EVALUATION OF BIO KINETIC PARAMETERS FOR RATIONAL DESIGN OF ACTIVATED SLUDGE PROCESS FOR PHENOLIC WASTE

A DISSERTATION

Submitted in partial fulfilment of the requirements for the award of the degree of

MASTER OF ENGINEERING

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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FEBRUARY, 1999

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled, **"EVALUATION OF BIO KINETIC PARAMETERS FOR RATIONAL DESIGN OF ACTIVATED SLUDGE PROCESS FOR PHENOLIC WASTE"**, in the partial fulfillment of the requirements for the award of the degree of **MASTER OF ENGINEERING** with specialization in **Industrial Pollution Abatement**, submitted in the Department of Chemical Engineering, University of Roorkee, Roorkee, is an authentic record of my own work carried for a period of about six months, from August 1998 to January 1999 under the guidance of **Dr. DESH DEEPAK,** Associate Professor, Department of Chemical Engineering, University of Roorkee, Roorkee.

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

Rajesh Dwivedi

Dated : 5/2/99 **(RAJESH DWIVEDI)**

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude and appreciation to my supervisor Dr. DESH DEEPAK, Associate Professor, Department of Chemical Engineering, for his keen interest, guidance and encouragement throughout the course of the present Dissertation work.

I am highly grateful to Prof. SURENDRA KUMAR, Head, Department of Chemical Engineering, for providing necessary facilities during the course of present work.

I am grateful to all my teachers for their suggestions and constant encouragement.

I also feel it my solemn duty to express my indebtness and gratitude to all others who contributed their best in the completion of this Dissertation work.

Place : Roorkee

Dated :

Rajesh Dwivedi

(RAJESH DWIVEDI)

Evaluation of Biokinetic parameters for rational design of activated sludge process for phenolic waste

by

RAJESH DWIVEDI

ABSTRACT

Phenols are a group of waste products which cause serious taste and odour problems in water. The major industries producing phenolic wastes are oil refineries, coke oven plants, steel plants etc. Acceptable discharge limits for phenols vary depending on the nature of the phenols, the volume and the rate of discharge and the nature and volume of receiving water.

Treatment methods applicable to phenol removal include biological (activated sludge, trickling filter, oxidation pond and lagoons); chemical oxidation (air, chlorine, chlorine dioxide, ozone and H_2O_2); Physical (activated carbon adsorption, solvent extraction and ion-exchange) and physico chemical (incineration and electrolytic oxidation).

Activated sludge techniques are reported to be effective for phenol levels as high as 'thousands' mg/l. However in view of the high capital requirements for biological oxidation the method is most cost effective with high volume effluents.

Phenols are not among those organic wastes which are readily biodegrabable. To degrade the phenol the microorganisms were developed in the present study. These microorganisms were able to survive in the phenolic solution. These microorganisms used phenol as their food.

The experiments carried out in batch and in the bioreactor. The batch study was done to determine the optimum temperature for the removal of phenolic wastes. The temperature which was found optimum was 30^0C.

In the bioreactor studies, initially the phenolic waste and the seed culture was taken in the aspirator bottle and the reactor was kept running for a definite period of time. After that time the different parameters which are needed in Monod's equations were determined. The graphs were plotted and the values of biokinetic parameters were determined for different sets of data..

The average values of the biokinetic parameters were determined. The saturation constant (k_s) was found to be 297 mg/l based on phenol, the value of rate of substrate utilization (K) was found to be 5.02 per day, the value of maximum yield coefficient (Y) was found to be 0.38 mg VSS/mg COD, and the value of endogenous decay coefficient was found to be 0.56 per day.

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INTRODUCTION

Phenols are a group of waste products which cause serious taste and odour problem in water, even at extremely low levels down to nearly one millionth of a gram per litre. Phenols can kill microorganisms and may even kill fish.

Despite the fact that they are used as a bactericide in strong concentrations, weak phenol solutions are decomposed by bacterial and biological action in stream.

1.1 CHARACTERISTICS OF PHENOL

Phenol is a colourless, hygroscopic and crystalline substance and it gradually turns pink in air owing to its oxidation. Its solubility in water is 98 gm l^{-1} and its melting point is 181^0C. Phenols contain a polar-OH group attached to non polar organic group. The -OH group of a phenol acts as a very weak acid. For this reason it is commonly known as carbolic acid. It is not polar enough to keep the unionized phenol from dissolving in non polar solvents.

Phenolic wastes are highly soluble in water, alcohol, benzene and other organic solvents. Phenols dissolve most readily in water that is somewhat basic. A non polar solvent could be used to extract phenols from water only if the water is acidic.

1.2 PRESENCE OF PHENOLIC WASTES

Although phenol (C_6H_5OH) has been detected in decaying organic matter and

animal urine, its presence in a surface stream is generally attributed to Industrial pollution. Petrol refineries, coke plants and resin plants are major industrial sources of phenolic waste. The phenolic compounds and their derivatives used in the production of coatings, solvents, plastics, explosives, fertilizer, textiles, pharmaceuticals, soap and dyes.

1.3 TREATMENT METHODS FOR PHENOLIC WASTES

Treatment methods applicable to phenol removal include biological (activated sludge, trickling filter, oxidation pond and lagoons) ; chemical oxidation (air, chlorine, chlorine dioxide, ozone and H_2O_2) ; Physical (activated carbon adsorption, solvent extraction and ion exchange) and physico chemical; (incineration and electrolytic oxidation).

In the present report it has been dealt that how the evaluation of bio kinetic parameters can be done for the treatment of phenolic wastes through one of the biological treatment process, i.e. activated sludge process.

1.4 BIOLOGICAL TREATMENT

Biological treatment for phenol removal is practised in a number of Industries where the combined plant effluent is treated for the removal of BOD in addition to reduction in phenol concentration.

Phenol is, however, not readily biodegradable. It is toxic to most types of microorganisms at sufficiently high concentrations and at low concentrations, it can be inhibitory to the growth rate of even those species which have the metabolic capability of using it as a substrate for growth.

In the biological treatment, the microorganism capable of degrading phenol

are highly specialized and require a controlled, stable environment. Under ideal conditions several weaks are required to develop the proper biological sludge. The efficiency of an acclimated biological system treating phenolic wastes depends strongly on temperature ; pH ; nutrients (nitrogen, phosphorus, minerals) ; oxygen concentration, phenol concentration and other organics concentration in the waste water.

To degrade phenol, the microorganism population must be fairly stable. Fluctuation in any of the preceding variables shift the balance of this population, reducing the efficiency of the system and possibly killing the biological organisms. Optimum phenol removal occurs at neutral pH (7.0), 21^0C and constant phenol concentration.

1.4.1 Activated Sludge Processes

Type of Process	:Standard, extended aeration, high rate
Contactor or Aeration tank retention time (hrs.)	:3 to 5 standard, 12 to 24 extended, as low as 0.5 for high rate
Recirculation of activated sludge	:15 to 100 percent (25 percent normal) of incoming primary clarifier overflow
BOD_5 removal efficiency	:70 to 95 percent (90 percent standard)
Other removal efficiency	:70 percent, COD, 90 percent SS, 30 percent P,35 percent N.
Excess sludge produced	:0.2 to 0.7 kgs per kg of BOD_5 removed. (0.5 to 0.6 typical)
Organic loading (Kg BOD_5 per Kg MLSS-day)	:0.1 to 1.5 (0.2 to 0.5 standard, 0.1 extended, over 0.5 for high rate).
Solids conversion constant (C) variation	:0.15 to. 0.60
Respiration rate constant (K)	:0.1
Required Nitrogen content in the influent	:10 percent of volatile solids produced

Required phosphorous content in the influent	:20 percent of Nitrogen required
Operating pH range	:6.5 to 9.0
Operating temperature range	:10 to 30^0C
Typical sludge volume index (SVI)	:150 ml. per gram of settled MLSS
Typical mixed liquor suspended solids (MLSS) concentration (mg/L)	:2000 for standard or high rate ; 3000 for extended process
Aerator types	:(a) high speed surface aerator ; (b) low speed surface aerator ; (c) compressed air diffusers (d) submerged sparge turbine aerator.

The activated sludge process was developed in England in 1914 by Ardern and Lockett[1] and was so named because it involved the production of an activated mass of microorganisms capable of stabilizing a waste aerobically. Many versions of the original process are in use today, but fundamentally they are all similar.

In the design of the activated sludge process, consideration must be given to (1) selection of the reactor type, (2) loading criteria, (3) sludge production, (4) Oxygen requirement and transfer, (5) nutrient requirements, (6) control of filamentous organisms, and (7) effluent characteristics.

1.4.1.1 Microorganisms in Activated sludge

A Wide variety of microorganisms are found in activated sludge, eg; bacteria, filamentous growths, algae and protozoa, the chemical nature of a waste will determined which organisms will grow. Bacteria predominate in activated sludge because their diverse biochemical nature enables metabolism of most organic compounds found in industrial effluents.

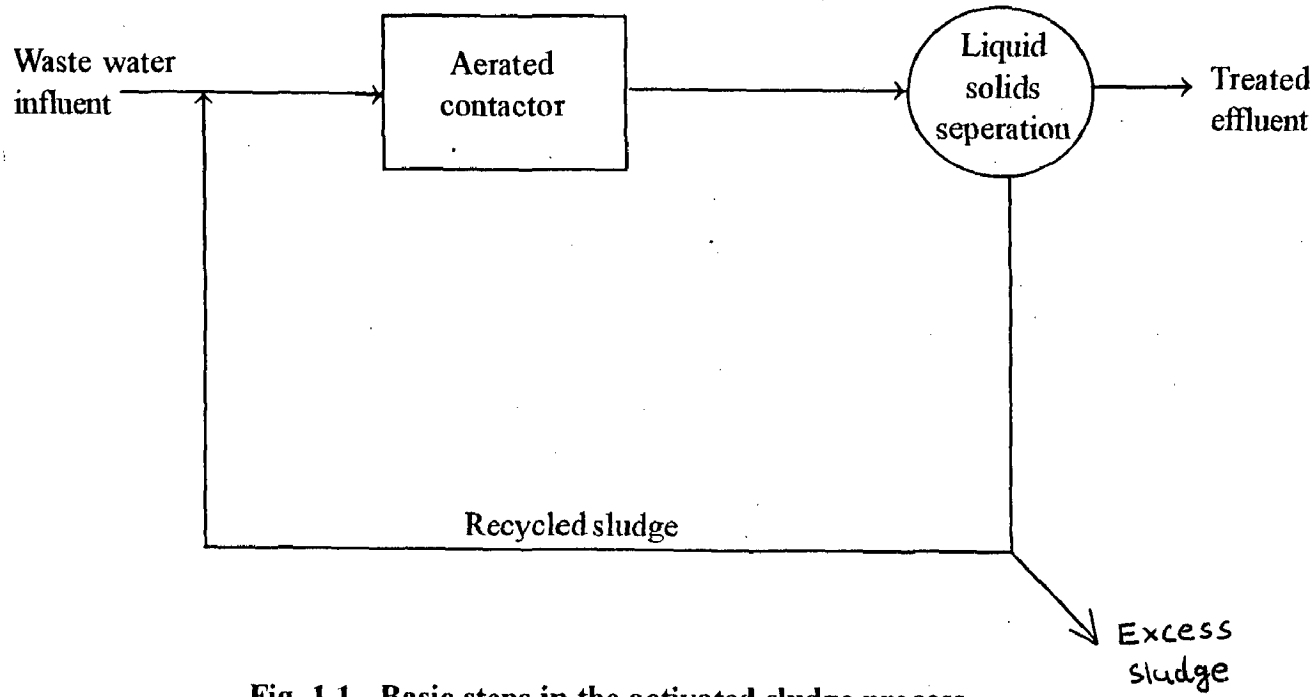


Fig. 1.1 Basic steps in the activated sludge process.

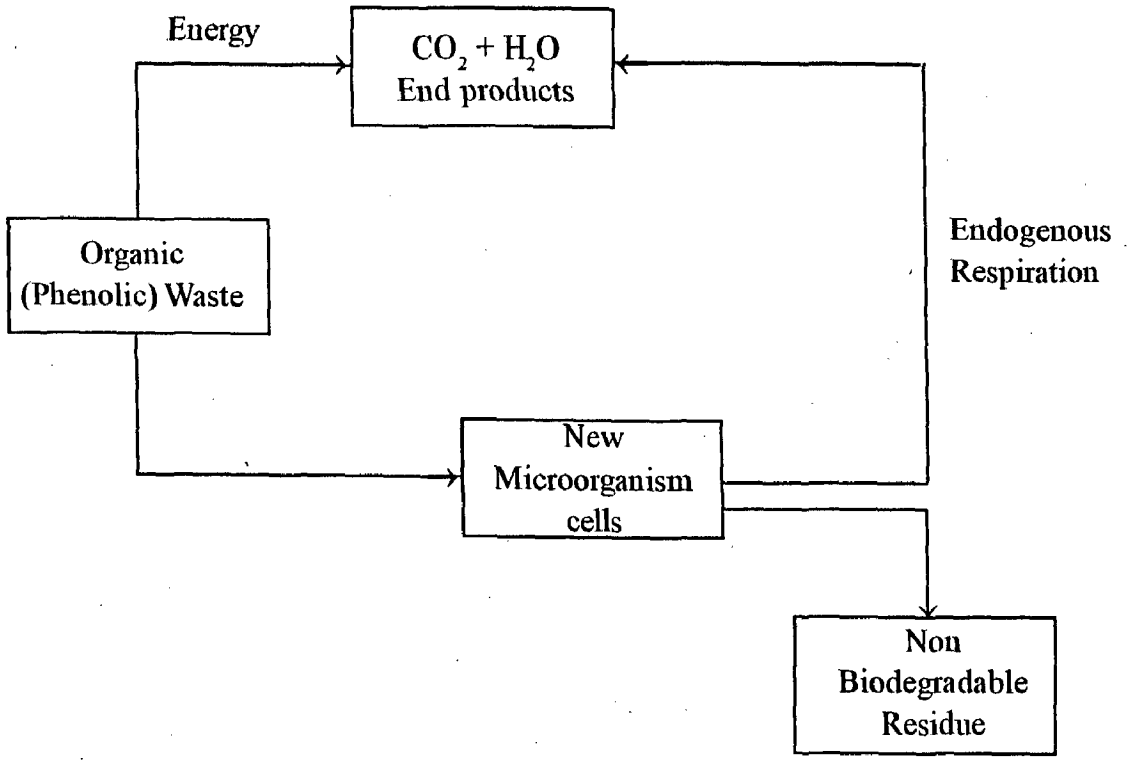


Fig. 1.2 Mechanism of Aerobic biological Oxidation of Organic (Phenolic) waste

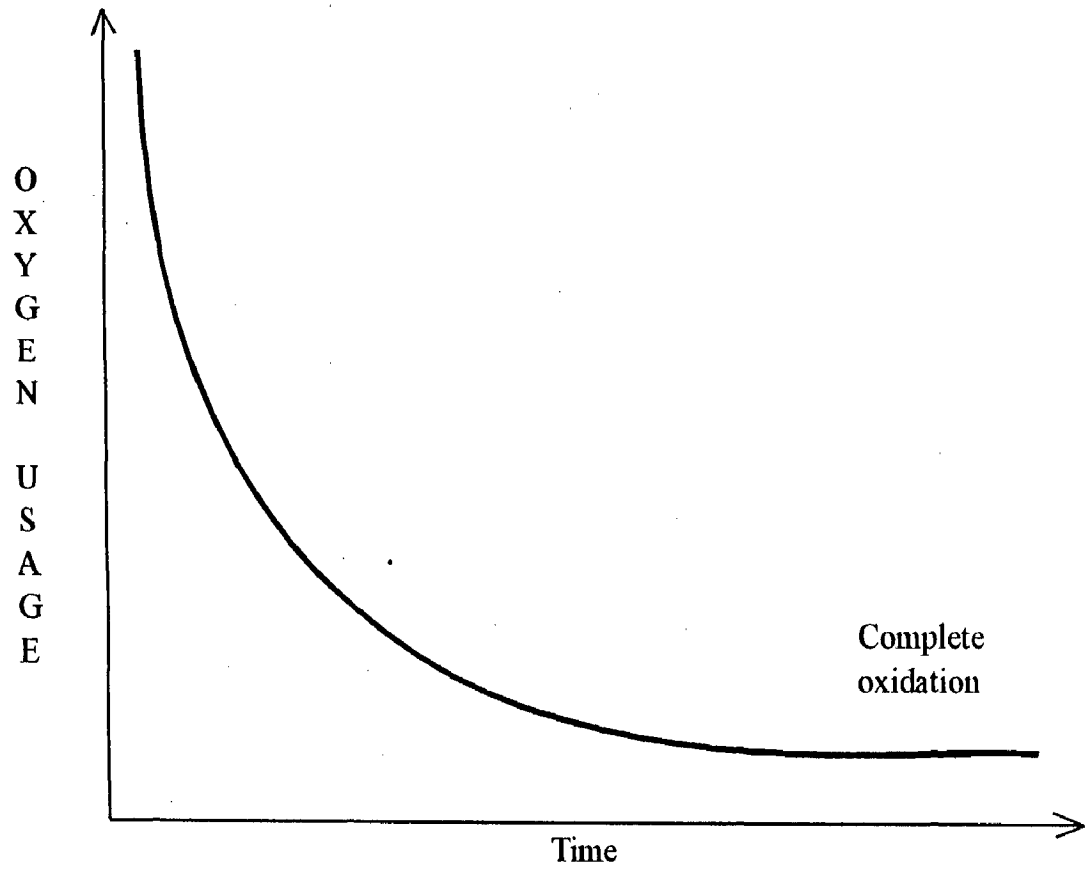


Fig. 1.3 Biological Oxygen Usage as a function of time in an activated sludge process.

In general the bacteria in the activated sludge process include members of the general Pseudomonas, Zoogloea, Achromobacter, Flavobacterium, Nocardia, Bdellovibrio, Mycobacterium, and two most common nitrifying bacteria, Nitrosomonas and Nitrobacter. Additionally, various filamentous forms, such as sphaerotilus, Beggiatoa, Thiothrix, Lecicothrix and Geotrichum, may also be present (Hawkes,1963 and Higgins,1975). While the bacteria are the microorganisms that actually degrade the organic waste in the influent, the metabolic activities of other microorganisms are also important in the activated-sludge system.

Even though excellent flock formation is obtained, the effluent from the system could still be high in biological solids as a result of the secondary settling unit, poor operation of the aeration units, or the presence of filamentous microorganisms such as Sphaerotilus, E. coli and fungi (Higgins, 1975, Jenkins et al, 1986 and WPCF, Manual , 1987).

1.4.1.2 Process Description

Operationally, biological waste treatment with the activated sludge process is typically accomplished using a flow diagram such as that shown in Fig.1.1.

Organic waste is introduced into a reactor where an aerobic bacterial culture is maintained in suspension. The reactor contents are referred to as the "mixed liquor". In the reactor, the bacterial culture carries out the conversion in general accordance with' the stoichiometry shown in equations (1.1) and (1.2).

Oxidation and Synthesis

$$\underset{\text{(Organic matter)}}{\text{COHNS}} + O_2 + \text{nutrients} \xrightarrow{\text{bacteria}} CO_2 + NH_3 + \underset{\text{new bacterial cells)}}{C_5H_7NO_2} + \text{other end products} \quad (1.1)$$

Endogenous respiration :

$$C_5H_7NO_2 + 5O_2 \xrightarrow{\text{bacteria}} 5CO_2 + 2H_2O + NH_3 + \text{energy} \quad (1.2)$$

113 160
1 1.42

In these equations, COHNS represents the organic matter in wastewater. Although the endogenous respiration reaction results in relatively simple end products and energy, stable organic end products are also formed. From equation (1.1), it can be seen that, if all of the cells can be oxidized completely, the ultimate BOD of the cells is equal to 1.42 times the concentration of cells.

The aerobic environment in the reactor is achieved by the use of diffused or mechanical aeration, which also serves to maintain the mixed liquor in a completely mixed regime. After a specified period of time, the mixture of new cells and old cells is passed into a settling tank, where the cells are separated from the treated waste water. A portion of the settled cells is recycled to maintain the desired concentration of organisms in the reactor, and a portion is wasted. The portion wasted corresponds to the new growth of cell tissue, r'_g, associated with a particular wastewater. The level at which the biological mass in the reactor should be kept depends on the desired treatment efficiency and other considerations related to growth kinetics.

If a biological system is to function properly, nutrients must be available in adequate amounts. The principal nutrients are nitrogen and phosphorous. Based on an average composition of cell tissue of $C_5H_7NO_2$, about 12.4 percent by

weight of nitrogen will be required. The phosphorous requirement is usually assumed to be about one-fifth of this value. These are typical values, not the fixed quantities, because it has been shown that the percentage distribution of nitrogen and phosphorous in cell tissue varies with the age of the cell and environmental conditions.

Other nutrients required by most biological systems are reported in Table (1.1). The inorganic composition of E.coli is shown in Table (1.2). The data in Table (1.2) can be used to estimate the concentration of trace elements required to form the maintenance of the proper biological growth. Because the total amount of nutrients required will depend on the net mass of organisms produced, nutrient quantities will be reduced for processes operated with long mean cell-residence times. This fact can often be used to explain why two similar activated sludge plants operated at different mean cell residence time may not perform in the same way when treating the same waste. (wood and Tchobanoglous, 1975).

Table 1.1 : Inorganic ions necessary for most organisms (Kimball,1968)

Substantial quantities	Trace quantities*
Sodium	Iron
Potassium	Copper
Calcium	Manganese
Phosphate	Boron
Chloride	Molybdenum
Sulphate	Iodine
Bicarbonate	Selenium
	Cobalt
	Vanadium

* Requirement depends on the type of the organisms.

Table 1.2 : Inorganic composition of E-Coli (Kimball, 1968)

Element	Percentage of dry-cell weight
Potassium	1.5
Calcium	1.4
Sodium	1.3
Magnesium	0.54
Chloride	0.41
Iron	0.20
Manganese	0.01
Copper	0.01
Aluminium	0.01
Zinc	0.01

1.5 ACCEPTABLE LIMITS OF PHENOLS

Acceptable discharge limits for phenols effluents vary, depending on the nature of the phenols, the volume and rate of discharge and the nature and volume of the receiving water.

The permissible limits for phenols in industrial effluent before being discharged into municipal sewers and surface waters are specified as 5.0 and 1.0 mg/l, respectively, by the regulatory agencies in India. In steel plants, coke oven plants, petroleum refineries etc., phenolic wastewaters are generated at several processing units with phenol concentration varying from 110 to 5000 mg l^{-1}.

1.6 TOXICITY EFFECTS OF PHENOLS

Problems created in receiving water by the presence of phenols in effluents may be classified into three areas :

1. Toxicity to aquatic life,
2. The introduction of BOD leading to oxygen depletion in the water,
3. Taste and odour in water subsequently abstracted and treated for potable purposes.

Generally it is concluded that simple phenols, cresols and xylenols at levels above 0.5 mg/l are unsafe to fish life and may lead to flesh taste. Toxic hazards are increased by a decrease in dissolved oxygen concentration, an increase in salinity and decrease in temperature.

Phenol is readily absorbed by all routes, though it is rapidly conjugated with either sulphate or gluconic acid, followed by elimination of urine. Significant amounts of phenol can be absorbed through the skin of the human forearm if present in concentration of 2.5-10 gl^{-1} in aqueous solutions. In man, the acute toxicity of phenol is characterized by its action on higher centres. Ingestion of large amounts can cause a burning sensation in the body, abdosominal pain, sweating, cyanosis, lowering of body temperature, decreased respiration, loss of reflux activity and it may lead to death due to respiratory failure. In an accidental spillage of a large quantity of phenol, symptoms of phenol poisoning such as burning of mouth, mouth sores, diarrhoea and dark urine were reported in some individuals who consumed contaminated well-water. During 8-months period the daily intake of phenol by these individuals was estimated to be about 10-240 mg/person/day. Chronic poisoning effects reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances. (Fawell and Hunt, 1988).

World Health Organization, recommends the permissible phenolic concentration of 0.001 mg l^{-1} in potable waters (WHO, 1963). A small amount of phenol (0.001 to 0.005 mg l^{-1}) on chlorination in water treatment plant, produces a medicinal taste and the odour of chlorophenol. Generally phenolic compounds are toxic to fish, but they also impact a disagreeable taste to the flesh far below toxic limits (Edmund, 1973). Commercial use of fish exposed for as little as one or two weeks to waters containing 0.02 mg l^{-1} of phenol is impractical because of odours and tastes imparted to the flesh (Resfjord, 1976).

CHAPTER - 2

LITERATURE REVIEW

As far back as 1929, Mohlmann reported that low levels of phenol could be successfully treated by activated sludge. Interest in the treatment of phenolic wastes has not waned and there are several papers available which discuss general design and operational guideline for biological treatment of wastes containing phenolic compounds. The general consensus is that the presence of phenolics enhances susceptibility of a biological process to periodical upsets (Lanoutte, 1977 ; Graves, 1960 and Short 1974).

T.Ide (1966) carried his study on an activated sludge process plant for the treatment of phenolic wastes which had been in operation in Japan since July 1964. Influent to the system, diluted with sanitary wastes and cooling tower water, contains approximately 500 mg/L of phenols. Nutrient nitrogen and phosphorous are added to the system at the ratio of 4.0 and 0.5 parts respectively, per 100 parts of phenols. Dissolved oxygen concentration is 2.0 mg/L and pH is 6.7 to 7.3. Phenols removal of an average of 99.8% have been obtained from this plant. This removal efficiency can be maintained only as long as the phenol sludge loading factor is less than 0.6 Kg phenol/day/kg VSS. At this value sludge production is also negligible. Above this critical loading, however, efficiency gradually decreases, and excess sludge starts to build up.

Phenols recovery is normally intended in cases of liquid wastes with flow rates larger than 10 m^3 h^{-1} and phenol concentration of at least 2000 mg l^{-1} (Wurm, 1968). In some of the industries phenol removal as a pretreatment process

involves the treatment of highly concentrated phenolic water prior to dilution by other process waste streams. For example there are two major techniques practised by petroleum refining industry for the pretreatment of phenols : biological treatment and the use of sour waters as make up to the desalter. Phenol removal efficiency from the desalted water will vary greatly depending on the type of crude being refined.

Activated sludge is an aerobic process, generally considered as most effective biological process for removing organic material with removal efficiencies in the range of 70 to 95% for BOD_5, 30 to 70% COD and 65 to 99% for phenols and cyanides. A large variety of microbes may be used in the process and many of these may be naturally present in the wastes initially. Those present may include various species of Bacillus, Clostridia, Pseudomonas, Myobacteria, Nocardia, such as Nocardia salmonicolor and Nocardia corallina, the yeast like Torula, and the filamentous fungi such as penicillium and phycomyces (Jones, 1973).

Alabaster, J.S.; Calamari, D.; Grande, M.; (1973) studied the water quality criteria with respect to phenols. They presented that the review of the literature concerning the occurrence and effects of phenols in the aquatic environment show that phenolic wastes can contain monohydric phenols, including phenol, the three cresol isomers, and the six xylenol isomers, together with other substances. Laboratory tests show that the toxicity of phenol is increased by decrease in dissolved oxygen, and decrease in temperature. For Fish cresols, xylenols and phenols are of similar toxicity and the toxicity of mixtures of phenols is apparently additive, although the toxicity of phenolic wastes may be greater than expected from chemical analysis, since these may not be equally

sensitive to all phenols and may neglect the contribution from other poisons.

Volesky (1974) found that effluent phenol concentrations of less than 0.2 mg/L could be produced using a 24 hr. mean hydraulic retention time for a combined waste in which the influent phenol concentration was 120 mg/L. Adams (1974) reported similar results using a 2-day detention time.

Phenolic wastewaters from coking plant, steel mill, air craft manufacturing, herbicide manufacturing, petroleum refineries etc. have been treated for many years by adopting activated sludge process and as well as by trickling filter (Hill and Robinson, 1975).

Capestany (1977) reported that an activated sludge plant fed phenol at 1000 mg/L and operated with a mean hydraulic retention time of 24 hr. produced an effluent phenol concentration of 0.5 mg/L. These writers also noted that sulfur was a key nutrient for success of the treatment process. Kostenbader and Flecksteiner (1969) also reported low effluent levels of phenol (less than 1 mg/L) for biological treatment of coke plant ammonia liquor.

In his Pilot plant studies, Holladay (1978) compared the performance of three types of biological reactors degrading phenol-stirred tank, fluidized bed and packed bed. He concluded that activated sludge was the least desirable since it exhibited the lowest degradation rate and was subject to operational upset.

In India none of the phenolic wastewaters bearing industries has identified seperate treatment process for phenol removal. However, biological treatment for phenol removal is practised in a number of industries at which the combined plant effluent is treated biologically for the removal of biochemical oxygen demand in addition to phenol reduction. In other countries, treatment for specific removal of phenol in the sour water stream by biological means has been

identified to be used in refineries.In general, most effective technique for biological treatment appears to be the completely mixed activated sludge process with detention times of about 24 hrs. in the aeration tank. This technique tends to minimize the adverse effects of shock loads of phenols or other pollution parameters (Sittig, 1978).

The results of several kinetic studies indicate conflicting conclusions regarding the need for incorporation of an inhibition function in model equations for predicting effluent substrate and biomass levels in fluidized (activated sludge) reactors treating inhibitory substrates. Neufeld and Valiknac (1979) reported that the Monod model for nonhibitory substrate could suffice for expressing the relationship between specific growth rate and substrate concentration for inhibitory substrates. Also, Beltrame et al. (1979) as a result of batch studies, reported finding no inhibition by phenol at high concentrations. However, a graph depicting some of the kinetic experiments shows a lower substrate utilization rate with increasing initial phenol concentration.Beltrame et al. also confirmed that the value of the advice given by some authors (Eckenfelder and Ford, 1970 ; Fredrickson & Tsuhiya, 1977), that kinetic measurements on degradation process by activated sludge be done in continuous steady-state conditions, rather than in batch, if the design of a continuous plant is of interest.In a second study (1980), these workers found no inhibition in a continuous stirred reactor employing cell recycle. They also felt that the normal Monod expression was sufficient to relate specific growth rate to substrate concentration. On the other hand, Sokol and Howell (1981) conducted batch growth studies using a pure culture harvested from a continuous growth reactor and found that the substrate (phenol) utilization rate increased

with increasing phenol concentrations upto a certain concentration, whereupon it then decreased with increasing phenol concentration.

A study was done by Rozich A.F. and Goudy A.F.(1985) to find the response to shock loads of phenol in an activated sludge pilot plant system with constant recycle sludge concentration. Results were compared to a prediction model. An increase from 500 to 1000 mg/l was tolerated well, which agreed with model predictions. A shock increase from 1000 to 2000 mg/L resulted in a specific growth rate near the critical value; after several days washout of the reactor occurred. The course of the transient following a shock load could not be predicted with satisfactory precision. The model equations can predict conditions which lead to total system failure. Recommendations for use of the model equations in design and operation to avoid such failures are presented.

Galil, N. and Rebhun, M. (1990) presented a comparative study of RBC and Activated sludge in biotreatment of wastewater from an Integrated oil Refinery. They concluded that R.B.C. produced an effluent of better quality, containing lower concentration of suspended ssolids, RBC was more resistant to disturbances caused by increased concentration of phenolic compounds. They finally concluded that the RBC was a promising alternative in the treatment of Industrial wastewater from integrated oil refineries.

Tur Mao-Yuan et al. (1990) in a paper presented in Purdue industrial waste conference discussed about the application of oxygen uptake rate in managing an activated sludge process for treating refinery wastewater. They established a monitoring system which could be used to predict food and microorganism ratio (F/M) and influent's COD; provide the criteria for judging abnormal influent characteristics and distinguish various types of shocks such as normal organic

shock, organic & toxic shock, and inorganic toxic shock.

Sheintuch, M. (1991) presented the design criteria for population selection in activated sludge. He found that the best sludge seperation is achieved when floc-forming bacterial and non-settling filamentous microorganisms co-exist in the reactor, with a small number fraction of filaments. Design criteria determining the largest recycle ratio which can still assure growth of the floc formation were derived for single substrate competition as well as for competition for oxygen and competition coupled with decay.

Lin, S.H. and Chuang, T.S. (1994) studied about the combined treatment of phenolic wastewater by wet air oxidation (WAO) and activated sludge. Their experimental results showed that over 90% removal of phenol or phenolic compounds could be effeciently achieved in the WAO process. Despite of the high treatment wastewater, however, still retained relatively high COD concentration and did not meet the safe discharge standard. Hence, further treatment of WAO treated wastewater by an aerobic biological treatment using acclimated activated sludge was necessary.

Nozaki, J. et al. (1994) in a study of biological removal of cyanide and organics from wastewater determined the performances of activated sludge process in removing toxic wastes. They determined the kinetic parameters, sludge yield, substrate and oxygen utilization, residence time, F/M ratio, COD and cyanide removal efficiency at different retention times and pH. They found that acclimated sludge took at least 10 days to achieve maximum efficiency. They presented that the COD removal efficiency was 84-95% and cyanide removal efficiency was 99.5%-99.8%.

Table 2.1 Phenol and its characteristics (Sax, 1968)

Parameters	Phenol
Molecular formula	C_6H_5OH
Structure	
Description	White crystalline mass which turns pink or red if not perfectly pure; burning taste, distinctive odour.
Toxicity	In acute phenol poisoning, the main effect on the central nervous system. Absorption of phenols by skin is very rapid and death results from collapse within 30 minutes to several hours. Where death is delayed, damage to kidneys, liver, pancreas, spleen and edema of lungs may result. At low concentration exposure results in digestive disturbance, nervous disorders and skin eruptions.
TLV	ACGIH (Accepted); 5 parts per million of air ; 19 mg m^{-3} of air can be absorbed through the intact skin.
Fire Hazard	Moderate, when exposed to heat or flame.
Explosion hazard	——— Nil ———
Disaster hazard	Dangerous; when heated it emits toxic fumes; can react with oxidizing materials.
λ_{max}	270 nm.

Table 2.2 Permissible limits for phenolic concentrations in industrial effluents

Source	Maximum permissible limits as phenols, mgl^{-1}
Public sewer (IS : 3306-1974)	5.0
Surface waters (IS : 2490-1974)	1.0
MINAS (Water bodies) (CPCB, 1981)	1.0
Marine coastal areas (IS : 2490-1974)	5.0

Table 2.3 Sources of phenols and other related aromatic compounds in wastewater (Kumaran and Paruchuri, 1997)

Source	Significant Phenolic Compounds
Petroleum refining	Hydrocarbons (alkanes, cycloalkanes, polyaromatic hydrocarbons), benzenes, substituted benzenes, toluenes, n-octanes, n-decanes, naphthalenes, biphenyls, phenol, cyanide, sulphide and ammonia Naphthalene, hepatanes, benzenes, butadiene,C-4 alcohols, phenol and resorcinol
Petrochemicals and basic organic chemical manufacture	m- amino phenol, resorcinol, dinitrophenol, p-nitrophenol, trinitrophenol, benzene sulphonic acids, anniline, chlorobenzenes, toluene and resorcinol
Coal refining	Phenol, catechol, o-m-,p-cresols, resorcinol, hydroquinone, pyrogallol, polyaromatic hydrocarbons, pyridines, pycolines, lutidines, xylenes, toluenes, benzoic acid
Pharmaceuticals	Toluenes, benzyl alcohols, phenyl acetic acid, chlorinated products of benzene, chloroform, ether, ethyl alcolhol
Tannery	Tannin, catechin,phenol, chlorophenol, nitrophenols
Pulp and paper mills	Lignin, vanillin, vanillic acid, dehydrodivanillin, ferulic acid, cinnamic acid, synringic acid, vieratic acid, protocatechuic acid, gentisic acid, benzoic acid, guadiachols, catechol, coniferyl alcohol, dehydrodihyroconiferyl alcohol, phenyl propionic acid, phenols and chlorophenols

Table 2.4 Concentration of phenolic compounds in coal carbonization and gasification wastewaters (Kumaran and Paruchuri, 1997)

Phenolics	Gas plant effluent ($mg\ l^{-1}$)	Low temperature carbonization effluent ($mg\ l^{-1}$)	Coke oven effluent ($mg\ l^{-1}$)
Phenol	131.25	3395	283.5
Catechol	31.90	1955	16.2
Cresols	114.50	1425	95.0
Resorcinol	11.25	770	14.8
Hydroquinone	1.55	61	21.9

Table 2.5 Maximum allowable limits of important pollutants in treated waste-waters from petroleum refineries (MINAS-Oil refineries, 1982)

Pollutants	Concentration mgl^{-1}	Quantum, kg/1000 tonne crude processed
Oil and grease	10.0	7.0
Phenol	1.0	0.7
Sulphide	0.5	0.35
BOD	15.0	10.0
Suspended solids	20.0	14.0
pH	6.0-8.5	6.0-8.5

Table 2.6 Discharge standards for phenols/phenolic compounds for different industries (CPCB, 1995)

Sl. No.	Industry	Parameters	Max. allowable concentration mg l^{-1}
1.	Oil refinery	Phenol	1.0
2.	Cotton & Textile	Phenolic compounds (as phenol)	5.0
3.	Composite and woollen Mills	Phenolic compounds (as phenol)	5.0
4.	Dye and dye intermediate	Phenolic compounds	1.0
5.	Coke ovens	Phenolic compounds (as phenol)	5.0
6.	Integarted iron and steel plant	Phenol	1.0
7.	Petrochemicals	Phenol	5.0*
8.	Pharmaceutical manufacturing and formulation	Phenolic (as phenol)	1.0
9.	Pesticide manufacturing and formulating	Phenol and Phenolic compounds	1.0
10.	Paint	Phenolics (as phenol)	1.0
11.	Common Effluent treatment plants	Phenolic (as phenol)	5.0

* Not to exceed 1.0 mg l^{-1} at the final disposal point.

KINETIC MODEL FOR ACTIVATED SLUDGE PROCESS

In the complete mix system shown schematically in Fig. 3.1, the contents of the reactor are mixed completely, and it is assumed that there are no microorganisms in the wastewater influent. Because of the solids separation unit, two additional assumptions must be made in the development of the kinetic model for this system :

1. Waste stabilization by the microorganisms occurs only in the reactor unit. This assumption leads to a conservative model (in some systems there may be some waste stabilization in the settling unit).
2. The volume used in calculating the mean cell residence time for the system includes only the volume of the reactor unit.

The mean hydraulic retention time for the system θ_S is defined as

$$\theta_S = \frac{V_T}{Q} = \frac{V_r + V_S}{Q} \qquad (3.1)$$

where, V_T = volume of reactor plus volume of settling tank

Q = influent flow rate

V_r = Volume of reactor

V_S = Volume of settling tank

The mean hydraulic retention time for the reactor θ is defined as,

$$\theta = \frac{V_r}{Q} \tag{3.2}$$

For the system of Fig. 3.1(a), the mean cell residence time θ_C, defined as the mass of organisms in the reactor divided by the mass of organisms removed from the system each day, is given by the following expression :

$$\theta_C = \frac{V_r X}{Q_w X + Q_e X_e} \tag{3.3}$$

where, Q_w = Flow rate of liquid containing the biological cells to be removed (wasted)from the system (in this case from the reactor).

Q_e = Flow rate of liquid from the separation unit.

X_e = Microorganisms concentration in effluent from solids separation unit.

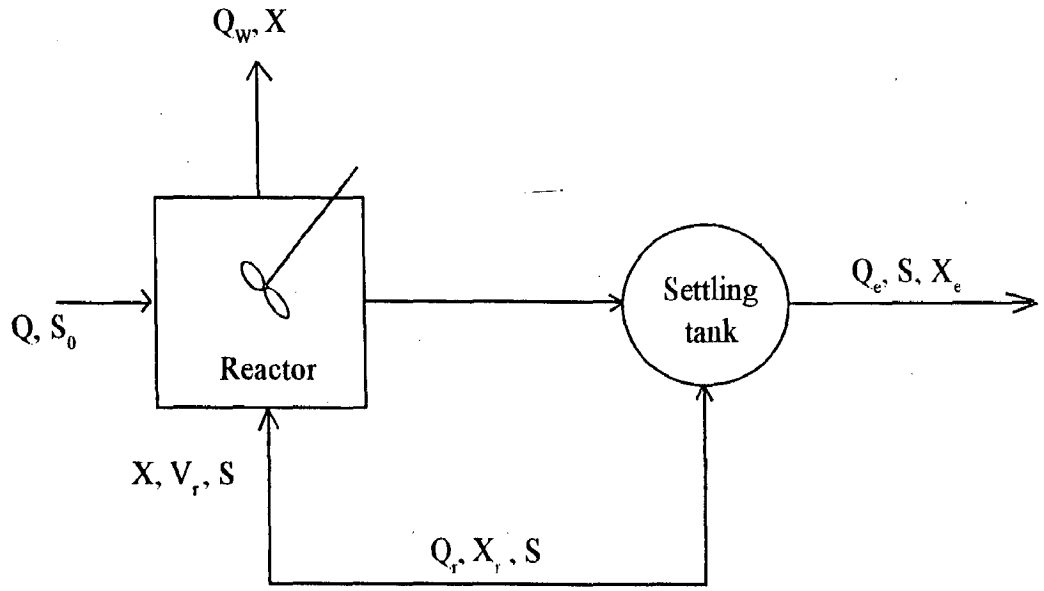
For the system in Fig. 3.1(b), the mean cell residence time θ_C is given by the following expression.

$$\theta_C = \frac{V_r X}{Q'_w X_r + Q_e X_e} \tag{3.4}$$

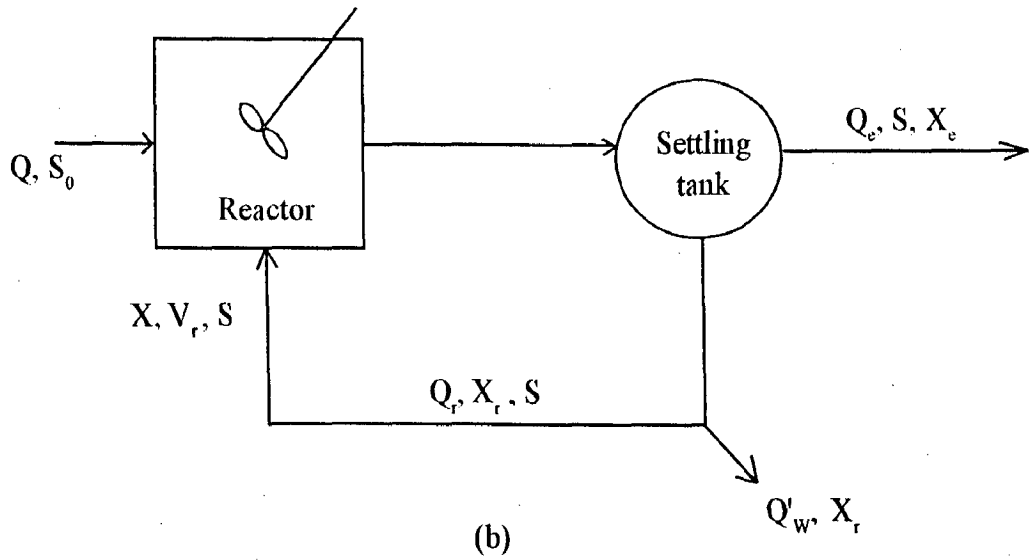
where, X_r = microorganism concentration in return sludge line

Q'_w = cell wastage rate from recycle line

Refering to Fig. 3.1(a), a mass balance for the microorganisms in the entire system can be written as follows :



(a)



(b)

Fig. 3.1 Schematic of complete mix reactor with cellular recycle and wasting (a) from the reactor and (b) from the recycle line.

Rate of accumulation of microorganism within the system boundary	=	Rate of flow of microorganism into the system boundary	-	Rate of flow of microorganism out of the system boundary	+	New growth of microorganism within the system boundary

i.e. Accumulation = Inflow - Outflow + Net growth

$$\text{or,} \quad \frac{dX}{dt} V_r = QX_0 - [Q_w X + Q_e X_e] + V_r (r'_g) \qquad (3.5)$$

where, X_0 = concentration of microorganisms in influent, mass VSS/unit vol.

X = concentration of cells, mass VSS/unit volume

r'_g = net rate of bacterial growth, mass/unit volume. time

r'_g can be mathematically represented as,

$$r'_g = -Y r_{su} - K_d X \qquad (3.6)$$

$$\text{where,} \quad r_{su} = -\frac{\mu_m X S}{Y (K_S + S)} \qquad (3.7)$$

r_{su} = substrate utilization rate, mass/unit volume time.

μ_m = maximum specific growth rate, time^{-1}.

S = substrate concentration in effluent mg/L.

Y = maximum yield coefficient, mg/mg.

K_d = endogenous decay coefficient, time^{-1}.

K_S = saturation constnat or half velocity constant, substrate concentration at one half of the maximum growth rate, mass per unit volume.

$\frac{\mu_m}{Y}$ = K, where K is maximum rate of substrate utilization per unit mass of microorganisms.

In equation (3.5) assuming that the cell concentration in the influent is zero and steady state conditions prevail (dX/dt=0) and substituting equation (3.6).

$$\frac{Q_w X + Q_e X_e}{V_r X} = - Y \frac{r_{su}}{X} - K_d \qquad (3.8)$$

or, $$\frac{1}{\theta_C} = - Y \frac{r_{su}}{X} - K_d \qquad (3.9)$$

The term r_{su} is determined using the following equation :

$$r_{su} = - \frac{Q}{V_r} (S_0 - S) = - \frac{S_0 - S}{\theta} \qquad (3.10)$$

where, $(S_0 - S)$ = mass concentration of substrate utilized, mg/L.

S_0 = substrate concentration in influent, mg/L.

θ = hydraulic detention time, d.

On solving the equations (3.9) and (3.10) for X, we have

$$X = \frac{\theta_C Y (S_0 - S)}{\theta (1 + K_d \theta_C)} \qquad (3.11)$$

Performing a substrate balance, the effluent substrate concentration is found to be equal to

$$S = \frac{K_S (1 + \theta_C K_d)}{\theta_C (Y K - K_d) - 1} \qquad (3.12)$$

Equations (3.11) and (3.12) are useful in predicting the effects of various system changes.

In laboratory, an aerobic treatment process carried out in a complete mix reactor without recycle (Fig. 4.1), such as a chemostat (Fig. 4.2).

As stated previously, for this case we can see,

$$\frac{dx}{dt} V_r = QX_o - QX + V_r r'_g \qquad (3.13)$$

substituting the value of r'_g from equation (3.6) in the above equation,

$$\frac{dx}{dt} V_r = QX_o - QX + V_r (-Y r_{su} - K_d X)$$

$$= QX_o - QX + V_r \left[\frac{\mu_m XS}{K_S + S} - K_d X\right] \qquad (3.14)$$

If it is assumed that the concentration of microorganisms in the influent can be neglected and that steady state conditions prevail (dX/dt = 0), equation (3.14) can be simplified to yield,

$$\frac{Q}{V_r} = \frac{1}{\theta} = \frac{\mu_m S}{K_S + S} - K_d \qquad (3.15)$$

where, θ = hydraulic detention time, V/Q

The term $1/\theta$ corresponds to $1/\theta_c$. In the field of wastewater treatment, θ_c may be defined as the mass of organisms in the reactor divided by the mass of organisms removed from the system each day. For the reactor shown in Fig. 4.1, θ_c is given by the following expression :

$$\theta_c = \frac{V_r X}{QX} = \frac{V_r}{Q} \qquad (3.16)$$

Performing a substrate balance corresponding to the microorganism mass balance given in equation (3.14) results in the following expression

$$\frac{dS}{dt} V_r = QS_o - QS - V_r \left[\frac{KXS}{K_S + S}\right] \qquad (3.17)$$

At steady state $\left[\frac{dS}{dt} = 0\right]$, the resulting equation is

$$(S_0 - S) - \theta \left[\frac{KXS}{K_S + S}\right] = 0 \qquad (3.18)$$

where $\theta = V_r/Q$

On solving the equations (3.15) and (3.18) the effluent steady state concentration is found to be given as

$$X = \frac{\mu_m (S_o - S)}{K(1 + K_d \theta)} = \frac{Y (S_o - S)}{(1 + K_d \theta)} \qquad (3.19)$$

Similarly, the effluent substrate concentration is found to be equal to,

$$X = \frac{K_S(1+\theta K_d)}{\theta (YK - K_d) - 1} \qquad (3.20)$$

The values of the biokinetic parameters such as Y, K, Ks and K_d can be determined with the help of the above equations.

Table 3.1 Typical kinetic coefficients for the activated sludge process for domestic wastewater (Metcalf and Eddy, 1995)

Coefficient	Basis	Value	
		Range	Typical
Maximum rate of substrate utilization (K)	day^{-1}	2-10	5
Saturation constant (K_s)	mg/L BOD_5	25-100	60
	mg/L COD	15-70	40
Maximum yield coefficient (Y)	mg VSS/mg BOD_5	0.4-0.8	0.6
Endogenous decay coefficient (K_d)	day^{-1}	0.025-0.075	0.06

EXPERIMENTAL WORK

4.1 WORK PLAN

The main object of the experiment was to establish biokinetic parameters for the biological oxidation of phenolic waste with the help of activated sludge process. In order to establish the biokinetic parameters, experiments were carried out in batch and in 2L bioreactor in the laboratory

The data so obtained were used to determine the different kinetic parameters i.e., maximum yield coefficient (Y), endogenous decay coefficient (K_d), saturation constant or half velocity constant (K_s) and maximum rate of substrate utilization per unit mass of microorganisms (K).

Kinetic parameters from the experimental data were obtained assuming that Monod's equations holds good in the present case.

4.2 STEPS INVOLVED IN THE EXPERIMENT

The various steps which were involved in the experimental work include preperation of seed culture, batch experiments and studies on 2L bioreactor. Details of these are given below:-

4.2.1 Preperation of seed culture

A seed culture for the present study was developed from a sewage obtained from the pumping station of the municipal wastewater plant at Machhi Manigram,

Roorkee. The seed was initially grown on glucose as a source of carbon and later on gradually acclimated to phenol as source of carbon.

4.2.2 Batch experiments

Batch experiments were conducted to get the optimum temperature for the removal of phenol. Five different concentrations (from 100 ppm to 800 ppm) of phenols were taken in 5 conical flasks. In each of the flasks one ml of seed culture was added and the COD of each of the flasks were determined. All of the flasks were kept at different temperatures of 20^0C, 28^0C and 37^0C , for two days. At the end of 2 days, the COD of the mixture in each of the flasks were defermined.

4.2.3 Experiments on bioreactor

The reactor was operated at a temperature of 30^0C. The study was done in four steps. In every step the initial phenol concentration was kept constant. In this way the initial phenol concentrations which were taken in each of the steps were 325 mg/l, 350 mg/l, 375 mg/l and 400 mg/l respectively.

For each of the initial phenol concentration the value of volatile suspended solids was kept varying. The residual phenol concentrations in the reactor were determined after 6 hrs., 24 hrs., 30 hrs., 40 hrs.

In this way we obtained different sets of data for initial phenol concentration (So), volatile suspended solids concentration (X), Final or residual phenolic concentration in the bioreactor (S) and hydraulic retentions (θ). These data are used in determining the value of biokinetic parameters.

4.3 SYNTHETIC PHENOLIC WASTE COMPOSITION

Set (i) Phenol = 325 mg

$(NH_4)_2\ SO_4$ = 118 mg

KH_2PO_4 = 4.33 mg

K_2HPO_4 = 11.19 mg

$Na_2HPO_4.12\ H_2O$ = 23.02 mg

Dissolved in 1L of tap water

C : N : P = 100:10:2

Set (ii) Phenol = 350 mg

$(NH_4)_2\ SO_4$ = 126 mg

KH_2PO_4 = 4.67 mg

K_2HPO_4 = 12.06 mg

$Na_2HPO_4.12\ H_2O$ = 24.79 mg

Dissolved in 1L of tap water

C : N : P = 100:10:2

Set(iii) Phenol = 375 mg

$(NH_4)_2\ SO_4$ = 135 mg

KH_2PO_4 = 5.0 mg

K_2HPO_4 = 12.92 mg

$Na_2HPO_4.12\ H_2O$ = 26.56 mg

Dissolved in 1L of tap water

C : N : P = 100:10:2

Set(iv) Phenol = 400 mg

$(NH_4)_2\ SO_4$ = 145 mg

KH_2PO_4 = 5.33 mg

K_2HPO_4 = 13.78 mg

$Na_2HPO_4.12\ H_2O$ = 28.33 mg

Dissolved in 1L of tap water

C : N : P = 100:10:2

4.4 EXPERIMENTAL SETUP OF BIO REACTOR

The experimental setup of bioreactor system is shown in detail in fig. (4.2). The reactor used in the present study was a 2 L capacity Aspirator bottle. To start with 1.3 L of the phenolic waste was taken in the reactor.

In order to maintain aerobic conditions within the reactor, compressed air was passed with the help of a porous diffuser.

4.5 CHEMICAL ANALYSIS

4.5.1 Phenol analysis

For the determination of the concentration of phenol the Direct photometric method (Manual, NEEERI) was used. The principle of this method is described below:-

First we removed the suspended solids from the sample by filtering it through a Whatman filter. Now small amount of filtrate was distilled. The amount of distillate could vary from 10 ml to 100 ml. This distillate reacted with 4-aminoantipyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide. Now we got a coloured antipyrene dye. This dye was kept in an aqueous solution and the absorbance was measured at 510 nm.

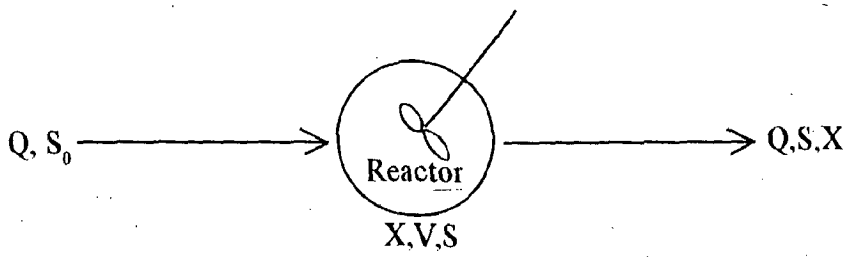


Fig. 4.1 Schematic of a complete mix reactor without recycle

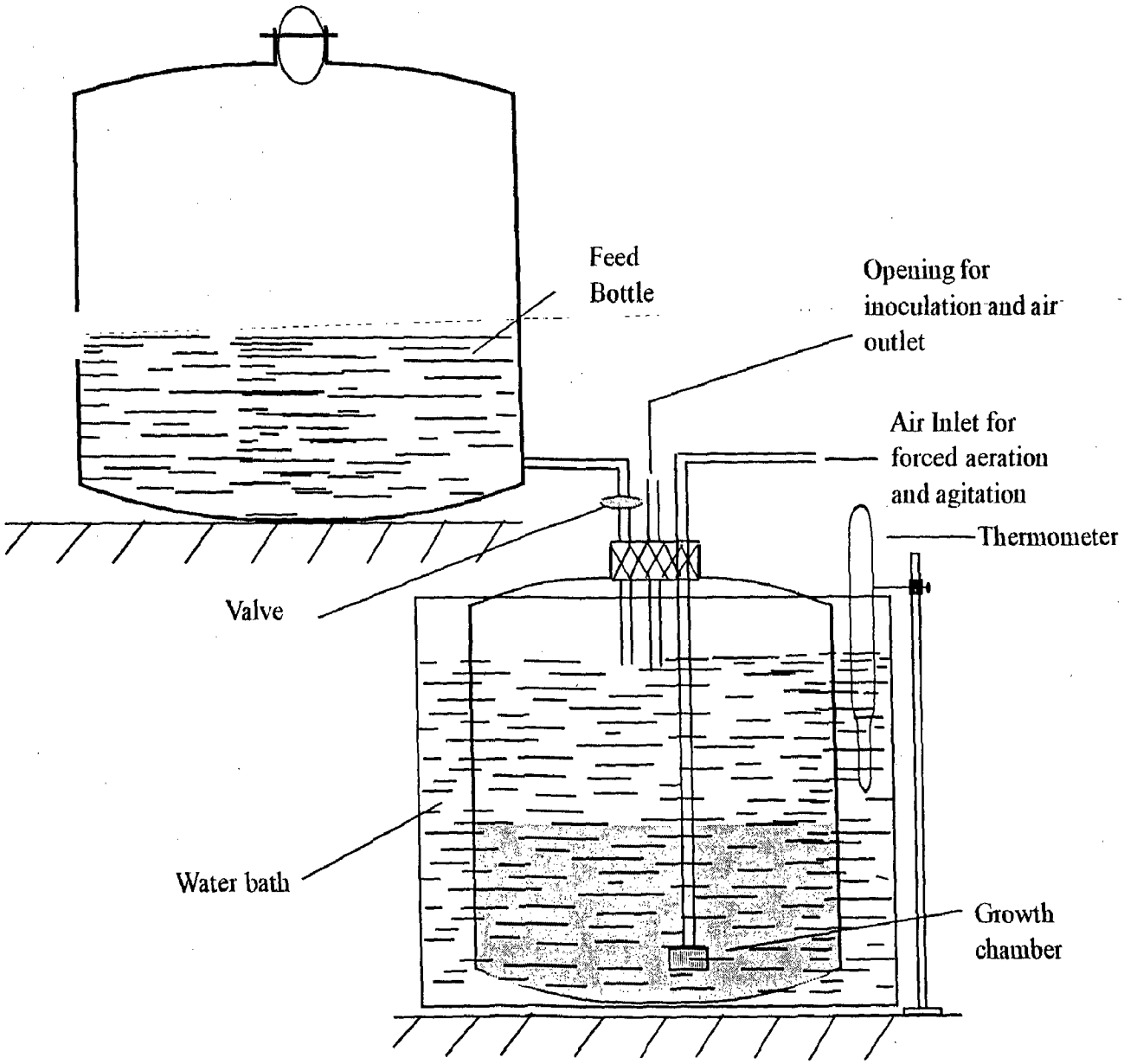


Fig. 4.2 Experimental setup of bioreactor

4.5.2 Analysis of Volatile suspended solids

In order to measure the concentration of volatile suspended solids the following procedure was adopted.:-

The sample was filtered through Whatman filter paper. This filter was dried at 100-105^{0}C. Now the weight of this filter paper was taken. Suppose it came out to be A mg. The filter paper was now heated at 500 ^{0}C for 20 minutes. After then we weighed the ash, suppose it came out to be B mg.

Now, the concentration of volatile suspended solids was calculated as,

$$\text{VSS (mg/l)} = \frac{\text{A(mg) - B (mg)}}{\text{Volume of sample (ml)}} \times 1000$$

4.5.3 COD estimation

The COD of the samples were determined as prescribed in IS 3025. The COD of the sample was calculated by formula :-

$$\text{COD (mg/l)} = \frac{\text{(A-B). C x 8000}}{\text{ml. of sample}}$$

where, A = ml. of Ferrous ammonium sulphate used for blank solution.

B = ml. of Ferrous ammonium sulphate used for the sample.

C = Normality of the Ferrous Ammonium sulphate.

CHAPTER 5

RESULTS AND DISCUSSIONS

The evaluation of the performance of bioreactor for the treatment of phenolic waste was done. First, the optimum temperature was determined for the removal of phenols through batch experiments. After then the study on bioreactor was started at that optimum temperature.

The effect of various operating factors such as temperature, initial phenol concentration in the bioreactor (S_0), the voltaile suspended solids concentration or microorganism concentration (X), the residual phenol concentration(S) and the hydraulic retention time (θ) were seen.

5.1 DETERMINATION OF OPTIMUM TEMPERATURE

The effect of temperature on the removal of phenol was seen at three different temperatures of 20^0C, 28^0C and 37^0C. The data obtained at these temperatures are shown in tables 5.1, 5.2 and 5.3. Fig.5.1 shows the plot of these data in terms of temperatures (^{0}C) Vs percentage removal of COD. From the plot we concluded that the optimum phenol removal occurred at around 30^0C.

Table 5.1

Batch experiments at $20^{o}C$

Flask No.	Initial COD (mg/l)	Final COD (mg/l)	Percentage removal
1.	1945	1945	0
2.	1470	620	58
3.	995	310	69
4.	515	88	83
5.	280	(≅30)	90

Table 5.2

Batch experiments at $28^{o}C$

Flask No.	Initial COD (mg/l)	Final COD (mg/l)	Percentage removal
1.	1945	1945	0
2.	1470	590	60
3.	995	280	72
4.	515	67	87
5.	280	(≅30)	90

Table 5.3

Batch experiments at $37^{o}C$

Flask No.	Initial COD (mg/l)	Final COD (mg/l)	Percentage removal
1.	1945	1945	0
2.	1470	660	55
3.	995	370	63
4.	515	135	74
5.	280	(≅30)	90

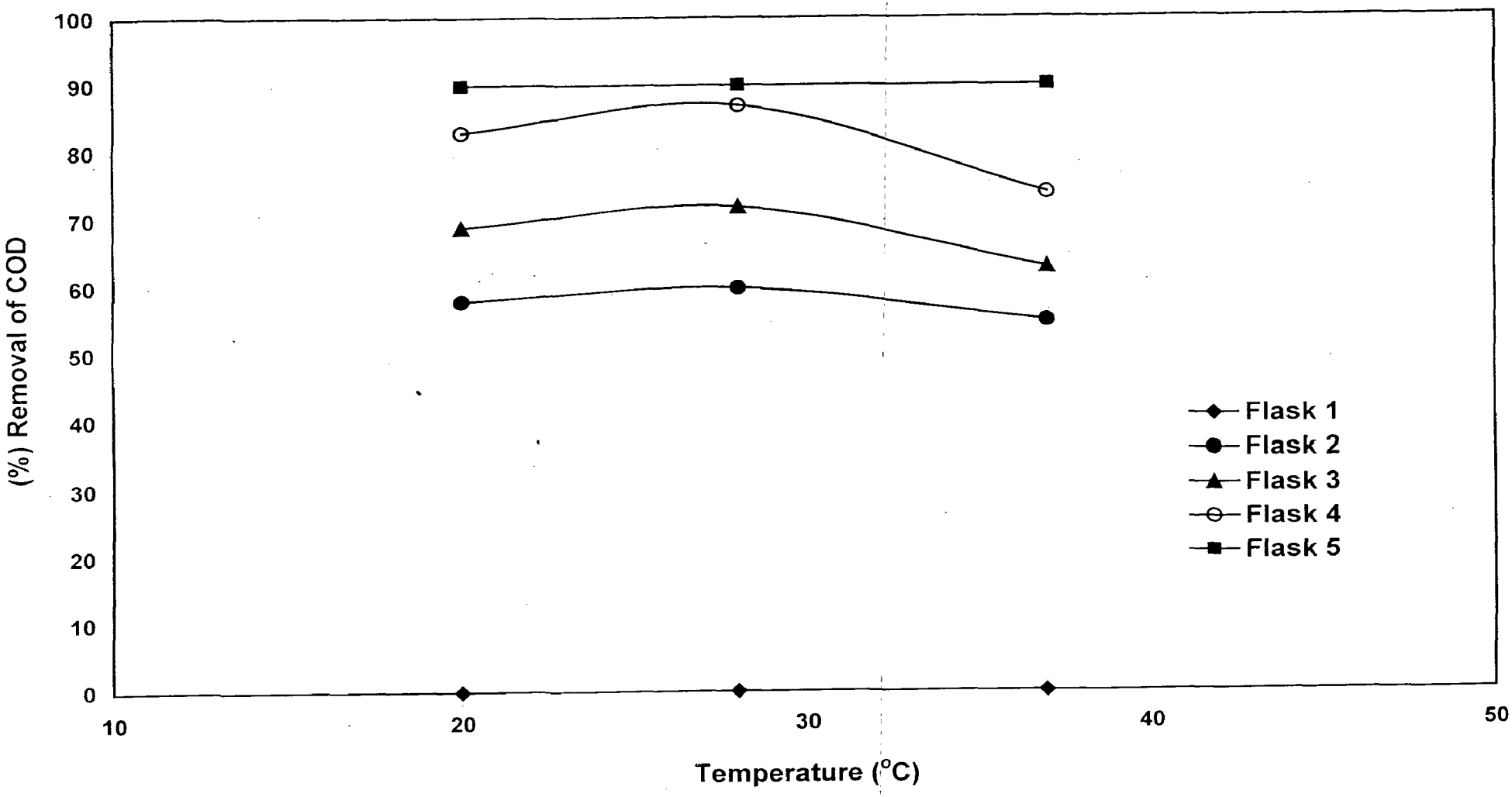


Fig. 5.1 : Percentage Removal of COD from Five Different Concentrations of Phenolic Solutions at Different Temperatures

5.2 MONOD'S EQUATION FOR THE BIODEGRADATION OF ORGANICS

Monod's equation for the biodegradation of organics in wastewaters can be expressed as :

$$\frac{X\,\theta}{S_0 - S} = \frac{K_S}{K}\frac{1}{S} + \frac{1}{K} \qquad (5.1)$$

$$\frac{1}{\theta} = \frac{Y\,(S_0 - S)}{X\,\theta} - K_d \qquad (5.2)$$

where,

K_S = half velocity constant,

K = rate of substrate utilization,

K_d = decay coefficient.

Equation (5.1) shows a linear relation between $\frac{1}{S}$ and $\frac{X\theta}{S_0 - S}$.

Equation (5.2) shows a linear relation between $1/\theta$ and $\frac{(S_0 - S)}{X\,\theta}$.

5.3 DETERMINATION OF BIOKINETIC PARAMETERS

Figure (5.2) shows the plot of 1/S and $\frac{X\theta}{S_0 - S}$ when S_0 = 325 mg/l. After plotting the data a straight line is obtained whose equation is

$$\frac{X\theta}{S_0 - S} = 54.12\,\frac{1}{S} + 0.20 \qquad (5.3)$$

On comparing the above equation with equation (5.1), the values of K_S and K are obtained as,

K_s = 266.5 mg/l,

K = 4.92 per day.

Table 5.4

Kinetic runs at $30^{o}C$,

with phenol concentration

at zero time (S_0) = 325 mg/l

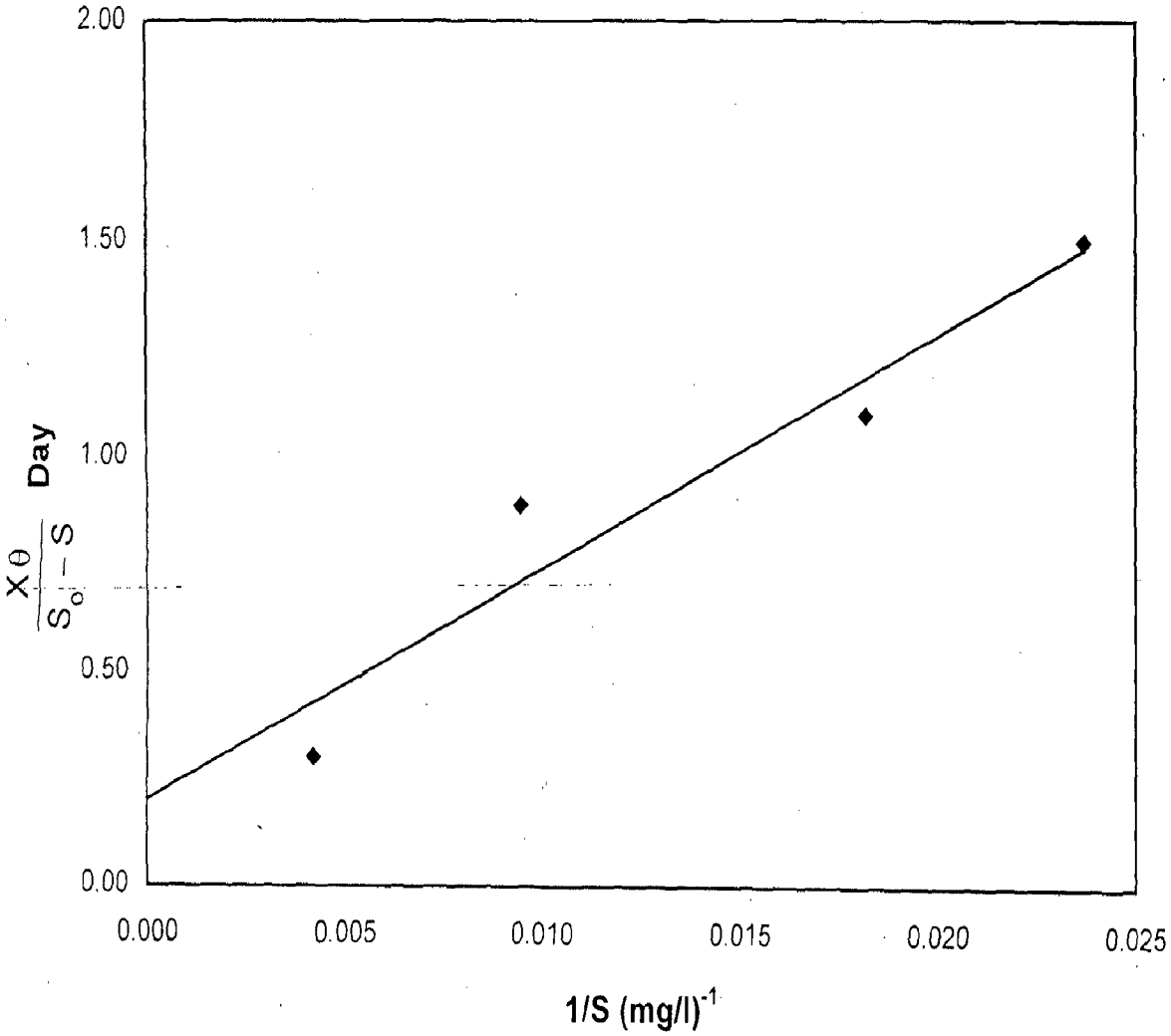
Phenol concentration in reactor (S),mg /l	Time(θ) Days	MLVSS(X) mg/l	Percentage removal (%)
240	0.25	105	27.0
105	1	195	67.7
55	1.25	240	83.0
40	2	210	87.1

Table 5.5

$1/S,(mg/l)^{-1}$	$\frac{X\theta}{(S_0-S)}$, day
0.0042	0.30
0.0095	0.89
0.0182	1.10
0.0237	1.50

Table 5.6

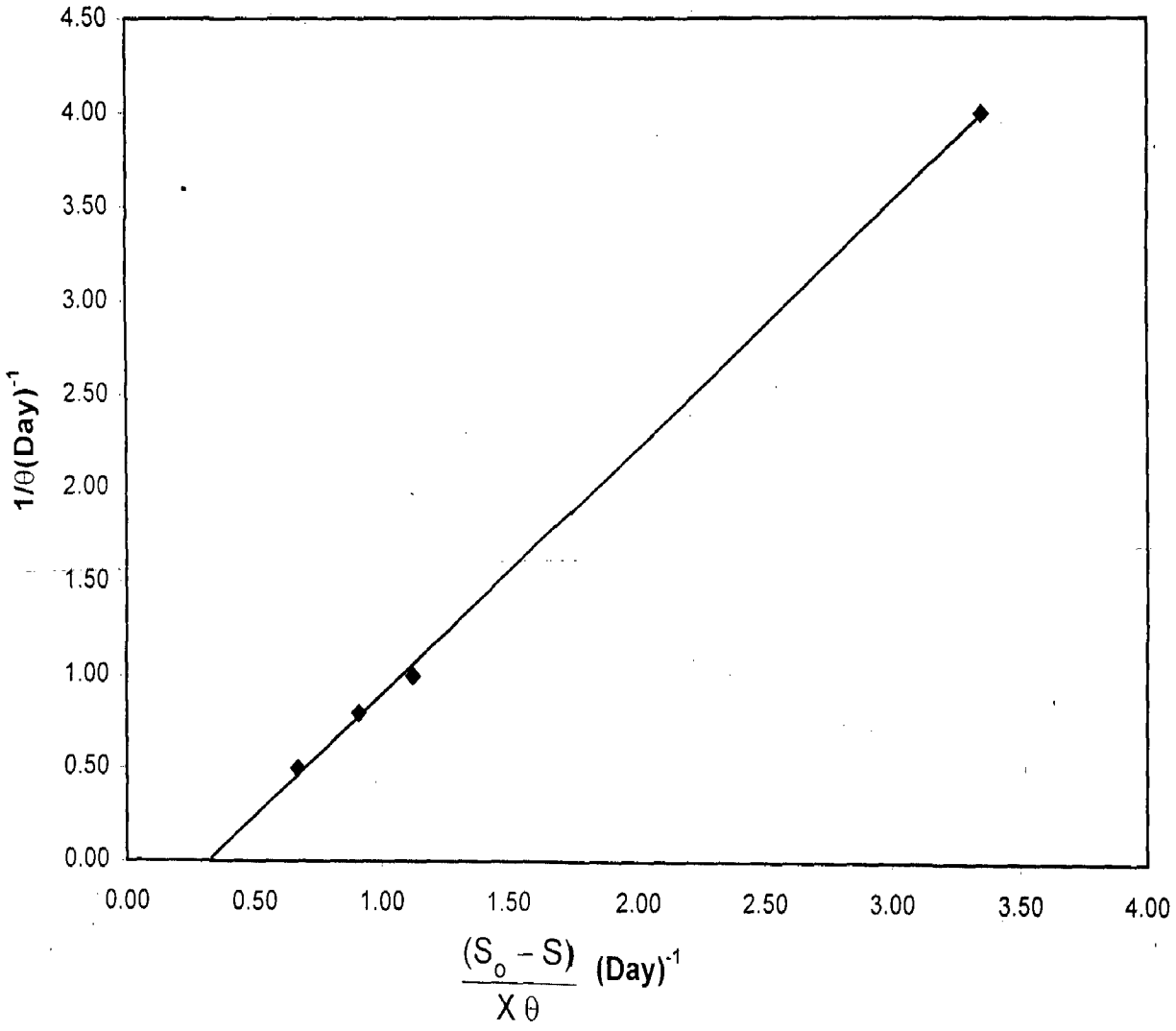
$\frac{(S_0-S)}{X\theta}$, day^{-1}	$1/\theta$, day^{-1}
3.35	4
1.124	1
0.91	0.8
0.67	0.5



Equation of Line

$$\frac{X\theta}{S_o - S} = 54.121\frac{1}{S} + 0.20$$

Fig. 5.2 : Plot of Monod's First Equation at S_o = 325 mg/l



Equation of Line

$$\frac{1}{\theta} = 1.316\left(\frac{S_o - S}{X\theta}\right) - 0.42$$

Fig. 5.3 : Plot of Monod's Second Equation at S_o = 325 mg/l

Table 5.7

Kinetic runs at 30^0C,

with phenol concentration

at zero time (S_0) = 350 mg/l

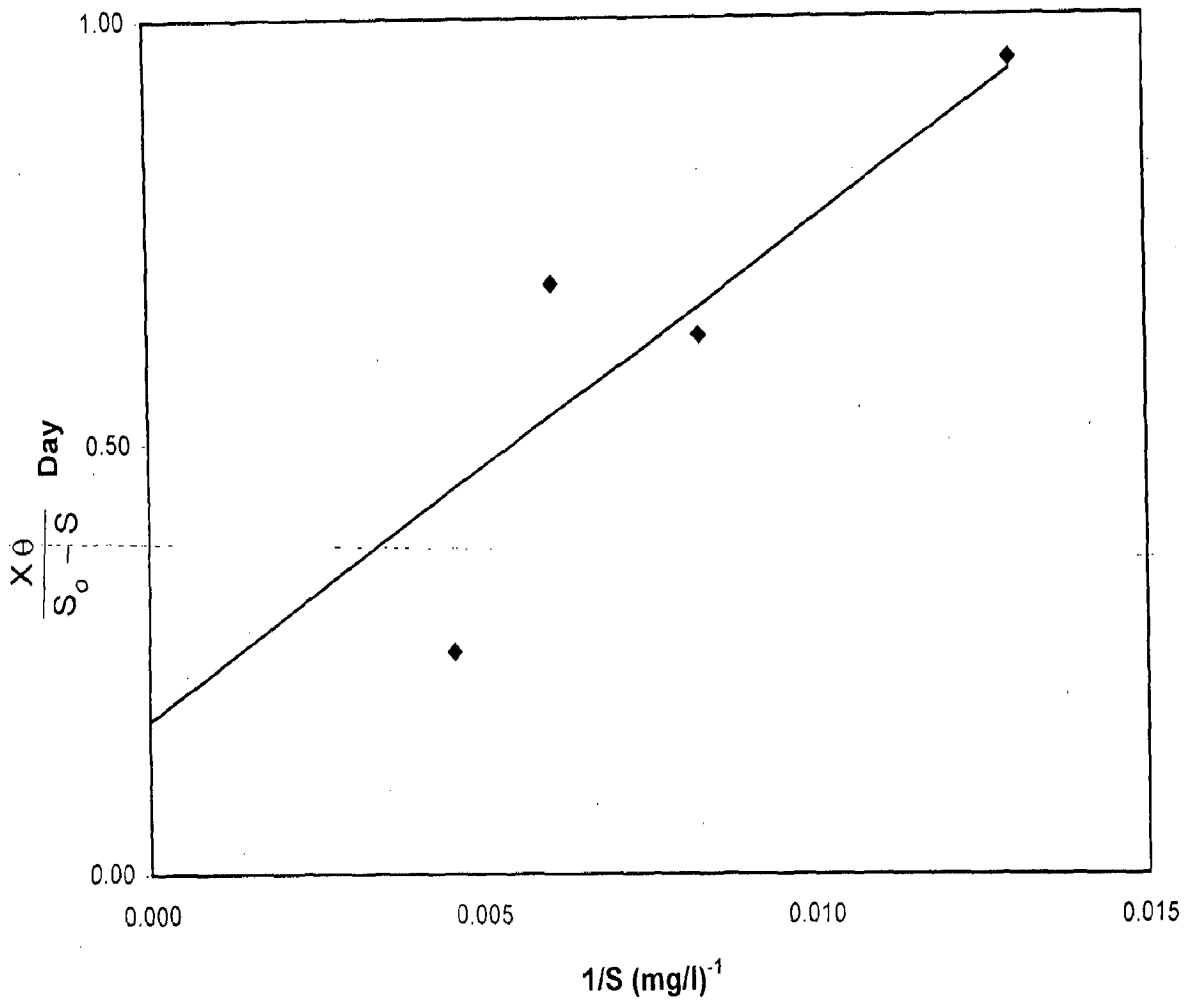
Phenol concentration in reactor (S),mg /l	Time(θ) Days	MLVSS(X) mg/l	Percentage removal (%)
200	0.25	140	42.0
120	1	145	65.4
165	1.25	100	53.1
75	2	130	78.0

Table 5.8

$1/S$, $(mg/l)^{-1}$	$\frac{X\theta}{(S_0-S)}$, day
0.0046	0.23
0.0083	0.63
0.0061	0.66
0.0130	0.95

Table 5.9

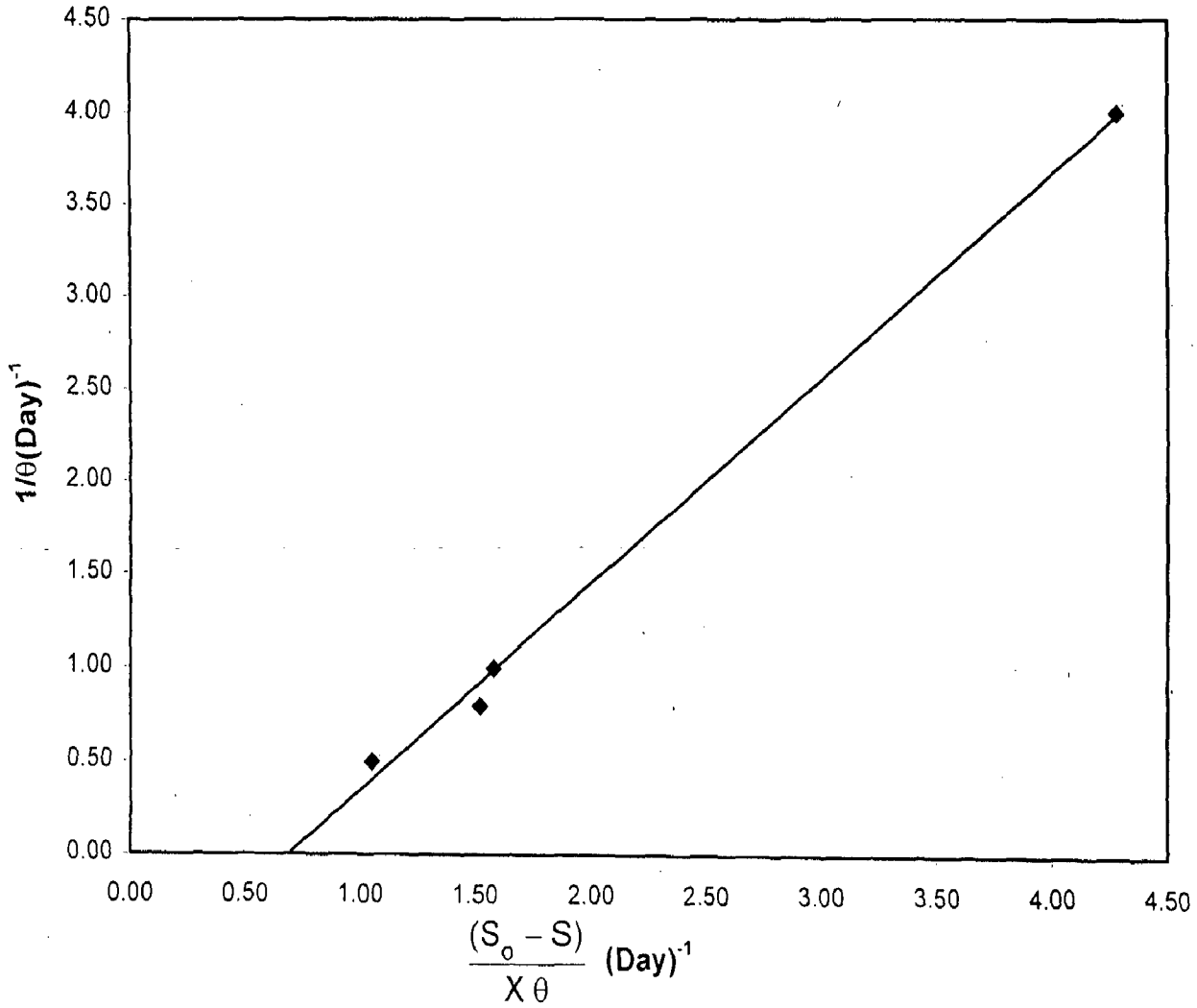
$\frac{(S_0-S)}{X\theta}$, day^{-1}	$1/\theta$, day^{-1}
4.28	4
1.58	1
1.52	0.8
1.05	0.5



Equation of Line

$$\frac{X\theta}{S_o - S} = 57.055\,\frac{1}{S} + 0.18$$

Fig. 5.4 : Plot of Monod's First Equation at S_o = 350 mg/l



Equation of Line

$$\frac{1}{\theta} = 1.025\left(\frac{S_o - S}{X\theta}\right) - 0.76$$

Fig. 5.5 : Plot of Monod's Second Equation at S_o = 350 mg/l

Table 5.10

Kinetic runs at 30°C,

with phenol concentration

at zero time (S_0) = 375 mg/l

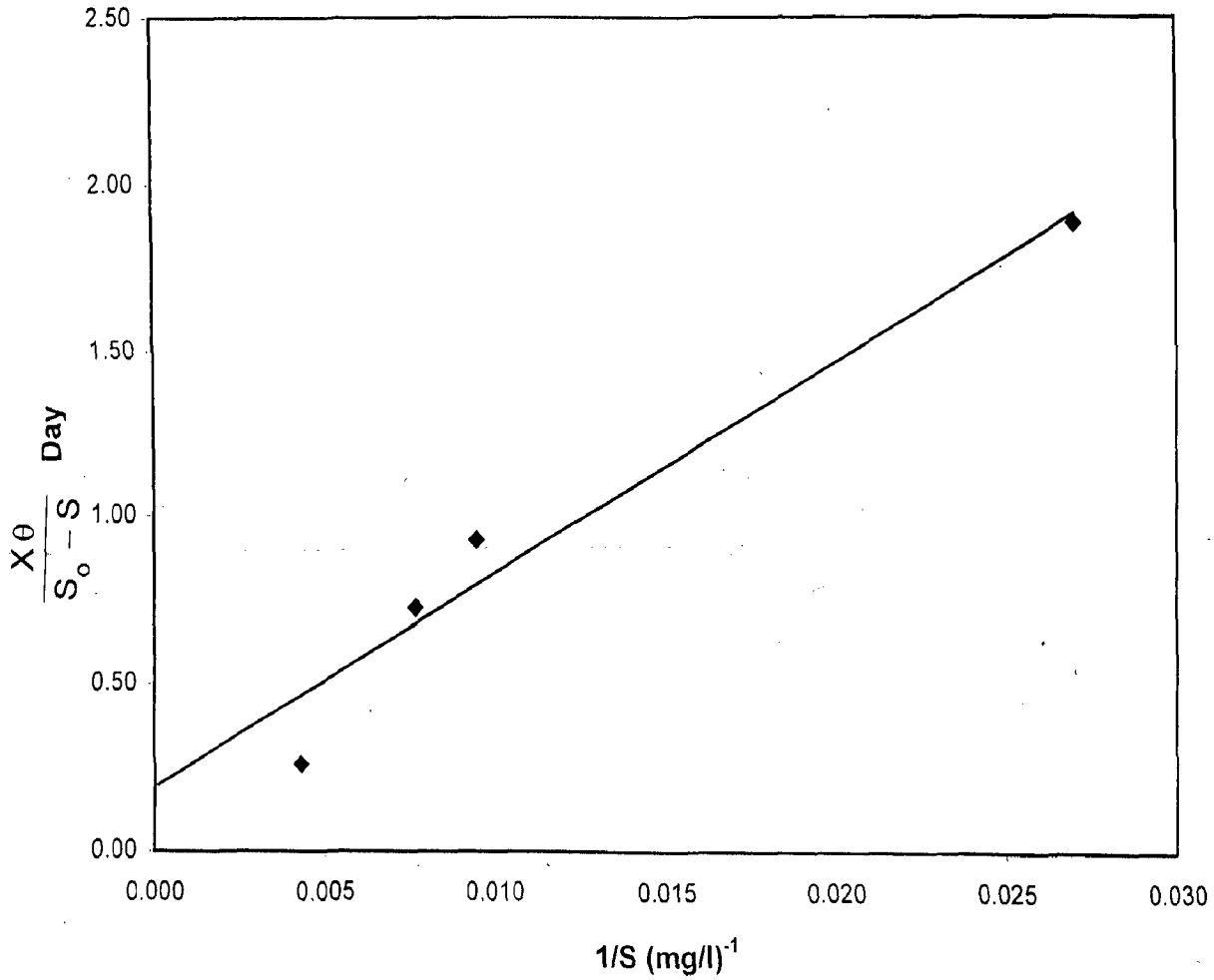
Phenol concentration in reactor (S),mg /l	Time(θ) Days	MLVSS(X) mg/l	Percentage removal
235	0.25	145	37.3
130	1	180	65.6
105	1.25	200	72.0
35	2	320	90.1

Table 5.11

$1/S$, $(mg/l)^{-1}$	$\frac{X\theta}{(S_0-S)}$, day
0.0043	0.26
0.0077	0.73
0.0095	0.93
0.0270	1.89

Table 5.12

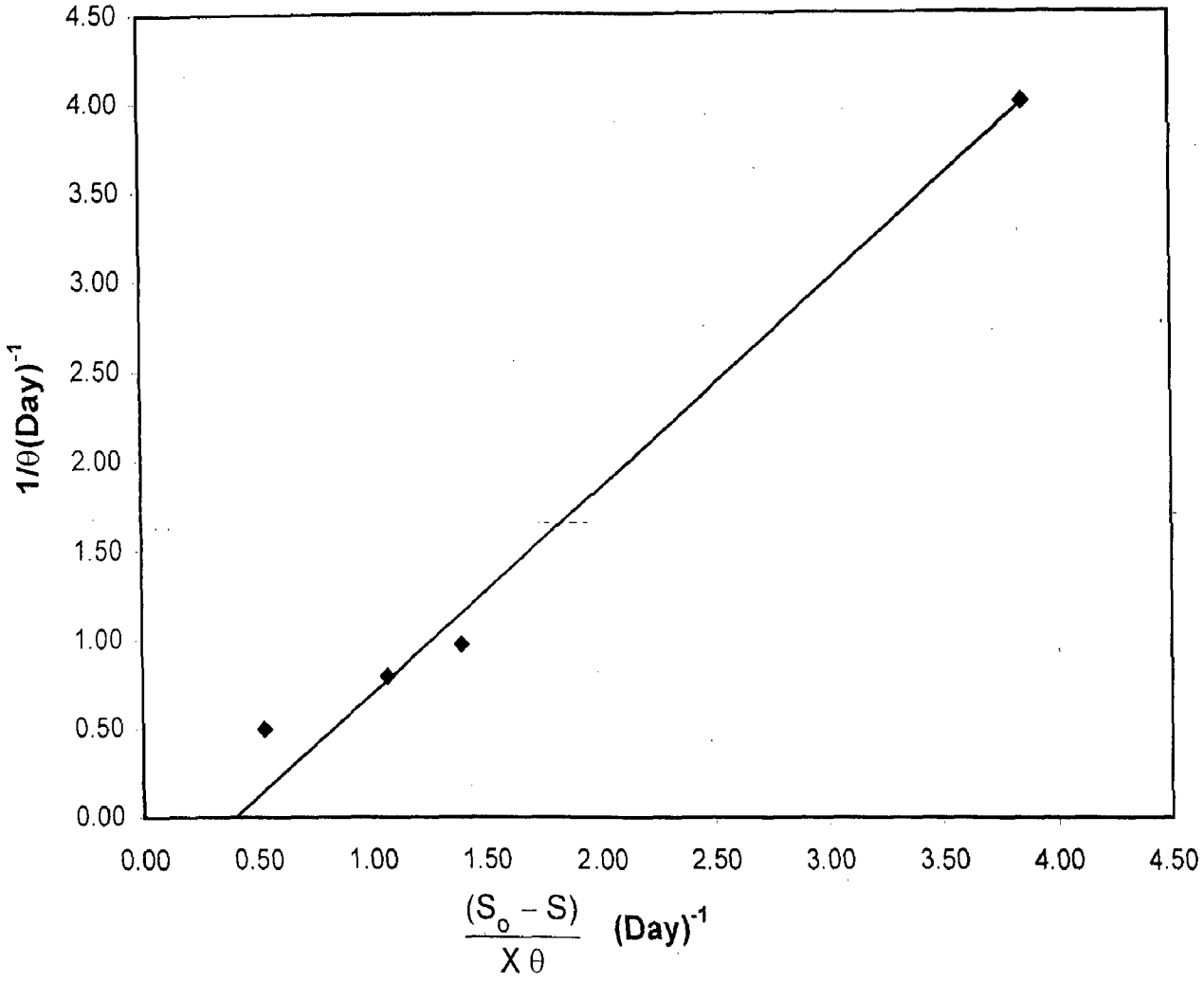
$\frac{(S_0-S)}{X\theta}$, day^{-1}	$1/\theta$, day^{-1}
3.86	4
1.37	1
1.07	0.8
0.53	0.5



Equation of Line

$$\frac{X\theta}{S_o - S} = 63.977\frac{1}{S} + 0.19$$

Fig. 5.6 : Plot of Monod's First Equation at S_o = 375 mg/l



Equation of Line

$$\frac{1}{\theta} = 1.058\left(\frac{S_o - S}{X\theta}\right) - 0.46$$

Fig. 5.7 : Plot of Monod's Second Equation at S_o = 375 mg/l

Table 5.13

Kinetic runs at $30^{o}C$,

with phenol concentration

at zero time (S_0) = 400 mg/l

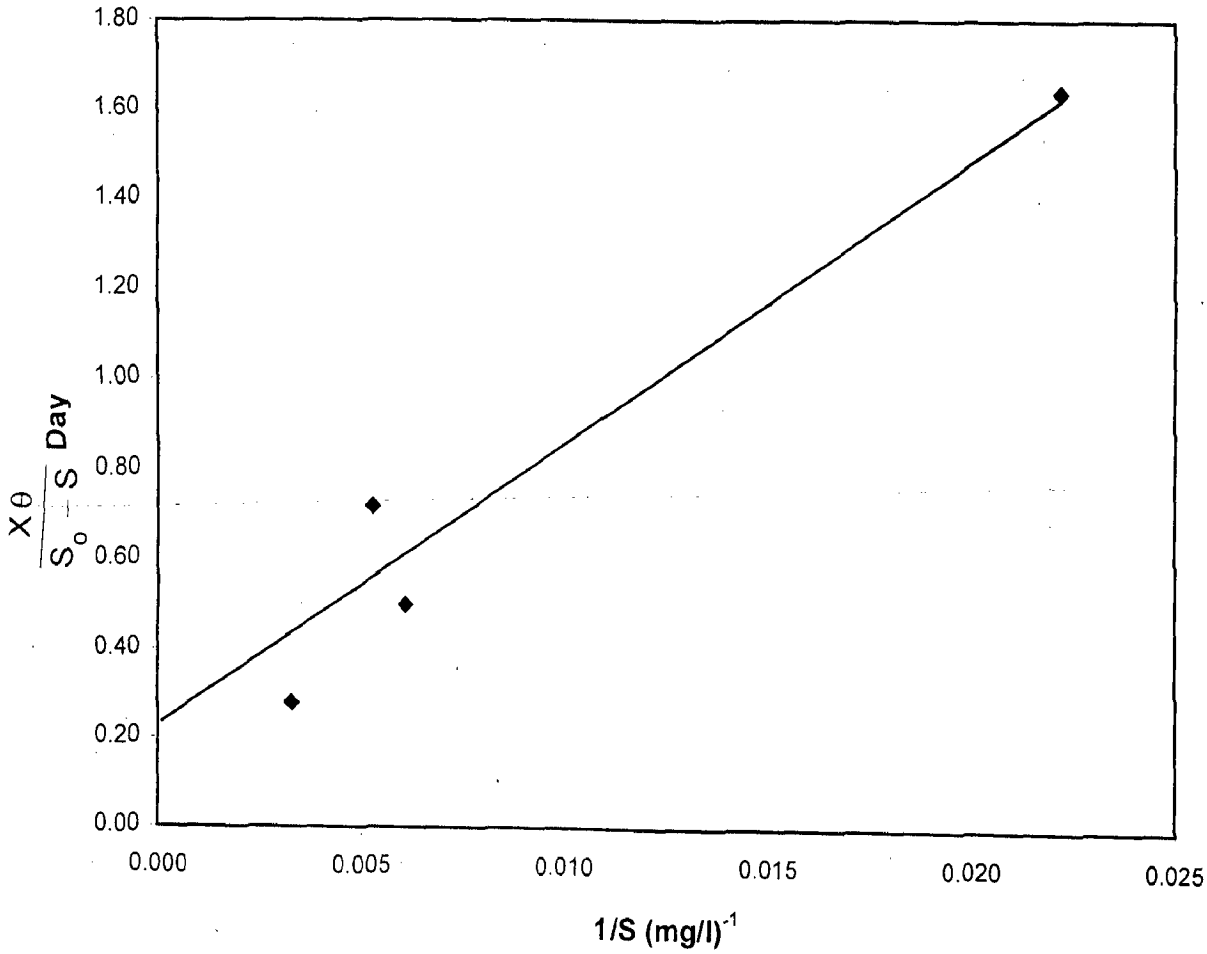
Phenol concentration in reactor (S),mg /l	Time(θ Days	MLVSS(X) mg/l	Percentage removal
265	0.25	140	33.7
165	1	115	59.2
190	1.25	120	52.5
45	2	295	88.7

Table 5.14

$1/S$, $(mg/l)^{-1}$	$\frac{X\theta}{(S_0-S)}$, day
0.0038	0.26
0.0061	0.48
0.0053	0.70
0.0222	1.64

Table 5.15

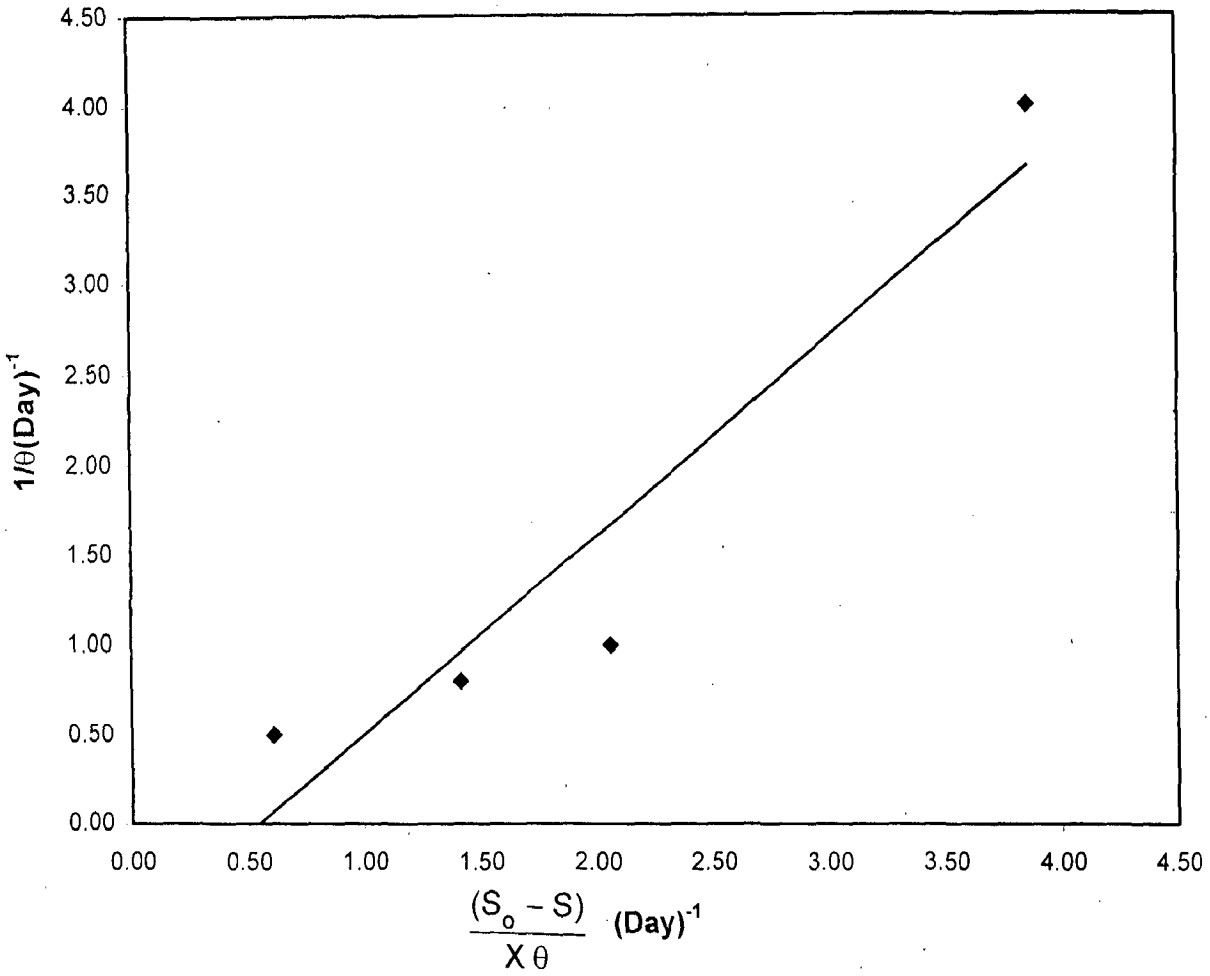
$\frac{(S_0-S)}{X\theta}$, day^{-1}	$1/\theta$, day^{-1}
3.86	4
2.06	1
1.42	0.8
0.61	0.5



Equation of Line

$$\frac{X\theta}{S_o - S} = 61.881\frac{1}{S} + 0.23$$

Fig. 5.8 : Plot of Monod's First Equation at S_o = 400 mg/l



Equation of Line

$$\frac{1}{\theta} = 1.011\left(\frac{S_o - S}{X\theta}\right) - 0.60$$

Fig. 5.9 : Plot of Monod's Second Equation at S_o = 400 mg/l

Figure (5.3) shows the plot of $\frac{(S_0 - S)}{X\,\theta}$ and $1/\theta$ at the same initial phenol concentration of 325 mg/l. The equation of line so obtained is

$$1/\theta = 1.316\,\frac{(S_0 - S)}{X\,\theta} - 0.42 \qquad (5.4)$$

On comparing the above equation with equation (5.2) the values of Y and K_d are obtained as,

Y = 1.316 mg VSS/ mg phenol,

K_d = 0.42 per day.

Fig. (5.4) shows the plot of 1/S and $\frac{X\theta}{(S_0-S)}$, when S_0 = 350 mg/l. After plotting the data, a straight line is obtained, whose equation is,

$$\frac{X\theta}{S_0-S} = 57.06\,\frac{1}{S} + 0.18 \qquad (5.5)$$

On comparing the above equation with equation (5.1), the values of K_s and K are obtained as

K_s = 317 mg/l,

K = 5.56 day^{-1}.

Figure (5.5) shows the plot of $\frac{(S_0-S)}{X\theta}$ and $1/\theta$ at S_0 = 350 mg/l. The equation of line so obtained is,

$$1/\theta = 1.025\left[\frac{S_0-S}{X\theta}\right] - 0.76 \qquad (5.6)$$

On comparing the above equation with equation (5.2), the values of Y and K_d are obtained as

Y = 1.025 mgVSS/mg of phenol,

K_d = 0.0.76 day^{-1}.

Figure (5.6) shows the plot of 1/S and $\frac{X\theta}{(S_o-S)}$, when S_0 = 375 mg/l. After plotting the data, a straight line is obtained, whose equation is,

$$\frac{X\theta}{S_0-S} = 63.98\,\frac{1}{S} + 0.19 \qquad (5.7)$$

On comparing the above equation with equation (5.1), the values of K_s and K are obtained as

K_s = 336.7 mg/l,

K = 5.26 day^{-1}.

Figure (5.7) shows the plot of $\frac{(S_0-S)}{X\theta}$ and $1/\theta$ at S_0 = 375 mg/l. The equation of line so obtained is,

$$1/\theta = 1.058\left[\frac{S_0-S}{X\theta}\right] - 0.46 \qquad (5.8)$$

On comparing the above equation with equation (5.2), the values of Y and K_d are obtained as

Y = 1.058 mgVSS/mg of phenol,

K_d = 0.46 day^{-1}.

Figure (5.8) shows the plot of 1/S and $\frac{X\theta}{S_o-S}$, when S_0 = 400 mg/l. After plotting the data, a straight line is obtained, whose equation is,

$$\frac{X\theta}{S_0-S} = 61.9\,\frac{1}{S} + 0.23 \qquad (5.9)$$

On comparing the above equation with equation (5.1), the values of K_s and K are obtained as

K_s = 269 mg/l,

K = 4.35 day^{-1}.

Figure (5.9) shows the plot of $\frac{(S_0-S)}{X\theta}$ and $1/\theta$ at S_0 = 400 mg/l. The equation of line so obtained is,

$$1/\theta = 1.011\left[\frac{S_0-S}{X\theta}\right] - 0.60 \qquad (5.10)$$

On comparing the above equation with equation (5.2), the values of Y and K_d are obtained as

Y = 1.011 mg VSS/mg of phenol,

K_d = 0.60 day^{-1}.

The values of Y which are calculated in terms of mg VSS/mg of phenol can be converted in terms of mg VSS/mg of COD. Since from experimental determination, we have, 1 mg phenol = 2.76 mg COD.

5.4 AVERAGE VALUES OF BIOKINETIC PARAMETERS

The values of different biokinetic parameters are showing variations for different sets of data. Since the variations in these values are not very high, so the means of the different values are taken (Table 5.16). These mean values are the representative values of different biokinetic parameter.

Table 5.16

Average Values of Biokinetic Parameters at 30^0C

	K_S(mg/l)	K (day^{-1})	Y $\frac{\text{mg VSS}}{\text{mg COD}}$	K_d(day^{-1})
S_0=325 mg/l	266.5	4.92	0.40	0.42
S_0=350 mg/l	317.0	5.56	0.37	0.76
S_0=375 mg/l	336.7	5.26	0.38	0.46
S_0=400 mg/l	269.0	4.35	0.37	0.60
Average :	297.3	5.02	0.38	0.56

CHAPTER -6

CONCLUSIONS

Major conclusions which could be drawn on the basis of present investigations are given below:-

1. Phenol was degraded by an adapted mixed seed culture with kinetics not much different from those reported for other cases of mixed culutre aerobic waste treatment (Metcalf & Eddy).

2. Kinetics of phenol removal by activated sludge process could be presented by Monod's equations.

3. No substrate inhibition was seen in the phenol concentration range covered upto 400 mg/l.

4. The maximum removal of phenol occurred at a temperature of 30^0C.

5. The large value was found for the saturation constant (K_S = 297.3 mg/l). This larger value indicated that while treating phenolic waste, achieving low phenol concentration was more difficult.

6. The relatively lower average value of maximum rate of substrate utilization per unit mass of microorganism (K = 5.02 day^{-1}) was due to the effect of initial phenol concentration on the microgranisms.

7. The value of maximum yield coefficient for phenol was found to be 0.38 mg VSS/mg of COD.

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2. A copy of M.E. Dissertation entitled **"Evaluation of Bio Kinetic Parameters for Rational Design of Activated Sludge Process for Phenolic Waste "**

The above is for your kind information and necessary action.

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(SURENDRA KUMAR)
PROF. & HEAD

Encl. As above.

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