ASPECTS OF BIOLOGICAL TREATMENT OF OIL REFINERY AND PETROCHEMICAL WASTE WATER

by

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ABSTRACT

Petrochemical and refinery liquid wastes were investigated on a laboratory scale with regard to their amenability to biological treatment by means of a completely mixed, high-rate, activated sludge process. The principal study consisted in designing and operating a model bio-treatment facility serving as a secondary step in the whole detoxification process after a pretreatment designed to free the raw waste from excessive amounts of ammonia and hydrogen sulfide by air-stripping and neutralization. An acclimated sludge was developed, capable of more than 70% COD removal and practically total elimination of phenol and sulfides. Analyses for COD, MLSS, phenol, D.O., and biomass characteristics were carried out daily and response of the system to altering operating parameters was recorded, so that optimal levels of these parameters were obtained:

Detention Time 8 hr.	MLSS 1400 mg/l
pH 7	Sludge recycle 67%
T 25°C	SVI 37-49
O_2 Uptake Rate 66.5 mg/l-hr.	Sludge yield 1.788 mg MLSS/mg COD

Also examined were nutrient requirements, high-ion concentration effects and the relationships among COD, BOD and TOC in raw, pretreated waste and in effluent.

The qualitative and quantitative information gathered from the study should serve for scaling up the process to a field-scale bio-oxidation facility.

ABRÉGÉ

Nous avons étudié en laboratoire des eaux résiduaires provenant des opérations de raffinage de pétrole, en ce qui concerne leur susceptibilité au traitement biologique au moyen d'un procédé de boues activées complètement mixte.

L'étude principale consistait à la mise en point et l'opération d'une installation de traitement biologique servant comme un étape secondaire dans le procédé de détoxification entier, après un traitement préliminaire prévu pour libérer les eaux usées originales de quantités excessives d'ammoniac et de sulfide d'hydrogène au moyen d'"air-stripping" et de neutralization. Nous avons developé une boue acclimatizée qui permettait une élimination de DOC jusqu'à 70% et l'élimination presque totale de phenol et sulfide. Nous avons effectué d'analyses quotidiennes de DOC, solides biologiques, phenol, O.D. et characteristiques de la boue activée et la réponse du système aux variations de paramètres d'operation était enregistrée de façon à obtenir le niveau optimal de ces paramètres:

Temps a détention: 8 hr	MLSS: 1400 mg/l
pH 7	Recyclage de boue: 67%
T 25°	SVI: 37-49
Taux de consommation d'O_2: 66.5 mg/l-hr.	Productivité de la boue: 1.78 mg MLSS/mg DOC

Nous avons aussi examiné les exigences en éléments nutritifs, l'effet de grosse concentration d'ions et les rélations de DOC, DOB et COT en l'eau résiduaire d'origine et celle après le traitement préliminaire et au effluent.

Les informations qualitatives et quantitatives obtenues per cette étude permettraient l'extention du procédé de traitement biologique au niveau operationnel.

To Shadie A.

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Montreal, August 1975 Spiro Agathos

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INTRODUCTION

The diversity of the characteristics and toxicity of industrial effluents contribute to the problems associated with their purification. Treatment procedures of industrial waste waters become far more involved and research-demanding than relatively well established procedures for municipal-type wastewater decontamination.

Industrial waste waters from oil-refining operations present a very specific problem in terms of detoxification and suitable treatment which would render them acceptable for discharge into the receiving stream:

The similarity of any two refinery raw effluents is highly unlikely due to the wide range of potentially polluting substances present at various concentrations in the waste streams collected in refinery sewer facilities. The characteristic compounds for the typical refinery waste water may often include:

(a) Dissolved organic materials exerting high BOD and COD, often of toxic nature (phenolics, mercaptans, hydrocarbons, oils, etc.)

(b) Potential biological inhibitors as inorganic ions in high concentrations (chlorides, sulfides, sulfates, sodium cations, etc.)

(c) Potentially toxic metal ions originating from refinery catalytic operations (chromium, copper, nickel, zinc.)

(d) Physical contaminants (suspended solids, oil globules, etc.)

Processes for biological oxidation and removal of contaminating substances from refinery effluents have been widely used and are well-

established. They have been proven to be very effective in attaining significant reductions in oxygen demand, organic load, toxicity, odor and general appearance of the treated waste stream. However, relatively little is known of some basic phenomena and relationships involved in biological treatment of industrial wastes and due to its complexity the process lends itself to a more in-depth investigation.

Biological treatment techniques make use of microorganisms to metabolize organic matter into harmless end-products such as CO_2 and water. Principles of basic biochemistry and microbiology involved have been described in considerable detail in the literature. On the other hand the general engineering approach to testing and optimization of the performance of biological treatment facilities in oil refineries has been rather empirical and of a trial-and-error nature, due to lack of adequate understanding of the mechanisms involved at a microscopic level.

The objective of the present research work has been to study the effects of some physical and chemical parameters upon the performance of an Activated Sludge process as it is applied to the treatment of oil refinery effluents.

CHAPTER I

TREATABILITY EVALUATION:
A SURVEY OF CURRENT PRACTICES AND TRENDS

I.1. Petrochemical and Oil Refinery Waste Treatment

Waste water streams originating from petrochemical and oil-refinery plants have been the subject of particular concern as effluent criteria imposed by the various regulatory authorities become more stringent. Efforts towards the effective handling of these liquid wastes have been intense in the past decade not only because of their extremely diverse toxic, inhibitory or simply objectionable ingredients, but also because of their volume, as the oil-refining and processing industry represents one of the largest and still expanding areas of industrial enterprise, particularly in North America.

There is a vast literature on problems and practices in the field of refinery and petrochemical waste treatment dispersed in a variety of technical journals, conference proceedings, individual treatises and reports. However most of the information available in these sources consists of case histories on waste abatement of a mainly descriptive nature. [e.g. Skogen (1967), Huber (1968), Armstrong (1968), Denbo and Gowdy (1971), Harrison (1972), Ross (1972), etc.]

A strikingly common feature among them is the absence of rational design approaches derived from basic engineering (and possibly bio-chemical and microbiological) principles. This is especially true in the area of secondary (biological) waste treatment.

Certain reports, while not quite fitting the above-mentioned "descriptive" majority in that they attempt a more systematic evaluation of the waste's amenability to bio-treatment still show no direct link between bench- or pilot-plant scale data and actual (or proposed) design. [e.g. Stensel et al. (1973), Rose and Gorringe (1974)].

There exist only a few actual treatability studies in published form, which show how the field-scale facility can be designed on the basis of information gathered from lab-scale (or pilot-plant) studies [Riemer et al. (1972), Volesky et al. (1974)].

The above findings from the existing literature reflect the fact that the design of bio-treatment facilities (activated sludge processes and their modifications, trickling filters, aerated lagoons and oxidation ponds) has been and still is generally based on "rule-of-thumb" relationships that have been obtained from experience with successfully operated units. [Jorden et al. (1971)]. Municipal and military facilities of biological waste treatment have provided the bulk of this information and as a result these "rule-of-thumb" design values are naturally biased toward design for domestic waste water treatment plants.

It is being increasingly recognized that a rational approach to the design of secondary treatment facilities in the petroleum processing industry should be based on results of treatability tests (of the actual waste streams that are to be controlled) and should be evaluated in the light of sound chemical engineering and biochemical kinetics considerations, with regard to inherent limitations to the treatment imposed by the waste in terms of:

rate of biological degradation

possible nutrient deficiencies

aeration requirements

production of biological sludge.

The adoption of this approach assumes the detailed knowledge of the waste streams' characteristics. Beychok (1967) authored an almost complete and still up-to-date guide to the various types of refinery and petrochemical waste waters and the complete spectrum of treatment possibilities, including design-oriented recommendations. The publication of the new, revised edition of the "Manual on Disposal of Refinery Wastes" by the American Petroleum Institute [API, (1969)] made available a wealth of information on the characteristics and treatment of various refinery and petrochemical effluents that should serve as a good basis for the initial investigation of a particular treatability problem. However much of the supporting literature is outdated especially as far as biological treatment is concerned.

The relatively recent reports published by regulatory authorities such as EPA* are indicative of the current trend towards more design-oriented treatability investigations. The volume on "Preliminary Investigational Requirements" [EPA, (1971)] is a clearly written and adequately comprehensive guide on the compilation, meaningful interpretation and effective presentation of the important aspects constituting a good treatability study for the petrochemical and oil refinery effluents.

Another useful report by EPA (1972) points to the direction of successful treatability tests, including the description of polluting problems and abatement procedures, classification of wastes and general suggestions as to pertinent treatment techniques including biological treatment.

McKinney (1967) has also given a comprehensive survey on the evaluation of waste characteristics, effluent requirements, waste water pretreatment, selection of biological treatment systems and some basic design criteria that could be still useful, although based on "case histories" from already successful refinery wastewater treatment units.

Continuous completely mixed activated sludge systems are becoming increasingly common in the process industries, however there are

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*U.S. Environmental Protection Agency

very little experimental data available in the literature to help guide their design for petroleum refinery waste water treatment. Most closely-controlled lab-scale studies of waste treatment are still being conducted on synthetic (hence well-defined) wastes.

In developing the design parameters it is best to use data derived from continuous studies rather than from batch studies: interpretations of batch-unit derived data and their extension to the design of continuous system is difficult and usually misleading because of largely uncontrolled environmental factors (Volesky et al. 1974). Also in batch techniques the initial loading is much higher than for the CSTR system operating at steady-state. For a refinery waste this can lead to inaccuracies due to the toxic effects of the waste on the biota at the initial high loadings.

Moreover the continuous units simulate much more closely the commercial-scale plant in operation [EPA (1971)].

I.2. Theoretical Considerations

It is increasingly felt that a rational approach towards the quantitative description of a continuous-flow biological treatment system should be based on valid mathematical relationships of the kinetics of microbial growth and substrate removal.

Several formulations of models for the bio-oxidation of a soluble substrate (liquid waste) in the completely mixed activated sludge process have been proposed and accepted in the current practice of waste water treatment of both municipal and industrial origin. The most widespread among the models--in their most recent forms--include that of Eckenfelder and Ford (1970), of McKinney and Ooten (1969)*, of Goodman and Englande (1974)--which is actually a demonstration of the fundamental mathematical identity between Eckenfelder's and McKinney's equations that are based on the concept of "food-to-microorganism ratio"--and that of Lawrence and McCarty (1970)--employing the concept of "mean cell residence time" and based significantly on the kinetics of the chemostat as developed originally for pure microbial cultures by Monod (1949). While many bench- and field-scale systems of activated sludge have been tested and found to fit, to various extents, all the above models, there are certain weak theoretical points in them with implications on their general usefulness in the design of treatment facilities. For example the empirically since long known and well-substantiated idea [Cf. Weddle

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*Basically the same as reported later in McKinney (1974).

and Jenkins (1971), Nutt (1974)] that only a portion of the microorganisms in the sludge flocs is viable has led Eckenfelder, McKinney and Goodman to incorporate in their models the concept of inactive, non-biodegradable solids, which if not disposed of through sludge wastage, they would build up with increasing mean cell residence times, causing a reduction in the active cell fraction of the biomass. This has been disproved through experimentation by many researchers including Gaudy and co-workers [e.g. (1970), (1971)], Erickson, Fan and their associates (1972), Grady and Roper (1974), etc. The trouble with models such as Eckenfelder's and McKinney's lies in that they were conceived mainly along traditional hydraulic engineering lines without an adequate insight into the biological facts of the process. Also the model of Lawrence and McCarty, although far more compatible with the facts and concepts of continuous microbial culture, predicts that the biomass resulting from the treatment of a completely soluble waste (substrate) will be 100% viable, which does not happen in actuality [Grady and Roper (1974)].

It is increasingly felt that the systematic approach to the study of the completely-mixed activated sludge process should be based on the simple and adequately tested formulations of continuous culture theory as proposed and advanced by Monod (1949), Novick and Szilard (1950), Herbert (1956) and Herbert et al (1956), along with operational assumptions for the peculiarities encountered in a heterogeneous population of microorganisms functioning within certain ranges of

environmental conditions. This approach has been successfully employed by Gaudy and his associates [Refs. (1969), (1971), etc.] and Erickson, Fan and their co-workers [Refs. Chiu et al (1972)a and b] who have been working mainly with synthetic wastes. Jorden et al (1971) have exemplified the applicability of these concepts in testing the treatability of actual industrial wastes.

The following formulation is based on material balances in terms of cell population and substrate (organic load to be removed) around a completely-mixed, continuous-flow reactor with cell recycle from the cell separator (see Fig. I-1). In addition, the kinetic model of Monod relating specific growth rate μ with limiting substrate concentration S is employed, not only because it is the most commonly in use, but also because it has been shown to be satisfactory in both pure and mixed microbial cultures [Cf. Gaudy et al (1967), Ramanathan and Gaudy (1969), Gaudy et al (1971), Chiu et al (1972) a, b, Surucu et al (1975), etc.] and besides describing experimental data mathematically, it offers mechanistic implications about the process [Chiu et al (1972)a].

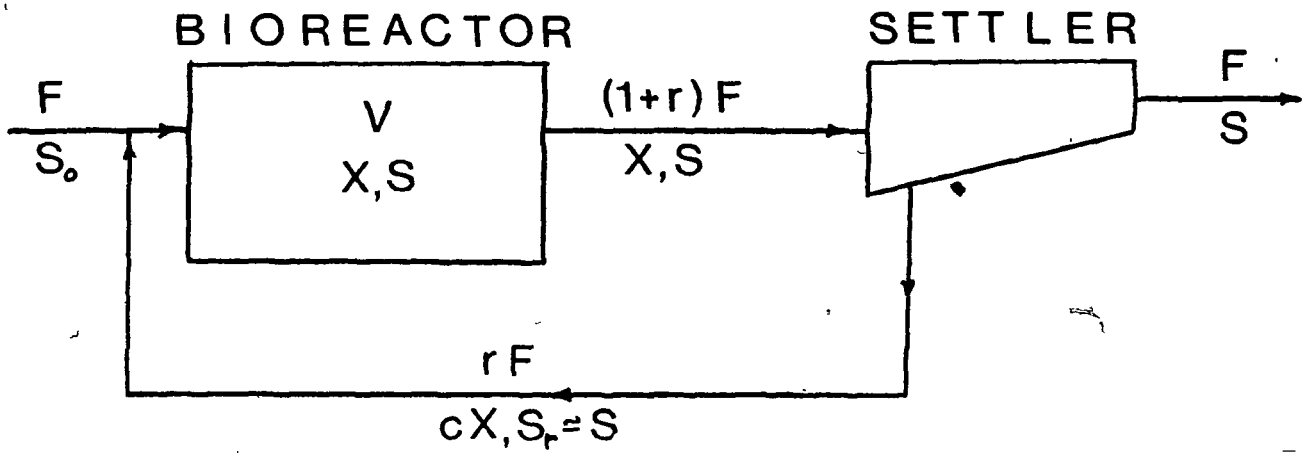
The cell mass balance around the reactor can be written as follows, since the rate of change in the amount of cells present in the system is equal to the sum of the rates of increase in cells due to inflow, recycle and growth minus the rate of outflow and cell death (decay):

$$\text{Increase} = \text{inflow} + \text{recycle} + \text{growth} - \text{outflow} - \text{death}$$

$$V\frac{dX}{dt} = FX_o + rFcX + \mu XV - (1+r)FX - k_dX \qquad (1)$$

Figure I-1: Flow Diagram of a Completely Mixed Activated Sludge Process

[Symbols explained in text]


BIOREACTOR
SETTLER
F
S_o
V
X,S
(1+r) F
X,S
F
S
r F
cX, S_r = S

where: V: volume of bioreactor (broth volume)

F: volumetric inflow rate of wastewater

X_o: influent biological solids (cell) concentration

X: cell concentration in reactor at any given moment

μ: specific growth rate of cells

r: recycle ratio (= ratio of underflow rate from cell separator to waste inflow rate)

c: concentration factor (= ratio of the biological solids concentration in the cell separator underflow to the biological solids concentration in the reactor)

k_d: cell death or decay constant

Assuming no biological solids in the inflow ($X_o = 0$) and setting F/V = D = diluting rate, equation (1) becomes:

$$\frac{dX}{dt} = DrcX + \mu X - (1+r)DX - k_d X \qquad (2)$$

Under steady-state operation dX/dt = 0, hence equation (2) can be rearranged to give:

$$\mu = D(1+r-rc) + k_d \qquad (3)$$

or, if we set $1 + r - rc = A$

$$\mu = D(1+r-rc) + k_d \rightarrow \mu = DA + k_d \qquad (3a)$$

Equation (3) or (3a) shows that the net growth rate, i.e. $\mu - k_d$ is not wholly controlled hydraulically as in a once-through system, where $\mu = D$, but is also subject to the effect of a non-hydraulic factor, namely the concentration factor c.

The substrate (or organic load) mass balance around the reactor

can be written as follows:

(Increase) = (inflow)+(recycle)-(outflow)-(consumption for growth)-(concumption for maintenance)-(consumption for product formation)

$$V\left(\frac{dS}{dt}\right) = FS_o + rFS_r - (1+r)FS - \mu\frac{X}{Y} - mX - \frac{q_p X}{Y'} \qquad (4)$$

where:

S_o = influent substrate concentration

S_r = recycle substrate concentration

S = substrate concentration in reactor

$Y = (dX/dt)_{growth}/(-\frac{dS}{dt})_{growth}$ = cell yield, i.e. ratio of the concentration of substrate consumed for growth [as is known $(\frac{dX}{dt})_{growth} = \mu X$, hence the fourth term of e.g. (4)]

m = cell maintenance coefficient

q_p = specific product formation rate

Y' = product yield

Usually the effects of substrate consumption for cell maintenance and intermediate product formation are negligible compared to the term of substrate consumption for growth. In the limited cases when their order of magnitude is significant, they can be also dropped with the understanding that their effect is conceptually "lumped" into the cell yield constant Y. It can also be assumed that essentially $S_r \simeq S$. With the above assumptions and with steady-state operation (i.e. $dS/dt=0$) eg. (4) leads to

$$X = \frac{DY\ (So-S)}{\mu} \qquad (5)$$

after some rearrangement.

Combining equations (3) and (5) we get the following expression for the relationship between steady state cell concentration and steady state substrate concentration:

$$X = \frac{DY\ (So-S)}{DA + k_d} \qquad (6)$$

If we invert and rearrange equation (6) we obtain:

$$\frac{So-S}{X} = \left(\frac{k_d}{Y}\right) \cdot \left(\frac{1}{D}\right) + \frac{A}{Y} \qquad (7)$$

This equation is of the general form $y = ax + b$, i.e. the "specific removal" $\frac{So-S}{X}$ is a linear function of the detention time $\bar{t} = \frac{1}{D}$; therefore if $\frac{So-S}{X}$ is plotted vs. the inverse of dilution rate the equation (7) should produce a straight line with a slope of k_d/Y and an intercept of $\frac{A}{Y}$. Thus from experimental data of $\frac{So-S}{X}$ and D the biological constants Y and k_d can be evaluated.

Now in order to obtain the steady state concentration of substrate as a function of the dilution rate D we use the growth model of Monod:

$$\mu = \mu_m \frac{S}{K_s+S} \qquad (8)$$

where μ_m is the maximum growth rate of the cells and K_s is the saturation constant, numerically equal to the substrate concentration at which $\mu = \frac{1}{2}\mu_m$; substituting for μ in the above equation from eq. 3a and solving for S we obtain

$$S = \frac{K_s(AD + k_d)}{\mu_m - (AD + k_d)} \qquad (9)$$

By inverting eq. (9), multiplying both sides by $\frac{K_s}{\mu_m}$ and rearranging we

arrive at

$$\frac{1}{AD + k_d} = \frac{K_s}{\mu_m} \frac{1}{S} + \frac{1}{\mu_m} \qquad (10)$$

Equation (10) shows that the reciprocal of the specific growth rate ($\frac{1}{\mu} = \frac{1}{AD + k_d}$) is a linear function of the reciprocal of substrate concentration, and, in a manner evocative of Lineweaver-Burk reciprocal plots in enzyme kinetics, one could plot experimental data of $\frac{1}{AD + k_d}$ (k_d is already known from the plot of eq. (7)) vs. $\frac{1}{S}$ to obtain estimates of the remaining biological constants μ_m (from the intercept $\frac{1}{\mu_m}$) and K_s (from the slope $\frac{K_s}{\mu_m}$).

It should be emphasized that in applying chemostat theory to the activated sludge process the problems of

(a) identification of the growth-limiting nutrient

(b) variations in species predominance

(c) changes in the concentration of organic matter in the influent

are always present, especially in the case of complex industrial waste waters.

With regard to "problem (a)" a generalized assay for dissolved organic matter such as COD (or even BOD_5 or TOC) is used, assuming this as representing the limiting substrate. The above "problem (b)", which has been adequately demonstrated by Jannasch (1967) and subsequently by Chiu et al. (1972)b as the "selective pressure" of the chemostat for different organisms even at steady state, is probably

the most serious limitation in the general successful application of deterministic chemostat models such as the one formulated above. Thus when the values of the kinetic parameters or "biological constants" [μ_m, K_s, Y and k_d] are measured for heterogeneous populations it has been found that they are best represented by ranges rather than by unique values, even for a single substrate [cf. Gaudy and Gaudy (1966) and (1971)]. In actual treatability tests such as the ones reported in the present work this limitation must be recognized when deriving values of biological constants. Hence no systematic use of the chemostat model presented previously was made in the "Results" section of this study, as it was judged of more importance to deduce the bio-treatability profile of the particular refinery wastes directly from the continuous flow long-term experimentation with varying controllable parameters.

Finally the above "problem (c)" reflects the fact that it is not possible to predict the final steady-state conditions (in terms of biomass and substrate levels) for various substrate (or organic load) inputs, since continuous culture theory shows that the effluent substrate concentration is independent of the influent substrate concentration [see Equation (9) above], despite the rather common experimental fact of some degree of dependence [see e.g. Eckhoff and Jenkins (1966), Grady et al. (1972)]. Statistical correlations have been developed and there is evidence that the measurement of substrate through a generalized assey (such as COD) contributes to this discrepancy from chemostat theory [Grady et al. (1972)].

I.3 Scope of Investigation

In accordance with the principles outlined above, the central idea behind the present work was to examine in a rational and organized way the biological treatability of actual real-life oil refinery and petrochemical waste water by means of a completely-mixed activated sludge process on a laboratory scale in order to derive optimal ranges of design parameters; these should be readily available and utilizable in the scaling-up of the treatment process.

It should be pointed out here that, given the particular type of waste, the treatability studies were not undertaken to decide the best (i. e., most economical and efficient in terms of meeting pre-existing public health standards) mode of treatment, but rather were a priori confined to the notion of biological treatment, so that they could serve as an operational guide or model in cases where preliminary investigations would show that the activated sludge process is actually the treatment method of choice.

In this spirit it was decided to first demonstrate the amenability of a particular waste water to biological degradation through a completely mixed activated sludge process by developing a biomass appropriately acclimated to the waste, with the desirable properties

of removal efficiency, flocculation and compaction characteristics, and effective self-maintenance of the system, i. e., attainment of a reasonably steady state. Only after establishing this would it seem appropriate to proceed with the exploration of interaction of variables and the response of the overall treatment to various perturbations.

To illustrate the importance of this primary step a Preliminary Study was undertaken on a high-phenol mixed (i. e., oil refinery and petrochemical) waste water originating from the Montreal East Works of Gulf Oil Canada Ltd. Following the analytical characterization of the raw waste liquor, the feasibility of a stable performance of the bio-treatment was explored in a simple chemostat by periodical assessing of the levels of residual substrate (as COD), of cell concentration and of residual phenol in the effluent, on a regular basis.

Experience from the coarse overall behaviour of this facility was helpful in the design and operation of the final system, in which the Main Treatability Studies were conducted.

The objective of these latter investigations has been to develop a reliable, stable and closely controlled bio-oxidation process on an oil refinery waste water, which should previously be proven clearly susceptible to treatment in a high-rate completely mixed activated sludge lab-scale reactor (fermentor), so that the optimal operating conditions including the biological constants could be assessed and confirmed subsequently in a series of long-term continuous-flow experiments. The waste water chosen to be tested came from the Montreal East

Works of Petrofina Canada Ltd.; in order to have an absolutely bio-treatable feed to the fermentor it was judged that, after an adequate analytical characterization of the raw waste liquor, it should be pre-treated physically-chemically in case of excessive presence of toxicants that are known to interfere with the biological oxidation process.

The continuous-flow experiments on the bioreactor comprised:

Hydraulic Studies: Examined was the effect of dilution rate, D, (or mean reactor residence time) on the characteristics of the system (i. e., residual COD, phenol, sustained level of biological solids and general settleability of biomass) and the measured amounts of substrate and biomass in the broth at various dilution rates served for the calculation of "mean" biological "constants" (i. e., yield of biomass per unit of substrate removed, cell death or decay constant, maximum growth rate and substrate saturation constant). In this connection it appeared desirable to increase the dilution rate to the maximum possible value with essentially the same quality of overall treatment performance, as such an increase, given a constant flow-rate of waste liquor, would entail a corresponding reduction of reactor volume and, hence, of capital cost in the full-scale facility envisaged. Also examined was the effect of the recycling of biological solids from the sedimentation vessel back to the bio-reactor.

Sludge Characteristics: Qualitative and quantitative appraisal of settleability and compactability of the biomass, was expressed by the Sludge Volume Index (SVI), under different operating

conditions.

Oxygen Requirements: These were evaluated by recording maximum oxygen utilization rate per unit of biomass, by calculating the constants indicating the distribution of O_2 between growth and maintenance (average values), and finally by assessing the ratio of O_2 transfer coefficient in the broth vs. the same in tap water, all useful in sizing aeration equipment when upscaling the treatment process to a field-scale facility.

Nutrient Requirements: Examined was whether there are adequate levels of readily useable N and P in the mixed liquor for an efficient bio-degradation of the pollutional load of the waste.

Selection of a parameter reflecting activity of the biomass: The Oxygen Uptake Rate (OUR) was chosen and monitored in an effort to evaluate and possibly predict the effects of perturbations imposed on the system.

Finally, an introductory examination of the effects of variations of Temperature, pH, and High Ion Concentration on the performance of the bioreactor in terms of substrate removal, residual phenol, oxygen uptake rate and sludge flocculation-compaction was performed.

It is recognized that further long-term experimentation is required for the accumulation of detailed results on the exact patterns of the system's response to variations in temperature, pH and various ionic species concentrations, lying outside the scope of the present work.

CHAPTER II

EXPERIMENTAL LAY-OUT

II.1. Materials and Methods

II.1.A. Description of Equipment

i. Preliminary Studies

The Preliminary bio-treatability tests using the strong phenolic waste liquor were conducted in a simple continuous-flow system consisting of a 30-liter aeration tank, a 6-liter sedimentation vessel, two variable-speed metering pumps for feeding and recycling and reervoirs for the liquid waste feed and the treated effluent. A schematic diagram of the system is shown in Figure II-1.

The cylindrical aeration vessel was made of 1/4" thick plexiglass, had a diameter of 16 inches and a height of 25 inches, and it was equipped with four built-in evenly spaced baffles of 1-1/2 inch width along the inside walls.

Agitation was provided by a manufactured steel flat-blade turbine-type impeller with the following characteristics: six blades, overall diameter--3 inches; blade width--1 inch. The impeller was powered by a variable angular velocity 1/3 HP motor ("Lightin Mixer," Greey Mixing Equipment Ltd., Toronto, Ont.).

Aeration was provided through a single nozzle in the center of the bio-reactor's bottom, directly from the laboratory air line. Laboratory air was filtered with an oil-trap and glass wool prior to its introduction into the aeration tank.

A working volume of 25 liters was employed in the bio-reactor and one of 5 liters in the settler. Both volumes were strictly maintained

Figure II-1: Experimental Set-up for Preliminary Studies ("crude" system)

R: Reactor

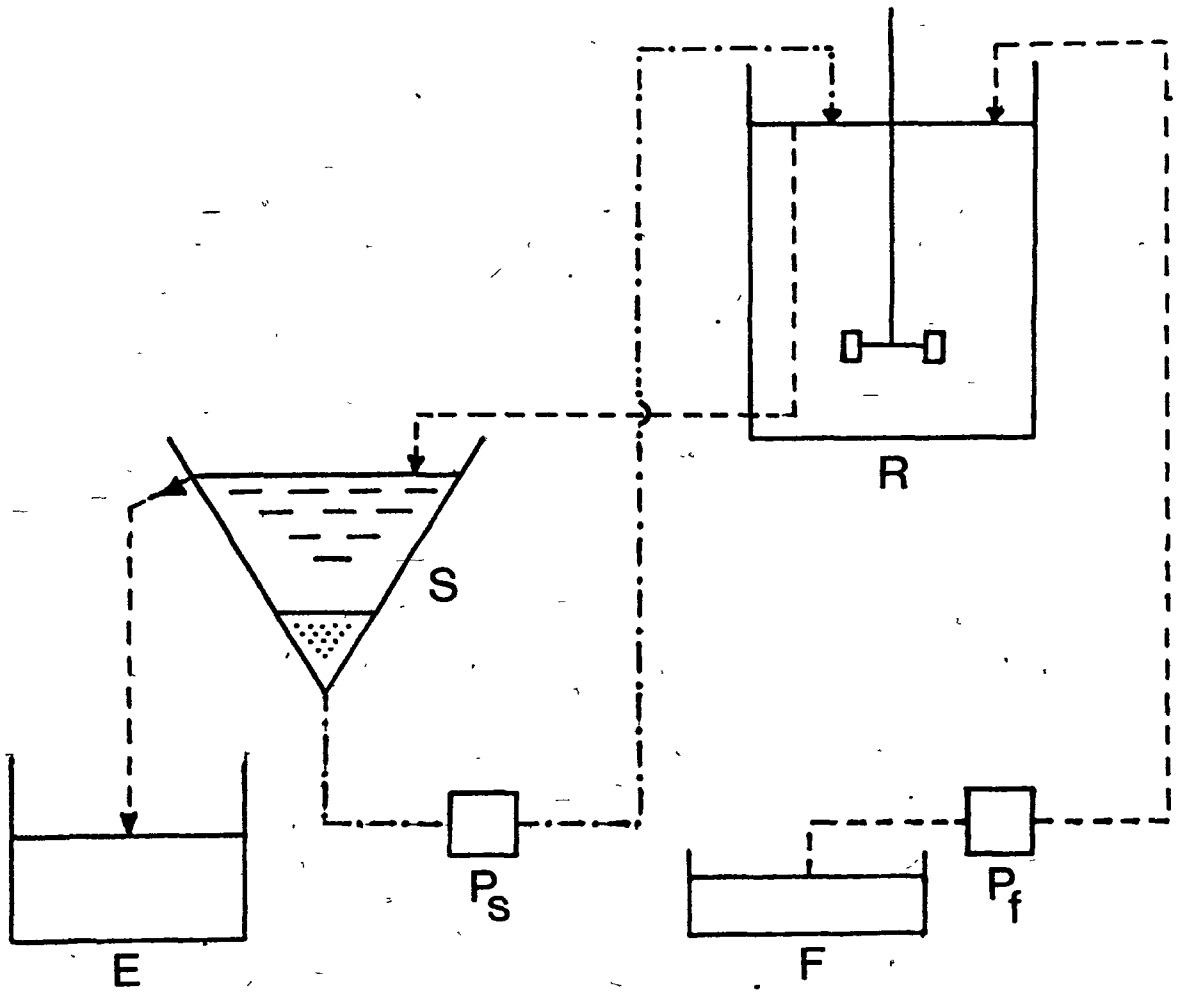
S: Settler

F: Waste Feed

E: Effluent

P_f: Feed Metering Pump

P_s: Sludge Recycling Pump


R
S
E
P_s
F
P_f

constant by level control, using thin pieces of plexiglass tubing and keeping the settler at a lower level with regard to the level of the mixed liquor inside the bio-reactor, so that circulation of the mixed liquor from the aeration tank and of the treated supernatant from the settler were accomplished freely by overflow. The sedimentation tank was fabricated by modifying a six-liter Erlenmeyer flask. Simple gravity separation was used.

The pumps for regulating accurately the flow in the feed and recycle lines were of the "kinetic clamp" type (Sigmamotor Pumps, Model AL-4E, manufactured by Sigma Motor Inc., Middleport, N. Y.). pH control was exercised intermittently by manual corrections using diagnostically an Orion Research pH-meter (model 407). No temperature control was used in these preliminary tests. However, the temperature of the mixed liquor never exceeded 24°C, and never dropped lower than 19°C.

ii. Main Treatability Studies

The physical-chemical pretreatment of the Petrofina waste took place in either of two plastic (chemically inert) cylindrical vessels of a capacity of 20 IG and 100 IG respectively, according to the temporal quantity of raw waste water per batch available for treatment.

The aeration-stripping-flotation-neutralization process was accomplished through a ring-shaped sparger of a 1-foot diameter constructed from 1/2-inch copper tubing, bearing 1 mm. mozzles evenly spaced around the ring. Adequate mixing and agitating were provided

in the 20 IG vessel simply by the action of the pressurized swarm of air bubbles, whereas complete mixing was obtained in the 100 IG vessel through a peristaltic pump used for forced circulation of the raw waste liquor inside the tank.

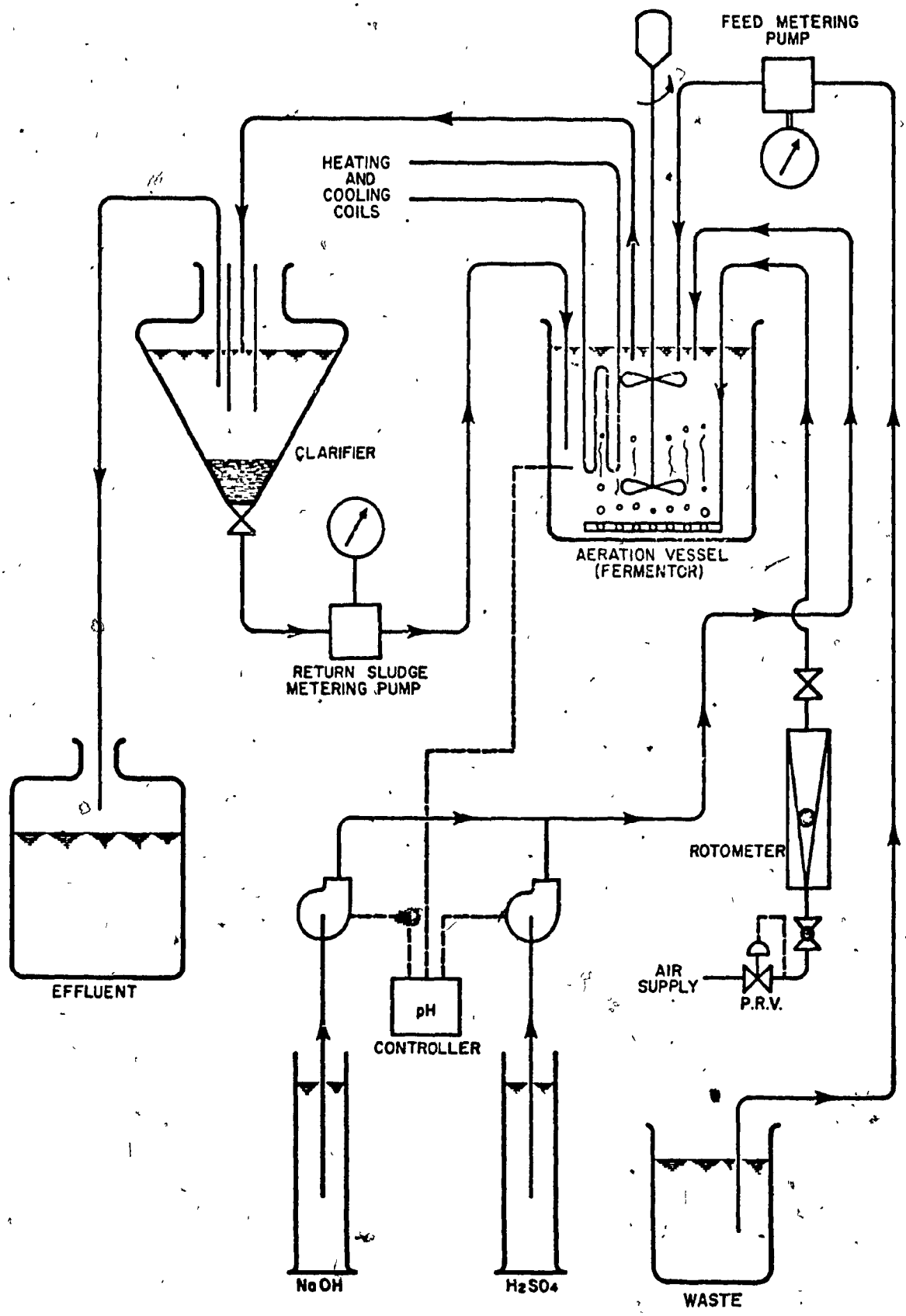
The basic experimental unit for the bio-treatment process was the "Microferm" bench scale fermentor (Model MF-114, manufactured by New Brunswick Scientific Co., Inc., New Brunswick, N. J.) supplied with accessory equipment to ensure continuous monitoring and control of operating parameters such as pH, temperature; D_2O was monitored too, but no automatic controller was available. Figure II-2 is a schematic diagram of the model bio-ox unit.

The reaction vessel of the fermentor (pyrex glass jar) was cylindrical and of a 14-liter maximum capacity. The bio-reactor was of the conventional standardized New Brunswick scientific design: four vertical baffles agitation through two flat-blade turbine impellers (6 blades each) adjustable on the shaft of the mixer which was mechanically coupled to a variable angular velocity motor; heating-cooling system and air-sparging system incorporated in the design of the baffles. Details of the exact specifications can be found in the user's manual provided by the manufacturer.

The temperature control system (thermistor-thermo couple) allowed maintenance of steady temperature with a fluctuation of less than $\pm$ 0.5°C.

The pH was regulated through a New Brunswick Scientific pH-

Figure II-2: Experimental Set-up for Main Treatability Studies ("well-controlled" system)


FEED METERING PUMP
HEATING AND COOLING COILS
CLARIFIER
AERATION VESSEL (FERMENTOR)
RETURN SLUDGE METERING PUMP
EFFLUENT
ROTOMETER
AIR SUPPLY
P.R.V.
pH CONTROLLER
NaOH
H2SO4
WASTE

controller (model pH-22) within ±0.3 of the preset value on the pH-scale.

The Dissolved Oxygen level was continuously monitored by way of a New Brunswick Scientific D. O. analyser (model DO-40) connected to its respective polarographic sterilizable D. O. sensing probe. During the latter part of the studies dissolved oxygen measurements were conducted intermittently through an YSI Dissolved Oxygen Meter (model 54PP manufactured by Yellow Springs Scientific Instrument Co., Inc., Yellow Springs, Ohio). Its polarographic probe was modified to fit exactly (air-tightly) the standard 300-ml. BOD bottle and was also provided with a mechanical stirrer and a temperature sensor (thermistor), thus allowing direct measurements of Dissolved Oxygen under both equilibrium and transient conditions; this was particularly useful in the determination of Dissolved Oxygen utilization rates by the microbial populations in samples of mixed liquor drawn directly from the reactor.

A 2-liter pear-shaped separatory funnel (pyrex glass) served as the sedimentation tank.

The working volume of the fermentor was kept at 10 liters throughout the Main Treatability Studies, except for the final period of experimentation on the effect of increased concentrations of ionic species on the biosystem when a 7-liter effective volume was employed.

Level control, i. e.,const. volume was achieved in both the reactor and the settler by keeping the whole system slightly "over-

pressurized", due to the head of compressed air admitted for aeration of the mixed liquor in the fermentor, which exited via the same line as the liquid. Liquid level was maintained by adjusting the length of the exit-exhaust pipe skimming the liquid surface.

The pre-treated liquid waste was fed in continuously from a 13 IG plastic (linear polyethylene-Nalgene) bottle to the bio-reactor through a variable speed "kinetic clamp" type flow-metering pump (Sigmamotor, Model AL-4E) with a maximum flow of 3000 cc/hr. A similar pump was used on the recirculation line in order to readmit into the bio-reactor the biological solids settled out in the clarifier. (Maximum flow was 1200 cc/hr.) The variable speed feeding and recycling pumps served as dilution rate (or mean reactor residence time) regulating devices in the investigation of the bio-system's hydraulics and the derivation of the biological kinetic constants.

Because of the inherently difficult task of simulating a gravity sedimentation tank on a laboratory scale (volume and configurational limitations resulting in considerable hindrance of and deviation from the "quiescent settling" of the biological solids), better separation of the biomass from the mixed liquor was gained by imparting a slight momentary swaying motion into the tip of the--freely suspended from a stationary stand--separatory funnel at regular time intervals, after having loosely connected the tip of the funnel through a clamp to the piston of a reciprocating pump, whose motion was determined by a preset timer device. The clear supernatant from the sedimentation tank was collected in a plastic 5 IG carboy.

Transparent flexible plastic tubing was used in the feeding, harvesting and circulating lines, which were replaced regularly throughout the long-term experimentation period with new ones, to correct for losses of flexibility impairing proper pump functioning and for accumulation of active and inert solids on the inside walls.

II.1.B. Operating Procedures (Experimental Design)

i. Preliminary Studies

The strong phenolic raw waste which was the subject of the preliminary bio-treatability tests was used directly in the bio-reactor for processing after its pH had been brought down from its alkaline value (pH=8.5-9.5) to a level close to neutrality (pH=6.5-7.5), by 85% concentrated "technical" grade phosphoric acid.

As an inoculum for the biological oxidation of the waste activated sludge from the field scale Extended Aeration facility of Gulf Oil Ltd. (Montreal East) was used. Although the Extended Aeration Plant, operating at retention times in the range of 42 to 48 hours was known to be suffering periodic spells of poor functioning, mainly in terms of sludge settling capacity and, less often, phenol and organic load removal, it was decided to use sludge from that facility as the initial seeding material for the lab-scale process, as it was judged to be generally better adjusted to the particular waste water.

In principle fresh sludge was employed, i. e., it was added to the waste not later than two hours after it had been collected from the field installations. Whenever it was necessary for the sludge to be

used later, it was assured of storage at 0°C to +4°C.

To initiate a continuous-flow experiment the reactor was filled with raw waste liquor and seeded with the heterogeneous biomass at 10% on a volume basis: thus 2.5 liters of fresh activated sludge was used as an inoculum for a 25-liter volume of broth inside the bio-reactor. The system was subsequently operated in batch (i. e., only aeration and agitation without feeding, harvesting and recycling) for several hours (typically 18 hours), and then continuous pumping was begun and the system was allowed to approach a steady-state equilibrium. To this effect in three long-term continuous flow experimental "runs" mean residence times of between 26 & 48 hrs. were used, with an exceptional use of a longer retention within the same experimental "run" at times when poor phenol (and/or COD) removals were observed, as a corrective approach to relieve the stress off the bio-system.

Immediately following the arrival of a new batch of waste water in the laboratory a set of chemical analyses were carried out in order to characterize the quality of the raw influent liquor. These analyses included the determinations of pH, organic load as COD, concentration of phenolics, suspended and dissolved solids, and selected ionic species, such as $C\ell^-$ or Na^+.

The performance of this system was followed quantitatively by regular daily and, at times, semi-diurnal assays of biological solids, residual substrate concentration in terms of COD and phenol in the effluent, as well as measurements of D. O., pH and temperature levels on

the broth.

The approachment to steady state was judged by the apparent constant levels of volatile suspended solids, COD and phenol concentration, observed several hours after the initiation of the continuous flow operation.

A high aeration rate was used, providing Dissolved Oxygen concentrations close to saturation (≥80% of the saturation value or, generally, not less than 6.5 ppm of D.O.) and also contributing to the adequate mixing of the broth as only a single turbine impeller was employed. Normally aeration was ≤ 1 vvm; agitation speed~400 rpm.

A recycle ratio of .25 or less was used according to the observed settling characteristics of the biomass and also in order to reduce the rate of oxygen utilization.

No temperature control was exercised throughout the Preliminary Studies, but the temperature remained most of the time within a range of between 20 and 24°C (ambient-room temperature).

Manual correction of the pH was taken up when it was observed, almost from the beginning, that the mixed liquor inside the bio-reactor had a reduced buffering capacity and its pH was dropping at a rather quick pace, resulting in dispersed growth and extensive deflocculation of the mixed microbial biota. pH control was carried out intermittently and was aimed at keeping its levels to values between 6.5 and 7.5. To this end concentrated "technical" grade solutions of ammonium hydroxide or phosphoric acid were employed, according to the corrective direction

required, thus contributing at the same time to meeting the nutrient requirements of the biomass in N and P.

The close approximation of complete mixing conditions with regard to biological solids was accomplished by maintaining the fermentor free from wall growth. Thus, once a day or, at times even more often, growth of biota along the walls of the aeration vessel, the baffles (sidewise) and the shaft of the impeller were scraped away meticulously.

Finally the sludge condition was assessed from time to time (not on a regular basis but upon circumstantial evidence of necessity) by determining SVI on a sample of mixed liquor directly drawn from the bioreactor.

ii. Main Treatability Studies

Pretreatment. The Petrofina refinery and petrochemical effluent that was chosen for the main bio-treatability tests was initially characterized analytically in the Fermentation Lab of the Dept. of Chemical Engineering at McGill by this investigator and also in the Analytical Lab of an external consulting firm. The analyses included determinations of pH, COD, TOC, phenolics, dissolved solids, suspended solids, ammonia, sulfides and globules of free oil. From the analyses of both laboratories (see "Results," Table III-9) it became obvious that, because of the relatively high concentration of pollutants and toxicants such as ammonium and sulfide ions and free oil and the decidedly alkaline range of the waste water's pH, a physical-chemical pretreatment would be in order. To this end the simple aeration-

stripping system described above in the Equipment section was devised.

As the raw Petrofina effluent had an alkaline pH of around 8.5, its excess ammonia content was first driven out by raising the pH to between 11 and 12 (according to the $_pK_{OH}$ of $NH_4^+OH^-$) through the addition of highly concentrated NaOH. The equilibrium:

$$OH^- + NH_4^+ \rightleftharpoons NH_3 + HOH$$

was thus shifted far to the right and the ammonia released was continuously expelled by the stripping action of the aeration. Subsequently, in a similar manner, excess hydrogen sulfide was removed by continuous aeration of the waste after shifting the simultaneous chemical equilibria:

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{--}$$

far to the left by lowering the pH to around 2 through the addition of concentrated H_2SO_4.

A period of 30 to 40 minutes for each air-stripping procedure was employed according to the loading of the particular batch of raw waste liquor to be pre-treated.

Apart from a substantial reduction in the ammonia and hydrogen sulfide content of the raw waste water, the swarm of air bubbles generated from the ring-shaped sparger was utilized for removal of free oil globules by air flotation as discussed by Volesky and Agathos (1974). The simulation of air-flotation ("induced") on this small scale was aided by the high pressure of the particular laboratory air line

employed (80 psi). The free oil droplets accumulated in the form of oily scum were mechanically skimmed from the surface of the pre-treatment vessel. The efficiency of the process was markedly enhanced at an alkaline pH, so most of the free oil was collected during the air-stripping of ammonia. Finally, the air-stripped waste water was brought to neutrality (pH: 6.7-7.3), by addition of NaOH, thus providing the feed for the bio-reactor.

In the very first continuous-flow experiments when the unambiguous bio-treatability of the Petrofina effluent was sought to be established, the waste water was simply subjected to the above series of physical and chemical operations by way of primary treatment.

However, as it became obvious from the analytical data that the phenol content was rather low (typically less than 20 ppm.) it was decided to present the mixed microbial population of the bio-reactor with the challenge of a more realistic phenol level, often encountered in refinery and petrochemical industrial effluents. Thus the principal portion of the Treatability Tests (i.e., Hydraulic Studies-Determination of Process Parameters--studies of perturbations in feed) was effected on a waste feed pre-treated in the above described physical-chemical way and in the stated sequence, but with the spiking addition of phenol right after the neutralization step, making up to predetermined levels of 30 ppm., 60 ppm., and 100 ppm. of phenol.

Seeding-Acclimation-Biotreatment. In the first part of the Main Treatability Study, in which continuous flow experimentation was

carried out in the well-controlled bio-reactor to verify the extent of bio-oxidation and the potential of the system in terms of reduced retention times, the sludge developed in the Preliminary system was used as an inoculum. However, in the principal hydraulic studies and the detailed investigations of process variables the seeding material was obtained from the recycle line of a secondary clarifier of the municipal sewage treatment plant at Vaudreuil, Que., 20 miles west of Montreal, as it was necessary for the long-term studies to have a reproducible inoculum and a fairly broad mixed population of microbial species in order for an efficient acclimation to the industrial waste to occur. Also an increased diversity of species increases the ecological scope of potentially successful response to shocks (Gaudy 1975).

As in the Preliminary Studies, fresh sludge was always used to initiate a continuous flow experiment in the bio-reactor, i. e. the sludge was used less than 2 hours after its collection. In the beginning the waste feed was mixed with the sludge inoculum in the fermentor at a proportion of biomass at one third of the working volume and of waste water at two thirds of the working volume, and the broth was subjected to aeration and mixing only, for 24 hours. The continuous flow was assumed for at least 3 to 4 retention periods until a (pseudo-) steady state performance was reached. Initial retention times of around 24 hours were employed.

The attainment of acclimation was ascertained in conjunction with the relative stability of the steady-state performance: repeated

samplings and subsequent analyses were made for biological solids (as MLSS and MLVSS) and residual substrate (as COD and phenol content) on the effluent from the reactor while reasonably constant values for MLSS, ratio of MLVSS to MLSS and for COD were established (i. e., fluctuating not more than around ±10%). The same procedure was followed whenever a new steady-state was sought to be established after imposed perturbations of operating variables, as in the portion on hydraulic studies and in the studies on high ion concentration effects.

Complete mixing with regard to biomass (which is known for its tendency to sediment in the absence of sufficiently vigorous agitation and efficient mixing regimes) in the bio-reactor was verified by checking the equality of cell concentrations in the fermentor and in the effluent before sedimentation in the cell separator, via optical density measurements. Mixing with regard to substrate was assumed to be "complete," as residence time distribution studies in commercial New Brunswick fermentors have confirmed (cf. Chiu et al., 1972b).

The same efforts to minimize cellular growth in the tubing system and on the reactor walls were practiced here as mentioned above in the Preliminary Studies. It was also seen that the volumetric flow rates of influent waste water and recycle activated sludge would be maintained by regularly examining the performance of the pumps regarding their rate of delivering fluid and by correcting appropriately to the desired values whenever deviations were discovered. The working volume of the aeration vessel was fixed at 10 liters, except in the latest

experiments, on high ion concentration effects when a broth volume of 7 liters was employed.

The clarifier had an effective volume of 2 liters. Throughout the Main Treatability Studies, the rate of agitation was maintained at 360 rpm. The temperature of the continuous culture was controlled at 25±0.5°C, except in tests where the effects of temperature itself were examined. The pH of the culture was controlled at 6.8±0.3, except in instances when pH was left to fluctuate freely in order to monitor its effects. Controlling buffering solutions were 3N KOH (or NaOH) and 3N H_2SO_4(or NaH_2PO_4).

A relatively high aeration rate was employed in order to maintain sufficient Dissolved Oxygen concentrations in the broth, i. e., at 70% of the saturation level or higher (≥5.5 ppm. of D.O.) in the bioreactor*.

Finally, after mainly qualitative observations of the biomass flocculation and sedimentation of the sludge blanket inside the cell separator, a cell recycle ratio of 0.67 was empirically chosen and maintained nominally throughout the main bio-treatability study. It is a well-known fact that a relatively high recycle ratio is employed in systems in which a biological solids concentration considerably greater than can be supported in active growth by the available substrate (organid load of industrial waste water) is sought [compare Gaudy(1975)].

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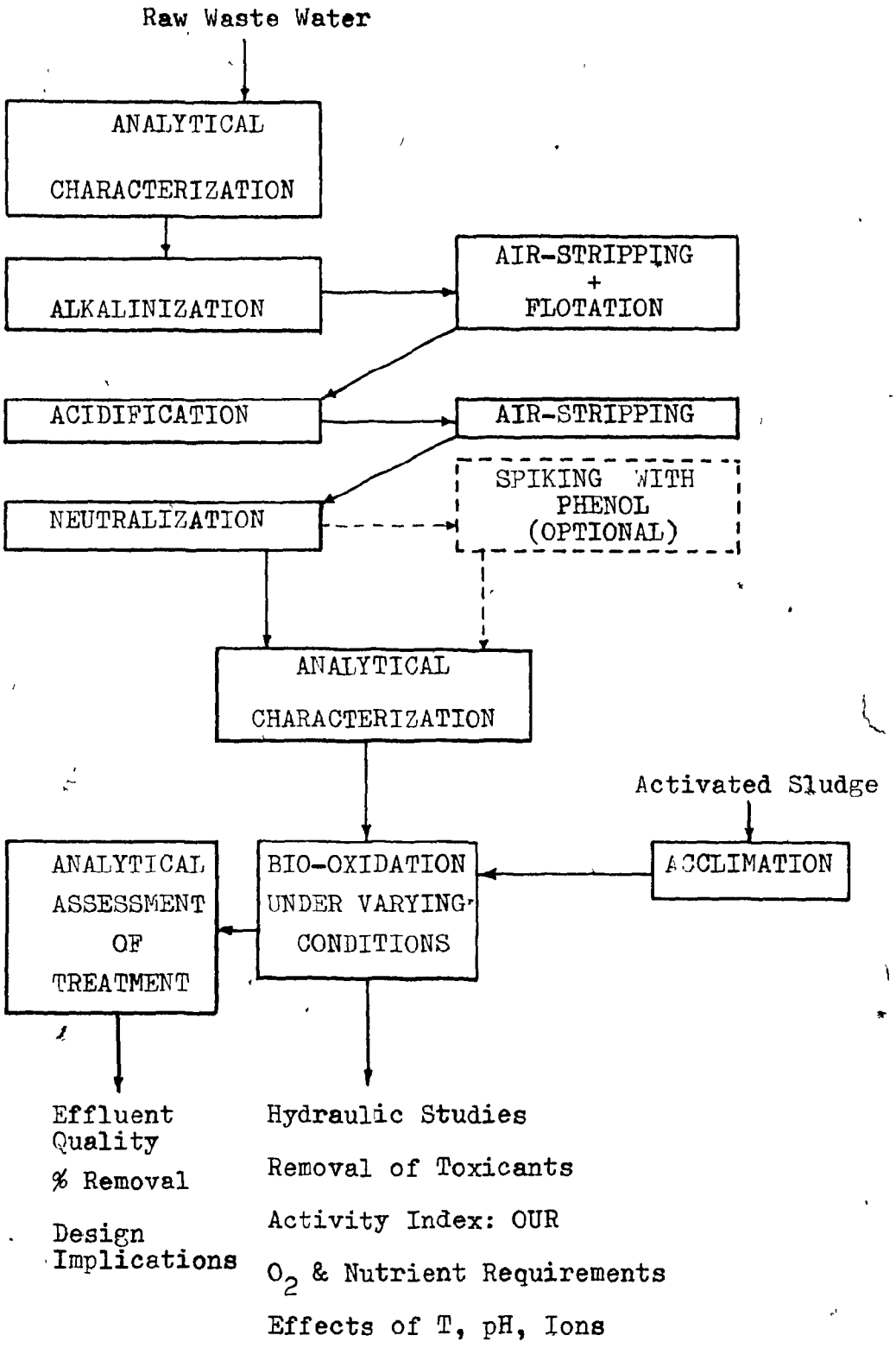
*This aeration was equivalent to 4±5l/min. at 14.7 psi and 70°F.

Figure II-3: Operational Sheet of Main Treatability Studies


Raw Waste Water
ANALYTICAL CHARACTERIZATION
ALKALINIZATION
AIR-STRIPPING + FLOTATION
ACIDIFICATION
AIR-STRIPPING
NEUTRALIZATION
SPIKING WITH PHENOL (OPTIONAL)
ANALYTICAL CHARACTERIZATION
Activated Sludge
ACCLIMATION
BIO-OXIDATION UNDER VARYING CONDITIONS
ANALYTICAL ASSESSMENT OF TREATMENT
Effluent Quality
% Removal
Design Implications
Hydraulic Studies
Removal of Toxicants
Activity Index: OUR
O_2 & Nutrient Requirements
Effects of T, pH, Ions

An overall schematic diagram of the various operations of which the Main Treatability Studies consisted can be seen in Figure II-3.

II.1.C. Analytical Methods

Measurements of Substrate

The organic concentration in the influent and treated effluent waste water (filtered and unfiltered) was ordinarily assessed by Chemical Oxygen Demand (COD) analyses, using the dichromate method according to Standard Methods (1971).

The filtrate obtained after a sample of broth had been separated from its suspended solids through Millipore Membrane filters was used for "dissolved COD" analysis. Such data were employed throughout the hydraulic studies on the performance of the bio-reactor as a chemostat and, specifically, for the estimation of mean values for the biological kinetic constants of the system.

Samples of effluent drawn directly from the supernatant in the cell-separator were used for the determination of COD on the biologically treated waste liquor when the gross organic load removal was sought to be assessed, as was the case in the Preliminary Studies and in Part 1 of Main Treatability Studies. Notwithstanding the limitations of the COD test as an index of both pollutional load and biologically degradable substrate, it is still regarded as a valuable parameter for estimating these physical entities [refs.: EPA-Preliminary Investigational Requirements (1971); Neufeld (1974); Surucu et al. (1975)]. Actually the COD

test is appropriate to use when the substrate is heterogeneous in nature [refs.: Jorden et al.(1971); Surucu et al. (1975)] as is the case in most industrial waste waters.

However, given the fact that in many reports in the literature of industrial waste water treatment indexes such as Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC) are also used, with an increasing tendency towards the widest use of the latter mainly on grounds of its simplicity and rapidity see EPA-Preliminary Investigational Requirements, (1971), an effort was made to tentatively correlate these two parameters with COD towards the end of the Main Treatability Studies.

The dichromate method for COD analysis was modified by proportional addition of $HgSO_4$ in the reaction mixture, as suggested in Standard Methods (1971), to allow for the relatively high concentration of chloride ions in the raw waste from Gulf Oil (see "Preliminary Studies"). BOD was determined by the method of dilutions, also described in Standard Methods (1971).

Finally, TOC was measured by using a Beckman organic carbon analyser (model 115) according to Standard Methods (1971) and user's manual [see also EPA-Preliminary Investigational Requirements, (1971)].

Measurements of Biomass

Microbial cell concentrations were estimated by routinely carrying out the gravimetric tests for MLSS (Mixed Liquor Suspended Solids) according to Standard Methods (1971). Gravimetric measurements were conducted directly by weighing the dried suspended solids

retained from vacuum filtration of samples drawn from the bio-reactor, through Millipore membrane filters (or equivalent Gelman filters) of a 0.45μ pore size. Less regularly the volatile portion of the suspended solids was determined, also according to Standard Methods, through combustion of the samples at 515°C and subsequent estimation of MLVSS (Mixed Liquor Volatile Suspended Solids) by difference between the weight of the ashed residue and the previously determined MLSS. The MLVSS determination was conducted as a check for the relative stability of the % volatile portion of the solids assumed to be an adequate estimate of cellular material.

The shortcomings of Dry Weight Measurements are recognized [see e. g., Weddle and Jenkins,(1971);Nutt,(1974)]-however, their use is proven quite satisfactory not only in full-scale plant operation but also in modelling of mixed population kinetics in closely-controlled laboratory scale systems [see continuing work by Gaudy and his associates (1967, 1969, 1971, 1973, 1974, 1975) and by Erickson, Fan and their associates (1972a, 1972b, 1973); also Goodman and Englande (1974), etc.] as other more "biologically rational" indexes of viable cell concentration such as enzyme activity or ATP are not as yet adequately refined or even conclusively capable of furnishing this type of information [Jordan et al.,(1971);Chiu et al.,(1973)].

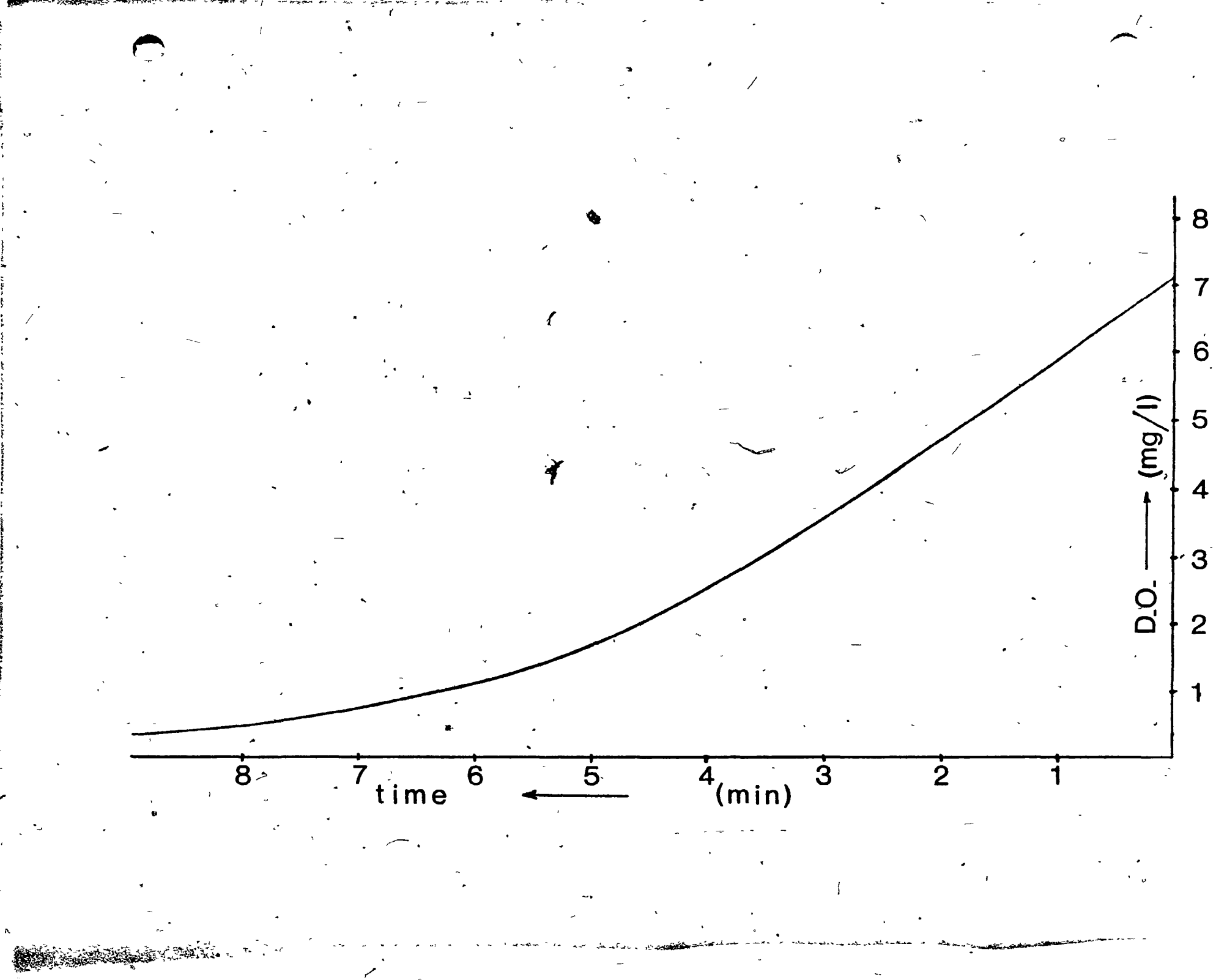
Selected rapid estimations of microorganism concentration were carried out photometrically, especially in the routine assessment of the attainment of a steady-state after initiating a new continuous-flow

experiment from operation in batch; the optical density was measured at 540 nm in a Spectronic 21 Spectrophotometer (manufactured by Bausch and Lomb).

Dissolved Oxygen Concentration-Oxygen Uptake Rate. For these measurements the YSI portable D.O. meter (model 55) described in the Equipment section was used. The oxygen uptake rate was determined as follows: Dissolved Oxygen levels were read off the meter at various time intervals on the particular sample of mixed liquor and a continuous profile of D.O. vs. time was visually observed from a recorder attached to the output of the D.O.-sensing polarographic probe. In this way the portion of the profile where D.O. depletion was linear could be used to obtain the oxygen uptake rate (OUR) as the slope -d(DO)/dt of the curve. The asymptotic approach to a lower but fixed rate of Dissolved Oxygen utilization represented simply the eventual depletion of D.O. to levels near zero after a few minutes of vigorous uptake. A representative diagram obtained directly from the recorder strip of the D.O. monitoring system which depicts these concepts is shown in Figure II-4.

To ensure sensing of D.O. concentration in the bulk of the sample agitation was provided to the sample solution captive inside a 300-ml. standard BOD bottle, whereas it was made sure that no air bubbles were entrapped inside the bottle, in order to avoid surface aeration of the monitored solution and a false low reading of oxygen utilization.

Figure II-4: Oxygen Consumption by the Aerobic Biomass of a Sample of Mixed Liquor Drawn from the Bio-reactor


8
7
6
5
4
3
2
1
D.O. ⟶ (mg/l)
8
7
6
5
4
3
2
1
time ⟵ (min)

Determination of Phenols. The levels of phenolic compounds were determined by means of the amino-antipyrine colorimetric technique in its two forms: i. e., the direct photometric method and the chloroform extraction method--for extreme sensitivity--always going through an all-glass distillation step as suggested in Standard Methods (1971). The chloroform extraction method was modified to accommodate a smaller total volume of sample or reaction mixture, i. e., 250 ml. rather than the 500 ml. recommended by Standard Methods: no discrepancy was found in the accuracy of this determination. In both procedures an addition of specified volumes of phosphoric acid and copper sulfate solutions is recommended by Standard Methods, serving the purpose of effectively eliminating or reducing to a minimum the interferences from oxidizing and oxidizable soluble species present in the sample and also guarding against spontaneous biodegradation of phenols upon storage of samples to be analyzed. It was found that, both in samples with relatively high (close to or more than 100 ppm.) and relatively low ($\lesssim$10 ppm.) phenol concentrations, the acidification of the sample with H_3PO_4 solution and the subsequent addition of copper sulfate solution before the distillation were unnecessary in most cases where the samples were assayed within a couple of hours or less from their collection, either from the field facility (raw waste water) or from the laboratory bioreactor and cell-separator. The results from assays of the same sample with and without H_3PO_4 and $CuSO_4$ addition were practically identical. However this addition did prove to be necessary, and was therefore

practised, in the case of particularly high-phenol and "complex" waste water samples (such as the ones originating from the Gulf Oil facility) or turbid distillates requiring a second distillation step in the all-glass apparatus.

In the Main Treatability Studies, the direct photometric procedure was chosen over the chloroform extraction method for reasons of relative rapidity and small sample volume requirements (i. e., samples or aliquots of 100 ml.) and also because of proven good reproducibility.

Finally, it was found that, as a means of tentative rapid estimation of the phenol content in a given sample or aliquot of waste water or treated effluent (particularly in the case of a sample relatively free from suspended matter) the distillation step could be omitted altogether, yielding results within 10-20% of the phenol concentration as determined by the Standard procedure which includes distillation as a necessary stage in order to separate the volatile phenolic species from the non-volatile impurities that tend to interfere with the eventual colorimetric determination.

Although the amino-antipyrine colorimetric technique in either of its two forms discussed above is clearly the most sensitive procedure for phenol assays, its chief disadvantage is the relatively long time it requires, mainly because of the distillation step. Thus a less cumbersome and far more rapid analytical technique for phenol determinations appears to be a gas-liquid chromatographic assay, which is actually in use in most industrial quality-control laboratories.

Selected Anion Species

Ammonia. Nitrogen in the form of ammonium ions was determined in samples obtained from the outlet of the raw waste water on field and from the treated effluent by a direct electrometric technique using a gas-sensing ammonia electrode manufactured by Orion Research, Inc. (Cambridge, Mass.), model 95-10, according to the user's manual The electrode was used in conjunction with an Orion Specific Ion Meter (Ionalyzer, Model 407A), and was standardized by employing a 0.1 M NH_4Cl standard solution, also provided by Orion Research, Inc. The direct electrometric method was chosen over the traditional kjeldahl determination of organic Nigrogen due to the former method's extreme rapidity, versatility and accuracy, which has prompted the U. S. Environmental Protection Agency (EPA) to endorse it since 1974 (cf. Analytical Method Guide, Orion Research, 7th edition, May 1975-Ref.)

Phosphates. The presence of phosphorous in waste water and treated effluent samples was quantified in the form of orthophosphates by employing the Vanadomolybdate colorimetric technique, according to Standard Methods (1971). Particular caution was exercised with respect to the glassware used in the assay: these were rinsed with hot dilute hydrochloric acid before and after each phosphate measurement and were specifically reserved for this particular analysis (detergents were avoided as most of them contain phosphates which obviously interfere with the analysis at hand).

Sulfides, Chlorides. Sulfide ions such as $[HS^-]$ and $[S^=]$ were

determined through a direct electrometric procedure using a solid-state specific ion electrode (silver/sulfide, Model 94-16, manufactured by Orion Research, Inc.) according to user's manual.

In a similar manner, the occasional determination of chloride ions [Cl^-] was carried out by means of a solid-state selective ion electrode (chloride electrode, model 96-17, manufactured by Orion Research, Inc.) following instructions in user's manual. Both electrodes were used on the Orion Specific Ion Meter (Ionalyzer, model 407A), which also served as precision pH-meter.

Metal Ions. During the Preliminary Studies phase on the high-strength phenolic waste water (Mixed Feed from Gulf Oil) the levels of metal ions such as Cu, Zn, Pb, Fe, and Na were determined via atomic absorption spectroscopy, according to Standard Methods (1971). The instrument used was an automated Perkin-Elmer Atomic Absorption Spectrophotometer, Model 403. However, the measurements of Na^+ concentrations during the studies of high ion concentration effects on the biological treatability of the Petrofina effluent were performed by utilizing a specific ion electrode (Sodium, Model 94-11 manufactured by Orion Research, Inc.) in a direct electrometric assay. The accuracy of this particular analysis was tested and confirmed by cross-checking with the results obtained on the same samples through atomic absorption spectroscopy.

Miscellaneous Analyses. Occasional or secondary analyses such as dissolved solids content, sludge volume index (SVI), effluent turbidity, were performed according to the specifications of Standard Methods (1971).

CHAPTER III

RESULTS AND THEIR DISCUSSION

III.1. Preliminary Studies

III.1.A. Feed Origin and Composition

The raw waste water used for the preliminary series of experiments was obtained from a mixed stream (from now on to be referred to as "Mixed Feed") at the Gulf Oil facilities in Montreal East. Three main streams of liquid wastes made up the Mixed Feed; the first one originated from Oil Refining Operations with a flow rate of 3000 gallons/hr, the second one from the Bisphenol production installations with a flow rate of 1200 gallons/hr and the third one from the Phenol/Acetone (via Cumene) production plant, with a flow rate of 4000 gallons/hr. The Oil Refinery waste stream accounted for around 200 ppm or more of the Mixed Feed's content in phenolic species (typically around 1000 ppm) while the waste liquor from the Acetone/Phenol plant contributed with the bulk of the sodium ion concentration (mainly as Na_2SO_4).

A typical composition of the Mixed Feed is shown in Table III-1, based on analyses performed at the Analytical Laboratory *in situ* by the Company's staff before and during the time of the study. The values of pH, COD, BOD, solids, hydrogen sulfide, ammonia and phenol were confirmed by the author's own analyses, performed on each batch of new waste liquor that was to be treated in the model Bio-oxidation

Table III-1

Typical Characteristics of High-Strength Waste Water Used in Preliminary Studies (Gulf Oil Waste)

PARAMETER	AMOUNT
pH	9.4
BOD (average)	1700 ppm
COD (average)	2900 ppm
Total Solids	5000 ppm
Hydrogen Sulfide	30 ppm
Ammonia Nitrogen	160 ppm
Phenol	900 ppm
Acetone	270 ppm
α-methyl-styrene	62 ppm
Acetophenone	40 ppm
Dimethyl-benzyl-alcohol	20 ppm
Cumene	27 ppm
Mesityl Oxide	10 ppm
Isopropyl Alcohol	17 ppm
Sodium (mainly as Na_2So_4)	2500 ppm

unit at the Fermentation Laboratory (Dept. of Chemical Engineering, McGill University).

It should be noted that the characteristics of the Mixed Feed liquor fluctuated considerably in the months before and throughout this portion of the investigation. According to figures obtained from the company's Analytical Laboratory the ranges of these fluctuations were as shown in Table III-2, with regard to BOD, COD, hydrogen sulfide, total solids, sodium (chiefly as Na_2SO_4) and selected heavy metals.

The rather heavily laden, in terms of COD and phenol content waste liquor, was fed continuously to an on-field biological oxidation facility of the Extended Aeration type (mean residence time about 50 hours) and, notwithstanding the wide range of fluctuations in the feed it had been previously reported to operate satisfactorily. However major upsets and even total failure of this field-scale facility, mainly in terms of settling properties of the biological solids and less often in terms of % removal had been occurring at the time of the present investigation.

As pointed out previously ("Scope of Investigation)" the rationale behind these preliminary research efforts was positively <u>not</u> the search for a remedy to the field-scale problems; these problems, however, were apparent too in conjunction with our primary task of achieving a <u>stable</u> high-rate activated sludge treatment (detention times of 24 hrs. or less) in our 30 liter laboratory unit, aiming at COD removals of 60% or better and residual phenol concentrations $\leq$ 1 ppm.

Table III-2

Ranges of Selected Pollution Parameters

of High-Strength Mixed Feed (Gulf Oil)

[Fall 1974 - Winter 1974-75]

PARAMETER	RANGE (in ppm)
BOD	1600-3600
COD	2780-4363
Total Solids	4762-5743
Hydrogen Sulfide	20-40
Sodium (mainly as Na_2SO_4)	1500-3000
Copper	0.15-0.43
Zinc	0.02-0.58
Calcium	14-34
Magnesium	2.6-6.8
Iron	1.2-8.0

III.1.B. Continuous Flow Experiments

Over a period of two months approximately, three continuous flow experiments were carried out. The Mixed Feed was kept relatively uniform in each of the experiments, through storage of each batch* at a temperature near the freezing point, and was also confirmed by performing "grab"-type occasional analyses of the raw waste water throughout the duration of the continuous-flow experiment at hand.

Run No. 1

This first series of tests on a continuous basis, also referred to as Run No. 1, was started up at a detention time of 26 hrs. (dilution rate D = 0.038 $hr.^{-1}$) using as inoculum an activated sludge acclimated to the high strength phenolic waste water from the field-scale treatment process. The biomass inside the lab reactor was adjusted at a level close to 3000 mg/l of MLSS developed at detention times progressively lowered from 48 to 32 hours in the two days before inoculation. The characteristics of the Mixed Feed used in Run No. 1 are shown in Table III-3.

A recycle ratio of 0.25 was employed and no sludge wastage was exercised, in an effort to keep the biomass at high levels owing to the relatively high organic load of the waste feed.

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*A batch of Mixed Feed to be treated at the laboratory would usually consist of 100 gallons of raw waste.

Table III-3

Characteristics of Influent Raw Waste in Run No. 1

PARAMETER	AMOUNT
pH	9.4
COD	2210 ppm
Phenol	1100 ppm
Dissolved Solids	5000 ppm
Suspended Solids	40 ppm
Sodium Ions	1300 ppm
Chloride Ions	270 ppm

Raw data of the analyses performed during this first experimental run are tabulated in Table III-4. The determinations were carried out on samples obtained from the bio-reactor and effluent at least once a day and often twice or even three times a day. The same data are represented graphically in Figure III-1.

Initially an acceptable steady-state performance could not be maintained for any appreciable length of time (i.e., in terms of a number of mean detention periods rather than just a few hours). The MLSS within three detention periods decreased from 2910 mg/l to 610 mg/l with a continuous trend downwards, while at the same time the residual substrate was stabilized at about 1400 mg/l showing a removal considerably less than satisfactory (removal of COD less than 37%). Also the phenol content of the effluent started rising almost immediately after the start-up of continuous operation to reach levels higher than 300 ppm, thus manifesting the total failure of the system to handle phenols effectively (the objective was $\leq$ 1 ppm of phenols in the effluent).

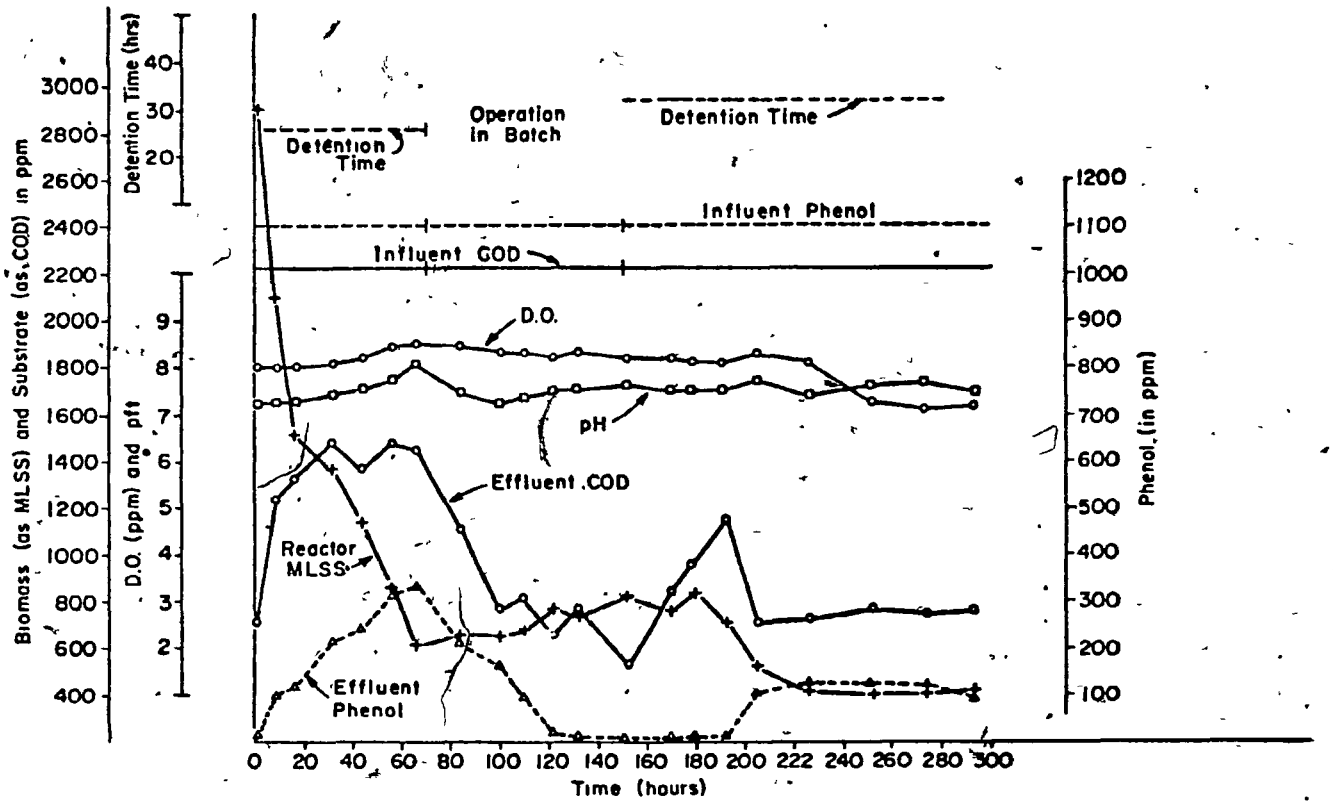
The gradual "kill" of the activated sludge population was corroborated by rising levels of D.O. due to a decrease in oxygen uptake and also by rising pH, clearly a consequence of continuous "dilute-out" of the broth inside the reactor, which was replenished by the highly alkaline Mixed Feed (the normal metabolic trend is for the pH to drop spontaneously in an aerobic bio-oxidation system treating a complex substrate such as petrochemical effluents, as can be shown from the results reported in the next section).

TABLE III-4

DATA FROM CONTINUOUS-FLOW RUN NO. 1

Time [hours]	Effluent		Bio-Reactor				Remarks
	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	
0	710	<1	2910	8.0	7.2	120	Continuous flow at detention time = 26 hrs
8	1235	100	2100	8.0	7.2		
16	1325	120	1510	8.0	7.2		
32	1480	215	1370	8.1	7.4	250	
44	1375	245	1140	8.2	7.5		
56	1480	320	860	8.4	7.7		
66	1450	330	610	8.5	8.0	290	Start operation in batch. Manual correction of pH
84	1110	230	660	8.4	7.4		
100	766	165	650	8.3	7.2		
110	811	95	680	8.3	7.4		
122	661	15	770	8.2	7.5	270	
132	777	10	750	8.3	7.5		Resume continuous flow at detention time = 32 hrs
152	524	2	810	8.2	7.6		
170	840	2	760	8.2	7.5		
178	966	<1	835	8.1	7.6	275	
192	1152	2	715	8.1	7.5		
205	706	118	520	8.3	7.7		
226	720	125	410	8.1	7.4		Decrease aeration
252	770	125	400	7.3	7.6		
274	750	110	400	7.1	7.7		
294	760	90	410	7.2	7.5		

Figure III-1: Continuous Flow Run No. 1


Biomass (as MLSS) and Substrate (as COD) in ppm
Detention Time (hrs)
D.O. (ppm) and pH
Phenol (in ppm)
Detention Time
Operation in Batch
Detention Time
Influent Phenol
Influent COD
D.O.
pH
Effluent COD
Reactor MLSS
Effluent Phenol
Time (hours)

Although the high phenol concentration of the Mixed Feed was the obvious suspect for this initial disruption of the bio-system at this rather high dilution rate, an analytical investigation, of the raw waste water with regard to heavy metal ions was carried out at that point.

Cu: 0.18 ppm

Zn: 0.27 ppm

Pb: 0.03 ppm

Fe: 3.25 ppm

The results shown above depict less than "troublesome" levels, since it is well-established that the first three heavy metals do not interfere with the bio-oxidation process unless in levels about 1 ppm and, in many cases levels of even orders of magnitude higher can be tolerated by the mixed microbial populations of the biological flocs. It should be noted here, in addition, that Cu, Zn and Pb were <u>not</u> detectable in the effluent, probably owing to concentration by the biomass. [Cf. EPA (1971), Neufeld (1974)].

The almost immediate signs of the system's deterioration were also apparent in the condition of the activated sludge. Whereas the sludge used as inoculum had an SVI of ≈120, it reached a value of 290 within the first three detention periods. Also this sludge "bulking" (with the appearance of floating aggregates in the secondary clarifier) was associated with a severe failure in the filterability of the biomass:

Standard Millipore or Gelman Membrane filters (0.45 μ pores) or even equivalent Whatman filter paper were proven impractical due to excessively long times of vacuum filtration required.

After the three initial detention periods it was decided to operate the system in batch (complete cut-off of the feed) in an attempt to provide the mixed microbial population with an additional period of acclimation to the high residual levels of phenol as well as of organic substrate (as COD). At the same time the pH was adjusted back to 7.1 with concentrated "technical grade" phosphoric acid.

By the end of almost four detention periods (accounting for an approximate turn-over of 95% of the liquid volume in the reactor) the phenol concentration had dropped to less than or around 1 ppm, with a marked dwindling in residual COD (oscillating around the 750 mg/l mark) and boosting in MLSS (approaching 800 mg/l), as seen in Fig. III-1. It can also be seen that the COD removal responded considerably more readily than the phenol removal after the complete feed cut-off.

When these signs of "healthy" performance were established the continuous feeding to the lab unit was resumed, this time round at a detention time of 32 hours.

It is interesting to note the response patterns of substrate and biomass concentrations, which showed, for the first time, the clear tendency to reach a steady state. The switch from batch operation in a nearly depleted medium to a continuous flow is equivalent hydraulically to a switch of a continuously operating bio-reactor to a higher

dilution rate. In this respect the response of the residual COD in our unit was qualitatively similar to the pattern observed by George and Gaudy (1973a) when studying the response of a completely mixed activated sludge system to increases in dilution rate, and it involved a distinct transient rise in effluent COD concentration to a local maximum before the establishment of an apparent steady state, at about the value achieved previously during the operation batchwise (750 mg/l). The response of the biological solids concentration was more gradual over the transient, did not involve the expected local minimum and stabilized to an all time low of ∿400 mg/l). This pattern may be explained if one takes into account the concurrent and continual loss of biological solids at the cell separator because of the poor compaction characteristics of the sludge, since even after the operation batchwise the SVI improved only marginally (SVI = 270). Finally the phenol content responded with an abrupt rise before the end of the second detention period (after the startup of the new continuous-flow phase) from 2 ppm to 118 ppm with a distinct tendency to stay around or closely above the 100 ppm mark for the next three detention periods in a quasi-steady state.

From an engineering point of view, while the COD removal is judged as quite satisfactory (66% COD removal), the plateau reached by the phenol concentration in the effluent (close to or above 100 ppm) is totally unacceptable in any practical sense. Still it appears that this poor removal of phenol (in conjunction with the high influent

phenol concentration and a preferential biodegradation of the rest of the organic load making up the substrate represented by COD) may be dictated by the metabolic potential of the particular mixed population at the dilution rate employed.

Also the values of MLSS attained are very low, given the persistent sludge "bulking"; this could not be conclusively identified in any particular class of poorly separating sludge cases as suggested by Pipes (1967), but it is possible that over-aeration was part of the problem, as a decrease in aeration (lowering the D.O. to 7.3 ppm from above 8 ppm) brought about a slight improvement in settling of the biomass, along with less foaming, which also had appeared to be a problem at times.

Run No. 2

A second continuous-flow experiment was conducted using as inoculum a sludge obtained also from the field-scale Extended Aeration facility of Gulf Oil, but differing in its characteristics from that of the previous "run": The sludge had good settling and compacting properties with an SVI of ∿100 but was darker in color and its flocs were more dispersed than fluffy.

This time a higher mean residence time was employed, i.e. 43.3 hours (dilution rate $D = 0.023$ hrs.$^{-1}$) with the expectation that if the system could reach some form of steady state and maintain it over a number of detention periods then the objective of high-rate treatment

could be achieved stepwise by gradually boosting the dilution rate, given the well-established (Cf. for example, Jannasch (1967), Stumm-Zollinger (1968), Chiu et al (1972)) selective pressure of the chemostat on the mixed microbial population for those species with higher growth rates.

Another feature of this second experimental "run" was that, for reasons of limited hauling capacity (from site of waste collection to our Fermentation Research Lab) a second batch of raw waste liquor with somewhat different characteristics had to be fed into the bioreactor after the first 190 hours of continuous operation (about 4½ detention periods), when the first batch had been used up. The characteristics of the two batches of Mixed Feed are presented in Table III-5.

Sludge recirculation was exercised at a ratio of 0.25 and there was no sludge wastage owing to the difficulties encountered in the flocculation of the biomass and also since here again an appreciable amount of biological solids in the reactor was aimed for.

Prior to the startup of the continuous operation of the bio-system, the pH was lowered to 7.1 with concentrated phosphoric acid and in the 18-hour period of additional* batch acclimation the concentration of biological solids was adjusted to 1300 mg/l. Average temperature of the process was around 22±2°C. Data on the values of the parameters tested

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*The sludge from the field-scale facility was assumed acclimated, but this 18-hour contact with the raw waste in batch was still exercised in view of the increased dilution rates to be encountered in the ensuing continuous-flow experimentation.

Table III-5

Characteristics of Influent Raw Waste in Run No. 2

	PARAMETER	AMOUNT
First Batch:	pH	9.1
	COD	2900 ppm
	Phenol	1225 ppm
	Suspended Solids	30 ppm
Second Batch:	pH	9.2
	COD	3600 ppm
	Phenol	1100 ppm
	Suspended Solids	33 ppm

during this "run" appear in Table III-6, while their graphical representation is given in Figure III-2.

As seen from this Figure there was an uneven initial period of about 2½ mean residence times for MLSS to build up to around 1500 mg/l after sagging to less than 1000 mg/l, for COD to reach a fairly constant level of around 700 mg/l after a "surge" to more than 1000 mg/l and for residual phenol to fluctuate to moderate levels between 2 and 5 ppm after an initial "surge" up to 18 ppm. All three parameters remained fairly steady for another two detention periods until pumping of the new batch was begun into the system at the same dilution rate.

Apparently this perturbation resulted in immediate deterioration of phenol removal already within the first detention period after the influx of the new batch, despite the fact that the influent phenol was now somewhat lower than before (1100 ppm compared to an initial 1225 ppm); on the other hand the COD removal not only was not impaired but it was excellent (around 81%) although the organic load was now considerably higher (3600 mg/l compared to an initial 2900 mg/l). It seems possible that some unspecified component of the new feed had an inhibitory effect on the segment of organisms particularly responsible for phenol removal or that the bulk of the mixed population of the sludge switched to the more readily biodegradable components of the organic substrate represented by COD.

As corrective action for this Phenol removal failure it was decided to discontinue the feed as in the previous experiment and operate the

TABLE III-6

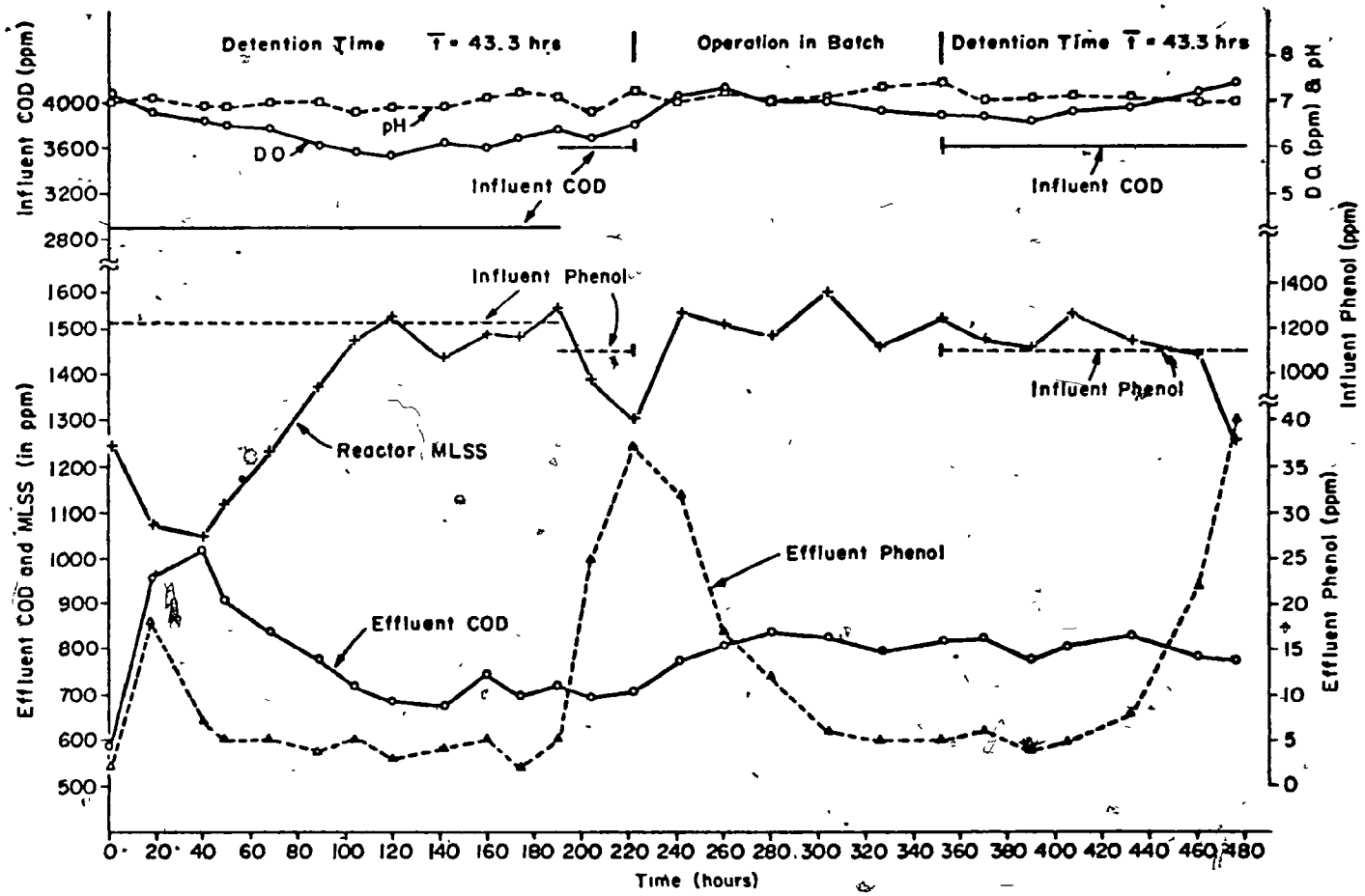
DATA FROM CONTINUOUS-FLOW RUN NO. 2

Time [hours]	Effluent		Bio-Reactor				Remarks
	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	
0	596	2	1244	7.2	7.0	100	Continuous flow at detention time $\bar{t}$ = 43.3 hrs
19	954	18	1072	6.8	7.1		
40	1015	7	1050	6.6	6.9		
49	903	5	1117	6.5	6.9		
68	837	5	1233	6.4	7.0		
89	774	4	1372	6.1	7.0		
104	716	5	1476	5.9	6.8		
120	683	3	1525	5.8	6.9		
142	675	4	1437	6.1	6.9		
160	744	5	1483	6.0	7.1	175	
174	697	2	1480	6.2	7.2		
190	721	5	1546	6.4	7.1		New Batch of Mixed Feed
204	698	25	1386	6.2	6.8		
222	707	37	1305	6.5	7.2		Start operation in Batch
242	775	32	1532	7.1	7.0		
260	810	17	1510	7.3	7.2	230	
280	840	12	1485	7.0	7.0		
304	827	6	1580	7.0	7.1		
326	790	5	1460	6.8	7.3		

TABLE III-6: Continued

Time [hours]	Effluent		Bio-Reactor				Remarks
	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	
352	818	5	1520	6.7	7.4		Resume continuous flow at detention time $\bar{t}$ = 43.3 hrs
370	825	6	1478	6.7	7.0		
390	778	4	1460	6.6	7.1	310	
407	803	5	1528	6.8	7.1		
432	833	8	1475	6.9	7.1		
460	781	22	1448	7.2	7.0		
476	776	40	1260	7.4	7.0	330	

Figure III-2: Continuous Flow Run No. 2


Detention Time $\bar{T}$ = 43.3 hrs
Operation in Batch
Detention Time $\bar{T}$ = 43.3 hrs
Influent COD (ppm)
D.O. (ppm) & pH
pH
DO
Influent COD
Influent COD
Influent Phenol
Influent Phenol
Influent Phenol (ppm)
Reactor MLSS
Effluent Phenol
Effluent COD
Effluent COD and MLSS (in ppm)
Effluent Phenol (ppm)
Time (hours)

system batchwise for a 130-hour period. By the third detention period of batch operation quasi-steady values of COD at ∿800 mg/l, of MLSS at 1500 mg/l and of Phenol at ∿5 ppm had been reached and were sustained by the system for another 2½ detention periods of continuous-flow operation at the same dilution rate. Failure of the bio-treatment was manifested again through sludge bulking (the SVI had deteriorated constantly from the time this experimental "run" was started) and serious impairment of phenol removal which was judged as being particularly dependent not only on the dilution rate, but also on the uniformity of the influent's characteristics. The "run" had to be terminated by the end of its 20th day of operation not only because of the poor sludge condition (manual intervention was needed to avoid losses of biological solids from the secondary clarifier into the effluent) but also since soon another batch of raw waste water with possibly different characteristics would have to be fed into the system, thus providing a new disruption. However the trends of the MLSS and Phenol concentration profiles indicate that these parameters were probably heading for a new steady state at the lower MLSS and higher Phenol levels dictated by the dilution rate employed (which has a direct bearing on the selective pressure exercised on the mixed microbial population of the sludge). Still the residual substrate (as COD) showed a remarkably small fluctuation and the COD removal was very good (∿78%) up until the time the "run" was discontinued.

Run No. 3

This series of observations on a continuous basis was conducted on a uniform influent raw waste liquor, whose characteristics are shown in Table III-7.

New apparently healthy (SVI = 115) sludge was used directly from the full-scale facility and a mean hydraulic residence time of 48 hours was employed initially (matching that of the full-scale facility), in an attempt to carry the reasoning of Run No. 2 one step further: Starting with an even lower dilution rate, i.e. with the same one on which the activated sludge inoculum had grown in the Extended Aeration Basin of the Refinery, and establishing an adequate steady state with satisfactory COD and phenol removals (a kind of scale-down of the field facility) we could work our way smoothly to higher dilution rates in the pursuit of a high-rate treatment. Here again manual pH correction was carried out and the average temperature fluctuated about the 24°C mark (±2°C). The data points obtained during this series of tests are tabulated in Table III-8 and are depicted graphically in Fig. III-3.

The MLSS initially adjusted to 2800 mg/l were maintained effectively constant at around 2600 mg/l for the first 5 days of operation and the average COD in the effluent was more or less steady around 1100 mg/l (removal 64% or better). During the same period the residual phenol concentration ranged between 2 and 8 ppm while the sludge quality was somewhat inferior in terms of settling and compaction (SVI = 165). After 2½ detention periods (5 days) a detention time of 40 hrs. was

Table III-7

Characteristics of Influent Raw Waste in Run No. 2

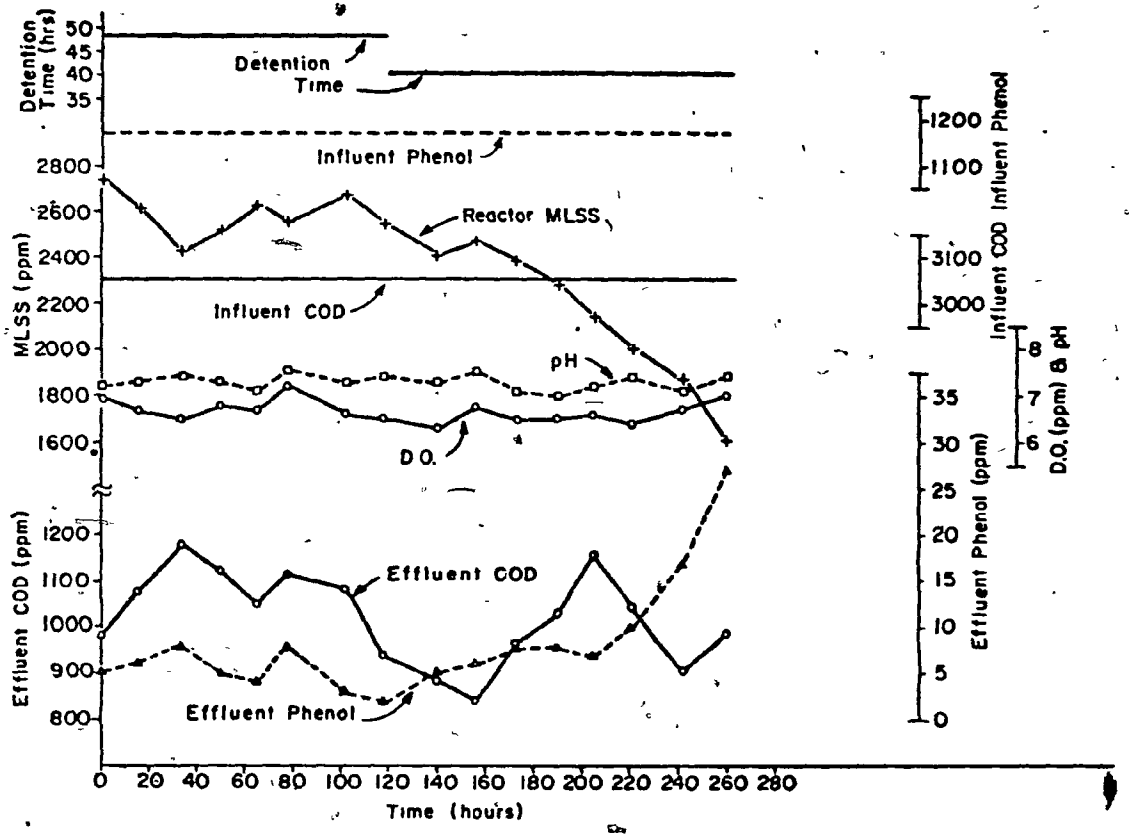
PARAMETER	AMOUNT
pH	9.3
COD	3050 ppm
Phenol	1170 ppm
Suspended Solids	47 ppm
Dissolved Solids	3100 ppm
NH_3-Nitrogen	187 ppm

TABLE III-8

DATA FROM CONTINUOUS-FLOW RUN NO. 3

Time [hours]	Effluent		Bio-Reactor				Remarks
	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	
0	982	5	2745	6.9	7.2	115	Operation at Detention time $\bar{t}$ = 48 hrs
16	1073	6	2610	6.7	7.3		
34	1180	8	2435	6.5	7.4		
50	1125	5	2515	6.8	7.3		
65	1050	4	2627	6.7	7.1	160	
78	1117	8	2560	7.2	7.5		
102	1083	3	2670	6.6	7.3		
118	940	2	2545	6.5	7.4		Operation at Detention time $\bar{t}$ = 40 hrs
140	885	5	2410	6.3	7.3		
156	843	6	2465	6.8	7.5		
173	967	8	2380	6.5	7.1	267	
190	1032	8	2278	6.5	7.0		
205	1160	7	2140	6.6	7.2		
221	1045	10	2004	6.4	7.4		Turbid effluent copious foaming
242	903	17	1870	6.7	7.1	360	
260	986	27	1610	7.0	7.4		

Figure III-3: Continuous Flow Run No. 3


Detention Time (hrs)
50
45
40
35
Detention Time
Influent Phenol
2800
2600
2400
2200
2000
1800
1600
MLSS (ppm)
Reactor MLSS
Influent COD
pH
D.O.
1200
1100
1000
900
800
Effluent COD (ppm)
Effluent COD
Effluent Phenol
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280
Time (hours)
1200
1100
Influent Phenol
3100
3000
Influent COD
35
30
25
20
15
10
5
0
Effluent Phenol (ppm)
8
7
6
D.O. (ppm) & pH

employed. While the COD in the effluent continued to fluctuate around 1000 ppm, there was a marked decline in MLSS not only due to the higher dilution rate, but also because of the deterioration of the characteristics of the biomass, and by the end of the 10th day of continuous operation it exhibited severe lack in settling and compacting capacity (SVI = 360) and excessively turbid effluent; at the same time there was copious foaming in the culture and phenol levels exhibited an upward trend well above the 10 ppm level.

The run was discontinued as the lack of sludge settling capacity was persistent, despite the trial use of a flocculant agent [$Fe_2(SO_4)_3$]. This multivalent salt had been previously used, reportedly successfully, on the field scale facility at times of dispersed growth and excessively turbid effluent. However, its use on the bench-scale system, even in excess of 200 ppm, was ineffective.

Following this last experimental "run" of the Preliminary bio-oxidation system, in conjunction with the observations made in the previous continuous-flow experiments it was concluded that:

In the strongly alkaline phenolic waste water from Refining and Petrochemical Operations (Phenol in excess of 1000 ppm, pH $\geq$ 9.0) adequate removals of organic load as COD could be achieved by high-rate activated sludge treatment, whereas the elimination of Phenol to levels below or around 1 ppm on a continuous basis was problematic.

Furthermore recovery of a disrupted bio-oxidation system seems to be far more responsive in terms of COD rather than phenol removals.

The long detention times required for the effective removals of phenolics combined with the instability of the activated sludge system (inability to attain a self-maintainable steady state) at such high phenol levels clearly points to the fact that the Activated Sludge Process might not be directly applicable to such feeds and that there might be a need for a preliminary reduction of high phenol concentrations, e.g. by air-stripping and/or dilution through equalization basin, multiple-stage bio-oxidation systems as reported by Adams (1974), etc.

Not only "short" (i.e. less than 40 hrs.) detention times, but also sudden changes in the feed make-up tend to disrupt the bio-treatability of high-phenol alkaline wastes both in terms of phenol elimination and sludge characteristics.

The toxic effect of phenolics at the high concentrations fed into the system seems to be powerful enough as not to warrant the investigation of interferences of ionic species such as heavy metals on the performance of the bio-system, as was also shown by the absence of such species in the tested case (Run No. 1).

The origin of the inoculating sludge and the concomitant question of its proper acclimation seemed to play a key role in the performance of the bench-scale system. Long-range acclimation tests are required in order that a highly potent mixed microbial population is developed, to be able to handle a high-strength petrochemical effluent and to better respond to shocks in hydraulic or environmental variables. This was probably the case in the present preliminary tests, as the sludge

obtained from the Extended Aeration Basin of the Gulf Oil Refinery was often shock-dosed at the time of its collection, and the point was confirmed later on, through the marked difference in system performance on the Petrofina Waste (Main Treatability Studies) between biomass developed form municipal sludge versus biomass developed from Gulf Oil sludge. (Effect of "past growth history".)

In addition to the above it was recognized that scaling down the activated sludge process from even a relatively successful prototype to a bench-scale unit that would simulate the performance of the prototype (as in Run No. 3) involves many complications, partially arising from the confined geometry and inadequate simulation of agitation, aeration, mode of feeding, etc.

Finally it was also recognized that, besides the need for a waste water clearly amenable to biodegradation in a high-rate activated sludge process without the above problems of the Gulf Oil effluent, a closely controlled bio-oxidation system should be built and operated in a way that parameter fluctuations could be interpreted meaningfully and that a basic process model based on material balances could be applicable.

III.2. Main Treatability Studies

III.2.A. Feed Origin and Composition

The waste liquor used for the Main Treatability Studies was obtained from the Refinery of Petrofina Canada Ltd. in Montreal East. Because it originated basically from common oil-refining operations (e.g. crude coker, desalter, catalytic alkylation and cracking units etc.) and was diluted with cooling water and "blow down" from boilers, it was not as heavily laden with organic pollutional load (as COD) and phenol as the Gulf Oil effluent studied previously.

On the field of the Refinery the main "oily" stream of waste water that was to be treated was first passing through a standard API gravity-type separator and subsequently through a Holding Basin which was also admitting a waste stream from a Polybutene unit, apart from serving as an "impounding basin" for storm waters; finally the stream coming out of the basin underwent an additional clarification by an air-flotation process through a Wemco-type Depurator, mainly for the elimination of residual oil globules and suspended solids. It was the stream originating from the Depurator that was used throughout the main treatability experimentation as the raw waste feed to our lab-scale physical-chemical pretreatment unit and subsequently, after its air-stripping and neutralization, as the feed to the fully-controlled fermentor. (There has been one exception, whereby one particular batch of waste liquor was obtained from an outlet before the Depurator (by-pass), as this latter unit happened to be out of order at that point.)

A list of the main characteristics of the raw waste water and their ranges is given in Table III-9. The data represent values from composite samples (over a 24-hour sampling period at the particular outlet) and were confirmed throughout the present investigation at our Fermentation Laboratory after their first evaluation at the analytical laboratory of a private consulting firm of Montreal.

Table III-9

Ranges of Characteristics of Waste Stream

Chosen for Main Treatability Studies

PARAMETER	AMOUNT
pH	8.2-9.1
COD	250-810 ppm
TOC	100-300 ppm
Total Suspended Solids	10-195 ppm
Dissolved Solids	2000-5800 ppm
Phenol	8-75 ppm
Hydrogen Sulfide	10-120 ppm
Ammonia	30-140 ppm
Oil	10-160 ppm

III.2.B. Hydraulics and General Treatability

This first part of the Main Treatability Studies was aimed at testing and establishing more qualitatively rather than quantitatively the susceptibility of the Petrofina Refinery waste water to high-rate activated sludge treatment in terms of obtainable quality of effluent and to gain some insight as a first approximation to the system's hydraulic behavior with regard to increasing dilution rates. This continuous-flow experiment, referred to as Run No. 4, lasted for more than a month (44 days). Initial sludge inoculum was obtained from the less sophisticated bio-oxidation unit that was still in operation, treating the high-strength phenolic Gulf Oil effluent, and it was subjected to additional batch-wise acclimation to the Petrofina Waste liquor, as described in the section on Operating Procedures. During this experiment mean hydraulic residence times of 24, 16, 15 and 13 hours, were employed, corresponding to dilution rates of 0.0417, 0.0625, 0.0667 and 0.0769 $hr.^{-1}$ respectively. Because of limitations in the hauling capacity from site of waste collection on field to our Fermentation Research Lab the waste liquor arrived in the Lab in batches collected at different points in time, thus differing somewhat in their characteristics. Also, because the physical-chemical pre-treatment unit in the Laboratory operated in batch, the final "stripped" waste water that constituted the actual feed to the bio-reactor was not absolutely uniform in its characteristics. In the results reported in this and the following section there is always mention of the quality of the "raw" and "stripped" feed for reasons of

Table III-10

Quality of Waste Water Batch "A"
fed at time t=0 (Detention time $\bar{t}$=24 hr & 15 hr)

Parameter	Raw	Stripped
pH	8.2	6.7
COD	340 ppm	285 ppm
Phenol	42 ppm	28 ppm
Susp. Solids	47 ppm	45 ppm
Dissolved Solids		4200 ppm

Table III-11

Quality of Waste Water Batch "B"
fed at time t=410 hrs. (Detention time $\bar{t}$=16 hrs)

Parameter	Raw	Stripped
pH	8.2	6.9
COD	322 ppm	266 ppm
Phenol	17 ppm	10 ppm
Sulfide	53 ppm	3 ppm
Ammonia	98 ppm	21 ppm
Dissolved Solids		5700 ppm

Table III-12

Quality of Waste Water Batch "C"
fed at time t=772 hr (Detention time $\bar{t}$=16 hr & 13 hr)

Parameter	Raw	Stripped
pH	8.8	7.2
COD	525 ppm	480 ppm
Phenol	12 ppm	8 ppm
Sulfide	37 ppm	Non-detectable
Ammonia	112 ppm	17 ppm
Susp. Solids		23 ppm
Dissolved Solids		3860 ppm

better comparison and interpretation of the resulting biological treatment.

The initial biomass concentration for the acclimation period and the first segment of this continuous run at a detention time $\bar{t}$ = 24 hours was adjusted at 1250 mg/l.

The performance of the system was quantified through the data of continuous operation listed in Table III-13 and graphically rendered in Figure III-4, while the characteristics of the batches of "raw" and "stripped" waste liquor fed at three different points in time during the run into the bio-system are shown in Tables III-10, III-11, and III-12, in the following pages.

Throughout the duration of this rather lengthy continuous flow run constant environmental conditions in terms of temperature (T = 25°C ± 0.2), agritation (360 rpm), aeration (70% of saturation) and cell recycle (67%) were maintained. The only variable that was not always controlled strictly at a preset level was pH, as in two occasions the only pH-controller available had to be used in a shorter-term project.

Following the course of variation of the monitored parameters (Table III-13 and Fig. III-4) one can discern the combined effects of dilution rate, feed make-up and pH variations and step-corrections on the levels of effluent COD and reactor biomass.

By the end of the fourth day of operation at a residence time $\bar{t}$ = 24 hours an increase in dilution rate was imposed ($\bar{t}$ = 15 hours). The initial overshoot of the residual COD is clearly the result of the hydrau-

TABLE III-13

DATA ON CONTINUOUS-FLOW RUN NO. 4
["Petrofina" Waste;
temperature = 25°C;
agitation = 360 rpm]

Time		Effluent		Bio-Reactor				
# day	[Hours]	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	Remarks
1	0	127	2	975	6.2	6.8		Detention time $\bar{t}$ = 24 hrs; Feed Batch "A"
2	25	105	1	920	6.5	6.7		
2	31	87	<1	935	6.3	6.9	120	
2	47	62	<1	875	6.8	6.8		
3	56	77	<1	855	6.5	6.7		
4	74	55	<1	785	6.7	6.5		
4	84	57	<1	795	6.3	6.8		
5	100	63	<1	785	6.2	6.8		Switch to Detention time $\bar{t}$ = 15 hr
5	112	110	<1	765	6.1	6.9		
5	120	92	≤1	710	6.5	6.7	130	
6	140	87	<1	640	6.5	6.6		
7	152	72	<1	730	6.1	6.9		
7	164	62	<1	750	6.3	6.7		
8	172	63	<1	717	6.4	6.9		Start manual control of pH
8	190	75	<1	682	6.2	6.4		
9	198	63	<1	667	6.0	6.6		
9	212	67	<1	518	6.2	6.2		Sludge: smaller flocs, more hindered settling

TABLE III-13: Continued

Time		Effluent		Bio-Reactor				
# day	[Hours]	COD. [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	Remarks
10	222	64	<1	475	6.3	6.1	144	
10	235	67	1	380	6.0	5.8		Step correction of pH to 7.2 with NH_4OH
11	248	55	2	360	6.2	6.8		
12	265	122	1	400	6.1	6.2		
13	295	83	1	425	6.7	6.6		
14	316	87	2	410	6.9	5.4		Step correction of pH to 7.1 with NH_4OH
14	332	79	1	527	6.3	5.9		
15	346	84	1	580	6.7	5.1		Step correction of pH to 7.1 with NH_4OH
15	358	85	<1	610	6.7	5.2		Step correction of pH to 7.2 with NH_4OH
16	369	85	<1	520	6.4	6.0		
16	380	87	<1	535	6.2	6.6		
17	387	92	<1	504	6.1	6.6		
18	410	52	<1	428	6.3	5.3		Automatic pH control; Detention time $\bar{t}$ = 16 hrs; Feed of Batch "B"
18	432	64	<1	425	6.2	7.1		
18	432	64	<1	425	6.2	7.1		
19	454	68	<1	387	6.3	7.0		
20	478	56	<1	422	6.2	7.0	92	Sludge; darker, excellent settling although too thin

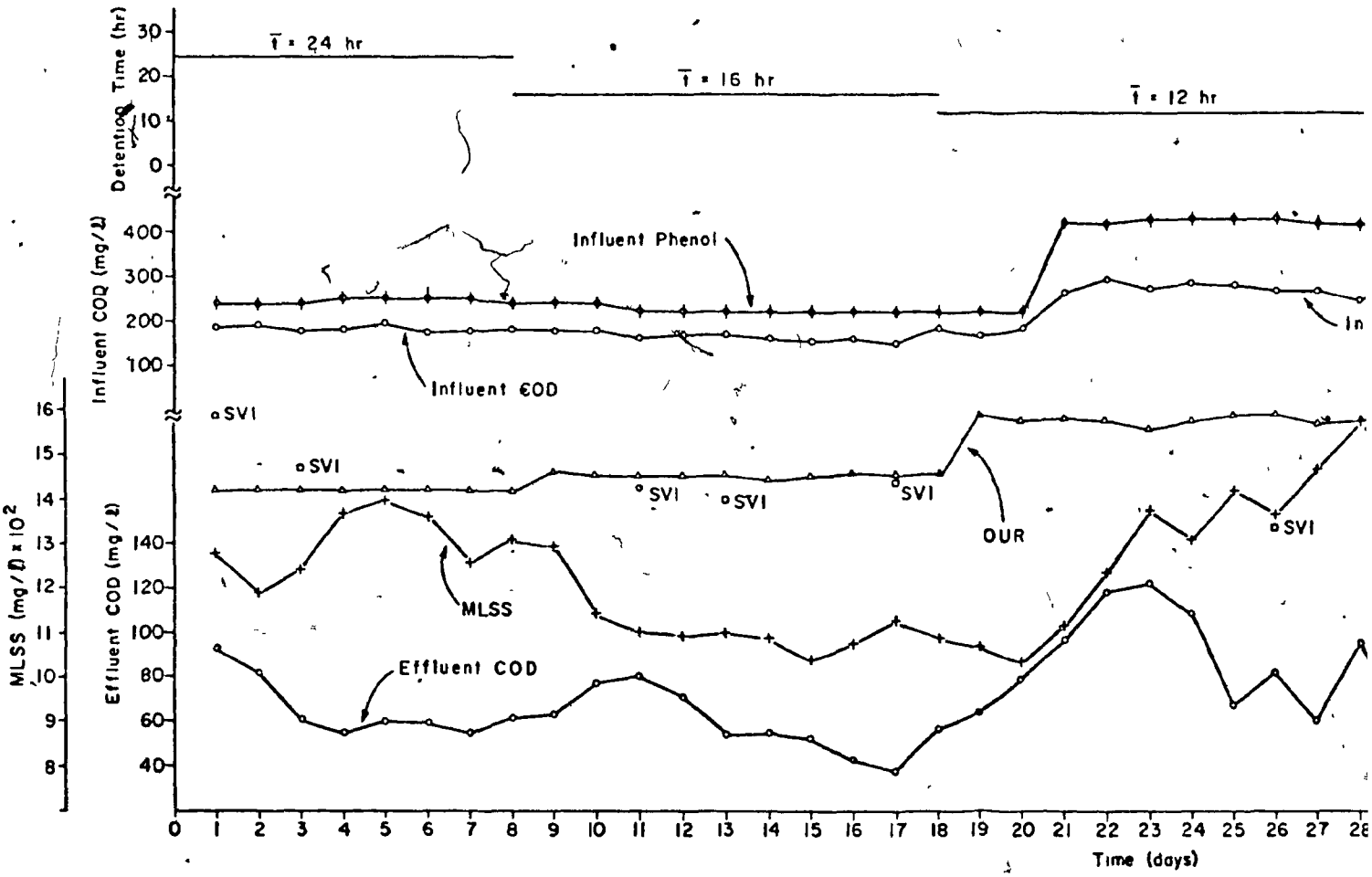
TABLE III-13: Continued

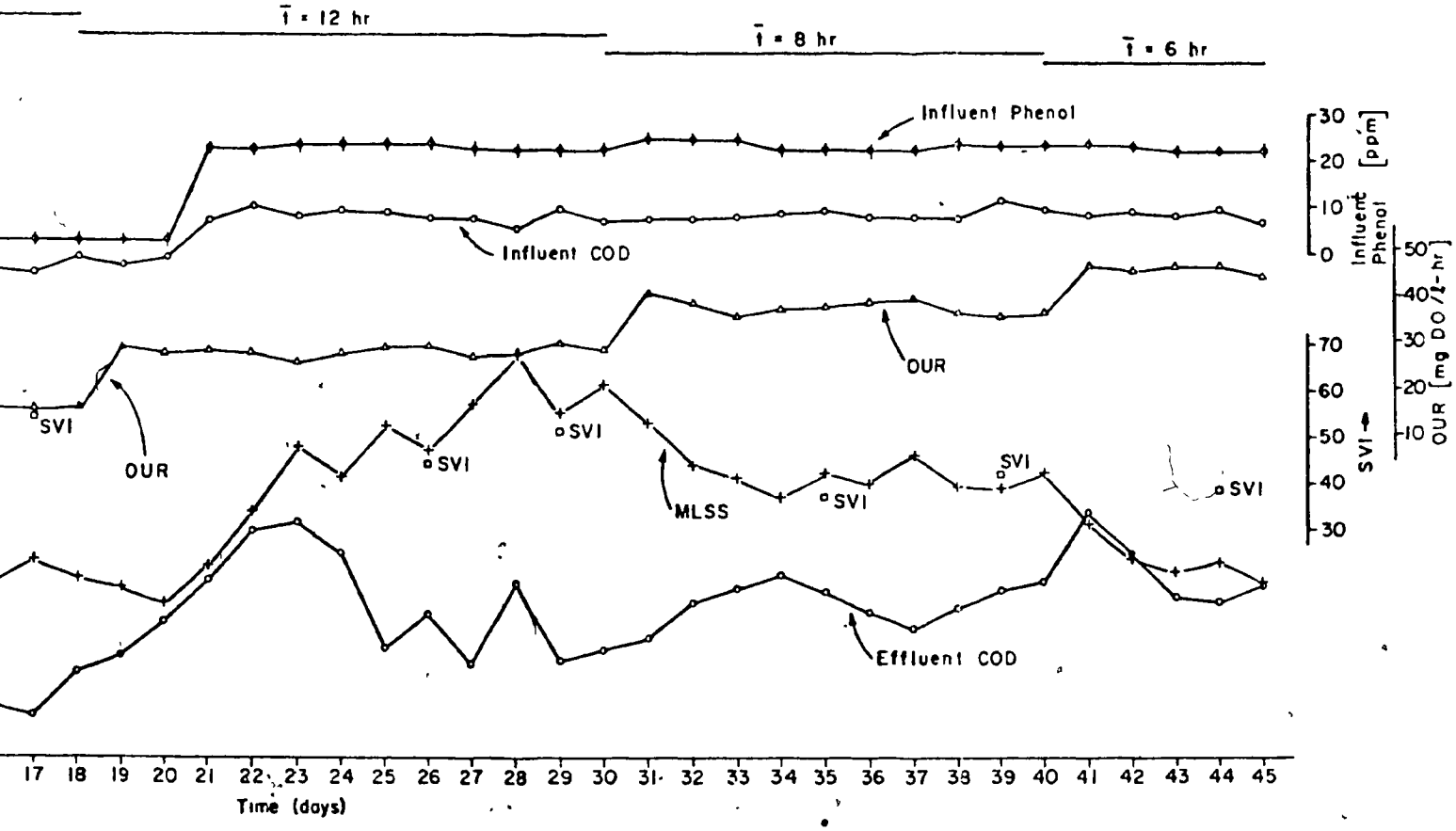
Time		Effluent		Bio-Reactor				
# day	[Hours]	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	Remarks
21	488	66	<1	405	6.1	7.1		
21	504	72	<1	400	6.3	7.0		
22	512	65	<1	410	6.2	7.0		
23	529	52	<1	383	6.1	6.8		Start manual pH control
23	536	70	<1	368	6.7	5.4		Step pH correction up to pH = 6.8 w/ NH_4OH
24	558	84	<1	375	6.5	6.2	130	
25	580	102	2	460	6.3	6.3		Thin sludge, dispersed
25	600	122	1	527	6.2	5.9		Automatic pH control
27	630	93	<1	612	6.5	7.1		
28	650	79	<1	600	6.3	7.0		Gradual shift in sludge color → yellowish brown
28	670	73	<1	820	6.3	7.0		
29	678	56	<1	834	6.5	7.1	122	
29	692	64	<1	783	6.1	7.0		
30	700	77	<1	770	6.3	7.1	110	
30	720	83	<1	757	5.9	7.1		
31	741	98	<1	762	5.8	7.1		
32	749	86	<1	740	5.9	7.1	110	
33	772	93	<1	715	5.7	7.0		Feed of Batch "C"
34	816	230	<1	630	5.7	7.1	100	
35	827	230	<1	640	5.6	7.1		

TABLE III-13: Continued

Time		Effluent		Bio-Reactor				
# day	[Hours]	COD [$\frac{mg}{\ell}$]	Phenol [ppm]	MLSS [$^{mg}/_{\ell}$]	D.O. [ppm]	pH	SVI	Remarks
35	837	210	<1	668	5.6	7.1		
36	856	193	<1	625	5.7	7.1		Excellent settling; large flocs.
36	864	206	<1	607	5.6	7.0	106	
37	884	188	<1	596	5.8	7.1		Switch to Detention time t = 13 hr
38	905	193	<1	635	5.6	7.1		
39	930	171	<1	590	5.5	7.1		
40	939	168	<1	565	5.3	7.2	90	Turbid supernatant
40	958	154	<1	622	5.6	6.9		
41	980	144	<1	625	5.3	7.0		
42	992	179	<1	575	5.6	7.0		
42	1002	196	<1	492	5.5	7.1	98	
43	1026	159	<1	634	5.3	7.1		
44	1038	184	<1	626	5.5	7.0		Turbid supernatant

Figure III-4: Continuous Flow Run No. 4


Detention Time (hr)
$\bar{t}$ = 24 hr
$\bar{t}$ = 16 hr
$\bar{t}$ = 12 hr
Influent COD (mg/ℓ)
Influent Phenol
Influent COD
oSVI
MLSS (mg/ℓ) x 10²
Effluent COD (mg/ℓ)
MLSS
Effluent COD
OUR
Time (days)


$\bar{t}$ = 12 hr
$\bar{t}$ = 8 hr
$\bar{t}$ = 6 hr
Influent Phenol
Influent COD
OUR
SVI
OUR
SVI
SVI
SVI
MLSS
SVI
SVI
Effluent COD
30
20
10
0
Influent Phenol [ppm]
70
60
50
40
30
SVI
50
40
30
20
10
OUR [mg DO/ℓ-hr]
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45
Time (days)

lic shock, as is the somewhat delayed "sagging" of the MLSS profile. However the residual COD retained a constancy relatively free of major oscillations for almost seven detention periods after the initial surge, whereas the biomass followed a distinct downward trend, being obviously far more vulnerable to the step changes in pH administered after the removal of the pH controller at the end of the fifth detention period after the dilution rate increase. Still the average results up until this point showed successful treatment of the influent waste:

$(COD)_{avg.}$ = 63 mg/l i.e. a removal of 78%;

$(MLSS)_{avg.}$ = 730 mg/l

(Phenol) < 1 mg/l

SVI : 130

Also the effluent had been particularly clear up until the 9th day of operation. A mild disruption was manifest by the second day of manual pH control as a result of the tendency of the broth to become more acidic, due to biodegradation intermediates. The mixed population remained under the influence of acidic pH for lengths of time (usually between 50% and 80% of one detention period) sufficient for ecological changes to occur, as could be seen by the change in sludge color, the distinctly smaller flocs and hindrance in settling. These changes are evidence of the established selection of the acidic environment for yeasts and molds, with an abundance of filamentous fungal species. [Cf. Gaudy (1975)]. Still the step corrections of pH to neutral by addition of NH_4OH exercised during these 10 days (between day #7 and day #17)

did not allow a transition to a clearly defined new steady state but maintained the environmental disruption in a way that for the first time there were detectable - though very low (1 and 2 ppm) amounts of phenol in the effluent for about 5 days. It can also be seen that this pH manipulation although not regular or reproducible, brought about some kind of adaptation on the part of the microbial population, as the biomass started building up again and the residual COD reached a new lower plateau in the last three days of manual pH regulation.

The reinstallation of the automatic pH controller followed the beginning of feeding with Batch "B" and also a slight increase in detention time ($\bar{t}$ = 16 hrs.). The relatively steady values of MLSS around 420 mg/l and COD around 65 mg/l changed markedly again when a new 3-day period of manual pH correction occurred. The transient surge of the residual substrate COD could be attributed to "substrate leakage" [George and Gaudy (1973a), (1973b); Gaudy (1975)] as can be also inferred by the transient appearance of residual phenol in the effluent. The adaptation of the biomass is exemplified by the build-up of biological solids level, which continued for almost 5 more detention periods after the new installation of automatic pH control (end of 25th day), reaching a steady state at about 770 mg/l. The average COD in the effluent was around 72 mg/l but fluctuated rather widely, while there was practical elimination of phenol again (<1 ppm). The biomass quality was good, with an SVI of about 110. On the whole the organic load removal was judged as very good at 73%.

In the beginning of the 32 d/day of continuous operation without any addition of new sludge the waste water Batch "C" was pumped into the biosystem at the same dilution rate of 0.0625 $hr.^{-1}$ ($\bar{t}$ = 16 hr.). Because this time the influent substrate level represented an increase of almost 45% over the previous inlet COD concentration, there was a sizeable immediate increase in effluent COD, clearly the effect of "substrate leakage," as the growth of biomass already existing in the fermentor could not handle this step increase in substrate level immediately. After reaching a peak value of 230 mg/l the effluent COD started decreasing towards some level that would be dictated by the then prevailing mean specific growth rate of the sludge population. The decrease in clarification efficiency of the cell separator (manifest also by the decrease in recycle cell concentration) which was reported by Chu et al (1973) while studying the dynamic behavior of a similar system to a step increase in influent organic load was also observed here and could be attributed to a change in the physiological state of the cells in the settler. However there was an initial reduction of cell concentration in the bioreactor, which gave way to relatively steady biomass values around the 600 mg/l mark, unlike the cell build-up observed by the above workers. This may be due to the subsequent decrease of residence time to $\bar{t}$ = 13 hrs., which was imposed on the system 5 days after the new feed was administered, but also the deviations in the quiescent settling mode of the clarifier have been responsible for regular losses of some solids over the weir, given the fact that no sludge wastage

was practiced throughout the experimentation. In the last 8 days of operation under the new dilution rate there were wider fluctuations in the residual COD and the reactor biomass than in previous steady states, but the overall treatment was judged satisfactory: Average values of COD at 172 mg/l (removal of organics: 64%), MLSS at 596 mg/l, residual phenol <1 and SVI between 90 and 106 were exhibited.

From a practical point of view this experimental series of tests in a continuous-flow mode served to establish unambiguously the biological treatability of the Petrofina Refinery effluent, under detention times between 24 and 13 hours, and under perturbations in organic composition of feed and in pH. The average values of parameters depicting the relative success of biotreatment are summarized below in Table III-14. Included is the average ratio of MLVSS over MLSS, following occasional analyses of MLVSS.

Table III-14

Profile of Biological Treatment of the

Petrofina Refinery Waste Water (Run No. 4)

Detention time t (hrs)	Influent Waste COD (mg/l)	Phenol (mg/l)	Reactor SVI	MLSS (mg/l)	MLVSS/MLSS	Treated Effluent COD (mg/l)	COD Removal %	Phenol (mg/l)
15	285	28	130	730	0.65	63	78	<1
16	266	10	110	770	0.63	72	73	<1
13	480	8	98	596	0.68	172	64	<1

III.2.C. Effect of Temperature on Biological Treatment

There have been thorough investigations on the effects of temperature and temperature changes in continuous systems with pure cultures of microorganisms and also, recently, detailed reports on temperature effects on mixed mocrobial populations. [George and Gaudy (1973c), Gaudy (1975)].

At the end of this continuous flow Run No. 4 it was decided to carry out a brief investigation of how the prevailing temperature of the bioreactor affects high-rate activated sludge treatment efficiency. No complete protocol of the process (in terms of other parameters) was kept as the main focus was on the degree of organic load removal from a strictly practical engineering standpoint, in view of the wide variation of temperatures in Quebec.

With the same feed from Batch "C" and the same controlled conditions of aeration, agitation, recycling and pH and at a detention time of $\bar{t}$ = 13 hrs. the temperature was varied upwards and downwards from 25°C. The results appear grouped in Table III-15. A graphic representation of the change of organic load removal with temperature is given in Figure III-5.

It is apparent, from these data, that temperatures below 23°C brought about a distinct deterioration in COD removal. At 12°C, which was the lowest temperature tested, the COD removal reached an unacceptable 40%, whereas for the first time detectable amounts of phenol (at 2 ppm) were observed in the effluent despite the relatively low influent phenol concentration (8 ppm). Difficulties in phenol removal were reported also

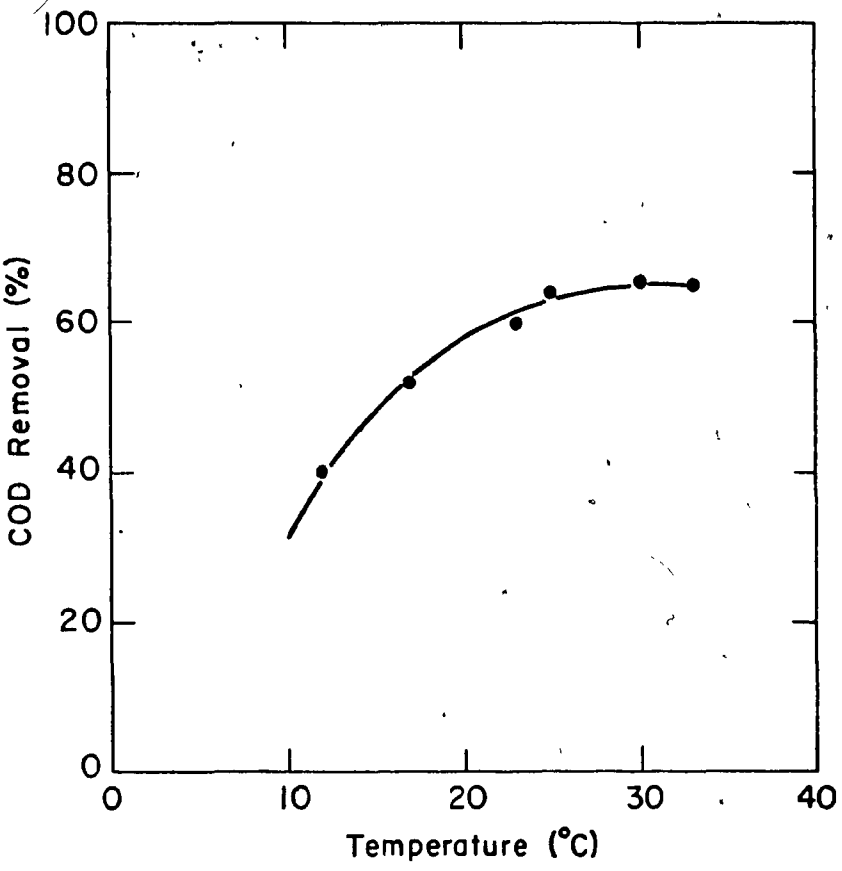
Table III-15

Effect of Temperature of Biological Treatment

[Feed: Batch "C"; Detention time $\overline{t}$ = 13 hrs.]

Temperature (°C)	COD Removal %	Effluent Phenol [ppm]
33	65	<1
30	65.5	<1
25	64	<1
23	60	<1
17	52	<1
12	40	2

Figure III-5: Effect of Temperature on Organic Load Removal


100
80
60
40
20
0
COD Removal (%)
0
10
20
30
40
Temperature (°C)

by Volesky et al (1974) in continuous-flow treatability tests on refinery waste water when the temperature was dropped at 18°C and 10°C. Above 25°C there was no impairment in COD and phenol removal up to and including 33°C, but no marked improvement either. So it was decided to keep the temperature control at 25°C for the remainder of the Main Treatability studies, as an optimum parameter value.

III.2.D Hydraulic Studies -- A Closer Look

A long-term continuous flow experiment referred to as "Run No. 5" in the following was designed and carried out in order to establish the effect of dilution rate on COD and phenol removal, sustained level of biological solids and sludge characteristics, and in order to derive estimates of the operational parameters on which the design of a commercial-scale facility should be based.

At the same time Oxygen Uptake Rate (OUR) values were monitored. Since this parameter has been described as a potential indicator of biomass activity [Heukelekian and Gillman (1955), Ford and Eckenfelder (1967), Washington et al. (1969), Nutt (1974)] and even of sludge viability [Weddle and Jenkins (1971)], it was felt that its pattern of change should have some bearing on perturbations imposed on the biosystem. Heukelekian and Gillman (1955) and Brezonik and Patterson (1971) have shown that OUR correlates satisfactorily with factors affecting the metabolic activity of the biomass, such as the concentration of heavy metals in the mixed liquor. Therefore, given the relative simplicity and directness of the determination of OUR (see Chap. II, Analytical Methods) compared to other proposed sludge activity indexes, such as ATP and dehydrogenase enzyme activity, it was decided to study at the same time the effect of changes in dilution rate and/or substrate concentration on OUR.

Initial sludge inoculum for continuous flow Run No. 5 as well as for the rest of the Main Treatability Studies was obtained from the municipal

treatment facility of Vaudreuil, Quebec, for reasons of reproducibility and in order that a wider spectrum of microorganisms be represented during the acclimation period, as pointed out in Chapter II. Apart from the closely controlled conditions in our model bio-oxidation lab-scale facility. the use of municipal sludge as inoculum had a distinct beneficial effect on the quality of the treatment, particularly with regard to attainment of steady states as compared to the previous results.

During the "run" mean hydraulic detention times of 24, 16, 12, 8, and 6 hours (i.e., dilution rates of 0.0417, 0.0625, 0.0834, 0.1250, and 0.1667 hr^{-1} respectively) were employed sequentially. Owing to the same problems of limited hauling capacity for raw waste water and of limited output of our batch pre-treatment process, there were frequent variations in the quality of the feed to the bioreactor. Given the large number of batches of "stripped" waste liquor fed into the bioreactor and their differences in characteristics, the quality of the influent stream in terms of COD and phenol is included in the following tabulations of continuous flow data from the biotreatment system. Although analyses for sulfide and ammonia were not run on a continuous basis the sulfide concentration in the "stripped" feed was less than 10 ppm and NH_3-nitrogen was around 25 ppm. The detailed performance of the system is shown in the data points from parameters monitored throughout Run No. 5 that appear in Table III-16, whereas their graphical representation is given in Figure III-6. The cumulative results from the same "run" appear in Table III-17. A recycle ratio of 0.67 was chosen empirically as in the previous

section (III.2.B) and maintained through all different detention times used. Occasional analyses of the concentration X_R of biological solids in the recycle stream revealed that the concentration factor c did not fluctuate appreciably, its average value being ~ 2.0. Thus the factor $A = 1 + r - rc$ (see "Theoretical Considerations," Chap. I) was around 0.33. Also the rest of the operating conditions were kept the same as previously (part III.2.B).

From the tabulated data and the graph (Fig. III.6) it is apparent that the residual COD follows the pattern exhibited previously upon increases in dilution rate, with a discernible "overshoot" and then the establishment of a steady-state situation. Also the characteristic "sagging" in the response of MLSS is present here again. It will be seen that there is, in general, wider fluctuation in the steady-state values of the biological solids rather than in the ones of the residual substrate. Also it can be observed that the attainment of a steady state was relatively easy in this closely controlled system, and even when the stripped feed had to be spiked with phenol, two days after changing the mean residence time $\bar{t}$ from 16 to 12 hours along with an increased organic loading, there was no detectable phenol in the effluent and the period of COD and MLSS fluctuation was almost less than 2 days (or 4 detention periods).

It was interesting to note that the condition of the sludge, although excellent from the beginning of the run, was even improved, in terms of settleability and compactability, as can be seen from the reduction of

TABLE III-16

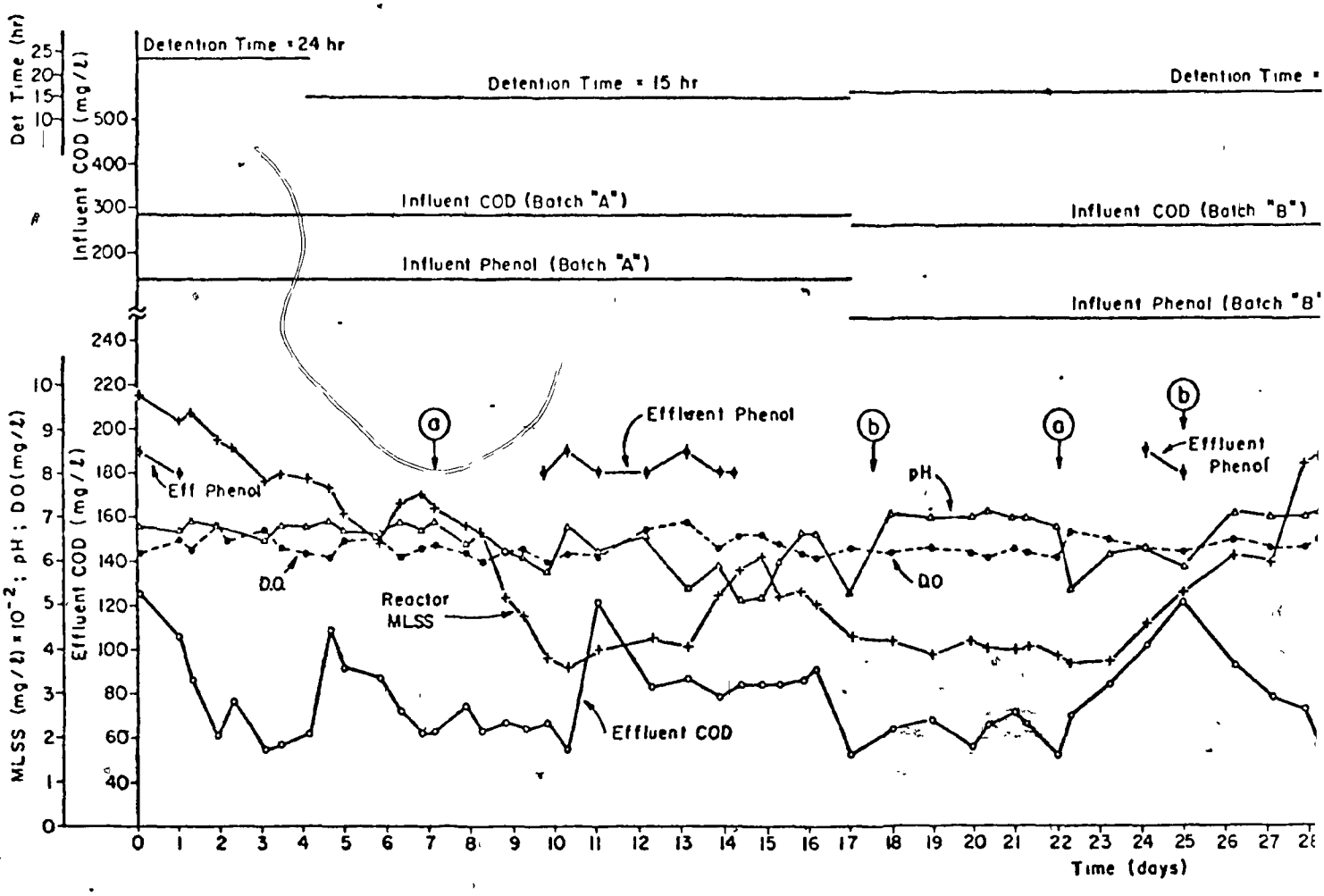
DATA ON CONTINUOUS FLOW RUN NO. 5
["Petrofina" Waste;
Temperature = 25°C;
Agitation = 360rpm]

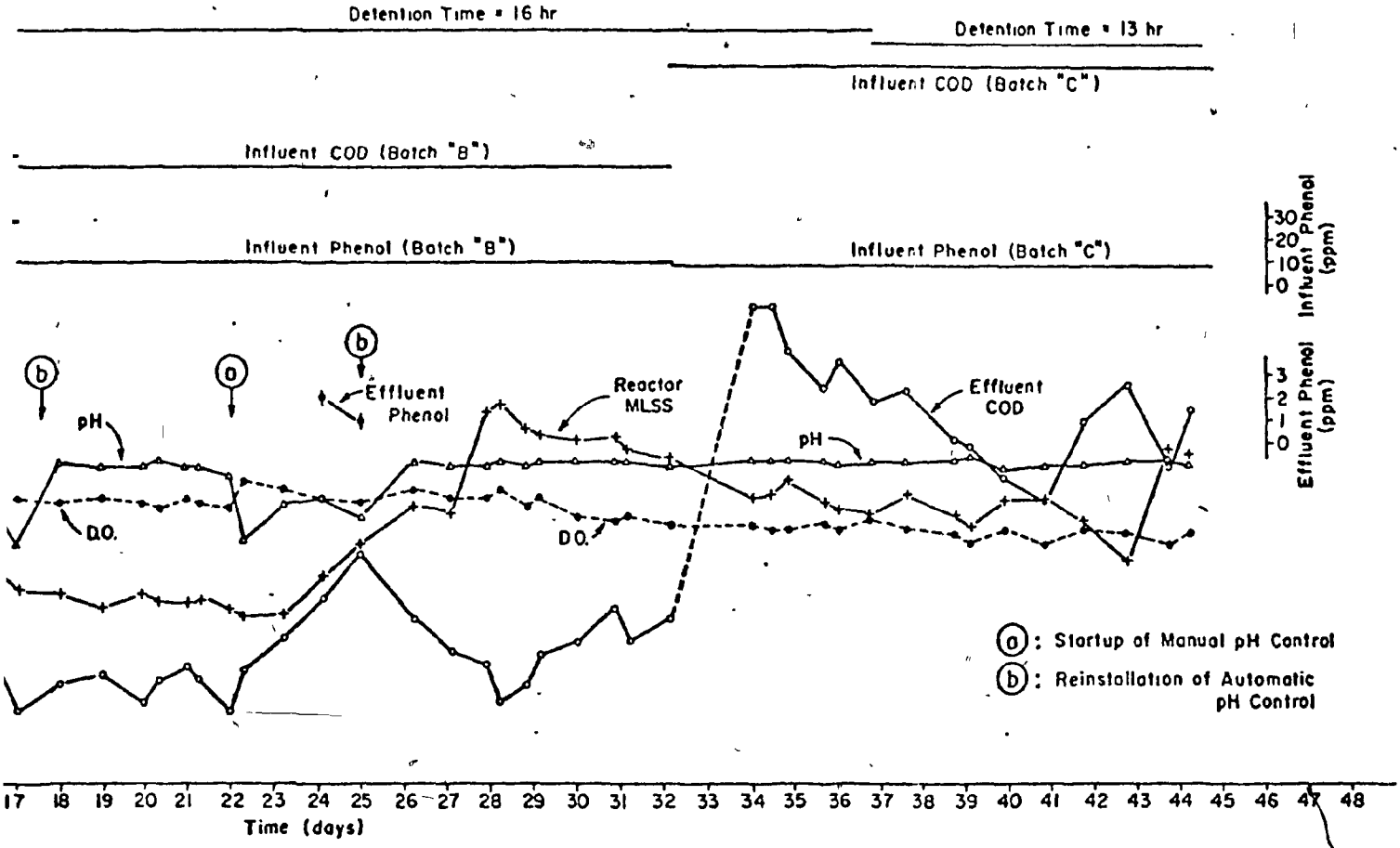
Day	Detention Time [hours]	COD in [mg/ℓ]	Phenol in [mg/ℓ]	COD out [mg/ℓ]	Phenol out [mg/ℓ]	MLSS [mg/ℓ]	SVI	OUR mg D.O./ℓ-hr
1	24	187	4	93	<1	1280	69	12.4
2	24	195	4	82	<1	1190		13.0
3	24	177	4	61	<1	1245	57	12.2
4	24	181	5	55	<1	1370		12.0
5	24	195	5	60	<1	1400		12.1
6	24	172	5	59	<1	1360		12.2
7	24	180	5	55	<1	1260		12.2
8	24	182	4	61	<1	1310		12.0
9	16	180	4	63	<1	1295		16.0
10	16	180	4	77	<1	1143		15.5
11	16	163	2	80	<1	1102	53	15.2
12	16	167	2	71	<1	1092		15.0
13	16	166	2	54	<1	1099	50	15.5
14	16	160	2	55	<1	1085		14.4
15	16	155	2	52	<1	1037		15.0
16	16	160	2	42	<1	1074		16.0
17	16	153	2	38	<1	1128	55	15.2
18	16	185	2	57	<1	1088		15.4
19	12	167	2	64	<1	1070		29.0
20	12	181	2	79	<1	1034		27.0
21	12	266	22	97	<1	1115		28.5
22	12	294	22	118	<1	1234		28.0
23	12	271	23	122	<1	1377		26.0
24	12	285	23	108	<1	1310		28.0
25	12	281	23	67	<1	1420		29.0

TABLE III-16: Continued

Day	Detention Time	COD in	Phenol in	COD out	Phenol out	MLSS	SVI	OUR
26	12	272	23	62	<1	1370	47	29.0
27	12	273	22	61	<1	1470		27.0
28	12	242	22	96	<1	1580		27.7
29	12	292	22	62	<1	1450	51	30.0
30	12	267	22	66	<1	1510		29.0
31	8	270	24	72	<1	1433		41.0
32	8	270	24	87	<1	1341		39.0
33	8	272	24	93	<1	1303		36.0
34	8	283	22	99	<1	1265		37.5
35	8	287	22	92	<1	1322	37	38.0
36	8	274	22	83	<1	1298		39.0
37	8	273	22	76	<1	1360		40.0
38	8	270	23	85	<1	1290		36.7
39	8	310	23	93	<1	1285	42	36.0
40	8	290	23	97	<1	1320		37.0
41	6	277	23	127	<1	1210		47.0
42	6	285	23	109	<1	1147		46.0
43	6	275	22	90	<1	1107		47.0
44	6	287	22	88	<1	1130	38	47.0
45	6	263	22	95	<1	1080		45.0

Figure III-6: Continuous Flow Run No. 5


Det Time (hr)
Influent COD (mg/l)
Detention Time = 24 hr
Detention Time = 15 hr
Detention Time =
Influent COD (Batch "A")
Influent COD (Batch "B")
Influent Phenol (Batch "A")
Influent Phenol (Batch "B"
MLSS (mg/l) x 10⁻²; pH; DO (mg/l)
Effluent COD (mg/l)
Eff Phenol
Effluent Phenol
pH
D.O
Reactor MLSS
Effluent COD
Time (days)


Detention Time = 16 hr
Detention Time = 13 hr
Influent COD (Batch "C")
Influent COD (Batch "B")
Influent Phenol (Batch "B")
Influent Phenol (Batch "C")
Influent Phenol (ppm)
30
20
10
0
Effluent Phenol (ppm)
3
2
1
0
b
a
b
pH
Effluent Phenol
Reactor MLSS
Effluent COD
pH
D.O.
D.O.
a : Startup of Manual pH Control
b : Reinstallation of Automatic pH Control
17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48
Time (days)

the SVI and also visually, with regard to the effluent from the clarifier, that was particularly clear. This was partly aided by the fact that during this run the settler was mechanically swayed at fixed time intervals, as explained in "Materials and Methods" (Chap. II).

Because of this particularly clear effluent there was a minimal discrepancy between effluent COD and residual COD. The improved sludge condition can be explained by the continuous selection-acclimation of the biomass during the length of the run and the relatively smooth reduction of mean detention times. Only the operation at $\bar{t}$ = 6 hrs could not be continued because of the amounts of feed that had to be available due to the high inflow rate.

The pattern of OUR change was somewhat similar to the variation of residual substrate, but the clear tendency was an almost immediate "overshoot" after imposing a higher dilution rate, which was followed, in a matter of hours, by a relatively steady state for the rest of the time in operation at a particular dilution rate. The new steady-state OUR value increased with increasing dilution rates as would be expected from a bioenergetic point of view [cf. Aiba et al. (1973)]. The above pattern of OUR variation is not obvious from Fig. III-6 because the time scale is in terms of days rather than hours, but it is better appreciated in Fig. III-9 and briefly discussed in the following section ("Variation of OUR"). The predicted increase of OUR with increasing dilution rates showed also the absence of inhibiting or toxic agents, overall, during this experimental run, whereas in at least two cases discussed in the

following parts (i.e., effect of continuous drop in pH and effect of high ion concentrations) the values of OUR decreased appreciably, thus confirming this parameter's merits as a rapid indicator of biomass activity. The occasional oscillations of OUR during the steady-state regimes (steady-state at least as described by the relative constancy in terms of residual substrate and biological solids) that were observed from time to time could be attributed to local transients, as it is known, for example, that agitation can affect OUR measurements [Rickard and Gaudy (1968)] and that the rpm of the impeller cannot be kept absolutely constant.

In computing the steady-state values of parameters such as substrate and biomass concentration and in averaging them in order to obtain the mean parameter values at each dilution rate as they appear in Table III-17, it was empirically decided to choose the last few points during at least five detention periods in the steady-state regime. Thus for detention times of $\bar{t}$ = 24 hrs and $\bar{t}$ = 16 hrs the values of the last five days were averaged; for $\bar{t}$ = 12 hrs the values of the last six days; for $\bar{t} \geq 8$ hrs the values of the last four days; and for $\bar{t}$ = 6 hrs the values of the last two days were averaged.

The profile of the biological treatment attained during this continuous flow Run No. 5 which lasted one-and-a-half months is given in Table III-17 in terms of the above-mentioned average values of COD and MLSS, the % COD removal, influent-effluent phenol, OUR, and ratio of volatile suspended solids to total suspended solids (MLVSS/MLSS). The

TABLE III-17

PROFILE OF BIOLOGICAL TREATMENT - RUN NO. 5

Detention Time $\frac{1}{t} = \frac{1}{D}$ [hr]	Influent COD S_o [mg/ℓ]	Influent Phenol [mg/ℓ]	Residual COD S [mg/ℓ]	Residual Phenol [$\frac{mg}{\ell}$]	MLSS SX [mg/ℓ]	$\frac{MLVSS}{MLSS}$	Specific Removal $\frac{S_o - S}{X}$ [$\frac{mg}{\ell}$ COD/$\frac{mg}{\ell}$ MLSS]	COD Removal %	$\frac{1}{\mu} = \frac{1}{AD + k_d}$ [hr]	OUR $\frac{mg\ D.O.}{\ell - hr}$
24	182	5	58	<1	1340	0.65	0.0925	68	47.39	12.1
16	168	2	49	<1	1082	0.67	0.1100	71	35.84	15.2
12	271	22	72	<1	1467	0.71	0.1354	73	28.74	28.6
8	286	23	88	<1	1314	0.70	0.1507	69	20.58	37.4
6	275	22	91.5	<1	1105	0.67	0.1661	67	16.05	46.0

Biological Coefficients

Biomass Yield	Cell Decay Coefficient	Max. Specific Growth Rate	Saturation Coefficient
$Y = 1.7857\ \frac{mg\ MLSS}{mg\ COD}$	$k_d = 0.0073\ hr^{-1}$	$\mu_m = 0.227\ hr^{-1}$	$K_s = 357 mg/\ell$

Figure.III-7: Graphic Derivation of Biomass Yield Y and Cell Decay Coefficient k_d

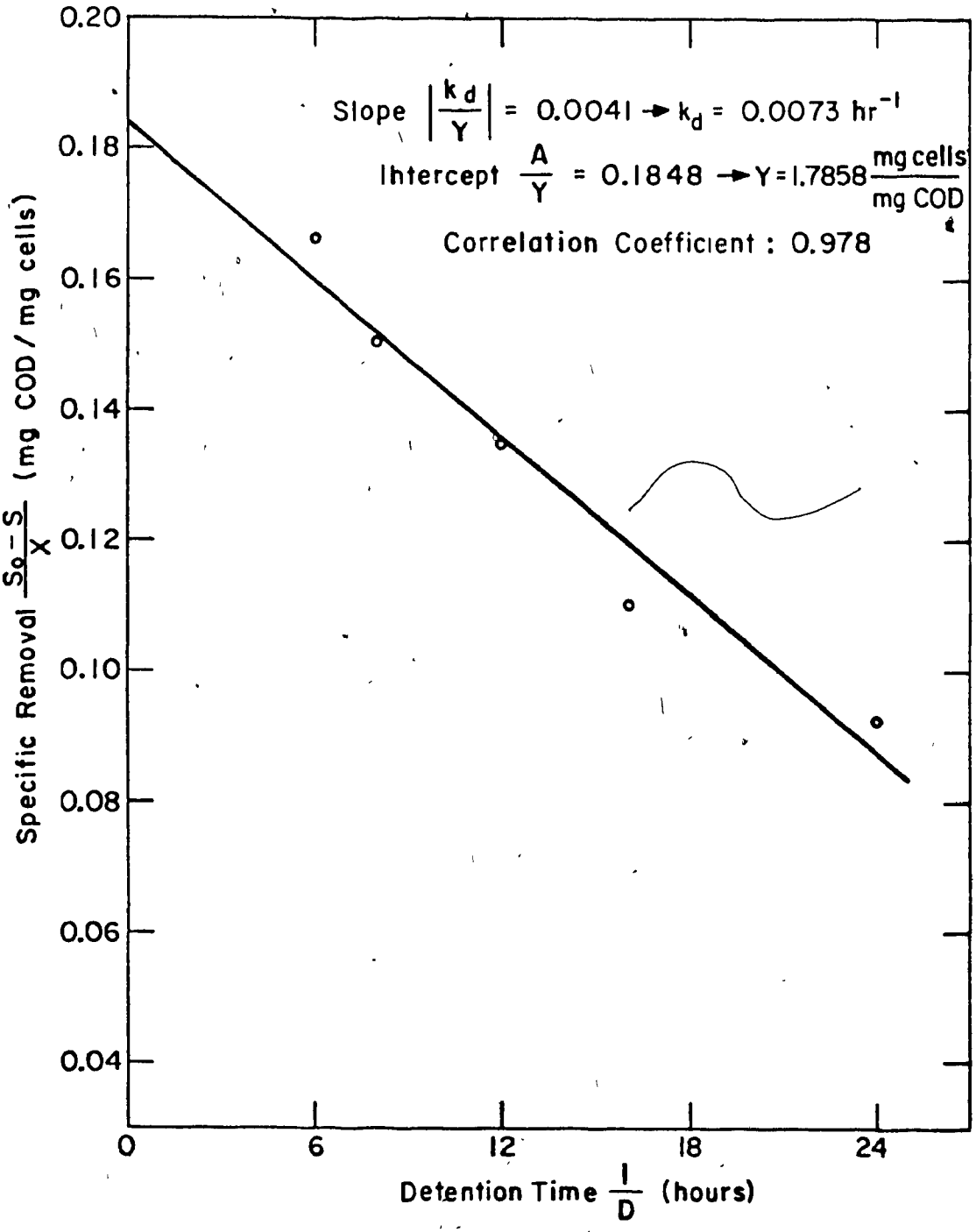
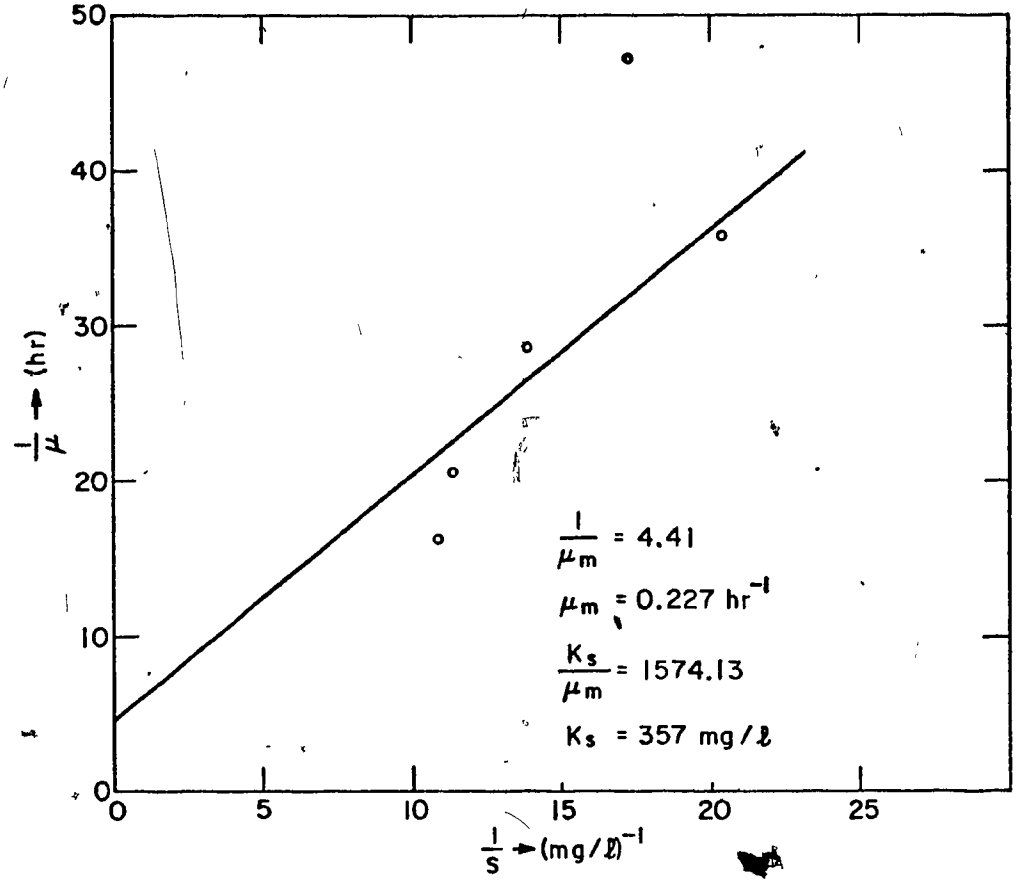

Slope $\left|\frac{k_d}{Y}\right|$ = 0.0041 → k_d = 0.0073 hr^{-1}
Intercept $\frac{A}{Y}$ = 0.1848 → Y = 1.7858 $\frac{mg\ cells}{mg\ COD}$
Correlation Coefficient : 0.978
Specific Removal $\frac{S_o - S}{X}$ (mg COD / mg cells)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0
6
12
18
24
Detention Time $\frac{1}{D}$ (hours)

Figure III-8: Graphic Derivation of Maximum Growth Rate μ_m and Saturation Constant K_s


50
40
30
20
10
0
0
5
10
15
20
25
$\frac{1}{\mu}$ → (hr)
$\frac{1}{S}$ → (mg/ℓ)$^{-1}$
$\frac{1}{\mu_m}$ = 4.41
μ_m = 0.227 hr^{-1}
$\frac{K_s}{\mu_m}$ = 1574.13
K_s = 357 mg/ℓ

parameter "specific removal," i.e., $(S_0 - S)/X = (COD_{in} - COD_{avg})/MLSS_{avg}$ is also tabulated in Table III-17 and is plotted versus the detention time $\bar{t} = 1/D$ in Fig. III-7 in order to obtain estimates of the cell yield Y and cell decay coefficient k_d, as described in Section "Theoretical Considerations" (Chap. I). As mentioned in that section, the biological "constants," including Y and k_d, are to be regarded only as indicative of a range of values rather than as "point values" and should be considered estimates of the relative magnitude of the parameters they represent.

After the cell decay coefficient k_d is derived from Fig. III-7 the parameter "inverse specific growth rate" $1/\mu = 1/(AD + k_d)$ is tabulated for different dilution rates D in the same cumulative Table III-17 and is also plotted against the inverse residual substrate 1/S in Fig. III-8. In evaluating the estimates of maximum growth rate μ_m and saturation constant K_S more weight was given the data points reflecting continuous operation at detention times of 16, 12, and 8 hours.

The values of the biological "constants" Y, k_d, μ_m, and K_S appear at the bottom of Table III-17.

The results accumulated during this Run No. 5, apart from describing the course of the bio-treatment, contain valuable information to be used in the design of a large-scale facility treating the particular waste water through a high-rate Activated Sludge Process. Specifically it is possible to derive design implications with respect to ranges of detention time , organic load removal, sludge production (through biomass yield)

and settling, and oxygen demand.

It was concluded that the most satisfactory operation in terms of stability (in achieving steady states), efficiency and high-rate organic load removal was achieved at a detention time of 8 hours ($D = 0.125\ hr^{-1}$). Subsequent short-term continuous "runs" confirmed this not only in terms of organic pollutional removal, but also in terms of phenol and sulfide elimination in all cases (cf. "Removal of Toxicants" in the following) as well as excellent sludge characteristics.

III.2.E Variation of Oxygen Uptake Rate

In one of the shorter-term continuous flow "runs" that followed the above Run No. 5 it was decided to examine the pattern of OUR changes upón increases in dilution rate in an effort to verify the observations made during the hydraulic studies.

Two step increases in dilution rate were imposed on the bio-system, after it had reached steady states: the first from a mean residence time of $\bar{t}$ = 16 hours to a new $\bar{t}$ of 12 hours, the second from $\bar{t}$ = 12 hours to $\bar{t}$ = 8 hours. The observed response of the OUR appears in Table III-18 and Figure III-9. Within only minutes of the administered hydraulic shock there was an increase in OUR, which, after reaching a maximum within the first hour, receded to a plateau of values higher than those of the previous steady state. The effect was more pronounced during the shift from $\bar{t}$ = 12 hours to $\bar{t}$ = 8 hours. It should be noted that the OUR reached steady values within the first hours of the first detention period in both cases, i.e. considerably earlier than required for a quasi-steady state in terms of COD and MLSS to set in. The absolute values of OUR in mg/ D.O./l-hr appear considerably lower than the ones reported for the same dilution rates in section III.2.D because of a lower biomass concentration in the present "run".

The initial "overshoot" characteristic of the OUR response could be indicative of a metabolic adaptation process on the part of the microbial population, as the organisms find themselves suddenly in an

TABLE III-18

RESPONSE OF OXYGEN UPTAKE RATE TO HYDRAULIC SHOCK

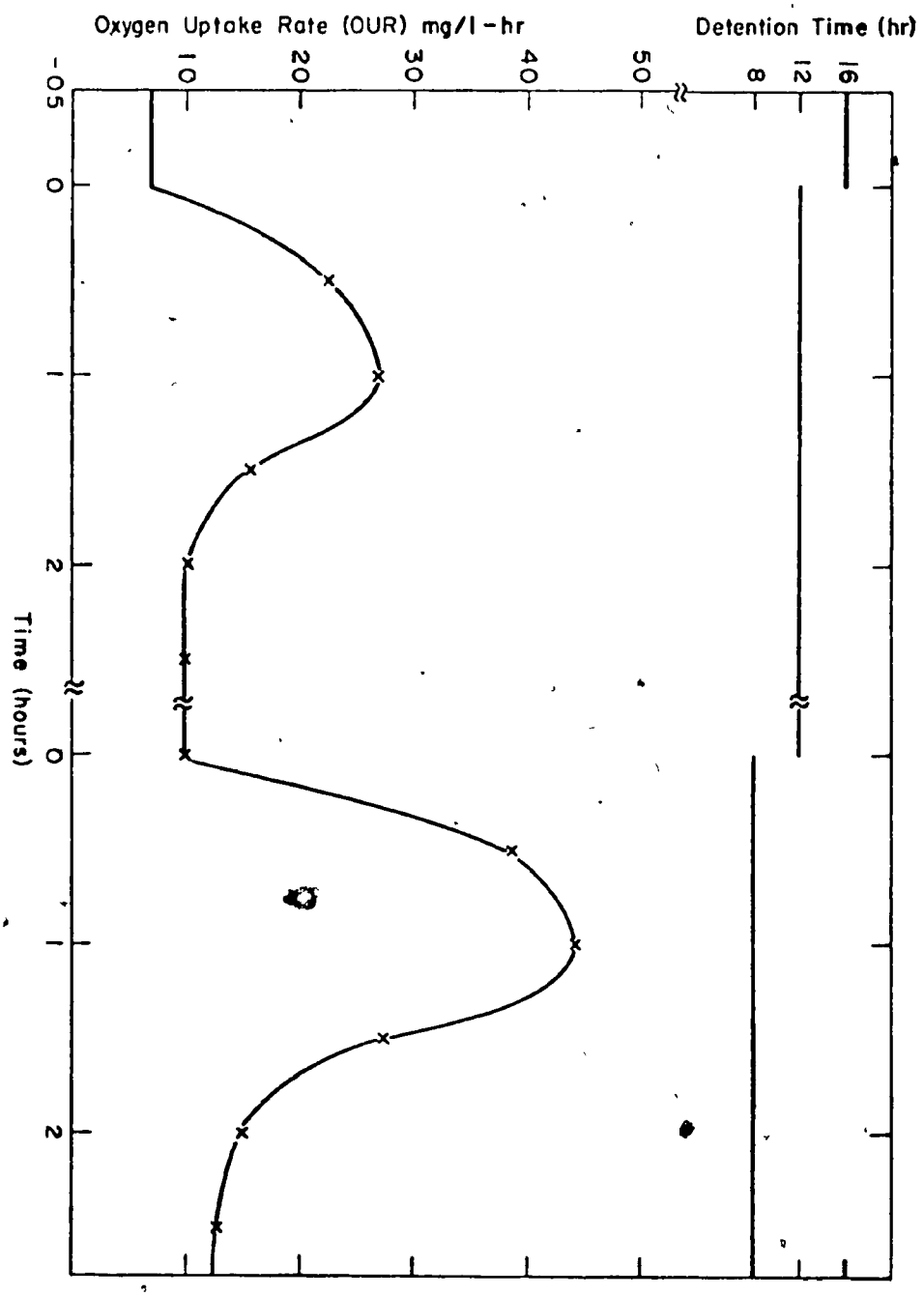
A. Shift from $\bar{t}$ = 16 hrs. to $\bar{t}$ = 12 hrs.

time [hr]	OUR $[\frac{\text{mg D.O.}}{\ell\text{- hr}}]$
0.0	7.5
0.5	22.5
1.0	27.0
1.5	15.5
2.0	10.0

B. Shift from $\bar{t}$ = 12 hrs. to $\bar{t}$ = 8 hrs.

time [hr]	OUR $[\frac{\text{mg D.O.}}{\ell\text{- hr.}}]$
0.0	9.8
0.5	38.5
1.0	42.0
1.5	27.5
2.0	15.0
2.5	12.5

Figure III-9: Variation of Oxygen Uptake Rate upon Changes in Detention Time


Oxygen Uptake Rate (OUR) mg/l-hr
Detention Time (hr)
10
20
30
40
50
8
12
16
-.05
0
1
2
0
1
2
Time (hours)

excess of substrate, whereas during steady-state operation the substrate concentration is growth-limiting. It has been shown before that a sizeable increase in OUR occurs upon administering an excess dose of carbon source to microbial cultures [e.g. Hospodka (1966)].

The Oxygen Uptake Rate can be equated to $\frac{\mu X}{Y_{O_2}}$

i.e. $OUR = \frac{\mu X}{Y_{O_2}}$

and at steady state without recycling

$$OUR = \frac{DX}{Y_{O_2}}$$

where: μ = specific growth rate
D = dilution rate
X = biomass concentration
Y_{O_2} = oxygen yield, $\left(\frac{\text{mass of cells}}{\text{mass of } O_2 \text{ consumed}}\right)$

A step increase in D will impart an immediate boosting in OUR, which should eventually level off, as the dilution rate is staying constant, since also Y_{O_2} is a function of D, assuming no sizeable reduction in biomass concentration due to washout.

However considerable oscillations in OUR might be observed in later stages of apparent steady-state operation and could be either circumstantial, due to local transients (e.g. unsteady agitation and aeration) or systematic, due to shifts in species predominance, or even to inherent limitations of the experimental technique.

III.2.F Oxygen Requirements

The rate of oxygen demand exerted by a mixed microbial population is related to the air supply required in a biological waste treatment facility and therefore very useful for design purposes.

It is made up of two parts:

(a) demand for oxygen to biologically oxidize the substrate removed for synthesis of new cells

(b) endogenous respiration required for basic cell maintenance

The first term is a function of substrate uptake $\frac{S_0-S}{\bar{t}}$ and the second term is a function of the microorganism concentration X inside the system, neglecting the effects of cell decay [Eckenfelder (1966)]:

$$OUR = a\,\frac{S_0-S}{\bar{t}} + bX \quad (1)$$

$$\text{i.e. } \frac{\text{mg } O_2 \text{ consumed}}{\text{hour}} = a\,\frac{\text{mg substrate removed}}{\text{hour}} + b\ (\text{mg biomass})$$

where OUR : Oxygen Uptake Rate (or rate of O_2 demand)
S_0 : Influent Substrate Concentration (e.g. COD)
S : Residual Substrate Concentration (e.g. COD)
$\bar{t}$: Mean Detention Time
X : Biomass Concentration (e.g. MLSS)
a,b : Constants

Constant b is known in particular as the endogenous respiration constant. If both sides of equation (1) are divided by X we get

$$Q_{O_2} = a\,\frac{S_0-S}{x\bar{t}} + b \quad (2)$$

where Q_{O_2} is the "Specific Oxygen Uptake Rate", i.e. OUR per unit mass of cells. Because of the linear relationship shown through equation (2) between Q_{O_2} and $\frac{S_o - S}{X\bar{t}}$ one could plot values of specific Oxygen Uptake Rates exercised at different dilution rates versus values of specific removal $\frac{S_o - S}{X}$ multiplied by the corresponding dilution rates in order to derive the values of the constants a and b. Specific Oxygen Uptake Rates have been computed from the data of Run No. 5 (see Table III-17) as have been Substrate Consumption values (i.e. Specific Removal x Dilution Rate) and are tabulated in Table III-19, whereas a plot of Q_{O_2} against $\frac{S_o - S}{X\bar{t}}$ is presented in Figure III-10.

The values of constants a and b obtained by this graphic method are: $a = 1.335 \frac{\text{mg } O_2}{\text{mg COD removed}}$

and $b = 0.00423 \frac{\text{mg } O_2}{\text{mg MLSS-hour}}$

Although the absolute values of OUR recorded during Hydraulic Studies (Run No. 5) generally reflected the magnitude of microbial oxygen demand exerted during subsequent tests, i.e. values ranging from $\sim$ 50 mg D.O./l-hr to 8 mg D.O./l-hr according to the dilution rate employed (values around 50 mg D.O./l-hr were encountered at detention times of 8 hours), for design purposes it should be noted that the highest OUR value encountered amounted to 66.5 mg D.O./l-hr, at a

TABLE III-19

DATA FOR THE DERIVATION OF OXYGEN DEMAND CONSTANTS
[Based on Results from Run No. 5]

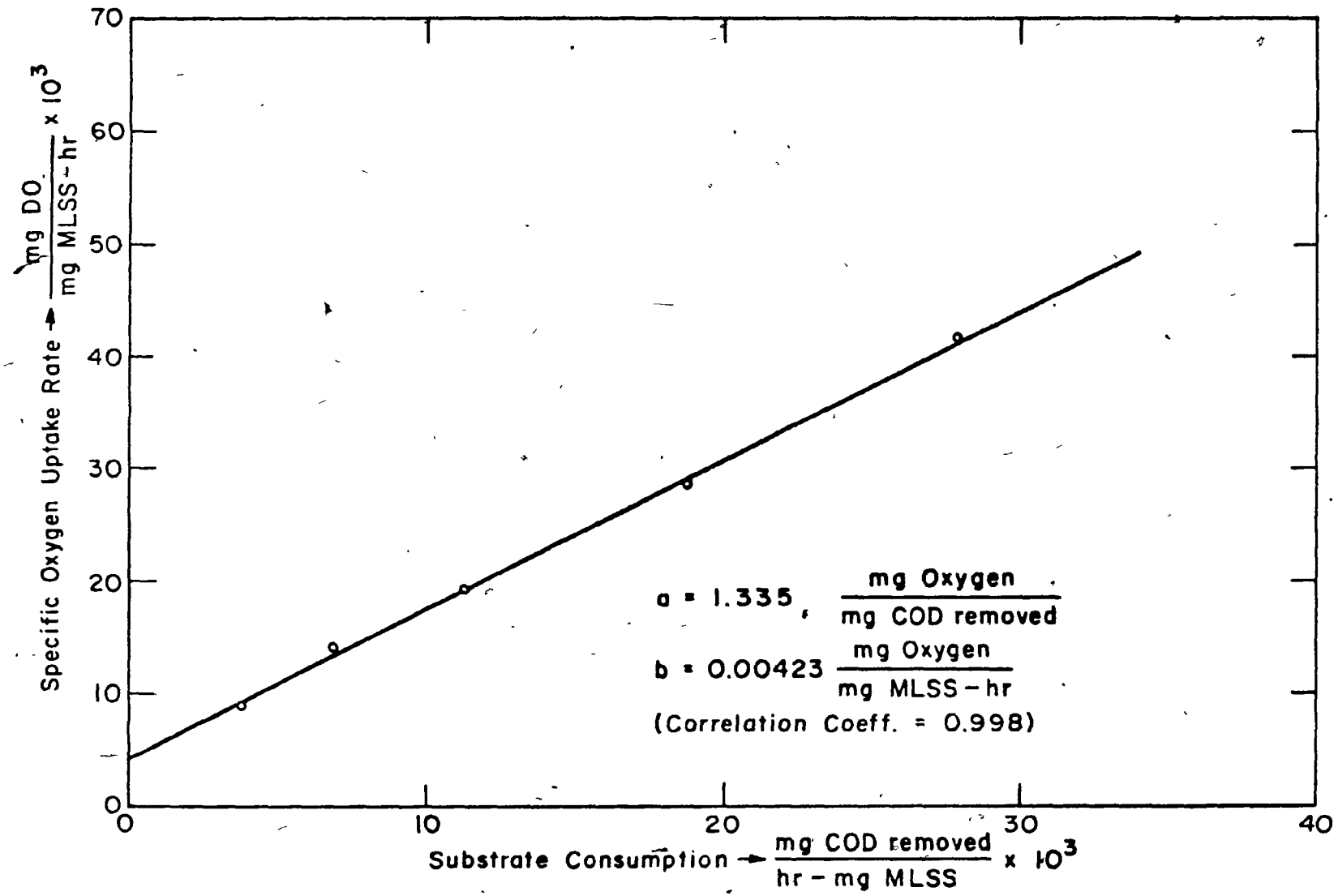
Detention Time $\bar{t}$ [hours]	Substrate Consumption $\frac{S_o - S}{X \cdot \bar{t}}$ $\left[\frac{\text{mg COD}}{\text{mg MLSS - hr}}\right]$	Specific OUR $\frac{OUR}{X}$ $\left[\frac{\text{mg D.O.}}{\ell\text{-hr}}\right] / [\text{mg MLSS}]$
24	0.0038	0.0090
16	0.0069	0.0140
12	0.0113	0.0195
8	0.0188	0.0285
6	0.0277	0.0416

Oxygen Demand Constants

$$a = 1.335 \quad \frac{\text{mg } O_2}{\text{mg COD removed}}$$

$$b = 0.00423 \quad \frac{\text{mg } O_2}{\text{mg MLSS - hr}}$$

Figure III-10: Graphic Derivation of Oxygen Utilization Constants a and b


70
60
50
40
30
20
10
0
0
10
20
30
40
Specific Oxygen Uptake Rate → mg DO / mg MLSS - hr x 10^3
Substrate Consumption → mg COD removed / hr - mg MLSS x 10^3
a = 1.335 mg Oxygen / mg COD removed
b = 0.00423 mg Oxygen / mg MLSS - hr
(Correlation Coeff. = 0.998)

detention time of $\bar{t}$ = 8 hours, whereas OUR at endogenous respiration levels was close to 4-5 mg D.O./l-hr.

Also the oxygen transfer properties of the waste water were briefly tested in an effort to assess the relative capacity of the waste liquor to absorb air from the aeration line. The volumetric oxygen transfer rate n'_{O_2} is given by the relationship $n'_{O_2} = k_L a(C^*-\bar{C})$

where k_L : mass-transfer coefficient in liquid film

a : interfacial area between liquid and gas (air) per unit volume of liquid (broth)

$\bar{C}$: D.O. (dissolved oxygen) concentration in bulk liquid

C^* : hypothetical value of D.O. in equilibrium with $\bar{C}$ in bulk liquid phase

In most fermentation systems it is common practice to evaluate the "lumped" volumetric oxygen transfer coefficient $k_L a$ with the ultimate purpose of calculating aeration and mixing power. However in biological waste treatment systems there have been developed correlations for sizing aeration equipment based on the ratio $\alpha = \frac{k_L a \text{ (filtered mixed liquor)}}{k_L a \quad \text{(tap water)}}$ of the volumetric oxygen transfer coefficients for the filtered mixed liquor of the bioreactor and for tap water, rendering the specific derivation of either $k_L a$ superfluous.

Filtered mixed liquor was "gassed-out", i.e. first stripped of dissolved oxygen by way of sparging with nitrogen (the depletion of D.O. was followed electrometrically through the YSI Dissolved Oxygen Meter) and then reaerated directly from the laboratory air-line and the D.O. concentration recorded until saturation was achieved. The same

technique was applied for tap water. The D.O. concentrations plotted in semilog paper vs. time (in minutes, linear scale) produced straignt lines whose slope ratio is α. The value of α was found to be 0.83 at $T = 25^{o}$ C.

Another constant used in the above-mentioned correlation for sizing aeration equipment for the field-scale facility to be designed is: $\beta = \dfrac{\bar{C}_S \text{ (waste water)}}{\bar{C}_S \text{ (tap water)}}$

i.e. the ratio of D.O. concentration at saturation in the waste water (feed to the bioreactor) over D.O. concentration at saturation in tap water. The value of β was found to be 0.97 at $T = 25^{o}$C.

III.2.G. Nutrient Requirements

Nitrogen and phosphorous are recognized as the two most important elements which must be present in the waste water, apart from the main carbon source, for an effective biological treatment to occur.

There was always an excess of nitrogen in the form of ammonia in the Petrofina raw waste water, which had to be reduced to non-toxic levels by the stripping pretreatment. Typically the concentration of ammonia in the raw waste water ranged from 120 to 150 ppm while that in the stripped feed was around 20-30 ppm, a concentration judged to be adequate, in view of the accepted proportion of organic load to nitrogen [according to Sawyer (1956) the BOD:N ratio should be at least 18:1].

As for phosphorous, because of the low levels in which it occurred in the stripped feed and also because of possible interferences in the method of analysis it was not always easy to measure its concentration. However in the analyses performed on the mixed liquor of the bioreactor there was a concentration of about 2-5 ppm P, whereas the maximum value recorded was 10 ppm. This P concentration was made possible not only because of the practical absence of any systematic sludge wastage except for the biomass withdrawn in the daily samplings of mixed liquor, but also because of the acid pH-controlling solution which consisted of 3N NaH_2PO_4. Thus the bio-treatment operation was assured of a satisfactory proportion of organic load to phosphorous [according to Sawyer (1956) the BOD:P ratio should be 96:1 whereas Sherrard and Schroeder (1972) propose a COD:P ratio equal to 130:1].

In view of the above it would seem recommended to use supplementary phosphorous source (e.g. phosphoric acid that could be combined in the pH-controlling scheme or a phosphate salt in the recommended proportion) for the full-scale facility to be designed.

III.2.H. Removal of Toxicants

As was outlined previously the pretreatment facility was instrumental in reducing the levels of toxicants, particularly ammonia and hydrogen sulfide to levels that could be harmlessly handled by the microbial population of the activated sludge.

The most serious case of heavily laden raw waste occurred during one of the shorter-term continuous flow experiments at a detention time of 8 hours that follows the principal Run No. 5. The raw waste was collected from an outlet situated before the Wemco Depurator on the Refinery field as the Depurator happened to be out of order. The sulfide concentration was 125 ppm and that of ammonia was 197 ppm. The air-stripping and neutralizing procedure was intensified and a lot of effort was invested towards reducing the free oil of the waste. The stripped waste contained 15 ppm sulfide and 30 ppm ammonia, levels which apparently did not disturb the normal course of the biological treatment inside the fermentor to any detectable degree.

During the operation of the bio-treatment facility at a detention time of 8 hours* the stripped feed contained on the average less than 10 ppm sulphide and between 20 and 32 ppm ammonia. At the same time it was invariably spiked with phenol at around 30 ppm. The effluent from the bioreactor was always free from both phenol and sulfide (<1 ppm).

---

*Including the corresponding portion of Run No. 5.

In an individual continuous flow experiment at a detention time of 8 hours the stripped feed was spiked with phenol first at 60 ppm and subsequently at 100 ppm. The biomass used in the first part of this "run" was already acclimated to 30 ppm of phenol from a previous continuous flow experiment and could handle the new phenol level without any disruption, not even a minimal one, in terms of residual phenol, COD and sludge characteristics. After a smooth operation at 60 ppm influent phenol over 4 detention periods the feed spiked at 100 ppm of phenol was pumped into the reactor. It seems that the mixed microbial population had already achieved a high degree of acclimation, as there was again no discernible upset of the system apart from a mere 2 ppm of effluent phenol in the end of the first detention period after the new feed was administered. The degree of organic load removed continued to fluctuate around the 72% mark (% COD removal) and there was excellent settling of sludge and clear effluent for the next 5 detention periods until all the spiked batch of waste was consumed.

III.2.I. Effect of pH

As was mentioned previously the normal course for the mixed liquor inside the bioreactor was a gradual drop in its pH when this was not externally controlled. This spontaneous pH drop may be explained by acidic metabolic intermediates accumulating during the process of biological treatment of the oil refinery waste water. It was found that the pH drop was detrimental to the efficiency of the treatment as the mixed microbial population could not reach the levels of organic load removals achieved around neutrality and there was a definite tendency for the sludge to deflocculate and for hindered settling to set in as was already exposed when dealing with continuous flow "runs"--or portions thereof--without pH control. The organic load (COD) removal was calculated between the influent and effluent (from the cell separator) COD, as the supernatant had a tendency to become turbid and entrain considerable amounts of dispersed biological solids over the weir. These symptoms started appearing at a pH between 6.5 and 6.0, but became quite obvious at pH's less than 6.0.

It is known that with relatively prolonged operation of mixed microbial systems such as activated sludge at acidic pH (e.g. 4.5-5.0) the selective pressure of the chemostat displaces bacterial species in favor of yeasts and molds and also that the concomitant dispersed growth can be attributed to filamentous fungi [Cf. Pipes (1967), Gaudy (1975)].

In an individual continuous flow experiment performed at a detention time of 16 hr. ($D = 0.0625\ hr^{-1}$) the pH was left to drop freely by

turning the pH-controller off after a steady state operation had already been established. Inflowing COD was 285 mg/l and residual COD around 50 mg, practically the same as that of the particularly clear effluent from the settler (% COD removal ≈82%). After shutting the pH-controller off pH was recorded at one-hour intervals and also the OUR was measured at the same time as an index of the sludge's activity. The results appear in Table III-20 and have been plotted as pH and OUR values versus time in Fig. III-11. These data show that initially the incremental drops in both pH and OUR were larger than the ones observed later. When the pH had reached a value of 5.2 five hours after the disconnection of the pH-control the OUR was already approaching endogenous respiration levels having been reduced by more than 50%. Measurements of residual substrate (on filtered mixed liquor drawn from the reactor) at points around pH = 5.0 did not show any dramatic increase (residual substrate ≈85 mg/l i.e. at 70% removal) but the COD of the effluent was more than 130 mg/l (less than 50% removal). Still the most serious effect was the loss of biological solids with the effluent from the settler. An elementary biomass balance, taking into account the mass of the samples withdrawn and the mass of solids collected in the effluent reservoir over the period between the onset of the perturbation and the time when pH = 5.0 (~6½ hours later) revealed that there was an actual overall increase in biomass but while the MLSS at t = 0 measured 1005 mg/l, 6½ hours later the MLSS amounted to only 435 mg/l, (i.e. a ~50% loss if we take into account the possible experimental error in MLSS determinations).

The above observations pointed clearly to the absolute necessity of a controlled pH around neutrality. Experience during the long-term continuous runs showed than an optimal pH range would be between 6.8 and 7.5.

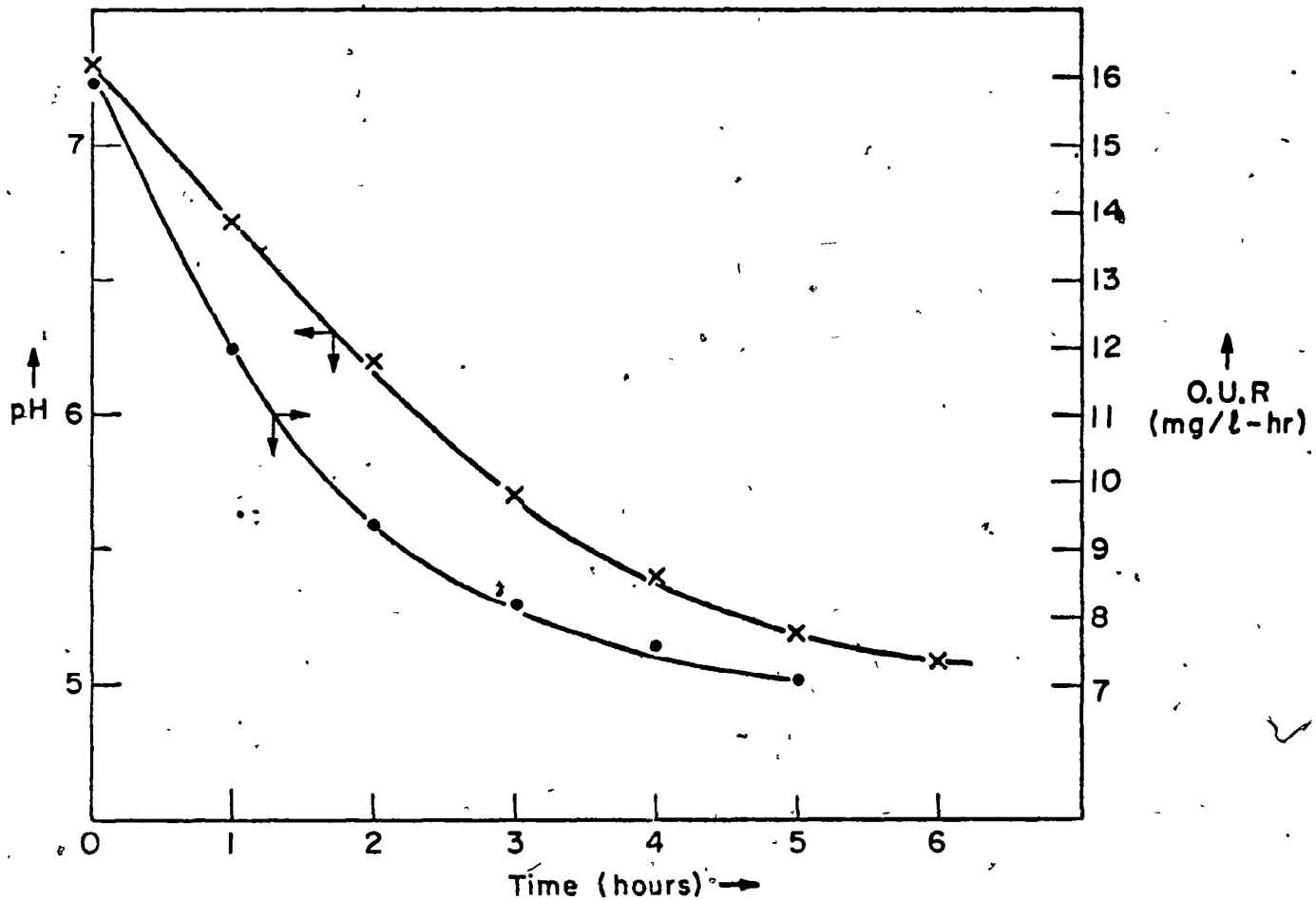
Table III-20

pH and OUR variation during operation

without pH control ($\bar{t}$ = 16 hr)

Time [hr]	pH	OUR mg/ℓ-hr
0	7.3	16.0
1	6.7	12.0
2	6.2	9.4
3	5.7	8.2
4	5.4	7.6
5	5.2	7.0

Figure III-11: Operation Without pH Control


pH
7
6
5
16
15
14
13
12
11
10
9
8
7
O.U.R
(mg/l-hr)
0
1
2
3
4
5
6
Time (hours)

III.2.J. Effect of Sludge Recycling

The cell recycle ratio employed throughout the Main Treatability Studies, namely r = 0.67, although chosen empirically upon observations of the settling properties of the acclimated sludge (degree of compaction) --concentration factor c) and also of the sustained level of biological solids at steady state, it still proved quite beneficial not only in terms of the successful lab-scale performance of the system, but also in terms of a more general design implication; i.e. that given this recycle ratio and the degree of compaction of the sludge dilution rates even higher than dictated by the maximum specific growth rate μ_m can be used, since the specific growth rate (of course the "mean" μ, as we are dealing with mixed populations) is not controlled by the dilution rate only, but by the factor $A = 1 + r - rc$ too.

In most field-scale applications of the Activated Sludge Process comprising the majority of municipal sewage treatment plants the above ratio would seem rather high (the usual figure is 0.25-0.30). Still many activated sludge systems do require high recycle ratios in order to maintain effectively a biological solids level considerably higher than can be supported in active growth by the available substrate, as noted by Gaudy et al. (1967); this was the case with the Petrofina waste (unlike the Gulf Oil waste in which increased recycle ratios tended to increase sludge "bulking"). At the same time the factor of cell decay k_d tends not to be negligible in systems with rather high recycle ratios and this is why it was taken into account in the formulation of the kinetic equations (in usual pure culture fermentations of

particularly rapid-growing microorganisms the cell decay factor is neglected).

Along these lines an attempt was made to compare our successfully operating bio-oxidation system (with cell recycle at r = 0.67 and a nominal detention time of $\overline{t}$ = 8 hours) with an identical system lacking only the cell recycle loop. A New Brunswick Microferm fermentor and its accessories happened to become available towards the end of the Main Treatability Studies and was used with the same waste feed and the same inoculum as the original system. In order to assure complete simulation of the rest of the system lacking the cell feedback it was decided that both systems be deprived of automatic pH control, as there was only one automatic pH controller available. In this way manual pH regulation was practiced on both units but both systems were followed closely in order to avoid as much as possible the detrimental effects of a sizeable pH drop. Feed to both systems: ~300 mg/l COD and 35 ppm phenol.

The absence of cell recycle brought about the predictable situation of very low levels of MLSS in the new system: Starting at about 1300 mg/l (for both systems) the new system ended up at less than 300 mg/l by the third detention period both because of the relatively high turn-over of feed--for a system lacking in recirculation*--and also because of considerable losses of solids in the effluent from the settler. Another possible advantage which the "once-through" system was also lacking

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*Since in this system μ was simply equal to D = 0.125 hr^{-1}.

was the simple fact, quoted by Gaudy (1975), that the cell recycle increases the cell concentration, X, in the reactor and that the presence of greater biomass concentration might be reinforcing the system employing cell recycle against leakage of carbon source.

It was further observed that although the removals of COD and phenol were not generally very different between the two systems (i.e. 75% COD removal and <1 ppm phenol for cell-recycle system and 65% COD removal and again <1 ppm phenol for "once-through" system) there was wide fluctuation in the values of the quasi-steady state established in the once-through system and the removal remained at the above level only when portions of acclimated sludge were added to complement for some of the losses of solids at the end of the fourth detention period. It should be noted here that the "removal" for the "once-through" system was computed in terms of residual rather than effluent COD (due to the solids included in the actual effluent).

The effluent from this non-recycle unit after separation from the entrained solids (quiescent settling as in the settler of the system with cell recycle) was still strikingly more turbid than the supernatant from the cell separator of the original system, although the SVI for both systems was comparable at around 50. A typical example is given in the following with regard to the % light transmittance observed through the settled supernatants from mixed liquor samples of the two systems (λ = 540 nm):

Table III-21 (a)

Effects of a slug dose of $[Na^+]$ = 10,000 ppm

on the performance of the Activated Sludge process

[D=0.125 hr^{-1}; T=25°C; pH=6.8; recycle: 67%]

influent COD=400

Time (hours)	Residual COD [mg/ℓ]	MLSS [mg/ℓ]	mg D.O./ℓ-hr	Remarks
- 8	74.0	1400	23	SVI: 53, excellent flocculation and compaction
0	75.6	1400	22	MLSS/MLSS = 0.68
2	86.9	1260	18	
10	90.7	2200	13	
24	98.3	1750	9	
48	104.0	1360	18	Shift in biomass color (brown to grayish)
56	95.0	1410	23.1	
64	98.0	1460	24	
72	86.0	1375	25	
80	92.0	1425	24	SVI: 42

	% Light Transmittance	
	Once-through system	Cell-recycle system
After 5 min. settling	63	87
After 15 min. settling	72	93

The beneficial effect of cell recycle on the flocculating and settling characteristics of the microbial population was noted by Ramanathan and Gaudy (1969) who have suggested that under recycle conditions the cells undergo a period of endogenous respiration or metabolic dormancy in the settler which may enhance flocculation tendencies and have also hinted that the higher average age of the cells in these systems may also be a contributing factor.

Finally it was suspected that the deflocculating tendencies of the once-through system might also reflect its reduced resiliency towards the almost perennial pH shock loadings brought about by the manual regulations of the pH, whereas the cell-recycle unit proved quite resistant to the above step changes in pH (these were not as pronounced as in Run No. 4, because of the close attendance given the two parallel systems).

III.2.K. Effects of High Ion Concentration

Unlike the abundance of published information on the biological treatment of industrial waste waters for the removal of organic pollutants, relatively little is known concerning the effects which the inorganic constituents of the waste have on the course of the removal of the organic pollutants and on the operational behavior of completely mixed activated sludge systems.

An introductory investigation was made on the effects of high concentrations of ionic species on the yield of biological solids and on the ability of a heterogeneous microbial population continuously cultured on the Petrofina refinery waste to remove substrate.

The ionic species specifically selected to be studied was sodium, since it is the most common cation to be encountered in Oil Refinery waste waters in large amounts. Sodium ions usually originate from saline waters used mainly for cooling purposes at refineries situated on the seashore and also from neutralizing operations (with NaOH) on acidic waste water streams and tank bottoms effluents, which, at times, can result in transient shock dosing of the bio-treatment facilities with sodium ion concentrations well into the thousands and even tens of thousands of ppm.

It was decided to spike the refinery waste water batch with neutral sodium phosphate ($Na_3PO_4 12H_2O$) first at a level of 10,000 ppm of Na+ and subsequently, if the system was not permanently disrupted, at a second level of 30,000 ppm of Na+. Both doses were to be administered in a "slug" manner, the step addition being only smoothed by the quasi-exponential

diluting-in of the ion. The choice of a phosphate salt was made over sodium chloride, as high chloride ion concentrations are known to impair the biological treatment unlike phosphates. Because the orthophosphate union PO_4 is a Lewis base with a conjugated Lewis acid which is relatively weak (phosphoric acid, H_3PO_4) hydrolysis of $Na_3PO_4 12H_2O$ occurs in acqueous solutions, resulting in an alakaline pH. Hence, after the spiking addition of the sodium salt the pH was adjusted back to neutral with sulfuric acid.

The waste water's characteristics were as follows:

COD = 400 mg/l
Phenol = 32 ppm
Susp. Solids = 77 ppm

whereas the bio-system was operated as usual at 67% total (i.e. no sludge wastage) cell recycle, at 25°C, pH=6.8 and 360 rpm.

Before the spiked waste water was started to be pumped into the bio-reactor at a dilution rate of $D=0.125\ hr^{-1}$ (mean residence time $\bar{t}$ = 8 hrs) a steady state of treatment had been reached with the unspiked liquor, at the same dilution rate, with the following parameter values:

Residual COD:	74 mg/l
Phenol:	<1 ppm
MLSS:	1400 mg/l
MLVSS/MLSS:	0.68
Oxygen Uptake Rate:	23 mg O_2/l - hr.
SVI:	53

The continuous flow data of the experiment appears in Tables III-21(a)

Table III-21 (a)

Effects of a slug dose of $[Na^+]$ = 10,000 ppm

on the performance of the Activated Sludge process

[D=0.125 hr^{-1}; T=25°C; pH=6.8; recycle: 67%]

influent COD=400 ppm

Time (hours)	Residual COD [mg/ℓ]	MLSS [mg/ℓ]	mg D.O./ℓ-hr	Remarks
- 8	74.0	1400	23	SVI: 53, excellent flocculation and compaction
0	75.6	1400	22	MLSS/MLSS = 0.68
2	86.9	1260	18	
10	90.7	2200	13	
24	98.3	1750	9	
48	104.0	1360	18	Shift in biomass color (brown to grayish)
56	95.0	1410	23.1	
64	98.0	1460	24	
72	86.0	1375	25	
80	92.0	1425	24	SVI: 42

Table III-21 (b)

Effects of a slug dose of $[Na^+]$ = 30,000 ppm

on the performance of the Activated Sludge process

[D=0.125 hr^{-1}; T=25°C; pH=6.8; recycle 67%; infl.COD=400 mg/ℓ]

System accliminated to $[Na^+]$ = 10,000 ppm

Time (hours)	Residual COD [mg/ℓ]	MLSS [mg/ℓ]	OUR mg/ℓ-hr	SVI	Optical Transmitt. %(supernatant)	Remarks
0 (80)*	92	1425	24.0	42		
2 (82)	103	1600	21.0		46	
8 (88)	115	1400	15.0		42	Color shift: greenish
16 (96)	159	1525	10.5	27	29	
24 (104)	229	2130	7.2		8.5	
40 (128)	245	2700	8.0	1.6	3.0	MLVSS/MLSS = 0.48 - 0.60
48 (128)	268	3200	7.0		3.0	"
60 (140)	293	3480	8.4		3.0	"
**(72)(152)						"
80 (160)	286	3100				"
90 (170)	252	2900	9.0	20		"

Table III-21 (b)
(cont.)

Time (hours)	Residual COD [mg/ℓ]	MLSS [mg/ℓ]	OUR mg/ℓ-hr	SVI	Optical Transmitt. %(supernatant)	Remarks
114 (194)	205	2780	14.0		5.0	MLVSS/MLSS = 0.48 - 0.60
144 (224)	188	2720	8.0	18		"

*Time in parentheses computed from introduction of 1st shock.

**Point when high-ion concentration feed was left to dilute out of system.

Figure III-12: Effect of High Na^+ Ion Concentrations on Biological Treatment

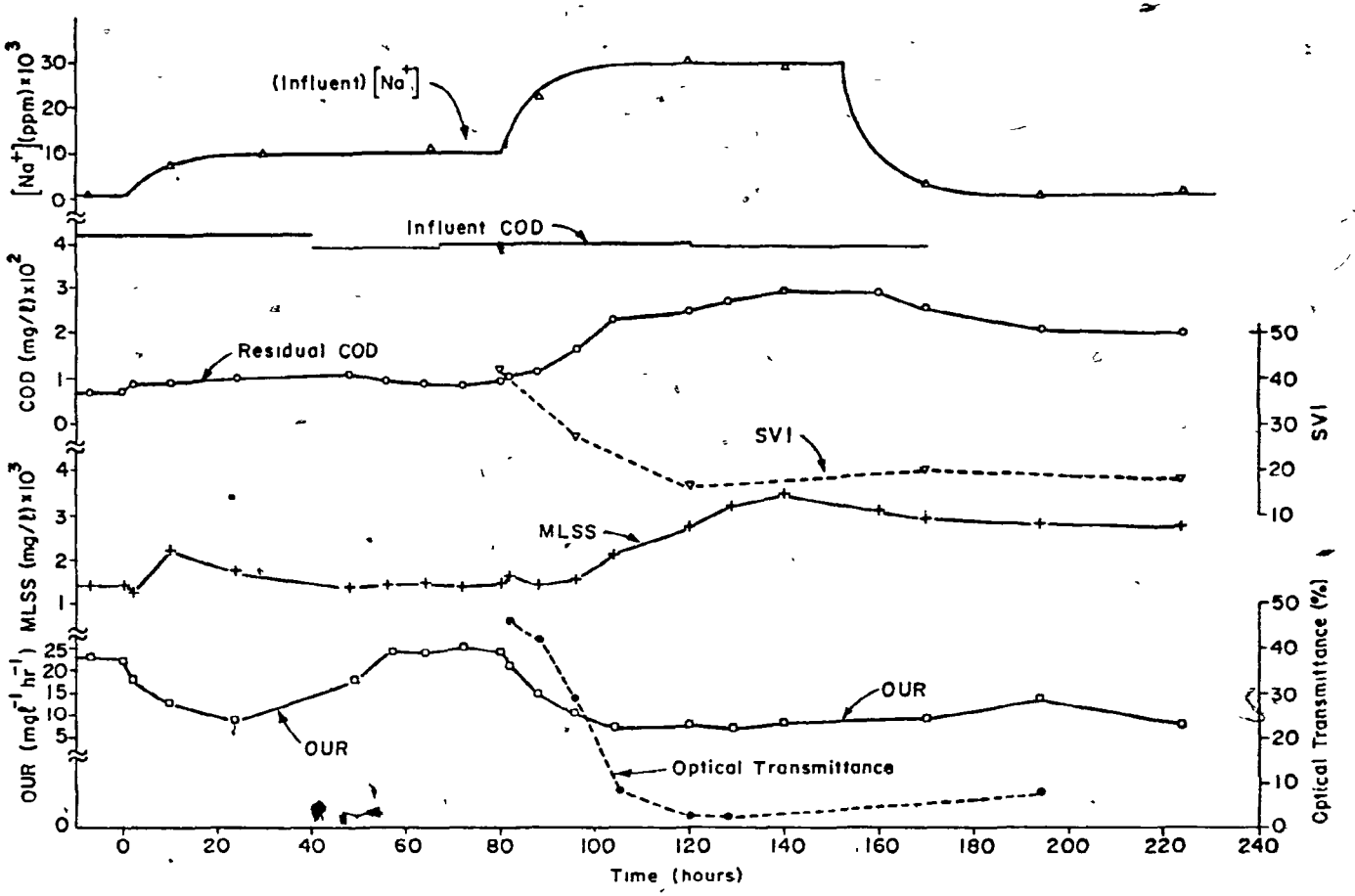
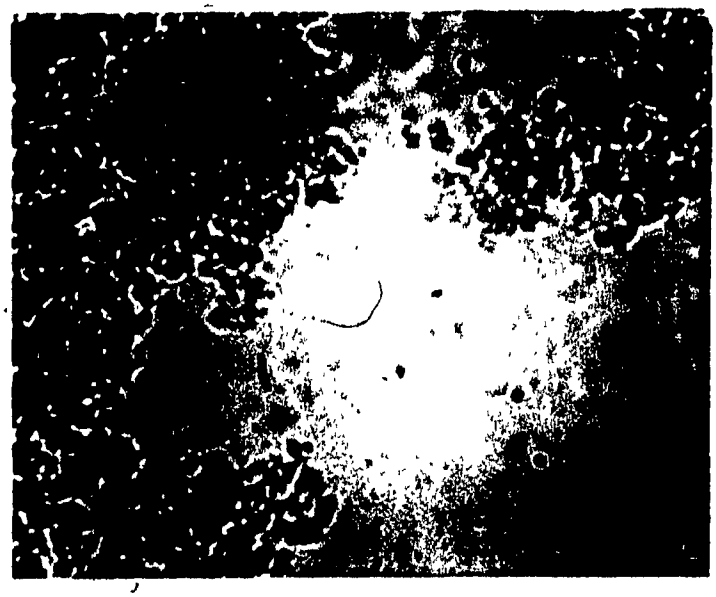

(Influent) [Na+]
[Na+](ppm)×10^3
Influent COD
COD (mg/ℓ)×10^2
Residual COD
SVI
MLSS
MLSS (mg/ℓ)×10^3
OUR (mgℓ^-1 hr^-1)
OUR
Optical Transmittance
Optical Transmittance (%)
Time (hours)

Figure III-13: (a) Photomicrograph of healthy settled activated sludge; Detention time: 8 hr.

(b) Photomicrograph of settled activated sludge 70 hours after a shock load of 30,000 ppm Na^+; Detention time: 8 hr.

(magnification x 600)



(a)

(b)

and III-21(b) while the course of the variation of the different parameters monitored throughout the run is shown graphically in Figure III-12.

The variation in substrate removal efficiency was only minor in the case of the first high-ion concentration shock: there was a consistent rise in residual COD in the first four detention periods, reaching a maximum of 104 mg/l, probably due to metabolic intermediates and/or end products according to evidence presented in cases of high sodium chloride dosing and activated sludge systems as reported by Kincannon and co-workers (1966 and 1968). By the fifth detention period after the sodium concentration had reached the 10,000 ppm level the system exhibited definite recovery and went on to stabilize itself at a residual COD concentration of 92 mg/l (i.e. a removal of 77% compared to 81% at the steady state prior to the slug does of sodium). As the sodium concentration in the fermentor increased there was a relatively small initial decrease in the biological solids level followed immediately by a sharp and sizeable increase (2200 mg/l) at the beginning of the second detention period. This could be explained in a way analogous to Kincannon's and Gaudy's (1968) proposal of an en masse increase in cell yield or a yield increase due to halophile species predominance in the heterogeneous microbial culture. There followed a smoother decrease in biomass concentration, which from the sixth up until the end of the tenth detention period remained practically stable at values around the 1425 mg/l mark, i.e. essentially the same level as that of the steady state existing prior to the introduction of the sodium salt. In Kincannon's system the new

steady-state level of biological solids was considerably lower than the initial one before the salt dosing, but there was no cell recycle. The cell recycle in the present system could also help explain the relative ease of adaptation of the activated sludge population to the step introduction of a 10,000 ppm concentration of sodium.

The initial upset of the biomass was also illustrated by a "sagging" profile of the Oxygen Uptake Rate (OUR) immediately following the diluting-in of the salt, but the final acclimation of the biota was seen in the stability of this parameter as well beyond the sixth detention period.

Although no systematic measurements of SVI were taken during this first portion of the experiment, the settleability of the biological solids was maintained at the same level as the prevailing in the salt-free operation. Still from visual inspection it could be inferred that new species predominance had occurred, as the color of the sludge had shifted from brown to light gray.

Waste water at a three-fold higher sodium concentration (30,000 ppm) was introduced at the end of the tenth detention period (at $\bar{t}$ = 80 hours) from the first shock loading. It is apparent from the tabulated and plotted data that the substrate removal ability of the system was severely impaired almost from the time the new high salt concentration started building up inside the reactor and even ten detention periods after the introduction of this second shock the residual substrate was around the 290 mg/l level (i.e. removal only 27.5%). In an attempt to see if the effect was reversible the salty waste feed was left to dilute out of the system starting at $\bar{t}$ = 72 hours after the shock.

A rather unexpected result was the apparent increase in the concentration of biological solids, which continued even after the influent sodium ions had reached the pre-set level of 30,000 ppm inside the bioreactor, attaining a peak value of close to 3500 mg/l (almost an increase by 150% over the previously established steady state) 60 hours after the shock. The MLSS level started decreasing slowly only a considerable time after the salt was left to completely dilute out of the reactor. It was suspected that the MLSS test might no more be a reliable estimate of viable cells, since Oxygen Uptake Rates had fallen to an all-time low plateau of around 7 mg O_2/l-hr., i.e. almost endogenous respiration levels. Still the MLVSS/MLSS ratio was between 0.48 and 0.60, which, although indicative of lower viability, still points out that there was a sizeable net increase in the microbial population. It can only be speculated that the high sodium and possibly the concomitant high phosphate level gave rise to increased yields of biomass, but the overall metabolic activity of this sludge was particularly low, as can be seen from the high residual substrate concentration and the low Oxygen Uptake Rate. Despite the excellent compaction which was exhibited by the biomass as can be seen from the steady decline of the SVI and its attainment of a plateau at values lower than 20, there was very dispersed growth, with a resulting effluent stream which was particularly turbid, as is shown by the optical transmission measurements on the supernatant from the cell separator. The decrease of MLSS during and after the diluting-out of the salty influent waste could also indicate a degree of lysis of cells after

this osmotic shock. Examination of the sludge under the microscope revealed minute dispersed flocs and aggregates of solid clay-like material, partly accounting for the greenish appearance of the biomass after the introduction of the second high ion level; two micrographs of healthy sludge and high salt-dosed sludge appear in Fig. III-13(a) and (b) for visual comparison. It was concluded that a 30,000 ppm level of Na^+ could not be handled by the mixed microbial population and led the system to irreversible damage, unlike the previous shock loading of 10,000 ppm of Na^+ which was effectively accomodated within only a few detention periods after it was imposed.

III.2.L. Correlation of Organic Parameters

The organic content of waste water being the main substrate utilizable by aerobic microorganisms is usually estimated in terms of "oxygen demand" using BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand) and TOD (Total Oxygen Demand) or in terms of carbon using TOC (Total Organic Carbon). These are the most common organic parameters for the characterization of industrial waste waters including those of oil refinery and petrochemical origin. Although there have been efforts to interrelate these parameters theoretically we can only have approximations, mainly in terms of accuracy (i.e. regarding percentage of Theoretical Oxygen Demand or of Theoretical Carbon Concentration). It is recognized therefore that the organic parameters all too often have serious limitations as to how well they represent the available substrate for biodegradation but they are very useful from the engineering standpoint. Consequently beyond the above-mentioned efforts at defining their accuracy in respect to some abolute measure of substrate there have been attempts to statistically correlate the organic parameters of particular categories of waste waters with relatively common origin and, presumably, approximately comparable distribution and composition.

The most comprehensive work on this type of correlations appears to be that of Ford et al. (1970) with applicability to oil-refinery and petrochemical effluents. The particular correlations between BOD, COD and TOC appear also in EPA (1971) and reflect results

from numerous analyses over a number of related industrial facilities.

As discussed in the section on Analytical Methods a few "grab"-type BOD and TOC tests on the raw Petrofina waste, the stripped feed and the final effluent were performed and they seem to generally fit the ratios and ranges suggested in the above-mentioned reports. Numerical values of ratios averaged over a set of five analyses of BOD and TOC on top of the routinely performed COD tests are given in Table III-22 as typical of an equal number of waste water batches (raw and stripped) that underwent continuous bio-oxidation runs at $\bar{t}$ = 8 hours.

It should be noted that the above correlations are to be considered as tentative rather and far from final or exhaustive, since the task of obtaining statistically significant ranges of such parameter values would constitute an entirely different project in itself. Still the above results are instructive in the following aspects:

The COD/TOC ratio for the raw waste reached beyond the maximum value 6.65 reported for chemical and refinery wastes by Eckenfelder and Ford (1970) indicating the presence of inorganic-reducing agents (it actually contains NH_3 and H_2S). Also in absolute values not reported here it was noted that the TOC of the stripped feed was considerably higher than that of the raw waste (see typical figures in next section) owing to the doubly boosting effect of the phenol-spiking and the release of most of ammonia and hydrogen sulfide during the pre-treatment. The COD/TOC ratio of the stripped feed

and the effluent are within the limits reported in the literature cited above.

The BOD/COD ratios for all three categories of water seem to fall within the limits reported in the literature. Note that the somewhat lower values of this ratio for the raw waste (and the effluent) show the relative scarcity of readily bio-oxidizable organic material in them, implying that it is possible for the raw waste liquor to be treated physically or chemically, at least partially.

Table III-22

Tentative Correlation of Organic Parameters

(Bio-oxidation at $\bar{t}$ = 8 Hr)

	COD/TOC	BOD/COD
Raw Waste:	6.0-8.0	0.30-0.40
Stripped Feed:	4.2-5.0	0.50-0.60
Bio-Treated Effluent:	4.5-5.5	0.15-0.25

III.3. Conclusions

Both the Preliminary Studies and the Main Treatability Studies provided valuable information concerning the effectiveness and the drawbacks of biological detoxification of each type of liquid waste examined.

The former revealed primarily the limitations imposed on the operation of a high-rate bio-oxidation process of the completely mixed activated sludge form as originating from:

- The characteristics per se of high-strength phenolic waste streams from petrochemical and oil refinery operations (hence: consideration of a pre-treatment step).
- The absence of closely-regulated environmental conditions such as pH.
- The dependence of the bio-system on hydraulic and feed make-up perturbations (variable chemical load).
- The effect of "past growth history" (incomplete acclimation) of inoculating sludge.

The same Preliminary Studies helped recognize some typical patterns of response of measured parameters, e.g. substrate and biomass, upon environmental shocks and were also instrumental in designing and operating the closely controlled experimental set-up for the Main Treatability Studies.

Through the latter the systematic investigations undertaken showed that after a physical-chemical pretreatment for the reduction

of the concentrations of trouble toxicants (NH_3 up to 85%, H_2S up to 92%) the well-characterized refinery waste was effectively amenable to biological oxidation achieving satisfactory steady-state operation of the Completely Mixed Activated Sludge Process at detention times from 24 hr. down to 6 hours, with % COD removals of generally more than 70% over the pre-treated feed (or more than 73% over the raw feed), excellent settling and flocculating capacity of biomass (SVI: 37-49), particularly if of municipal origin, and elimination of toxicants (e.g. H_2S, Phenol $\leq$ 1 ppm). These overall data derived as typical for the Petrofina waste water are tabulated in Table III-23.

In particular the hydraulic studies of the bio-treatment process (i.e. sequentially imposing different detention times and following the response of the system) either in themselves or in combination with individual investigations of variables furnished readily useable design information for upscaling of the bio-oxidation system (see also Table III-23) such as:

- Optimum range of detention times.
- Predicted (theoretical) maximum dilution rate by means of maximum specific growth rate and recycle constants.
- Predicted (theoretical) sludge production, through the cell yield (implication regarding sludge disposal).
- Predicted rate of substrate uptake of different dilution rates and hence degree of organic removal.

- Oxygen requirements (data on microbial oxygen demand and oxygen transfer constants).

Finally specific studies [redacted]ed on particularly useful aspects of the biological treatment revealing:

- Nutrient requirements to be extrapolated for field-scale facility.
- Capacity of system to eliminate up to 100 mg/l phenol to levels less than 1 ppm.
- Usefulness of OUR as a measure of biomass activity in hydraulic (increased D) and chemical (low pH, high Na^+ concentration) shocks.
- Relative resistance of the bio-system to high Ion Concentrations exemplified by 10,000 ppm and 30,000 ppm of Na^+.
- Tentative correlations of organic parameters COD, BOD and TOC for rapid estimations of waste water quality and treatment efficiency with implications on the make up of the particular stream or batch; and the suitability of physical-chemical vs. biological treatment.

Table III-23

Summary of Design Parameters

Determined from Main Treatability Studies

Stream Characteristics, (Average)

	Raw Waste	Stripped Feed (and Spiked Nominally at 30 ppm Phenol)	Effluent
COD	325 ppm	290 ppm	88 ppm
BOD	164 "	175 "	33 "
TOC	40 "	64 "	16 "
Phenol	9 "	33 "	<1 "
Hydrogen Sulfide	55-125 "	4-10 "	<1 "
pH	8.7	7.1	6.8

Bio-oxidation

Detention time:	8 hr
MLSS	1400 mg/ℓ
MLVSS/MLSS	0.65-0.71
Temperature, T	25°C
Recycle ratio, r	0.67
Concentration factor, c	2.00
SVI	37-49
OUR (max.)	66.5 mg D.O./ℓ-hr

Oxygen Uptake factor a = 1.335 mg O_2/mg COD removal

Oxygen Uptake factor b = 0.00423 mg O_2/ mg MLSS-hr

Oxygen Transfer ratio α = 0.83 (T = 25°C)

Oxygen Transfer ratio β = 0.97 (T = 25°C)

Sludge Yield, Y 1.7858 mg MLSS/mg COD

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