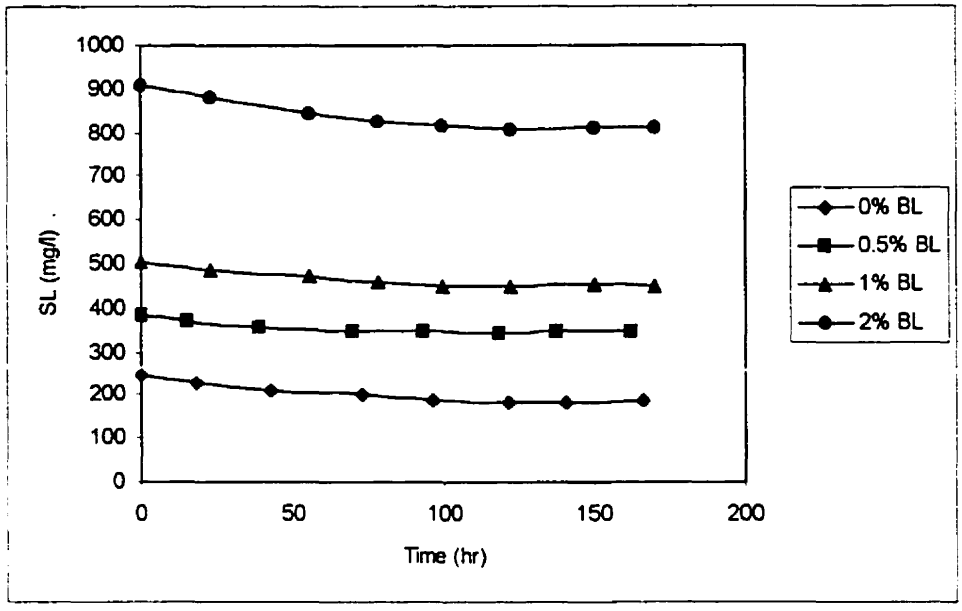


Figure 4.23 Variation of SL concentration with time for initial TSS ~ 250 mg/l

Figure 4.24 and Figure 4.25 show the variation of TOC and soluble lignin concentration with time respectively for the initial TSS of 500 mg/l. In this case the final decrease in TOC and soluble lignin concentration were higher than that for the case of initial TSS 250 mg/l.

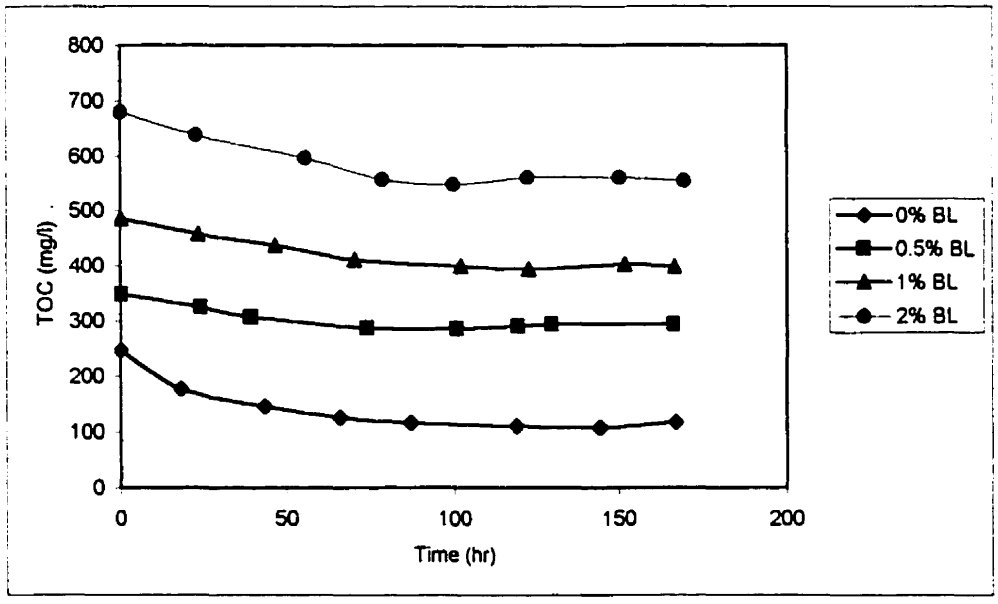


Figure 4.24 Variation of TOC with time for initial TSS ~ 500 mg/l

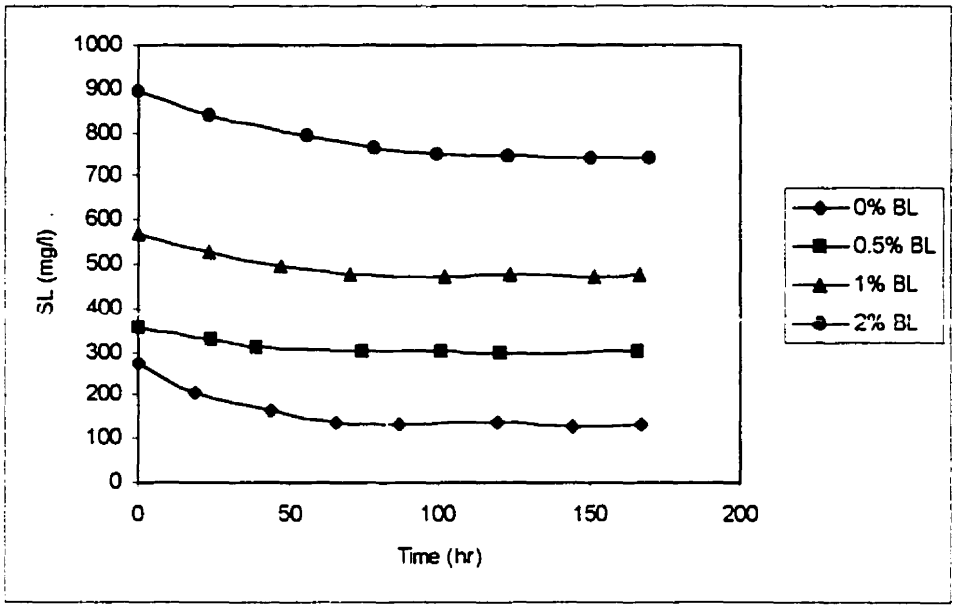


Figure 4.25 Variation of SL concentration with time for initial TSS ~ 500 mg/l

Figure 4.26 and 4.27 show TOC and soluble lignin concentration curves for initial TSS 800 mg/l respectively.

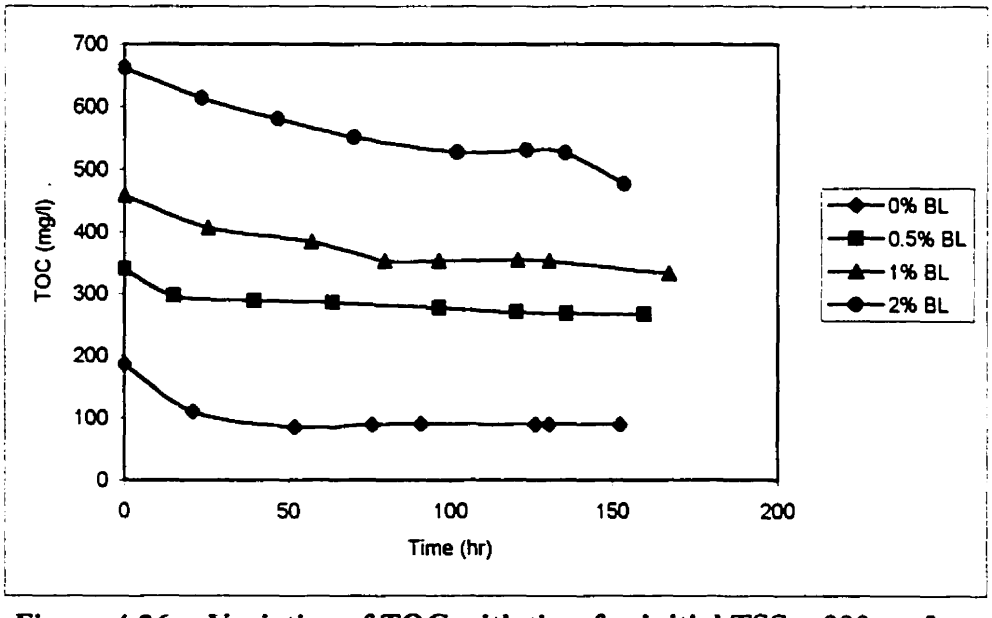


Figure 4.26 Variation of TOC with time for initial TSS ~ 800 mg/l

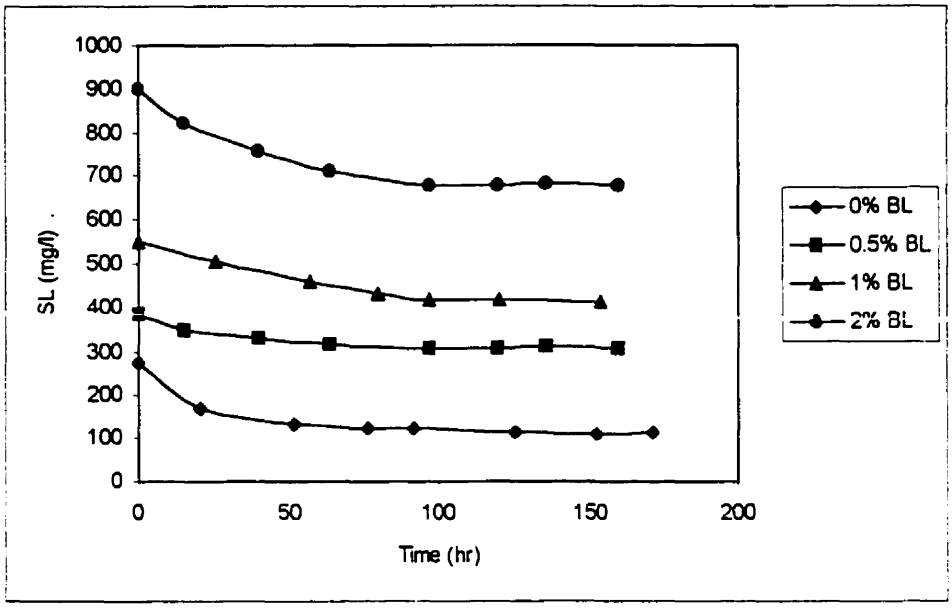


Figure 4.27 SL concentration vs. time for initial TSS ~ 800 mg/l

For all initial TSS values, all black liquor concentrations showed decrease in TOC and soluble lignin, which indicated that the activated sludge was able to degrade some of the compounds. However, the absolute final value for 0% black liquor was lower than other black liquor concentrations. This indicated that although black liquor increases TOC and soluble lignin of samples, not all the organic compounds present in black liquor are biodegradable.

Carbohydrate concentrations were also measured for the experiments with initial TSS of 250 and 800 mg/l. It was observed that carbohydrates were present initially at time zero but for the next sample time, its value was below the detection limit (10 mg/l). This suggested that carbohydrates were degraded first and they were responsible for the initial decrease of COD and TOC. Then the soluble lignins were consumed over the time resulting in decrease of COD and TOC. Biological oxygen demand (BOD) was measured for time zero and in the end. For all the concentrations and all initial TSS cases, BOD removal of 90-95% was observed. This indicates that the activated sludge was able to degrade almost all of BOD present in the samples.

4.2.2 *Initial Sludge Concentration of 1400 mg/l*

Initial TSS of 1400 mg/l was the highest concentration used for experiments. In actual mill, plant operation is carried out at average concentration of about 2000 mg/l. Initial TSS was restricted to 1400 mg/l because initial experiments with higher TSS than 1500 mg/l led to inconsistent results of TSS and VSS. This was because of the smaller system and foaming in the reactor caused removal of biomass from the system. Experiments were run for 160-180 hr. The pH was 7-9 depending on black liquor concentration, temperature was 24°C and dissolved oxygen was 6-7 mg/l in all experiments. Biolog microplates were prepared in duplicates for the starting sludge population and the final sludge population.

Variation of TSS and VSS with time

In contrast to the previous cases of initial TSS 250, 500 and 800 mg/l, TSS and VSS did not show any increase or decrease and remained constant. This was mainly due to low food to microorganism ratio. At such a high TSS value, substrate was available just for the sustenance of microorganism and not for their growth. Table 4.9 shows the starting and the final values for the TSS and VSS for all conditions and the average value for the VSS/TSS ratio. Average value of VSS/TSS was 0.75 and it remained same irrespective of the black liquor concentrations.

Table 4.9 TSS and VSS values for initial TSS ~ 1400 mg/l

BL conc. (%)	Initial TSS (mg/l)	Final TSS (mg/l)	Initial VSS (mg/l)	Final VSS (mg/l)	Average VSS/TSS
0	1776	1514	1459	1225	0.81
0.5	1275	1301	1112	1110	0.85
1	1414	1362	1151	1060	0.80
2	1551	1479	1385	1291	0.88
Average	1504	-	1277	-	0.83

Figure 4.28 shows growth curves based on TSS for all conditions and Figure 4.29 shows the growth curves based on VSS. As described earlier, growth in TSS and VSS was not observed and values of TSS and VSS were within ± 10 % of the original value.

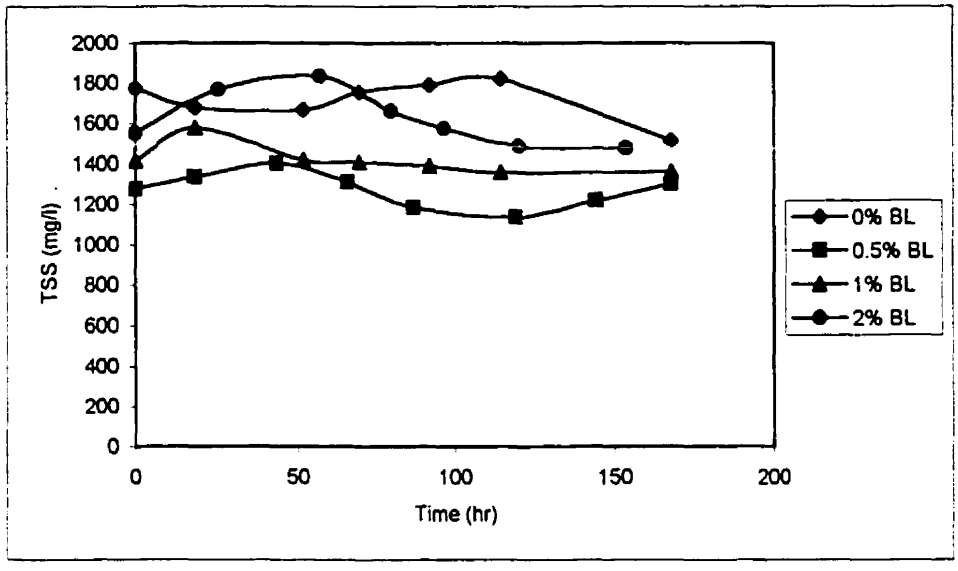


Figure 4.28 TSS Comparison for initial TSS ~ 1400 mg/l

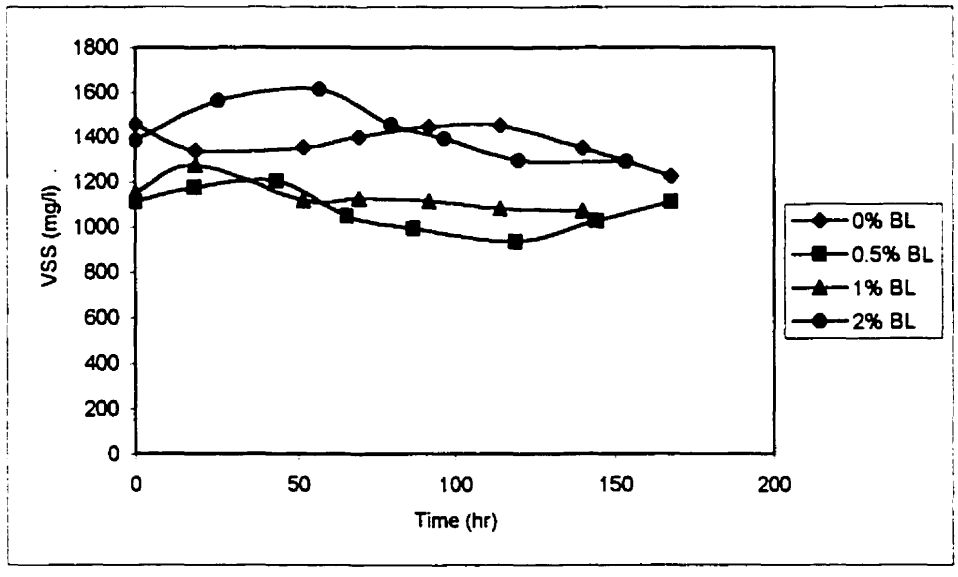


Figure 4.29 VSS Comparison for initial TSS ~ 1400 mg/l

Variation of COD, TOC and Soluble lignin (SL) concentration with time

COD, TOC and SL showed decrease in the first 60hr only and then remained constant. Table 4.10 shows the initial and final values and percentage decrease for these parameters. For 0% black liquor, the percentage decrease in these parameters were higher than those for other black liquor concentrations. In addition, the percentage change in COD, TOC and SL concentrations for black liquor concentrations 0.5%, 1% and 2%, were nearly the same. These changes were higher than that for the cases of initial sludge concentration 250, 500 and 800 mg/l. For example, the final percentage change for COD for initial TSS 1400 mg/l for 0.5, 1, 2% black liquor were in the range 27-34% while for initial TSS 250, 500 and 800 mg/l, the final change were in the range 14-15%, 19-20% and 22-24% respectively.

Table 4.10 COD, TOC and SL values (in mg/l) for initial TSS ~ 1400 mg/l

Parameter	Black Liquor Concentration			
	0%	0.5%	1%	2%
Initial COD (mg/l)	502	930	1511	2315
Final COD (mg/l)	213	648	990	1607
% decrease in COD	58	27	34	30
Initial TOC (mg/l)	184	341	474	646
Final TOC (mg/l)	87	243	333	477
% decrease in TOC	55	29	31	27
Avg. COD/TOC	2.73	2.73	3.19	3.58
Initial SL conc. (mg/l)	256	369	536	917
Final SL conc. (mg/l)	118	263	366	633
% decrease in SL conc.	54	29	32	31

Figure 4.30 shows the variation of COD and Figure 4.31 shows the variation of percentage change in COD values for various time intervals for different black liquor concentrations. The decrease in COD may appear to be small in Figure 4.30 but it can be as high as 60% as shown in Figure 4.31.

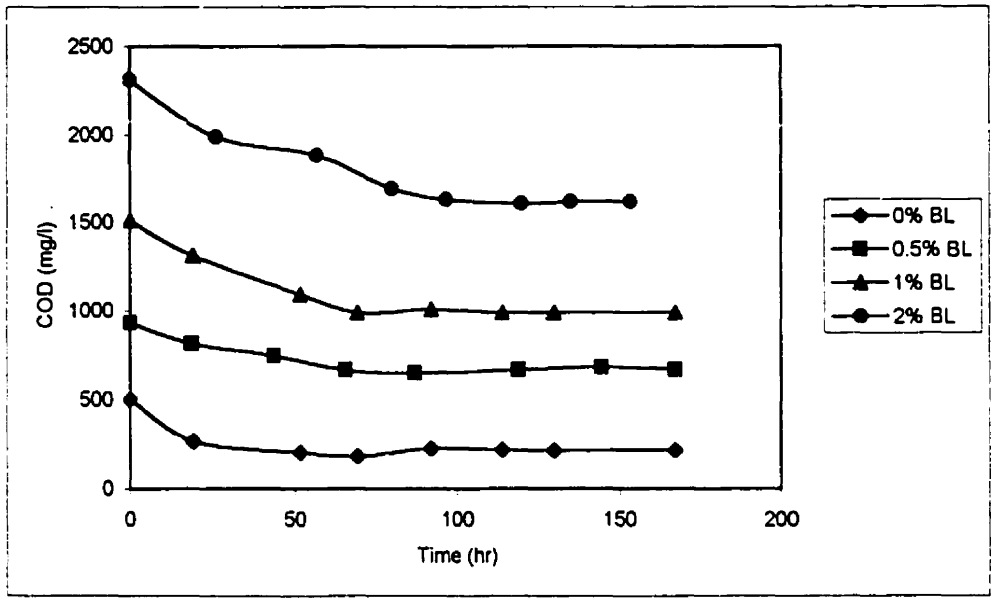


Figure 4.30 Variation of COD with time for initial TSS ~ 1400 mg/l

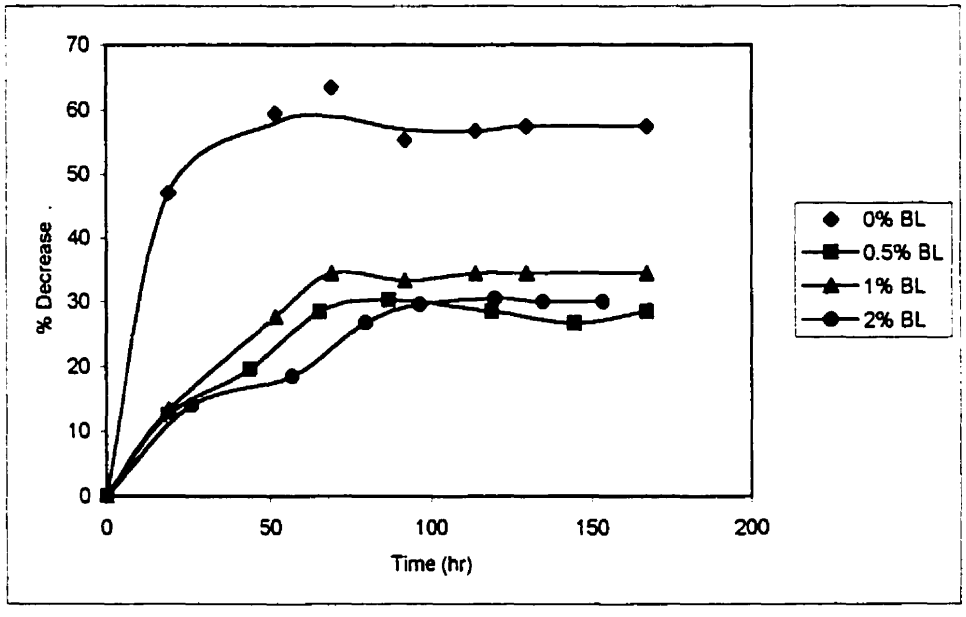


Figure 4.31 Variation of percentage decrease in COD with time for initial TSS ~ 1400 mg/l

Figure 4.31 shows that when black liquor is present even at low concentration of 0.5%, it adversely affects COD decrease. Figure 4.32 and Figure 4.33 shows TOC and soluble lignin concentration variation with time respectively.

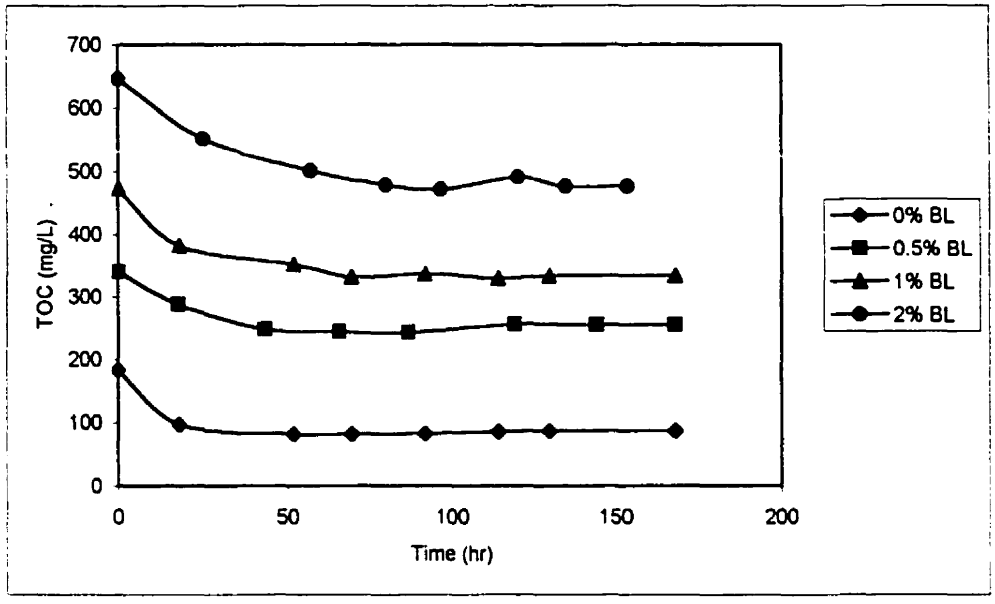


Figure 4.32 Variation of TOC with time for initial TSS ~ 1400 mg/l

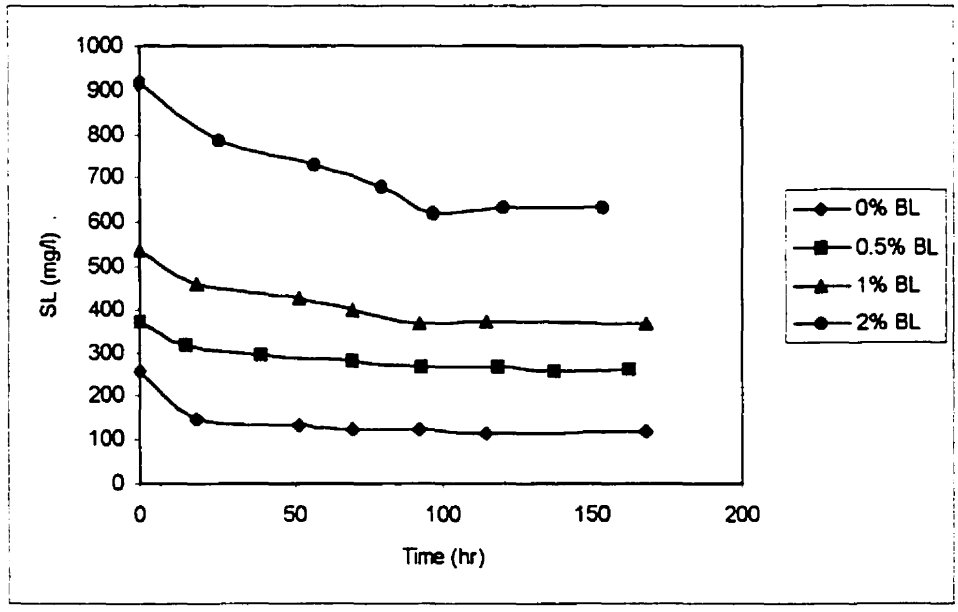


Figure 4.33 Variation of SL concentration with time for initial TSS ~ 1400 mg/l

Both TOC and SL show the behavior similar to COD. Again, as the black liquor concentration increases, initial rate of TOC and soluble lignin removal decreases showing the adverse effect of the black liquor. Figure 4.34 shows the graph for normalized TOC vs. time for different black liquor concentrations. Normalization of TOC was done using the initial TOC values.

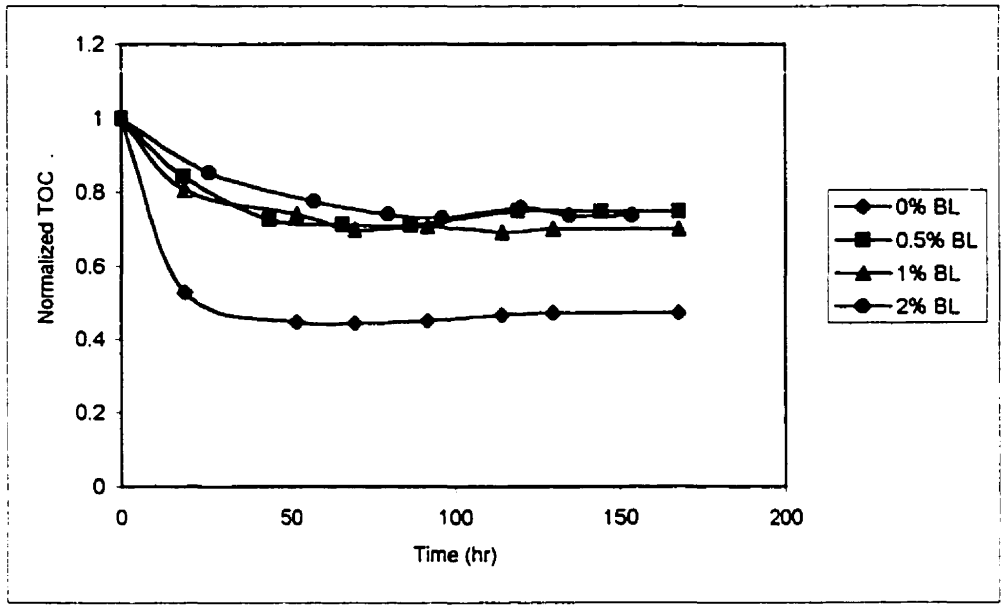


Figure 4.34 Variation of normalized TOC with time for initial TSS ~ 1400 mg/l

All concentrations of black liquor show a decrease in TOC, which indicates that the activated sludge was able to degrade some of the compounds. However, final absolute value for 0% black liquor was lower than those for other black liquor concentrations. Biological oxygen demand (BOD) was measured for time zero and in the end. For all the concentrations, BOD removal of about 90-95% was observed.

4.3 Discussion of Combined Results

Results of various rates values for different initial sludge concentrations were combined to see the overall effect of the black liquor concentration and the initial sludge concentration. To calculate different rate values, a polynomial trend line (usually 5^{th} or 6^{th} order) was added to data. Initial rate values were then calculated by calculating the first order derivative at time zero. Appendix B shows a sample calculation of initial rate.

Initial rates were used to make comparison because batch system was used in the study and conditions like black liquor concentrations were known exactly only at time zero. Initial rates for TSS, VSS, COD, TOC and soluble lignin concentrations were again calculated as shown in Appendix B.

4.3.1 Comparison for TSS

Comparison of Maximum Percentage Increase

To study the effect of black liquor and initial sludge concentrations, maximum percentage increase in TSS were compared. As it was shown in the previous section, the biomass in any experiments increased from the initial value to a maximum value and then started declining. Maximum percentage increase was calculated by using this maximum TSS value and the initial TSS value. Figure 4.35 shows results for the maximum percentage change for TSS with black liquor concentrations for various initial TSS.

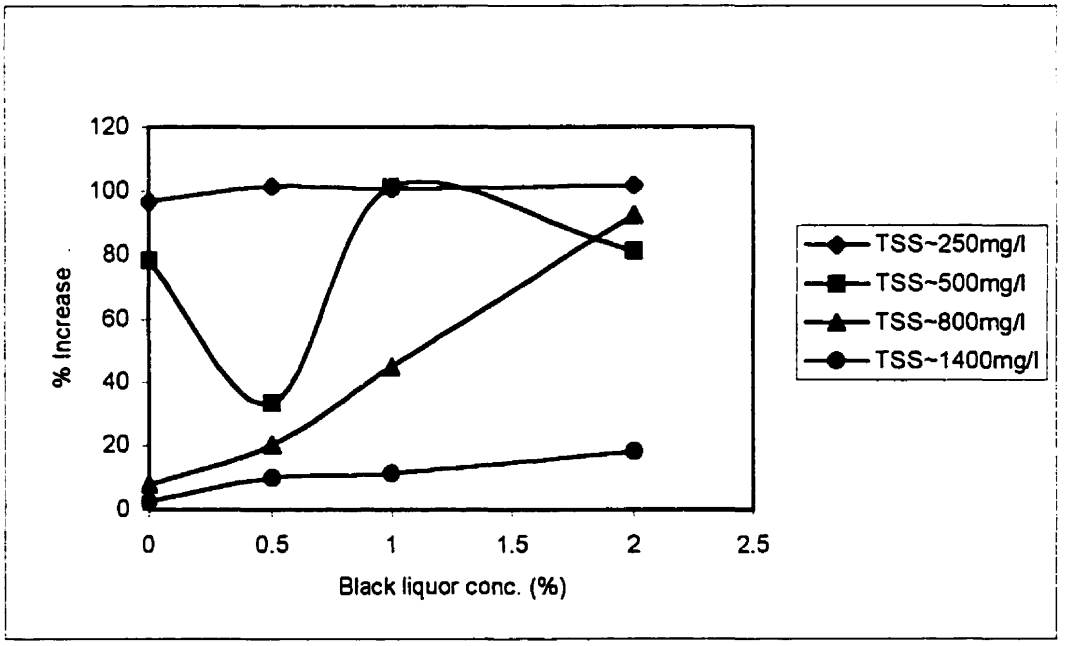


Figure 4.35 Maximum percentage increase in TSS

Figure 4.35 shows that as the black liquor concentration increases, the maximum increase in TSS also increases. This is due to the increase in food available for the growth of activated sludge. For example for the case of initial TSS 800 mg/l, the maximum

increase in TSS was 8% for 0% black liquor and was 45% and 90% for 1% and 2% black liquor concentrations respectively. In addition, as the initial sludge concentration decreases, the maximum value of increase in TSS also increases. This can be explained based on the food to microorganism ratio. At lower sludge concentrations, the food to microorganism ratio is higher. This implies that at the lower sludge concentrations, there is substrate available for both the sustenance and the growth of microorganisms but at higher concentrations of biomass, substrate is available just for the sustenance of microorganisms.

Comparison of Specific Rates of TSS Increase

The specific rate of TSS increase is defined as the amount of TSS increased per unit time per unit TSS. Figure 4.36 shows the graph for specific rates of TSS increase.

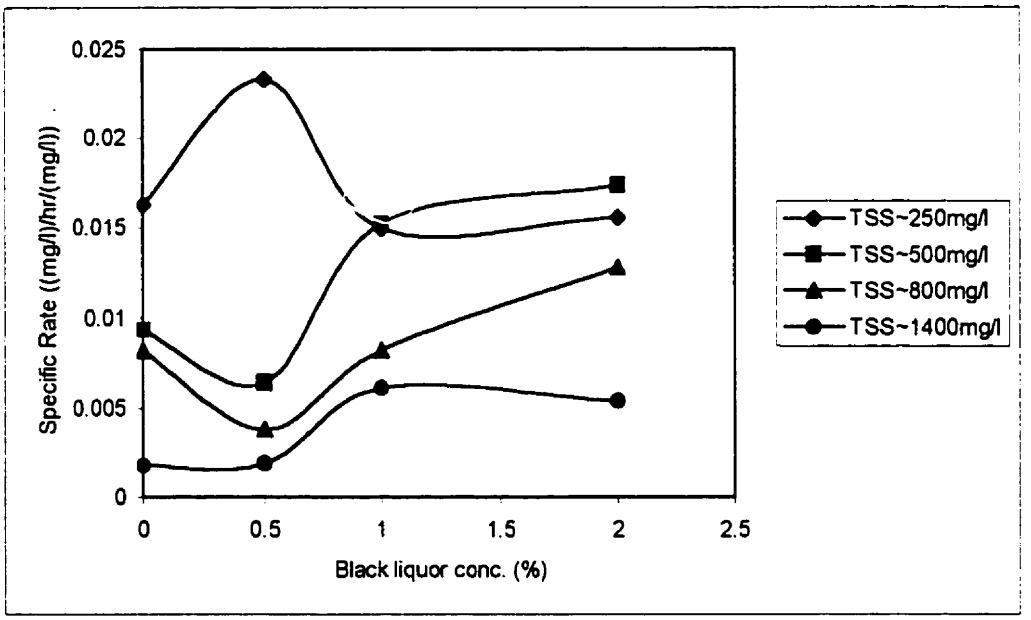


Figure 4.36 Specific rate of TSS increase

Specific rate represents the amount of sludge grown per unit time per unit amount of sludge present in the system. Specific rate values were calculated by calculating the initial rate of TSS increase and then dividing it by the initial TSS value. Again, all the values used were calculated at time zero as only at time zero the concentration of black liquor is known. Specific rate has units of (mg/l)/hr/(mg/l). As the initial sludge

concentration decreases, specific rate value increases implying that there is larger amount of sludge produced per unit time per unit biomass present. This is because at lower concentrations of TSS, growth of microorganisms was observed but at higher concentrations of TSS, no growth was observed.

Comparison of VSS Data

As described earlier, VSS and TSS showed similar trends. Results of the maximum increase for VSS increase were similar to that observed for TSS and they are summarized in Table 4.11. Table 4.12 shows the average value of VSS/TSS ratio for different conditions. Irrespective of initial TSS and black liquor concentration, ratio varied in a small range from 0.64 to 0.88. The average value was 0.79.

Table 4.11 Comparison of maximum percentage increase in VSS

Initial TSS (mg/l)	Black liquor concentration			
	0%	0.5%	1%	2%
250	71	64	6	2
500	81	32	10	8
800	90	99	39	11
1400	98	79	87	17

Table 4.12 Comparison of VSS/TSS ratio

Initial TSS (mg/l)	Black liquor concentration			
	0%	0.5%	1%	2%
250	0.81	0.76	0.86	0.81
500	0.81	0.78	0.80	0.85
800	0.73	0.81	0.72	0.80
1400	0.77	0.64	0.76	0.88

Specific rates of VSS increase were calculated for all conditions in similar way to that for specific rates of TSS increase. Figure 4.37 shows graph for the specific rate of VSS increase. It can be concluded that black liquor increases the specific rate of VSS and at lower sludge concentration, specific rates are higher as compared to higher sludge concentrations. This can be explained again based on the food to microorganism ratio.

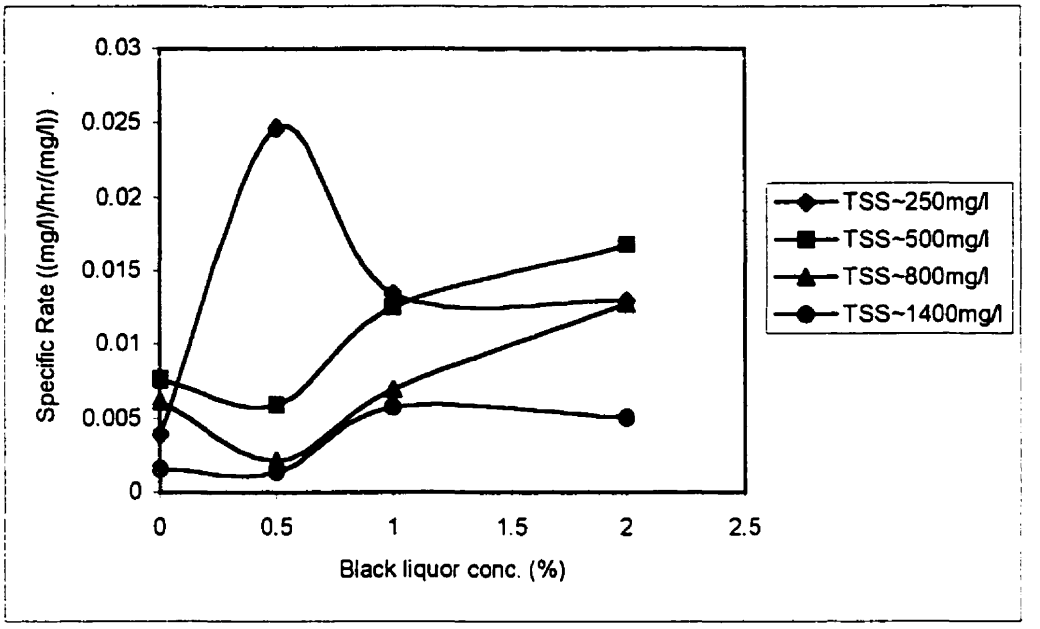


Figure 4.37 Specific rate of VSS increase

4.3.2 Comparison of COD and TOC Data

TSS and VSS represent the amount of biomass concentration in the system whereas COD and TOC give an indication of the amount of substrate available in the system. Initial rates, specific rates, instantaneous yields and yields based on COD and TOC were measured to understand the kinetics.

Results of Percentage Decrease in COD and TOC

The percentage decrease in COD was calculated using the initial COD and the final COD values over the experimental time. Percentage decrease in TOC was calculated in a similar way. Figure 4.38 shows graph of percentage decrease in COD vs. black liquor concentration for various initial TSS and Figure 4.39 shows the corresponding graph for the percentage decrease in TOC.

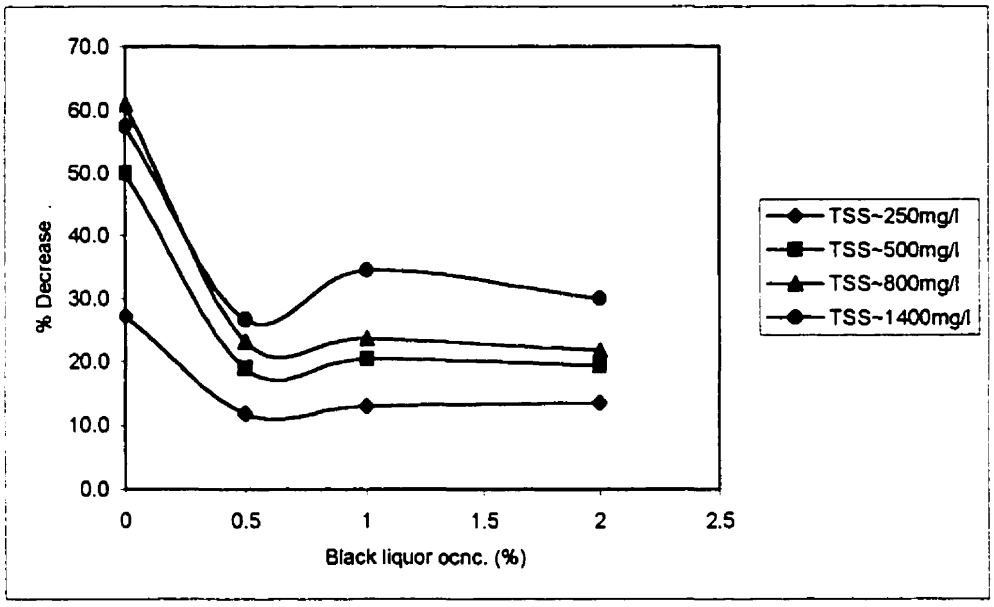


Figure 4.38 Percentage decrease in COD

In both cases, as the initial TSS increases, the percentage decrease in COD and TOC increases. This can be explained based on the number of microorganisms consuming food. At higher initial TSS, there are larger number of microorganisms utilizing available substrate, resulting in a larger decrease in COD and TOC. However, the percentage decrease for samples containing black liquor was always lower than that for TME for a given TSS. This was due to the toxicity of black liquor to the activated sludge and the fact that not all compounds present in the black liquor were biodegradable. For example for initial TSS of 1400 mg/l, the percentage decrease in COD was 58% for 0% while for 0.5% it was 27%.

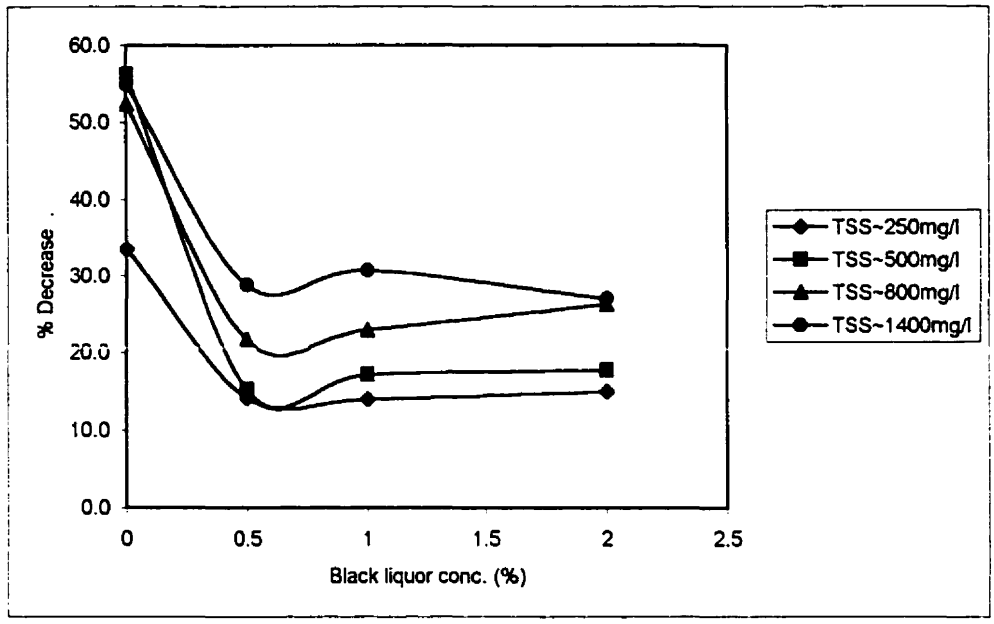


Figure 4.39 Percentage decrease in TOC

Results of Instantaneous Yield and Overall Yield

Instantaneous yield is the yield of activated sludge at time zero. Yield is defined as the amount of sludge grown per amount of food consumed. It was calculated based on TSS and both COD and TOC. Instantaneous yield was calculated using the initial rate of TSS increase and initial rate of COD decrease (or initial rate of TOC decrease).

$$Inst.\cdot Yield = \frac{Initial\cdot Rate\cdot of\cdot TSS\cdot increase}{Initial\cdot Rate\cdot of\cdot COD\cdot (or\cdot TOC)\cdot removal} \quad \text{.....(4.1)}$$

$$Inst.\cdot Yield = \frac{(mg/l)of\cdot TSS\cdot produced/hr}{(mg/l)of\cdot COD(orTOC)\cdot removed/hr} \quad \text{.....(4.2)}$$

Figure 4.40 shows the graph for the instantaneous yield based on COD vs. black liquor concentration for various initial TSS. Results of the instantaneous yield based on TOC were similar to COD and they followed same trends. Table 4.13 gives the yield values based on TOC values. From both the Figure 4.40 and Table 4.13, it is clear that the instantaneous yield values were higher for lower TSS values and were lower for the higher TSS values. For example for 1% black liquor, instantaneous yield based on TOC

for initial TSS of 250 mg/l was 1.51 while it was 3.81 for initial TSS 1400 mg/l. This was because at lower TSS, food was utilized for both the sustenance and growth of sludge but at higher TSS, food was used only for sustenance. Hence, at lower TSS there was no growth and therefore instantaneous yield values were lower. Also, as the black liquor concentration increased, the instantaneous yield value also increased which was due to increase in the food available to microorganisms.

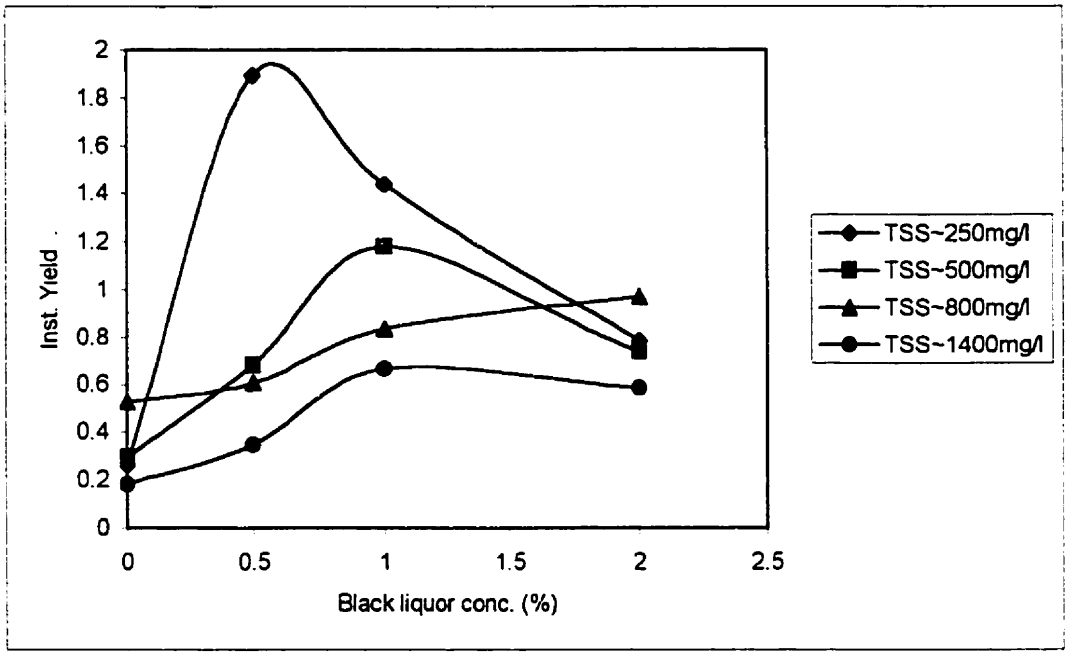


Figure 4.40 Instantaneous yield based on COD

Table 4.13 Instantaneous yield based on TOC

Initial TSS (mg/l)	Black liquor concentration			
	0%	0.5%	1%	2%
250	1.63	0.96	1.51	0.41
500	4.05	2.38	1.22	0.63
800	3.78	6.12	2.61	1.97
1400	2.92	3.34	3.81	1.82

Overall yield was calculated using the final change in COD or TOC and the maximum increase in TSS. It represents the amount of biomass produced per amount of food consumed. Figure 4.41 shows the graph for the overall yield vs. black liquor

concentration for various initial TSS and Table 4.14 shows the overall yield values based on the TOC. These results indicate that overall yields were lower for higher TSS but they were higher for lower TSS. This again could be explained based on food to microorganism ratio. At lower TSS, biomass utilized food for both their sustenance and growth but at higher TSS, food was available just for their sustenance. Therefore, at higher TSS, high growth was not observed and overall yield remained lower. In addition, the overall yield values were same irrespective of black liquor concentration for higher TSS 1400 mg/l, which was because of lack of growth.

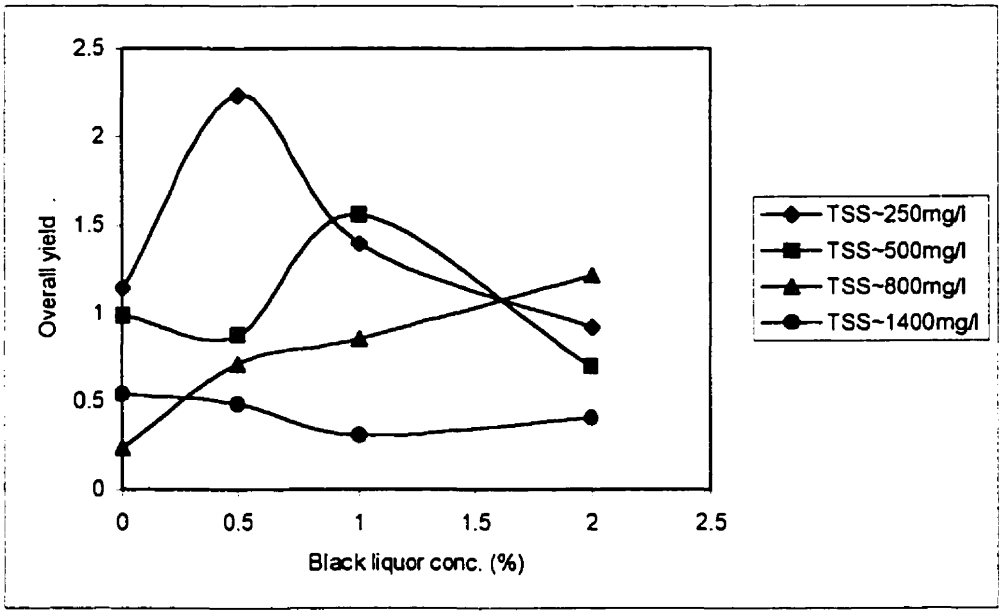


Figure 4.41 Overall yield based on COD

Table 4.14 Overall yield based on TOC

Initial TSS (mg/l)	Black liquor concentration.			
	0%	0.5%	1%	2%
250	2.69	2.66	0.80	1.58
500	4.85	2.82	2.38	1.30
800	4.45	6.18	3.28	0.86
1400	3.51	2.72	4.28	1.62

Results of Initial Rate of COD and TOC Decrease

Initial rate of COD (or TOC) removal was calculated from the slope at time zero of COD (or TOC) vs. time curve. Figure 4.42 shows graph of initial rates of COD removal with black liquor concentration for different initial TSS. Table 4.15 shows values of initial rate of TOC removal.

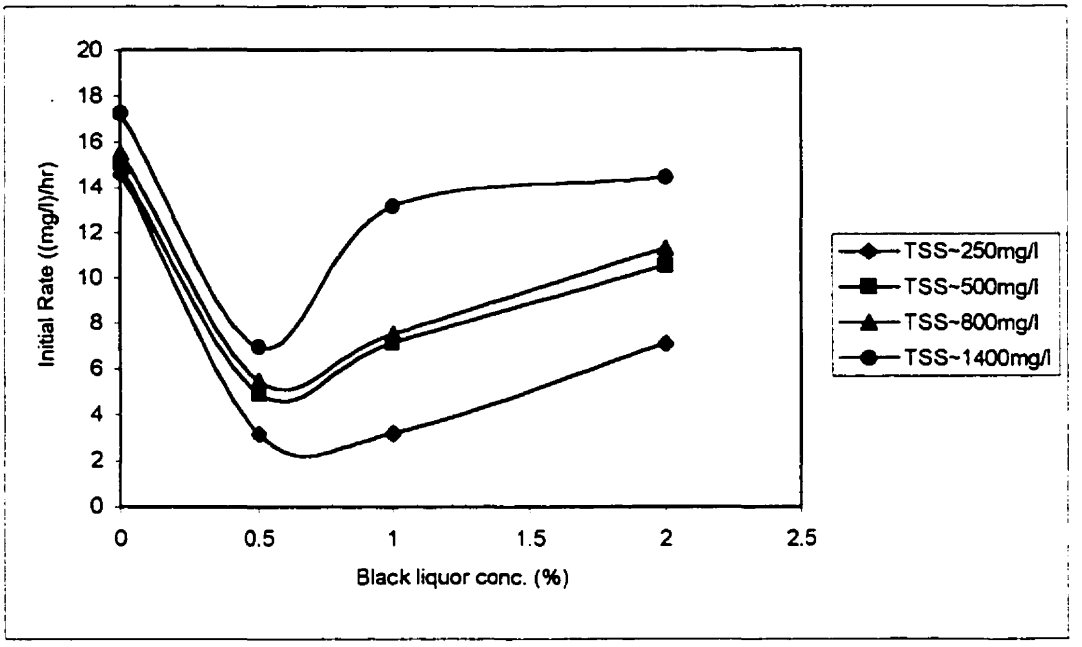


Figure 4.42 Initial rate of COD removal

Table 4.15 Initial rate ((mg/l)/hr) of TOC removal

Initial TSS (mg/l)	Black liquor concentration			
	0%	0.5%	1%	2%
250	2.35	4.59	5.39	7.65
500	1.49	1.42	2.72	3.86
800	1.21	1.38	2.41	4.43
1400	1.91	2.31	2.88	4.64

The above results indicate that as the initial sludge concentration increases the initial rate of COD (or TOC) removal also increases. This could again be explained by the number of microorganisms consuming the available food. At the higher TSS, larger

number of microorganisms were present to consume the food and therefore, the initial rate was higher than that for lower TSS.

In addition for a given initial TSS, as the black liquor concentration increased the initial rate of COD removal first decreased and then it increased. This could be explained by two effects of the black liquor. Black liquor increases the amount of food available for the growth of microorganisms however it has also toxic compounds in it. Increased food concentration promotes the growth while toxic compounds hinder the growth. At 0.5% black liquor, effect of toxicity was more dominant than the effect of the increased food. For other black liquor concentrations 1% and 2%, effect of increased food prevailed and therefore there was increase in the initial rate with increase in the black liquor concentration. However, the effect of toxicity was always present, since for black liquor concentrations the initial rates were always lower than that for 0% or TME for a given initial TSS.

Specific Rate of COD or TOC Removal

Figure 4.43 shows the graph for the specific rate based on the COD with black liquor concentration for various initial TSS.

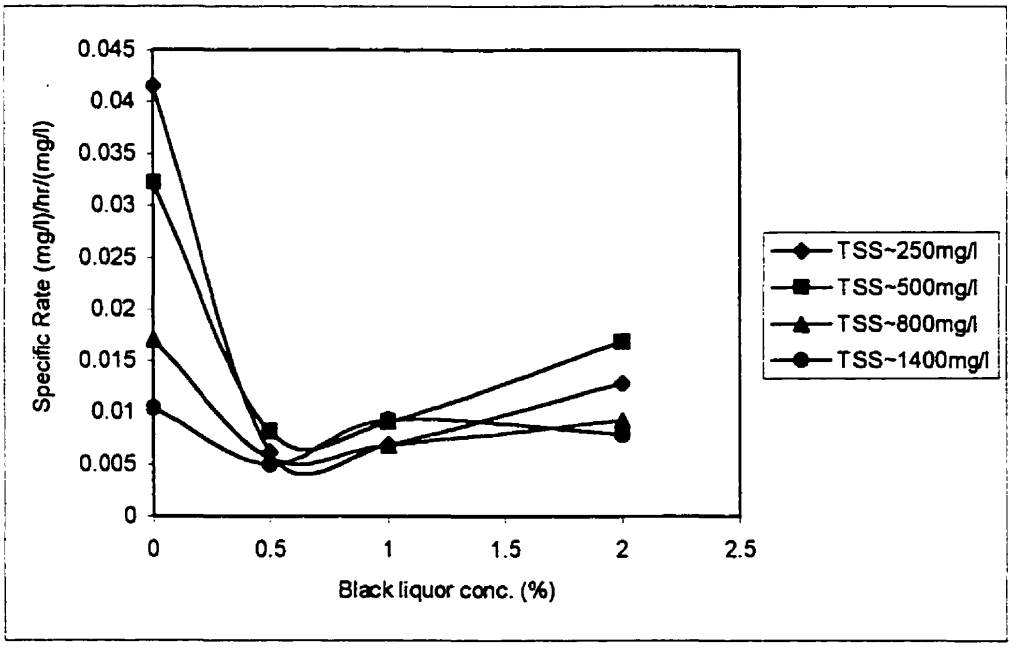


Figure 4.43 Specific rate of COD removal

Table 4.16 shows the values of specific rates based on TOC. In a analogous way to the specific rate of TSS increase, specific rate of COD (or TOC) removal is defined as the ratio of the initial rate of COD (or TOC) removal per initial TSS. It represents the activity of the microorganisms because this parameter indicates the amount of COD or TOC consumed per unit time by microorganisms. It has units of (mg/l)/hr/(mg/l).

Table 4.16 Specific rate of TOC removal ((mg/l)/hr/(mg/l))

Initial TSS (mg/l)	Black liquor concentration.			
	0%	0.5%	1%	2%
250	0.0100	0.0097	0.0055	0.0043
500	0.0058	0.0027	0.0031	0.0030
800	0.0040	0.0025	0.0032	0.0031
1400	0.0053	0.0050	0.0034	0.0030

Figure 4.43 and Table 4.16 indicate that for 0% black liquor, initial specific rates of COD (or TOC) removal (or the activity of microorganisms) are different for different initial TSS. In addition, for lower TSS, specific rates are higher, but for higher TSS, specific rates are lower. This implies that at lower TSS, microorganisms use larger amount of substrate per unit time because they use the substrate for both their sustenance and growth. This leads to higher initial rates of COD (or TOC) removal resulting in higher specific rates. For higher initial TSS, due to lower food to microorganism ratio, microorganism use the substrate mainly for their sustenance and therefore the activity or the specific rate is lower.

This trend however is not clear for the black liquor concentrations. For all conditions of TSS, the specific rate is nearly the same. Due to the toxicity of black liquor, microorganisms that can survive the toxicity shock or which can adapt to black liquor, may lead to a similar population in the system, resulting in the same specific rate or the activity of the microorganisms. This was confirmed by the Biolog technique, results of which are presented below.

In actual plant operation, the concentration of the sludge is approximately 2000mg/l. As Figure 4.43 shows at this higher TSS value the same specific rate was obtained for all black liquor conditions including 0% black liquor. The main adverse effect of black liquor is that it results in an increase in the biomass concentration (see section 4.3.1) while keeping the same specific rate. From the point of view of the plant operation, this increases the cost of sludge disposal, while from the point of view of the sludge population black liquor decreases its diversity as shown below by the Biolog results.

4.3.3 Biolog Results

Biolog analytical technique was used to characterize the activated sludge population. It used principal component analysis (PCA). After the statistical analysis, the score results were plotted on a scatter plot wherein each population is represented by a point. Thus, comparison among the various sludge populations can be made by the relative positions of these points on the scatter plot.

Biolog variability test results

Variability test was done to find out repeatability of the test. For this purpose, six biolog plates were prepared with the same sludge at the same time and then the results were analyzed. Figure 4.44 shows the position of each plate on the scatter plot using principal components one and two. Actually, three different principal components were obtained by statistical analysis.

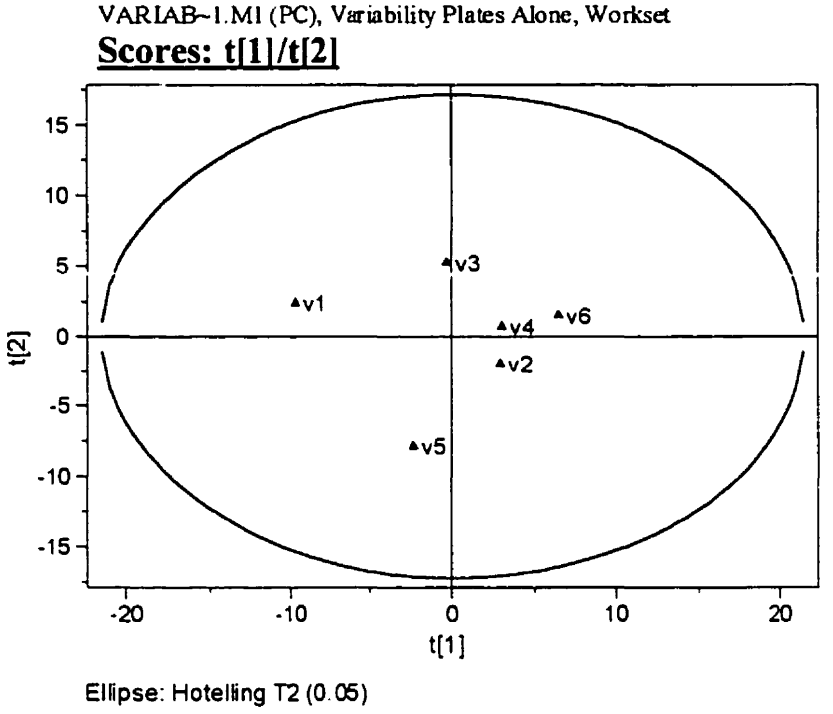


Figure 4.44 Biolog variability plates alone

From the Figure 4.45, it is clear that six points did not come to the same point although all represented the same sludge population. It was because Figure 4.44 represents the difference (variation) in six plates themselves but these points with respect to some other population, came to the same point as it is shown in the Figure 4.45. This showed that Biolog test had a good reproducibility and could identify two same populations or could distinguish between two different populations.

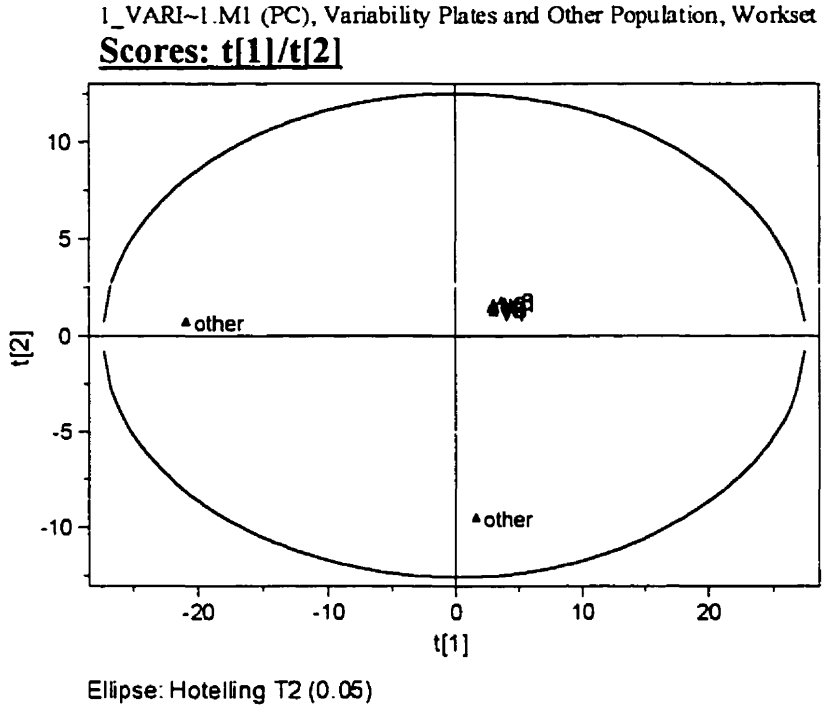


Figure 4.45 Biolog variability plates and one other plate

Biolog Results

Biolog plates were prepared for the start and the end population. An attempt was made to correlate the results of the kinetics (mainly the activity of microorganisms or the specific rate of COD removal) and the sludge population. Results of biolog analysis are presented in two sections. Results of the starting populations are presented first and then the results of the end populations are presented. Results of end population are presented in three sections. First results of the end populations for experiments with initial TSS of 250, 500, 800 and 1400 mg/l are presented. Then in the second section, results of end population of all experiments are combined together to see the effect of black liquor and then in the third section, results for end populations of 0% are presented.

Starting Population

Figure 4.46 shows the graph of principle components for the starting populations. The number in the figure after the point indicates the black liquor concentration and the initial TSS.

▲ X - Y

Where, X represents the black liquor concentration

Y represents the initial sludge concentration

Figure 4.46 shows the starting population data along with the variability data. The starting population data are scattered and they do not come to the same point. This indicates that the starting point is not same for all experiments and there is variability in the starting population. Samples for experiments were obtained from a paper mill on regular basis. There is a variation in the sludge population due to upsets or mill operation. This explains the variation in the starting population.

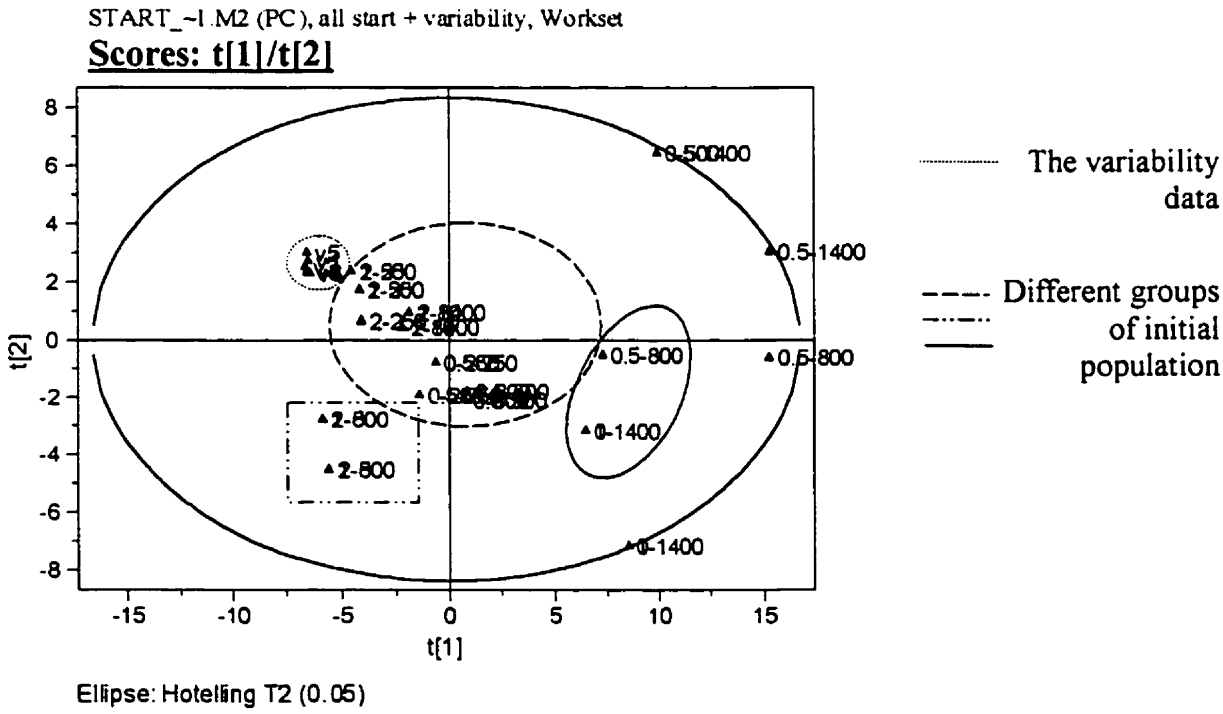


Figure 4.46 Starting population

End population for different initial TSS

Figure 4.47 shows the graph for the end population for initial TSS ~ 250 mg/l and different black liquor concentrations. Terminology used for representing points is explained below.

▲ XenY

where, X represents the black liquor concentration in %

Y represents the duplicate sample number (1 or 2)

From the comparison of principle component t[2] it can be concluded that the final population for the black liquor concentrations, 0.5, 1, 2% is same but it is different from the final population of 0% or TME. This is in accordance with the activity or the specific rate data for initial TSS~250 mg/l. The activity of the microorganisms for black liquor concentrations 0.5, 1, 2% was nearly the same but it was different for 0% or TME.

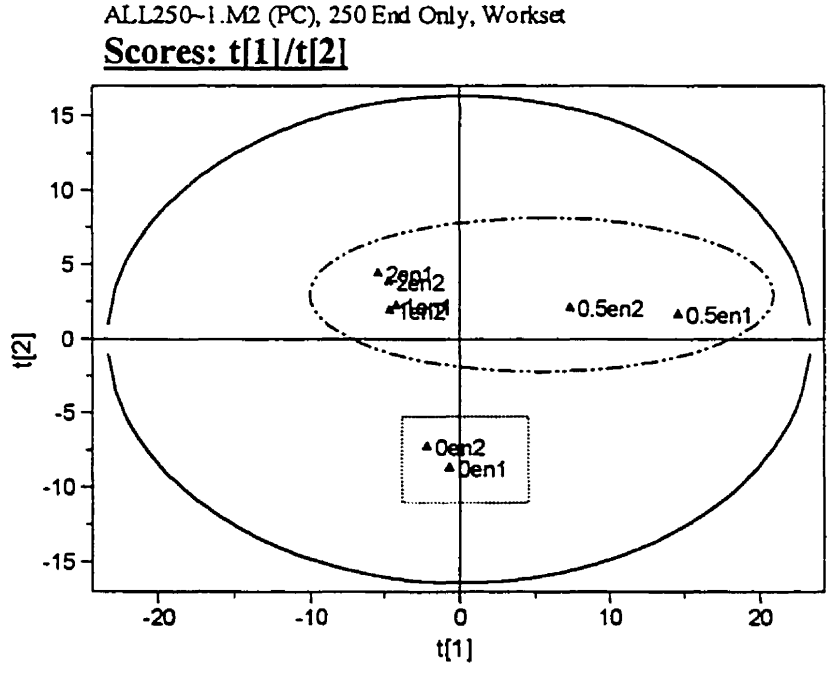


Figure 4.47 Final population for initial TSS ~ 250 mg/l

Similarly, end populations for the initial TSS of 500, 800 and 1400 mg/l were plotted. Again, the same results were obtained. Figure 4.48 to Figure 4.50 shows the graph for the final population for various conditions.

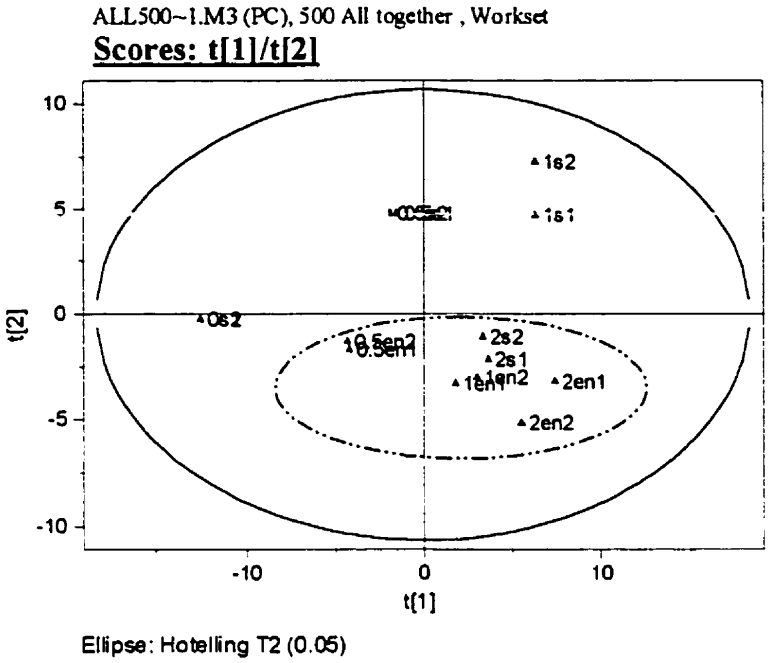


Figure 4.48 Final population for initial TSS ~ 500 mg/l

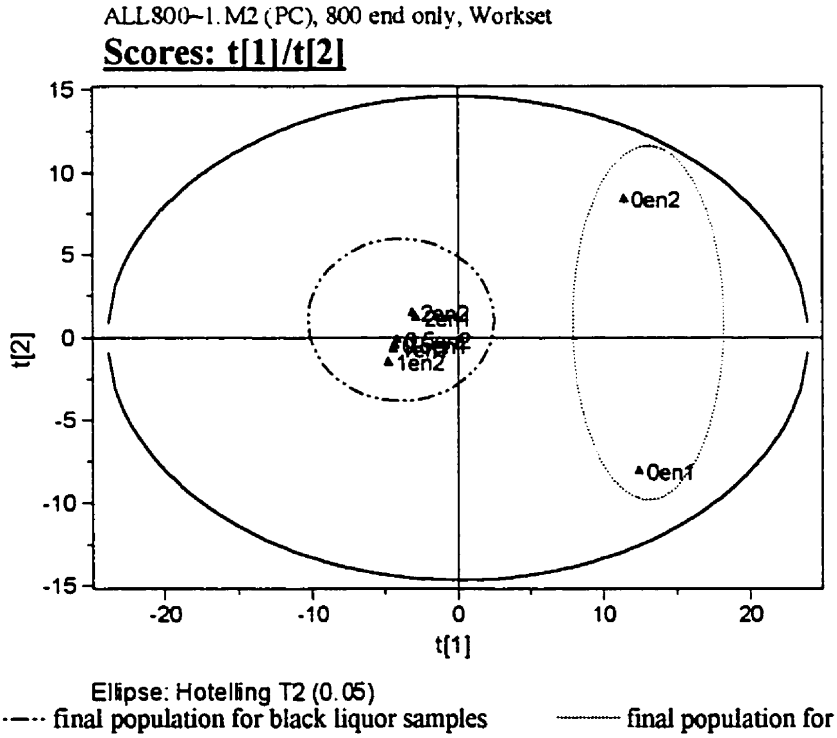


Figure 4.49 Final population for initial TSS ~ 800 mg/l

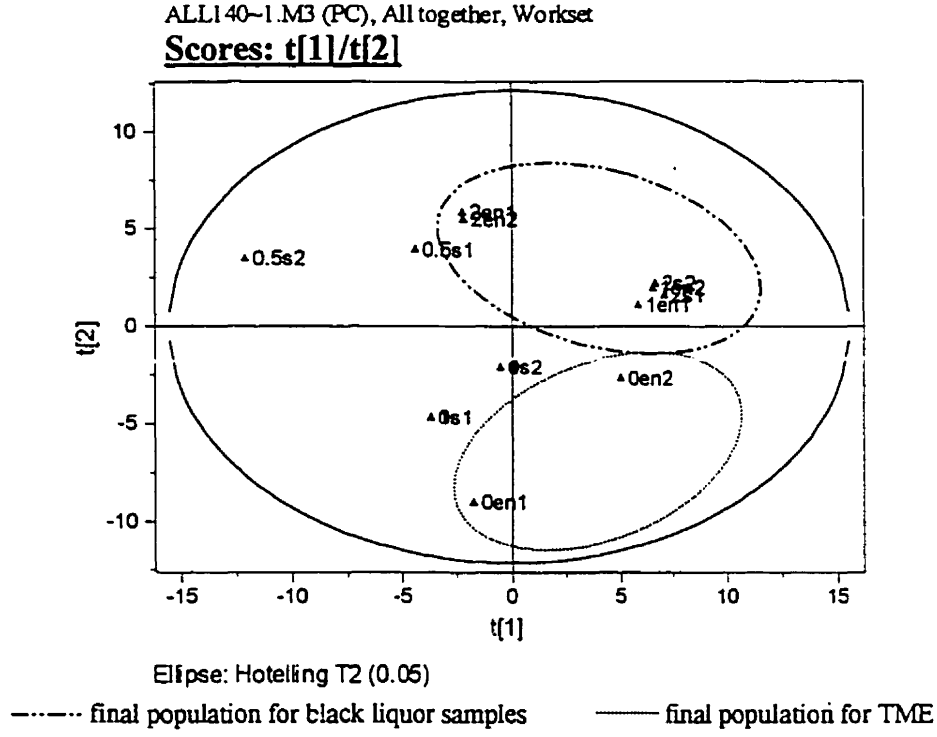


Figure 4.50 Final population for initial TSS ~ 1400 mg/l

End population of all the experiments

Figure 4.51 shows the graph of principle components for all the end populations combined. Points are represented in the same way as the Figure 4.44. All final population for black liquor samples come in the same area and are very close however for TME, the final populations are scattered. Hence, it is clear from the graph that the final population for the black liquor concentrations 0.5, 1 and 2% is the same irrespective of the initial TSS. However, this final population is different from the final population for 0%.

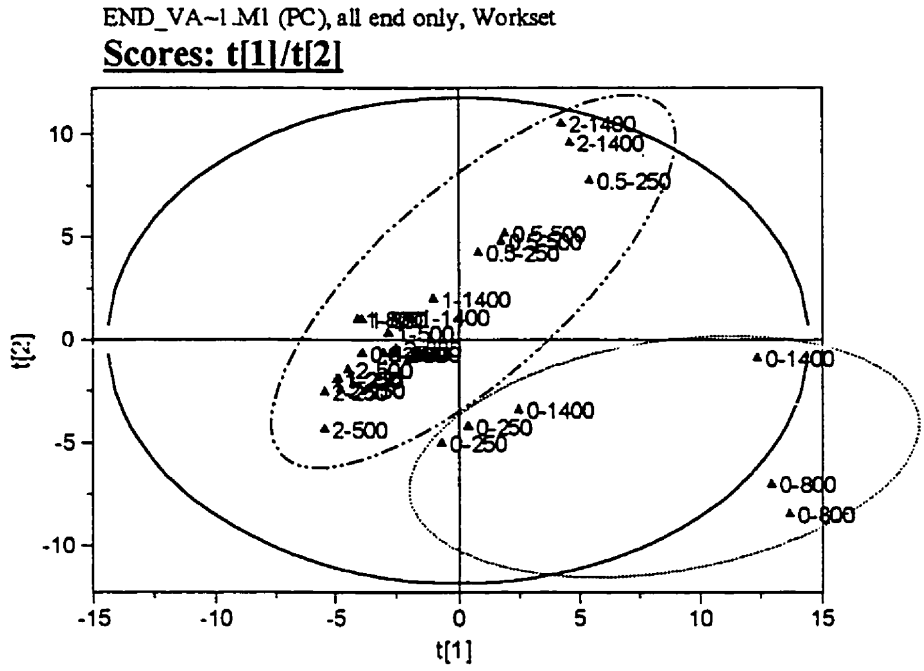


Figure 4.51 Final population for all experiments

End population of 0% or TME

Figure 4.52 shows the graph for principle components of 0% black liquor concentration and different initial TSS. The numbers represent initial TSS and duplicate values. The final populations are scattered around the point (0,0) and do not fall in the same area. Therefore, it can be concluded that the final population for 0% is different for different initial TSS. This indicates that the final population for 0% is a function of initial TSS. This is in accordance with the specific rate data as discussed in section 4.3.2 on page 73.

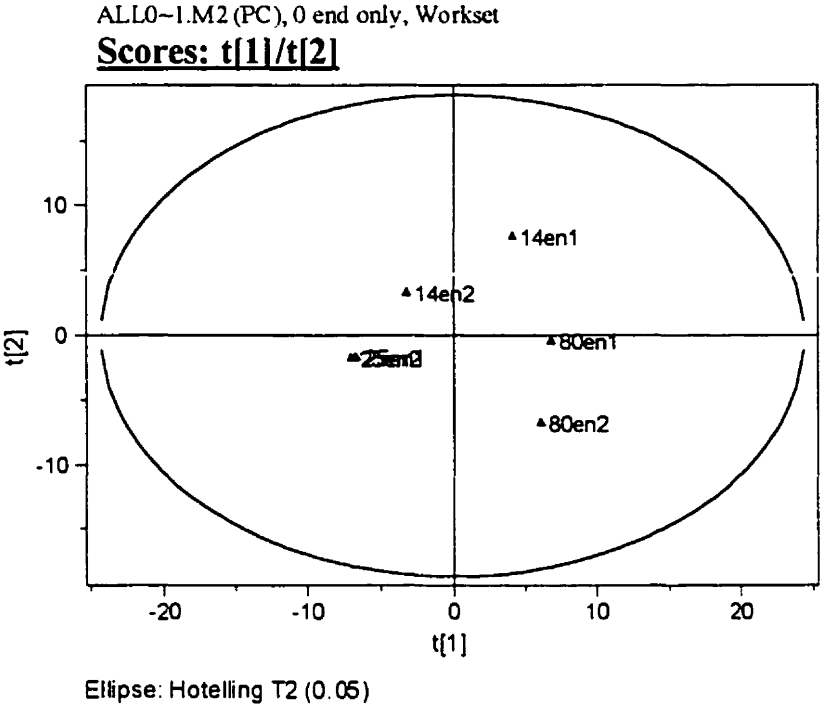


Figure 4.52 Final population for 0% black liquor or TME

CHAPTER 5

RESULTS AND DISCUSSION

(FOAM FRACTIONATION)

One of the objectives of the present work was to study the feasibility of using foam fractionation as a pretreatment step to activated sludge process. In this chapter, results from experiments studying the feasibility of foam fractionation are presented.

5.1 Initial Experiments

5.1.1 Effect of pH on Surface Tension

Surface tension is a function of pH. To study the effect of pH on surface tension, samples of TME and black liquor were prepared with various pH values. Figure 5.1 shows the effect of pH on the surface tension for TME and 2.5% black liquor. Surface tension values were in the range of 56 to 61 dynes/cm for pH range of 7.5 to 11 for TME and 2.5% black liquor samples.

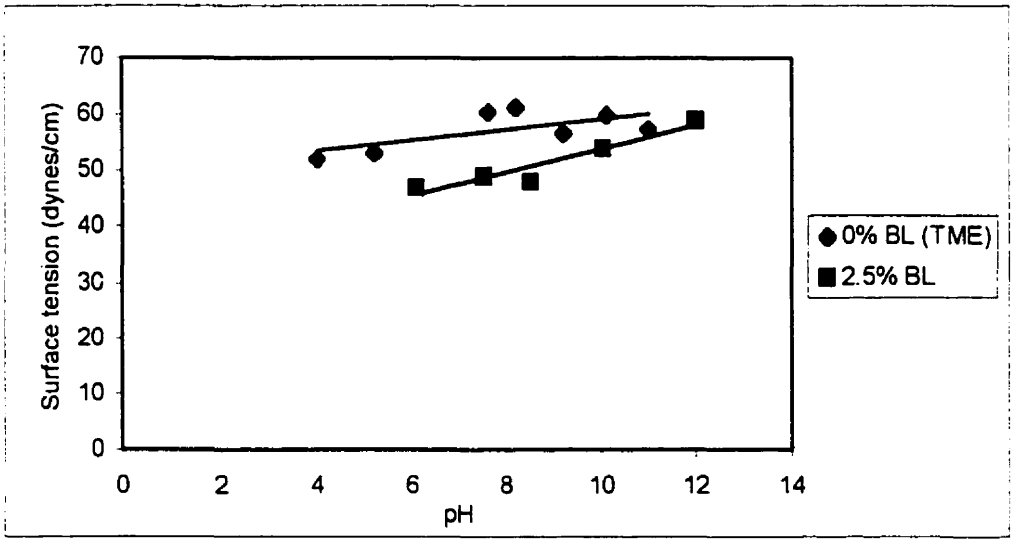


Figure 5.1 Effect of pH on surface tension

5.1.2 *Effect of Black Liquor Concentration on Surface Tension*

Surface tension is a function of the surfactant concentration and hence it is a strong function of black liquor concentration. As seen above, surface tension is a function of pH and pH depends on the black liquor concentration. Hence, two calibration curves were established. One for surface tension vs. black liquor concentration without pH control and other at constant pH of 9.5. In the acidic range of pH (pH < 7) for black liquor samples, precipitation of black liquor occurred with evolution of gases which indicated that black liquor samples were not stable in the acidic range. In addition, from the literature (Walden et al, 1972), it was found that pH of 9.5 gave optimal separation for foam fractionation. Therefore, pH of 9.5 was selected for all foam fractionation experiments. Figure 5.2 shows the graph of surface tension vs. black liquor concentration without pH control. The Figure indicates that black liquor decreased the surface tension for all samples. Surface tension initially decreases and then attains a limiting value at higher black liquor concentrations as the critical micelle concentration is exceeded. For lower concentrations, surfactants are present in free liquid and reduce surface tension. However, at higher concentrations of surfactants (or black liquor), they form micelle and then they do not decrease surface tension.

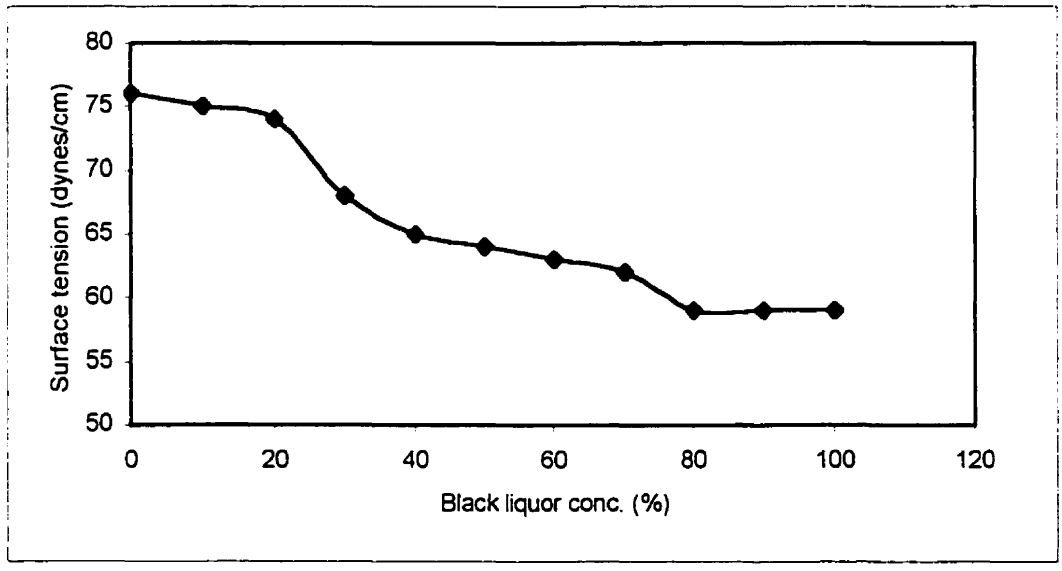


Figure 5.2 Surface tension vs. black liquor concentration without pH control

Figure 5.3 shows the surface tension vs. concentration of black liquor with pH of 9.5. This curve shows that for a given pH, as black liquor concentration increases surface tension decreases and this decrease is more than the case in Figure 5.2. Only the range from 0% to 5% of BL was relevant for the activated sludge process. Hence, consideration was given to this range only in all further analysis.

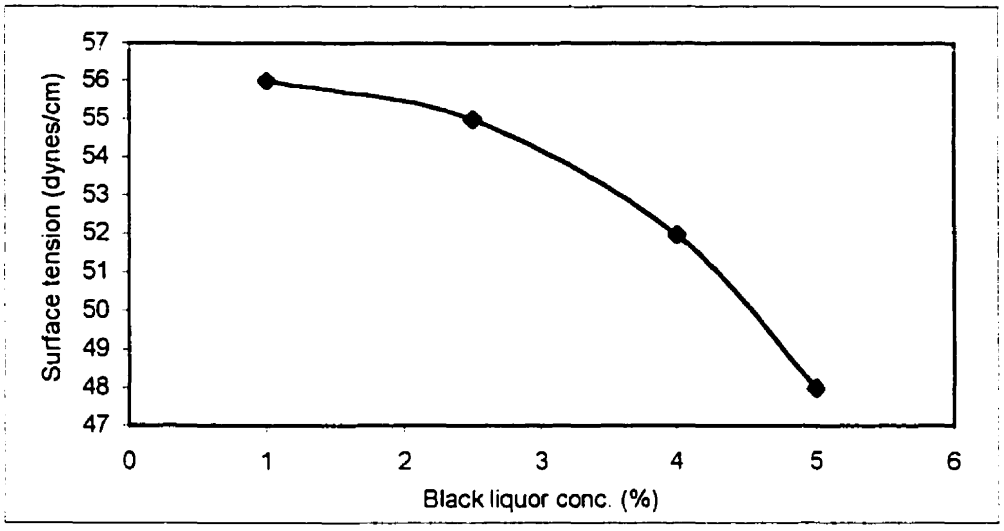


Figure 5.3 Surface tension vs. black liquor concentration at pH = 9.5

5.1.3 Time needed for the Complete Foam Fractionation

As foam fractionation is carried out, surfactants are transferred from the liquid phase to the foam phase and because of this, the surface tension of the liquid increases. Therefore, as the time for foam fractionation increases, surface tension of liquid increases. However, once all removable surfactants are removed from the liquid phase then further foam fractionation does not lead to any separation. Therefore, the surface tension does not change after that point. Experiments were carried out to find the time for foam fractionation after which further foam fractionation does not lead to any separation. Figure 5.4 shows the graph of surface tension vs. time for foam fractionation for 2.5% black liquor. Gas flow rate was kept at 182 ml/min and foam fractionation was carried out at pH 9.5. Experiment was run for 6 hr. It is clear from the graph that initially surface tension increases with time but after 3 hr surface tension remains constant. This implies that the whole separation took place in first three hours. Therefore, all foam fractionation experiments were carried out for 4 hr.

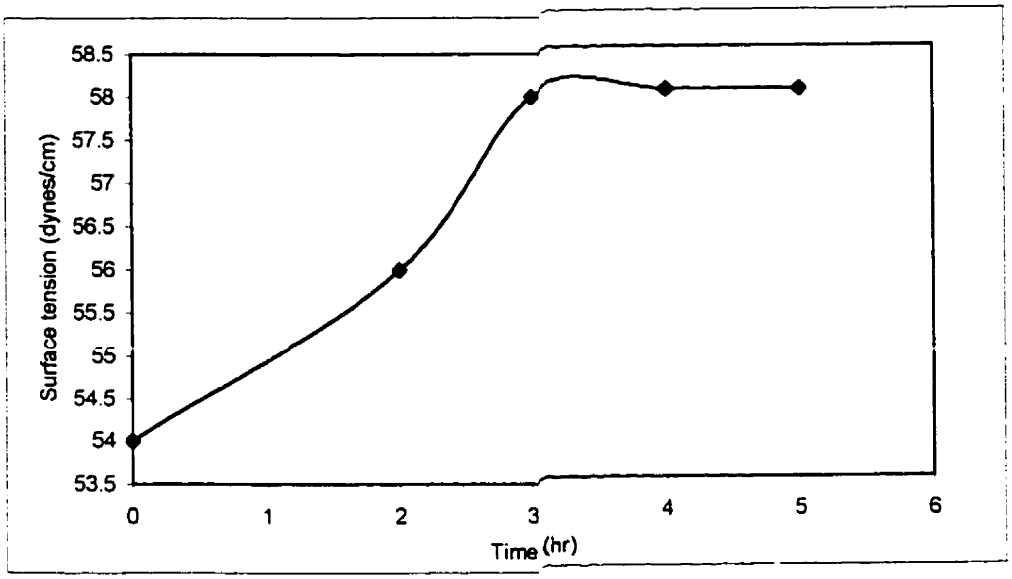


Figure 5.4 Time needed for Foam Fractionation

5.1.4 Initial Foam Fractionation Experiments

Foam fractionation experiments were carried out with various black liquor concentrations. To study the effect of foam fractionation, foam volume and total volume were measured at various times. In addition, the surface tension analysis was done. Experiments were carried out for the range of 0% to 5% black liquor. Other parameters like gas flow rate, pH and initial liquid volume were kept constant at values 100 ml/min, 9.5 and 500 ml respectively. Inlet pressure for air was 1.4 psig. Experiments were carried out for 1%, 2.5%, 4% and 5% black liquor. Since, foam volume stabilized after 1 hr., these experiments were carried out for only 1 hr.

Variation of Foam Volume and Foam Height with Time

Figure 5.5 shows the graph of foam volume vs. time curves for various black liquor concentrations. As the foam fractionation is carried out, gas liquid interface is generated. Because of gas, foam is formed and total volume (sum of liquid volume and foam volume) increases. As time progresses more and more foam is generated. However, simultaneously foam also breaks. These leads to equilibrium foam volume and then foam volume and hence total volume remains constant. At this condition, rate of foam generation is same as rate of foam breakage.

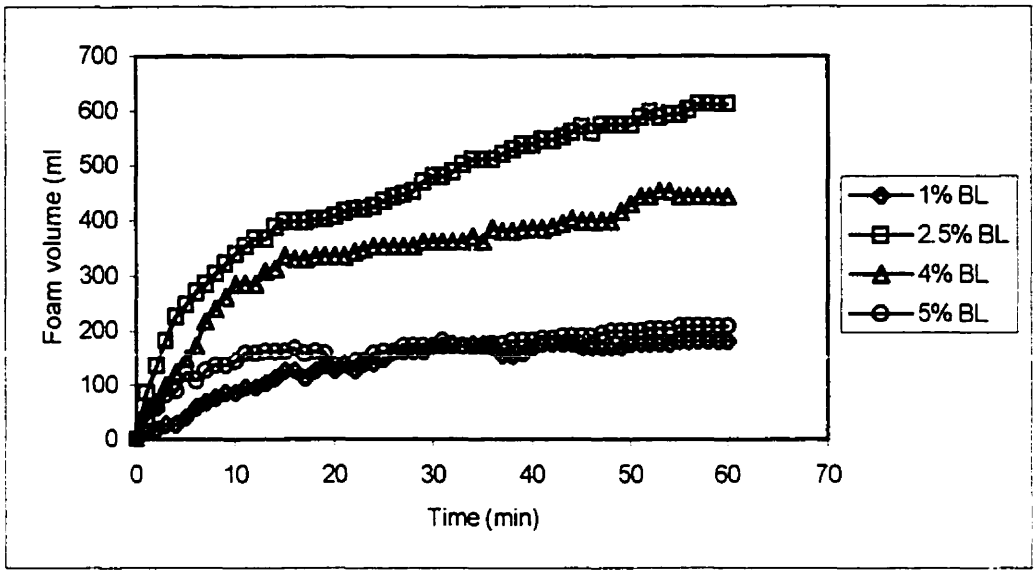


Figure 5.5 Variation in foam volume with time

Foam Volume and Black Liquor Concentration

Figure 5.6 shows the graph between the foam volume and black liquor concentration. The foam volume is the final equilibrium value for given black liquor concentration. The foam volume increases as the black liquor concentration increases but then it attains a maximum value for 2.5% and then foam volume actually decreases. This nature can be explained by the stability of foam. Higher concentration of surfactants makes the foam rigid and less elastic, which leads to more breakage of foam, and foam becomes unstable. Therefore, although concentration of surfactant increases with increased black liquor concentration, foam volume does not increase.

Effect of foam fractionation on surface tension

Figure 5.7 shows the graph of surface tension vs. black liquor concentration. It is clear form the graph that after 1 hr. of foam fractionation, increase in surface tension is same for all conditions though the absolute values are different. Actual foam fractionation experiments were carried out for 3 hr. and that time surface tension was found to increase by 10 dynes/cm.

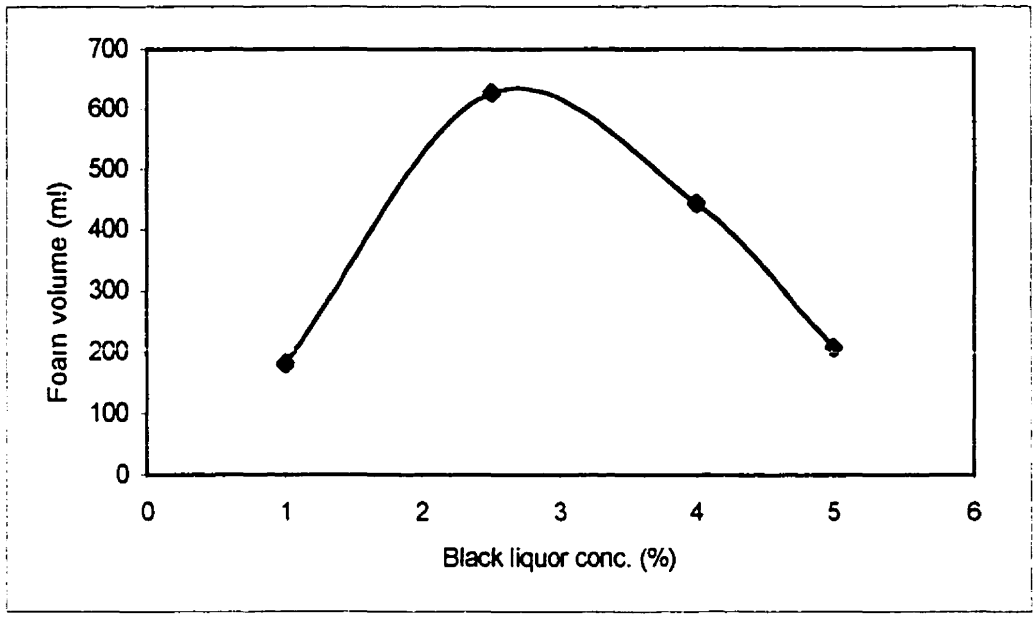


Figure 5.6 Foam volume v/s black liquor conc.

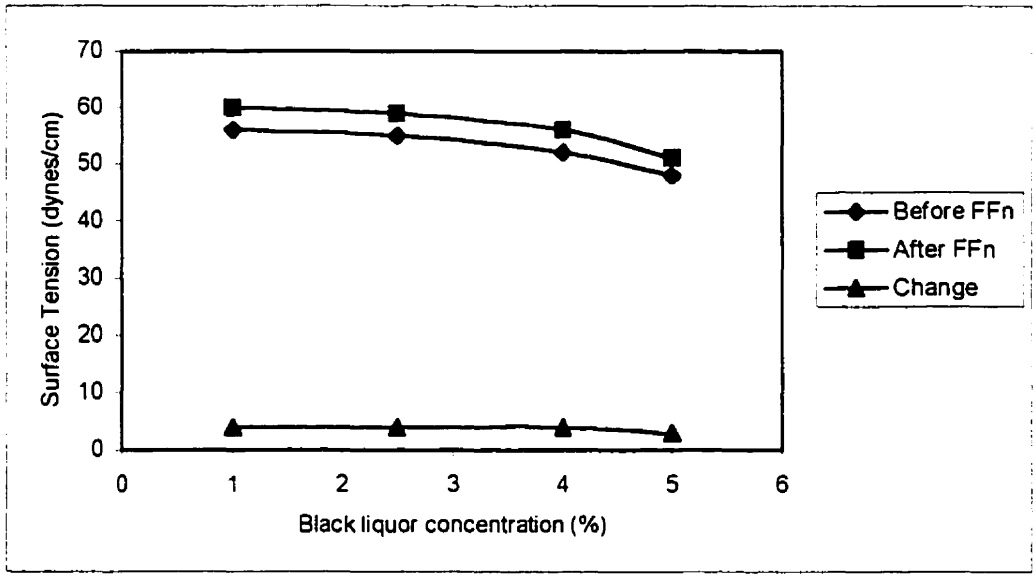


Figure 5.7 Effect of foam fractionation on surface tension

2.2 Activated Sludge Kinetics Experiments with Foam Fractionated Effluents

To study the effect of foam fractionation on growth kinetics of activated sludge and on kinetics of COD, TOC removal, experiments were carried out in batch reactors. For the feasibility study of foam fractionation, experiments were carried out for only 1% black liquor concentration. Figure 5.8 shows the normalized value of TSS for 1% black liquor effluents before and after the foam fractionation It is clear from the graph that increase in the TSS value is less in the case of foam fractionated effluent. This is due to the removal of substrate due to foam fractionation. Foam fractionation actually removes some of the organic compounds from effluents and thus decreasing the amount of food available to the biomass. Hence, growth is lower in case of foam fractionated effluent.

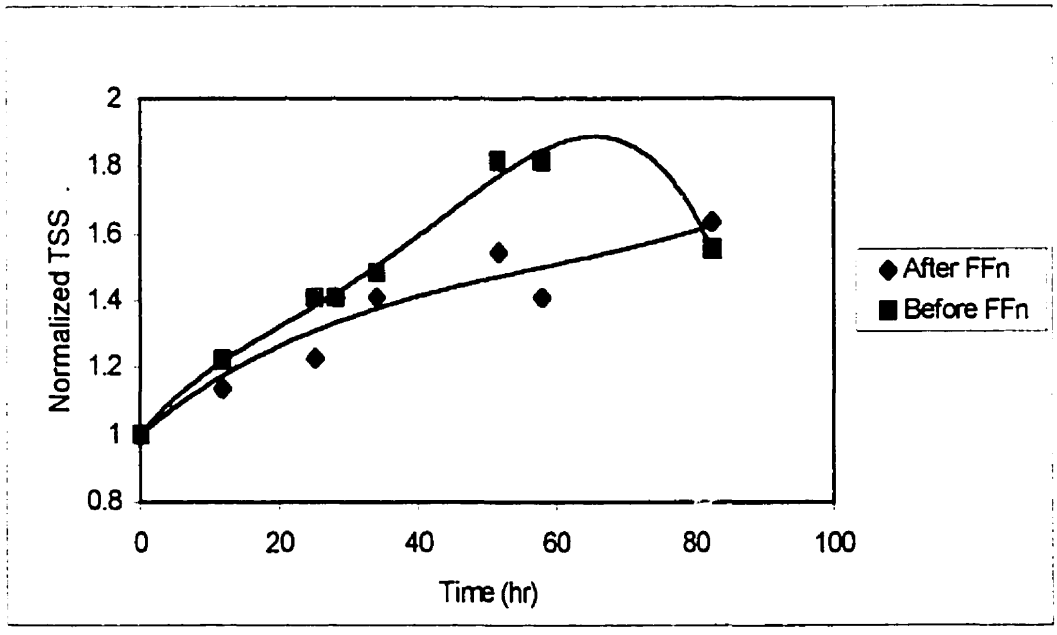


Figure 5.8 Effect of foam fractionation on the growth kinetics

Figure 5.9 shows the normalized value of COD for the samples. Actual starting value of COD were 1159mg/L for effluent sample without foam fractionation while COD value was 729mg/L for foam fractionated effluent. This shows that foam fractionation decreases COD by removing some compounds. In addition, from the graph it is clear that initial rates of COD removal were nearly same.

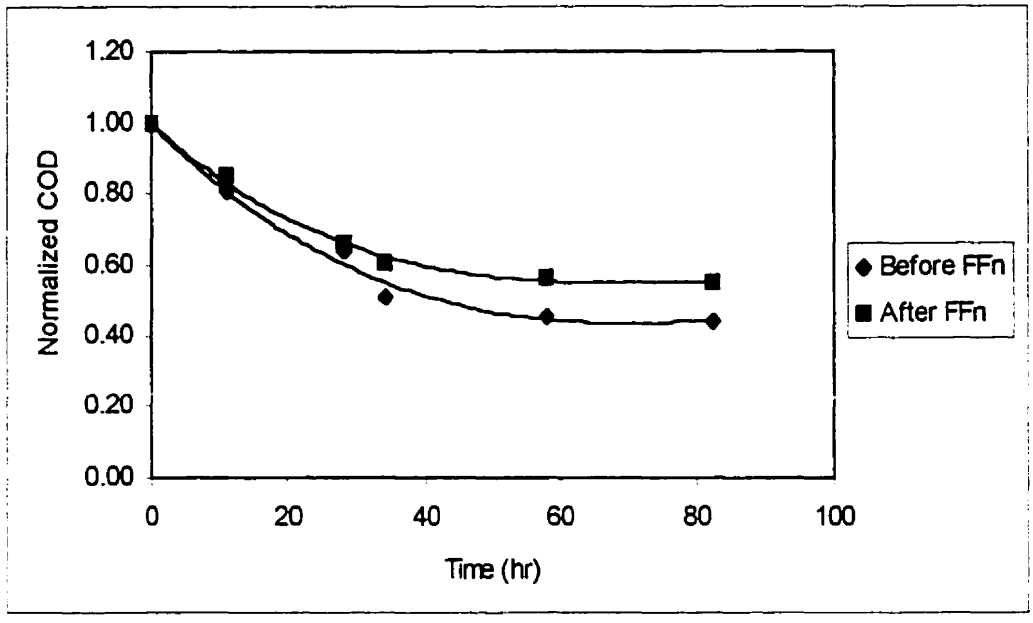


Figure 5.9 Effect of Foam Fractionation on COD removal

In addition, final percentage decrease for the foam fractionation case was lower than the without foam fractionation case. This indicates that foam fractionation does not help the kinetics of activated sludge. This can be explained by the source of effluents. Effluents for experiments were obtained form a kraft mill. The kraft mill uses hardwood as its raw material. Hardwood generally does not yield any extractives such as resin acids and fatty acids, which contribute significantly to toxicity. Foam fractionation actually removes the extractives, which are surface active in nature. Since, they are absent in effluents, foam fractionation does not help improve the kinetics of activated sludge.

Hence, from the preliminary analysis, it was concluded that foam fractionation did not improve the kinetics of activated sludge for the mill effluents used for the study.

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions:

For the given kraft mill effluents and activated sludge, the effect of black liquor was studied. This was achieved by studying various concentrations of black liquor with different initial sludge concentrations. In addition, preliminary feasibility study of foam fractionation as a pretreatment step to activated sludge process was carried out. The maximum black liquor concentration of 2% was studied but typical upsets in the plant operation rarely lead to black liquor levels as high as 2% in total mill effluent. Results from all experiments indicate that activated sludge was able to reduce the BOD and COD of the effluents. The COD removal was found to be a strong function of initial sludge concentration.

Results from the batch experiments indicate that black liquor adversely affects the activated sludge population. Results of specific rates (activity of microorganisms) indicate that despite the diversity of the initial population, same value was obtained for all black liquor concentrations. In all cases, even for the lowest concentrations of black liquor, the final population appeared to be same. This shows only those organisms survive which can adapt to black liquor. This was confirmed by the sludge characterization technique Biolog. It showed same activated sludge population for black liquor concentrations. However, for the total mill effluent the specific rate was found inversely proportional to the initial sludge concentration. In addition, the sludge characterization technique Biolog indicated different final sludge population for different initial sludge concentrations for TME.

The preliminary study indicated that foam fractionation did not improve the kinetics of activated sludge for the mill effluents used for the study.

6.2 Recommendations:

The present study of black liquor was done in a batch assay. However, further study is required in a continuous assay. In the present study, only the effect of black liquor on the activated sludge was established. However, this type of study on the effect of various streams from the plant should be carried out with other toxic effluent streams such as bleached plant liquor. Sludge characterization was done using the biolog analytical technique. This technique gives only qualitative results. Further study is needed to establish quantitative results.

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APPENDIX A

(PRELIMINARY CALCULATIONS)

Experiment: Asp21
Date: October 17th '98

Black Liquor Concentration: 1%

Reactor Used: A ~~or B~~

Foam Fractionation Done: ~~Yes~~ / No

(If yes check the sheet with title Foam Fractionation Data)

Conductance: - ms

Initial COD (mg/L): 2500

Actual Sludge Concentration: 15020 mg/l

COD: N: P = 100: 3: 1

Initial BOD: -

Initial pH: 9.72 After Adjustment: 9.10

Other Information:

Batch Volume Used (ml): 1600
Amount of Sludge Used (ml): (1600 x 1500) / (1000 x 15.02) = 159.79
Concentration of Phosphoric Acid: 20 times diluted 85% Phosphoric Acid
Concentration of Urea Solution: 30.0214 mg/ml

Conc. Of P required = 0.01 * COD = 0.01 x 2500 = 25
Conc. Of N required = 0.03 * COD = 0.03 x 2500 = 75

Volume of Phosphoric Acid Used:

$$V_{acid} : \frac{\text{Conc. of P} * 98 * \text{Volume of Batch}}{31 * 1000 * d_{acid}} = \frac{25 * 98 * 20 * 1600}{31 * 1000 * 1685 * 0.85} = \mathbf{1.7657\ ml}$$

Volume of Urea Solution Used:

$$V_{urea} = \frac{\text{conc. of N} * 60.06 * Vt}{28 * 1000 * \text{Curea}} = \frac{75 * 60.06 * 1600}{28 * 1000 * 30.0214} = \mathbf{8.5738\ ml}$$

APPENDIX B

(CALCULATION OF INITIAL RATES)

Initial rate values for various parameters were calculated using the procedure shown below. Example of calculation of initial rate of TOC removal is shown here. Same procedure was used for calculating initial rate of TSS, VSS, TOC, COD and SL concentration.

Data of TOC vs. time:

Time (hr)	TOC (mg/l)
0	680.4
22.9	638.6
55.6	596.1
78.4	556.5
99.6	547.8
122.7	559.9
150.1	560.1
169.9	554.8

Data are plotted on X-Y scatter plot using Microsoft Excel 97 with time as the X-axis and TOC (or other parameter) as the Y-axis. Trendline was added to data using a 5^{th} or 6^{th} order polynomial curve. R^2 value was also calculated. A polynomial fit that gave R^2 value close to 1 was selected and the equation of that polynomial curve was used to calculate initial rate. Equation was differentiated with respect totime. Then derivative value was calculated at time zero. This value is the initial rate value.

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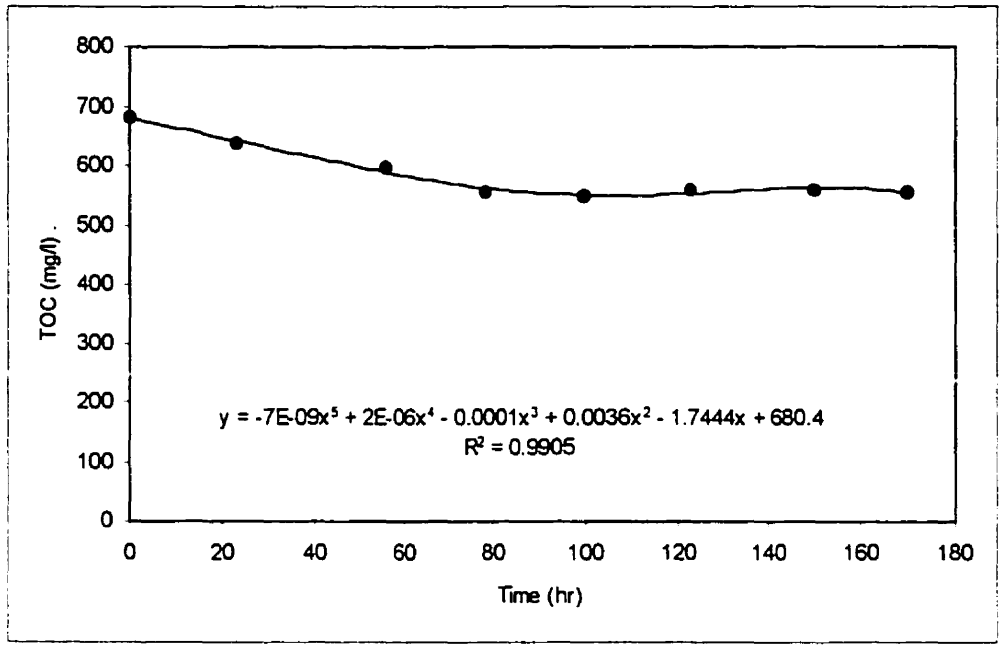

Fig.B.1 TOC vs. time curve

Equation of the polynomial is:

$$y = -7 * 10^{-09} * x^5 + 2 * 10^{-06} * x^4 - 0.0001 * x^3 + 0.0036 * x^2 - 1.7444 * x + 680.4 \quad \text{.....(B.1)}$$

$$R^2 = 0.9905 \quad \text{.....(B.2)}$$

1st order derivative of equation is:

$$\frac{dy}{dx} = -5 * 7 * 10^{-09} * x^4 + 4 * 2 * 10^{-06} * x^3 - 3 * 0.0001 * x^2 + 2 * 0.0036 * x - 1.7444 \quad \text{.....(B.3)}$$

$$\therefore initial \cdot rate = \left(\frac{dy}{dx}\right)_{x=0} = -1.7444 \quad \text{.....(B.4)}$$

Negative sign indicates that as time increases TOC decreases. Thus, initial rate of TOC removal is 1.7444 (mg/l)/hr