TREATMENT OF STRIPPABLE AND NONSTRIPPABLE SUBSTRATES BY THE ACTIVATED SLUDGE PROCESS

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CHAPTER I

INTRODUCTION

It may seem inconceivable at first glance, but it is true that mankind is faced with the dire threat of thirst, despite an abounding affluence in the form of mighty rivers, clear mountain streams, and verdant meadows. In the United States alone there is on the average 4300 billion gallons of rainfall each day (1), a quantity far in excess of that which can be used; yet, 40 million Americans are subject to a menacing situation in the form of critical water shortages. Furthermore, in a recent year of subnormal rainfall, water rationing was practiced in one quarter of the states. The population explosion is part of the reason for the ever-increasing demand. It has been estimated that by 1980 the population of the United States will probably reach 245 million and the demands on the nation's water resources will have almost doubled (2). By the year 2000, water demands will have tripled. Besides population growth, technological advances leading to elevated standards of living contribute significantly to the increase of water usage. Man, through his activities, has further worsened the already acute water shortage problem by polluting the available water resources. The importance of this aspect of the water problem cannot be overemphasized. To alleviate such aggravating situations, measures such as conservation of water usage and prevention and/or abatement of pollution of the

existing water resources are well under way.

To an industry or manufacturing concern, wastes produced are a liability unless there is a profitable means of saleable byproduct recovery. As a result, an industry endeavors to dispose of its wastes at a minimum cost. Oftentimes such wastes are channeled to a domestic sewer, a stream, a creek, or other water course. The same water course may serve downstream users as a source of municipal drinking water supply, or industrial or agricultural supply. Today untreated waste in the United States waterways from municipalities alone is three times as great as in 1900. Industrial wastes make the problem even more critical. Many cities are now taking water from sources carrying twice as much pollution as was considered safe in 1955. This situation points toward either of two possibilities: we are not adequately equipped with the technical know-how regarding treatment processes for the pollutants arising out of modern industrial activities or, possessing such knowledge, there is a lack of implementation of the acquired skill toward preventing pollution of the nation's water bodies. The current surge of research activity and the new pollution control laws and enforcement powers given to federal regulatory agencies may be expected to do much to foster rapid progress; however, meaningful and successful implementation of knowledge and enforcement of the laws depend to a large extent on public awareness of the dire consequences of leaving pollution problems unsolved.

In regard to waste water treatment for the removal of organic pollutants, the activated sludge process occupies a unique position in the sense that it is regarded as one of the most effective methods for the treatment of domestic and industrial wastes. Developed over half

a century ago, it has been realized for some time that this process owes its tremendous waste treatment ability solely to the biological and biochemical activities of microorganisms which compose the "activated" sludge. Even in the area of tertiary treatment, attainment of treatment by biological means is an ideal goal. Compared to other physical and/or chemical means of treating aqueous wastes, the biological method is usually cheaper, and so long as conditions for maintaining a viable microbial population are attained, removal of organic matter is feasible.

While the biological mechanism of activated sludge has been well-established, and while it seems reasonable to conclude that there is in nature a type of organism(s) which can metabolize almost any organic compound, an understanding of the process and translation of such understanding to useful engineering parameters is not a simple matter. Also, man has created many new organic compounds which may form part of waste water streams and thereby complicate the problem of understanding and describing the course of waste water purification. Also, the organic composition of waste water streams does not stay constant. In addition, some organic constituents are volatile in the sense that they can escape from the aqueous waste due to agitation, mixing, heating, etc. The escape of such compounds to the atmosphere during treatment by the activated sludge process may constitute a health hazard to plant personnel, as well as adding to the complexity of describing the course of purification. When one contemplates the rapid and continuing growth of the petrochemical industry which produces some of the newer "man-made" chemicals and a variety of volatile compounds, and when one realizes the fact that the product line (and hence the waste stream) can change

rapidly at such plants, the engineering justification for the research interest pursued in the present investigation seems amply demonstrated.

The work reported in this thesis was accomplished in an attempt to gain a better understanding of the kinetics and mechanisms of purification of wastes containing low molecular weight (volatile) aldehydes and ketones during treatment by the activated sludge process. During such treatment the course of waste water treatment can be effected concurrently by chemical oxidation (autoxidation) as well as physical stripping and microbial metabolism. Various aspects of these three processes were investigated. A portion of the research effort was also directed to studying the possibility of biological production and elaboration of volatile metabolic products which might subsequently be stripped from the aeration tank. Concern over the possible formation of strippable compounds from an originally nonvolatile substrate during aerobic metabolism by heterogeneous biological populations is fairly recent, and stems primarily from observations made during the course of various experiments in the Bioengineering Laboratories of Oklahoma State University. Very little information on this aspect is available in the literature. Some reports pertaining to the treatment of initially volatile substrates (especially of acetone and methyl ethyl ketone) by biological methods are available. Work in this area consists largely of the contributions of Gaudy, Turner, and Pusztaszeri (3), who conducted experimental laboratory investigations under batch conditions. To the author's knowledge, there has been no work which has attempted to distinguish between removal by stripping and biological treatment of volatile aldehydes and ketones in a laboratory-scale continuous flow operation.

In the present study, production of strippable compounds from a nonvolatile substrate during aerobic metabolism by heterogeneous populations of sewage origin was studied using glucose as the initially nonvolatile carbon source (batch conditions). In studies on initially volatile substrates (both batch and continuous flow), three aldehydes (propionaldehyde, butyraldehyde, and valeraldehyde) and two ketones (acetone and methyl ethyl ketone) were employed. Removal by stripping alone at various airflow rates was determined; then removal by stripping and microbial metabolism was investigated. The responses of a biological population to shock loadings, consisting of a series of changes in the feed compound, were studied under continuous flow conditions. System performances under both batch and continuous flow operations were assessed by analysis for COD, biological solids, and detection of possible intermediates as well as initial carbon source by gas liquid chromatography.

While some difficulties were encountered in working with these volatile substrates (particularly with regard to clumping of cells), and while the complexity of kinetics and mechanistic description under three possible modes of action on the substrates (autoxidation, physical stripping, and biological activity) militated against obtaining all of the information which was originally hoped for, a considerable amount of knowledge was gained which it is felt contributes significantly to furtherance of understanding of treatment of volatile waste components by the activated sludge process.

CHAPTER II

REVIEW OF LITERATURE

General

Concern over the possible formation of strippable compounds from an originally nonvolatile substrate during aerobic metabolism of heterogeneous microbial populations is fairly recent. As a result, literature pertaining to this aspect is rather scant. The major impetus for seeking information pertinent to this possible phenomenon arose as a direct outcome of extensive research carried out in the Bioenvironmental Engineering Laboratories of the Oklahoma State University. In making aerobic materials balances (4)(5) especially at high biological solids concentrations, it was observed that more COD was removed than could be accounted for by oxygen uptake and biological solids production. It was thought that this imbalance could be due to rapid production of volatile compounds and their subsequent stripping during aeration. For this reason it was felt that before initiating the research on initially volatile compounds, an investigation of the possible production of volatile compounds would be useful. It is important to note that there are many data which indicate that microorganisms can excrete various organic compounds into the medium during metabolism, and that these compounds can accumulate in the medium. If they are strippable compounds, it is to be expected that they will be partially removed in the

aeration process. In most cases the products found in the medium fall into the general category of "volatile acids," but these are not strippable compounds under normal aeration conditions in the activated sludge process. The fact that strippable compounds have in general not been detected is, however, no guarantee that they are not produced since there have been (to the author's knowledge) no studies designed to assess their production; such detection requires a specific experimental design, i.e., an attempt to capture the stripped materials. In the present research an effort was made to gain an insight into the possible production and escape of strippable components, and the magnitude of such occurrences under conditions akin to those existing in the activated sludge process.

The related problem of health hazard to the treatment plant personnel from the intermediary derivatives arising out of the biodegradation of initially nonvolatile carbon sources cannot be overlooked. Ledbetter (6) reviewed the air pollution aspects of aerobic waste treatment processes. It was his conviction that offensive odor prevailing in the neighborhood of aerobic waste treatment processes was due to the volatilization of complex organics and intermediate derivatives. The inorganic endproducts of aerobic biological degradation were inoffensive.

In all kinds of aerobic waste treatment, aeration of one kind or another is employed; for example, in the present research, aeration of the solution of strippable aldehydes and ketones in water and their admixture with acclimated microorganisms is achieved by diffused aeration. In either case, aerosols in the form of mist or droplets emerge from the main body of the liquid waste. Under most atmospheric conditions these droplets evaporate, leaving the nuclei of the solid

wastes, which may contain materials detrimental to the health of human beings and other forms of life. Vector organisms and other irritating materials have in the past been propagated by this mode of transmission; this has been well documented by Woodcock (7), and Greenberg and Kupka (8).

The primary concern of the present research is to study the kinetic behavior and factors affecting the degree of purification for substrates which are strippable, e.g., volatile aldehydes and ketones. Such compounds may be found in certain industrial wastes, e.g., refinery and petrochemical wastes. In an activated sludge process it is conceivable that such compounds could be acted upon in three distinct ways. They may be partially oxidized chemically; they may be subject to physical stripping; and they may serve as carbon and energy sources for the microorganisms which constitute the activated sludge. The susceptibility of "volatile" aldehydes and ketones to stripping or to oxidation (either chemical or biochemical) is in large measure dependent upon the structure of the compound. Therefore it seems appropriate here to note some of the distinguishing characteristics of these types of compounds.

The general formulas for aldehydes and ketones are usually written as RCHO and RR'CO, respectively. The groups R and R' may be aliphatic or aromatic (in the present research only aliphatic compounds were studied). Aldehydes and ketones contain the carbonyl group, C = O, and are referred to as carbonyl compounds. It is this potent group which largely determines the chemistry of aldehydes and ketones. Aldehydes and ketones resemble each other closely in most of their properties; however, certain differences are manifested because of the location of the carbonyl group. This difference in structure affects their

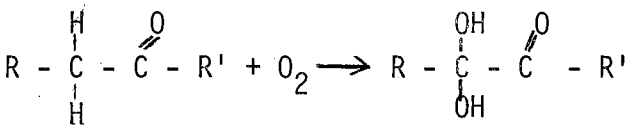
properties in two ways: (a) aldehydes are quite easily oxidized, whereas ketones are oxidized with less ease; (b) aldehydes are usually more reactive than ketones toward nucleophilic addition--the characteristic reaction of carbonyl compounds.

Regarding physical properties, the lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about 5 carbons. Aldehydes and ketones are soluble in the usual organic solvents, such as ethanol and ether. Aldehydes are most easily oxidized to carboxylic acids, not only by reagents like permanganate or dichromate, but also by such weak oxidizing agents as silver ion or cupric ion (9). Oxidation by silver or cupric ion requires an alkaline medium to prevent precipitation of the insoluble metal oxide or hydroxide.

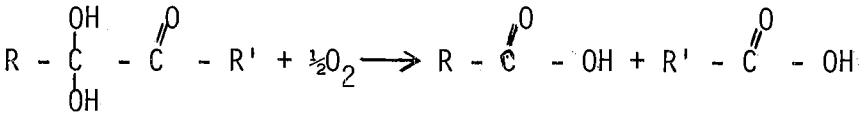
Oxidation of ketones requires the breaking of carbon-carbon bonds, and hence takes place only under more severe conditions. Aldehydes and ketones differ in their case of oxidation, because with ketones there is no hydrogen attached to the carbonyl group. As a result, oxidation must initiate in one of the alkyl groups; the molecule is cleaved and two or more acids are formed.

$$CH_3COCH_3 + 2O_2 \longrightarrow CO_2 + H_2O + CH_3COOH$$

In the case of acetone, CO_2 and acetic acid are formed. Theoretically, formic acid should be formed but it is so easily oxidized that it is converted under the prevailing conditions to CO_2 and H_2O (10). Higher ketones such as di-ethyl-ketone (3-pentanone) are oxidized as follows:



Compounds with two hydroxyl groups on the same carbon atom are unstable and decompose with further oxidation to produce two acids



According to Stewart (11), pH is an important factor in the oxidation of aldehydes. The rate constants for permanganate oxidation of C_6H_5CHO and $(C_6H_5)_2CHOH$ are approximately equal at pH 12. At pH 12.8, the alcohol is oxidized at about seven times the rate of the aldehyde; at pH 11, the effect is reversed. This occurs because aldehydes, both aliphatic and aromatic, are oxidized at reasonable rates even in neutral solution, whereas alcohols are oxidized rapidly only via the alkoxide ions. Electron withdrawing groups have a considerable accelerating effect on the oxidation of both alcohols and aldehydes, but especially on the latter.

In view of the use of some of these aldehydes and ketones as solvents, their increasing prominence in industrial operation, and the attendant health hazards, the Industrial Hygiene Subcommittee of the National Association of Mutual Casualty Companies (12) has outlined the explosive limits, threshold limits, fire hazards, etc., of some of these compounds and some other compounds which are the products of biological degradation of the aldehydes and ketones.

Compound	Flash Point	Fire Hazard Group	Explosive Limits % by Volume in Air LEL*	UEL**	Threshold Limit Values - ppm
acetaldehyde	-36	4	4.1	55	200(A)
acetic acid	104	2	5.4	-	10(A)
acetone	0	4	3.0	11	1000(A)
n-butyraldehyde	20	4	2.5	-	-

*LEL = lower explosive limit
**UEL = upper explosive limit

Some of the properties and terminology given above require explanation; for example, the flash points are "closed cup" determinations unless otherwise specified and are given in degrees Fahrenheit. "Closed cup" determinations involve heating of the solvent in a standard closed container. The temperature at which a flash is seen in the vapor above the surface of the solvent upon introduction of a small flame is called the "flash point" of the solvent under study. Such procedures are standardized as per specifications by the American Society for Testing Materials and National Fire Codes (13). Fire hazard is indicated by a numerical rating which is related to the compound's flash point, as shown below:

Flash Points	Fire Hazard Group
nonflammable	0
above 140°F	1
100° - 140°F	2
73° - 100°F	3
less than 73°F	4

The threshold limit values above are from the recommendations of the American Conference of Governmental Industrial Hygienists, and for the

sake of brevity, are indicated by (A).

Certain aldehydes and ketones exhibit distinct physiological action. As pointed out by Spiegel (14), acetaldehyde shows a distinctly hypnotic action. This effect is exhibited in pronounced degree by the polymeric paraldehydes $(C_2H_4O)_3$. Ketones exert even greater hypnotic properties than aldehydes when there is an ethyl group in the compound. Dimethyl ketone causes a hypnosis like that observed in drunkenness, an excitation of the heart and a subsequent paralysis of the central nervous system; whereas diethylketone is a bonafide sleep producer with no effect whatever on heart action. The hypnotic action of dipropyl ketone is less pronounced than the two ketones previously mentioned. The intensity of the action is essentially determined in all cases by the aliphatic component group rather than by the aromatic group.

In view of the fact that "volatile" aldehydes and ketones either in solution as pure solvents or as constituents of waste streams arising out of hydrocarbon processing or treatment of petroleum refinery wastes are subject to removal by physical process as "stripping" and are often associated with the mechanism of "autoxidation" in their elimination process, certain clarifications with regard to semantics are in order.

Autoxidation

Lundberg (15) defined autoxidation as the "spontaneous reaction between atmospheric oxygen and many types of organic compounds." He concluded that light has a minor effect upon autoxidation (and consequently upon stripping). According to him, the phenomenon of autoxidation is applicable mainly to unsaturated compounds, wherein the nature of reaction of oxygen with the double bond system can be viewed in the light of the following theories:

1. cyclic peroxide theory
2. ethylene oxide theory
3. hydroperoxide theory

Autoxidation can be regarded as a chain reaction of the type

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

where $R^{\cdot}$ = organic radical. In general, chain reactions of the above type have kinetic features which distinguish them from other reaction sequences. In simpler cases, the oxidation reaction proceeds in three well-defined sequences as initiation, propagation, and termination. Commenting on the mechanisms of oxidation of organic compounds, Waters (16) concluded that autoxidations are promoted by light and small quantities of many catalysts, notably the oxides and oil-soluble salts of heavy metals as well as by various peroxidic substances. Further, they can be markedly retarded by mere traces of oxidizable organic substances such as phenols and amines, many of which occur naturally as protectants of unrefined plant and animal products. Wieland (17) as early as 1934, in dealing with the mechanism of oxidation, stressed the role of unsaturated bonds and sometimes a labile hydrogen, which brings about the autoxidation reaction.

Later works in 1960 (18) showed that such a labile hydrogen could mean the hydrogen atom attached to the carbonyl group, which readily reacts with the free radical (derived from the aldehydic or ketonic waste source) thus bringing about the hydrogen abstraction step of the chain reaction which is a characteristic feature of the autoxidation mechanism. Wieland (17) further commented that the oxidizing activity of the oxygen in solution is appreciably enhanced by the formation of a

labile primary oxide which subsequently acts as a strong oxidizing agent. For example

$$A + O_2 \longrightarrow AO_2$$

$$AO_2 + A \longrightarrow 2AO$$

where A is the unsaturated compound. Thus Wieland (17) by "lability" meant the presence of a reactive atom or compound and its facile availability in carrying out the oxidation steps.

Commenting on autoxidation, Gilman (19) was of the opinion that the phenomenon was common with aldehydes but was occasionally encountered with ketones. Although he (19) did not cite the example of a straight chain aliphatic aldehyde, from his example of benzaldehyde (aromatic ring aldehyde) oxidation to benzoic acid, it was clearly demonstrated that the reaction with oxygen (autoxidation) was initiated by the formation of peroxy acid (in this case, perbenzoic acid) which acted as a hydrogen acceptor. This justifies one of the theories (cyclic peroxide theory) of Lundberg (15) in bringing about autoxidation reaction.

Bolland and Gee (20) from their work on ethyl linoleate and ethyl linolenate attributed the oxidation of these compounds to autoxidation, a chain reaction catalyzed by the initial formation of hydroperoxide by reaction of oxygen with the starting compounds. The essential mechanism of autoxidation with regard to the two olefins under study was outlined by the authors (20) as

(i) formation of hydrocarbon radical

(ii) absorption of oxygen

(iii) reaction with another molecule of olefin to give a hydroperoxide plus an additional free radical and thus propagation of the chain reaction. In this work another postulation (hydroperoxide theory)

of Lundberg (15) concerning autoxication finds verification.

Following the work of Bolland and Gee (20) in 1946, Woodward and Mesorbian (21) in 1953 reported the autoxidation of the hydrocarbon tetralin (1, 2, 3, 4-tetrahydronaphthalene) wherein the same scheme of chain reaction for autoxidation as that proposed by Bolland and Gee (20) was observed. The initial product of reaction with oxygen was a hydroperoxide. Furthermore, it was found from their (21) experimental studies that heavy metals like cobalt ion could accelerate oxidation of the tetralin as well as of the hydroperoxides. Initiation here again was stemming from the formation of free radical. The experimental findings of the enhancement of the key reactions leading to autoxidation by cobalt ion in the present study is in line with the remarks of Waters (16), who predicted the promotion of autoxidation reactions by many catalysts, among which oxides of heavy metals were also mentioned.

Stewart, et al. (22) demonstrated a reaction prevailing in bacterial hydrocarbon oxidation which forms a product similar to autoxidation products of hydrocarbons. Even though this piece of work, being bacteriological, belongs to the biological works referred to in another part of the literature review, it was thought appropriate to refer to it here since the oxidation of hexadecane involved the formation of 1-hexadecylhydroperoxide as the first intermediate. The final product identified by infrared spectroscopy and mass spectrometry was cetyl palmitate, which was interpreted to have been formed by the esterification of cetyl alcohol and palmitic acid which, in turn, were produced from the 1-hexadecylhydroperoxide. Thus, bacterial oxidation of alkane is similar to autoxidation. In this experiment, atmospheric oxygen participated in the reaction. The organism employed was a gram-

negative coccus previously grown and isolated from hexadecane enrichment culture. Later, Stewart and Kallio (23) reported similar results indicating evidence of a similar oxidation as an intermediary step toward the bacterial degradation of octadecane.

Thus far the role and mechanism of autoxidation has been presented in the case of hydrocarbons in general, and it is pertinent now to see how such findings may be corroborated in the case of whole wastes. The waste streams of petrochemical industries and refinery treatment processes can be looked upon as sources of "volatile" aldehydes and ketones in particular (among other components). In this regard, Prather (24) in 1962 compiled and reviewed literature pertaining to autoxidation, and defined autoxidation as the chemical oxidation reaction responsible for bringing about the degradation of small concentrations of hydrocarbons present in petroleum refinery wastes. He believes that autoxidation has its place as a secondary or final treatment of the clarified refinery waste water and outlined three basic requirements toward successful implementation as follows:

(i) plentiful and cheap source of oxygen

(ii) initiators to ensure a source of free radicals, and

(iii) escape routes for volatile degradation products of autoxidation.

Volatile degradation products can be best routed by "stripping" from the solution. A report of three months of study by the author (24) with pilot plant towers indicated that on the average over fifty per cent COD removal was obtained on the clarified waste water during its passage through an aeration tower.

As previously reported, volatile degradation products of

autoxidation can be routed through "stripping." This leads to a discussion of the "stripping" process; considerations of autoxidation will also be discussed, inasmuch as they are not invariably separated from each other.

Stripping

Stripping has been defined by Haney (25) as "negative absorption" where absorption is looked upon as addition of gas to a liquid. In other words, stripping involves removal of gases from a liquid. Eckenfelder, Kleffman, and Walker (26) defined stripping as a process of mass transfer from the liquid to the gas phase, which is quite in accordance with the views of Haney (25).

Eckenfelder, Kleffman, and Walker (26) conducted some stripping studies on solvents and mixtures of solvents. Since the present study includes some of the components and mixtures of compounds used by these workers, a careful review of their work is warranted especially with regard to methodology and operational parameters. Dilute aqueous solutions containing approximately 1000 mg/l of various solvents were aerated in one-liter cylinders in a temperature-controlled water bath. Solvents included ethyl alcohol, acetone, and methyl ethyl ketone (MEK). Aeration studies were also conducted for mixtures of these solvents. Reduction in solvent concentration was measured using a modified COD method, employing oxidation at 165-170^{o}C in the presence of potassium dichromate, sulfuric acid, orthophosphoric acid, and silver sulfate. In calculating rate constants from a plot of log of COD remaining in the aqueous phase versus time of aeration, assumption was made that the equilibrium concentration at the interface was negligible in comparison to the concentration in the bulk of the solution. Acetone removal was

studied at airflow rates of 200, 250, and 400 cc/min/l at temperatures of 21, 35, 50, and 70°C. MEK removal by aeration (200, 250, 400 cc/min/l) was studied at 21, 35, 50, and 67°C. Since these workers did not analyze for the specific compounds undergoing stripping, they could not determine whether any autoxidation occurred under the mild oxidizing conditions provided by aeration.

Stripping by batch acidification and aeration was one of the processes employed by Zabban, et al. (27) in removing hydrogen cyanide from plating wastes. The batch volatilization method for the disposal of cyanide could be effected in two ways, namely, by impounding cyanide waste solutions in large shallow ponds, or by acidifying the waste solution to a pH value at which most of the cyanide (CN) is present as hydrogen cyanide, and accelerating the evolution of the HCN by aerating the solution or by passing steam through it. Monitoring of the atmosphere is essential in order not to exceed the limiting concentration of HCN in the atmosphere. Such methods for CN disposal are dangerous, and most probably will be outlawed in the future. From batch experiments (75 gallons) a correlation equation was developed for predicting final concentration of HCN in ppm from related variables such as concentrations of HCN, aeration time in hours, airflow rate in cubic feet per cubic foot of solution per hour, and temperature in degrees Fahrenheit. Airflow rate ranged from 50 to 1400, and temperature between 78-144°F. Using this correlation, they were able to predict with a considerable degree of accuracy the result of other experiments conducted in the 75-gallon apparatus. These authors did not mention the method used to determine the concentration of HCN.

Engelbrecht, Gaudy, and Cederstrand (28) studied air stripping of

acetone and butanone at various rates of airflow; they employed eight liters of reaction volume and the compounds were dissolved in distilled water. The kinetic expression used by these authors was in line with those detailed by Haney (25). COD was used as the parameter for evaluating the stripping or transfer constants from observed data at airflow rates of 156, 469, and 781 ml/min/l. It was found that both acetone and butanone were stripped in accordance with first order kinetics. An arithmetic relationship was developed between the transfer coefficient and unit airflow rate for acetone and butanone from experiments conducted on these compounds at airflow rates from 40 to 780 ml/min/l. Their linear expression contrasted to the exponential function derived by Eckenfelder, et al. (26) for these compounds. However, use of both expressions was concluded to be within the practical limits of engineering accuracy, if the range in airflow rates employed was not great. The transfer coefficient was found to be appreciably constant for a range of concentration of 250 to 2000 mg/l COD, a characteristic feature of first order kinetic expressions. In experiments with methyl ethyl ketone, it was found that the stripping rate remained virtually unaltered with the addition of inorganic salts at concentrations required for biological growth. Specific analyses for acetone and butanone were not made.

Gaudy, Engelbrecht, and Turner (29) concluded from their aeration studies on volatile organic compounds that first order kinetics could not be expected for all volatile compounds. While acetone, butanone, and propionaldehyde at 25°C obeyed first order kinetics in removal, butyraldehyde and valeraldehyde at 25°C and propionaldehyde at 40°C did not. The non-first order removal of propionaldehyde at 40°C was

theorized to be due to the conversion of propionaldehyde to its immediate oxidation product, i.e., propionic acid, which is not a strippable compound at the temperature and airflow rate which were employed. Propionaldehyde concentration was estimated by a method outlined by Carter, et al. (30). For studies with butyraldehyde and valeraldehyde at 25°C, separate determinations for aldehydes were not made and the nonlinearity of the semilog plot of COD versus time of aeration was attributed to partial conversion of the aldehydes to nonstrippable oxidation products.

Biological

Apart from the physical (stripping) and chemical (autoxidation) methods of treatment of volatile aldehydes and ketones in particular, and, in general, of whole wastes which consist of such compounds, biological methods have been used in the utilization of these compounds. Data on determination of the BOD (biochemical oxygen demand) of the aldehydes and ketones or of a whole waste comprising such compounds (among other constituents) would point toward the amenability of biological treatment of these compounds by certain microbial populations. On the other hand, use of conventional biological treatment processes like activated sludge and trickling filters in the treatment of whole wastes abounding in aldehydes and ketones would attest to the biological mode of removal of aldehydic and ketonic wastes. According to Sawyer (10), oxidation of both aldehydes and ketones is accomplished readily by many microorganisms. It appears that the oxidation process proceeds via the corresponding acids; however, since organic acids themselves serve as a good food supply for microorganisms, Sawyer (10) concluded that the final end products of biological oxidation of aldehydes and

ketones were carbon dioxide and water.

Mills and Stack (31) compared the theoretical BOD of many ketones to the 10-day BOD at 20°C. It was observed from their studies that the degree of biological oxidation (using 10-day BOD at 20°C), with the exception of methyl phenyl ketone, was related to the size of the molecule, the BOD for ketones decreasing with increasing molecular weight. The 10-day BOD value at 20°C for acetone was 54.5 per cent of the theoretical BOD. From similar studies with aldehydes it was found by these authors that benzaldehyde above 400 mg/l was toxic to biological organisms.

Lamb and Jenkins (32) determined the percent theoretical BOD satisifed after various days of incubation at 20°C for acetone and butyraldehyde (among other compounds). In each case 2.5 ppm of the chemical were used in the BOD bottle, with mineralized dilution water; two different kinds of seeding material were employed. One was settled sewage and the other acclimated sludge. They concluded that acclimated seed yielded higher BOD values than an unacclimated settled sewage, but this statement was not in agreement with their findings on butyraldehyde. With settled sewage the 10-day (20°C) BOD was 59.8 per cent of the theoretical, whereas the corresponding value with acclimated sewage was 54.1 per cent. This trend persisted for the 5, 15, and 20-day (20°C) BOD values. For acetone, with 2.5 ppm of chemical in the BOD bottle, using mineralized dilution water and settled sewage as seed, the 10-day (20°C) BOD value was 71.8 per cent of the theoretical value.

BOD data on aldehydes and ketones have been compiled by Heukelekian and Rand (33). BOD values were expressed as grams/gram of the chemical used. All data were for 20°C, most of the data reported being for a

5-day incubation period; some were for a 10-day incubation period. In general, the standard dilution method was used with sewage as seed. For MEK and butyraldehyde, the BOD values reported were 2.14 and 1.06 g/g, respectively, while for acetone there were some glaring inconsistencies and variations in the reported BOD values (compiled from various sources) which ranged from 0 to 1.63 g/g.

Weston and Eckenfelder (34) compiled thermochemical and stoichiometrical data for various compounds, including acetone and methyl ethyl ketone, to explain the behavior of oxidative biological treatment from a theoretical point of view. Three general equations were used, i.e., organic matter oxidation, cell material synthesis, and cell material oxidation. Cell material was represented by the empirical formula $C_5H_7NO_2$. It is debatable whether such generalization as to the assumption of a common formula for cell material is valid regardless of the type of substrate used. Sludge production was related to the ultimate BOD of the compounds, and was expressed as oxygen demand in grams per gram of sludge. Values reported for MEK and acetone were 2.34 and 2.21, respectively. From a hypothetical standpoint, Weston and Eckenfelder (34) also estimated the minimum fraction of the compound that would be oxidized by way of producing sludge. Such values (as percentage) were 16.7 and 14.65 for MEK and acetone, respectively. These figures are indicative of low yield values for these strippable ketones. When a major portion is airstripped, only a relatively small amount is left for channelling into sludge synthesis.

The effect of temperature on removal of BOD from a waste containing acetone and MEK in addition to other solvents and nonvolatile organic constituents having an average BOD of 25,000 ppm and COD of

45,000 ppm was studied by Eckenfelder, Kleffman, and Walker (26). At an airflow of 250 cc/min/l an increase of 27 to 70 per cent BOD removal was observed (after seven hours) when temperature was increased from 27 to 68°C. On the other hand, for a chemical waste from a laboratory, containing solvents and other organics, the BOD removal after five hours of aeration increased from 49 to 88 per cent as the temperature increased from 24 to 49°C. Initial BOD was 236 ppm; no mention was made of the airflow rate during this investigation.

Hatfield (35) studied the biological oxidation of a number of organic compounds representing constituents of typical petrochemical wastes of which formaldehyde, acetaldehyde, propionaldehyde, and acetone are of particular interest to the present investigation. The batchwise fill-and-draw method was employed in developing acclimated cultures from domestic sewage seed. The analytical parameters employed were BOD and COD; in the case of formaldehyde, substrate removal was followed by Schiff's test for formaldehyde. Formaldehyde was removed more rapidly than BOD and COD, giving indication of the production of intermediate products (either by chemical or biochemical oxidation) and their subsequent utilization by the bacteria. Hatfield (35) commented that formaldehyde readily goes to some intermediate state, possibly to formic acid, or it may undergo Cannizzaro dismutation to formic acid and methanol. These compounds, in turn, are further oxidized or assimilated by the bacteria. Formaldehyde was completely removed from the system after six hours, whereas about 8 to 10 hours were required for the BOD to attain zero value. No mention was made of the suspended solids concentration in the unit. From an initial BOD value of about 400 ppm, both acetaldehyde and propionaldehyde were

reduced to a level of 50 ppm after five hours' aeration. The remainder persisted for three additional hours, at which time the experiment was terminated. The initial suspended solids concentration in the acetaldehyde and propionaldehyde systems were 2400 and 3460 ppm, respectively. No mention was made of the airflow rate, and since no specific substrate tests for acetaldehyde and propionaldehyde were made, the mode of biological removal (intermediate products) cannot be assessed, as was possible in the case of formaldehyde. Using an aeration solids concentration of 2370 mg/l, the COD of acetone was reduced from about 475 to 75 ppm in approximatly four hours, and this value (75 ppm) persisted in the effluent for four additional hours, at which time the experiment was terminated. No airflow rate was mentioned, nor was a specific test for acetone employed, so that it cannot be said whether acetone removal led to any accumulation of other products in the medium. For the acetone system, BOD values were not reported since, according to Hatfield, the incubation bottle contained toxic concentrations of acetone at the low cell concentrations employed in the BOD seed population. From previous works quoted by Strong (35), Strong and Hatfield (36) had concluded that more than 2 ppm of acetone in the BOD incubation bottle was toxic to non-acclimated organisms. Below 2 ppm, the BOD of acetone solutions (using sewage seed) was 64 per cent of theoretical BOD.

Stodola (37) has outlined the various forms of oxidation of organic compounds by microorganisms. Since the starting compound and the possible intermediates and endproducts are given, they are of much help in tracing the metabolic pathway of volatile compounds by the joint mechanism of air stripping and biochemical metabolism.

Reference to the biological treatment of wastes containing aldehydes is rather scant in the literature. In the manufacture of synthetic resins, formaldehyde constitutes much of the COD of the waste stream. Work by Dickerson (38) indicated that combined treatment with domestic sewage caused decay of the biological growth in a pilot plant trickling filter. This was due probably to the toxicity of the formaldehyde to the sewage microorganisms. Chemical treatment of formaldehyde proved to be very costly, and the endproduct was more difficult to handle than the original. Ozone treatment of formaldehyde was investigated, but was abandoned due to prohibitive costs. The ultimate treatment was provided by controlled operation of a high-rate trickling filter pilot plant, and based on the pilot plant data, a full scale plant was installed. Results of the full scale plant operation given by Dickerson (39) indicated that although the filter efficiency averaged about 16.5 per cent, overall system efficiency was fairly good (76 per cent removal). Formaldehyde comprised 90 per cent of the load. It was found that further reduction of formaldehyde concentration was possible by lagooning the filter effluent. It is important to note here that the author (39) has repeatedly mentioned the low removal efficiencies of the filter, but has nevertheless reported higher values for overall efficiency or system efficiency. He claimed the high-rate trickling filter as the answer for the predominantly formaldehyde waste (along with other components including sanitary sewage). From his article, however, it appears that a major portion of the waste was removed prior to the application of the wasteload to the filter.

Waste water consisting chiefly of methyl ethyl ketone was successfully treated on trickling filters by Degnan, et al. (40). The waste

which originated from an MEK solvent dewaxing and de-oiling unit also contained some oil. The MEK content of the waste water was 93 ppm. With adjustments of temperature, loading, and recycling ratio (1.4:1), excellent treatment efficiency was obtained. The general trend was that with increasing MEK concentration in the influent, the percent BOD and MEK reduction decreased. No mention was made by these authors (40) as to the strippability of this compound.

Elkin reported on the use of cooling towers for the biological oxidation of refinery waste water (41). For phenol-bearing waste, 99 per cent phenol removal was obtained, and there was a substantial reduction of the total chemical oxygen demand. Even though the system was not seeded with phenol-consuming organisms, the presence of bacterial sludge was noted several hours after applying the phenol-bearing wastes to the tower. Microscopic examination indicated that a wide variety of biological life was present, including rod-shaped bacilli, cocci, protozoans, and traces of algae. Oxygen transfer in the tower was enhanced by the mechanical draft. Nitrogen derived from ammonia in catalytic cracking process water and polyphosphates used in the cooling system for corrosion inhibition supplied, respectively, the N and P for the organisms.

Bacterial attack on the petroleum hydrocarbons has been mentioned by Beerstecher (42) in his text Petroleum Microbiology. He has (42) compiled a list of various organisms isolated by different workers on the utilization of individual hydrocarbons as constituents of various processes of a petroleum industry. Formation of a variety of aldehydes and ketones in cultures of hydrcarbon-oxidizing bacteria were reported, and the most probable mode of utilization of the aldehydes

and ketones was suggested as via their oxidation to acids.

Gaudy (43) in a discussion of the treatment of petrochemical wastes, concluded that petrochemical wastes, because of their predominantly soluble organic content, are readily suited for treatment of biological oxidation.

Combined Studies

Gaudy, Turner, and Pusztaszeri (3) studied the removal of acetone and butanone by the joint mechanisms of physical stripping and biological metabolism by running experiments concurrently in the Warburg apparatus (where there was no physical stripping) and in an activated sludge aeration tank (biological metabolism plus physical stripping). In previous experiments they had studied stripping in the same tank. Biological removal of acetone in the Warburg apparatus could be plotted in accordance with either first order or zero order kinetics. Using rate constants determined for biological removal in the Warburg study and rate constants for stripping determined in separate stripping studies, they were able to predict the kinetic course of purification for acetone and butanone when these rate constants were inserted into kinetic equations which they derived from combinations of zero and first order reactions. Such equations developed by the authors (3) for predicting the removal of acetone and butanone in activated sludge aeration tanks subject to stripping and biological metabolism have been found to apply over a range of 0 to 90 per cent removal of the waste constituents based on COD values. These authors did not show plots of biological solids produced during the dual removal experiments in the activated sludge aeration tank; however, it was observed that the percent of substrate channelled into synthesis was rather low. Specific

tests for acetone or butanone were not run (removals were assessed by the COD test) for these compounds. The possible effect of accumulation of oxidation products (either chemical or biochemical) on the observed kinetics cannot be assessed. To the author's knowledge this is the only batch study on "dual" removal of these two ketones reported in the literature.

Treatment of Whole Industrial Wastes Containing Large Amounts of Aldehydes and Ketones

Examples of whole waste treatment by the combined processes can be seen in the realm of petroleum refinery works, petrochemical waste treatment processes, and other chemical or industrial processes dealing with solvents and synthetics.

Petrochemical wastes may be regarded as a representative of wastes containing significant amounts of aldehydes and ketones. Many methods have been suggested for use in treating petrochemical wastes, depending on the nature of the waste components. Stripping and biological oxidation have been mentioned prominently (among other processes) by Elkin (44). When stripping is the sole treatment, steam rather than air stripping has been practiced. For example, in a styrene plant, catalytic dehydrogenation of ethyl benzene was carried out in the presence of steam. The resulting condensate was saturated with 0.1 per cent aromatics which were removed by steam stripping. However, air stripping is an important consideration because of its occurrence in the activated sludge process.

Steam stripping has been used in the treatment of hydrogen cyanide and acrylonitrile, as pointed out by Morris (45). Hydrogen cyanide is reasonably volatile; disposal of a waste gas stream containing HCN has

been accomplished by flaring it through a stack. The surrounding area was air-monitored for HCN to abate air pollution, and the effluent concentration of HCN at the stack was set at 40 ppm, which is the stack threshold limit for this compound under the atmospheric and climatic conditions prevalent at the plant site. Steam stripping was employed to remove acrylonitrile from water, since oxidation with chlorine proved to be uneconomical at the concentrations of the contaminant which were present.

Solvent stripping has also been employed for wastes other than petrochemical, for example, in a nylon waste (46) in which acetone and MEK comprised 1.31 and 0.56 per cent (maximum) of the whole waste. Full scale treatment was provided (after investigation on a laboratory scale) by steam stripping, fractional distillation, aeration, and biological oxidation. Two stripping processes were investigated; aeration at elevated temperatures, and submerged combustion. Methodology included aeration of one-liter samples in the laboratory at airflows ranging from 0.05 to 1.00 SCFM over a temperature range of 27 to 86^{o}C. In the study conducted by Remy and Lauria (46) on a nylon waste, samples were taken at periodic time intervals and COD was determined until no further reduction was observed. COD removal coefficients were determined by plotting the log of COD remaining in solution versus time of aeration and measuring the slope of the curve.

Petrochemicals have been defined by Bateman (47) to be products or components arising primarily from the chemical processing of petroleum and natural gas hydrocarbons. Mention has been made of aldehydes and ketones as typical oxidation products of paraffins in petrochemical industries by Ruggles (48). These aldehydes and ketones are used

extensively as solvents in the manufacture of dyes and plastics.

Wright (49) has listed the causes for the appearance of organic compounds in petrochemical waste streams as pollutional components as follows: byproduct formation, side reactions, incomplete reactions, and mechanical loss problems.

Garrett (50) discussed applicable disposal measures for petrochemical wastes and hazards of air and water pollution due to these wastes. Pertinent to the present study are air stripping and biological metabolism. Treatment of a pertrochemical waste having a COD of 30,000 ppm and formaldehyde concentration of 6000 ppm by the activated sludge process has been reported by Strong and Hatfield (51). By increasing the rate of flow of return sludge and maintaining an unusually high concentration of suspended solids in the aerator, and by using a high rate of recirculation of treated effluent, BOD could be removed with excellent efficiency at applied loads many times greater than those handled by domestic sewage plants. BOD removals were 99 and 80 per cent for loads of 183 and 365 lbs/day/1000 cu ft aeration volume, respectively. Because of this high efficiency of BOD removal, Strong and Hatfield (51) termed this system a "superactivated" sludge process.

Biological treatment of petrochemical plant waste products has been described by McKinney (52). Activated sludge, trickling filters, and oxidation ponds have all been employed as petroleum waste treatment systems. Seeding organisms are easily obtained, since soil in a refinery is usually saturated with bacteria capable of metabolizing refinery waste materials. Some components of refinery wastes contain ample nitrogen and phosphorus, while others do not. When biological waste treatment is recommended for certain waste streams, an ample supply of

nitrogen and phosphorus is necessary for maximum stabilization. When biological treatment of petrochemical wastes is planned, some precautions are in order to take care of the usually toxic substances like phenol, chromium cyanides, copper, etc., in the waste effluent stream. The sulfide stripper employed inthe manufacturing process results in some reduction of phenol. Two refineries (53)(54) have in the past reported 30 per cent phenol reduction through sulfide strippers. One refinery (54) obtained a further reduction of phenol by employing the stripper effluent in the electric desalter, which gave a 90 per cent reduction in phenols.

Commenting on the role of bio-oxidation, Elkin (44) is of the opinion that many oils and chemical wastes previously thought to be toxic to biological treatment systems are today considered to be amenable to biological treatment. Indeed, phenol would fall into this category. In general, primary and secondary alcohols and aldehydes are readily oxidized with a major portion of the BOD and COD removed within four hours of aeration time. Tertiary alcohols, methylals, and glycols on the other hand are more resistant and require a longer period for sludge acclimation (44).

The concept of combined chemical, physical, and biological processes in the purification of whole refinery wastes was investigated at the Sunray DX Oil Company Refinery in Tulsa, Oklahoma, by Prather and Gaudy (55). An attempt was made to determine the role of stripping and chemical oxidation. Taking advantage of the pressurized flotation unit at the refinery, the occurrence of autoxidation at elevated temperatures and pressures was investigated. Employing infrared spectroscopy, the authors concluded that chemical changes did occur during aeration.

Their data indicated that many of the components of the waste were strippable. Their results also indicated that, under the experimental conditions employed, both autoxidation and stripping were operative, and that biological activity played a minor role in reducing the COD.

In previous studies in which refinery waste was passed over a cooling tower, Prather (24) indicated that 54 to 60 per cent COD removal could be effected on whole wastes by chemical oxidation or stripping, or both. Prather (24) did not attribute any of the COD removal to biological action, because the tower was dosed periodically with 200 ppm sodium pentachlorophenate. The work of Prather and Gaudy (55) is very significant, since it relates in a practical way (whole wastes) three separate removal mechanisms which may be operative concurrently in the treatment of a highly complex waste, and although of necessity a preliminary study, it may never have been attempted had it not seemed a reasonable approach based upon the results of more basic studies using pure compounds (synthetic wastes).

From the foregoing review it can be seen that some laboratory-scale work has been reported by Hatfield (35) and Strong and Hatfield (51) on the amenability of acetone and propionaldehyde to biological treatment without any attempt to distinguish removal by stripping from removal by biological processes. Also, it is noted that the work of Gaudy, Turner, and Pusztaszeri (3) on ketones (in batch system) has provided some information on the kinetics of joint stripping and biological removal. These authors did not do any similar work on aldehydes. Also, there has been no work reported on stripping and joint stripping and biological removal in continuous flow systems.

From both a basic and a practical standpoint it seems extremely

important to know whether a viable active microbial population can be maintained in continuous culture on a feed consisting of strippable compounds such as aldehydes and ketones. Unlike a batch operation, the cells in a completely mixed continuous flow reactor are constantly washed out of the unit and if the population is to exist, a steady state in which the logarithmic growth rate constant, μ, is equal to the dilution rate, must be maintained. Also, it seems possible that cyclic changes in microbial species in the reactor could at times lead to predominance of organisms which rapidly convert the original exogenous carbon source to intermediate products which may be more (or less) strippable than the original feed component. Also, since aldehydes and ketones are fairly labile compounds, it is possible that they may undergo some degree of autoxidation due to aeration.

Through the experimental results of the research conducted in the present study it is hoped that further insight into the understanding of the kinetics and mechanisms of biological treatment processes may be attained, and that the knowledge gained can serve as a guide to better pilot plant and prototype design for industrial wastes containing strippable organic components.

CHAPTER III

MATERIALS AND METHODS

Phase I.

Studies on the Possible Production and Subsequent Stripping of Volatile Compounds During Aerobic Metabolism of an Initially Nonstrippable Carbon Source in High Solids Batch Systems

Experimental Apparatus

The experimental unit with volatile acid trapping assembly is shown in Figure 1. For some experiments an additional absorbing flask was connected in series with the one shown.

Operational Sequences

A batch activated sludge unit was started using seed from the municipal treatment plant at Stillwater, Oklahoma. The unit was maintained on the 24-hour batch feeding cycle, using glucose at 5000 mg/l as the sole carbon source. The constituent chemicals of the synthetic waste used in the study are shown in the following table:

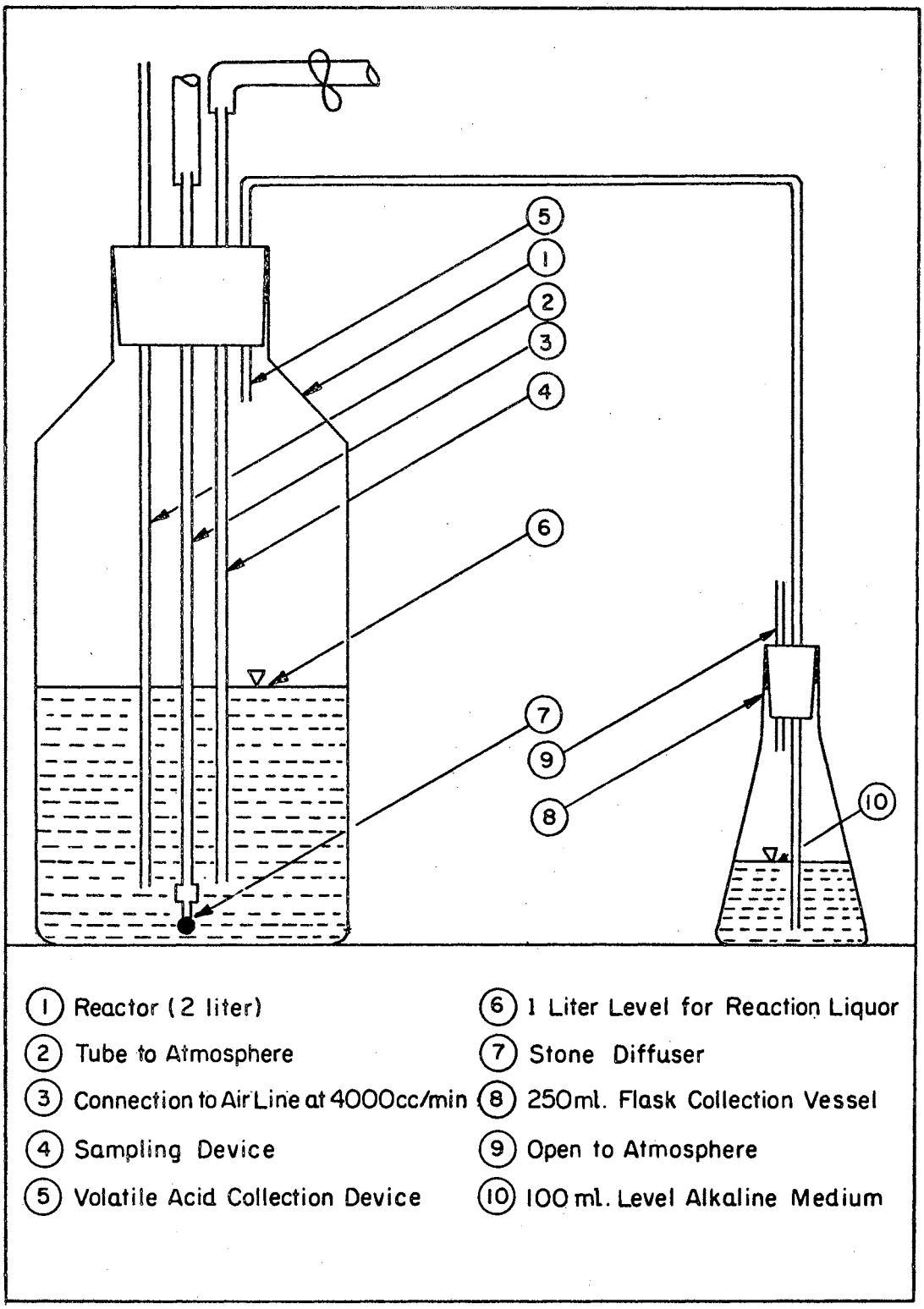


Figure 1 - Schematic representation of the experimental unit with volatile acid-trapping assembly.

TABLE I

COMPOSITION OF SYNTHETIC WASTE WITH GLUCOSE

Constituent	Concentration
glucose	5000 mg/l
$(NH_4)_2SO_4$	2500 mg/l
$MgSO_4 \cdot 7H_2O$	500 mg/l
$CaCl_2 \cdot 2H_2O$	37.5 mg/l
$MnSO_4 \cdot H_2O$	50 mg/l
$FeCl_3 \cdot 6H_2O$	2.5 mg/l
trace elements (tap water)	100 ml/l
1 M potassium phosphate buffer, pH = 7.0	60 ml/l
distilled water	to 1 liter

On the day of the experiment sludge was centrifuged, washed twice in 0.05 M potassium phosphate buffer, and resuspended in inorganic salts medium of the composition given in Table I (without glucose). Twenty-five ml of the suspension were then filtered (0.45 μ Millipore filter) for measurement of initial biological solids concentration. The chemical oxygen demand of the filtrate was determined to detect the presence of any carryover COD. To the remaining sludge suspension a concentrated solution of glucose was added to yield the desired substrate concentration. The same amount of concentrated substrate was added to an equal volume of the inorganic salts medium devoid of cells and a sample was taken for analysis of COD and substrate to determine the exact concentration of carbon source present at the beginning of

the experiment. This concentration, added to the carryover COD or substrate, represented the initial COD and substrate of the particular system.

Thirty seconds after adding the carbon source to the system containing the sludge, a sample was withdrawn for analysis of COD, substrate, and solids concentration. The values of COD and substrate thus obtained were subtracted from their corresponding initial values and the difference was recorded; thus the percentage of substrate taken up in thirty seconds could be calculated. Following the thirty-second sample, samples were withdrawn every fifteen minutes during the first hour, every thirty minutes during the second hour, and less often during succeeding hours. Samples were immediately placed in pre-chilled test tubes held in an ice water bath. Previous experience by Krishnan and Gaudy (5) indicated that this procedure was a necessary precaution in order to arrest the reaction at the high biological solids level employed. After cooling for one-half hour, the sample was centrifuged, the pellet was partially re-suspended, and the suspension was passed through a Millipore filter.

For all experiments, oxygen uptake was also measured. A portion of the cell suspension was placed in 140 ml Warburg flasks, and after equilibration, substrate was tipped in from the flask side arm. Initial cell and substrate concentrations were the same as those in the aeration tube from which samples were taken for solids production and substrate removal. The Warburg shaker rate and temperature were 104 oscillations per minute and 25^{o}, respectively. The aeration rate and the temperature in the aeration tube were 4000 cc/min/l and 25^{o}C.

In all experiments, absorbing flasks contained 100 ml distilled

water made alkaline to a pH ranging between 8.9 and 10.7 by the addition of one to two ml of 0.05 N NaOH. Each time a sample was withdrawn from the aeration tube, an absorbing flask was taken off and another placed in position for the next sample. An aliquot of the absorbate was analyzed for COD and later a 5 µl sample of the absorbate was analyzed for acids by gas liquid chromatography, hereinafter called GLC. The pH of the absorbate was also measured.

Phase II.

Studies on the Removal of Strippable Organic Compunds by Stripping and by Combined Stripping and Biological Treatment

A. Treatment of Strippable Compounds by Stripping Alone in Batch Units

Experimental Equipment

All batch experiments with volatile compounds were conducted in a reactor placed in a water bath thermostatically controlled at 25 ± 0.5°C by a "Precision Lo-Temptrol" (Precision Scientific Company). The schematic representation of this setup is shown in Figure 2. Air was controlled by a Fisher and Porter rotameter graduated in SCC/min air at STP through fritted cylinder gas dispersion tube. The volume of the aerator was 2.5 liters, but the volume used for all batch studies was one liter. One gas dispersion tube was used in all cases. The air pressure in the manifold was 33 psi.

Preliminary Studies

Prior to physical stripping studies in the batch unit for the compounds mentioned here, the suitability of each compound to COD analysis was investigated. For this purpose a standard solution of each compound was made in distilled water and its "theoretical" COD was computed, i.e.,

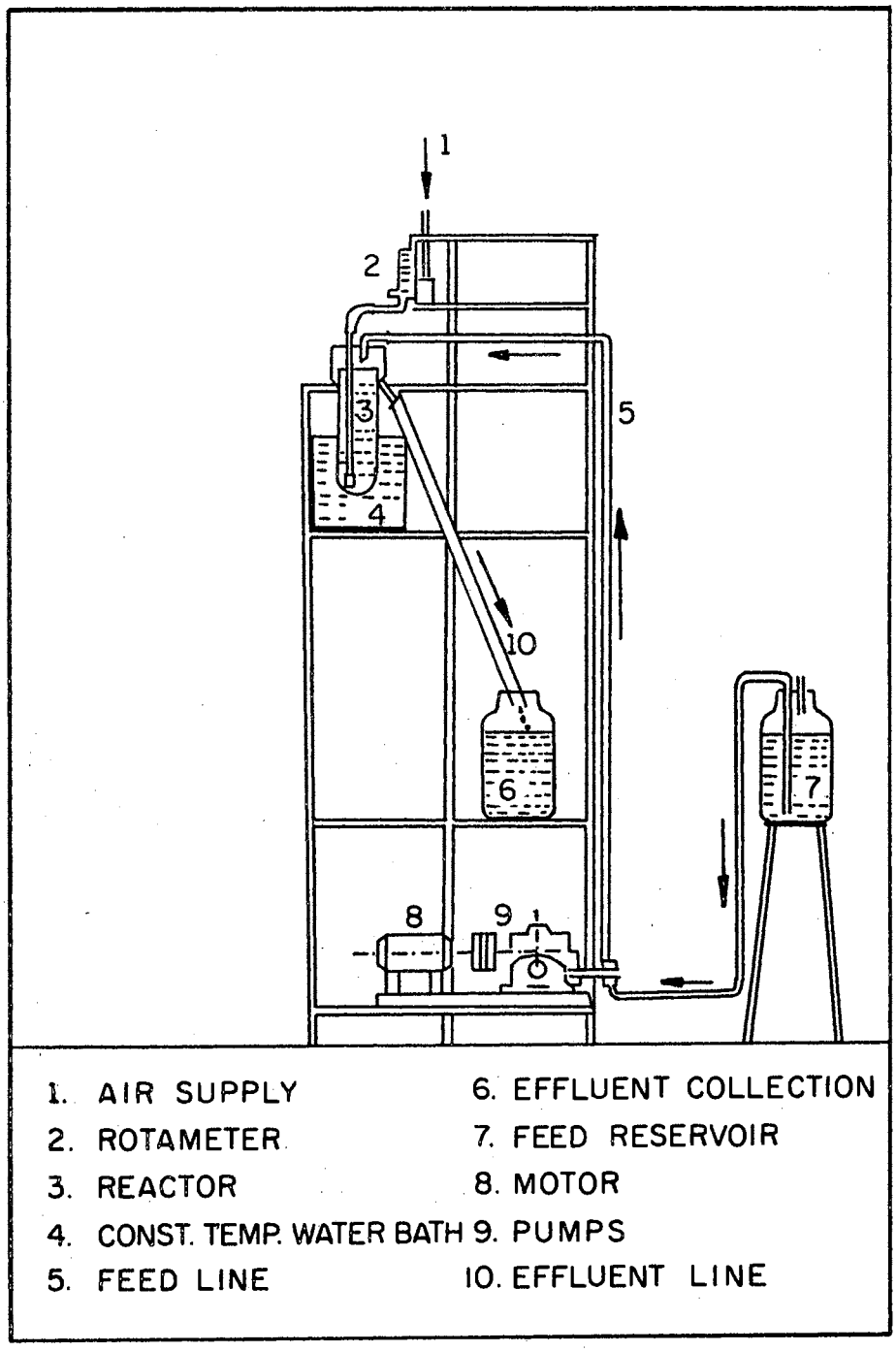


Figure 2 - Schematic representation of the experimental unit for conducting batch and continuous flow studies for strippable organic compounds.

the amount of oxygen required to oxidize the compound to CO_2 and H_2O was calculated. Triplicate samples of each solution were analyzed by the COD test as outlined in Standard Methods (56). The ratios of theoretical COD to observed COD (termed percentage recovery) for the various compounds were as follows:

acetone	97
methyl ethyl ketone	95
propionaldehyde	96
butyraldehyde	99
valeraldehyde	99

Operational Sequences

All compounds were studied at airflow rates of 4000, 2000, 1000, 500, and zero (quiescent state) cc/min. In addition, the effect of disodium hydrogen phosphate (Na_2HPO_4) was investigated at an airflow rate of 500 cc/min for all of the compounds. In the experimental studies of Prather (57) with refinery waste waters, 0.4 to 0.5 lbs of this phosphate salt per 1000 gallons increased COD removal from 70 to 92 per cent. The above dosage corresponds to 60 mg/l. Accordingly, a stock solution of 6000 mg/l of disodium hydrogen phosphate was made and 10 ml (= 60 mg) from this stock was added to the one-liter volume of reaction liquor in the reactor; these studies were run in duplicate.

For each run, after making the solution of the test compound in distilled water, a sample was added to a COD flask. This sample served to measure the initial COD of the compound to be stripped. The solution was placed in the reactor, and aeration started at the desired airflow rate. Samples were withdrawn every fifteen minutes during the first hour; every thirty minutes during the second (and, at times, until the fourth) hour, and less often in succeeding hours. The samples were placed in previously prepared COD flasks. For some runs, aliquots of

some samples were analyzed by GLC the same day of the experiment. Most experiments were continued for twelve hours, and some were run for as long as twenty-four hours. For the quiescent state experiments, samples were withdrawn from the reactor every hour. Stripping kinetics (order and rate) were determined from semilogarithmic plots of COD remaining at various times.

For studying stripping characteristics of a mixture of acetone and methyl ethyl ketone, a solution of the two compounds in approximately equal concentrations (1000 mg/l as COD of each) was prepared in unbuffered distilled water. Initial concentration of this mixture was determined from the COD analysis on an aliquot. To determine the exact contribution of each of the components in the mixture, solutions of each (1000 mg/l as COD) were made separately in unbuffered distilled water and COD and GLC analyses performed on aliquots. These served as standards for calculation of acetone and MEK concentrations in the mixture by GLC analysis.

The prepared mixture of the two components was placed in the reactor and aerated at the rate of 2000 cc/min/l. Samples were withdrawn every fifteen minutes during the first hour, every thirty minutes until the fifth hour, and every hour thereafter until the experiment was terminated. The samples were placed in previously prepared COD flasks. For all samples up to five hours, GLC analysis was performed on the same day of the experiment. From the semilogarithmic plot of the COD of the mixture remaining versus time, the stripping kinetics of the mixture was determined, whereas the stripping kinetics of each compound in the mixture was determined from similar plots utilizing the GLC analyses.

B. Treatment of Strippable Compounds by Stripping and Acclimated Biological Solids in Batch Units

The experimental setup was the same as shown in Figure 2. The same aerator was used, the volume of the mixed liquor at all airflow rates for study of dual removal was one liter, and only one gas dispersion tube was used in all cases.

Operational Sequences

Activated sludge systems were developed from sewage seed (2 per cent of reaction volume) obtained from the primary clarifier effluent of the municipal treatment plant at Stillwater, Oklahoma, using volatile organic compounds as sole carbon source. These volatile organic compounds were acetone, methyl ethyl ketone, propionaldehyde, butyraldehyde, and valeraldehyde. Each compound was fed as sole carbon source to separate activated sludge systems maintained on the 24-hour batch feeding cycle. The constituents of the synthetic waste are shown in Table II.

TABLE II

COMPOSITION OF SYNTHETIC WASTE FOR VOLATILE SUBSTRATES

Constituent	Concentration
ketones or aldehydes	1000 mg/l as COD
$(NH_4)_2SO_4$	500 mg/l
$MgSO_4 \cdot 7H_2O$	100 mg/l
$MnSO_4 \cdot H_2O$	10 mg/l
$CaCl_2 \cdot 2H_2O$	7.5 mg/l
$FeCl_3 \cdot 6H_2O$	0.5 mg/l
trace elements (tap water)	100 ml/l
1 M potassium phosphate buffer	10 ml/l
distilled water	to 1 liter

Prior to daily feeding, certain routine checks as to pH and growth of biological solids were made. The pH of the mixed liquor was measured by a Beckman Zeromatic pH-meter to determine if the amount of buffer added at the dosage shown in Table II was sufficient to hold the desired pH. It was found that for activated sludge growing on valeraldehyde, it was necessary to increase the buffer dosage from 10 ml/l to 15 ml/l to maintain the pH between 6.5 and 7.1. For all other compounds, maintenance of pH within the above range was obtained at the 10 ml/l buffer dosage. To examine the growth of biological solids in the medium, optical density (OD) measurements were conducted on an aliquot of the reaction liquor prior to daily feeding (Spectronic 20 colorimeter at 540 mμ wavelength, using a light path of 1 cm).

There was no appreciable increase of OD for a period of five to six days after inoculation with sewage seed. Physical stripping of the substrates (in the form of fine aerosols) could be visually detected. For ketones, during this five-to-six-day period, the unit appeared to be dense white in color, and the diffuser was sparkling clean when withdrawn from the unit. For aldehydes, especially for butyraldehyde and valeraldehyde, during aeration, oily particles became localized on the surface of the reaction liquor and frequent agitation of the surface (with a plastic spatula) was necessary in order to disperse the substrate evenly in the medium. About three weeks were required for each of these systems to approach solids balance.

Prior to the day of a particular experiment with a specific substrate, a preliminary biological solids concenration was determined by the membrane filter technique. This served as the guide for obtaining the desired biological solids concentration in an experiment which was

run on the following day. Experiments for each substrate with acclimated biological solids were carried out at four different airflow rates, 4000, 2000, 1000, and 500 cc/min. On the day of the experiment, sludge was centrifuged (Sorvall Superspeed RC2-B Automatic Refrigerated Centrifuge), washed twice in 0.05 M potassium phosphate buffer, and resuspended in an inorganic salts medium (as given in Table II) containing distilled water. Twenty-five ml of the suspension were then filtered (0.45 μ Millipore filter) for measurement of initial biological solids concentration; COD determination on the filtrate indicated the amount of carryover COD. The desired amount of substrate (as COD) was added to the remainder of the sludge suspension. The same amount of concentrated substrate was added to an equal volume of the inorganic salts medium devoid of biological solids; a sample was taken for analysis of COD and an aliquot preserved for GLC analysis to determine the exact concentration of carbon source present at the beginning of the experiment. This initial feed concentration when added to the carryover COD represented the best estimate of initial COD. Samples from the aerator were taken every fifteen minutes during the first hour, every thirty minutes during the second hour, and less frequently during the subsequent hours. Depending on the settleability of the sludge, samples were passed either directly through a Millipore filter or centrifuged prior to passing through the Millipore filter. An aliquot of filtrate was placed in a COD flask and the remainder preserved for analysis by GLC. When centrifugation of samples prior to filtration was imperative during high frequency of sampling, samples were preserved in chilled test tubes in an ice water bath to arrest activity during the time lag for processing consecutive samples. The dissolved oxygen (DO)

concentration in the aerator during the experiment was measured for some runs at lower airflow rates by a galvanic cell oxygen analyzer (Precision Scientific Company). The sensitivity coefficient of the DO probe was previously established at the temperature of the batch unit. The aeration period was varied during this phase of the experimentation. Based on experiences from the earlier experiments, the aeration periods for later experiments were reduced. However, in no case was an experiiment terminated earlier than three hours after the exogenous substrate was exhausted.

C. Treatment of Strippable Compounds by Stripping Alone and by Stripping and Acclimated Biological Solids in Continuous Flow Reactors

Experimental Apparatus and General Operational Procedure

All continuous flow experiments were conducted in the same experimental setup as shown in Figure 2. The volume of the Pyrex aeration vessel was 2.5 liters. It was provided with a circumferential overflow weir at this level. The net aeration volumes after correcting for the volume change due to the air stream at airflow rates of 4000, 2000, 1000, and 500 cc/min were 2353, 2415, 2446, and 2461 ml, respectively. This was determined by running the continuous flow unit at a detention time of eight hours, with acetone-distilled water mixture both in the feed reservoir and in the aeration basin. Pumping was disrupted, the volume of the aeration liquor was measured, and the pumping was resumed after filling the aerator to the 2.5-liter volume mark. The reported net effective aeration volume is the average of three such values. The same procedure was repeated for all airflow rates.

All continuous flow experiments were conducted at a nominal

dilution rate of 1/8 hr^{-1}; the flow rate employed was 312 ml/hr. Prior to each experiment, this flow rate was set by careful adjustment of the stroke length of the small capacity controlled volume pump (mini Pump, Model MM-2-B-96R, Milton Roy Company). Two such pump and motor assemblies with appropriate tubing were used; while one was in operation, the other was cleaned by pumping two per cent (by volume) Clorox solution first, then pumping distilled water. This procedure was employed to keep the tygon feed and delivery lines free of contamination. The feed reservoir was filled every twenty-four hours; the volume remaining in the reservoir was noted as a check on the constancy of flow rate to the reactor. Whenever a pump needed slight adjustment, the alternate pump (which was previously calibrated) was placed on the line. At times the pumping rate was found to be very exact; however, on the average, the pumping rate was ±5 per cent of the nominal or desired rate. Air was supplied by a gas dispersion tube; flow rates were measured and adjusted using a Fisher and Porter rotameter. The reaction liquor was maintained at a constant temperature of 25°C, using a "Precision Lo-Temptrol" unit. Suction and delivery lines were made of tygon tubing joined with unions. Care was taken to ensure that the right-angled glass nozzle used to deliver the feed to the reactor was centered and located above the zone of aerosol and foam splatter in order to help prevent back contamination of the feed. During experimental runs employing a biological population, whenever an accumulation of solids was observed in the bottom of the reactor, it was mixed periodically by a rubber spatula attached to the end of a wooden handle. Also, at times the entire reactor contents were placed in a Waring blender in order to break up floc particles and help mix the system.

This procedure was necessary at times because of the nature of the biological floc which developed on the substrates employed. Diffusers were cleaned periodically with sodium dichromate solution in concentrated sulfuric acid, followed by overnight bubbling in distilled water. Feed bottles were similarly cleaned.

Experimental Procedure

For continuous flow studies of stripping alone, the desired feed was pumped to the reactor and enough samples were taken to determine the average steady state concentrations.

For initiating experiments in which both stripping and biological treatment were studied, an acclimated biological population was first grown in a batch reactor. The composition of the synthetic waste was the same as that used for the batch studies (Phase II-B). To initiate a continuous flow experiment, biological solids from the batch tube were suspended in 2.5 liters of the inorganic salts medium. A portion was then filtered for measurement of initial biological solids concentration, and the COD of the filtrate was determined. The rotameter was adjusted to the desired airflow rate, and the feed pump turned on.

An aliquot of the daily feed was analyzed for COD. Periodically, the system was checked for complete mixing by measuring optical density of two unfiltered samples, one from within the reactor and another from delivery to the effluent bottle. In general, samples were withdrawn once daily (sometimes every two or four hours) for determination of biological solids and chemical oxygen demand of the filtrate, and an aliquot was refrigerated for later analysis by GLC. The pH of the mixed liquor or filtrate and the DO in the reactor were checked periodically. At times samples of the sludge were examined under microscope.

Tests for Complete Mixing in the Reactor

Complete mixing in the reactor vessel can be checked by comparing observed "wash-in" and/or "wash-out" curves with the theoretical curves generated for the unit from equations based upon the hydraulic mixing pattern which must exist if the reactor is truly completely mixed. The theoretical dilute-in equation has been given by Komolrit and Gaudy (58):

$$C = C_o(1-e^{-Dt}) \qquad (i)$$

and the dilute-out equation (58) can be expressed as follows:

$$C = C_o(e^{-Dt}) \qquad (ii)$$

The above equations permit calculation of the concentration, C, of material in the reactor at any time t for a given dilution rate. In Equation (i), C_o represents the concentration of substrate in the inflowing feed, whereas in Equation (ii), C_o represents the concentration of substrate in the reactor at zero time. Both dilute-in and dilute-out curves were obtained for the experimental reactor used in the continuous flow studies. Instead of using a dye as is sometimes done (58), glucose was employed in the present study and the COD was run on samples of the reactor effluent. It is seen in Figures 3 and 4 that the observed and computed dilute-in and dilute-out patterns for the reactor are in close agreement. Hence, the system was completely mixed with respect to substrate. One or more of the volatile substrates selected for study was not employed in the check on complete mixing, since these compounds are subject to stripping. During all continuous flow experiments on joint treatment by stripping and biological mechanism, the units were checked for complete mixing with respect to

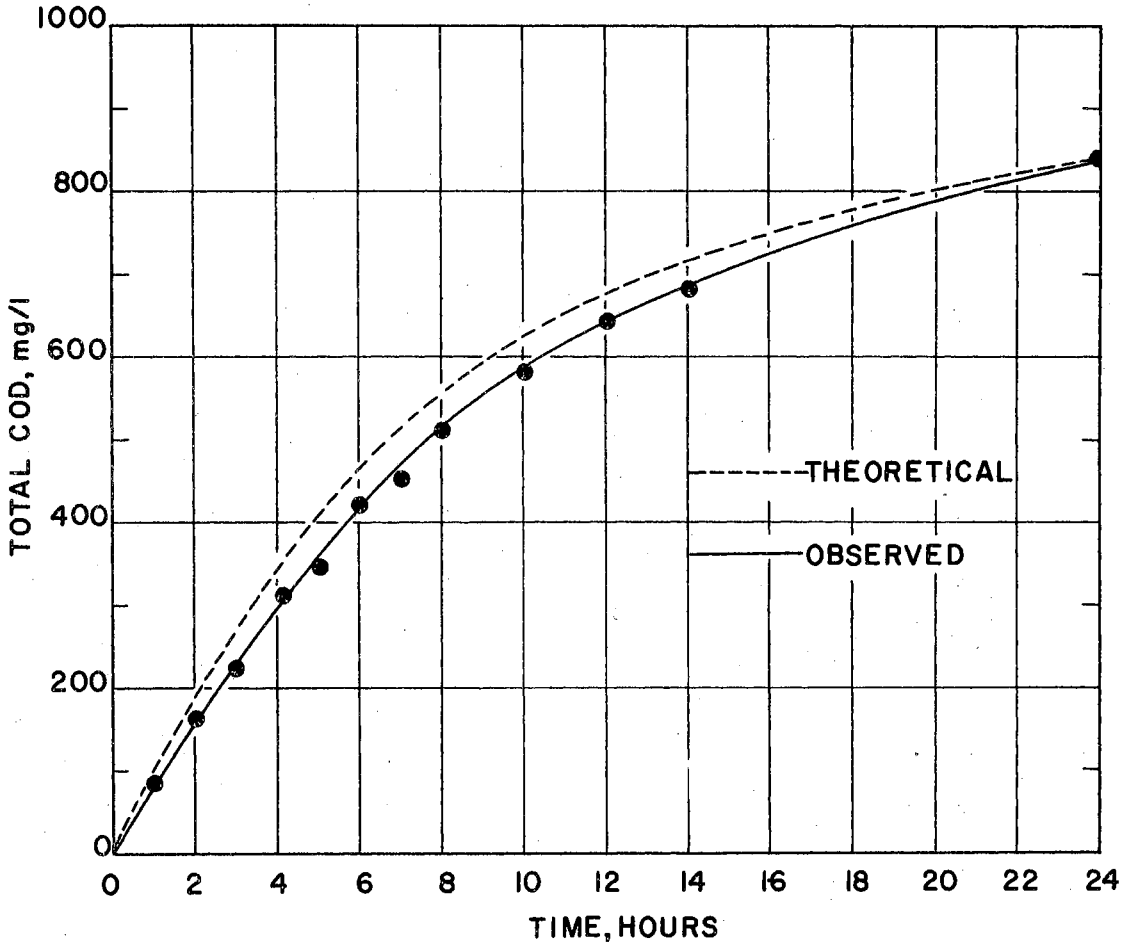


Figure 3 - Theoretical and observed dilute-in patterns for glucose in continuous flow unit. D = 1/8 hr^{-1}. Airflow rate = 4000 cc/min.

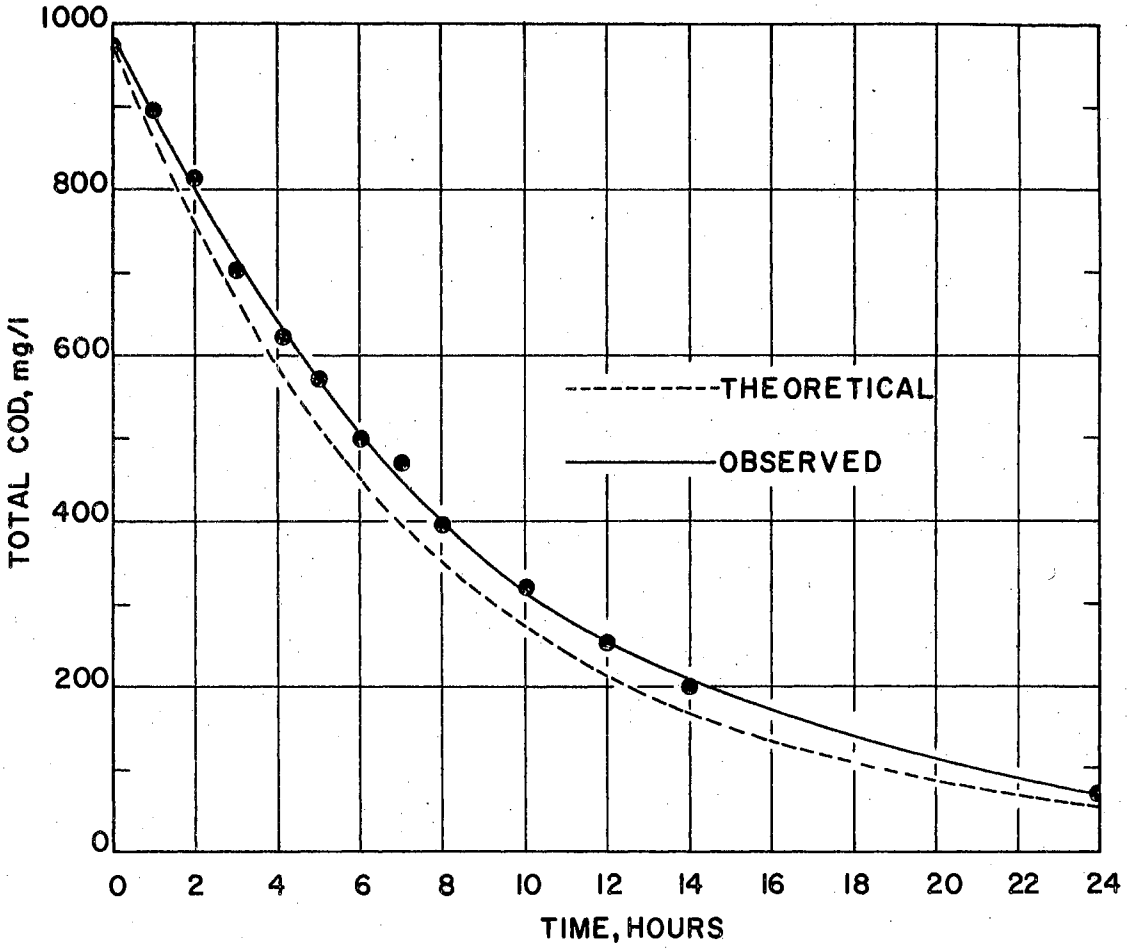


Figure 4 - Theoretical and observed dilute-out patterns for glucose in continuous flow unit. D = 1/8 hr^{-1}. Airflow rate = 4000 cc/min.

suspended solids by comparing the optical density in the reactor and the reactor effluent. If the OD values were the same, it was taken as evidence that the reactor was completely mixed with respect to biological solids concentration.

Shock Load Studies

In order to gain some insight into the ability of a heterogeneous population to assimilate low molecular weight compounds under varying conditions, a population acclimated to MEK was continuously fed this compound ($D = 1/8\ hr^{-1}$). Then after a period of such operation, the feed was changed to acetone, then MEK, then butyraldehyde, then propionaldehyde, and finally acetone. Experimental parameters examined during the study were biological solids, pH, and COD. Filtrates were also analyzed by GLC to evaluate concentrations of substrate and metabolic intermediates.

Analytical Techniques

Methods for the determination of the experimental parameters are given below.

(a) Chemical Oxygen Demand (COD) Test

The COD technique was used to measure substrate remaining in solution after passing the mixed liquor through a membrane filter (Millipore HA 0.45 μ). The procedure followed for running the COD test was the same as outlined in the 11th edition of Standard Methods (59) for Phase I of the study. COD determinations for Phase II were done in accordance with the procedure outlined in the twelfth edition of Standard Methods (56).

(b) Anthrone (Total Carbohydrate) Test

Carbohydrate remaining in solution was measured by the anthrone test using the procedures given by Gaudy (60). This test, together with the COD test, enables one to obtain information on the possible release of intermediates and/or endproducts during the process of substrate removal. This test was employed only in Phase I of the research.

(c) Glucostat Test

This analysis, which is based on an enzymatic reaction, is specific for glucose. The test was run in accordance with procedures outlined by Worthington Biochemical Corporation (61), and was used in Phase I of the research.

(d) Biological Solids

The synthesis of biological solids was determined by the membrane filter technique wherever applicable, using 0.45 μ white plain 47 mm diameter Millipore filters. The procedure used was the same as outlined in Standard Methods (59).

(e) Oxygen Utilization (Warburg Technique)

Oxygen uptake was measured with a Warburg respirometer using 40 ml of mixed liquor in the flasks and 1.0 ml of KOH (20%) in the center well. A 10-minute equilibration period was allowed before the manometers were closed. In general, readings were taken at 15-minute intervals during the period of oxygen uptake. The detailed techniques and calculations were those given in Standard Methods (59) and Manometric Techniques (62). This analytical technique was used only in Phase I of the study.

(f) Volatile Acid Determination (GLC)

Volatile acids were analyzed (qualitatively and quantitatively) by gas liquid chromatography. A Model 810 "Research Chromatograph" (Hewlett Packard Company, Avondale, Pa.) was used for this analysis. A ¼-inch glass column packed with 20% (by weight) diethylene glycol adipate polyester and 2% phosphoric acid on 60 to 80 mesh Chromosorb W as adsorbent was used. This column was capable of detecting acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids. Before injecting either filtrate or absorbate samples on any day of GLC analysis, a sample from a mixture of volatile acids of known concentration was injected to determine the resolution of independent peaks in the mixture. The retention times of these discrete peaks were later compared with the peaks obtained on the samples. Once the various operational parameters were established for the elution of the mixture of the standard acids, they were not changed during the analyses of filtrates and absorbates. This is a necessary condition, and was strictly adhered to in all GLC analyses. The operational parameters for a typical elution pattern of a mixture of standard volatile acids (100 mg/l each) were as follows: The oven temperature was maintained at 125^{o}C, the injection port and detector temperatures were held at 272^{o}C and 287^{o}C, respectively; carrier gas (helium) was supplied at 60 psi and controlled at the #4 position on the rotameter yielding a flowrate of 140 ml/min; hydrogen and air were supplied at 30 psi and 33 psi, respectively. The acids are eluted on the basis of number of carbon atoms, i.e., the higher the number of carbon atoms, the greater is the retention time. A semilogarithmic plot of the retention time versus number of carbon atoms yielded a straight line (Figure 5). It

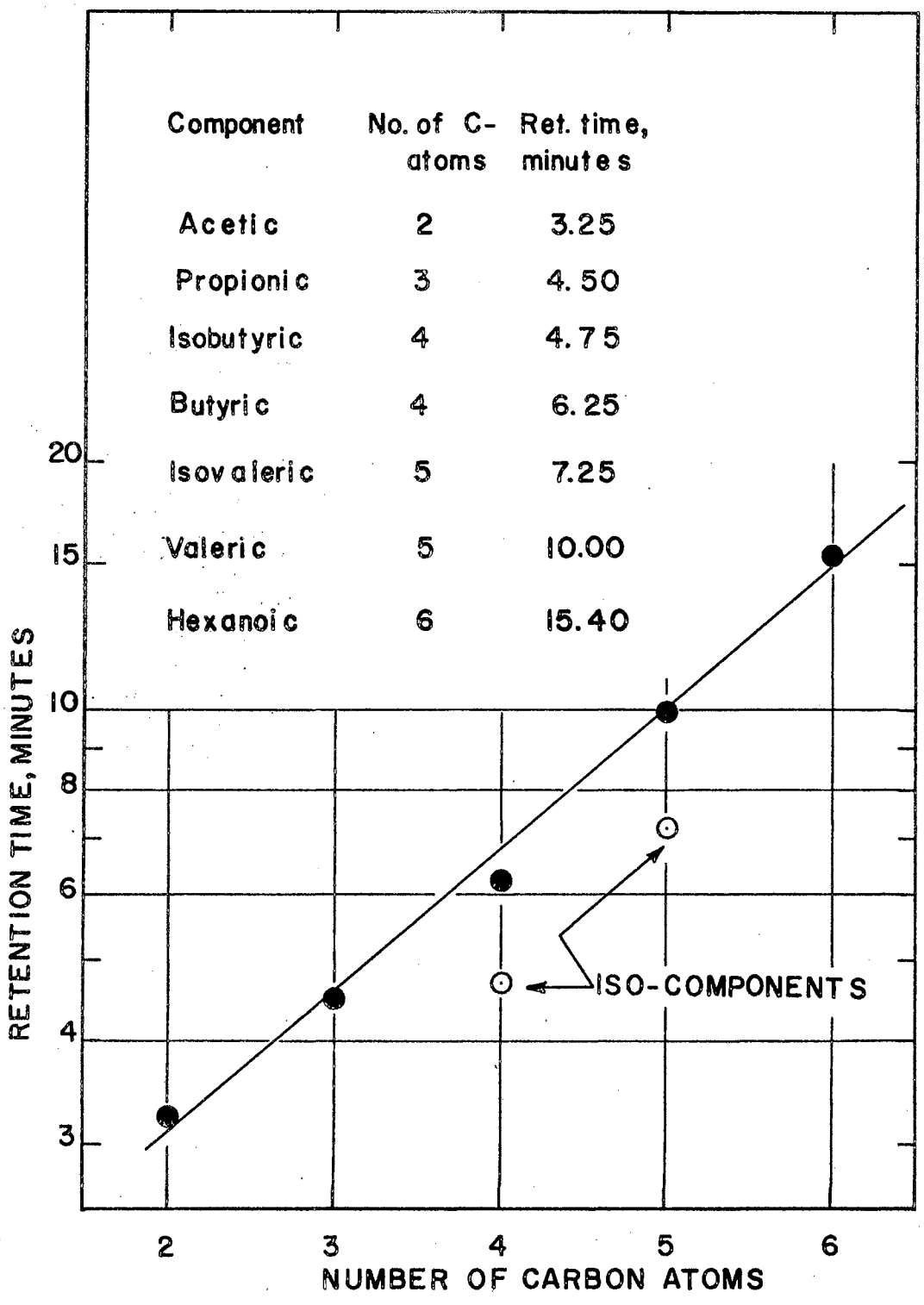


Figure 5 - Elution pattern of standard volatile acids on a gas liquid chromotographic (GLC) column.

is to be noted that the iso- compounds were eluted faster than the corresponding straight chain compounds. The detailed method of analysis and quantitative estimation by peak area measurement was that given by Nogare and Juvet (63).

The column described above was used only for the studies of Phase I. For the studies conducted in Phase II of the thesis research, a different column was employed. This column was capable of detecting aldehydes and ketones in addition to the volatile acids. A ¼-inch glass column was packed with a polymer packing, "Poly Pak-2" (80/120 mesh). This material is thermally stable at 300°C in an oxygen-free atmosphere. The other relevant properties of this packing material are as follows:

surface area	= 300 m^2/gm or 120 m^2/cc
average pore diameter	= 90 Angstroms
density	= 0.4 gm/cc
color	= white

Elution patterns of some compounds of interest are shown in Figure 6, where retention time in minutes for compounds analyzed were plotted (semilogarithmic) against numbers of carbon atoms. The plotted retention times were based on the average of multiple injections of different concentrations of the particular compounds. Retention time is independent of the concentration of compound injected. Retention time was calculated as the time from the point of injection to the point of appearance of the peak. Knowing the recorder chart speed, retention time could easily be scaled out. It should be mentioned here that the retention time of a particular compound can increase as the column ages with continued use. Therefore, whenever samples were analyzed, corresponding standards were also injected. Analysis of samples was made immediately, i.e., on the same day the sample was obtained. The GLC

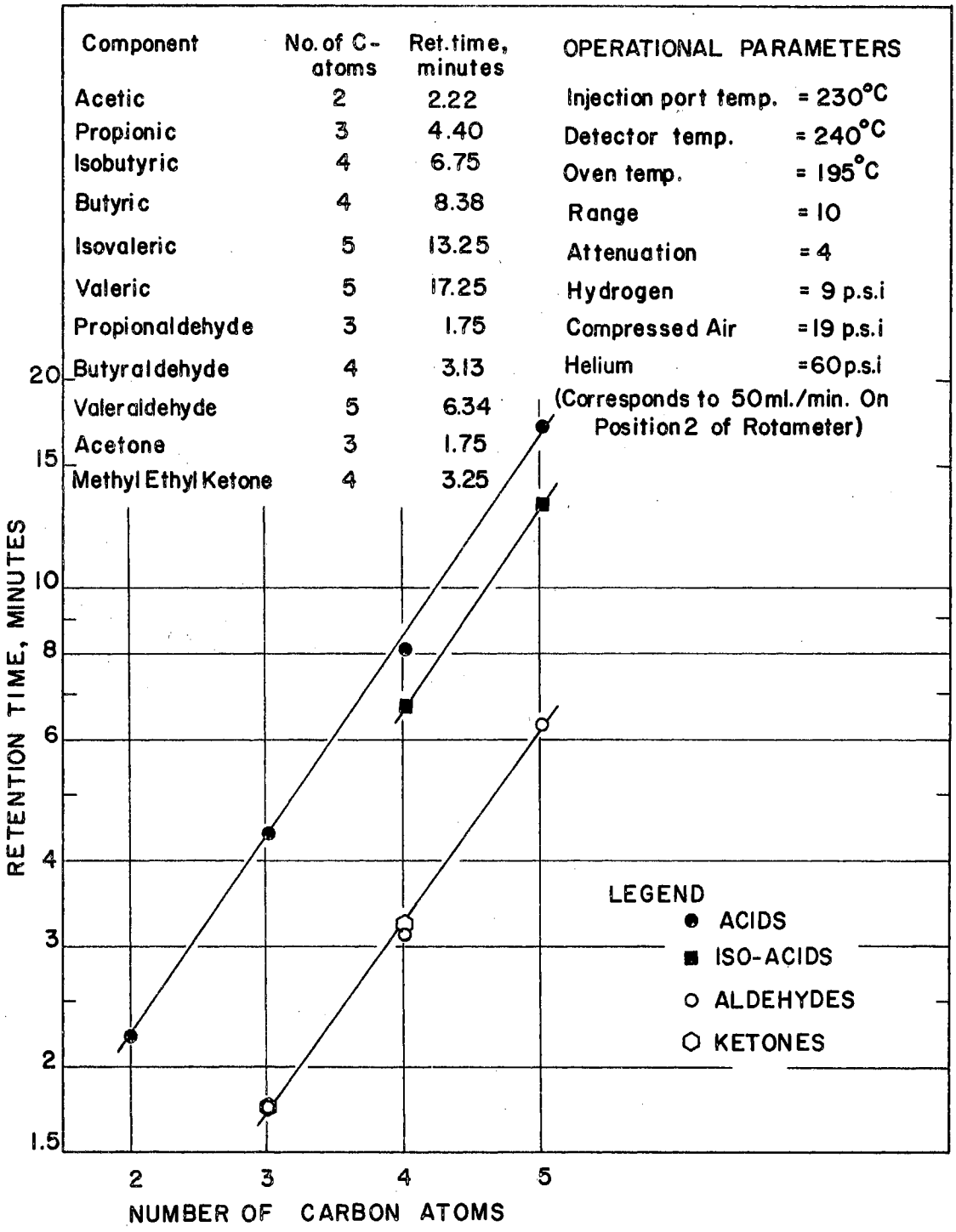


Figure 6 - Elution pattern of standard volatile compounds by gas liquid chromatography (GLC) on a Poly Pak-2 column.

analyzer was turned on the night before the experiment was to be conducted in order that injection and detector temperatures could attain a desired steady value. On the following morning, i.e., the day of the experiment, the oven was turned on and shortly afterward, gas flow was initiated which triggered the lighting of the hydrogen flame. When no appreciable drifting in the base line was observed, the apparatus was assumed to be ready for injection of samples. In nearly all cases standard or sample size was 5 µl. Samples were carefully injected using a Hamilton Microliter Syringe #701 (capacity 10 µl). Range and attenuation were adjusted in order to accommodate the peaks for compounds present in high concentrations, and to obtain a well-defined measurable peak for the compounds present in low concentrations. It may be pointed out here that retention times are independent of attenuation but are inversely proportional to the carrier gas flow rate. The suggested carrier gas flowrate for this column was 50 ml/min, which corresponds to the #2 position on the rotameter with pressure of 60 psi on the helium cylinder. These settings with regard to carrier gas flowrate were strictly adhered to. When the chromatograph was employed to assess the stripping rate of a compound, the initial concentration (as COD) was determined by the COD test, and the peak area obtained by GLC on this initial sample was taken as the standard for comparing with peak areas of samples taken as the experiment proceeded. Peak areas were measured with a planimeter (Gelman Instrument Company).

In preliminary studies the applicability of GLC analysis to a wide range of concentrations of compounds of interest was investigated. Also, the effect of attenuation setting on peak areas for particular concentration levels of the compounds was investigated. This was

deemed necessary to streamline calculations of concentrations of samples later on in cases where standards and samples of low concentrations could not be run at the same attenuation. For all compounds examined (acetone, methyl ethyl ketone, propionaldehyde, butyraldehyde, and valeraldehyde) there was a direct relationship between peak area and concentration. An example of the relationship obtained is presented in Figure 7 (acetone).

For analysis of filtrates which might contain volatile fatty acids, it was desirable to determine whether the sample should be acidified prior to injection into the column, since almost all filtrates were at neutral pH (7.0). Accordingly, stock solutions of acetic, propionic, butyric, and valeric acids were made in distilled water. The highest concentration employed in each case was 800 mg/l of the corresponding acids. Serial dilutions (in each case) of 400, 200, 100, and 50 mg/l were made. The acid pH of these samples was determined and recorded. Solutions with alkaline pH were made by careful addition of 0.05 N NaOH, the pH was measured and recorded. Five microliter samples were injected from both acidic and basic solutions of all concentrations of each acid at identical and compatible attenuations to obtain well-defined measurable peaks. Then plots were made with all areas converted to attenuation = 1. The data indicated that acidification of neutral (pH 7.0) samples prior to injection in the GLC column would not be necessary. An example of the type of relationship obtained is given in Figure 8.

For studies under continuous flow conditions it was not possible to perform GLC analyses immediately after obtaining each sample. Such a procedure would require continued use of the apparatus over an

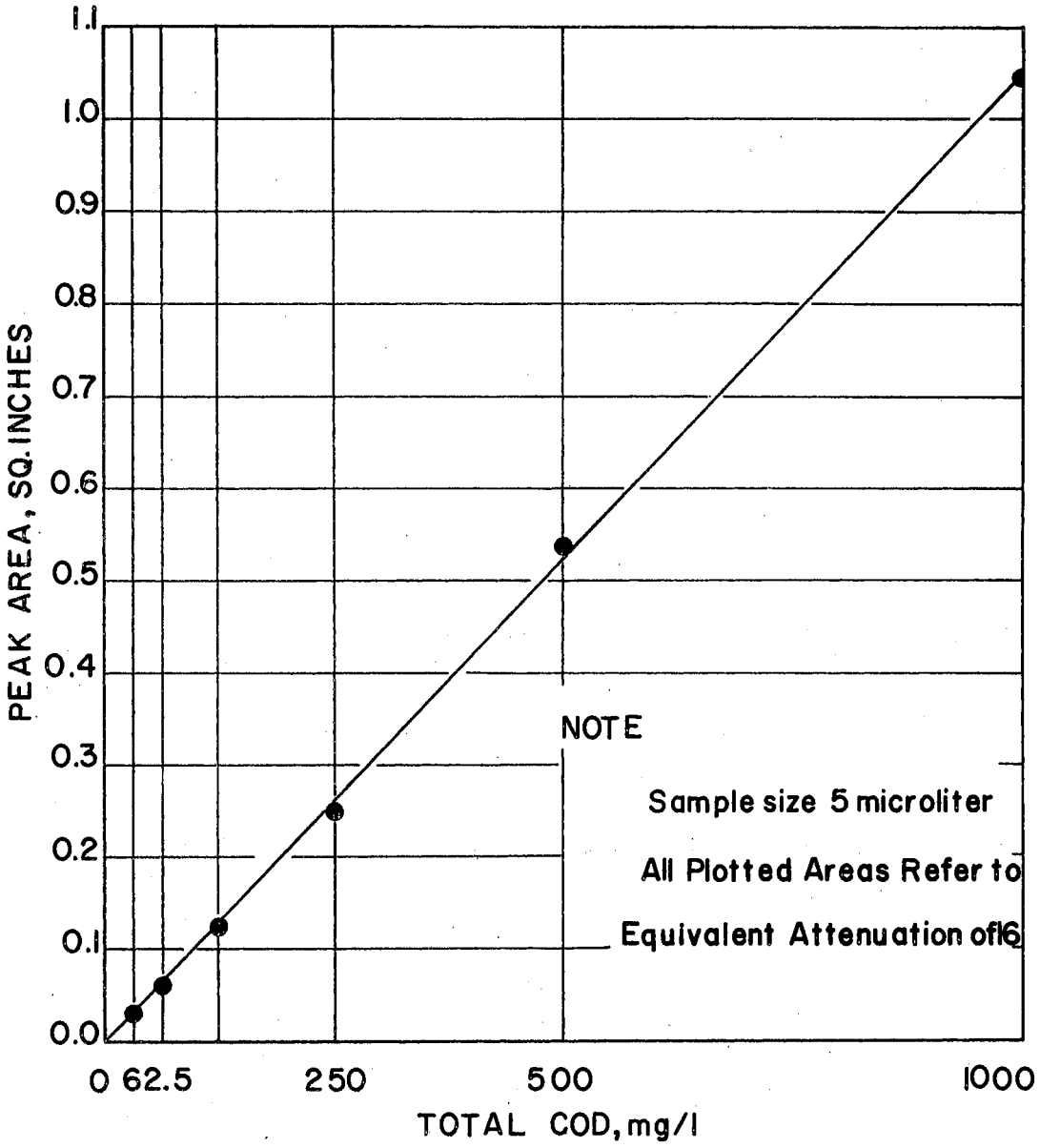


Figure 7 - Peak area-concentration relationship of acetone by gas liquid chromatography (GLC) on a Poly Pak-2 column.

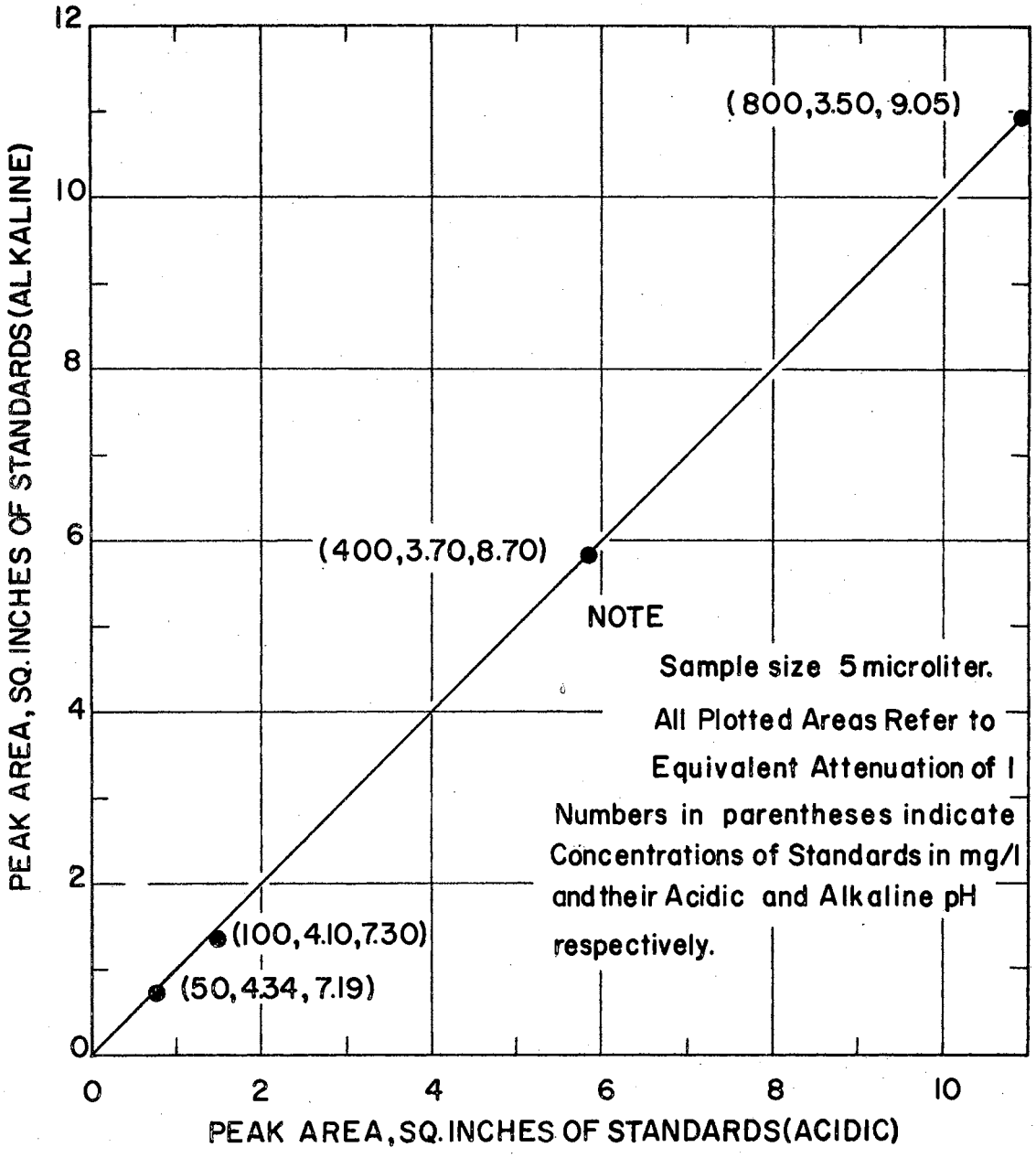


Figure 8 - Effect of H^+ ion concentration on peak area of acetic acid standards by gas liquid chromatographic (GLC) technique on a Poly Pak-2 column.

extended period of time and the instrument had to be scheduled for use by other researchers in the laboratory. Accordingly, samples were frozen for later analyses. There was some evidence for a slight loss in peak areas for volatile substrates during storage, so the standard solutions were subjected to the same storage procedure as the samples in an effort to minimize inaccuracy due to storage. It is emphasized that the major reason for running GLC analyses during continuous flow experiments was to detect, if possible, the presence of either oxidation products or metabolic intermediates formed due to stripping and due to combined stripping and biological metabolism of the volatile substrates. Such products (acids were anticipated) are not really volatile compounds and would not be expected to be "stripped" during the storage period. In cases where the GLC analysis on the original volatile compounds could be employed as a test for substrate removal it was realized that losses due to storage could cause inaccuracy and that differences between the COD analysis and GLC analysis (converted to equivalent COD) were not necessarily due entirely to chemical changes in the substrate due to stripping, but were due in part to losses during freezing and storage. Studies were undertaken to estimate losses during frozen storage, and it was found that the maximum expected loss was ten per cent of the COD. In experiments under conditions of combined stripping and biological removal of volatile substrate, it was realized that a portion of the volatile compound could be stripped during the filtering operation on the membrane filter apparatus. Special studies were undertaken using valeraldehyde and methyl ethyl ketone (the most rapidly stripped of the compounds under study) to determine losses due to filtering. It was found that the maximum expected loss for valeraldehyde was ten per cent, and for MEK, five per cent.

CHAPTER IV

RESULTS

Phase I

Studies on the Possible Production and Subsequent Stripping of Volatile Components During Aerobic Metabolism of an Initially Nonstrippable Carbon Source in High Solids Batch Systems

The results of this phase of the study are summarized in Tables III and IV arranged in ascending order of substrate:biological solids, the so-called F:M (food:microorganisms) ratio. In this series of experiments, biological solids concentrations greater than 2000 mg/l were employed. In the interest of brevity, only one typical experiment is presented in kinetic detail.

Figure 9 shows the detailed results for run No. 14 of Table III, the experiment with the highest F:M ratio employed in the series. Measurement of filtrate COD of a sample thirty seconds after initiation of the experiment yielded an apparent initial COD removal of 14.5 per cent. The thirty-second solids data show a slight drop from the initial solids level. Thereafter the biological solids concentration continued to rise and attained a maximum level as the COD approached exhaustion. The biochemical efficiency of substrate removal (as COD) was 96.4 per cent. Substrate removal is exhibited in three well-defined profiles, namely,

TABLE III

EFFECT OF F:M RATIO ON BIOCHEMICAL CHARACTERISTICS DURING SUBSTRATE REMOVAL

1	2	3	4	5	6	7	8	9	10	11	12	13		
					Maximum Intermediates as Difference of			Absorbate		Time to Attain 95% COD Removal (Minutes)			30-Sec. Parameters	
Run No.	Initial Solids mg/l(M)	Initial COD mg/l(F)	F:M Ratio	Immediate Uptake as % Initial COD	(Total COD - Anthrone COD) mg/l	(Total COD - Glucostat COD) mg/l	By GLC COD mg/l	Total COD mg/l	By GLC as COD mg/l	Total COD	Based on Anthrone COD	Glucostat COD	Solids mg/l	COD mg/l
1	15575	2544	0.16	66.6				95	206	29	<0.5		16495	846
2	7355	2485	0.34	57.1				225	40	34	15		7525	1065
3	5520	2408	0.44	31.0				64		92				1661
4	4530	2090	0.46		826			360		79	18			
5	4620	2994	0.65		1471			78	50	120	45			
6	5825	4530	0.78		1134			8	146	86			6890	
7	4325	4305	1.00	7.6	1066	1056		74	24	112	47	50	4640	3980
8	4390	4423	1.01	6.2	541	592	64	135	79	>240	103	105	4400	4150
9	4000	4240	1.06		2035	1969	198			>210	50	45		
10	3920	4540	1.16		3906	3644	13	115		126	13	27		
11	3960	4784	1.21		1470			265	112	128	45		4875	
12	2695	4288	1.59	7.7	2378	2519	252	1295	97	152	61	75	3005	3960
13	2825	4577	1.62		1888	1980	945	198		≫210	107	91		
14	2735	4735	1.73	14.5	2073	2142	106	158	15	198	108	84	2640	4050

TABLE IV

EFFECT OF F:M RATIO ON BIOCHEMICAL CHARACTERISTICS DURING SUBSTRATE REMOVAL

(Explanatory Notes for Columns 8 and 10 in Table III)

Components by Gas Liquid Chromatography

Run No.	In Filtrate*	In Absorbate**
1		propionic (7.8), butyric (7.81), valeric (190.54)
2		isobutyric (39.56)
3		
4		
5		acetic (44.12), propionic (3.72), isovaleric (2.58)
6		isovaleric (145.6)
7		acetic (23.57)
8	acetic (52.2), isovaleric (11.39)	acetic (79.10)
9	acetic (181), propionic (17.2)	
10	acetic (13.1)	
11		valeric (88.24), hexanoic (24.1)
12	acetic (191), propionic (50.5), butyric (trace), isovaleric (10.92)	isobutyric (97.30)
13	acetic (945)	
14	acetic (21.6), propionic (47.5), isovaleric (5.6), hexanoic (31.2)	acetic (14.65)

*Numbers in parentheses indicate concentration of a particular compound as its equivalent COD, mg/l, constituting the total at the point of maximum intermediate and/or endproducts. The multiplying factors for the various compounds for equivalent COD, mg/l are given in the Appendix.

**Numbers in parentheses indicate allocation of different compounds as their equivalent COD, mg/l, in the cumulative production of intermediate and/or endproducts.

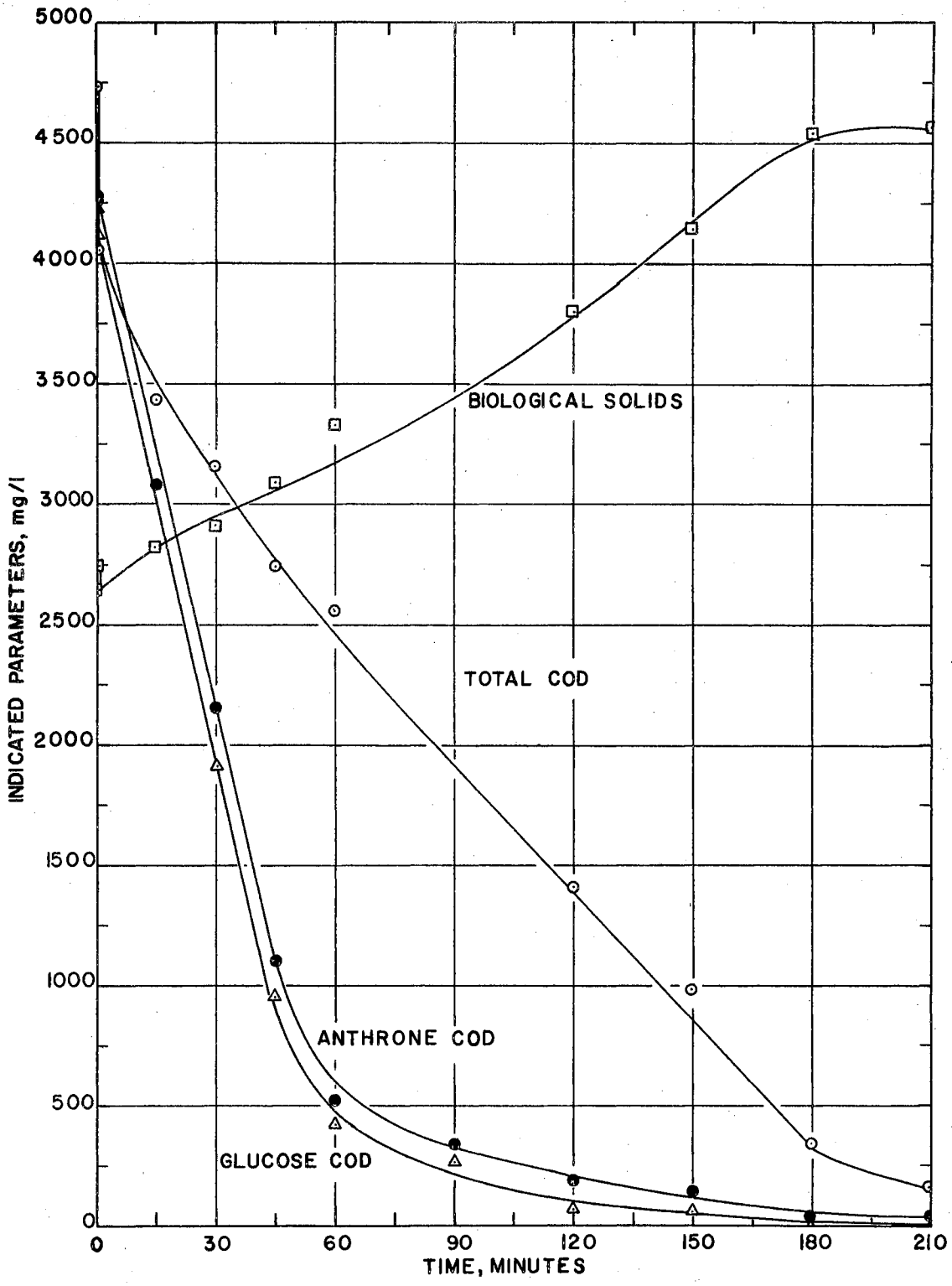


Figure 9 - Utilization of glucose in aeration reactor at initial biological solids concentration of 2735 mg/l.

total COD, anthrone COD, and glucostat COD, determined on the filtrates at various time intervals during the course of the run. The curves for anthrone COD and glucostat COD are essentially the same, whereas there is a considerable difference between these curves and the total COD curve, indicating a significant accumulation of metabolic intermediates and/or endproducts. Also, it may be discerned that the bulk of these products was not carbohydrate. The time required to attain 95 per cent overall treatment efficiency on the basis of anthrone COD was 108 minutes, whereas on the basis of glucostat COD, 84 minutes were required. The concentrations of metabolic intermediates and/or endproducts were calculated as the difference between total COD and COD calculated from the glucostat and anthrone analyses. These values are plotted in Figure 10. It can be seen that the intermediates and/or endproducts accumulated in the medium during the first 75 minutes of the experiment during which time most of the original carbon source was exhausted. The maximum amounts of intermediates and/or endproducts were 2073 (anthrone basis) and 2142 mg/l (glucostat basis). Also shown in this figure are the results of analyses of the filtrates using gas chromatography. Peaks were identified as acetic, propionic, isovaleric, and hexanoic acids. For purposes of plotting and ease of comparison, the various acids were converted to their equivalent COD values and summed. The maximum amount of intermediates and/or endproducts obtained in this way was 105.9 mg/l COD, and occurred at the 45-minute sampling time. These acids account for only 6.5 per cent of the total intermediate accumulation at this time. It is interesting to note that these products, as in the case of the other intermediate products, were later metabolized. Figure 11 shows the cumulative results of the analyses

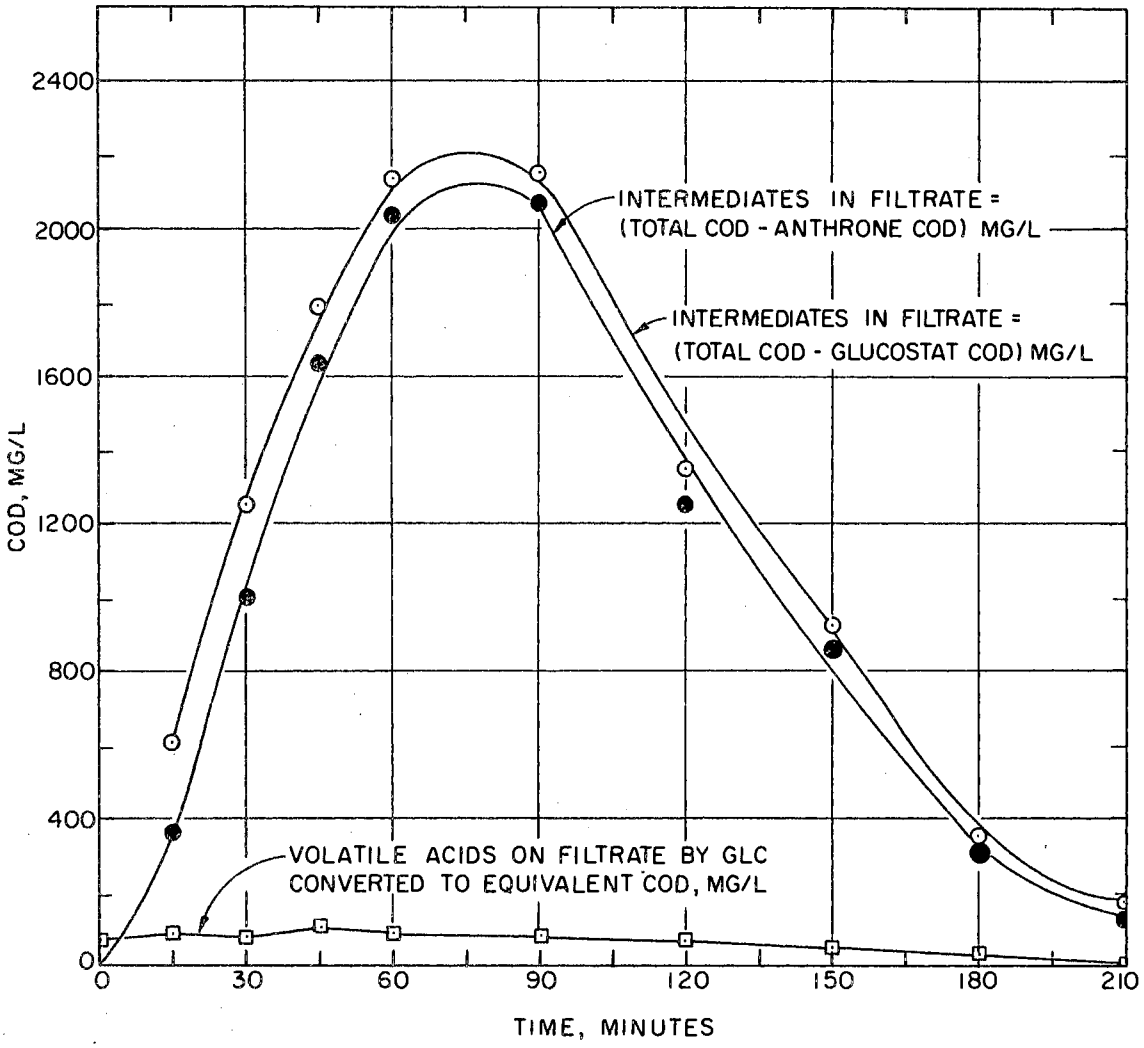


Figure 10 - Metabolic intermediates and/or endproducts during aerobic utilization of an initially nonvolatile carbon source in high solids batch system.

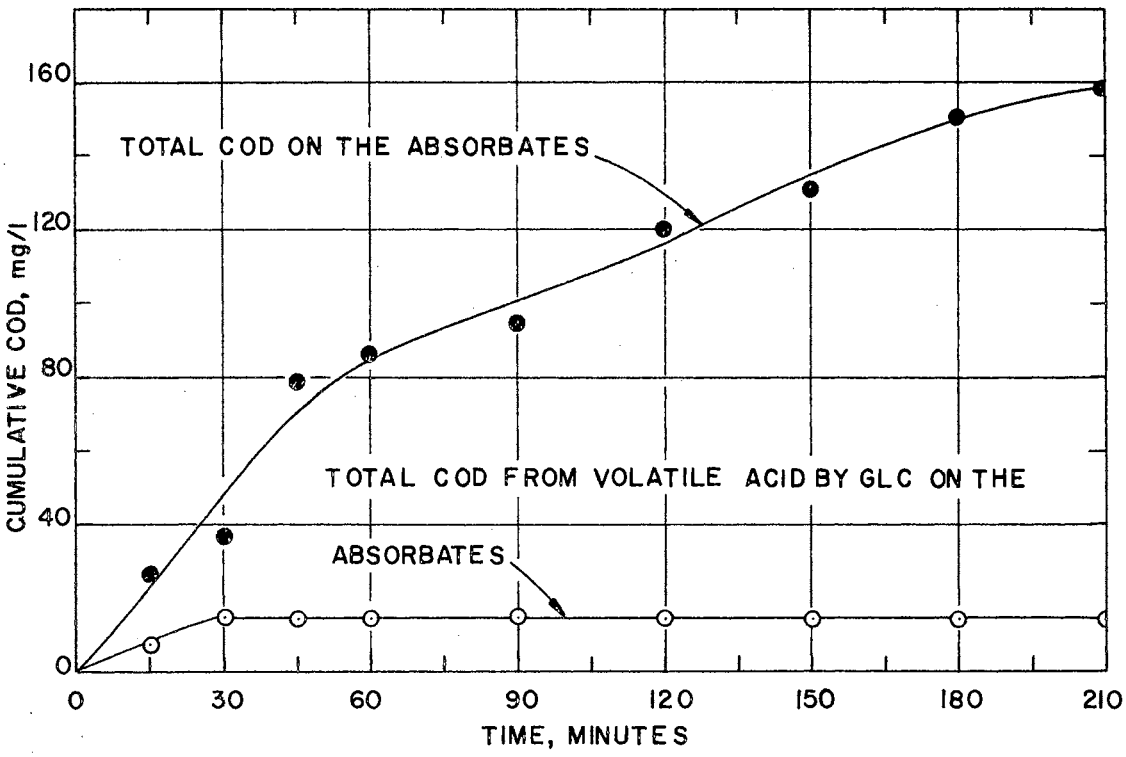


Figure 11 - Cumulative results on absorbates by COD and gas liquid chromatographic (GLC) analyses.

performed on absorbates. In this experiment two absorbing flasks were used in series to ensure more complete absorption of aerosols emerging from the aerator. The COD values of the absorbates which are plotted represent the sum of values from both absorbing flasks; the chromatographic (GLC) values also represent the sum of both absorbing flasks in the train. It is emphasized that the plot is a cumulative one. Whereas both absorbing flasks contributed toward total absorbate COD, there appears to be no distinct correlation or pattern regarding the discrete COD contribution by either absorbing flask on the total COD. Acetic acid was the only compound detected in the 15 and 30-minute samples, while the remainder contained trace amounts of acetic acid, not warranting peak area measurement. The equivalent COD of the acid detected accounts for only 9.3 per cent of the total COD in the absorbates.

Although oxygen uptake was measured using the Warburg respirometer in all experiments, the results are not presented because it has been found by Krishnan and Gaudy (5) that, at biological solids levels exceeding 2000 mg/l, the Warburg oxygen uptake data cannot be taken as representative of the O_2 uptake in the batch aerator tube under the conditions of shaking rate and airflow rate employed in this study, i.e., the Warburg system is limited by shaker rate. Twelve other experiments similar to the one shown in Figures 9, 10, and 11 were performed. The results are summarized in Tables III and IV. Columns 1, 2, and 3 need no explanation. Column 4 shows the F:M ratio which is the ratio of the two previous columns, i.e., $\frac{\text{column 3}}{\text{column 2}}$. For experiments in which a thirty second sample was taken, immediate COD uptake expressed as percent of the initial COD is entered under column 5.

Columns 6, 7, and 8 deal with the evaluation of intermediates

and/or endproducts in the filtrates. Columns 6 and 7 relate to the amount of intermediates and/or endproducts obtained by the method of difference between total COD and anthrone COD, and total COD and glucostat COD, respectively. Column 8 shows the amount of intermediates and/or endproducts obtained by GLC analysis. The analyses on absorbates are shown in columns 9 and 10. Column 9 shows the cumulative COD of the absorbates; column 10 shows the cumulative COD of the compounds detected by GLC analysis. Columns 11, 12, and 13 provide an insight into the kinetic aspects of carbon source removal based on three substrate analyses, i.e., total COD, anthrone COD, and glucostat COD. The time to attain 95 per cent removal was used as the basis of comparison. For runs where initial anthrone COD and glucostat COD were absent, initial total COD was used for calculations of percentages of anthrone COD and glucostat COD remaining with time.

Table IV shows the results of GLC analyses on filtrates and absorbates in greater detail. This serves to break down the total values for GLC analyses reported in columns 8 and 10 of Table III to discrete components and their respective concentrations. It is to be emphasized that the components and their concentrations followed by a number within paranthesis under the filtrate column denote those observed at the point of maximum intermediates and/or endproducts production, whereas those under the absorbate column relate to the cumulative values at the end of the run.

Phase II, A and B

Treatment of Strippable Compounds by the Activated Sludge Process (Batch Studies)

For each of the compounds studied, the sequence of presentation of

results is the physical stripping characteristics at various airflow rates, effect of addition of disodium hydrogen phosphate at an airflow rate of 500 cc/min, stripping under quiescent conditions, and removal of the compounds by the joint removal mechanisms of physical stripping and metabolism by acclimated biological solids.

Acetone

Figures 12, 13, and 14 show the effect of physical stripping of acetone at airflow rates of 4000, 2000, and 1000 cc/min. For each experiment, both arithmetic and semilogarithmic plots of the data are shown. It is seen that acetone was stripped in accordance with first order kinetics in each case. The values of stripping constants based on COD were 0.224, 0.142, and 0.105 hr^{-1} for airflow rates of 4000, 2000, and 1000 cc/min, respectively. Also in Figure 12 are plotted the GLC analyses for samples taken at selected time intervals. As can be seen, these values are consistently slightly lower than the corresponding values by COD determination; however, when plotted on the semilog scale, these GLC data yield the same slope as the one obtained using values from COD analyses. After twelve hours of aeration, stripping efficiencies were of the order of 99, 98, and 94.6 per cent for airflow rates of 4000, 2000, and 1000 cc/min, respectively.

Figure 15 shows the effect of stripping at an airflow rate of 500 cc/min with and without addition of disodium hydrogen phosphate. Considering the 12-hour period, disodium hydrogen phosphate seems to have an inhibitory influence on the overall removal of acetone. At the end of this period the removal efficiency without disodium hydrogen phosphate was 82.5 per cent, whereas with its addition the removal efficiency was 75 per cent. Stripping with air alone permitted a fairly

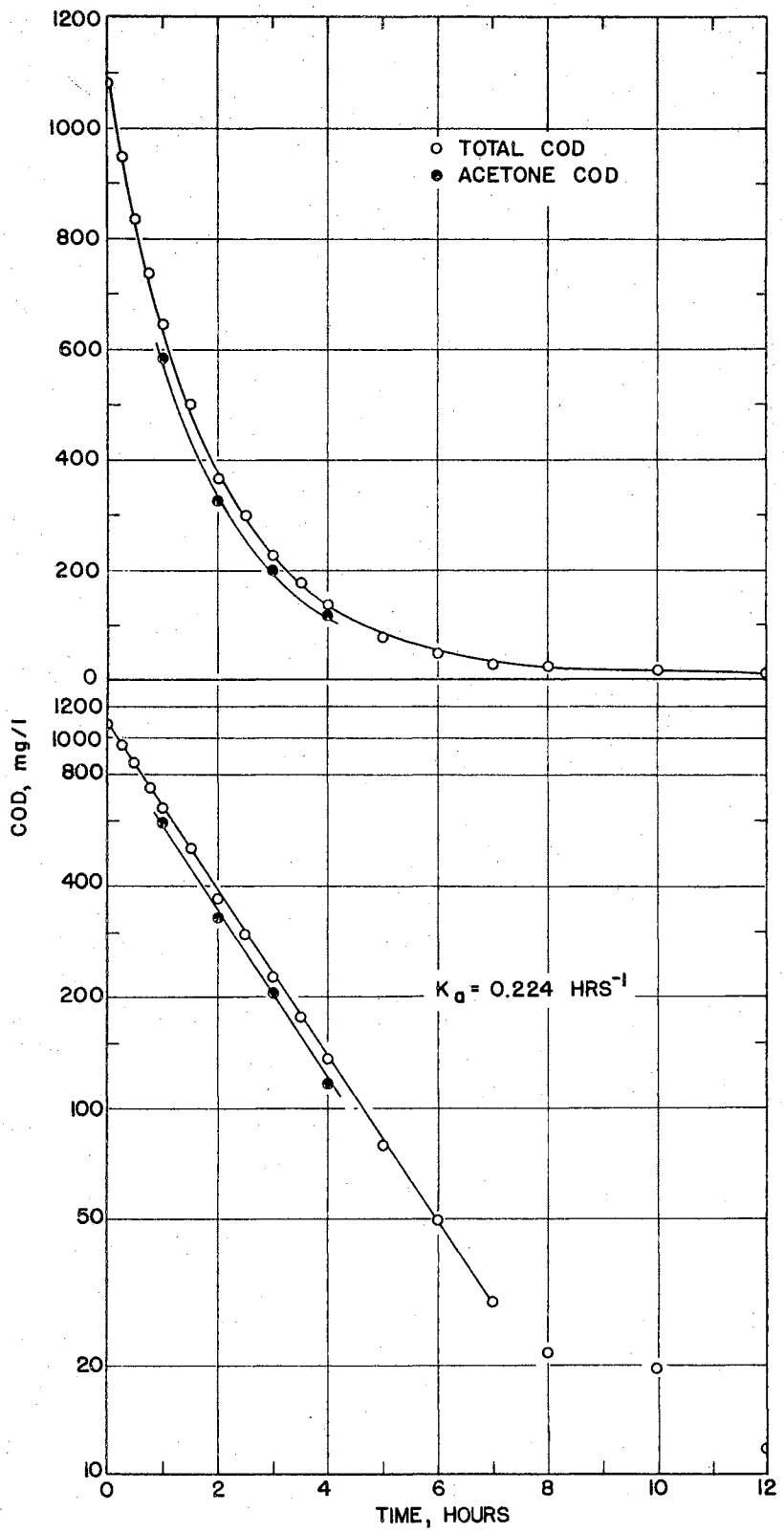


Figure 12 - Air stripping of acetone under batch conditions at 4000 cc/min/l.

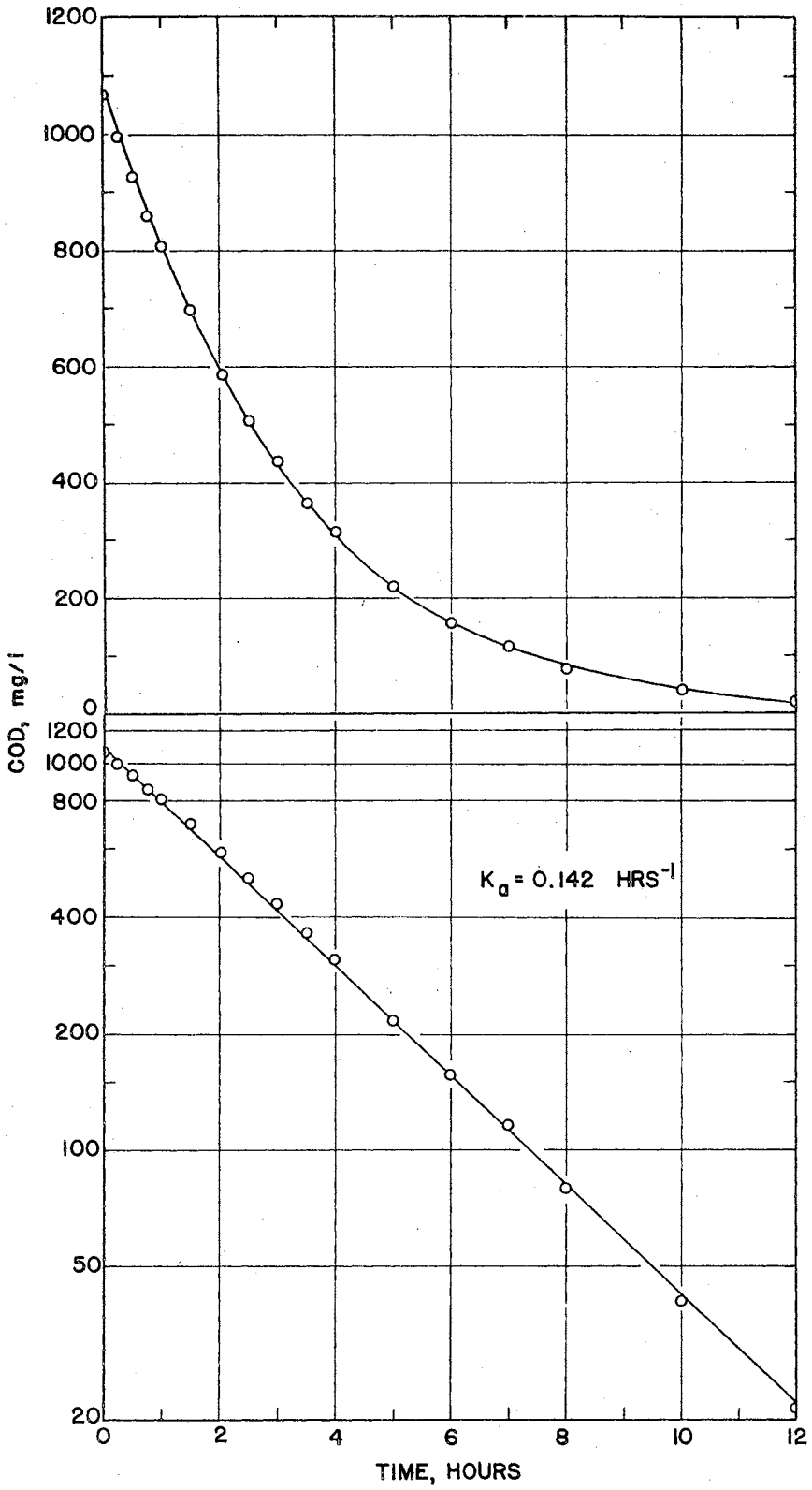


Figure 13 - Air stripping of acetone under batch conditions at 2000 cc/min/l.

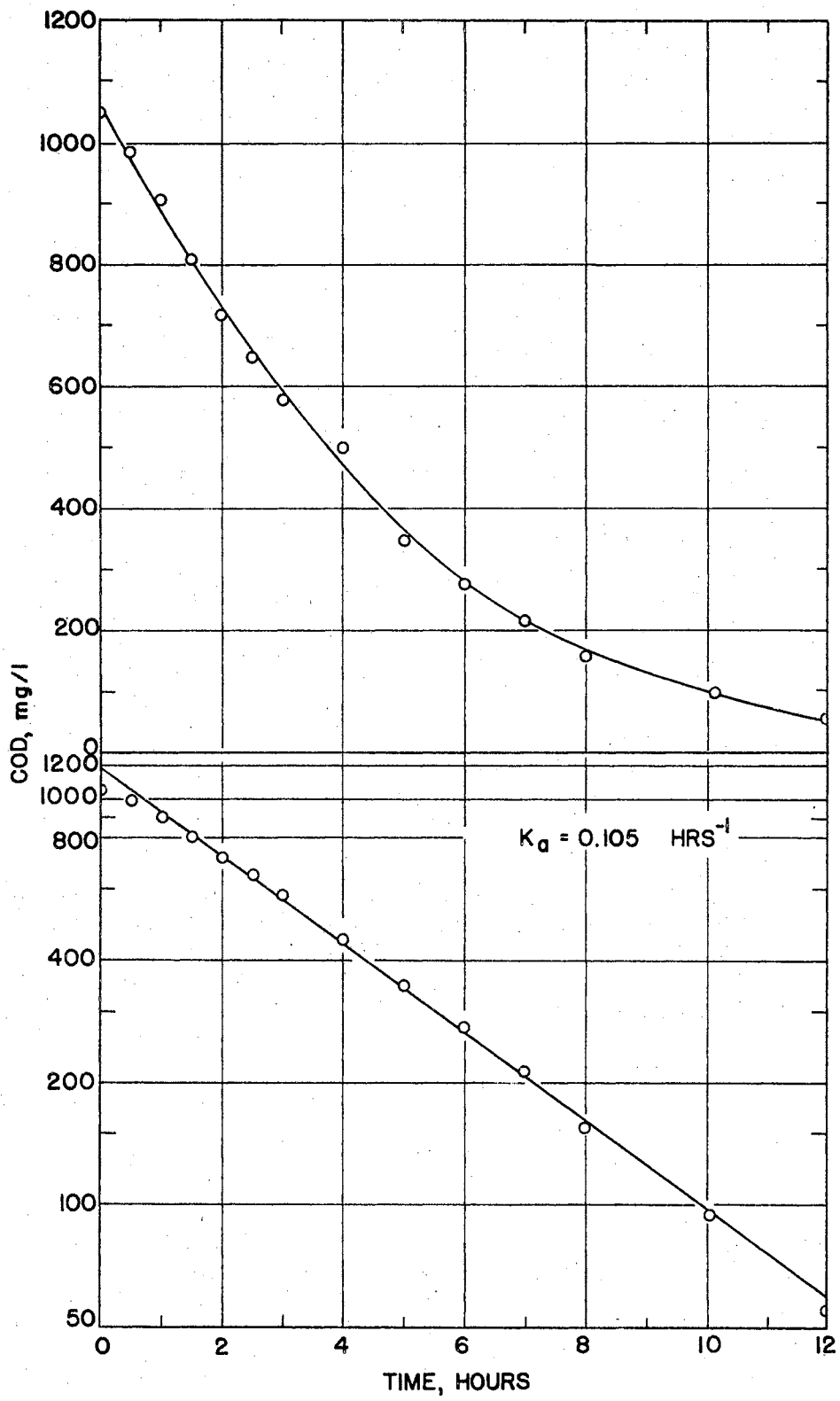


Figure 14 - Air stripping of acetone under batch conditions at 1000 cc/min/l.

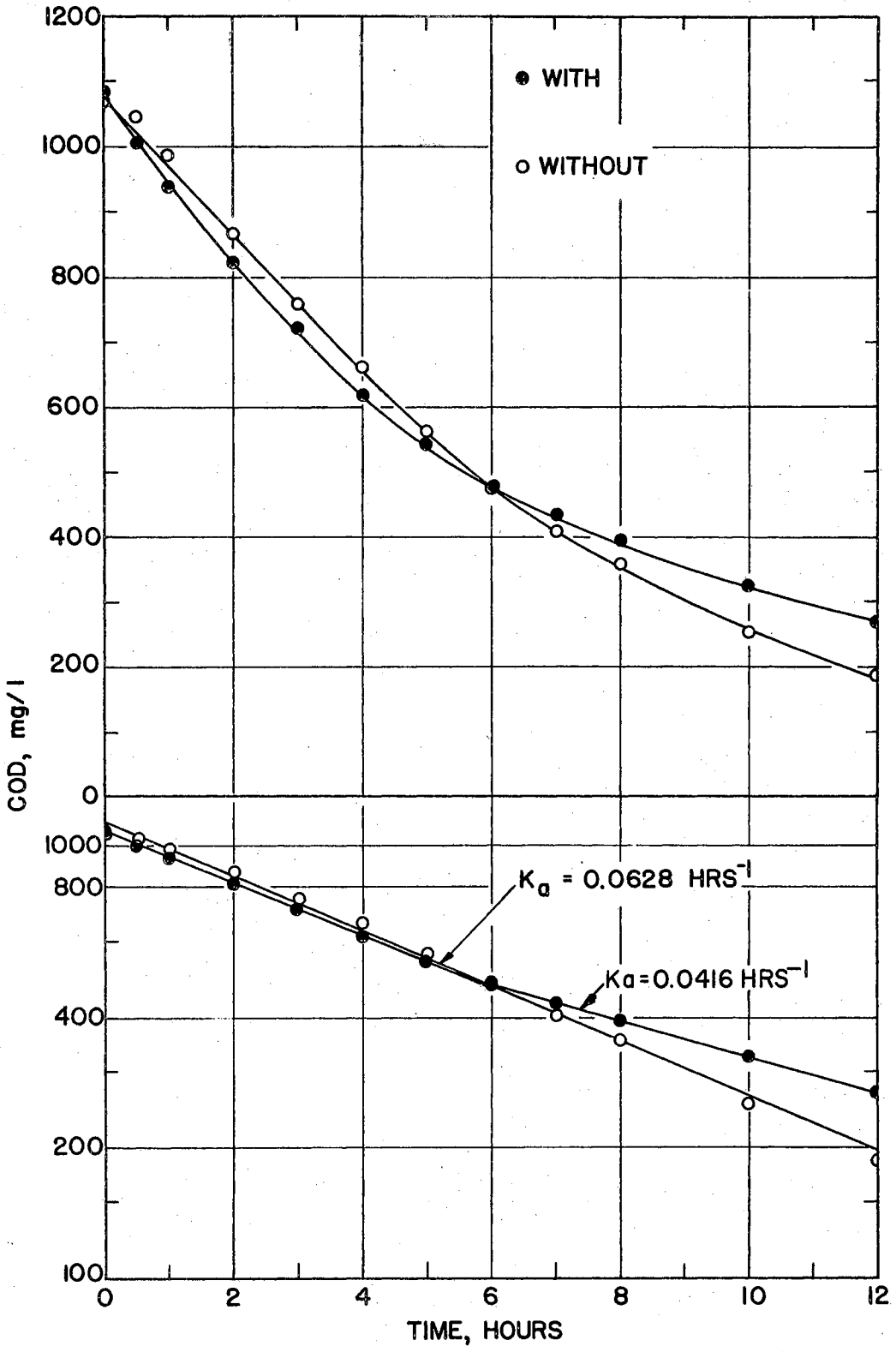


Figure 15 - Air stripping of acetone with and without disodium hydrogen phosphate under batch conditions at 500 cc/min/l.

good fit of the data to a first order plot, and the constant calculated from the semilogarithmic graph was 0.0628 hr^{-1}. However, with the addition of disodium hydrogen phosphate, the semilogarithmic plot does not yield a straight line through all points. There appears to be a break in the semilogarithmic plot at the sixth hour. The first order removal rate constant for the latter portion of the experiment was 0.0416 hr^{-1} as compared to the first order rate of 0.0628 hr^{-1} for the entire duration of the run without disodium hydrogen phosphate. The same trend (break at the sixth hour) was exhibited in another run with disodium hydrogen phosphate at 500 cc/min of air, and an initial acetone COD of 897 mg/l, the detailed results of which are not shown here.

Figure 16 shows the behavior of acetone at zero airflow rate (quiescent conditions). The COD removal was slight and a straight line fit could be obtained from both the arithmetic and the semilogarithmic plots. The slope of the semilogarithmic plot is 0.00708 hr^{-1}. The experiment was conducted for twenty-four hours, and COD removal followed the trend established during the 12-hour period shown. At the end of twelve hours, efficiency of acetone removal under quiescent conditions was 17.2 per cent.

The results of acetone removal by the joint action of physical stripping and metabolism by an acetone-acclimated biomass are represented in Figures 17, 18, 19, and 20, at airflow rates of 4000, 2000, 1000, and 500 cc/min, respectively.

In these experiments certain common features were observed regardless of the airflow rate and level of initial biological solids concentration. Aceone, as measured by GLC, was removed more rapidly, and hence was exhausted earlier than the total COD. Although this result

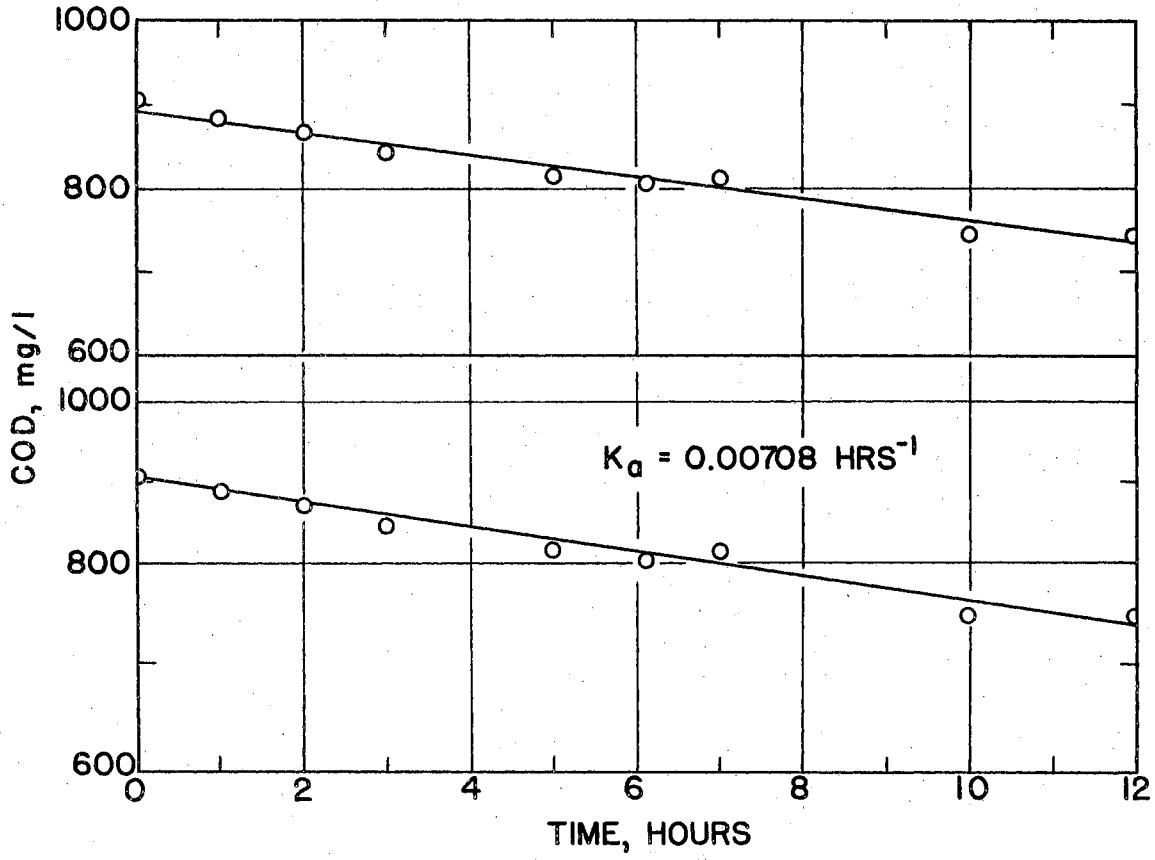


Figure 16 - Stripping of acetone (batch experiment) under quiescent conditions (zero airflow rate).

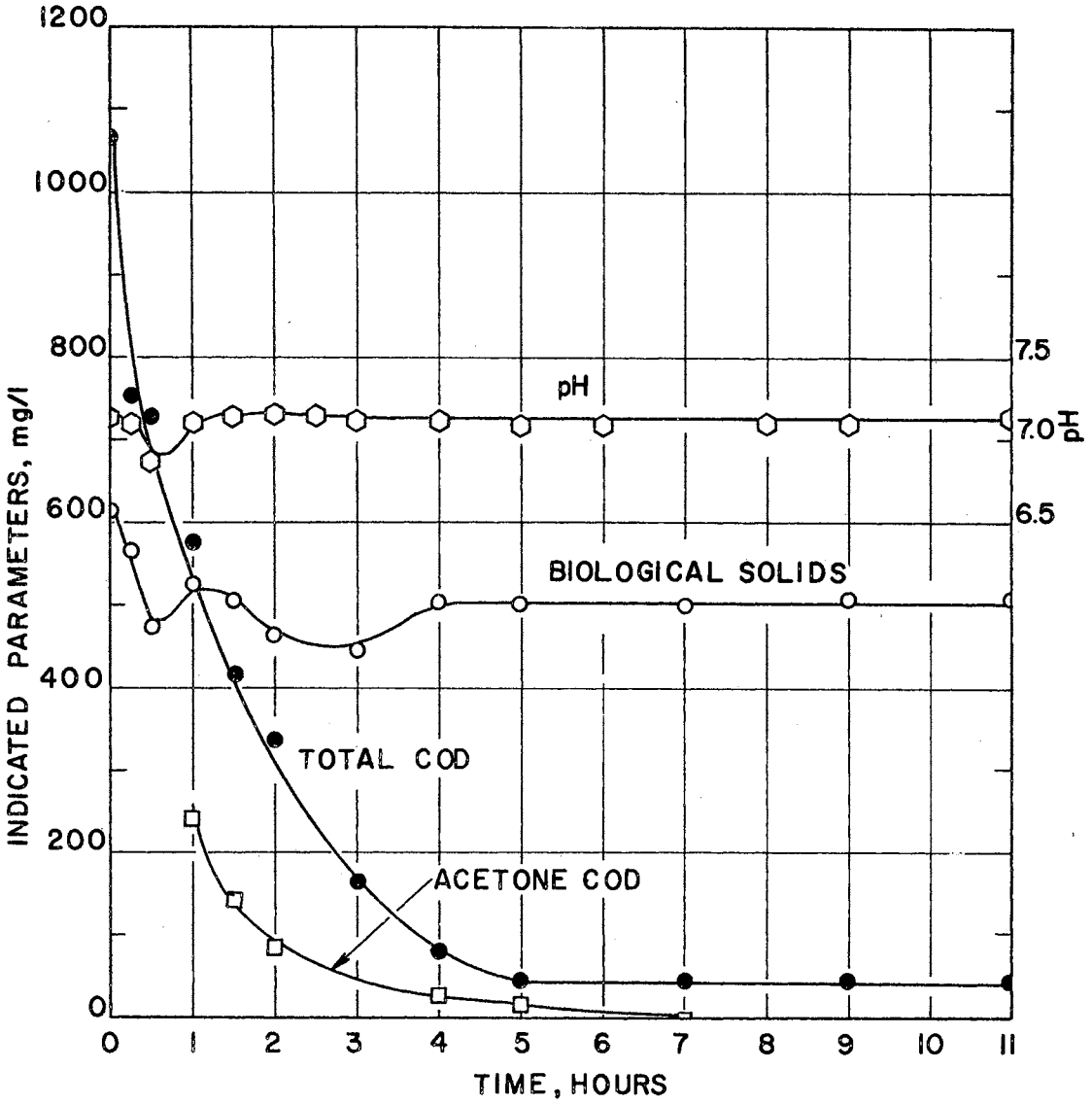


Figure 17 - Removal of acetone by stripping and biological metabolism (batch experiment) at an airflow rate of 4000 cc/min/l.

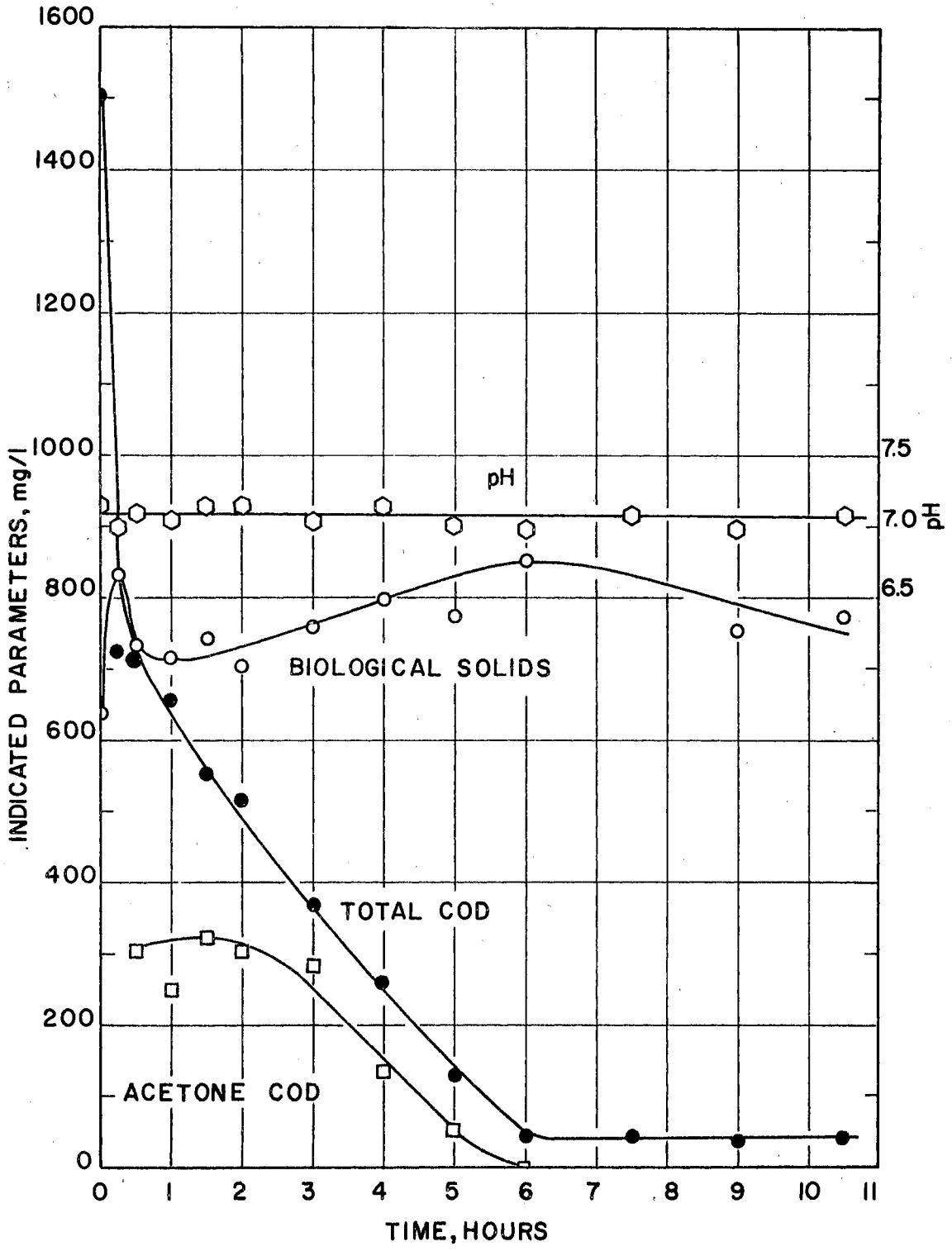


Figure 18 - Removal of acetone by stripping and biological metabolism (batch experiment) at an airflow rate of 2000 cc/min/l.

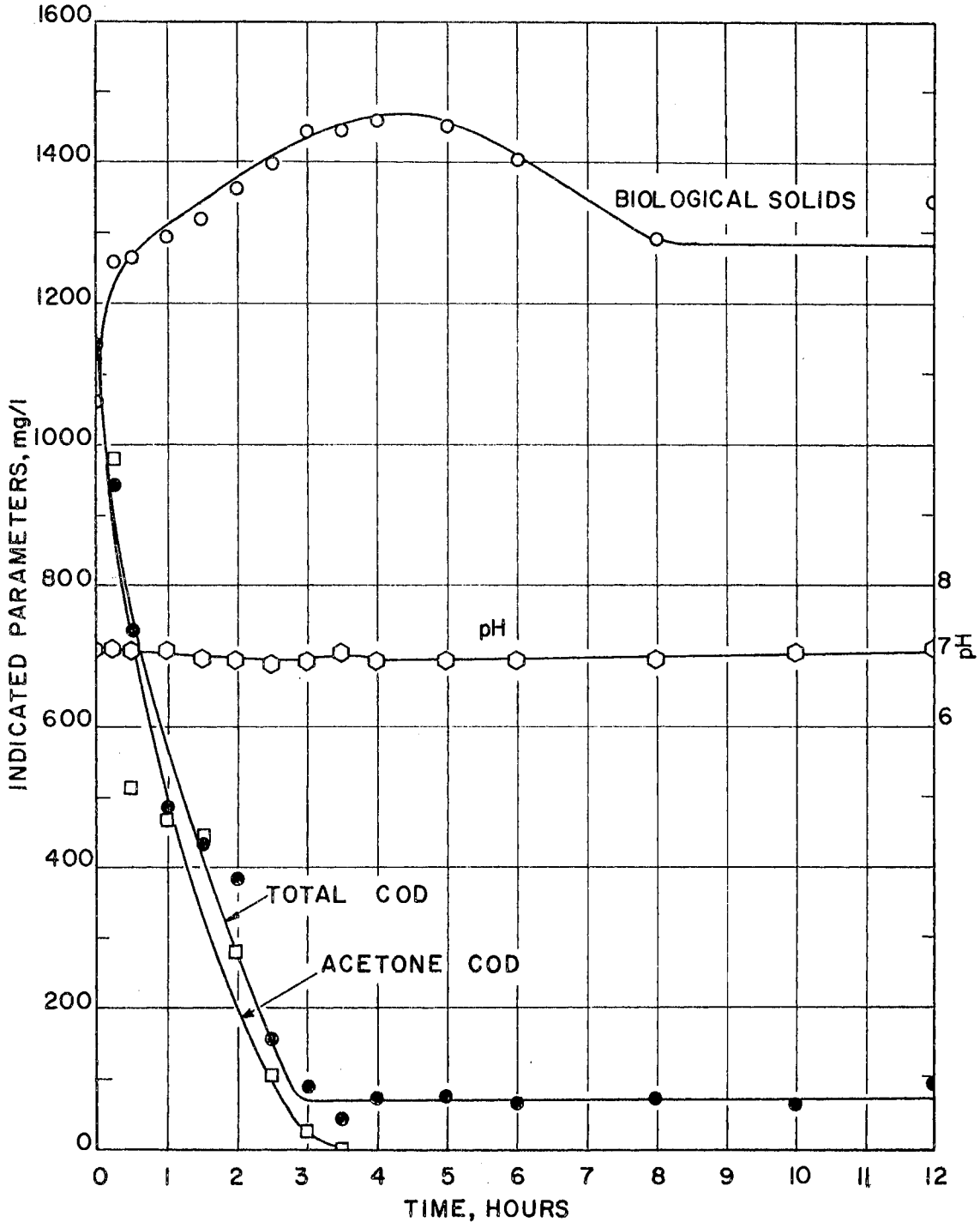


Figure 19 - Removal of acetone by stripping and biological metabolism (batch experiment) at an airflow rate of 1000 cc/min/l.

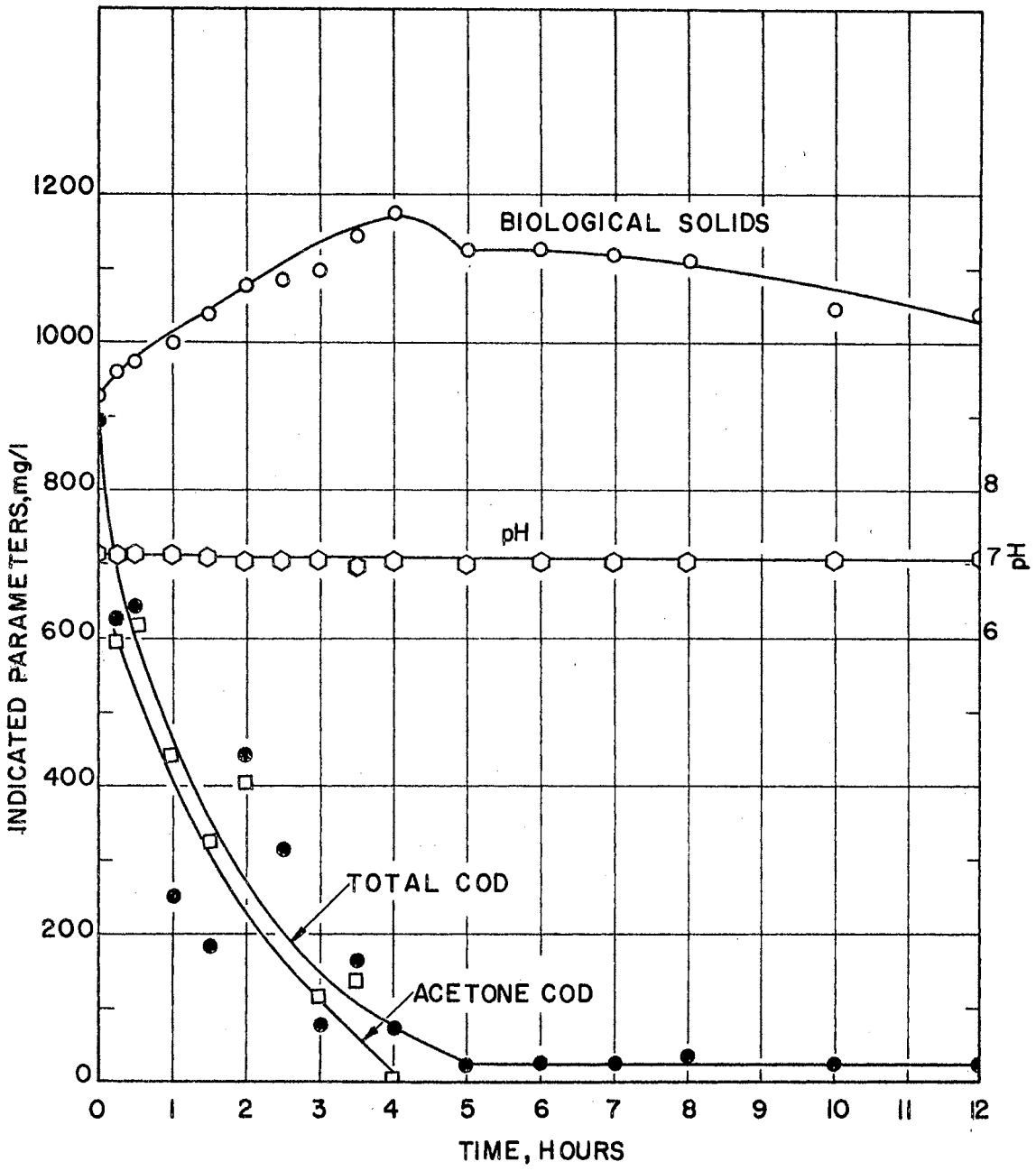


Figure 20 - Removal of acetone by stripping and biological metabolism (batch experiment) at an airflow rate of 500 cc/min/l.

attests to the accumulation of metabolic intermediates and/or endproducts, they were not detected by the GLC analyses on filtrates, i.e., no peaks other than acetone were found. However, only the Poly Pak-2 column was used. Except during the experiment at 4000 cc/min airflow rate, biological solids increased until the exogenous carbon source approached exhaustion, and thereafter declined and later attained a relatively stable value during the remainder of the run.

The pH of filtrates in all cases remained at approximately 7.0. From Figure 17, the overall treatment efficiency at five hours after the start of aeration is 96 per cent. A residual COD of 45 mg/l persisted in the system. This experiment was conducted for twenty-four hours, but the residual COD did not decrease any further.

For Figures 18, 19, and 20, the combined efficiencies at the point of maximum solids production are 97, 93.6, and 92 per cent, respectively. Another experiment for dual removal by stripping and biological solids was run at an airflow of 1000 cc/min with 450 mg/l of initial solids; the results are not shown here. The overall removal efficiency at the point of maximum solids production for that run was 96.6 per cent.

Methyl Ethyl Ketone

The stripping of methyl ethyl ketone at airflow rates of 4000, 2000, and 1000 cc/min is shown in Figures 21, 22, and 23, respectively. It is obvious from the semilogarithmic plots that methyl ethyl ketone was stripped in accordance with first order kinetics.

Two additional experiments were made at 4000 cc/min airflow with different initial COD concentrations (2317 and 920 mg/l MEK). The stripping constants calculated from these runs were in close agreement with the value calculated for the data shown in Figure 21. The values

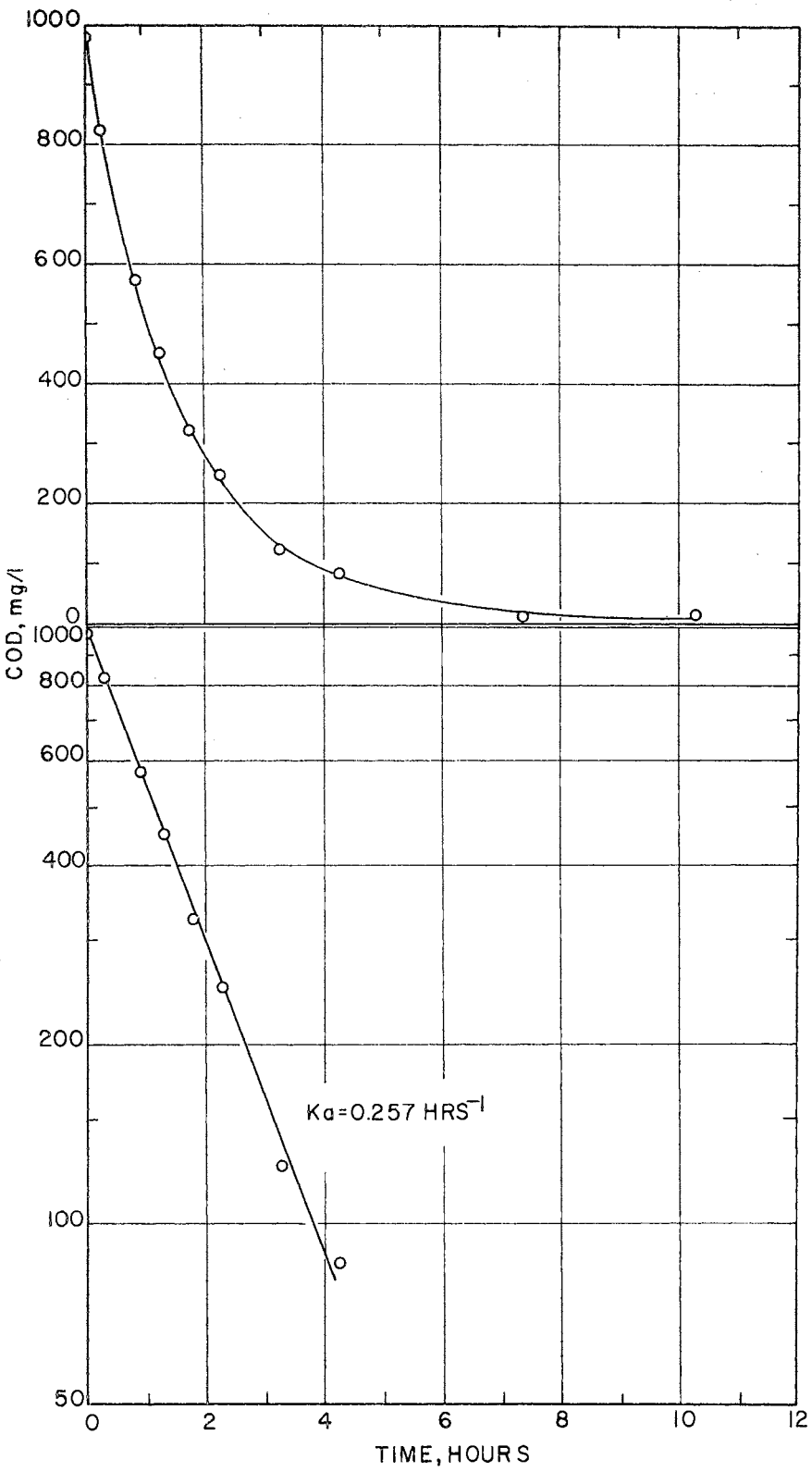


Figure 21 - Air stripping of methyl ethyl ketone under batch conditions at 4000 cc/min/l.

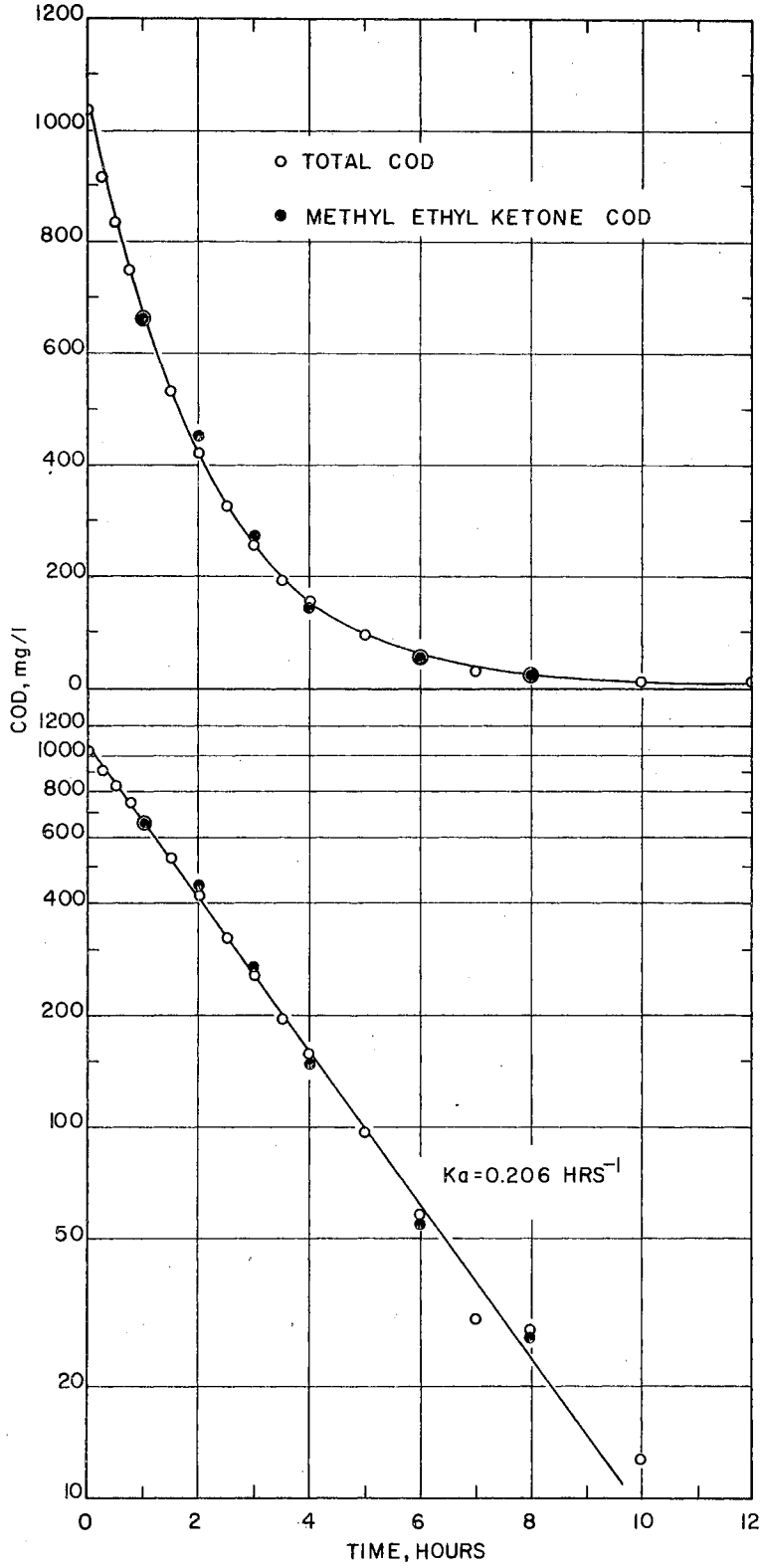


Figure 22 - Air stripping of methyl ethyl ketone under batch conditions at 2000 cc/min/l.

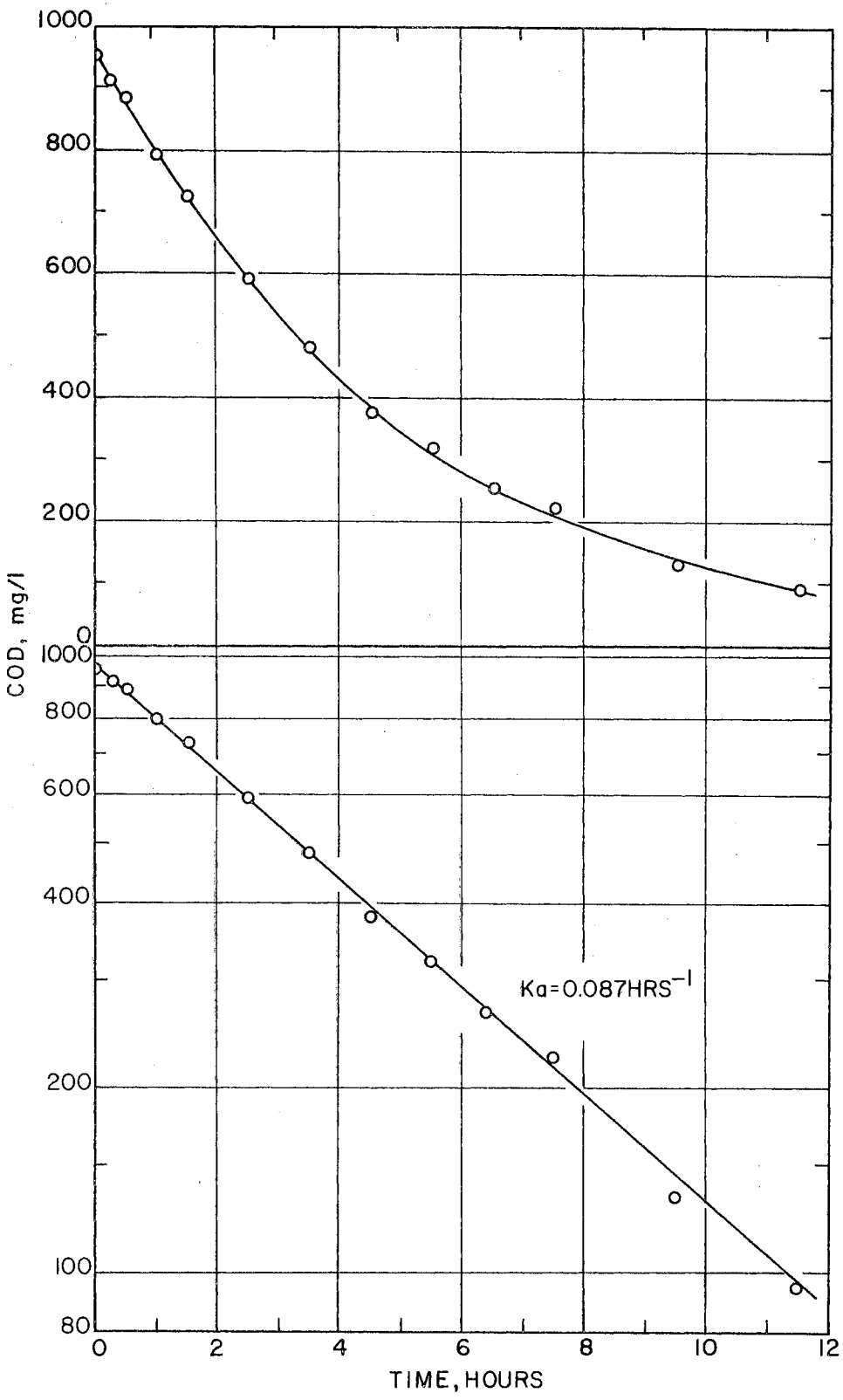


Figure 23 - Air stripping of methyl ethyl ketone under batch conditions at 1000 cc/min/l.

of the stripping constants are given on the semilogarithmic plot in each figure; they are 0.257, 0.206, and 0.087 hr^{-1} for airflow rates of 4000, 2000, and 1000 cc/min, respectively.

Figure 22 (airflow = 2000 cc/min) shows the results of GLC analysis performed on samples to check for evidence of possible oxidation products during stripping. As can be seen from both the arithmetic and semilogarithmic plots, there was no indication for the autoxidation of MEK under the mild oxidizing conditions of the stripping experiment.

The stripping characteristics of methyl ethyl ketone at an airflow rate of 500 cc/min with and without addition of disodium hydrogen phosphate are shown in Figure 24. It is apparent from the semilogarithmic plot that the addition of the disodium hydrogen phosphate accelerated the removal rate. Both systems obey first order rate kinetics. With MEK alone, the stripping constant was 0.0623 hr^{-1}, whereas with the addition of disodium hydrogen phosphate the constant was 0.0795 hr^{-1}, representing a 1.28-fold increase in the removal rate.

Figure 25 shows the methyl ethyl ketone removal curve under quiescent conditions. Both the arithmetic and semilogarithmic plots could be fitted as straight lines. The slope of the line calculated from the semilogarithmic plot yielded a stripping constant for methyl ethyl ketone of 0.00718 hr^{-1}. Eighteen per cent of the methyl ethyl ketone was removed by the end of twelve hours, compared to 99 per cent in $7\frac{1}{3}$ hours at an airflow rate of 4000 cc/min, 99 per cent in ten hours at an airflow rate of 2000 cc/min, 89 per cent in eleven and one-half hours at 1000 cc/min (97 per cent in twenty-four hours), 79.6 per cent in ten and three-fourths hours (97 per cent in twenty-four hours) at an airflow rate of 500 cc/min.

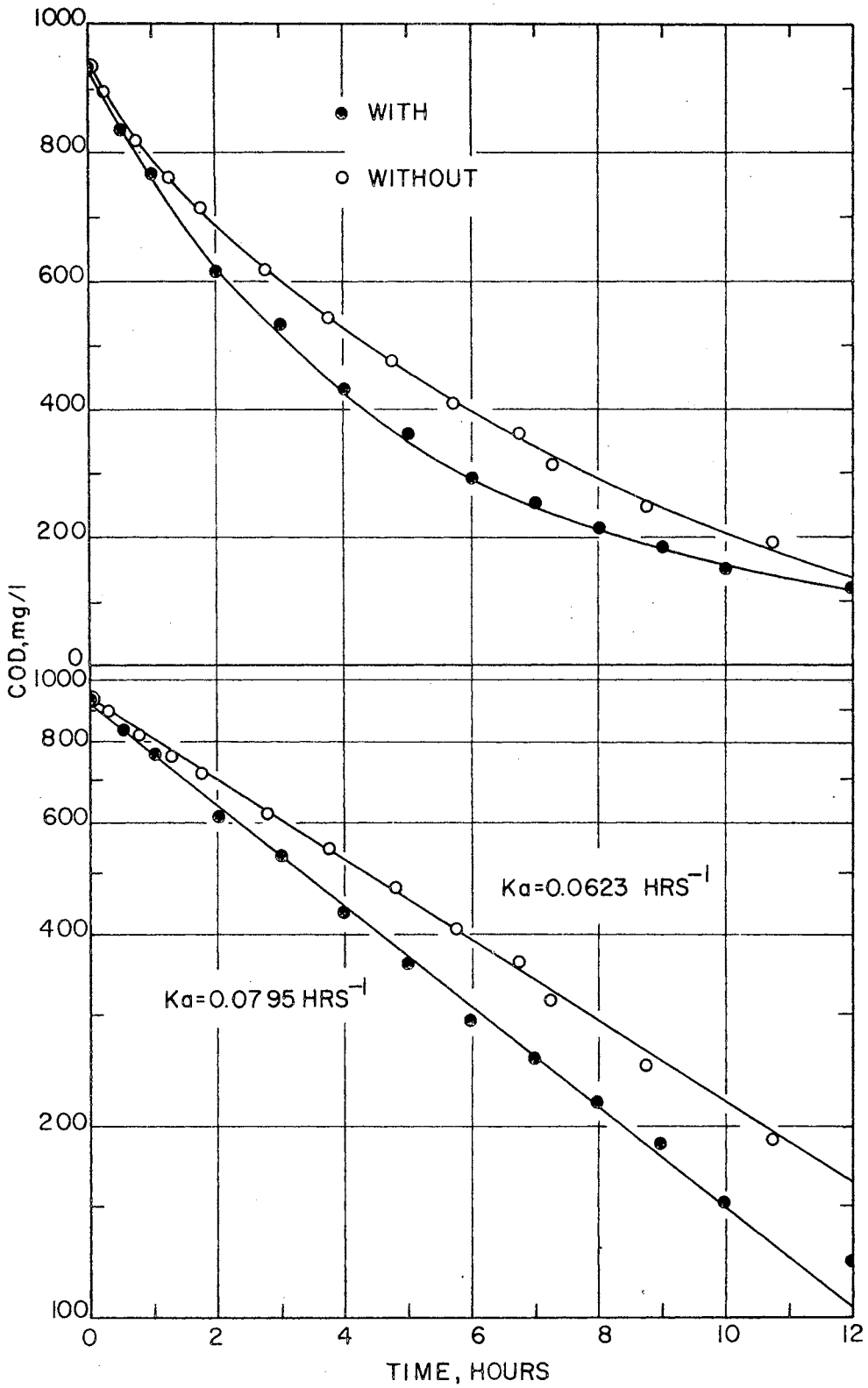


Figure 24 - Air stripping of methyl ethyl ketone with and without disodium hydrogen phosphate under batch conditions at 500 cc/min/l.

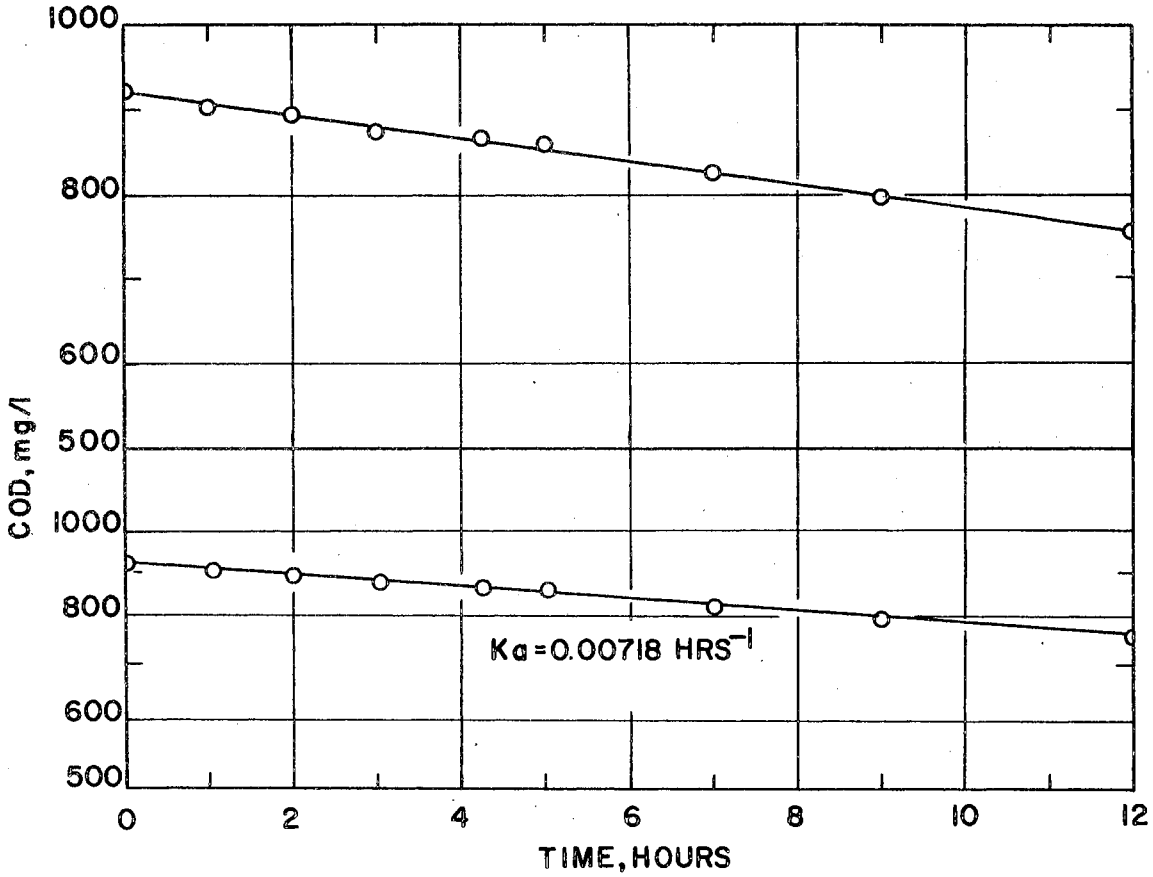


Figure 25 - Stripping of methyl ethyl ketone (batch experiment) under quiescent conditions (zero airflow rate).

Figures 26, 27, 28, and 29 show the removal patterns for MEK for combined stripping and biological actions at airflow rates of 4000, 2000, 1000, and 500 cc/min, respectively. In Figure 26 it is clearly shown that methyl ethyl ketone disappeared from the medium more rapidly than did the total COD. However, the results of the GLC analyses on the filtrates showed that except for the substrate peak, no others were detectible. In all systems the peak in biological solids production corresponded to the time of exhaustion of COD. The treatment efficiencies at these points were 96, 99.1, 97.5, and 94.1 per cent, respectively, for the systems shown in Figures 26, 27, 28, and 29. Except for the lowest airflow rate in the series, 500 cc/min, for which the removal efficiency was calculated at five hours, calculations were based on the 2½-hour sampling.

Mixture of Acetone and Methyl Ethyl Ketone

Batch stripping of a mixture of acetone and methyl ethyl ketone at approximately the same initial concentrations was investigated at an airflow rate of 2000 cc/min. The results are shown in Figure 30. From the semilogarithmic plots (Figure 30, lower half) it is obvious that the mixture as well as the individual compounds were stripped in accordance with the first order kinetics. Further, the stripping constants of the compounds calculated from the mixture are nearly the same as those when these compounds were stripped separately at an airflow rate of 2000 cc/min. From GLC analyses on samples from the mixture only acetone and methyl ethyl ketone peaks were detected, indicating that stripping of the mixture did not result in autoxidation. From pH measurements of samples during the course of the experiment it was evident that stripping occurred at constant and neutral pH (average 7.10),

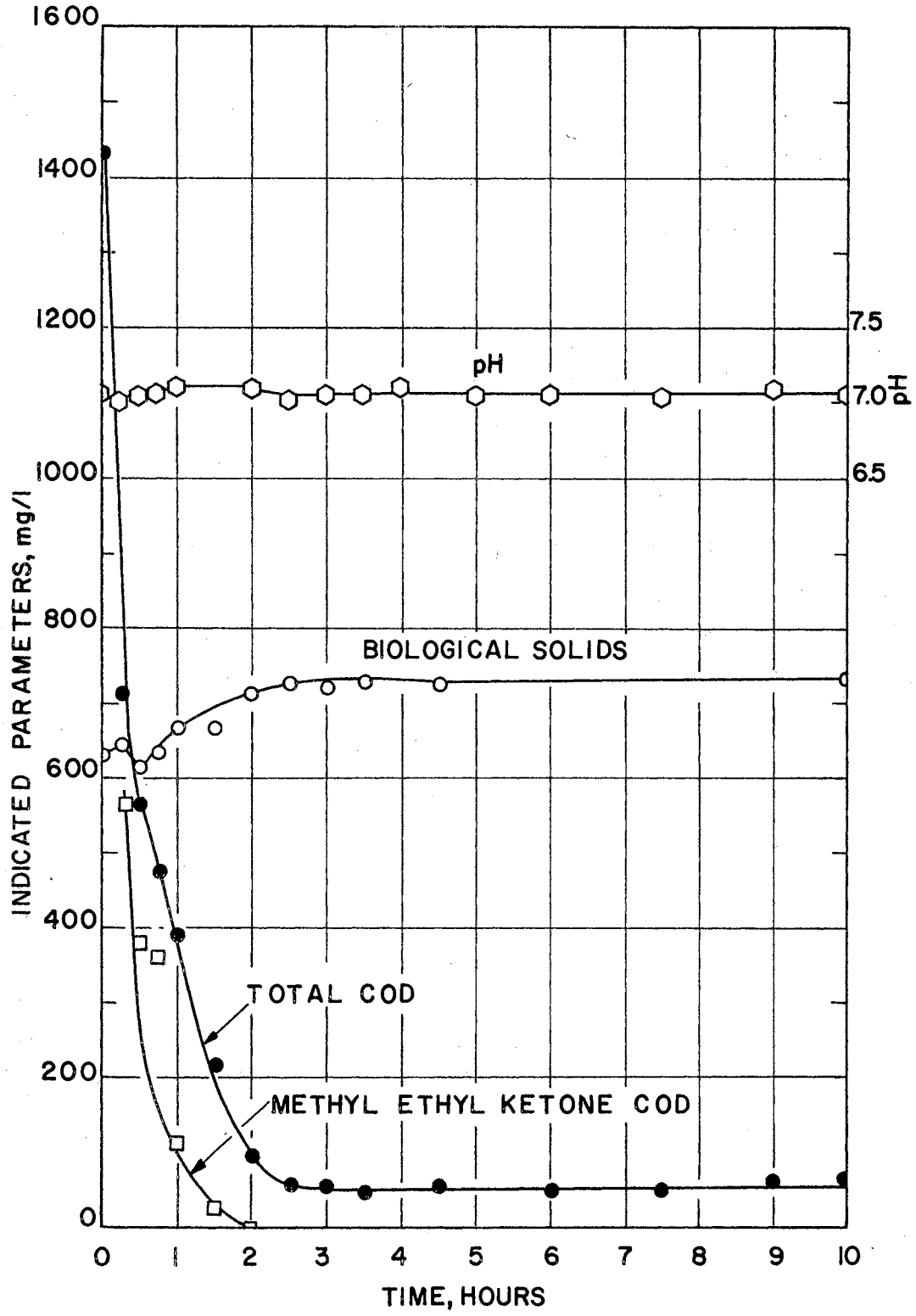


Figure 26 - Removal of methyl ethyl ketone by stripping and biological metabolism (batch experiment) at an airflow rate of 4000 cc/min/l.

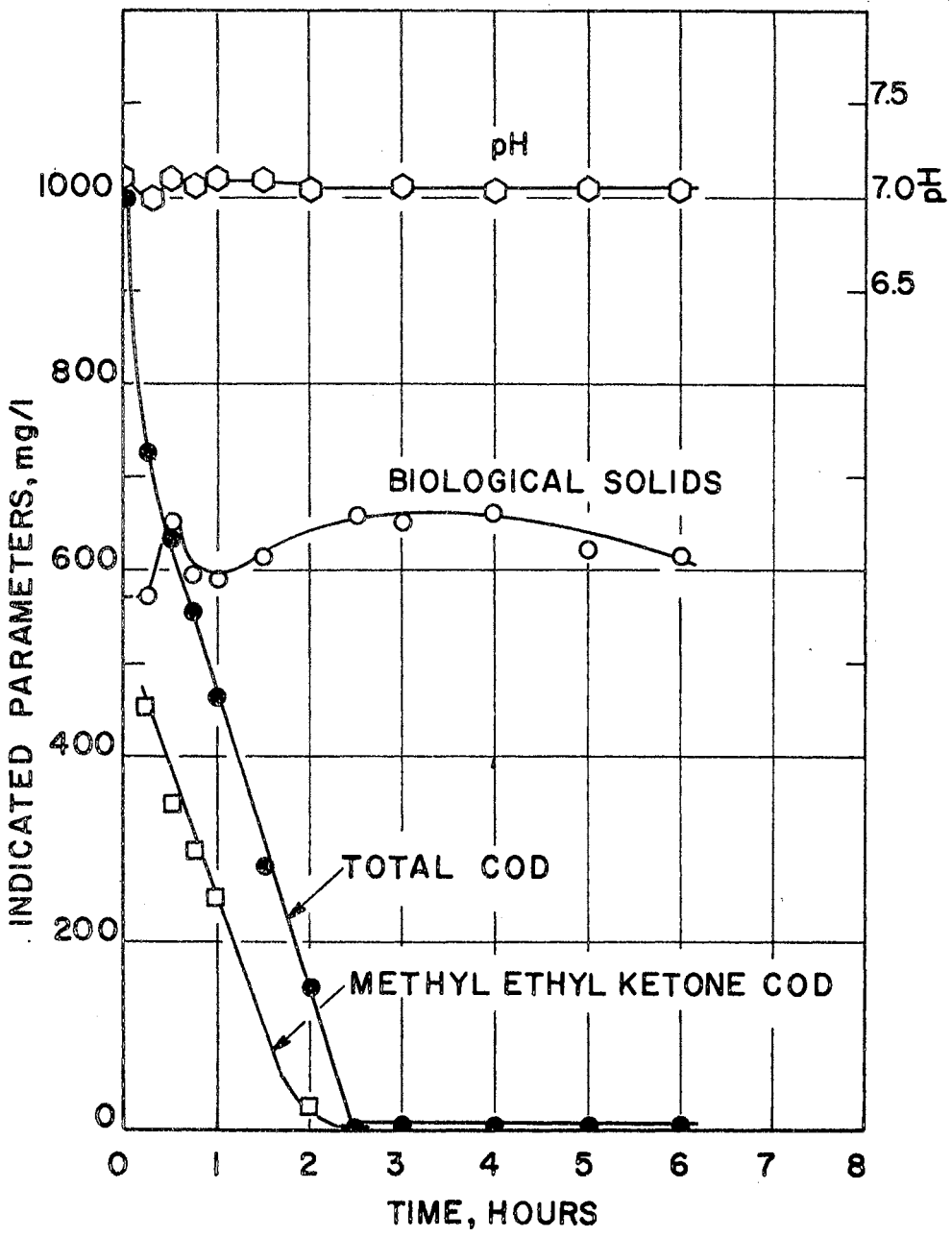


Figure 27 - Removal of methyl ethyl ketone by stripping and biological metabolism (batch experiment) at an airflow rate of 2000 cc/min/l.

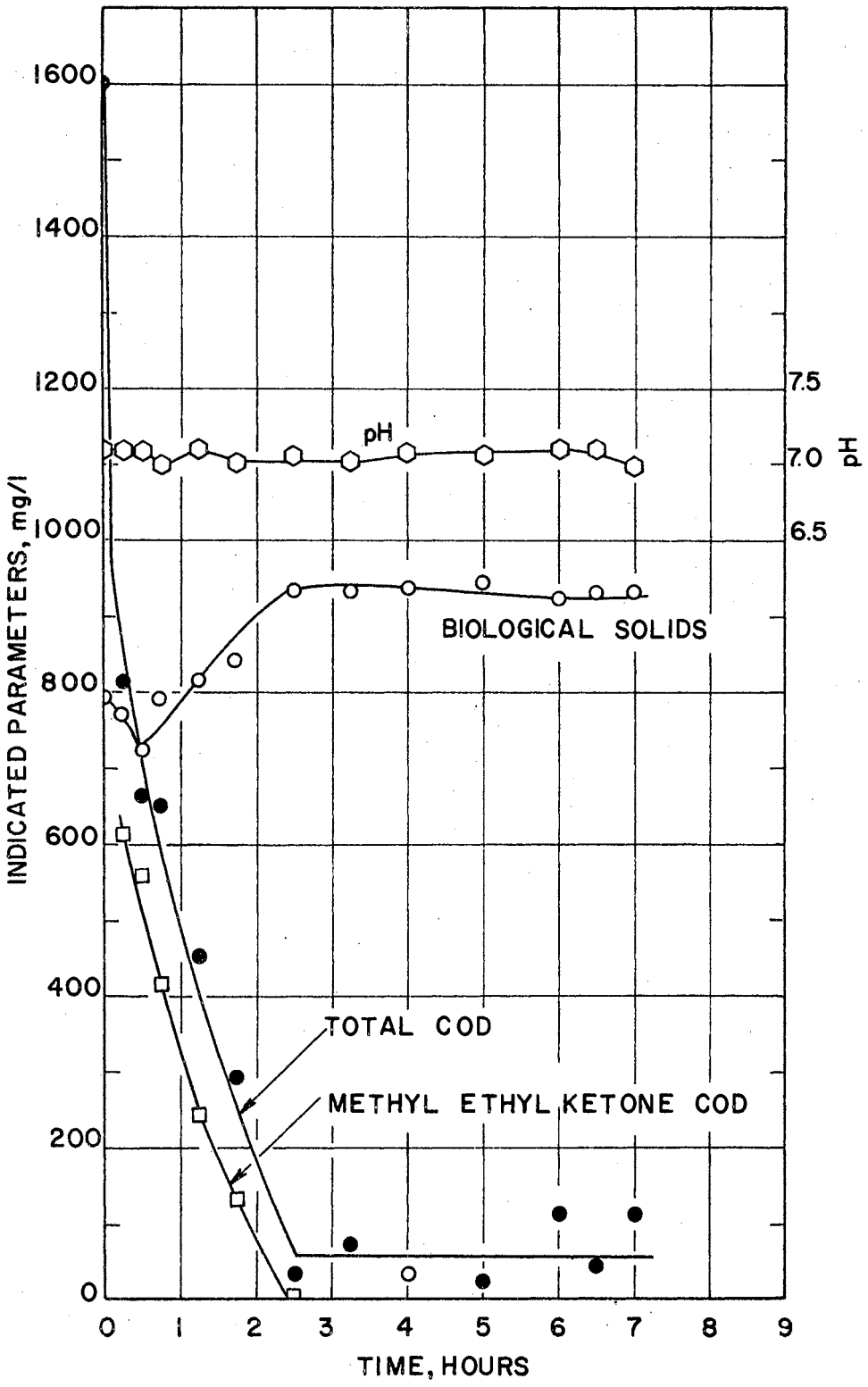


Figure 28 - Removal of methyl ethyl ketone by stripping and biological metabolism (batch experiment) at an airflow rate of 1000 cc/min/l.

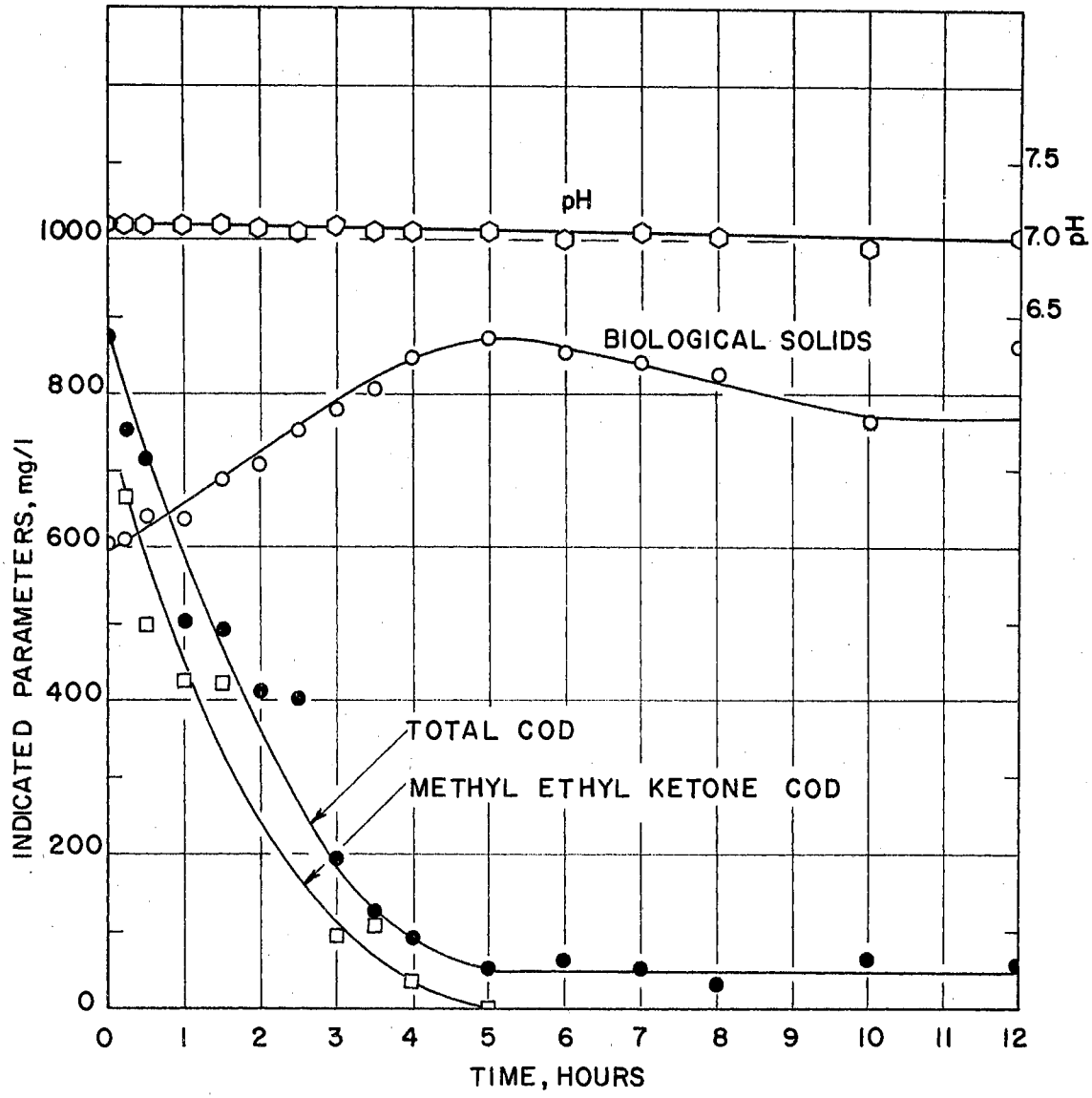


Figure 29 - Removal of methyl ethyl ketone by stripping and biological metabolism (batch experiment) at an airflow rate of 500 cc/min/l.

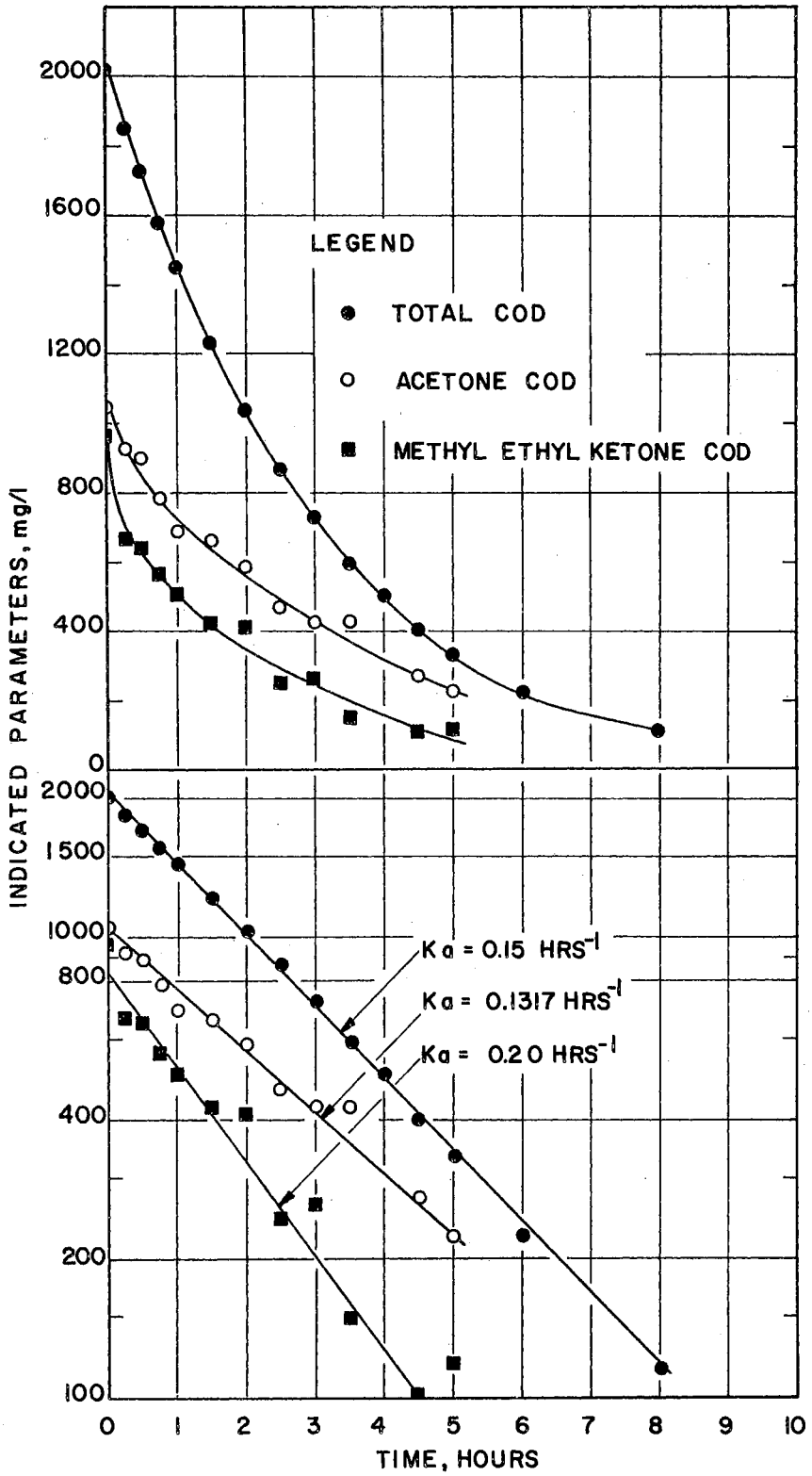


Figure 30 - Air stripping of a mixture of acetone and methyl ethyl ketone under batch conditions at 2000 cc/min/l.

i.e., there was no evidence for acid formation.

Propionaldehyde

The results for stripping propionaldehyde at airflow rates of 4000, 2000, and 1000 cc/min are shown in Figures 31, 32, and 33. From the semilogarithmic plot of the GLC data, shown in Figure 32, it appears that except at the lower concentrations, propionaldehyde was eliminated in accordance with first order kinetics and the removal constant thus calculated was 0.303 hr^{-1}. At lower concentrations there was a significant deviation between the COD data and the GLC data; however, no compound other than propionaldehyde was detected in any of the samples using the Poly Pak-2 column. On the basis of the COD data (see semilog plots) it would appear that at airflow rates of 4000, 2000, and 1000 cc/min, propionaldehyde was not stripped in accordance with first order kinetics. Since there was some evidence that the compound was eliminated at a first order rate, there would appear to be some basis for concluding that a small amount of autoxidation of propionaldehyde occurred and that the oxidation product was not strippable or, in any event, was less strippable than propionaldehyde.

Figure 34 shows the strippability of propionaldehyde at an airflow rate of 500 cc/min, with and without addition of disodium hydrogen phosphate. With the addition of disodium hydrogen phosphate, the removal of propionaldehyde is consistently slower than without it. Both the semilogarithmic plots indicate non-first order kinetics. At the end of ten hours the percent COD removal values are 85.4 without addition of phosphate compound, and 73.5 with the addition of phosphate compound. Thus, on this basis, there was an overall 1.6-fold retardation of removal efficiency, due to addition of disodium hydrogen phosphate.

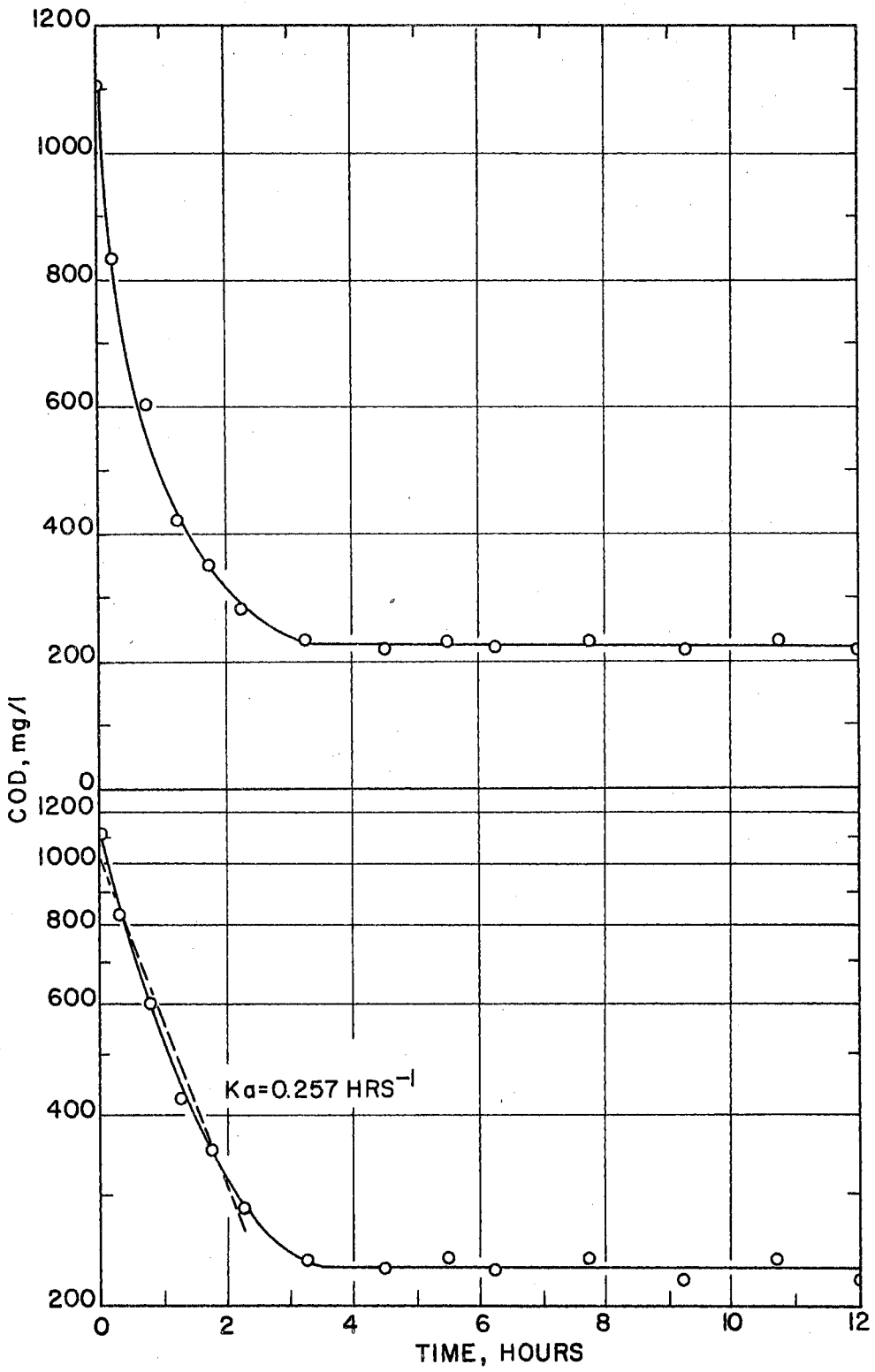


Figure 31 - Air stripping at propionaldehyde under batch conditions at 4000 cc/min/l.

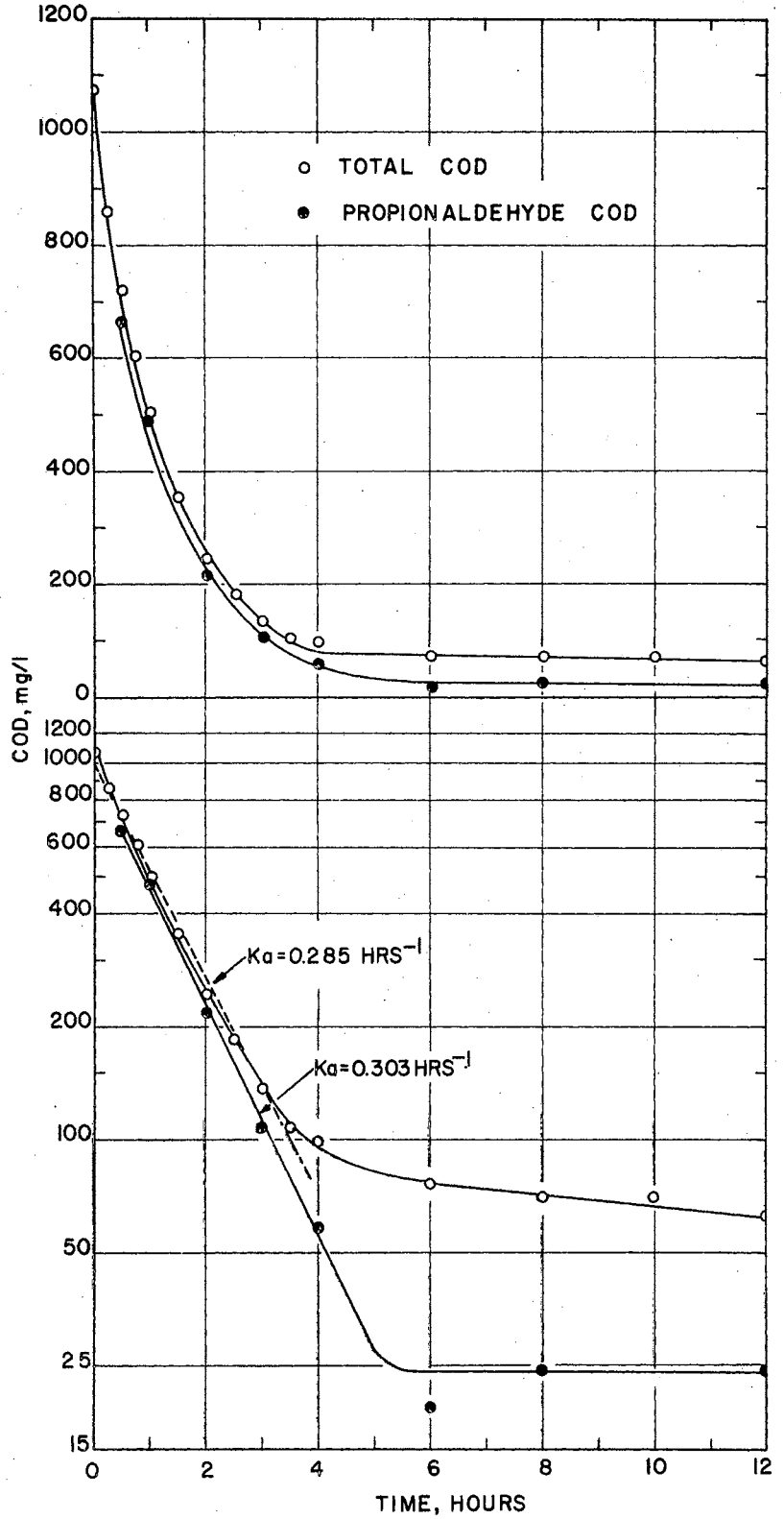


Figure 32 - Air stripping of propionaldehyde under batch conditions at 2000 cc/min/l.

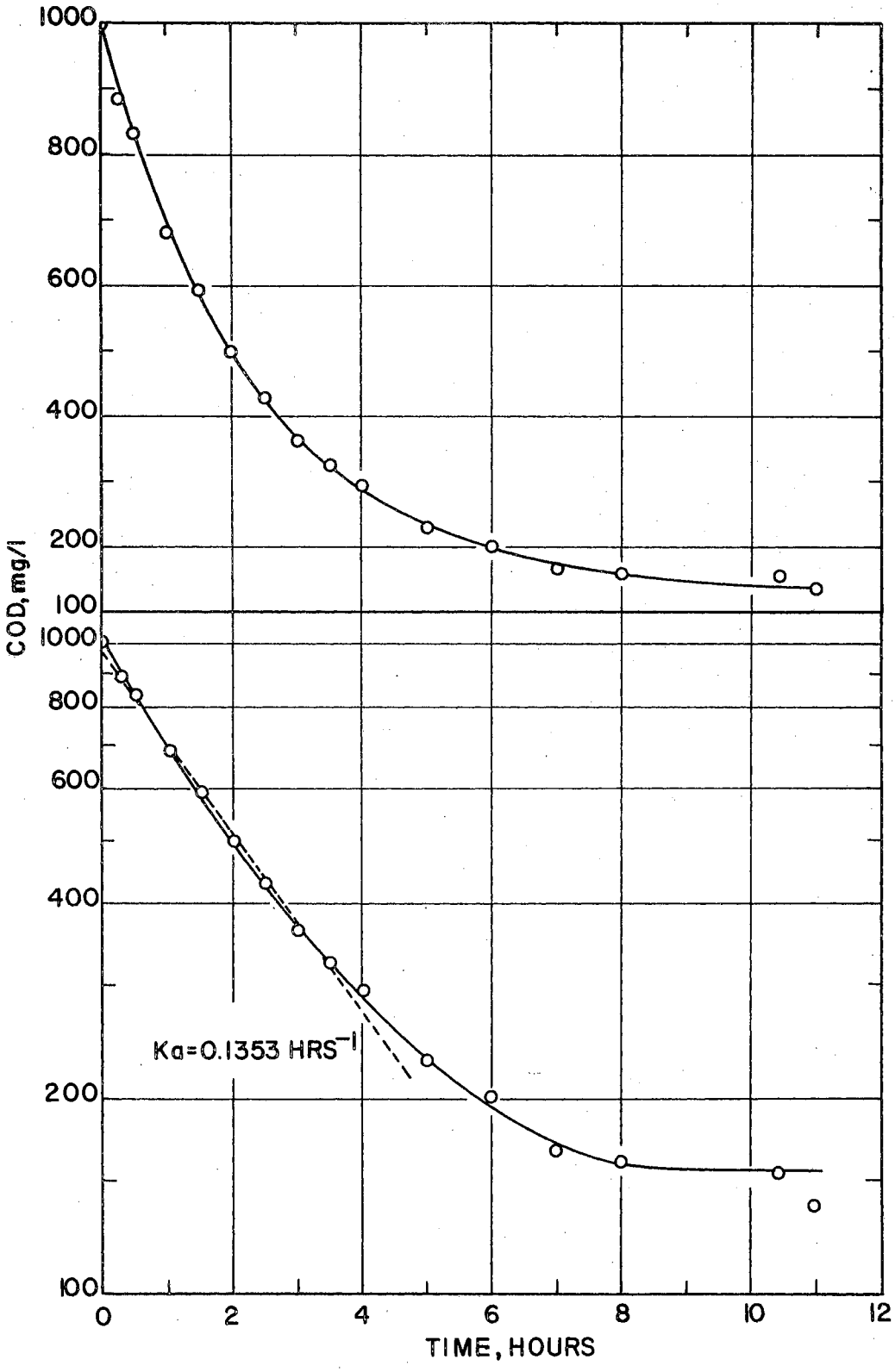


Figure 33 - Air stripping of propionaldehyde under batch conditions at 1000 cc/min/l.

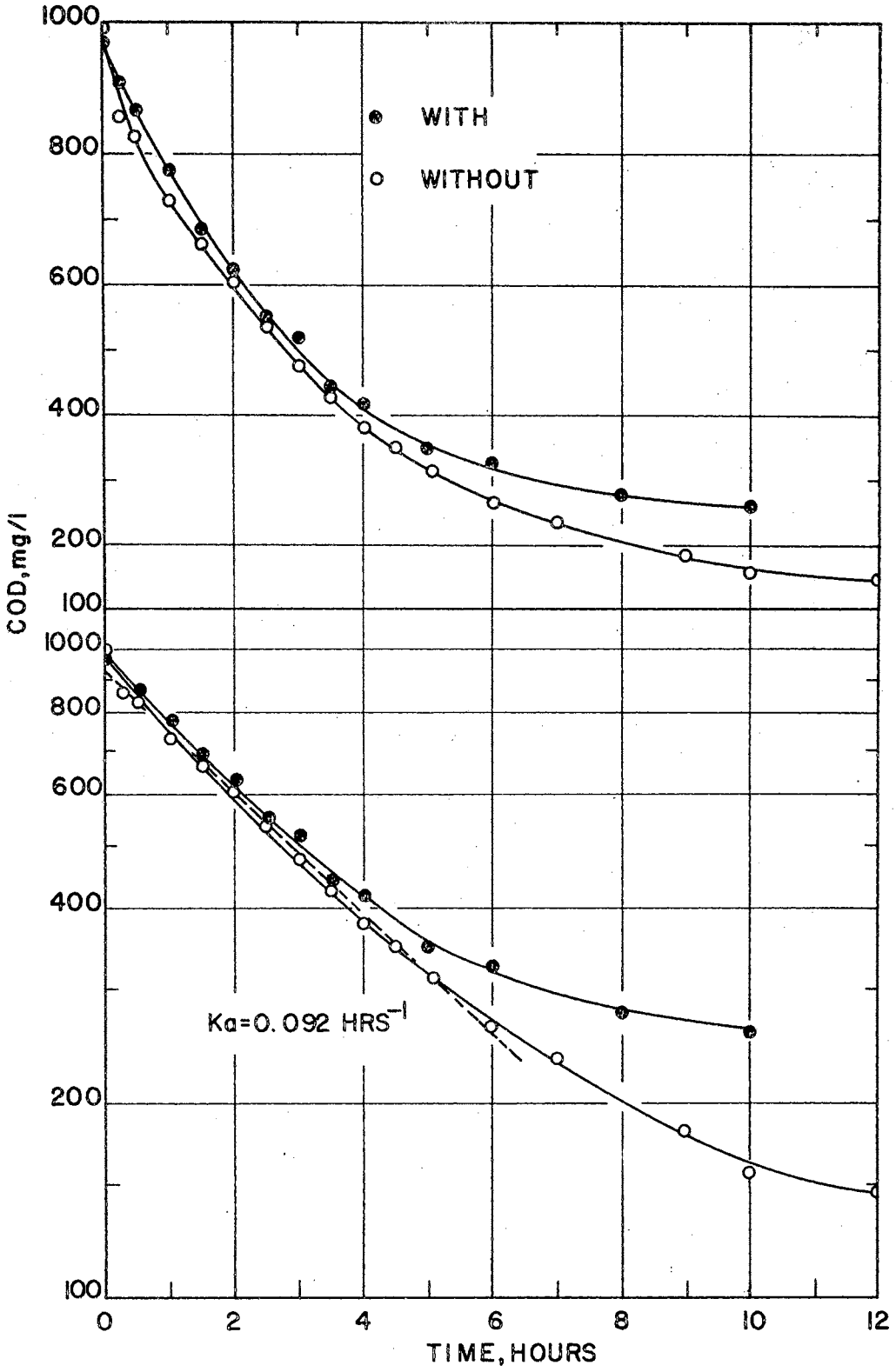


Figure 34 - Air stripping of propionaldehyde with and without disodium hydrogen phosphate under batch conditions at 500 cc/min/l.

The removal of propionaldehyde under quiescent conditions is shown in Figure 35. Both the arithmetic and the semilogarithmic plots give rise to a straight line. The stripping constant calculated from the semilogarithmic plot is 0.0115 hr^{-1}, and the propionaldehyde removal efficiency at the end of 11½ hours was 27 per cent.

The results for stripping plus biological action for propionaldehyde at airflow rates of 4000, 2000, 1000, and 500 cc/min are represented in Figures 36, 37, 38, and 39, respectively. Unlike the similar runs with ketones described previously, intermediates and/or endproducts in varying amounts were detected by GLC analysis on the filtrates. Certain characteristics were common to all four experiments; exhaustion of the externally-added substrate was much more rapid than that of the total COD and acidic metabolic intermediates and/or endproducts were produced. Intermediates and/or endproducts calculated as the difference between the total COD and the aldehyde COD are shown by broken lines to facilitate their comparison with the actual amount of intermediates and/or endproducts accounted for by the GLC analysis (shown at the top of the figures). From Figure 36 (airflow = 4000 cc/min), the COD removal efficiency at the point of maximum solids concentration was 92.1 per cent, and intermediates and/or end products detected were acetic, propionic, and isovaleric acids; acetic acid was present in the highest concentrations.

Figure 37 shows that the efficiency of propionaldehyde removal (calculated as COD at three hours) was 90.1 per cent, and the intermediates and/or endproducts detected were acetic, propionic, butyric, isobutyric, and isovaleric acids. Propionic, isovaleric, and acetic acids increased with time and were later exhausted from the medium.

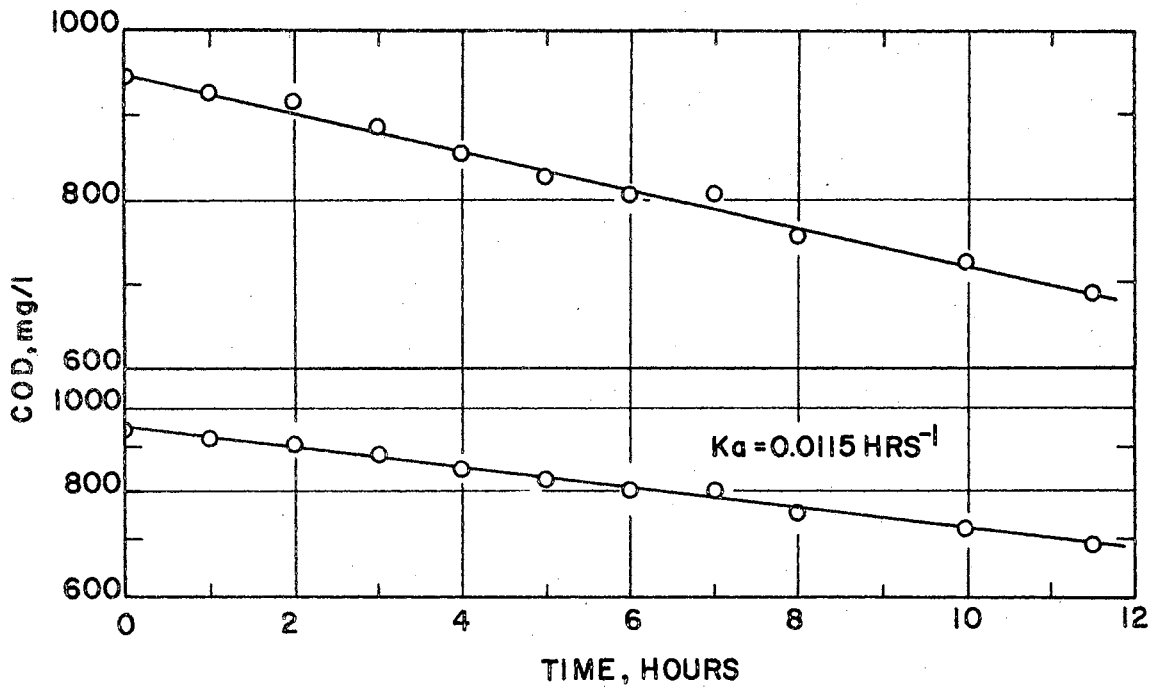


Figure 35 - Stripping of propionaldehyde (batch experiment) under quiescent conditions (zero airflow rate).

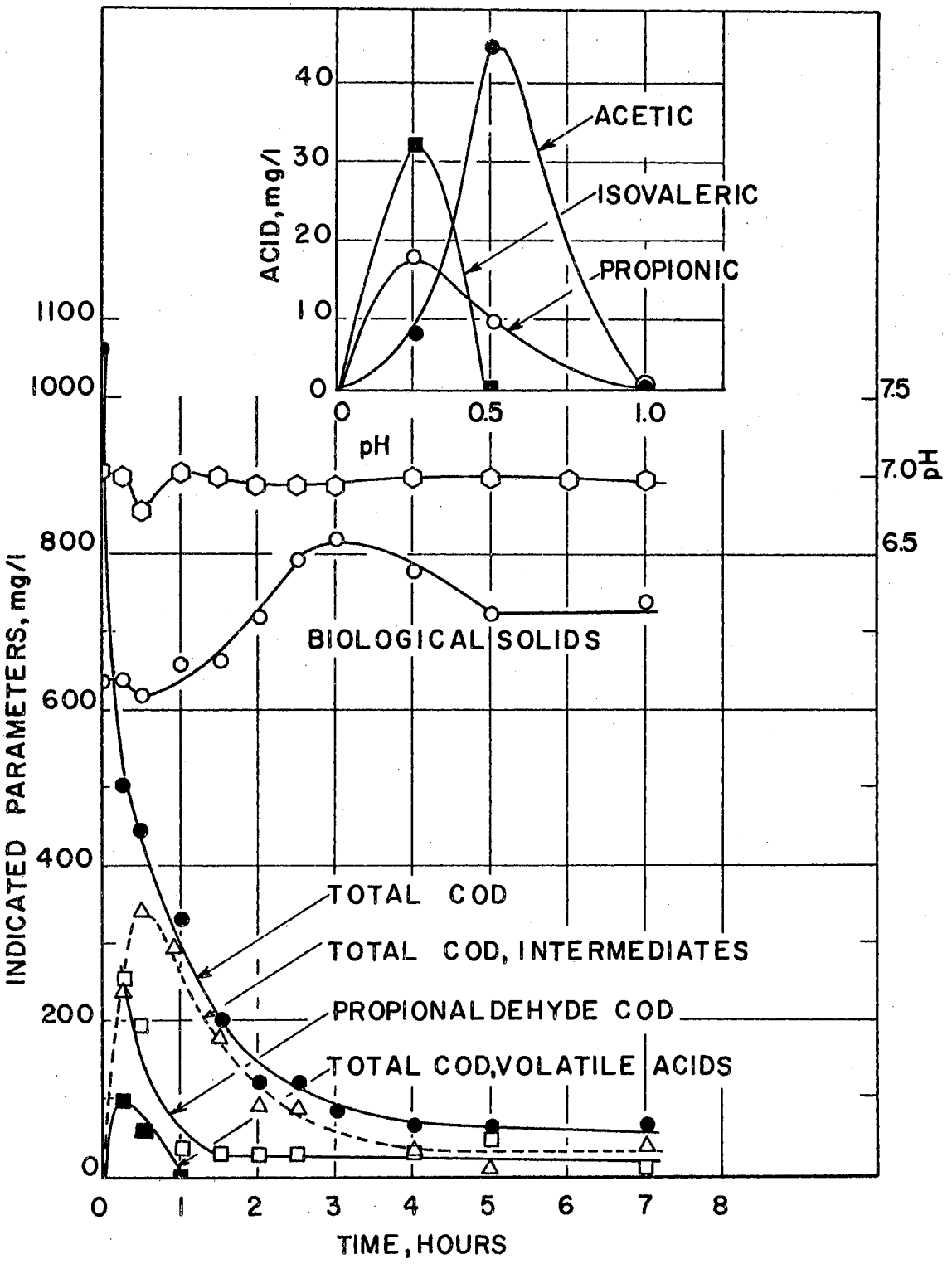


Figure 36 - Removal of propionaldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 4000 cc/min/l.

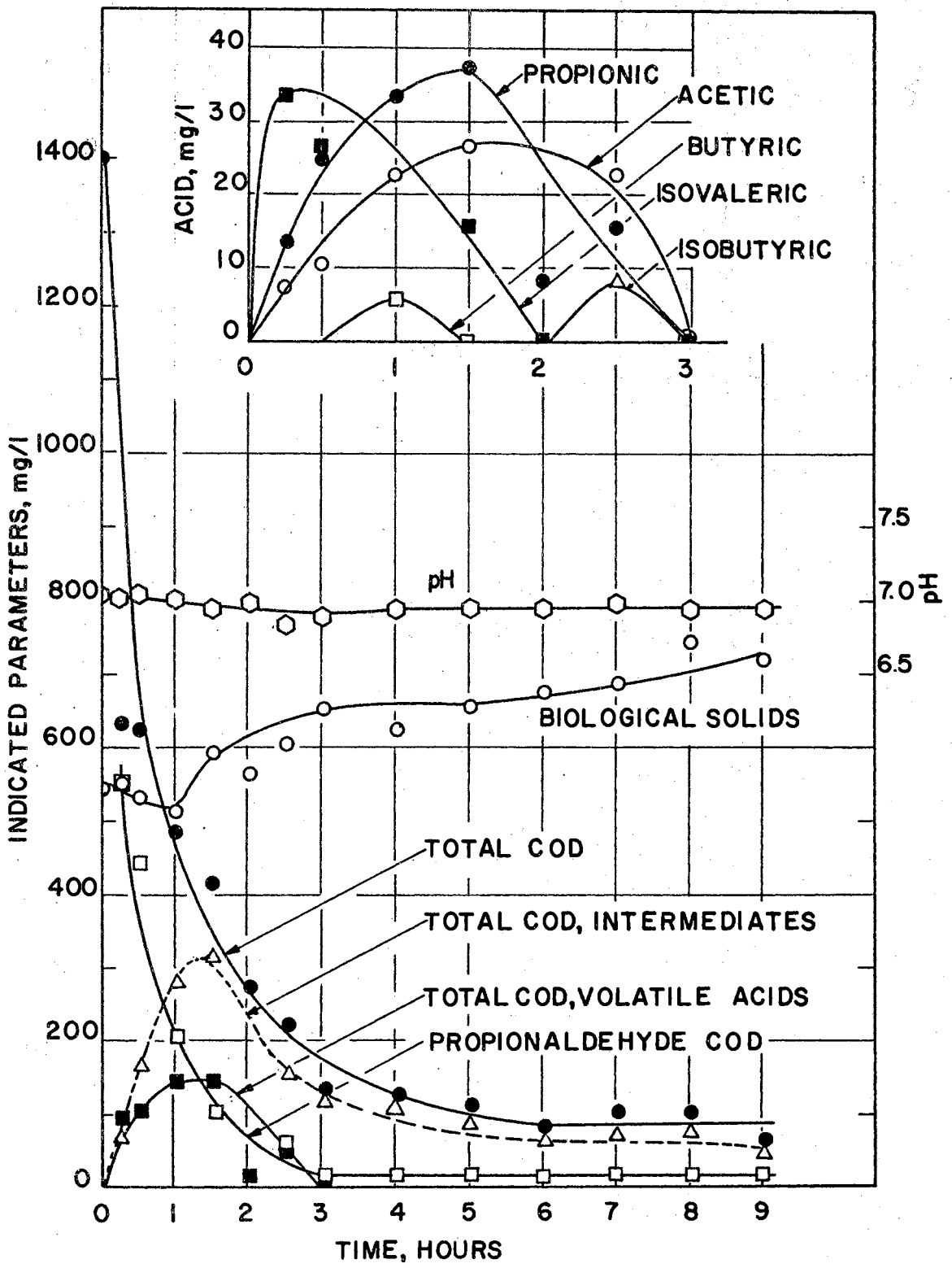


Figure 37 - Removal of propionaldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 2000 cc/min/l.

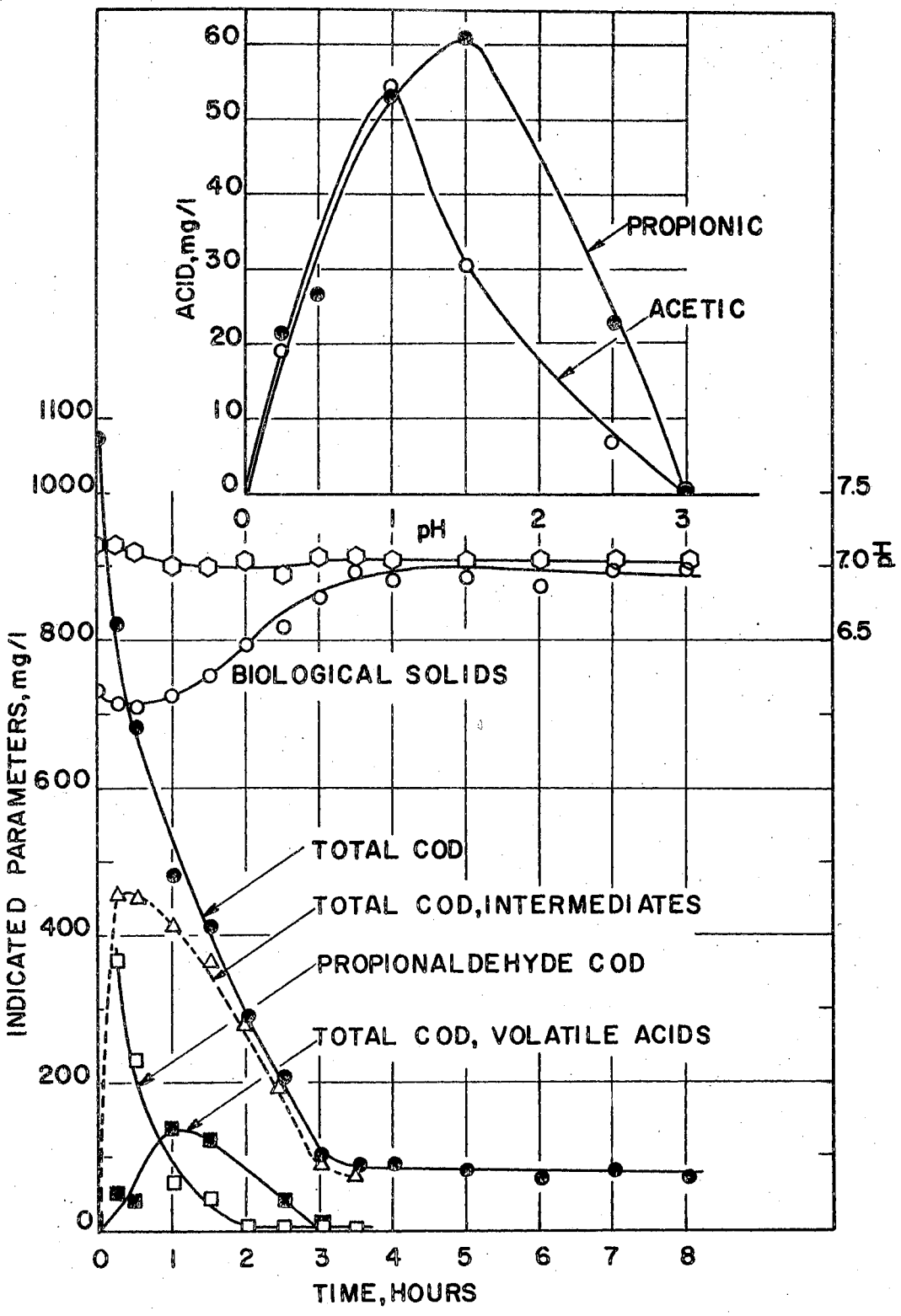


Figure 38 - Removal of propionaldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 1000 cc/min/l.

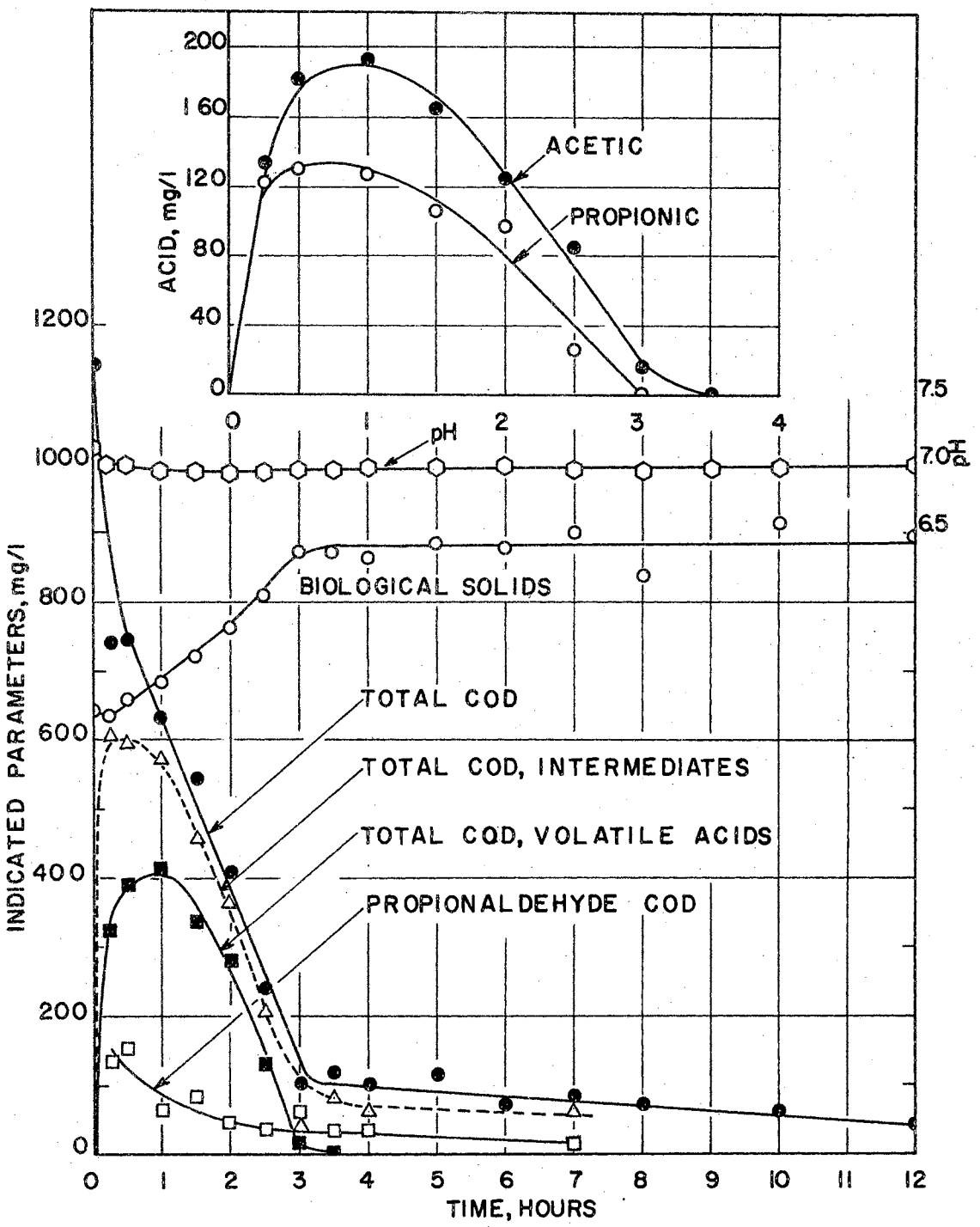


Figure 39 - Removal of propionaldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 500 cc/min/l.

Isovaleric acid was utilized completely at the end of two hours, whereas propionic and acetic acids were no longer detected in the filtrate at the end of three hours.

Figure 38 shows the results for stripping plus biological action at an airflow rate of 1000 cc/min. At the point of maximum solids production in the system, the overall treatment efficiency was 91.6 per cent. Acetic and propionic acids were detected in the filtrate and as the experiment progressed they were metabolized. In this case propionic acid attained a higher concentration than acetic acid.

At an airflow of 500 cc/min (Figure 39), acetic and propionic acids were detected in the filtrate during the period of active metabolism; they were later removed. In the latter part of the experiment most of the exogenous carbon source consisted of these carbon compounds.

Butyraldehyde

The stripping of butyraldehyde at airflow rates of 4000, 2000, 1000, and 500 cc/min is shown in Figures 40, 41, 42, and 43, respectively. In addition, Figure 41 shows the results of GLC analyses on samples taken during the experiment at an airflow rate of 2000 cc/min, and Figure 43 shows the effect of disodium hydrogen phosphate. From the semilogarithmic plots it may be seen that COD removal could be described by first order kinetics over approximately 90 per cent of the course of removal. However, as the COD remaining in solution decreased, there was an indication (at the lower concentrations) of divergence from first order kinetics. The fact that the butyraldehyde removal was not truly in accordance with kinetics of the first order is evident from a comparison of the COD and GLC data presented in Figure 41, which indicates that butyraldehyde was eliminated at a slightly faster rate than was the

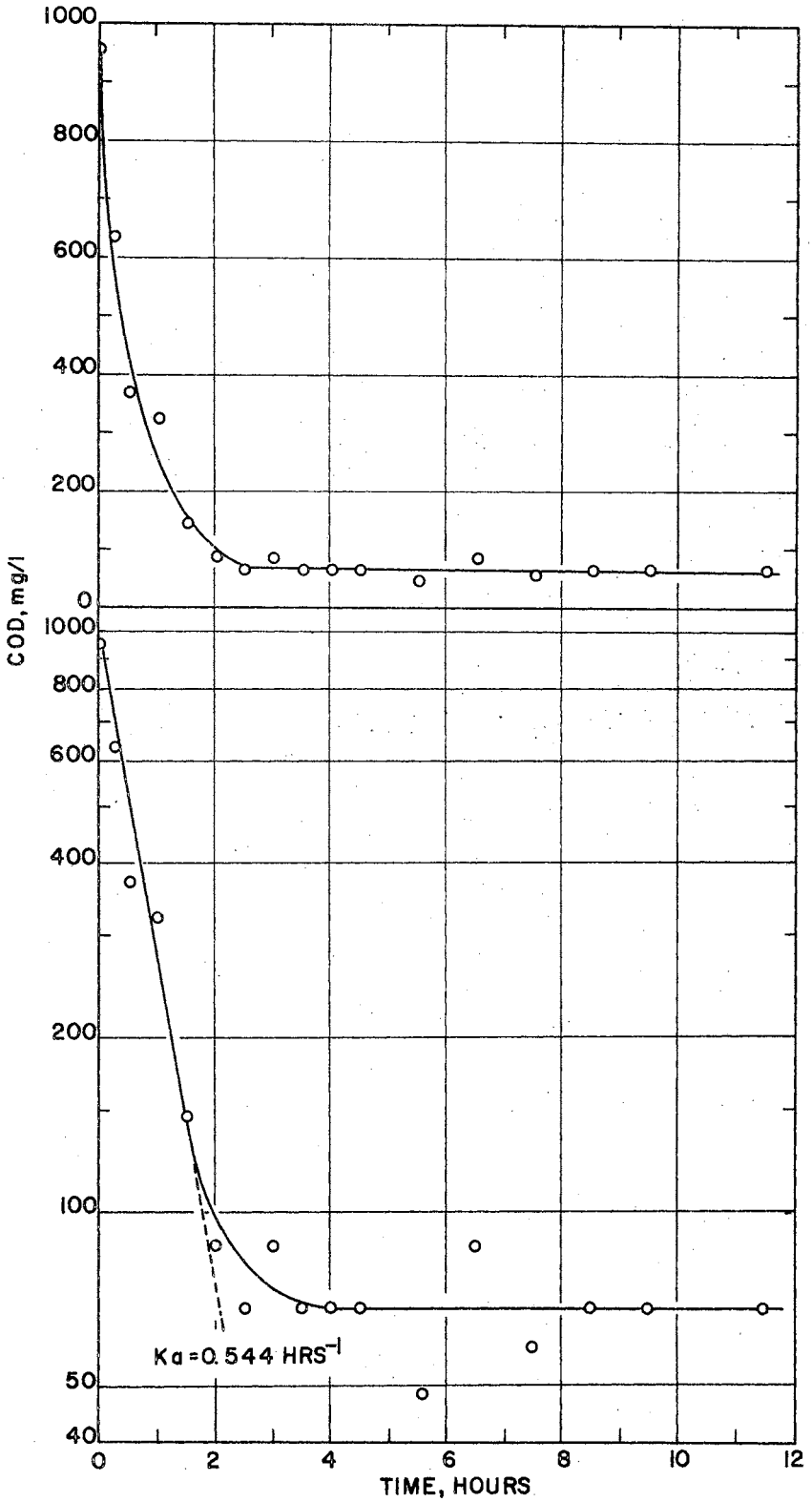


Figure 40 - Air stripping of butyraldehyde under batch conditions at 4000 cc/min/l.

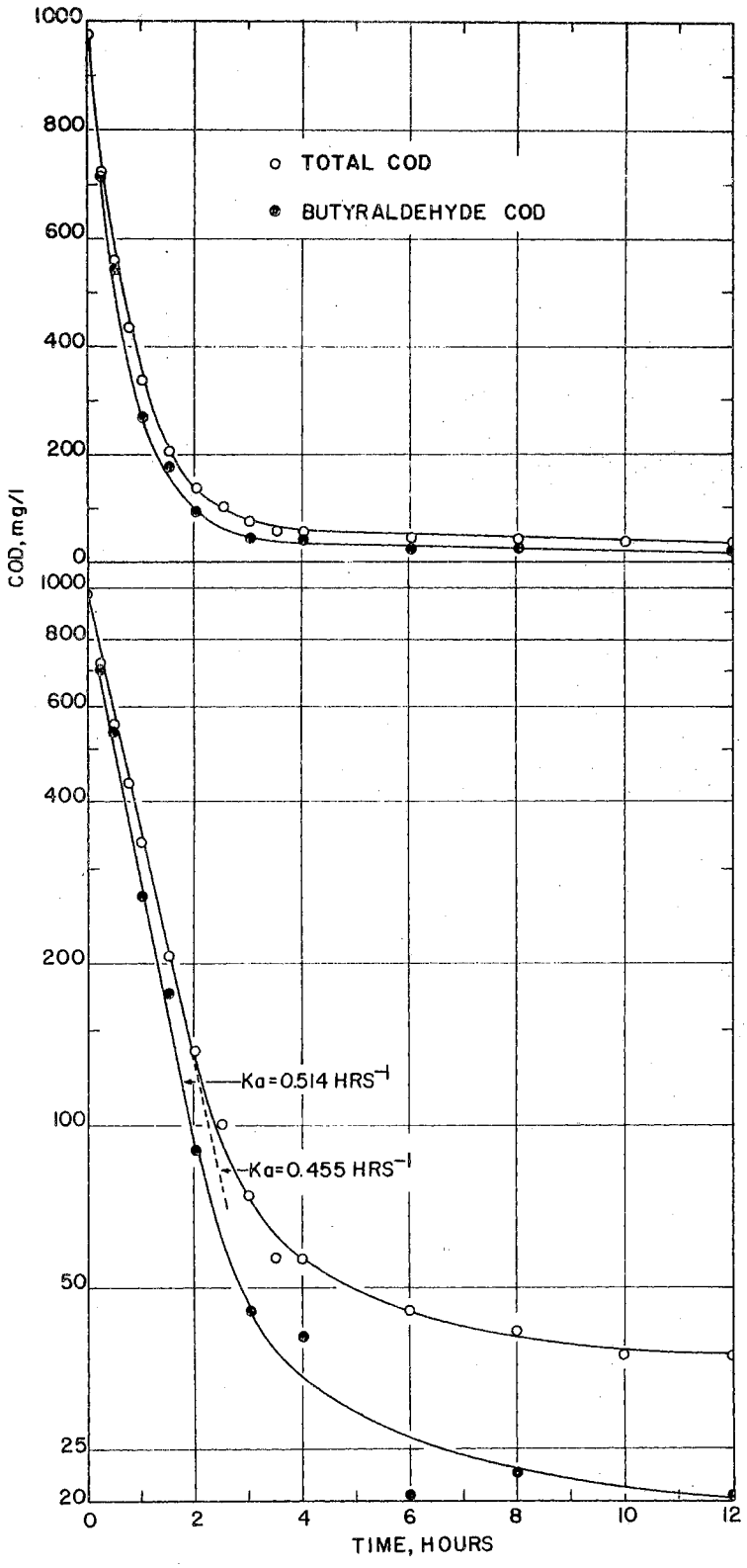


Figure 41 - Air stripping of butyraldehyde under batch conditions at 2000 cc/min/l.

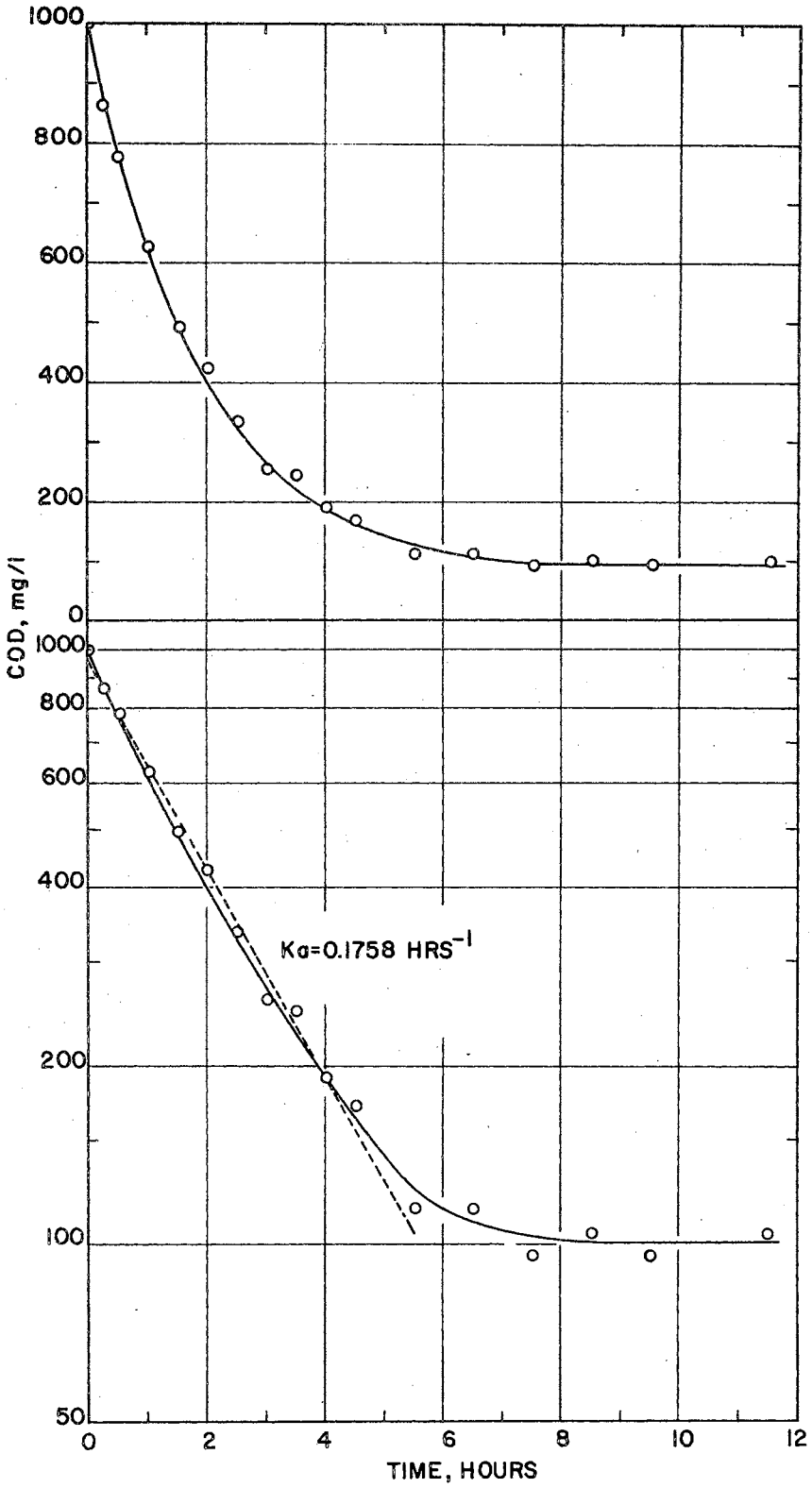


Figure 42 - Air stripping of butyraldehyde under batch conditions at 1000 cc/min/l.

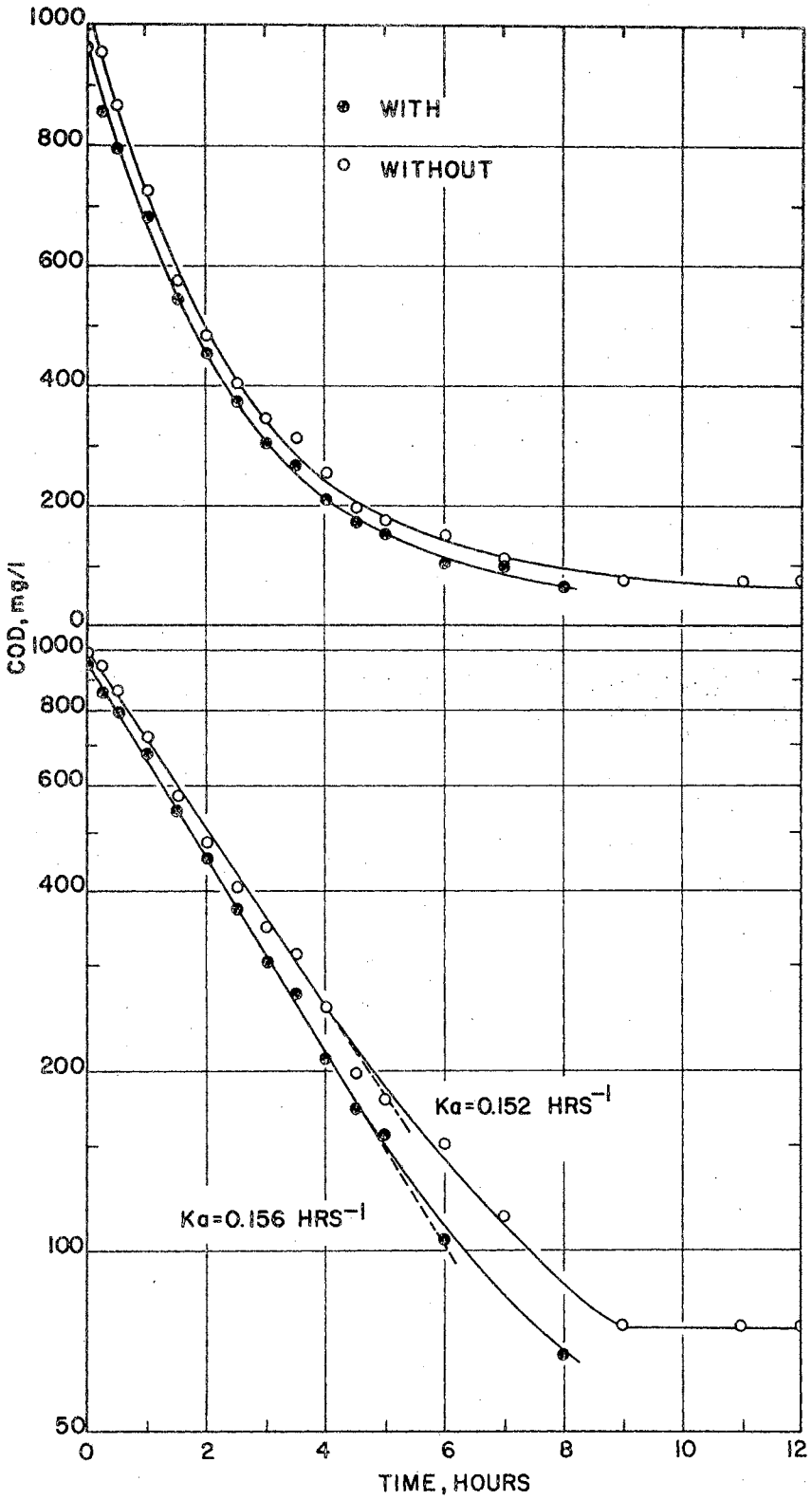


Figure 43 - Air stripping of butyraldehyde with and without disodium hydrogen phosphate under batch conditions at 500 cc/min/l.

total COD. In all cases of air stripping of butyraldehyde where conformation to first order kinetics was not observed for the entire course of operation, the slope of the straight line (indicated by a broken line) obtained from the early samples (semilogarithmic plot) was calculated and expressed as the first order rate constant.

In Figure 43 it can be seen that disodium hydrogen phosphate slightly enhanced the removal of butyraldehyde. Butyraldehyde removal under quiescent conditions (Figure 44) was higher than for any of the other compounds examined (32.8 per cent in 11½ hours). The stripping constant calculated from the semilogarithmic plot was 0.015 hr^{-1}.

The results of studies on butyraldehyde removal by the combined action of stripping and biological metabolism at airflow rates of 4000, 2000, 1000, and 500 cc/min are shown in Figures 45, 46, 47, and 48, respectively. The highest airflow rate studied (4000 cc/min, Figure 45) also corresponded to the system employing the highest initial biological solids concentration and as a result the substrate was removed very rapidly (90 per cent in two hours). However, it was possible to obtain sufficient samples to give an insight into the nature of the metabolic intermediates and/or endproducts elaborated during the metabolism of the original exogenous substrate. Compounds other than butyraldehyde found in the filtrate samples were butyric and propionic acids; butyric acid was found in much higher concentration than propionic acid. These compounds accounted for less than half of the total amount of intermediates accumulated in the medium. Accumulation and subsequent utilization of metabolic intermediates was also evidenced for the systems run at the other airflow rates. In all cases, butyric and propionic acids were detected, and in all but one system (Figure 46) butyric acid

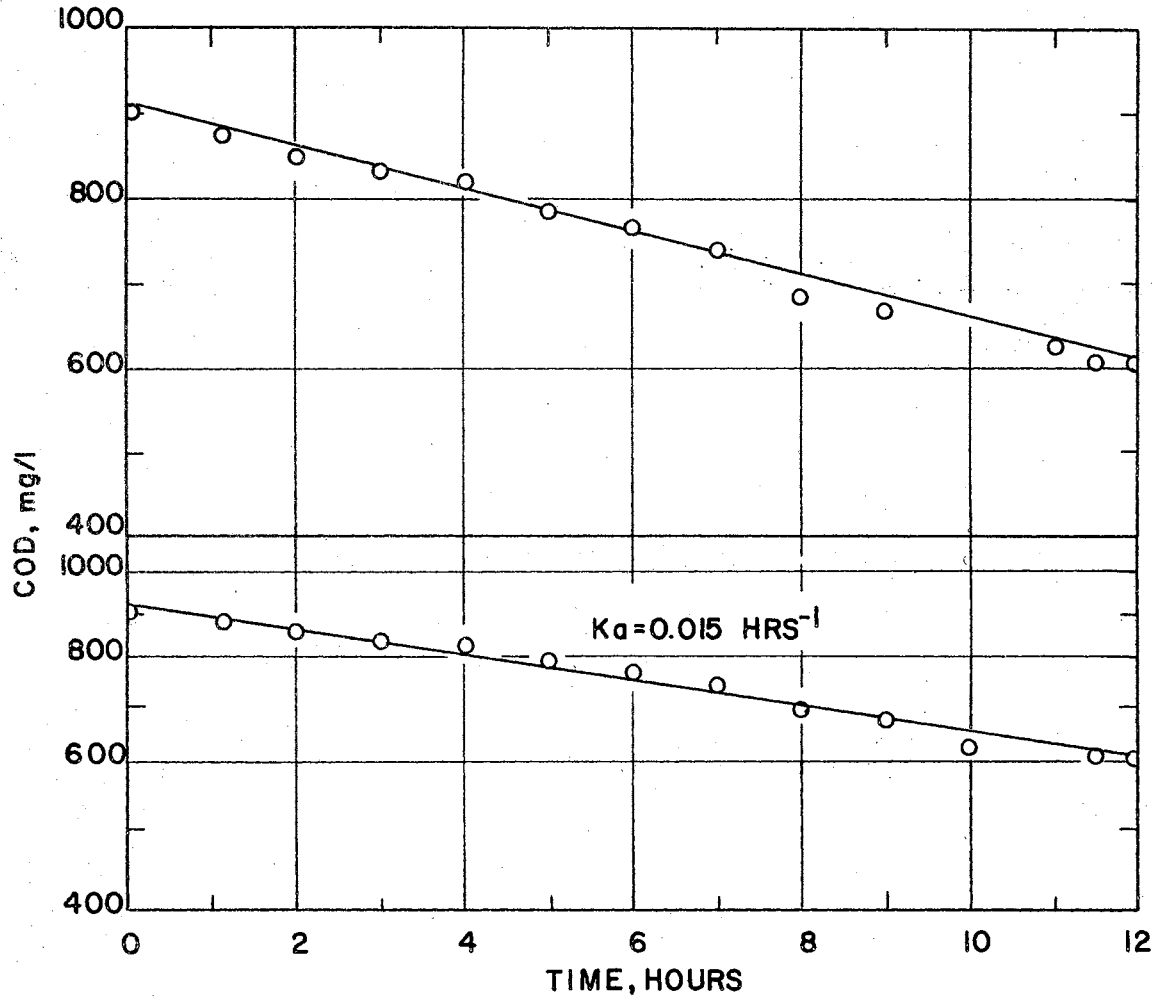


Figure 44 - Stripping of butyraldehyde (batch experiment) under quiescent conditions (zero airflow rate).

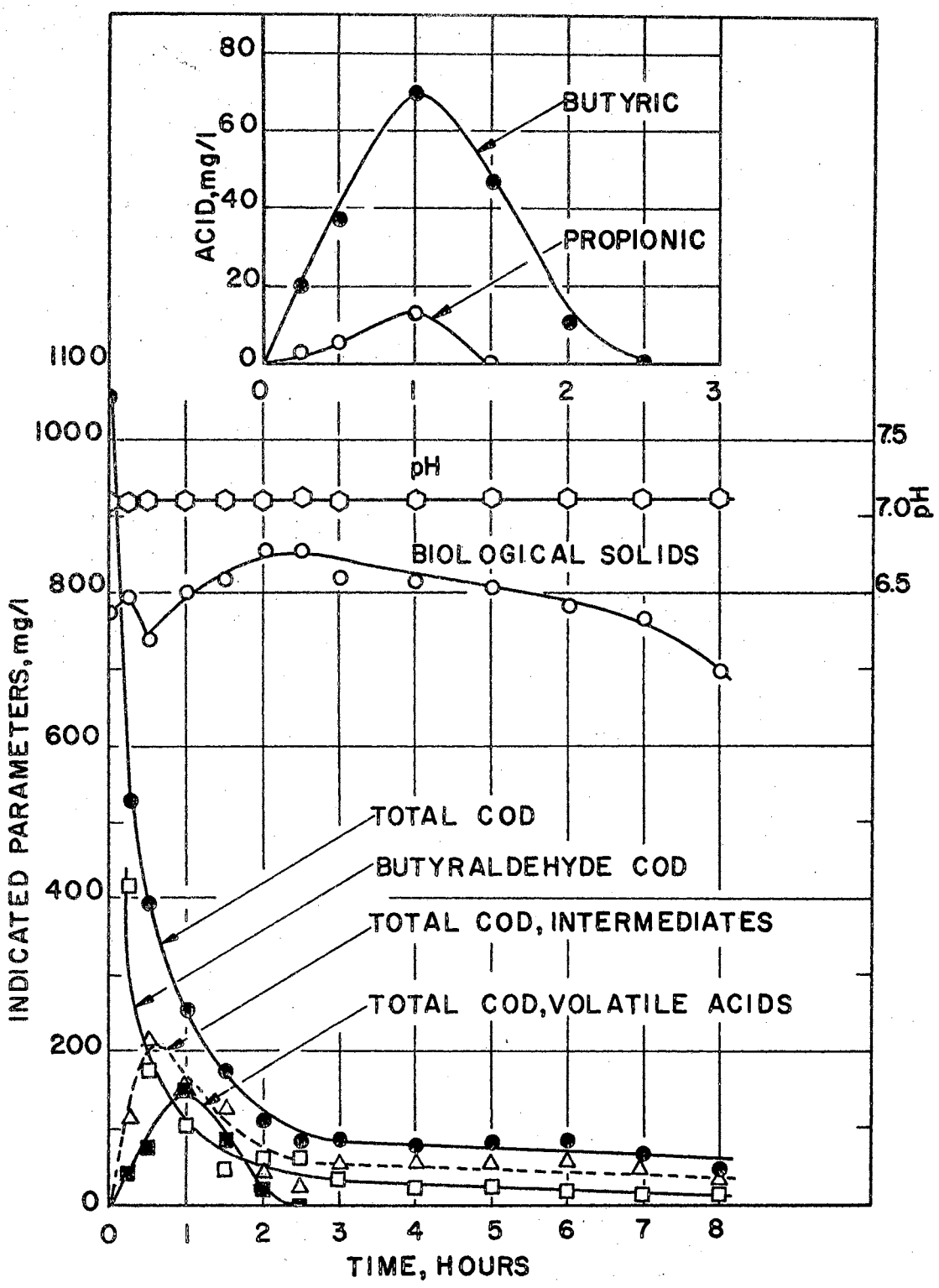


Figure 45 - Removal of butyraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 4000 cc/min/l.

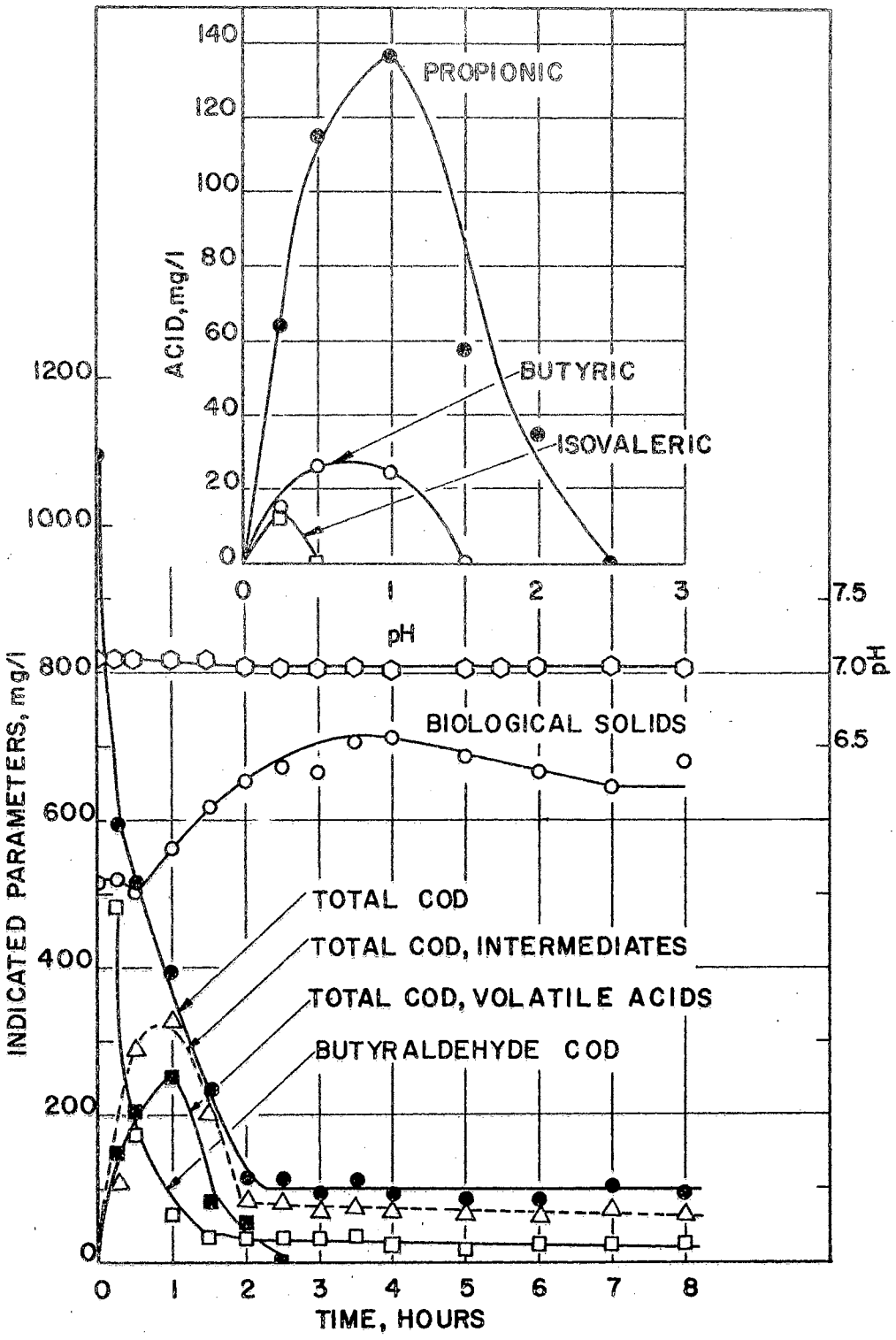


Figure 46 - Removal of butyraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 2000 cc/min/l.

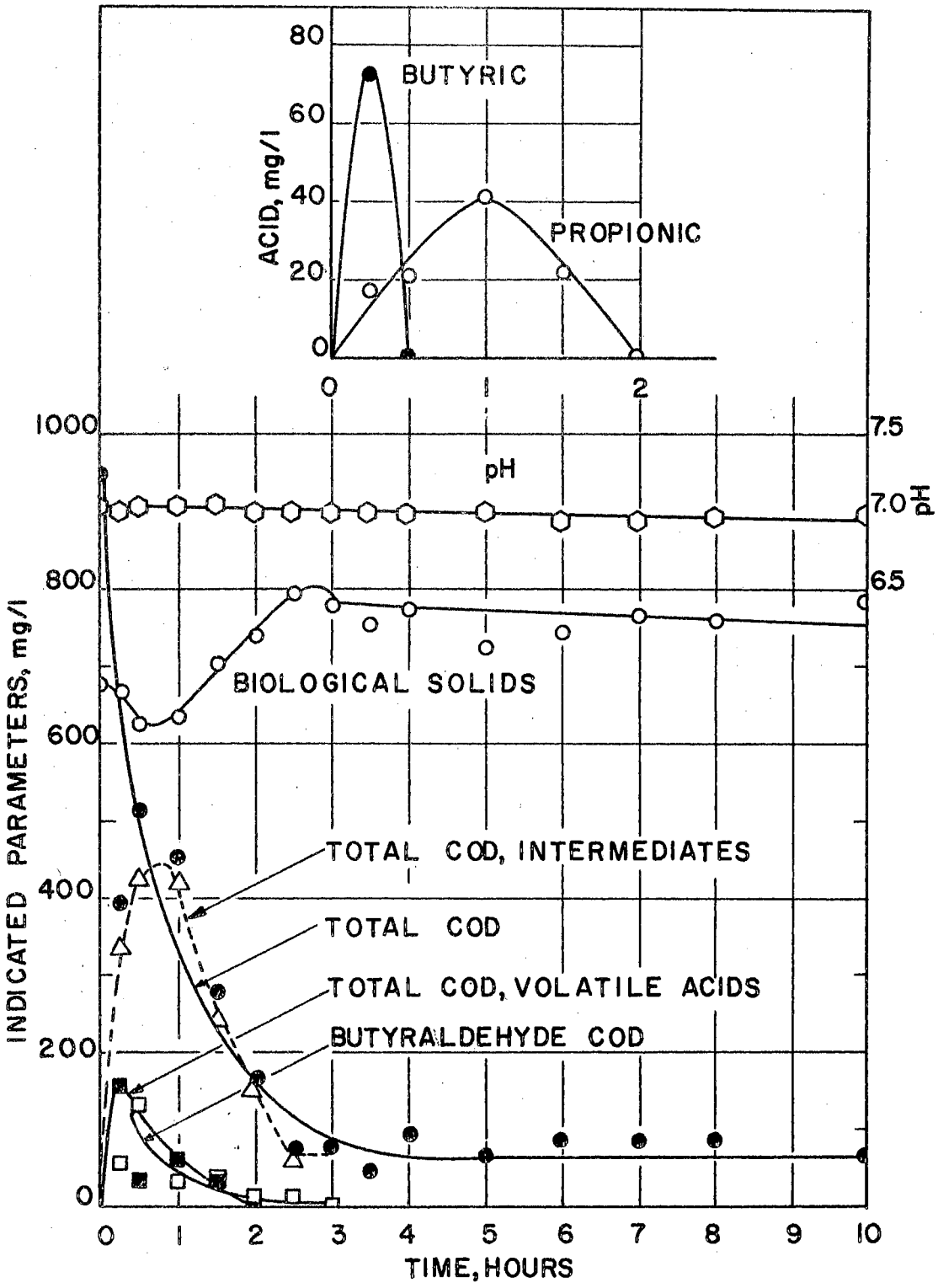


Figure 47 - Removal of butyraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 1000 cc/min/l.

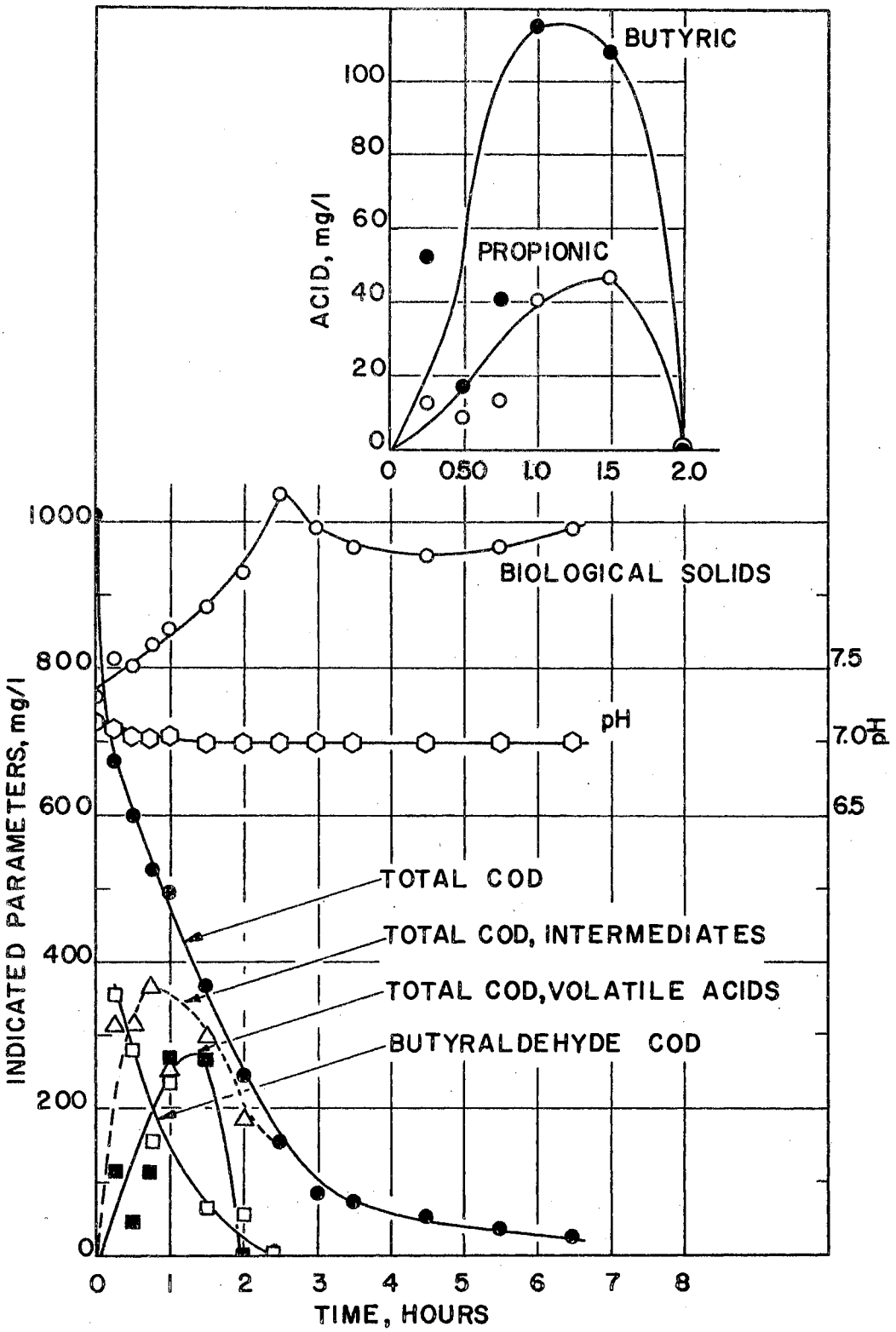


Figure 48 - Removal of butyraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 500 cc/min/l.

accumulated in greater amount. The dissolved oxygen was determined during the substrate removal period for the experiment at an airflow rate of 500 cc/min (Figure 48). The minimum dissolved oxygen recorded was 3.9 mg/l, indicating that the elaboration of butyric and propionic acids was not due to existence of anaerobic conditions.

Valeraldehyde

The stripping of valeraldehyde at airflow rates of 4000, 2000, 1000, and 500 cc/min is shown in Figures 49, 50, 51, and 52, respectively. Removal under quiescent conditions is shown in Figure 53. In general, the semilogarithmic plots of COD concentrations remaining in solutions indicate that first order kinetics did not prevail. Also, it is seen (Figure 50) from the experiment in which valeraldehyde was measured by both the COD test and GLC analysis that, on the basis of the GLC data, well-defined first order removal was exhibited. The velocity constant was 0.62 hr^{-1}. At lower concentrations there is a considerable divergence of the curves; however, no other component was detected on the Poly Pak-2 column.

As can be seen from Figure 52, disodium hydrogen phosphate slightly retarded the COD removal of valeraldehyde at an airflow rate of 500 cc/min. Under quiescent conditions (Figure 53), 35.3 per cent of the COD was removed at the end of twelve hours. Unlike propionaldehyde and butyraldehyde, the arithmetic plot for valeraldehyde did not give rise to a straight line. However, from the semilogarithmic plot a reasonably good first order fit was obtained. The slope of the line is 0.0125 hr^{-1}.

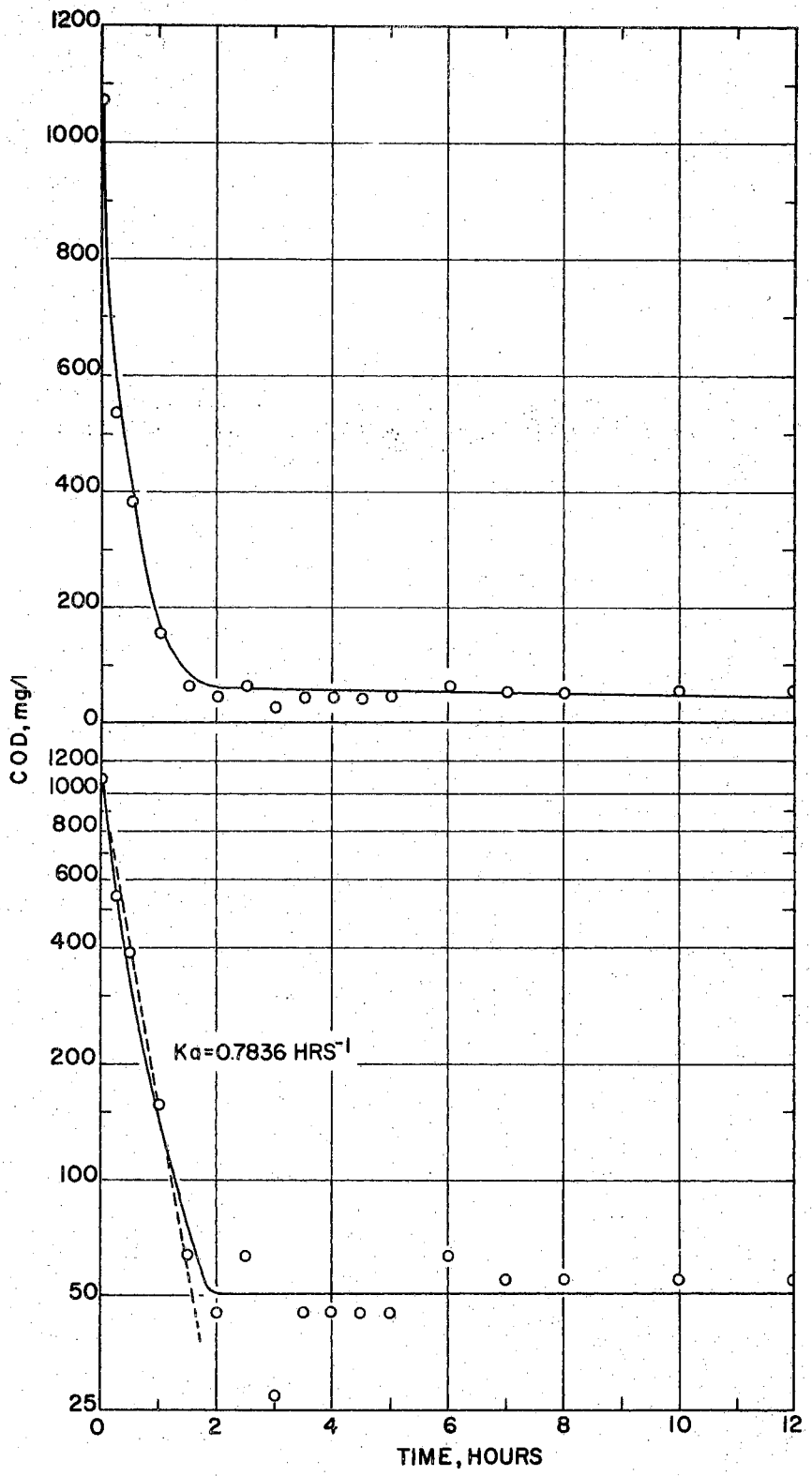


Figure 49 - Air stripping of valeraldehyde under batch conditions at 4000 cc/min/l.

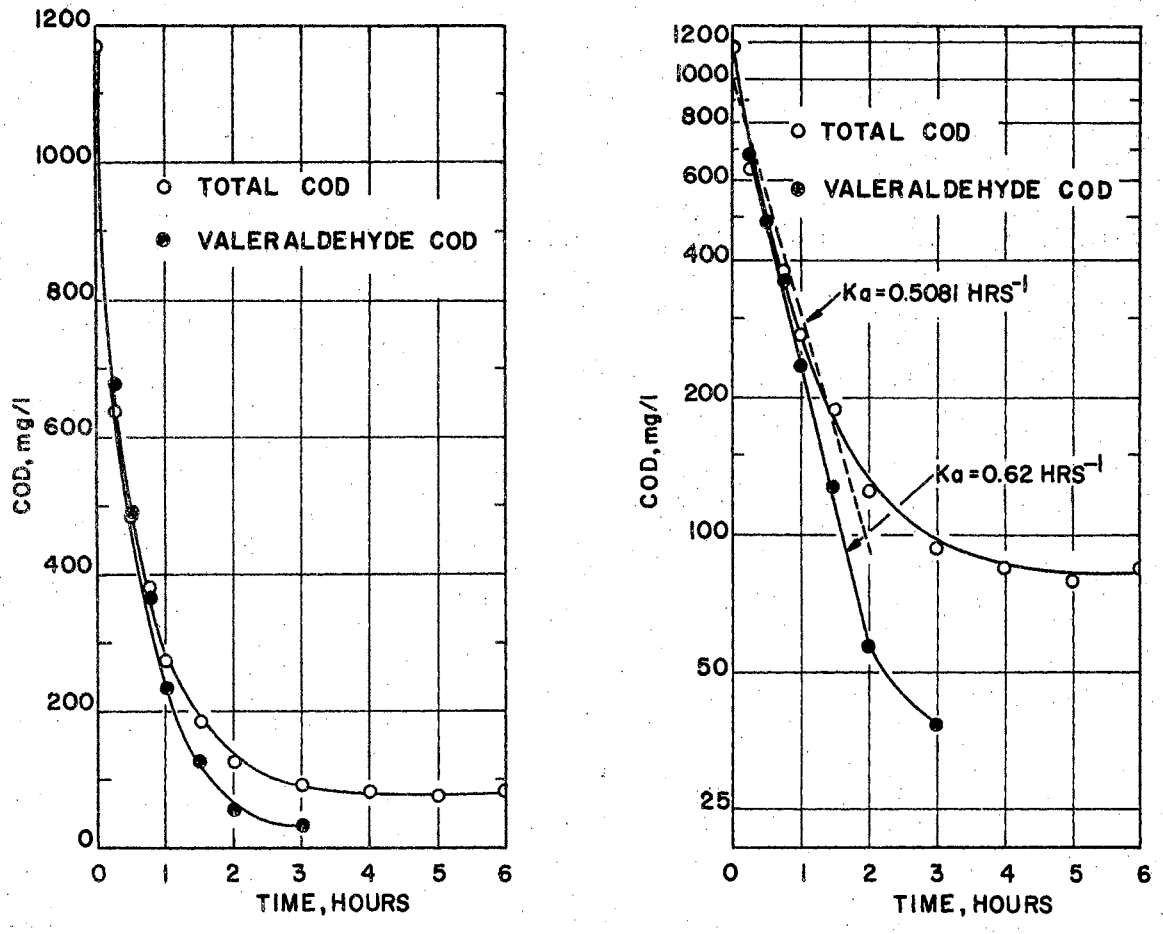


Figure 50 - Air stripping of valeraldehyde under batch conditions at 2000 cc/min/l.

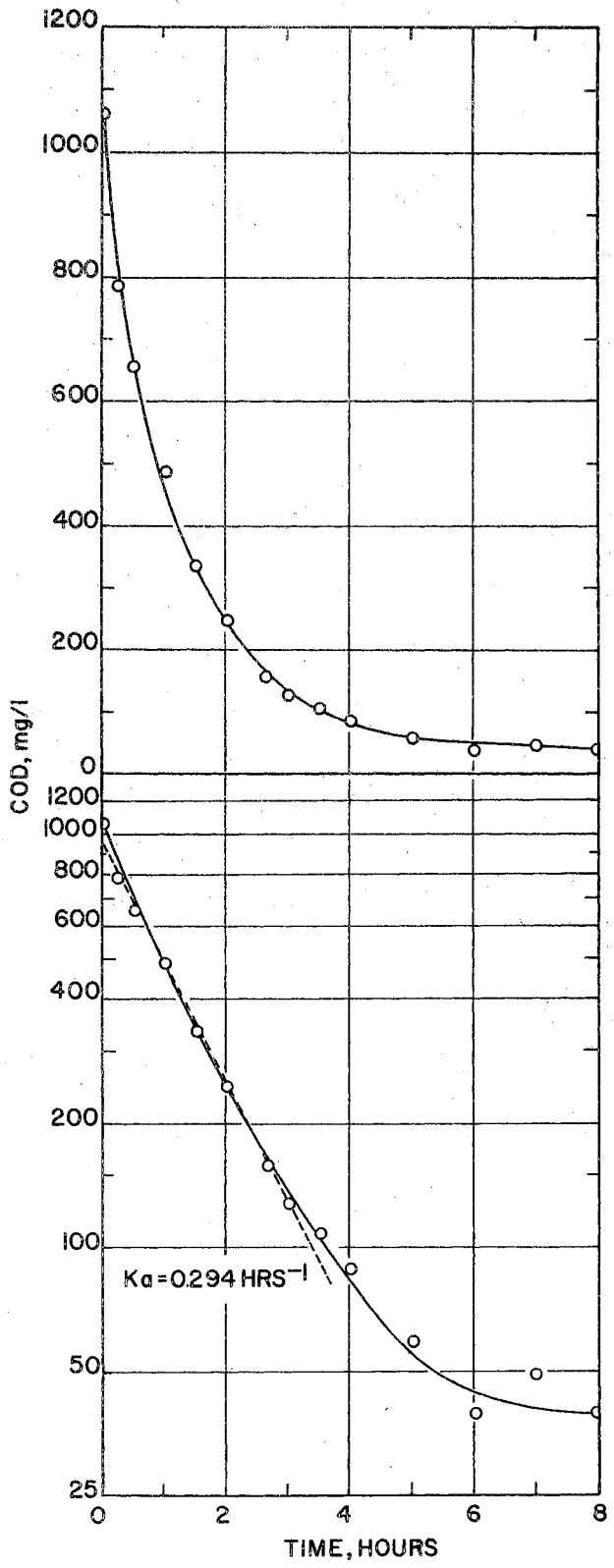


Figure 51 - Air stripping of valeraldehyde under batch conditions at 1000 cc/min/l.

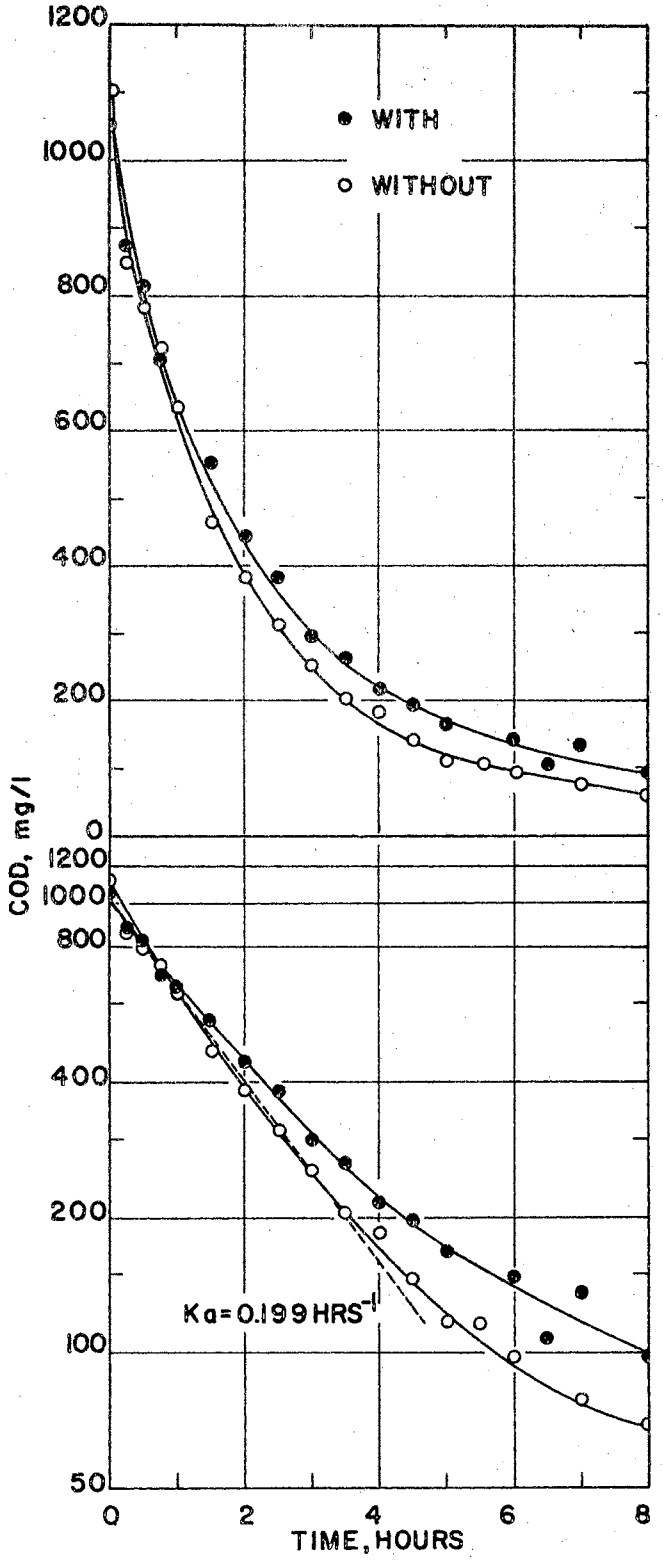


Figure 52 - Air stripping of valeraldehyde with and without disodium hydrogen phosphate under batch conditions at 500 cc/min/l.

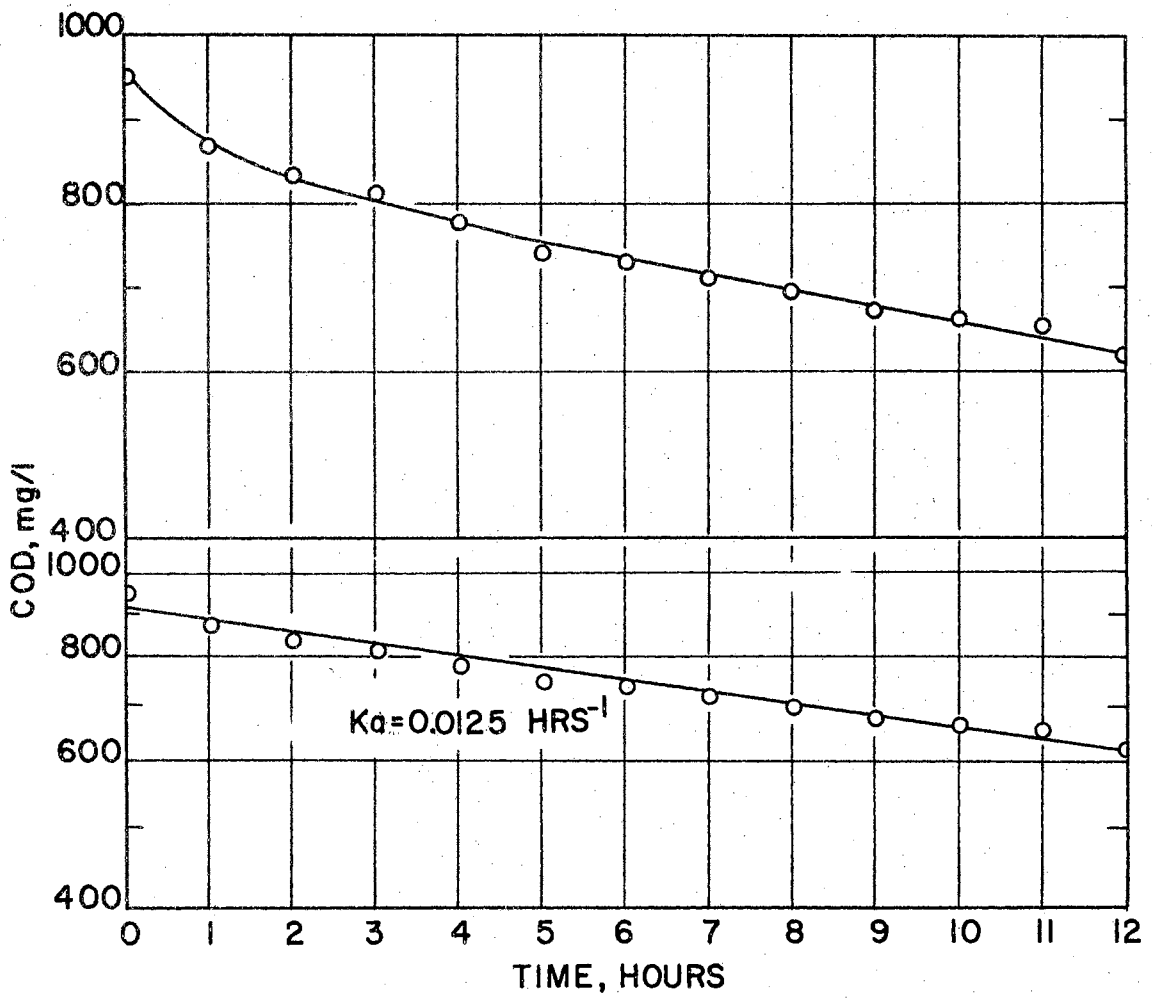


Figure 53 - Stripping of valeraldehyde (batch experiment) under quiescent conditions (zero airflow rate).

Joint stripping and biological removal of valeraldehyde at airflow rates of 4000, 2000, 1000, and 500 cc/min are shown in Figures 54, 55, 56, and 57, respectively. At an airflow rate of 4000 cc/min, valeraldehyde was removed from the system within one hour. Regarding intermediates and/or endproducts, acetic acid was detected only at the first sampling point (12 minutes); valeric acid was the only other compound detected. At an airflow rate of 2000 cc/min (Figure 55), propionic, butyric, and valeric acids were detected in the medium during the period of substrate removal. At an airflow rate of 1000 cc/min (Figure 56) the pattern of total COD removal was much the same as observed in the previous figure, i.e., there was a rapid decrease in COD during the first fifteen minutes, followed by a slow rate of removal. Since the slower rate of COD removal coincides in both cases to the period of buildup and subsequent metabolism of valeric acid (and to a lesser extent of butyric acid), the slower COD removal rate would appear to be an expression of characteristic rates for these compounds. The dissolved oxygen of 4.95 mg/l measured at the point of elaboration of these acids showed that the system was not anaerobic. Also, it should be recalled that these acids are not strippable to any large extent. Therefore, the removal mechanism becomes less dual as the run progresses.

A similar run at 1000 cc/min verified the results shown in Figure 56. In this check run acetic as well as butyric and valeric acids were detected in the filtrate. The results for the dual removal run on valeraldehyde at an airflow rate of 500 cc/min are shown in Figure 57. The same pattern of COD removal as in the previous two cases was exhibited in this experiment, i.e., rapid COD removal initially, followed by a distinctly slower rate approaching a zero order kinetic mode. The

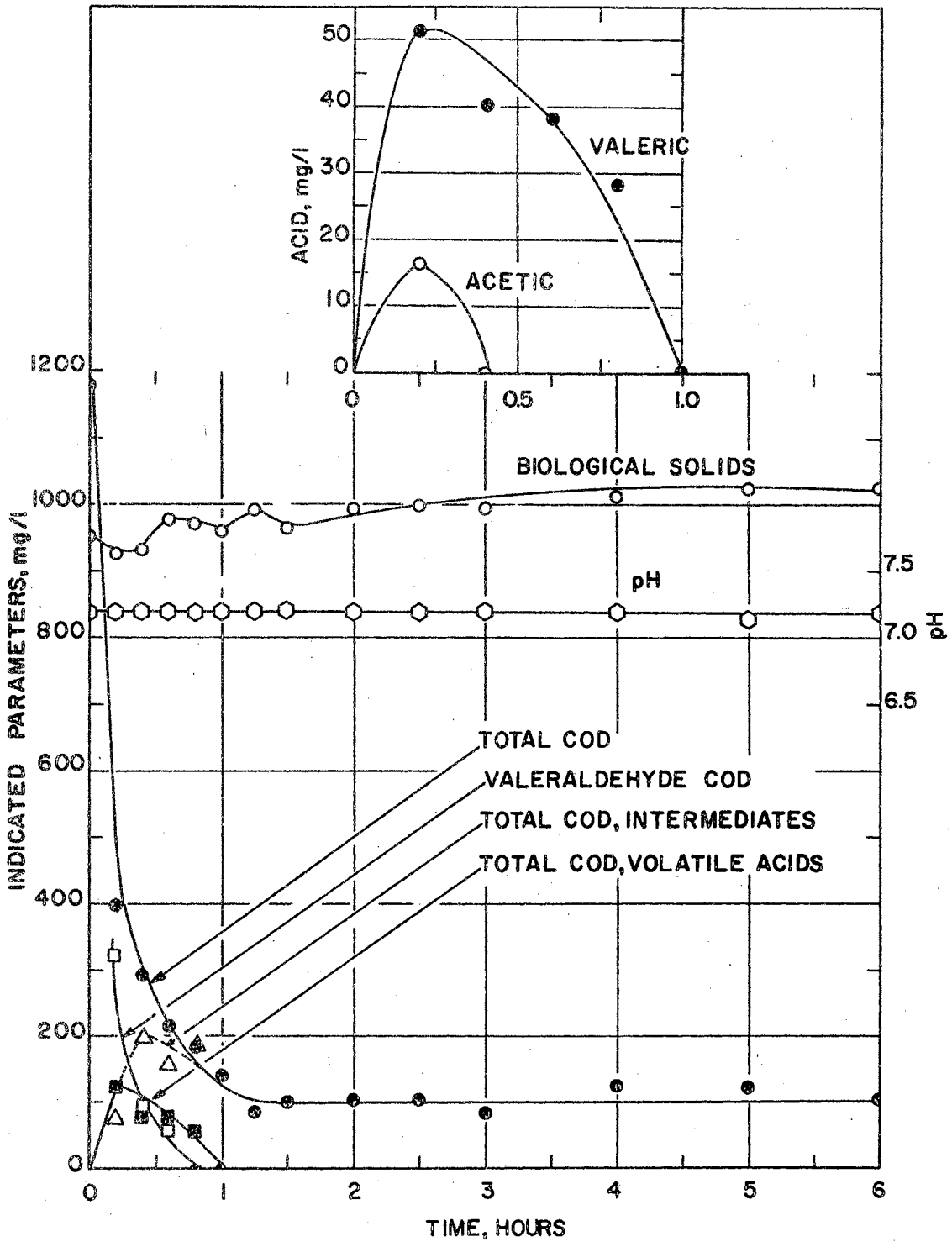


Figure 54 - Removal of valeraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 4000 cc/min/l.

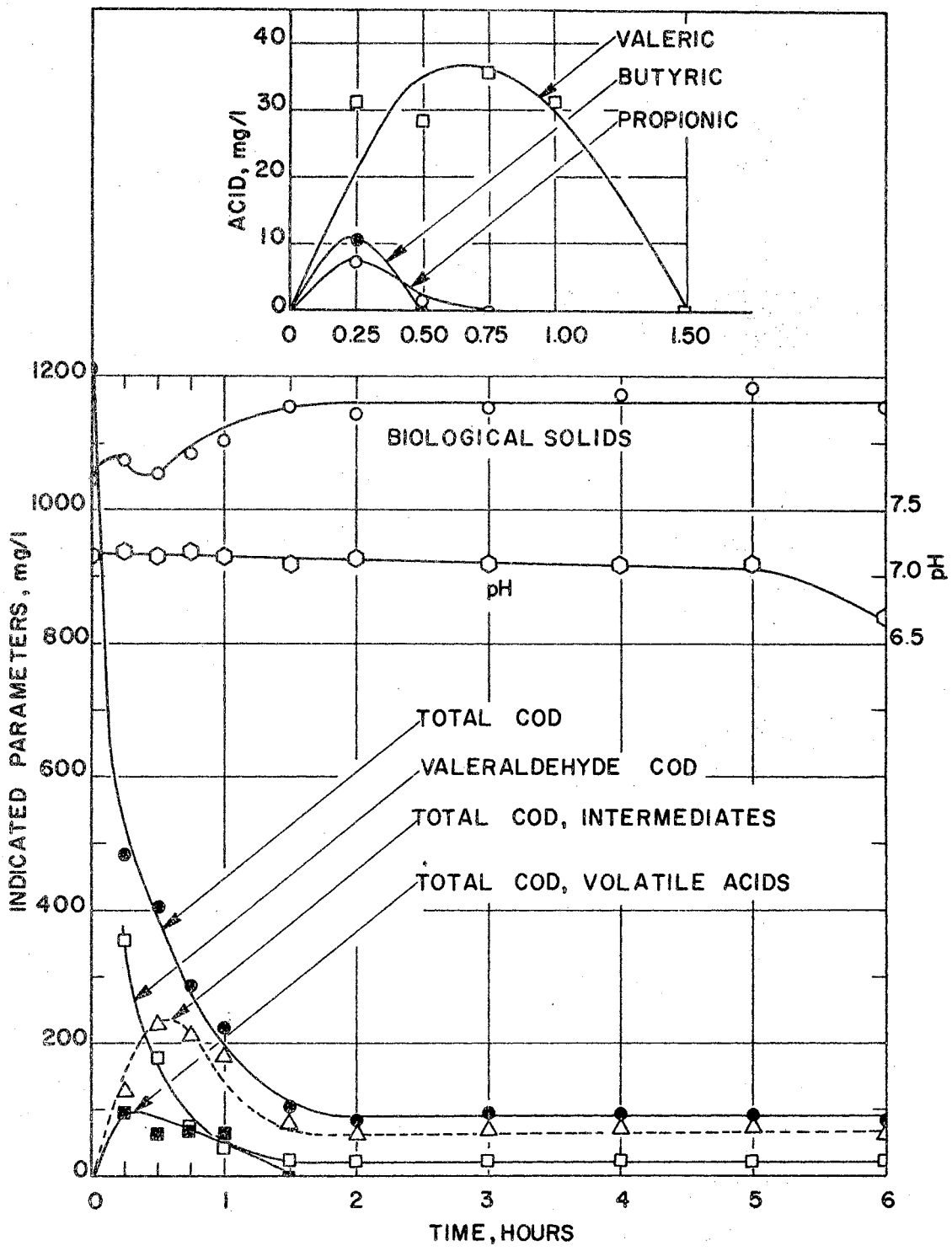


Figure 55 - Removal of valeraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 2000 cc/min/l.

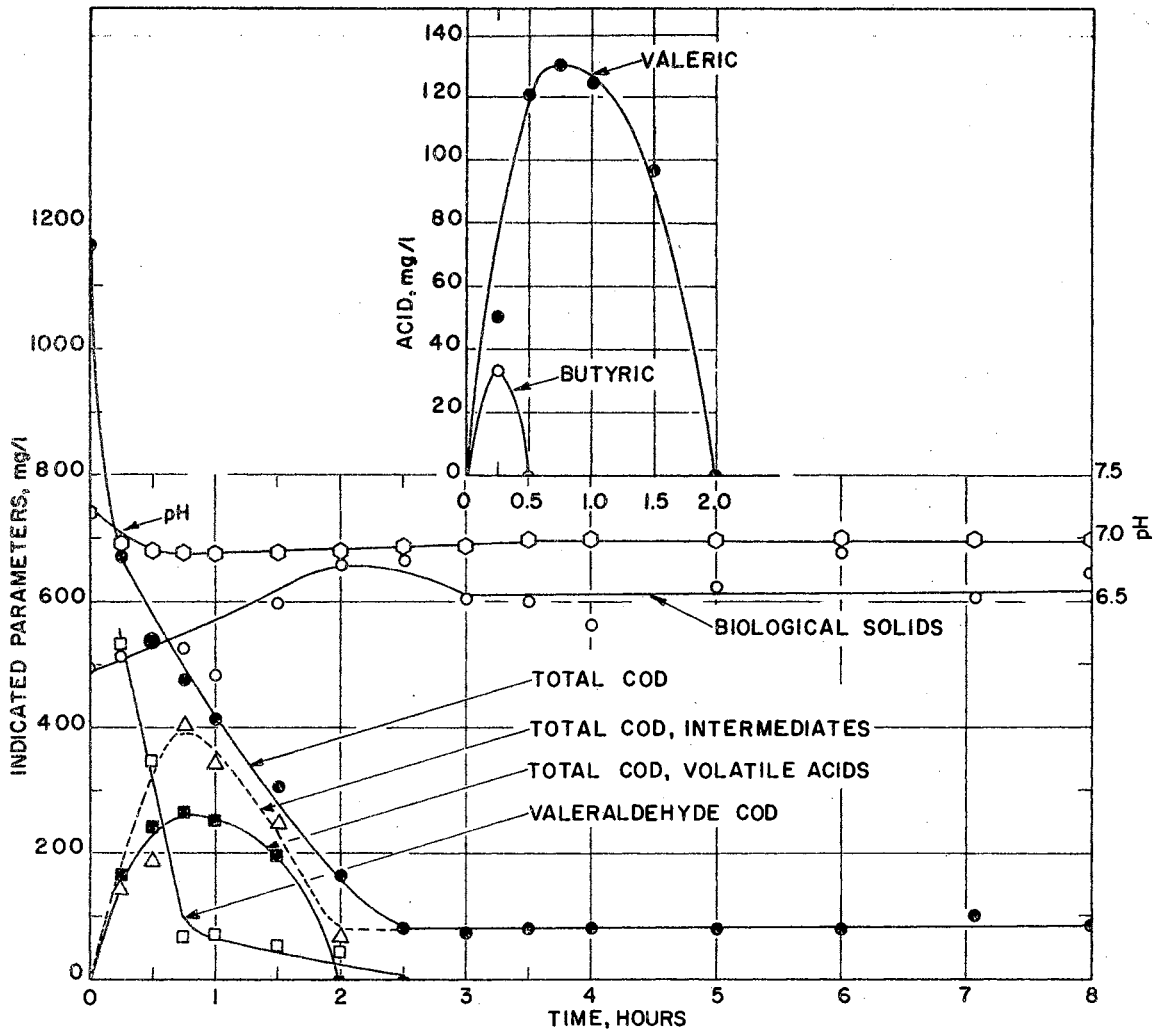


Figure 56 - Removal of valeraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 1000 cc/min/l.

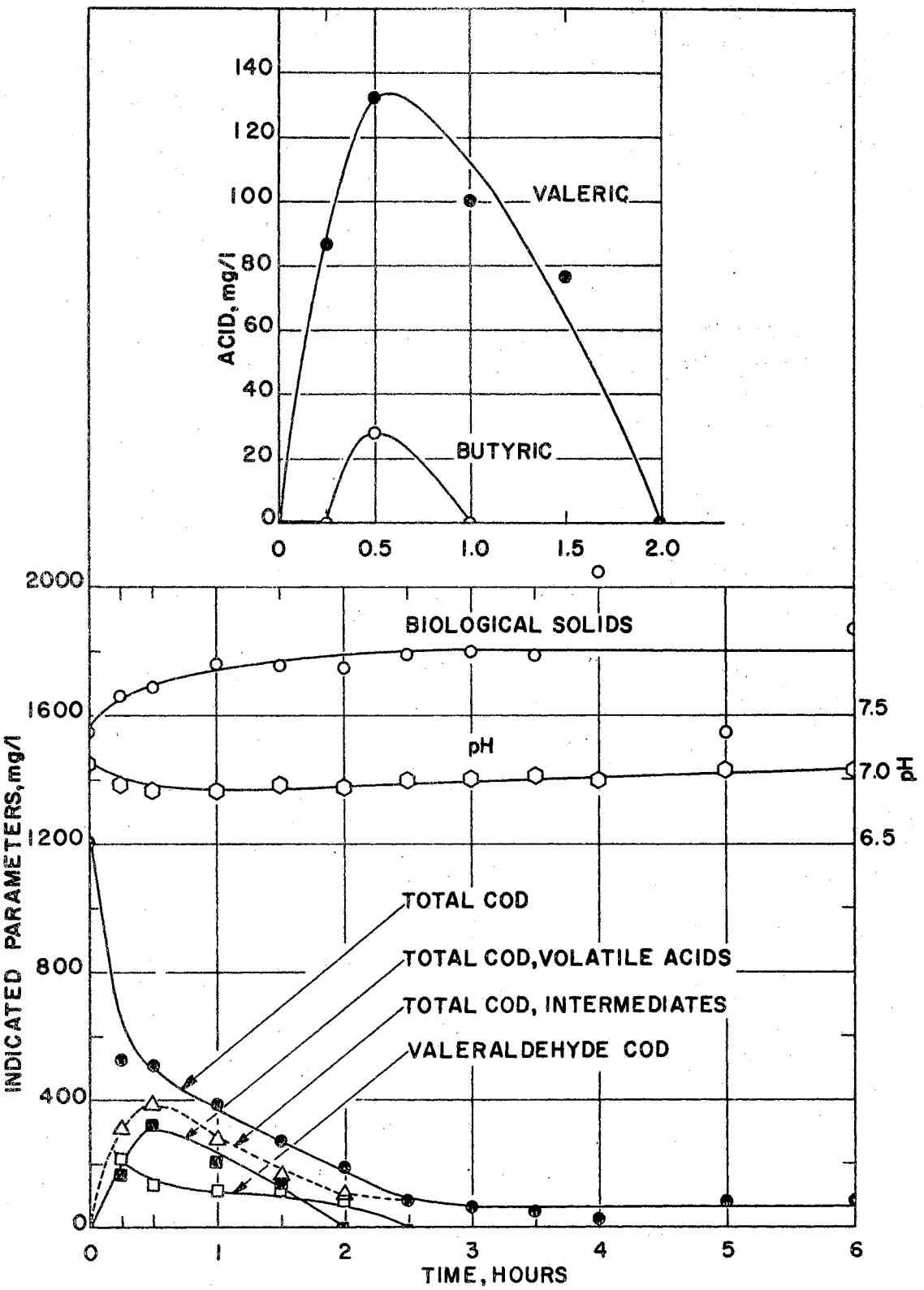


Figure 57 - Removal of valeraldehyde by stripping and biological metabolism (batch experiment) at an airflow rate of 500 cc/min/l.

aldehyde was removed from the system at an exceedingly fast rate (about 676 mg/l of aldehyde COD removed during the first fifteen minutes). This was probably due to the high initial biological solids concentration in the aerator. By GLC analysis, butyric and valeric acids were detected in the filtrates. As in the previous experiments using valeraldehyde, valeric acid was the predominant product detected.

Phase II, C

Stripping and Combined Stripping and Biological Treatment of Strippable Compounds in Continuous Flow Reactors

All experiments conducted in the continuous flow units were run at a dilution rate of 1/8 hr^{-1} (detention time eight hours). "Steady state" concentrations of the various compounds at various airflow rates were established for physical stripping alone, and air stripping plus metabolism by acclimated biological solids was also investigated.

Acetone

The stripping of acetone in the continuous flow unit at airflow rates of 4000, 2000, 1000, and 500 cc/min is shown in Figures 58, 59, 60, and 61, respectively. For the experiment run at an airflow rate of 4000 cc/min (Figure 58), the average feed COD for the period of operation was 1094 mg/l, whereas the average effluent COD was 439 mg/l. Thus 59.7 per cent of the feed in the unit was stripped by air alone. From GLC analyses, no peak other than acetone was detected on the samples, and the entire COD could be accounted for by the acetone COD as calculated from GLC analyses of acetone.

In another run at the same airflow rate which was continued for six days of operation at an average feed concentration of 680 mg/l, the

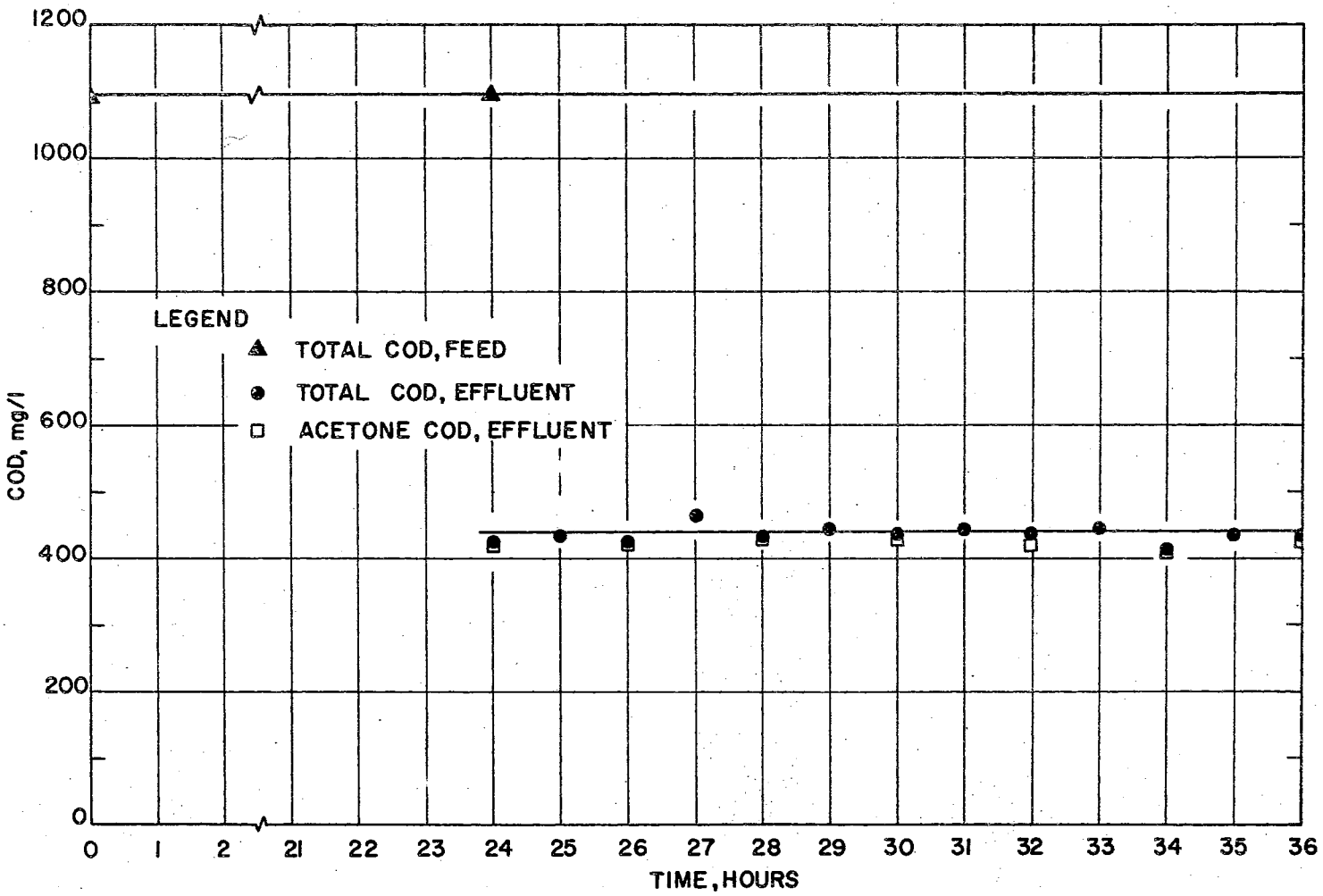


Figure 58 - Stripping of acetone in a continuous flow reactor at an airflow rate of 4000 cc/min.

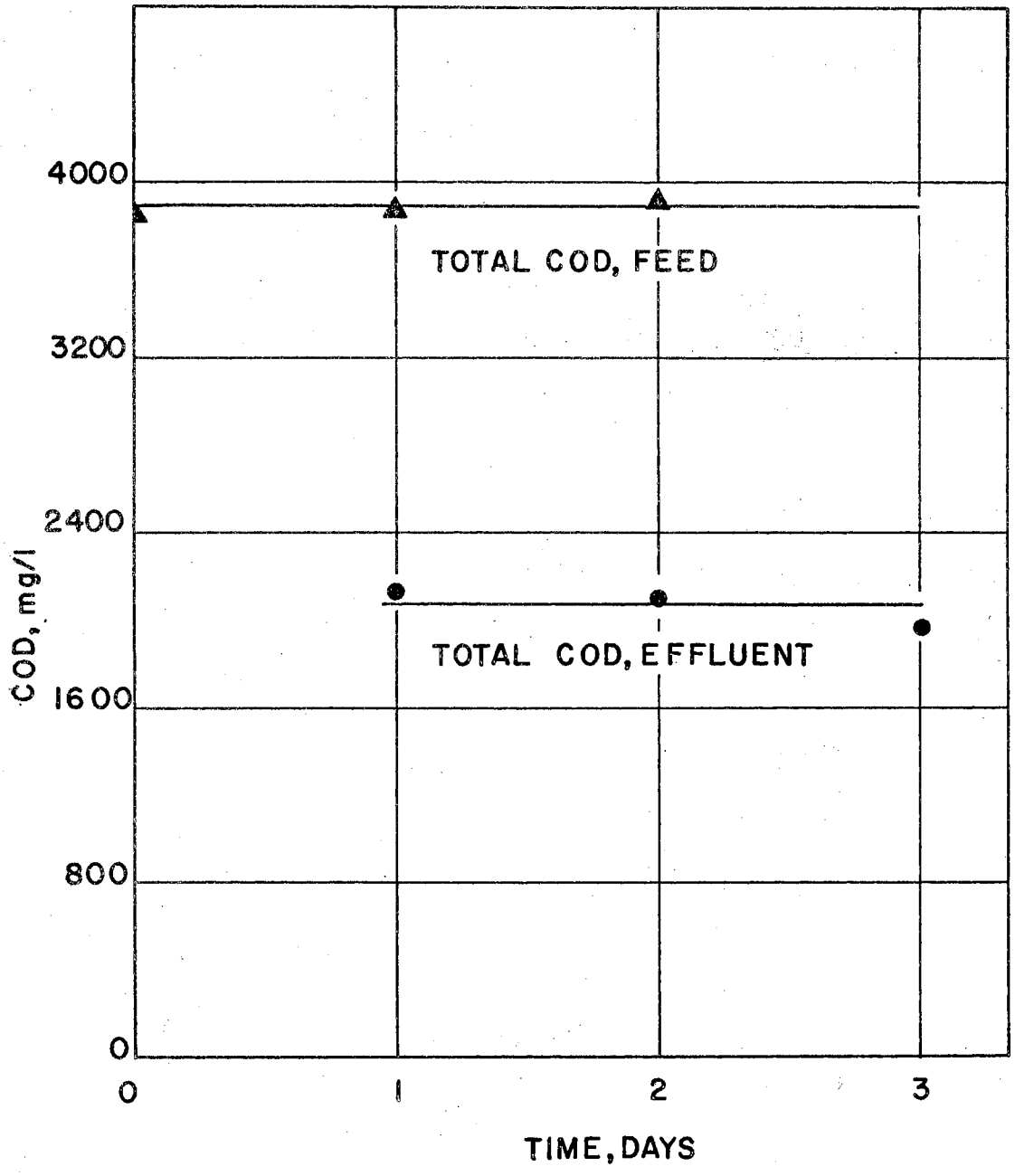


Figure 59 - Stripping of acetone in a continuous flow reactor at an airflow rate of 2000 cc/min.

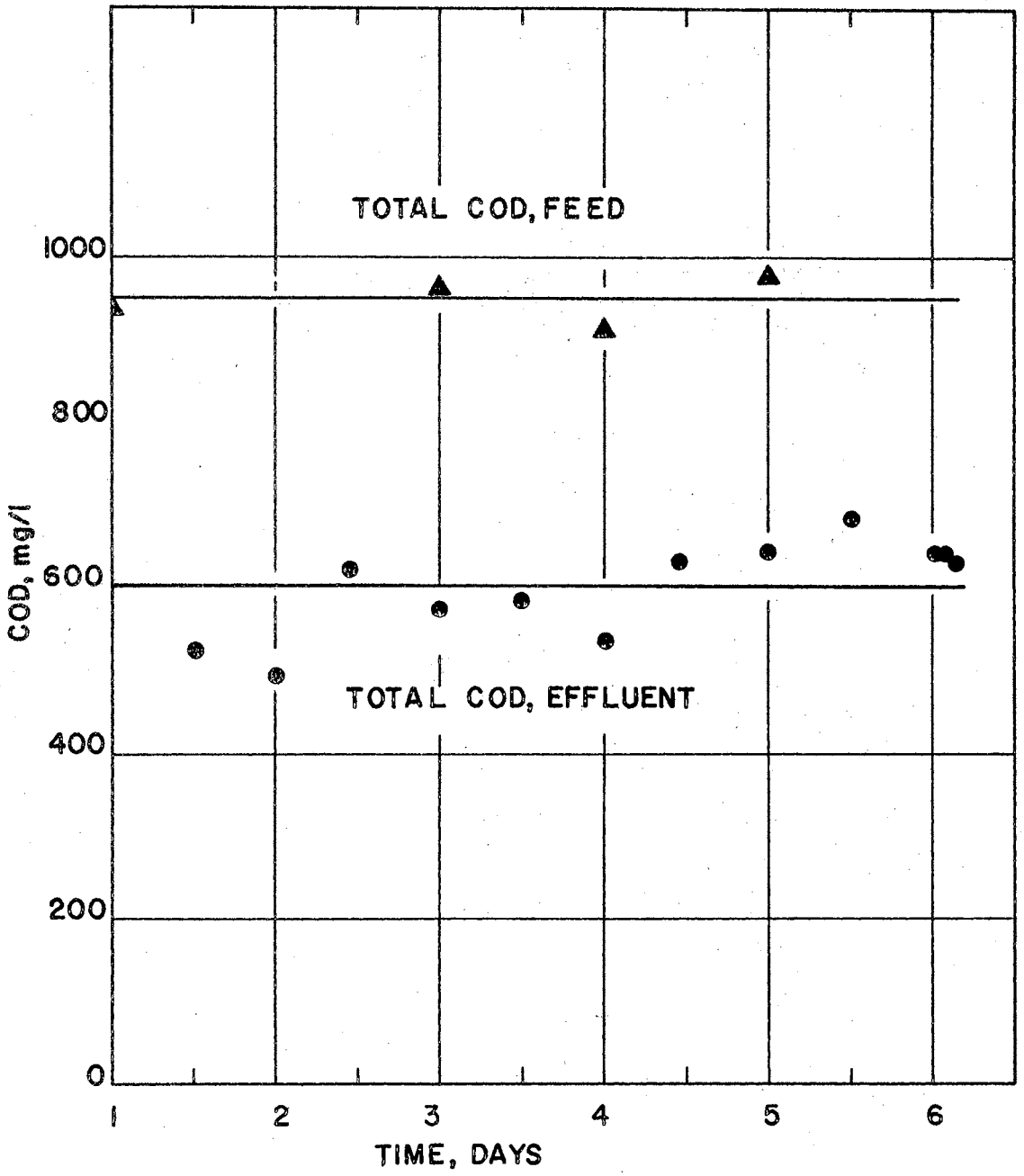


Figure 60 - Stripping of acetone in a continuous flow reactor at an airflow rate of 1000 cc/min.

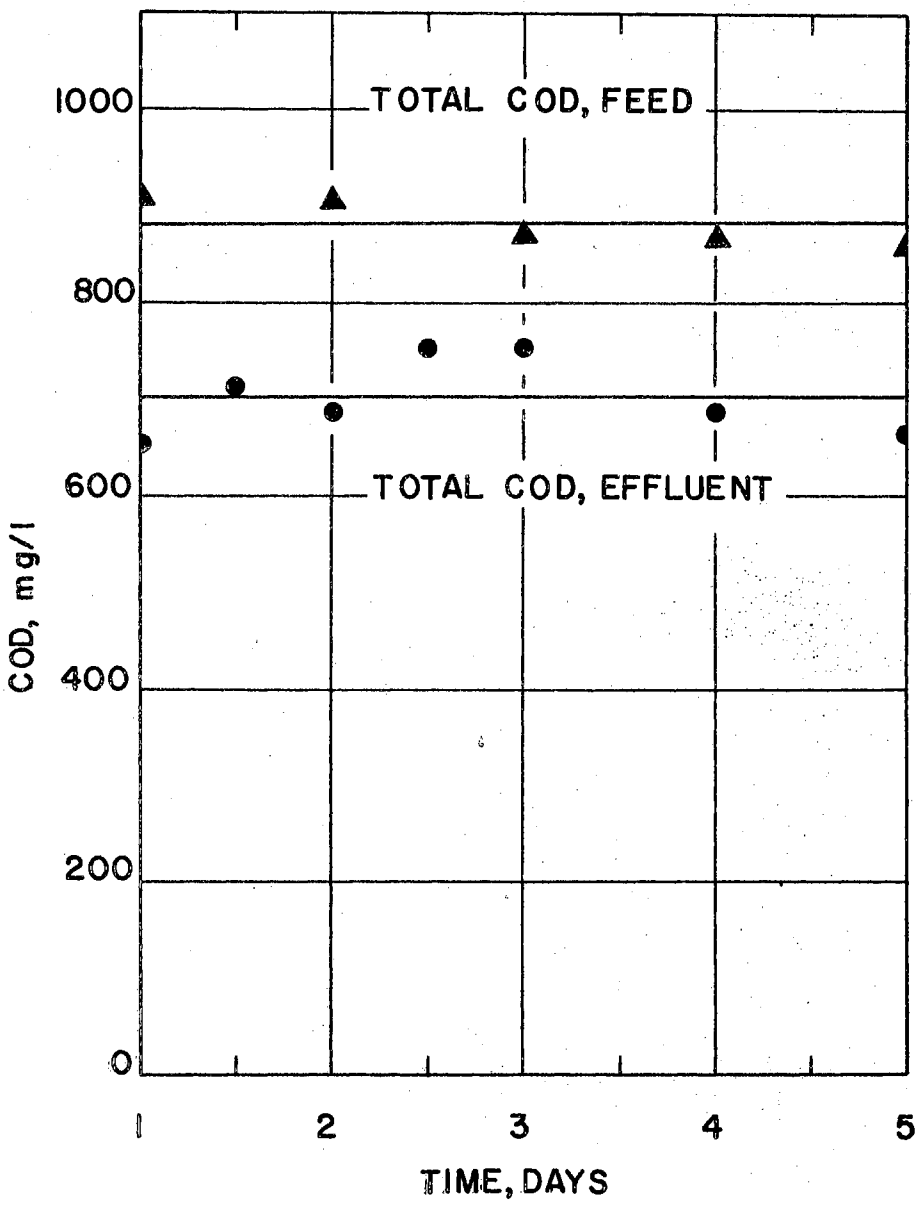


Figure 61 - Stripping of acetone in a continuous flow reactor at an airflow rate of 500 cc/min.

average effluent COD was 309 mg/l; 54.5 per cent of the feed was thus stripped by air alone. The average feed COD was 3890 mg/l for the run at an airflow rate of 2000 cc/min (Figure 59). The average steady state COD was 2064 mg/l; thus physical stripping removed 47 per cent of the feed COD. Figure 60 shows the stripping of acetone in the continuous flow unit at an airflow of 1000 cc/min. The average feed COD was 949 mg/l, whereas the average steady state COD value for the period of operation was 601 mg/l. Thus physical stripping alone removed 36.6 per cent of the feed COD. From Figure 61 it may be seen that when air was supplied at a rate of 500 cc/min, 20.5 per cent of the acetone was stripped. The average feed COD in this experiment was 881 mg/l, and the average steady state COD was 701 mg/l. The average pH of samples for different experiments at various airflow rates was 6.7.

The results of joint removal by stripping and metabolism by acclimated biological solids at an airflow rate of 2000 cc/min and an average feeding level of 3900 mg/l acetone COD are shown in Figure 62. The average solids in the system (initial solids on day zero were omitted) was 405 mg/l. The average COD in the effluent was 1575 mg/l, giving an overall treatment efficiency of 59.6 per cent, as compared to 47 per cent by stripping alone at this airflow rate (Figure 59). No intermediates and/or endproducts were detected in the filtrates by GLC analyses. In fact, the total COD of the filtrates can be attributed to acetone alone, as can be seen by comparing the GLC analyses and the total COD values. This is also clear from Figure 63, wherein the values plot fairly close to the 45^{o} line. Thus the relatively low system efficiency was not due to biologically refractive materials produced by the action of the microorganisms on acetone.

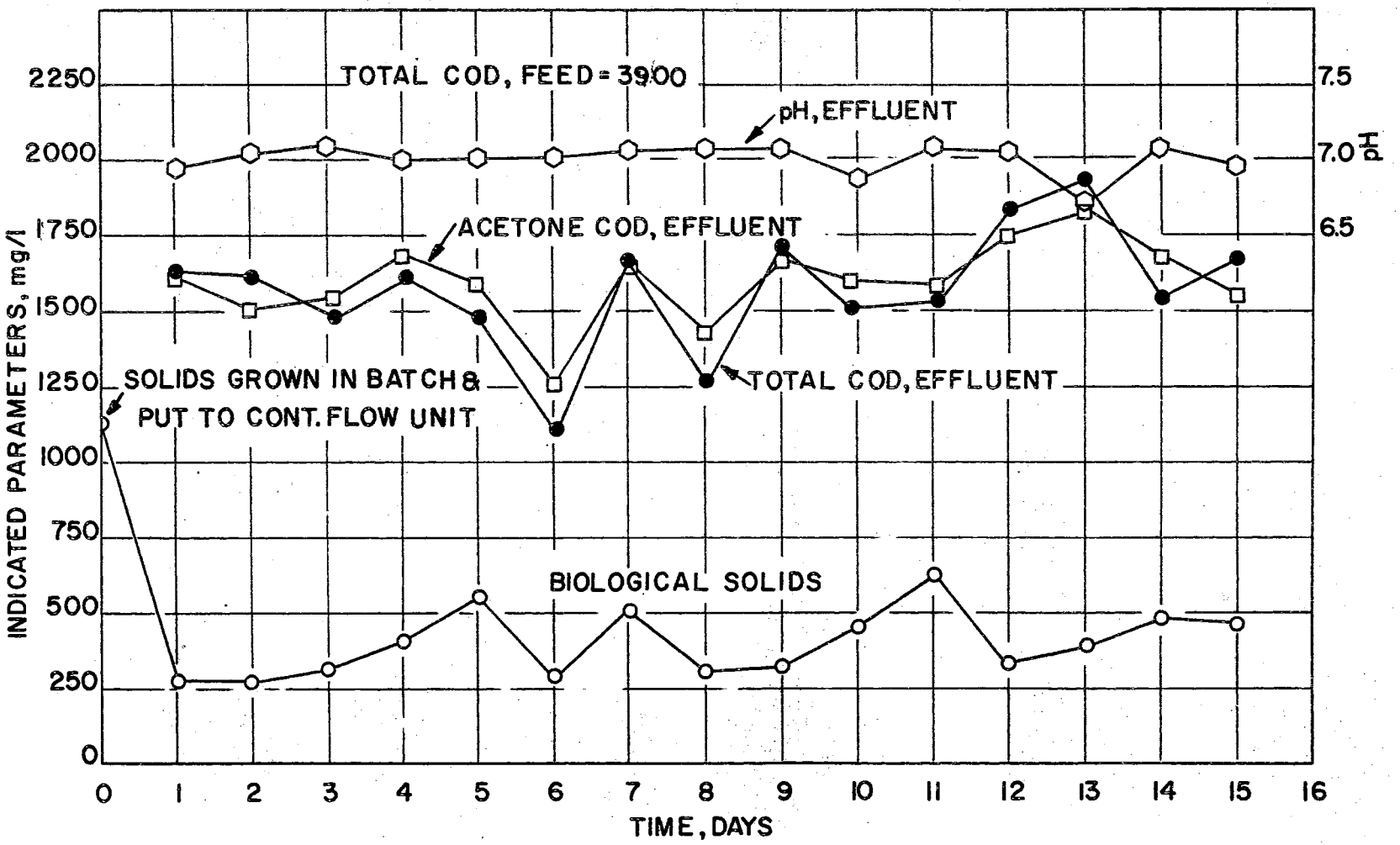


Figure 62 - Stripping and biological metabolism of acetone in a continuous flow reactor at an airflow rate of 2000 cc/min.

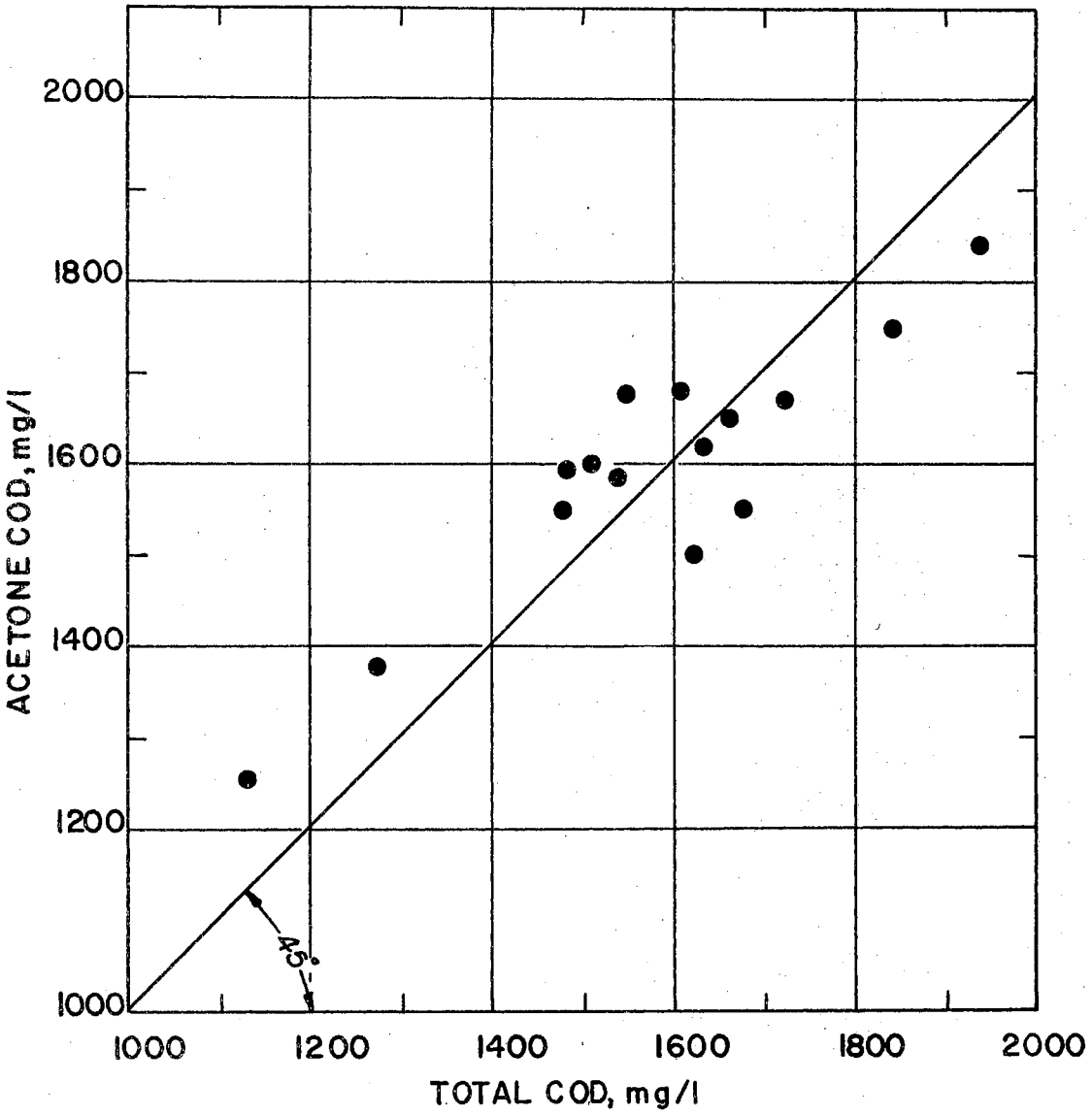


Figure 63 - Total COD versus acetone COD in filtrates of a continuous flow experiment with acetone at an airflow rate of 2000 cc/min during stripping and biological metabolism.

Methyl Ethyl Ketone

Results of physical stripping for methyl ethyl ketone at airflow rates of 4000, 2000, 1000, and 500 cc/min in continuous flow units are shown in Figures 64, 65, 66, and 67, respectively. At an airflow rate of 4000 cc/min, methyl ethyl ketone was 65 per cent stripped. The COD in the unit varied in an oscillatory manner. From an average feed of 666 mg/l, an average of 235 mg/l COD was maintained in the aerator during the six days of operation (Figure 64). For the experiment conducted at an airflow rate of 2000 cc/min, the average feed concentration (as COD) was 1068 mg/l, and the average effluent COD was 542 mg/l (see Figure 65). Thus the stripping efficiency for methyl ethyl ketone was 49.2 per cent at this airflow rate. It can be seen from Figure 65 that the entire COD could be accounted for by the COD due to methyl ethyl ketone quantitated from GLC analyses on samples. From a similar run at an airflow rate of 2000 cc/min for methyl ethyl ketone, 49.2 per cent of the feed COD was stripped for an operational period of six days after reaching a steady state at twenty-four hours. The average feed COD for this run was 673 mg/l, and the average steady state COD was 342 mg/l.

Results for stripping of methyl ethyl ketone at an airflow rate of 1000 cc/min are shown in Figure 66. The average feed COD was 696 mg/l, and average steady state concentration of COD was 373 mg/l, yielding a stripping efficiency of 46.5 per cent. Figure 67 shows the stripping of methyl ethyl ketone at an airflow rate of 500 cc/min; the stripping efficiency was 34 per cent. The average feed COD was 1227 mg/l, and average steady state concentration in the effluent was 808 mg/l COD. In all of these straight stripping runs on methyl ethyl ketone at various airflow rates, the pH of samples averaged 6.8. There was no change in pH

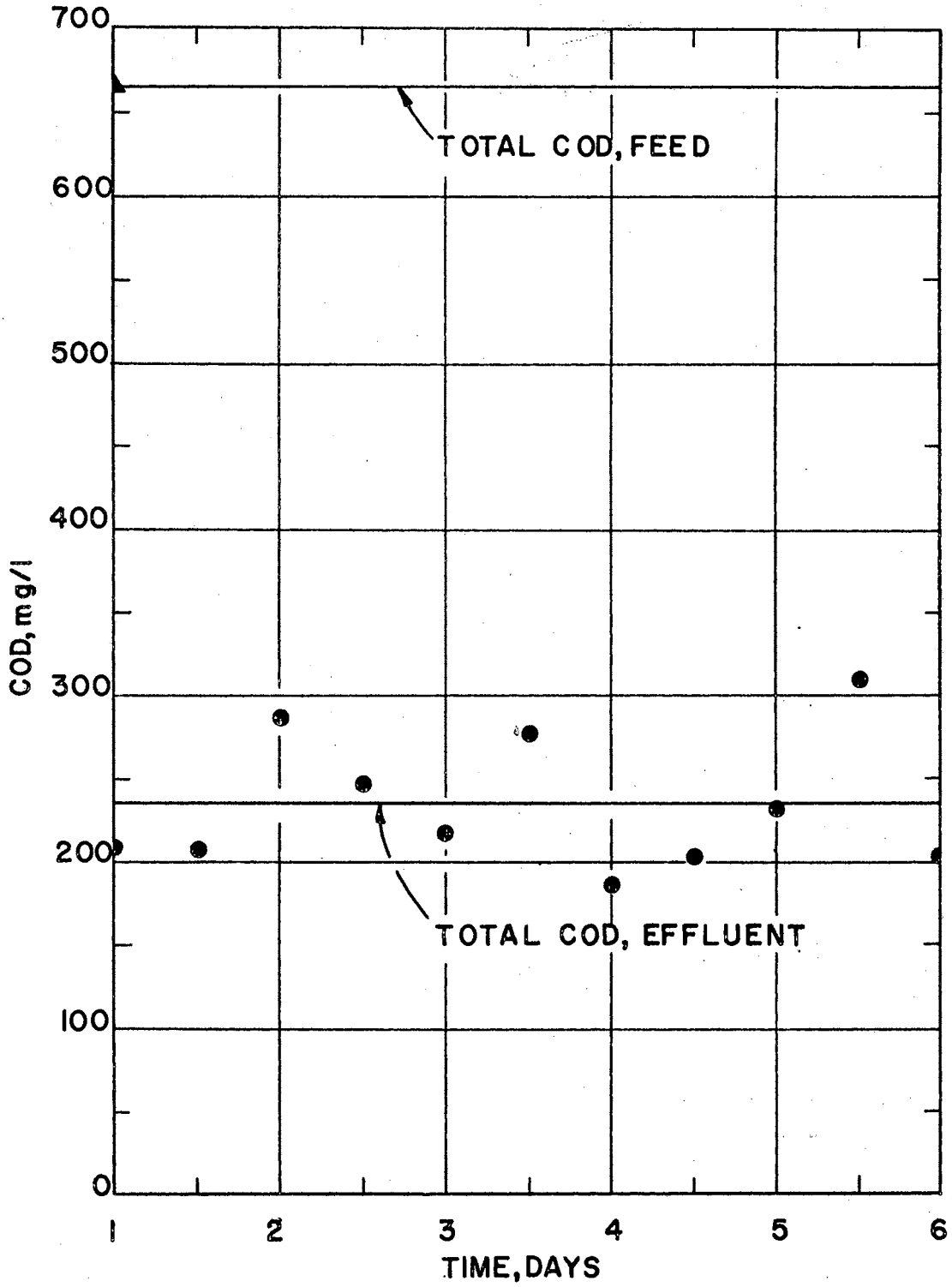


Figure 64 - Stripping of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 4000 cc/min.

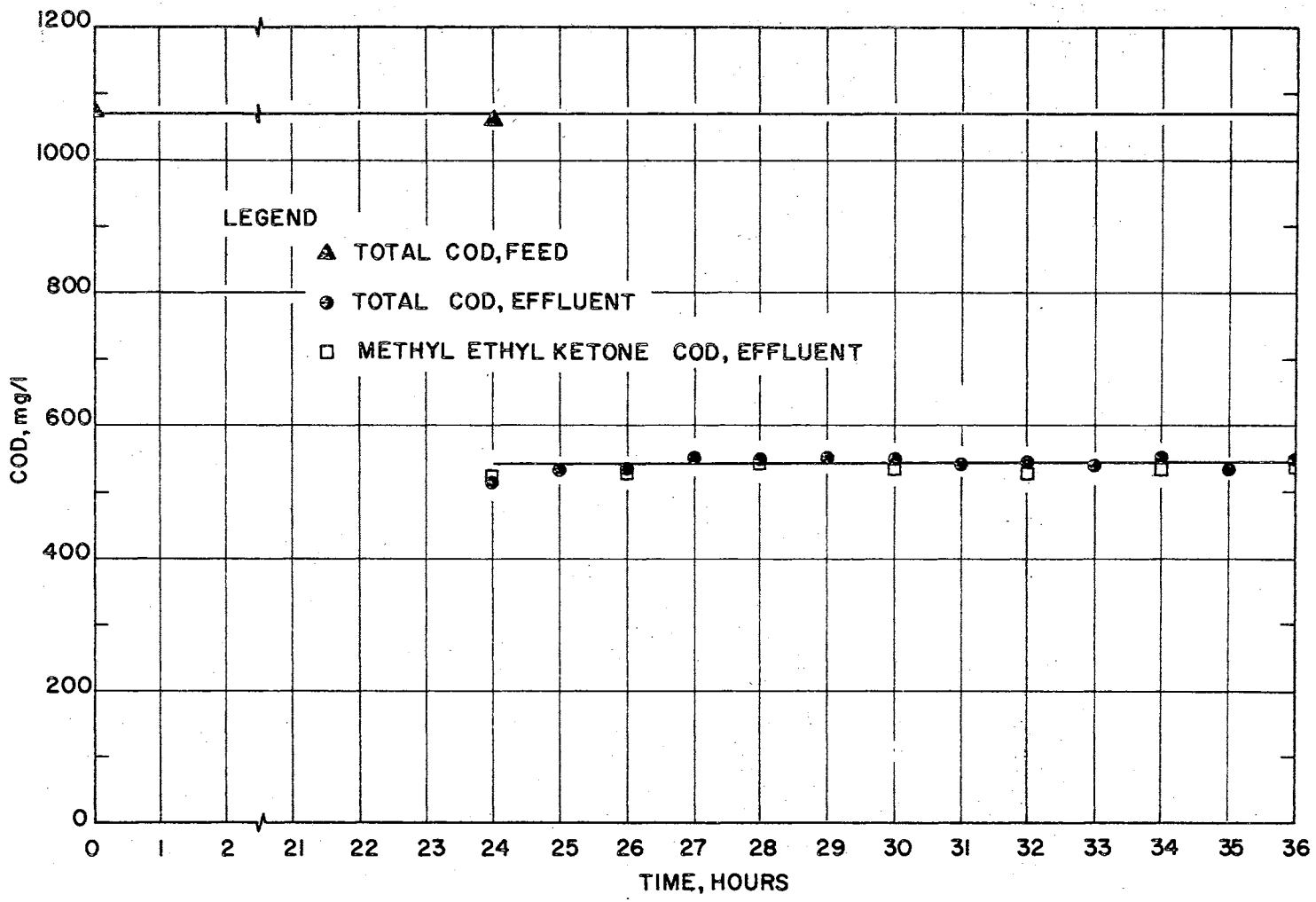


Figure 65 - Stripping of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 2000 cc/min.

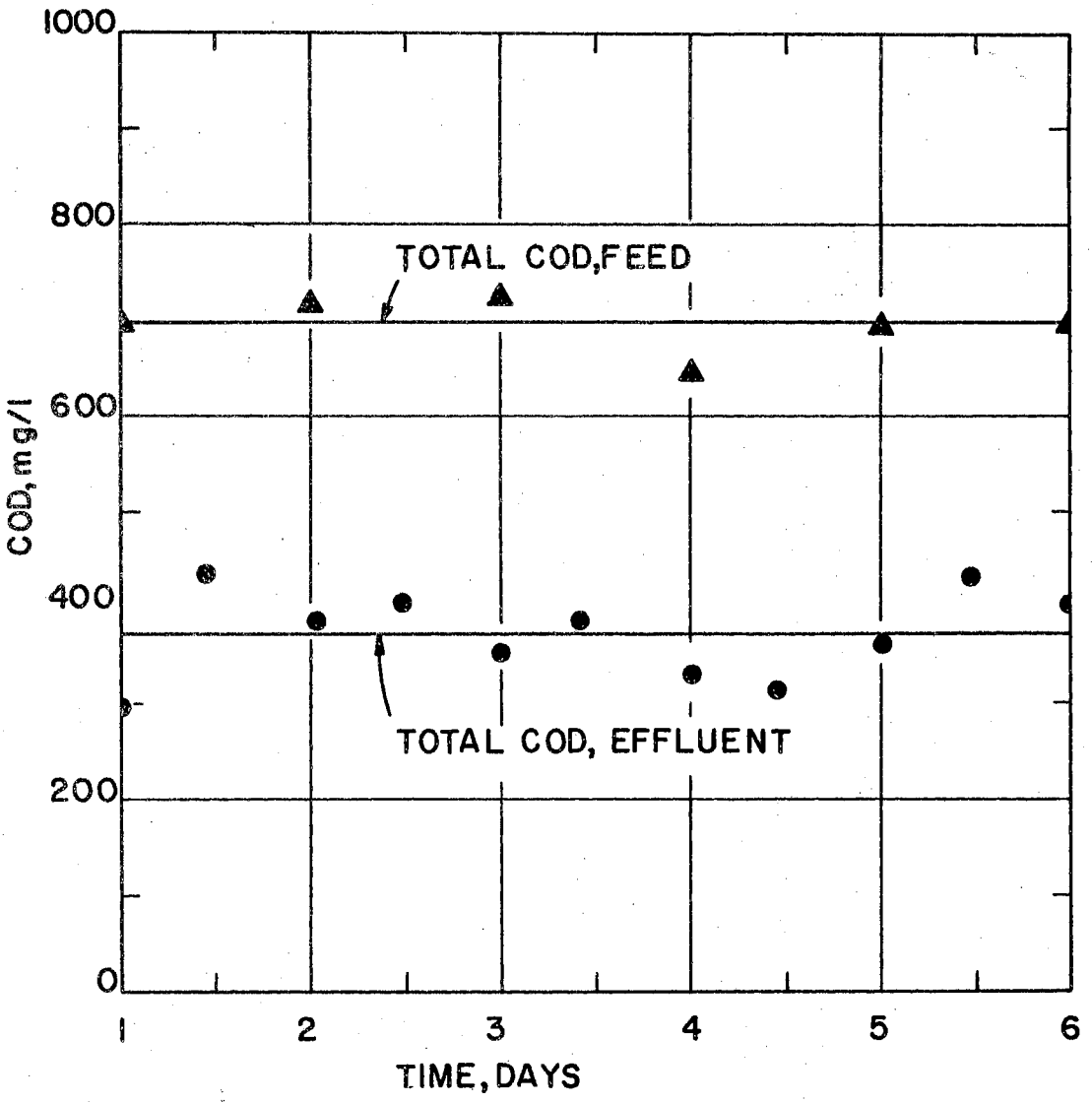


Figure 66 - Stripping of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 1000 cc/min.

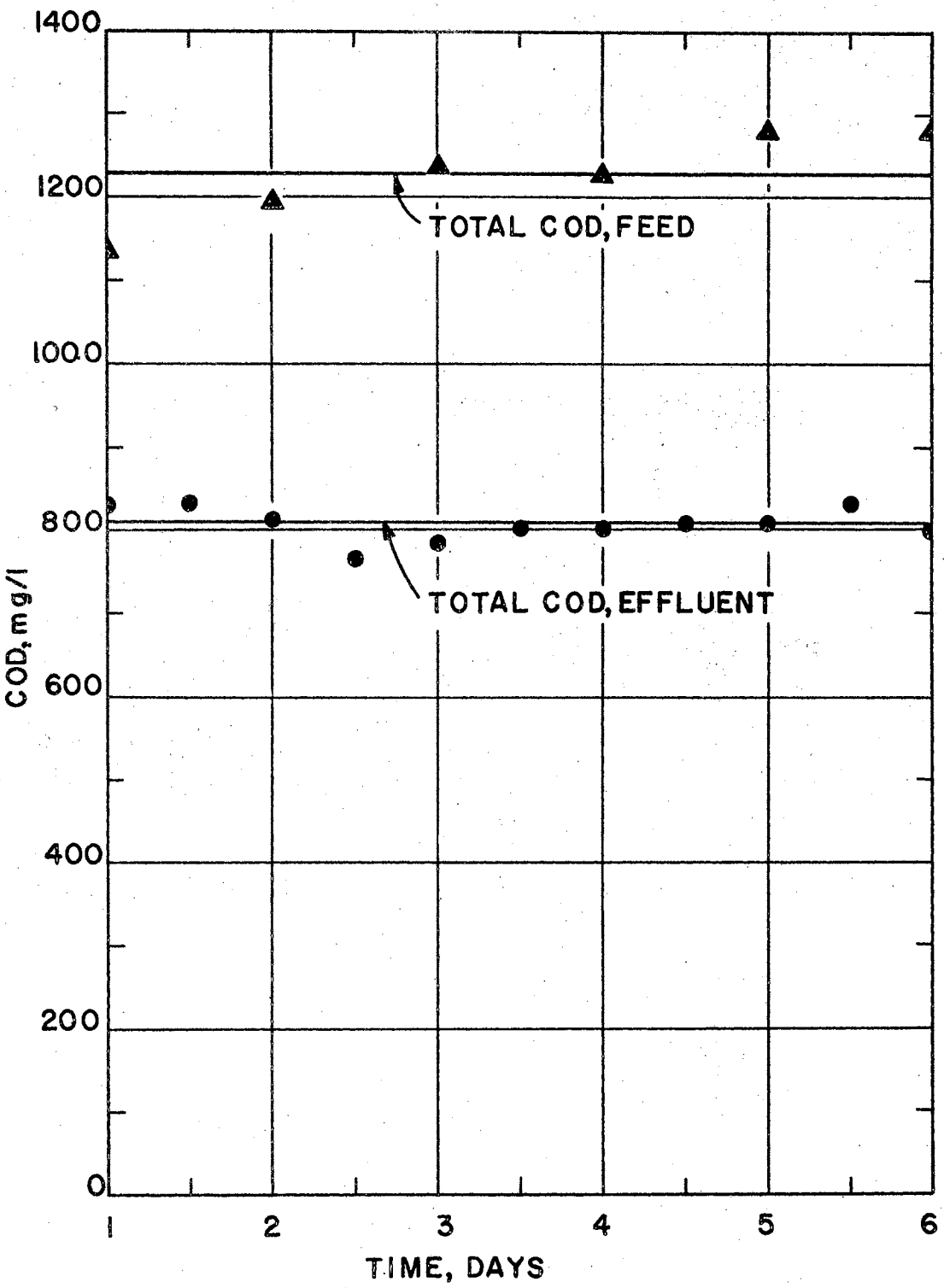


Figure 67 - Stripping of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 500 cc/min.

during any run. Any acidic oxidation product would have been expected to depress the pH, since the feed solution was made up in unbuffered distilled water.

Continuous removal of methyl ethyl ketone due to combined physical stripping and metabolism by an acclimated biomass with air applied at a rate of 4000 cc/min is shown in Figure 68. The average COD of the feed was 1788 mg/l and that of the filtrate was 368 mg/l, giving an overall treatment efficiency of 79.5 per cent due to joint physical-biological action. The average biological solids concentration was 268 mg/l. Regarding metabolic intermediates and/or endproducts, no compound other than MEK was detected by GLC analysis. On the fourth, fifth, and sixth day of operation about 50 per cent of the filtrate COD was accounted for by the untreated methyl ethyl ketone COD as obtained by GLC analysis. This was most probably due to the very low solids level prevailing in the aerator during this time. At all other times, methyl ethyl ketone was present in the system in only trace amounts. The biological solids concentration remained low for six days after starting continuous flow operations, and then increased and maintained a more or less "steady state" at a level between 400 and 500 mg/l.

Results of dual removal of methyl ethyl ketone at an airflow rate of 2000 cc/min are shown in Figure 69. The average feed COD was 603 mg/l, and the average filtrate COD was 22 mg/l, yielding an overall treatment efficiency of 96.4 per cent. No substrate, intermediates, or endproducts were detected in any of the filtrate samples by GLC analyses. The average biological solids concentration was 396 mg/l. Visually, the reactor contents during aeration appeared white, whereas the residue on the Millipore filter paper after filtration of a sample of

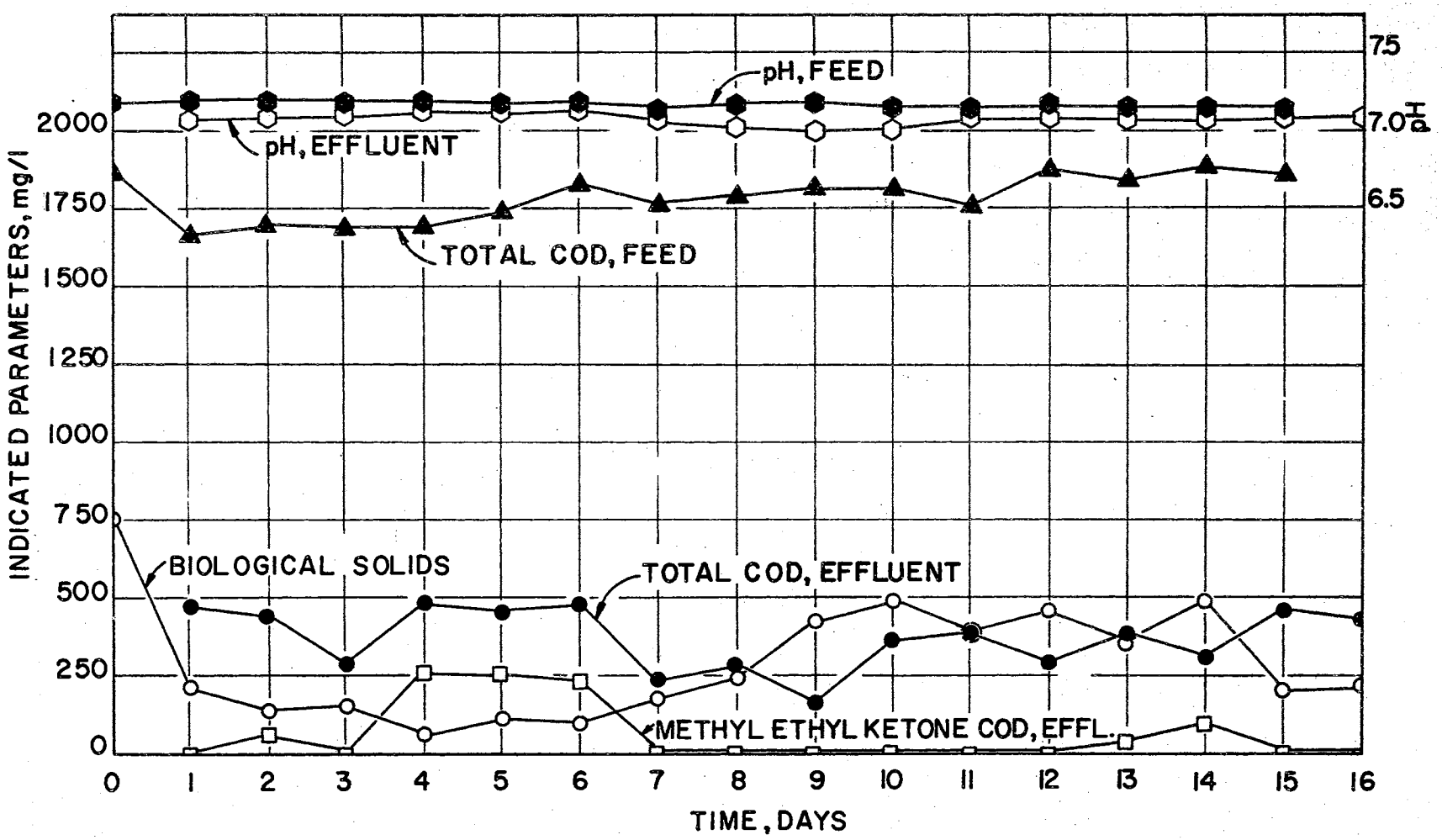


Figure 68 - Stripping and biological metabolism of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 4000 cc/min.

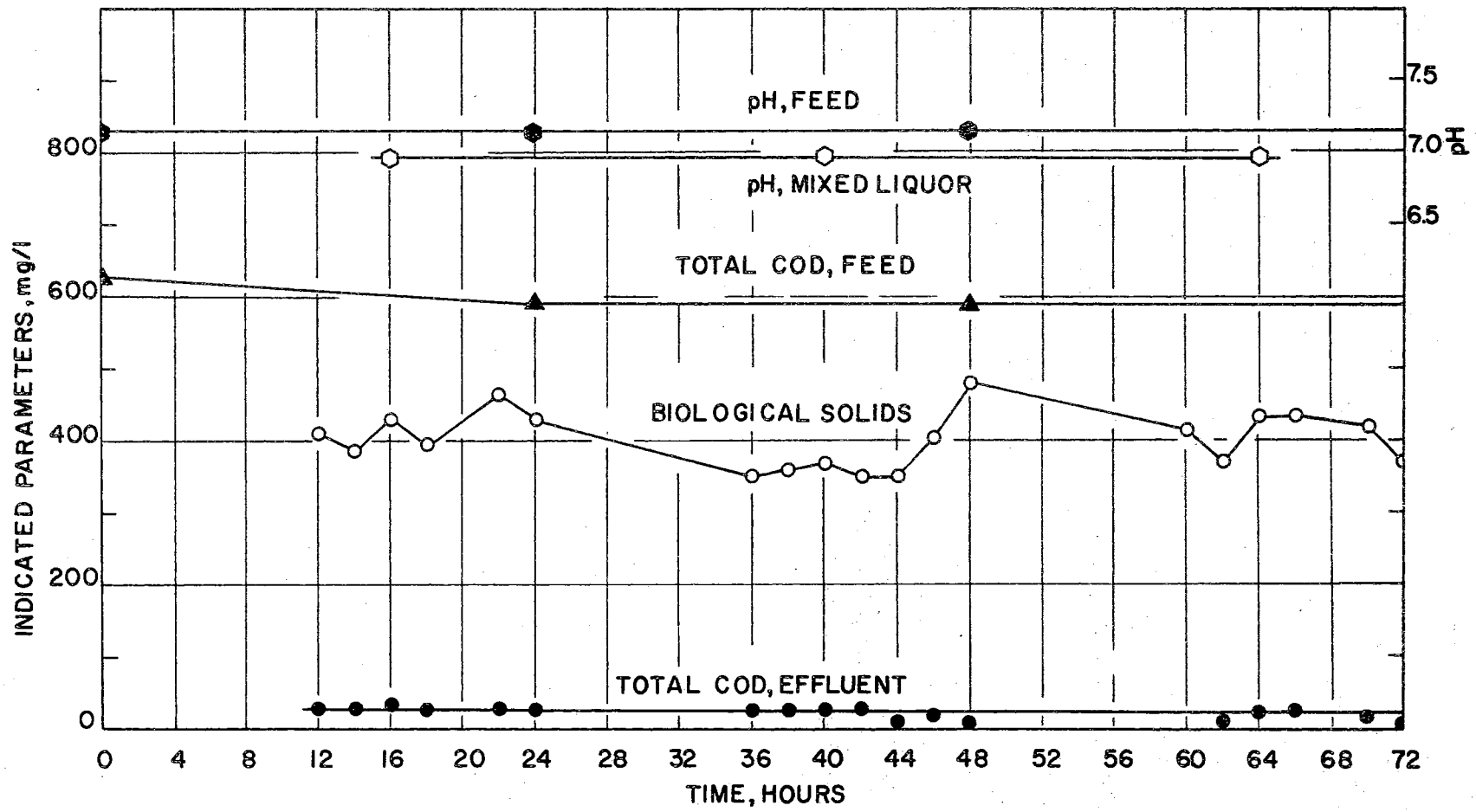


Figure 69 - Stripping and biological metabolism of methyl ethyl ketone in a continuous flow reactor at an airflow rate of 2000 cc/min.

mixed liquor was yellow in color. On the other hand, while the bottom of the reactor showed prevalence of some yellowish masses, mostly clinging to the sides, the entire reactor contents after blending by a Waring blender appeared white again. Microscopic examination of the mixed liquor at the 12th and 36th hours indicated the presence of filamentous organisms.

Propionaldehyde

Figure 70 represents the physical stripping of propionaldehyde at an airflow of 4000 cc/min. From an average feed COD of 884 mg/l, the steady state COD concentration averaged 333 mg/l, yielding a stripping efficiency of 62.3 per cent. Some of the feed concentrations were also checked by GLC analysis; their values on the plot are shown in open triangles. This unit was operated for six days under continuous flow conditions.

Figure 71 shows the results of stripping of propionaldehyde in the continuous flow unit at an airflow rate of 2000 cc/min. The feed concentration was checked periodically. From an average feed COD concentration of 998 mg/l and an average effluent COD concentration of 347 mg/l, the removal efficiency of propionaldehyde due to stripping amounted to 64.9 per cent. From GLC analyses, no compound other than propionaldehyde was detected in the samples. In fact, the total COD measurements were in close agreement with those by GLC analyses, except for slight variations (see Figure 71). In a similar run with propionaldehyde, where air was applied at the rate of 2000 cc/min, the stripping efficiency was found to be 66.1 per cent. For six days of continuous flow operation, the average feed and steady state effluent COD's were 831 and 282 mg/l, respectively.

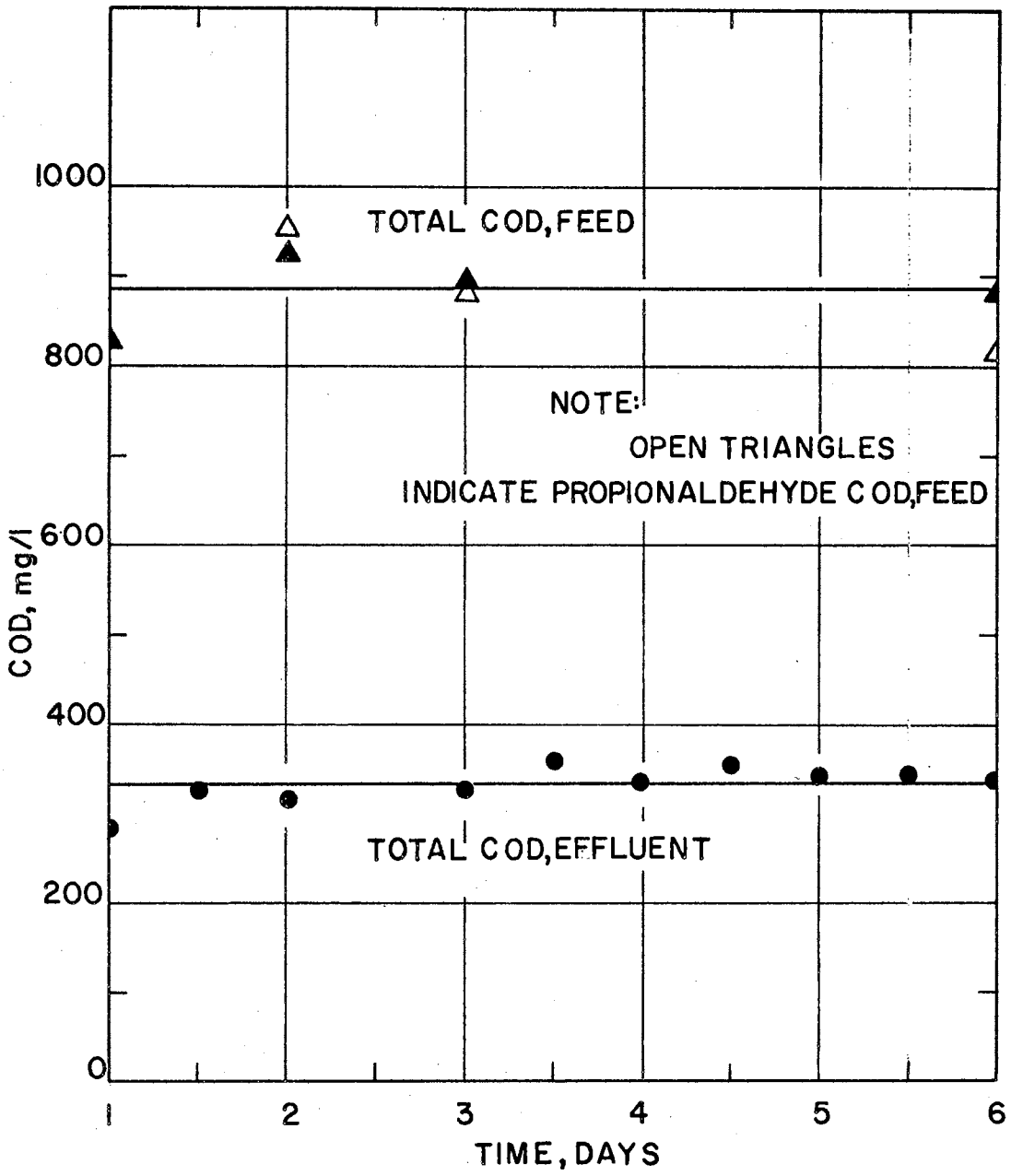


Figure 70 - Stripping of propionaldehyde in a continuous flow reactor at an airflow rate of 4000 cc/min.

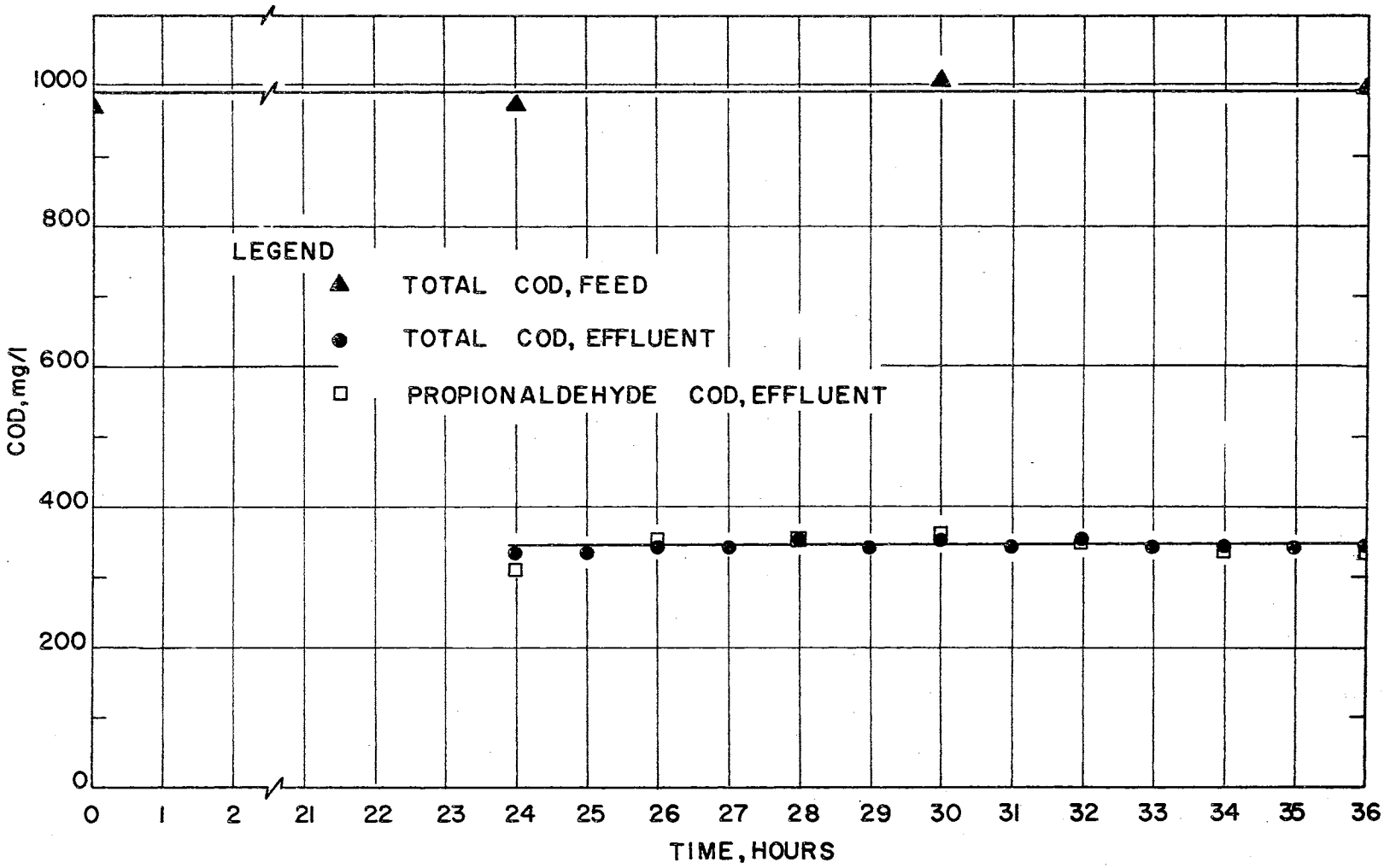


Figure 71 - Stripping of propionaldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min.

The stripping of propionaldehyde with air applied at 1000 cc/min is shown in Figure 72. The average feed COD was 913 mg/l. Fifty-one per cent of the feed propionaldehyde was stripped. With air applied at 500 cc/min, 40.8 per cent of propionaldehyde was stripped (see Figure 73). The average feed and steady state COD values were 833 and 493 mg/l, respectively. In all stripping experiments on propionaldehyde, the pH of the samples was approximately 7.0. In no case was there any drop in pH, indicative of acid oxidation products.

Figure 74 shows the results for the dual removal of propionaldehyde by stripping and biological action of acclimated cells with air applied at a rate of 2000 cc/min. Two distinct modes of behavior with respect to biological solids level and concentration of filtrate COD can be discerned in Figure 74. The average feed COD in the system for the entire period under study was 861 mg/l. The average filtrate COD up to 104 hours of operation was 323 mg/l. After this (until the end of the experiment) it was 135 mg/l. Correspondingly, the average solids concentration up to 104 hours of operation was 153 mg/l; after this time it was 356 mg/l. Overall treatment efficiency up to the transition was 62.5 per cent; it was 84.5 per cent thereafter. The high level of filtrate COD before the transition is accounted for by the relatively high amount of unremoved propionaldehyde. Also, during this period the biological solids level was rather low and propionaldehyde was partly oxidized to propionic acid. Propionic acid did not exist in the system after 46 hours. Approximately eight hours preceding the rise in biological solids level, propionaldehyde was no longer detected in the filtrate (except for trace amounts, not warranting peak area measurement). The average dissolved oxygen concentration was 6.7 mg/l, indicating

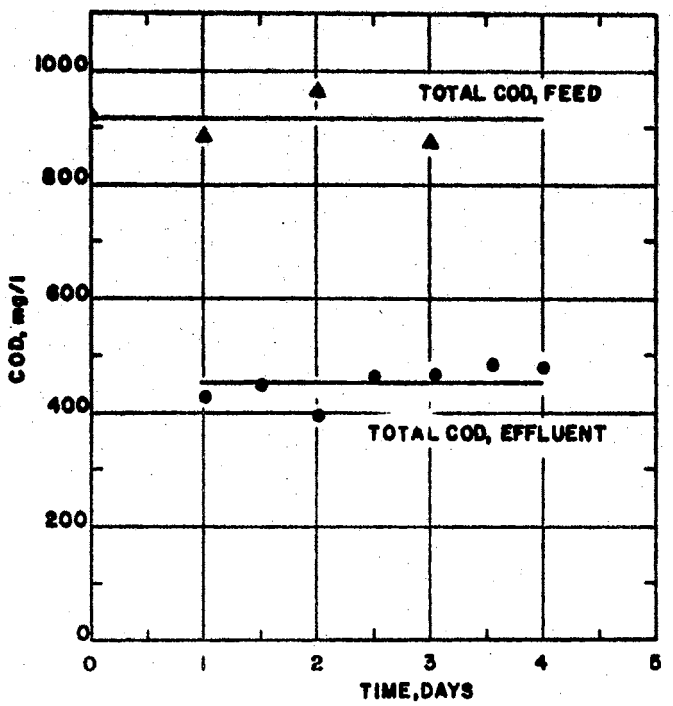


Figure 72 - Stripping of propionaldehyde in a continuous flow reactor at an airflow rate of 1000 cc/min.

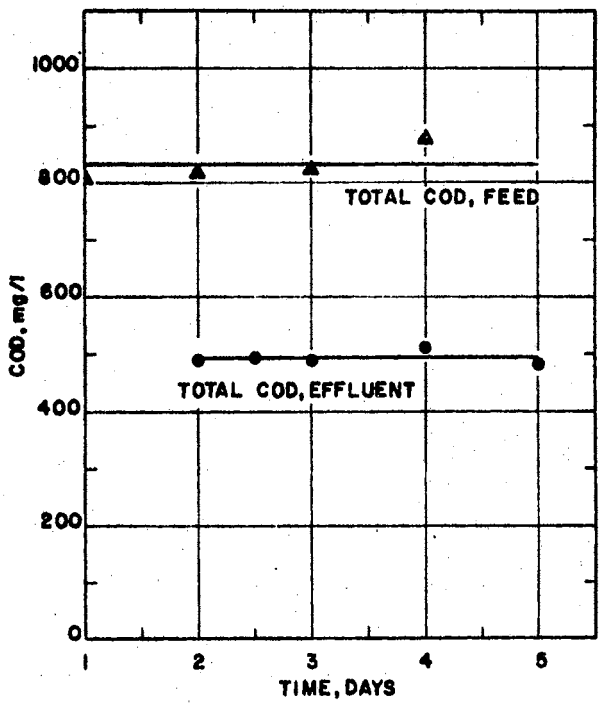


Figure 73 - Stripping of propionaldehyde in a continuous flow reactor at an airflow rate of 500 cc/min.

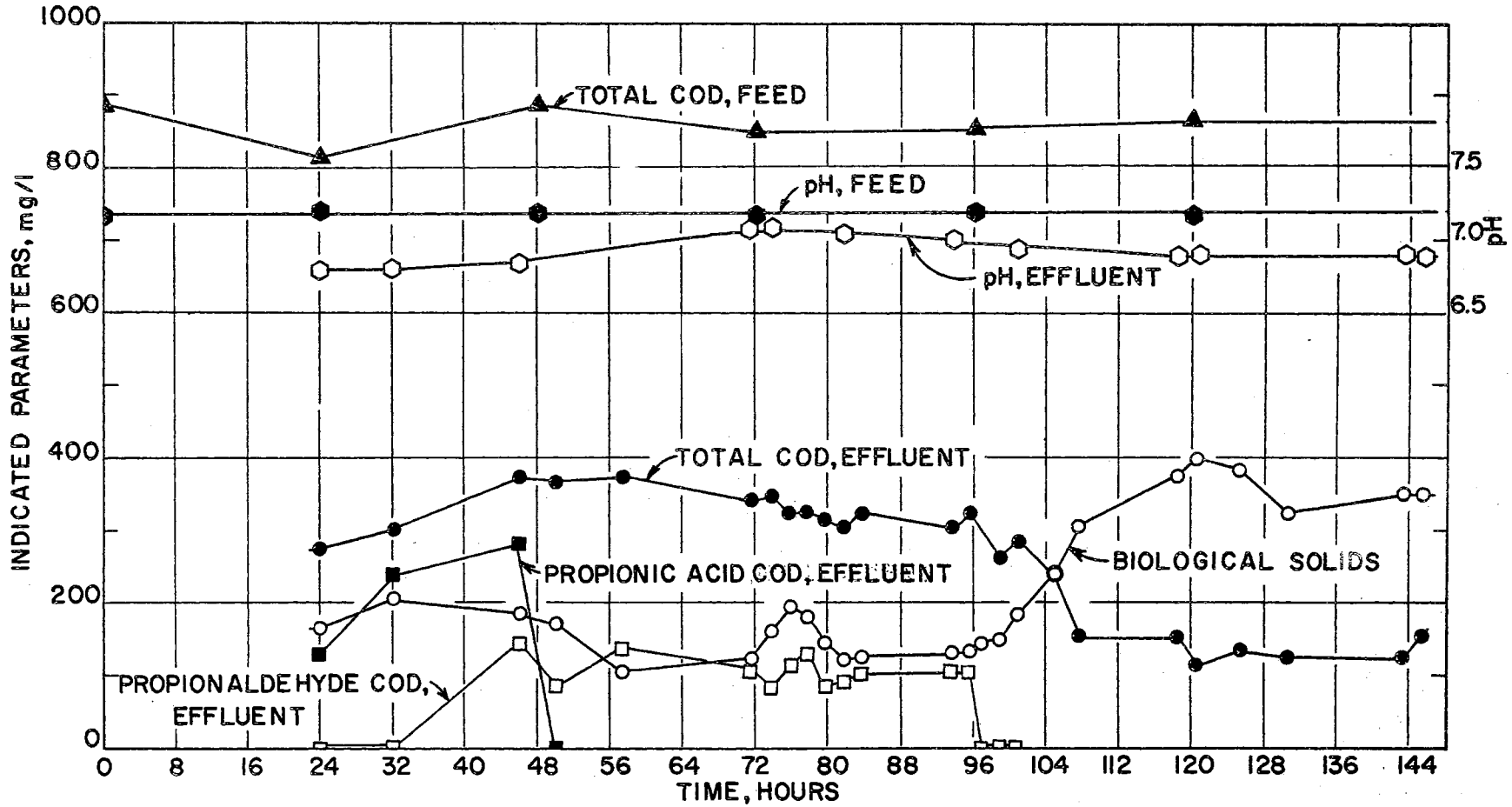


Figure 74 - Stripping and biological metabolism of propionaldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min.

sufficiently aerobic conditions prevailing in the reaction liquor at the biological solids concentration and airflow rate of the experiment.

Certain physical observations were made as time progressed. At twenty-four hours there was an abundance of foam above and around the peripheral overflow weir. At ninety-six hours of operation, flocs were seen in the unit; these disappeared on blending the reactor contents with a Waring blender. However, with progression of time, attached growth tended to develop around the thermometer inside the reactor as well as around the tygon diffuser tube immersed in the reactor. With the influent dropping inside the reactor, again there was formation of foam around the top rim of the aerator. At one hundred twenty hours of operation, and as observed earlier, the color of the reaction liquor was white, and the sludge had good settling characteristics. There was no visible indication of contamination of the feed, and solids in the unit exhibited an increase. From microscopic observations at one hundred forty-four hours of operation, mostly spherical organisms with some elongated rods were seen. Other than that, there were some entangled elongated masses. The color of the unit was milky white, and the sludge was not readily settleable. No flocs were seen at this time.

Butyraldehyde

The result of stripping butyraldehyde with air at 4000 cc/min is shown in Figure 75. The average feed COD was 788 mg/l, and the average COD in the aerator was 159 mg/l, yielding a removal efficiency of 79.8 per cent. From GLC analyses on samples, no peak other than butyraldehyde was observed. The apparent difference between the COD and GLC analyses on samples (of 46 mg/l) should not be taken as an indication of autoxidation products in this amount, since the feed concentrations by GLC

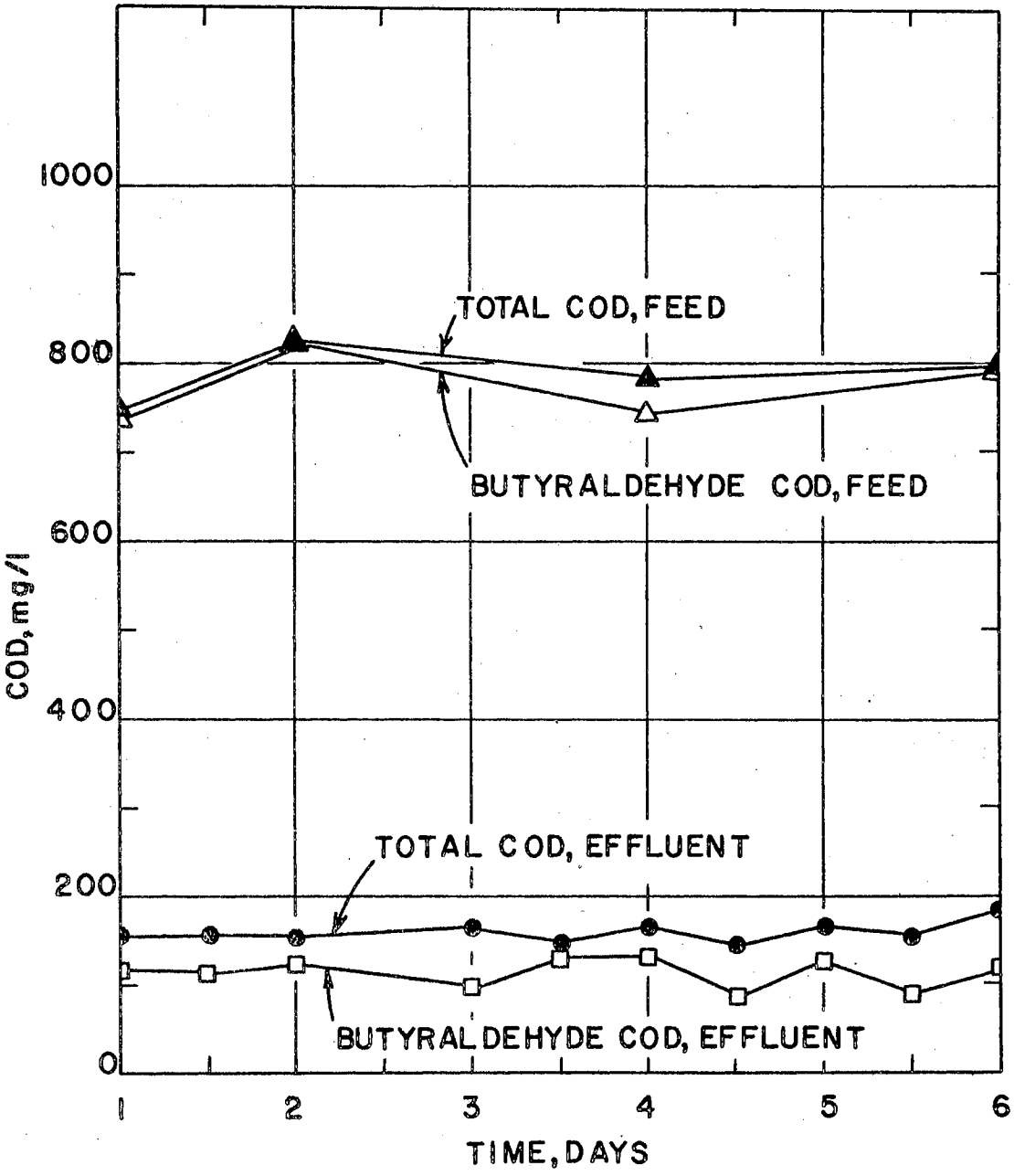


Figure 75 - Stripping of butyraldehyde in a continuous flow reactor at an airflow rate of 4000 cc/min.

were also correspondingly lower than their respective values by COD test. The pH of the samples was about the same as that of feed made up in unbuffered distilled water (pH = 5.50).

Results of butyraldehyde stripping at an airflow of 2000 cc/min are shown in Figure 76. Due to limited solubility of this compound in distilled water, feed concentrations were checked periodically for COD from the bottom of the feed reservoir, and between samples the reservoir contents were mixed by manual shaking. The average feed COD was 979 mg/l, whereas the steady state COD concentration was 263 mg/l, yielding a removal efficiency of 73.1 per cent at this airflow. All samples analyzed by GLC showed consistently lower values than attained by the COD test; however, no peak other than butyraldehyde was observed by GLC analyses on samples. The pH of the samples was the same as those of the feed (pH = 5.50) made up in unbuffered distilled water.

Valeraldehyde

The result of continuous stripping of valeraldehyde with air at 2000 cc/min is shown in Figure 77. Because of the limited solubility of this compound in distilled water, feed concentrations were checked periodically for COD; between such samplings the feed bottle was shaken for thorough mixing of the reservoir contents. Feed samples were also analyzed for COD concentration after such shaking (see Figure 77). The average feed COD was 920 mg/l, and the average steady state COD value in the aerator was 210 mg/l. The removal of valeraldehyde due to stripping alone at this airflow rate was 77.2 per cent.

From pH values of feeds (pH 5.8) made up with unbuffered distilled water, and samples (pH 4.45) it appears that stripping of valeraldehyde is accompanied by a drop in pH, indicative of acid oxidation products.

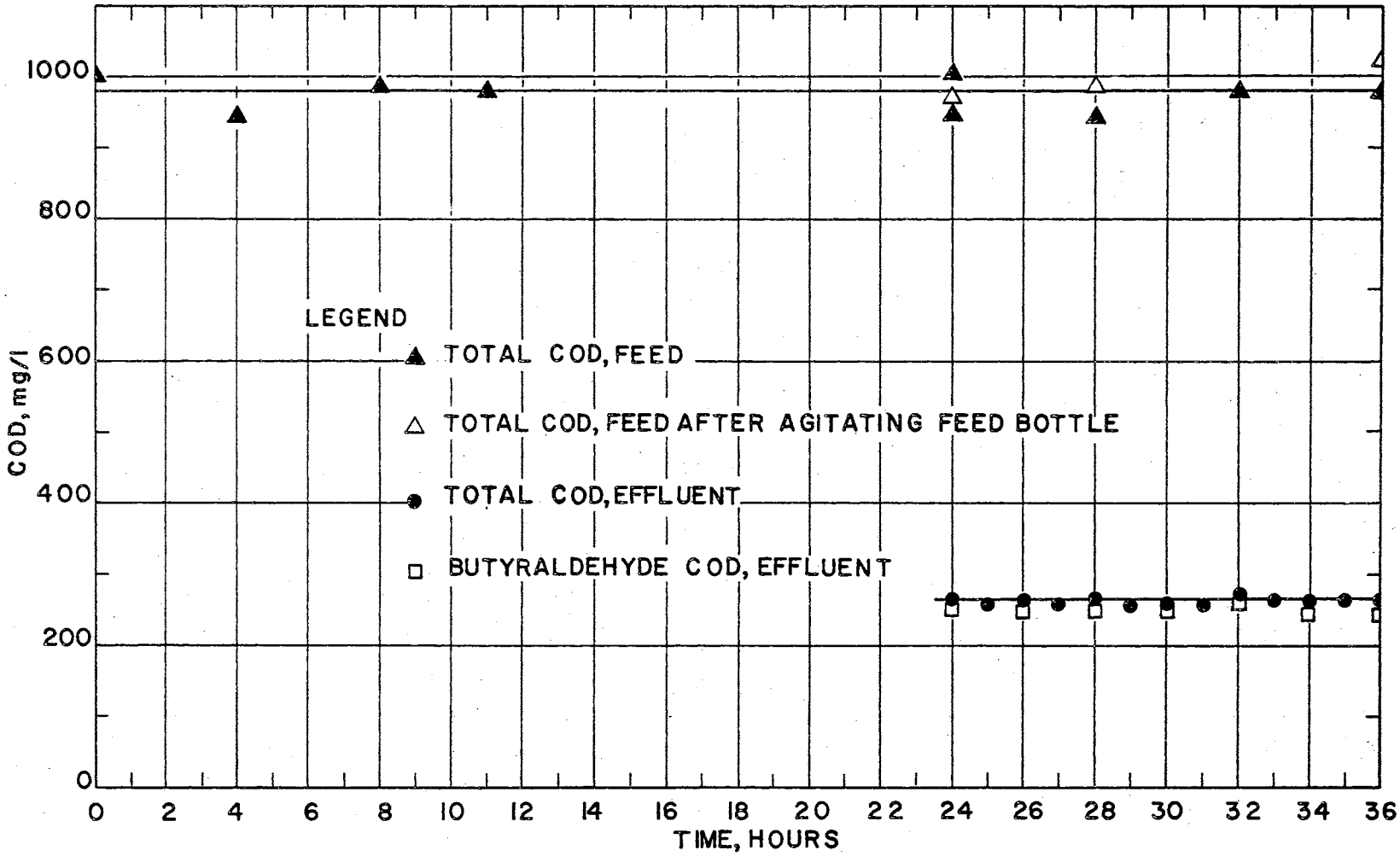


Figure 76 - Stripping of butyraldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min.

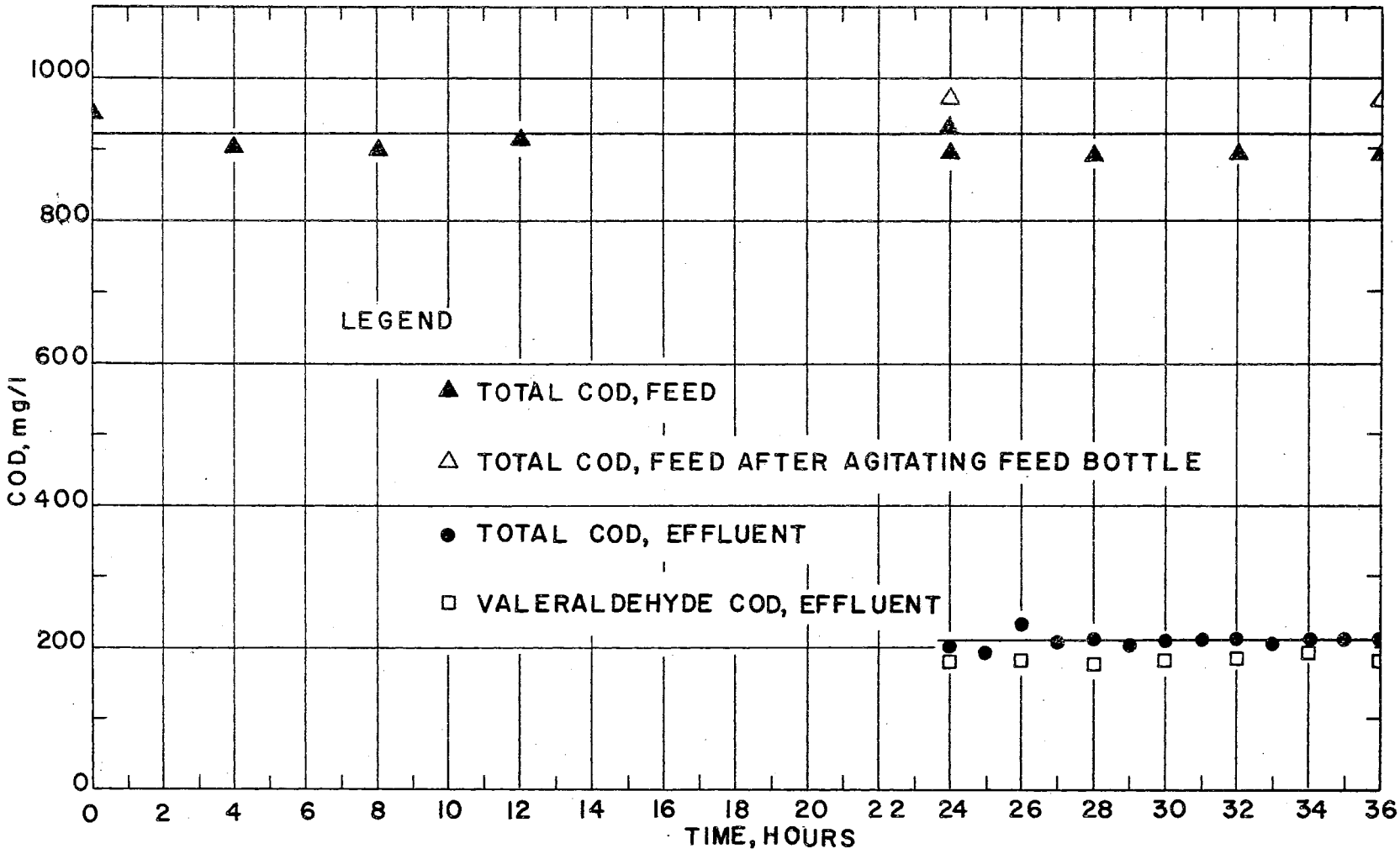


Figure 77 - Stripping of valeraldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min.

From GLC analyses of the samples it appeared that valeraldehyde COD was consistently slightly lower than the total COD values. In another run studying stripping of valeraldehyde at an airflow rate of 2000 cc/min, the average feed and steady state COD were 2184 and 605 mg/l, respectively. The percent stripping of valeraldehyde thus amounted to 72.3. This experiment was continued for five days. Feed was made up with distilled water plus nutrient salts and buffer. The average pH of the feed and samples was 6.95.

The results for valeraldehyde removal due to stripping at an airflow rate of 2000 cc/min plus metabolism by a valeraldehyde-acclimated microbial population are shown in Figure 78. The average feed concentration was 5025 mg/l (as COD). Average biological solids concentration after dilute-out of the high initial seed population was 476 mg/l, and average filtrate COD was 1941 mg/l. The overall removal efficiency of valeraldehyde by the dual mechanism was 61.4 per cent. There were severe fluctuations in cell parameters during this run. From the pH profile, it may be seen that throughout the experiment the pH was in the acid range. The average pH of the filtrate was 4.7. The usual amount of buffer in the synthetic medium was not sufficient to hold the pH in the neutral range. From analyses of filtrates by GLC it was found that a significant amount of the filtrate COD could be accounted for by the presence of valeric acid in the filtrate. Only small amounts of valeraldehyde were detected. It appears that valeraldehyde, under the experimental conditions which prevailed, was oxidized to valeric acid, which caused an acid pH. The results of two analyses, namely, COD and GLC on filtrates are shown in Figure 79. The results of the two measurements of valeric acid concentration are in good agreement. It

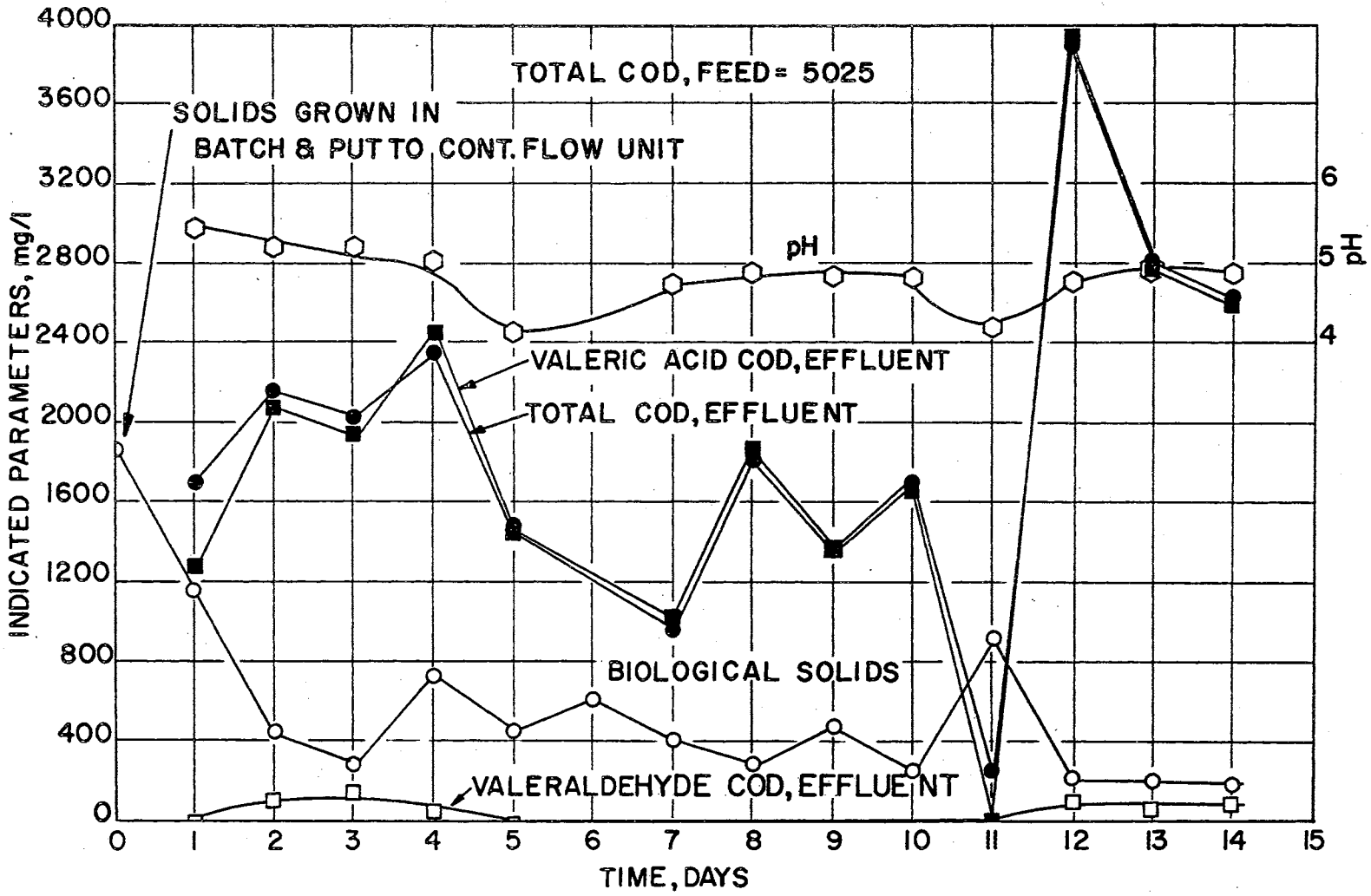


Figure 78 - Stripping and biological metabolism of valeraldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min at pH 4.7.

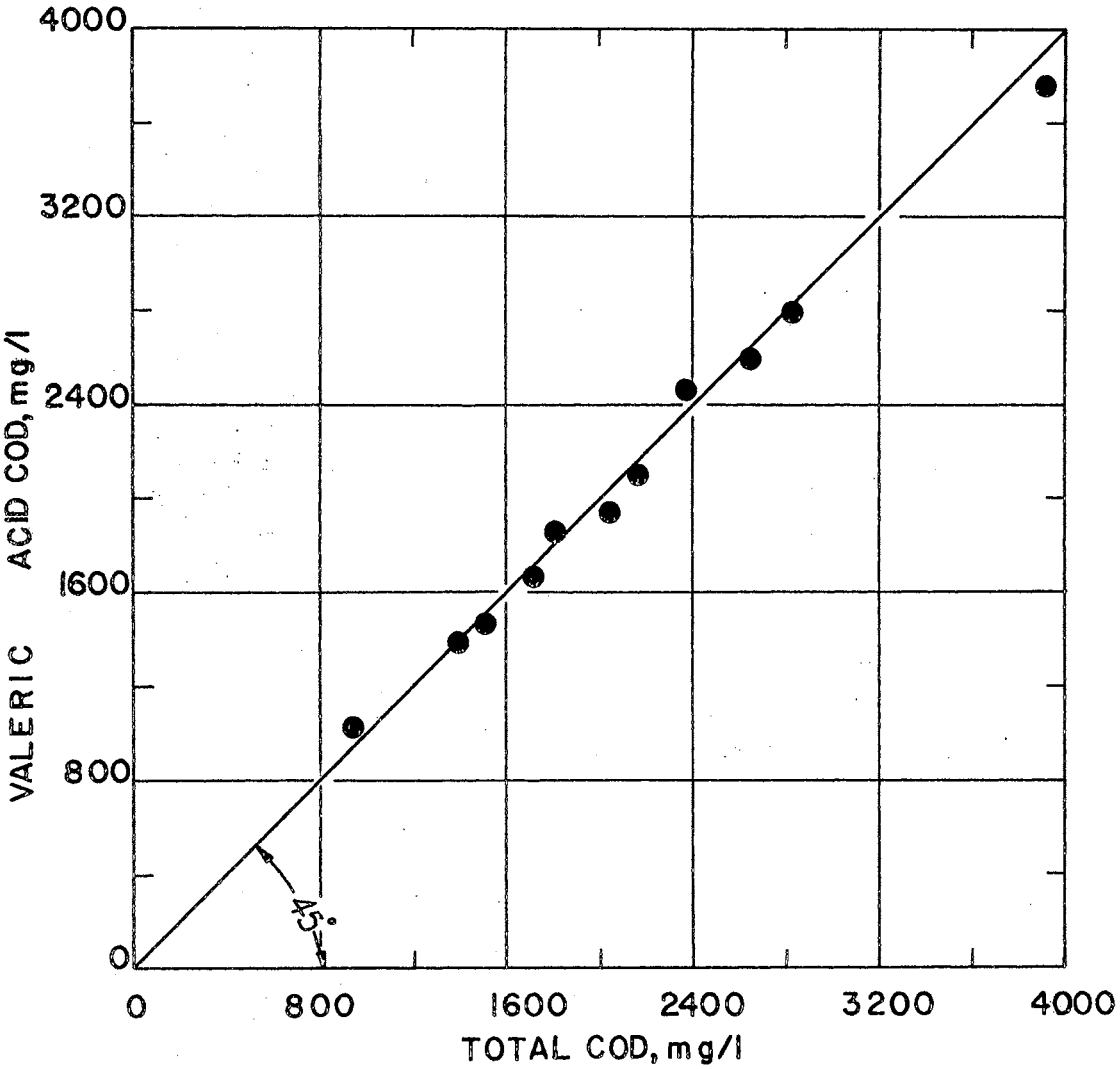


Figure 79 - Total COD versus valeric acid COD in filtrates of a continuous flow experiment with valeraldehyde at an airflow rate of 2000 cc/min during stripping and biological metabolism.

appears that valeric acid released in the medium was not actively metabolized by the biomass present in the system, nor was this acid very susceptible to physical stripping at 2000 cc/min of air.

The average valeric acid concentration in the filtrates was 2025 mg/l. Thus the strippability of valeric acid at a concentration of 2000 mg/l was investigated at an air supply of 2000 cc/min in a batch tube. The results are shown in Figure 80. It is obvious from Figure 80 that valeric acid is not susceptible to stripping, and the pH during aeration remains acidic and unaltered.

From results shown in Figure 78 it was reasoned that had the low pH level prevailing in the medium been brought to a more neutral level, microbial growth and COD removal efficiency might have been improved and the valeric acid produced by the population might have been metabolized. Another continuous flow experiment at an airflow rate of 2000 cc/min was conducted, the results of which are shown in Figure 81. The average feed COD (valeraldehyde) was 4340 mg/l. The average dissolved oxygen in the aerator during the run was 7.3 mg/l. At the start of the run, the pH of the mixed liquor was 6.8, dropping sharply to pH 5.0 after twenty-four hours. The pH of the mixed liquor was maintained at approximately 6.8 by addition of a larger amount of 1.0 M phosphate buffer. During the early part of the run, COD removal efficiency was rather high, and the biological solids level rose and was maintained above 1000 mg/l. Later, the biological solids level decreased and effluent COD increased. During this period both valeric and acetic acids were found in the filtrates. Most of the effluent COD could be accounted for as valeric acid. Acetic acid was detected only in the eighth and ninth samples, and in amounts of 22.8 and 127.5 mg/l of acid, respectively. From these

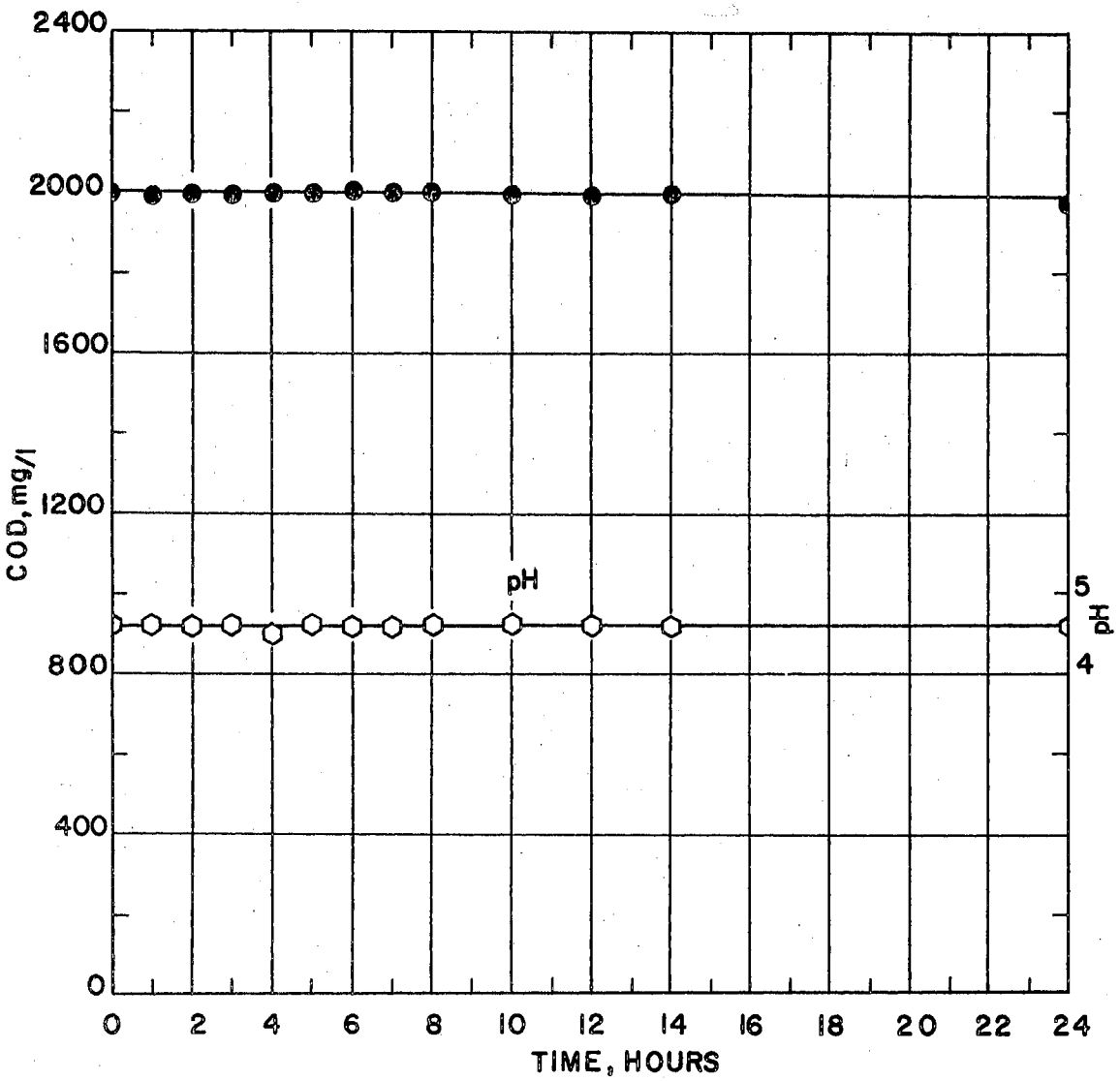


Figure 80 - Air stripping of valeric acid under batch conditions at 2000 cc/min/l.

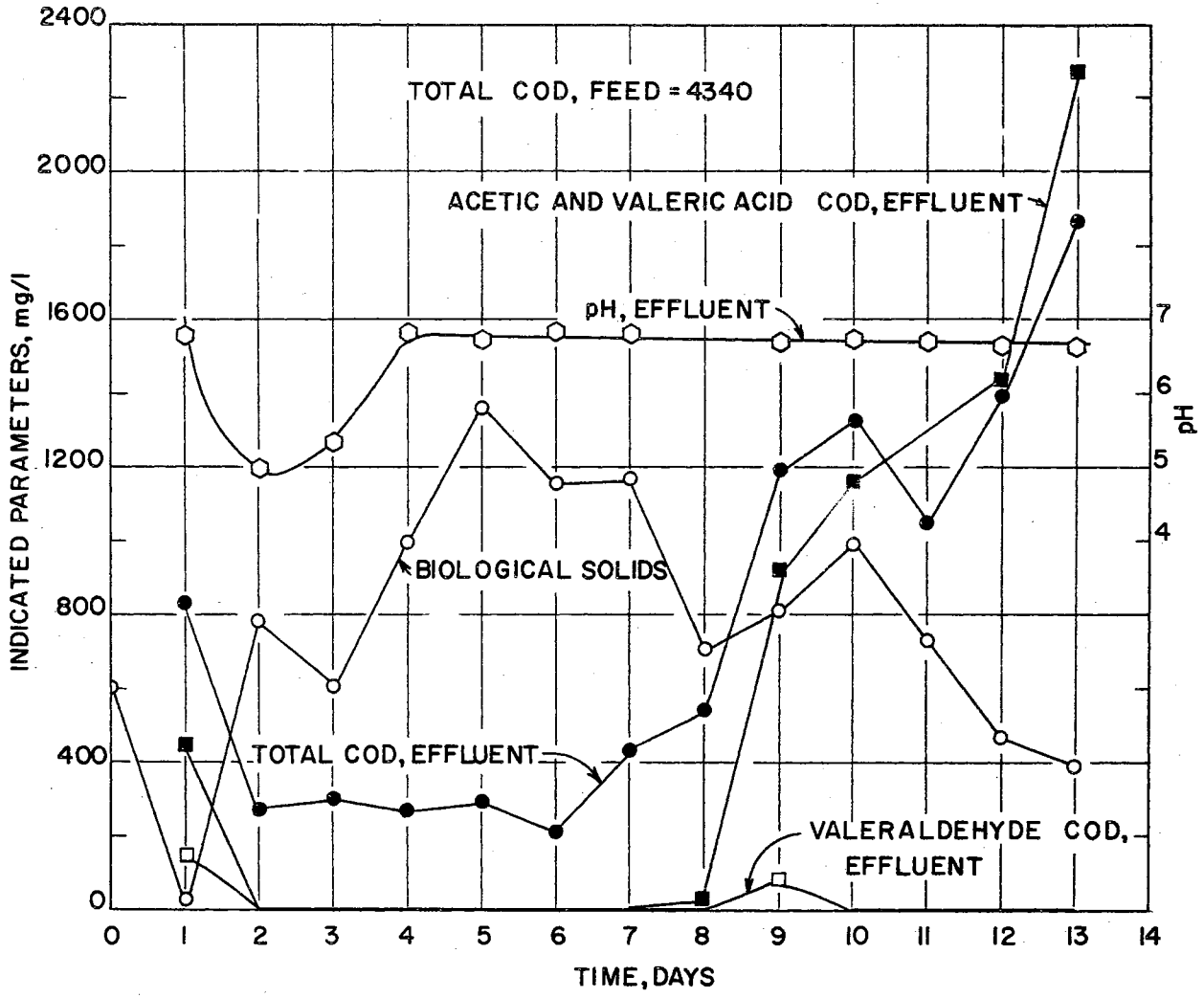


Figure 81 - Stripping and biological metabolism of valeraldehyde in a continuous flow reactor at an airflow rate of 2000 cc/min at pH 6.7.

results it would appear that the accumulation of valeric acid in the medium could not be prevented by maintenance of a pH (approximately neutral) more suitable for bacterial metabolism. The color of the unit was green, the reaction liquor was extremely thick. On blending the mixed liquor, it generated an abundance of foam and at times loss of biological solids was attributable to the escape of foam from the aerator. Because of the severely slimy nature of the mixed liquor, separation of biological solids by centrifugation and vacuum filtration demanded more time than usual. The consistency of the biomass retained on the filter paper was rather pasty and sticky. Microscopic observations of the reactor content under oil immersion revealed the presence of mostly rod-like organisms throughout, with some scattered lumps. It is interesting to note here that regardless of acid and neutral pH in the medium, in these two continuous flow experiments with valeraldehyde as substrate, the amount of acid intermediates attained their peaks at about the same time in either experiment; namely, on the twelfth day (Figure 78) and thirteenth day (Figure 81). This probably was due to the absence of acid-metabolizing organisms during these periods.

Biological Response in Completely Mixed Continuous Flow Reactor Subjected to Shock Loadings With Aldehydes and Ketones

The results of continuous flow operation by stripping and biological metabolism during a series of qualitative shock loading experiments are shown in Figure 82. Airflow during the entire operation was 500 cc/min, and only one diffuser was used. Cells were grown up in a batch system on MEK, then continuous flow operation was initiated on MEK. After a period of operation on MEK (average feed 897 mg/l COD) a series of shock loadings were applied consisting of acetone, MEK, butyraldehyde,

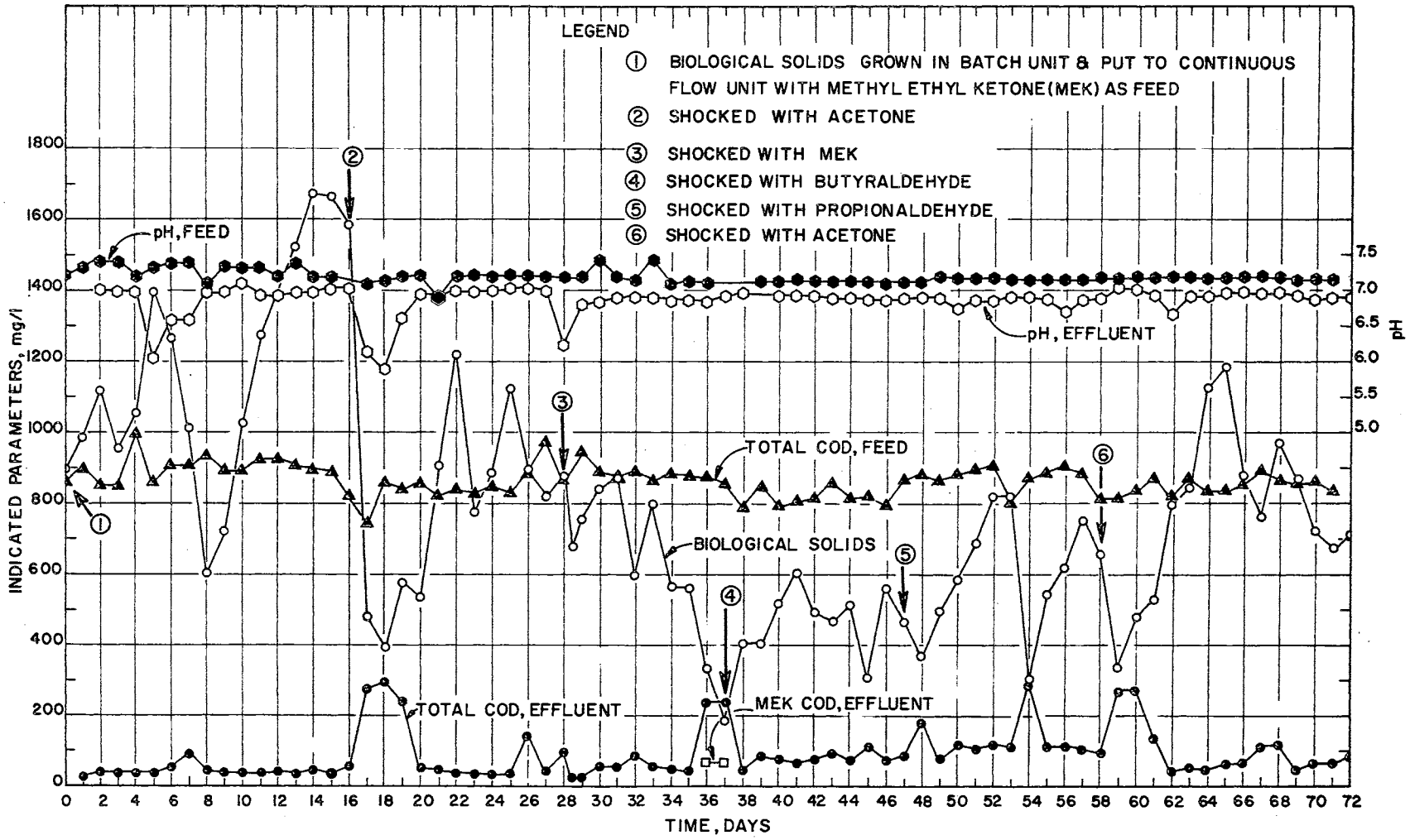


Figure 82 - Biological response in completely mixed continuous flow reactor subjected to shock loadings with aldehydes and ketones. Airflow = 500 cc/min, dilution rate = 1/8 hr^{-1}.

propionaldehyde, and acetone (average feed concentrations were 844, 883, 819, 887, and 846 mg/l COD,respectively). Under this qualitative shock operation, the biological solids in the system during the entire period of experimentation underwent severe fluctuations. The pH of the system was approximately neutral except at a few points where it dropped but was still within the optimum range for the activity of most common microorganisms.

The filtrate COD's were rather low except at some points immediately following a shock. For the entire period no metabolic intermediates and/or endproducts were detected by GLC analysis on filtrates; however, after shocking with MEK, during the last two days of operation when the biological solids decreased sharply, leakage of MEK was observed in the filtrates to the extent of 66 mg/l COD as compared with a total COD of 235 and 244 on these two days. The overall treatment efficiencies for the successive stages of operations were 95, 87, 81, 91, 85, and 87 per cent, respectively. These calculations were made taking into account the average feed and filtrate COD of each stage separately. Due to nonsteady state of the biological solids, yield calculations would be very unrealistic.

Certain observations with regard to the oscillatory nature of the biological solids seem warranted. The biological solids were heavily flocculated throughout the study and each day before sampling the unit contents were blended (in short bursts) in a Waring blender. While blending helped disperse the cells (to some degree), it did not really alleviate the problem and solids were retained in the unit. Periodically a dispersed condition would exist and the reactor would tend toward complete mixing; solids would begin to dilute out. The wide

fluctuations in biological solids concentration were thus caused largely by the flocing tendency of the cells and agitation at the airflow rate employed was insufficient to maintain complete mixing of the flocs.

Changes in predominating species also occurred during the experiment. On the 54th day of operation the color of the mixed liquor changed from deep yellow to a whitish flocculent mass.

CHAPTER V

ANALYSIS AND DISCUSSION OF RESULTS

Phase I

Studies on the Possible Production and Subsequent Stripping of Volatile Components During Aerobic Metabolism of an Initially Nonstrippable Carbon Source in a High Solids Batch System

A. Production of Intermediates and/or Endproducts and Their Dependence on F:M Ratio

From results presented in the preceding chapter, it becomes obvious that during substrate removal in high solids batch systems, metabolic intermediates and/or endproducts are released into the medium. Some of the metabolic intermediates and/or endproducts found their way, in the form of aerosols, to the absorbing flasks and exerted a COD; they were also detected by GLC. The amounts of metabolic intermediates and/or endproducts escaping from the aerator were much smaller than the amounts retained in the aeration unit. Essentially the same components found in the filtrates were found in the absorbates. For example, acetic, propionic, butyric, isovaleric, valeric, and hexanoic acids were detected by GLC in both filtrates and absorbates in varying degrees.

As can be seen from the ascending and descending limbs of the plots

of intermediates and/or endproducts in Figure 10 for the filtrate, these components accumulate in the medium, attain a maximum level, and then recede during the latter part of the run. This prevailing pattern of intermediates and/or endproducts is one which indicates that they continue to accumulate and ultimately reach a peak value at or near the time when the original carbon source has been removed from the system. At this time these products represent the only carbon source in the medium. In all cases examined in the present study, the new carbon source produced from the original substrate was then metabolized. It cannot be said from the observed data whether these products accumulate because they are not used concurrently with the original carbon source or whether they are simply produced at a much faster rate than they are used. However, it is known from other studies in the bioengineering laboratories that the presence of glucose (and other carbohydrates) can repress enzyme functions, leading to sequential removal. The results therefore suggest that the metabolic products were accumulated and not used until the original carbon source was exhausted. From a comparison of the anthrone and Glucostat analyses, it is clear that the accumulated products were not carbohydrates. The GLC analyses indicate that only a very small percentage of the intermediates and/or endproducts were short chain volatile acids. It is interesting to note that the small amounts of volatile acids which did accumulate were eventually removed. The peak value (at 45 minutes) for the run shown in Figure 10 was 6.5 per cent of the total intermediates and/or endproducts in the medium at this time. The F:M ratio seems to have a bearing on the amount of intermediates and/or endproducts released and/or accumulated; the higher the F:M ratio, the greater the production of intermediates and/or endproducts.

Regarding the immediate uptake of COD (expressed as a percentage of the initial COD) based on a thirty second sample, the results for the most part agree with those of Krishnan and Gaudy (5); however, at low F:M ratios, namely, 0.16, 0.34, and 0.44, the results reported herein deviate considerably from those of Krishnan and Gaudy (5). The immediate uptake as percent of initial COD for the three runs cited above were 66.6, 57.1, and 31.0, respectively. These high values can be related to the extremely high initial solids (15575, 7355, and 5520 mg/l, respectively) used in these three runs, and it is noted that they were much higher than those employed by Krishnan and Gaudy (5). It is interesting to note, although difficult to explain, that while an initial uptake or removal of COD was recorded, the COD which was removed in thirty seconds did not cause an equivalent rise in biological solids concentration. In all runs for which immediate uptake was measured (see Table III), the thirty second biological solids concentration was increased over the initial concentration (except for run 14), but to a lesser extent than would have been expected if the COD removed had been incorporated into the biomass.

B. COD Removed in Reactor Aerosols

From results presented in the preceding chapter (see Table III), it is clear that whenever arrangements were made to absorb the escaping aerosols, a significant amount of organic material was found in the absorbates regardless of the F:M ratio in the experiment. From gas chromatographic analysis the COD exerted was found to be due to acetic, propionic, isobutyric, isovaleric, valeric, and hexanoic acids. In two cases the COD's computed from GLC analysis exceeded the amount recorded by the total COD test. In one case (run 1) a considerable amount of

valeric acid was detected by GLC, and in the other (run 6) only isovaleric acid was detected by GLC. COD's run on these two compounds indicated that they were subject to chemical oxidation by acid dichromate. Therefore, they would be expected to be oxidized in the absorbate mixture; unexplainably, they were not. In all other cases the COD of the absorbate was higher than the sum of the COD values of the compounds detected by GLC. This type of result was expected, since the column which was used retains only volatile acids and some other low molecular weight compounds. Since the compounds which were detected are not strippable to any great extent by diffused air (the aldehydes and ketones of these compounds are strippable), it seems apparent that they were carried into the absorbate as an aerosol, not as a vapor. It is also possible that other organic metabolic products which existed in the medium in plentiful quantity (see Table III) and which could not be detected by GLC were also carried over in the aerosol.

From the results obtained it would not appear that the production of strippable compounds or, in any event, compounds easily carried away in aeration tank aerosols during the purification of a nonvolatile carbon source (e.g., glucose) accounts for a large portion of COD removal. Also, judging from the GLC analysis, it would not appear that the type and amount of compounds emitted to the atmosphere represent a serious health hazard to plant personnel. However, it is clear that the loss of COD due to "stripping" can affect the accuracy of a material balance written for the reactor. In one case (run 4) over seventeen per cent of the initial COD was found in the absorbate. From an operational and a research standpoint, it seems wise to consider this phenomenon where the major basis for a particular conclusion involves the results

of a material balance. It should also be noted that the COD values of the absorbates are conservative estimates of the COD stripped or carried over in the form of an aerosol because in the one experiment for which two absorbers were used in series, some COD was found in the second flask.

Phase II

A. Treatment of Strippable Compounds by Air Stripping Alone in Batch Units

Acetone

Acetone (at all airflow rates studied at 25°C) exhibited COD removal patterns in accordance with first order kinetics. This finding agrees with results of Gaudy and Engelbrecht (64). These authors used both conventional and "confined" column aerators in their study, and in both cases first order kinetics was observed. Their experimental setup for conventional and confined column aerators was as follows:

Conventional Aerator	Confined Column Aerator
depth = 15 inches	depth = 4 ft
volume = 28.3 liters (1 cu ft)	volume = 19.3 liters
1 diffuser in operation	4 diffusers in operation

In the present study only one diffuser was employed in a volume of one liter (depth of 6.25 inches) in a glass aeration tube. Also, the highest unit airflow rate employed in these studies was far in excess of that used by the previous authors. While these differences in aeration tank geometry and unit airflow rates did not affect the kinetic order of removal, the overall transfer coefficients or stripping coefficients at

comparable unit airflow rates were higher for the present studies than the values observed by Gaudy and Engelbrecht (64). In their studies an arithmetic plot of Ka (stripping constant) versus unit airflow rate for confined column showed the stripping constant at zero airflow (quiescent condition) to be 0.002 hr^{-1}. The corresponding value from the present work under quiescent conditions was found to be 0.00708 hr^{-1}. The value was obtained by measuring loss of COD under quiescent conditions. In the case of the conventional aerators, Gaudy and Engelbrecht (64) found the value of Ka at zero airflow was 0.023 hr^{-1}. The value was obtained by extrapolating the data to the axis. For the previous work, arithmetic plots of Ka versus unit airflow rate for conventional and confined column aerators yielded straight lines; however, the results of the present investigation, in which a wider range of airflow rates was employed, indicate that the data do not fit a straight line over the entire range of airflow rate. A plot of Ka versus unit airflow rate for the present investigation is shown in Figure 83.

Gas chromatography was also performed on samples at selected time intervals during a batch stripping run on acetone at an airflow rate of 4000 cc/min (Figure 12). It was found that the GLC data gave essentially the same removal rate as obtained by COD analysis. On the average, GLC values were 11.4 per cent lower than COD values, and no peaks other than for acetone were detected. It may be concluded that under the experimental conditions employed, acetone was not subject to any significant degree of autoxidation.

The fact that stripping did not materially alter the pH of the acetone-distilled water reaction liquor at any of the airflow rates provided further indication that an acidic oxidation product (resulting

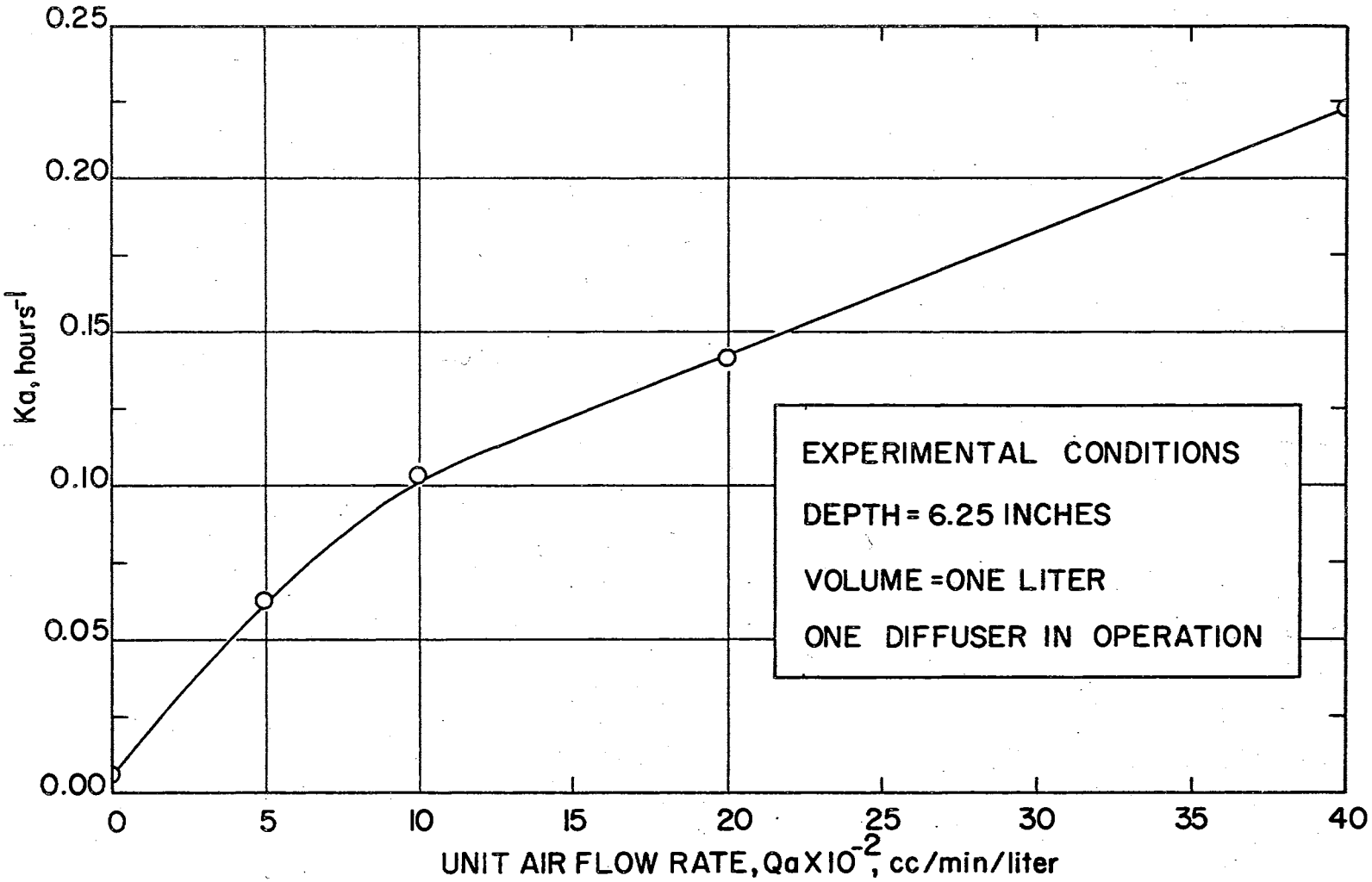


Figure 83 - Effect of unit airflow rate, Qa, on Ka for air stripping of acetone under batch conditions.

from autoxidation) was not formed to any significant extent.

At an airflow rate of 500 cc/min, disodium hydrogen phosphate seemed to have an adverse influence on the stripping of acetone (Figure 15). This compound had been very successfully used by Prather (57) in increasing COD removal from 70 per cent to 92 per cent for refinery waste waters. Disodium hydrogen phosphate is a very good emusifying agent and is used as a buffering agent in boiler water treatment and in cheese processing (65). While it may have enhanced stripping of whole refinery wastes, it did not enhance acetone removal.

Stripping of acetone under quiescent conditions gave interesting results, since the data could be plotted with equal facility in accordance with either first order or zero order kinetics (Figure 16). This occurred because, in the absence of artificial aeration or agitation, the system response was so sluggish that there was no appreciable difference between the successive remaining concentrations so that linear plots were possible in both arithmetic and semilogarithmic graphs. The loss of acetone COD amounted to 12.6 per cent of the initial COD after eight hours in the laboratory batch tube which had a surface area of 44 square inches (3.75" inside diameter). It is interesting to contemplate the effect for a surface area many times greater (for example, an oxidation pond). It would seem that much treatment efficiency could be achieved for very volatile compounds just by allowing the mixed liquor to stand (oftentimes at a temperature higher than 25^{o}C) subject to the turbulence provided by wind action.

Methyl Ethyl Ketone

Methyl ethyl ketone was removed from the methyl ethyl ketone-distilled water aeration liquor at various rates of airflow in

accordance with kinetics of the first order. This result was in accord with the findings of Engelbrecht, Gaudy, and Cederstrand (28). Both arithmetic and log-log plots of Ka versus unit airflow rate for MEK by these authors yielded straight lines. In the present study, however, neither type of plot resulted in straight lines over the range of airflow rates employed (Figures 84 and 85). The stripping values at comparable airflow rates were higher in the present study than reported by these authors (28). From the arithmetic plot the extrapolated stripping constant (0.0055 hr^{-1}) at zero airflow rate by these authors checked fairly well with that obtained under actual test conditions. This was achieved by these authors (28) by recirculating the methyl ethyl ketone-distilled water system through a pulsating pump. In the present investigation the corresponding experimental value under quiescent conditions was 0.0072 hr^{-1} (Figure 25). The agreement between the results of the two studies on acetone and methyl ethyl ketone seems rather good, and the differences which did occur seem to be due largely to tank geometry and the range of unit airflow rates employed.

As in the case of acetone, there was no evidence for autoxidation of MEK. It can be seem from Figure 22 that the COD and GLC data are practically superimposable. Disodium hydrogen phosphate at the dosage rate of 60 mg/l definitely increased the rate of MEK removal. It did not change the mode of kinetics of removal of the compound (Figure 24).

The behavior of acetone and MEK were similar in that both were stripped in accordance with first order kinetics, and there was no evidence of autoxidation of either compound. However, the overall transfer coefficients at airflow rates above 1000 cc/min were higher for MEK than for acetone.

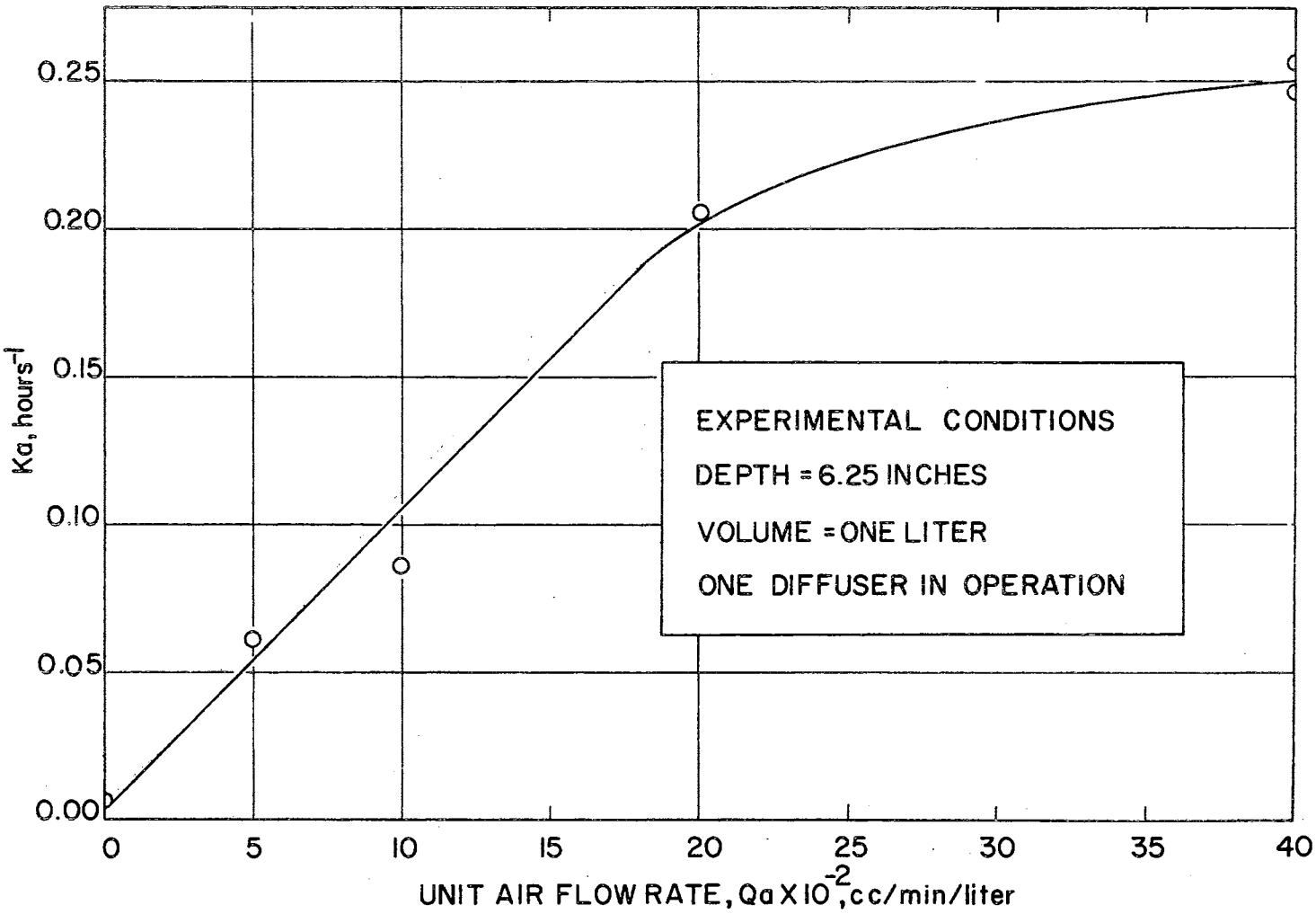


Figure 84 - Effect of unit airflow rate, Qa, on Ka for air stripping of methyl ethyl ketone under batch conditions.

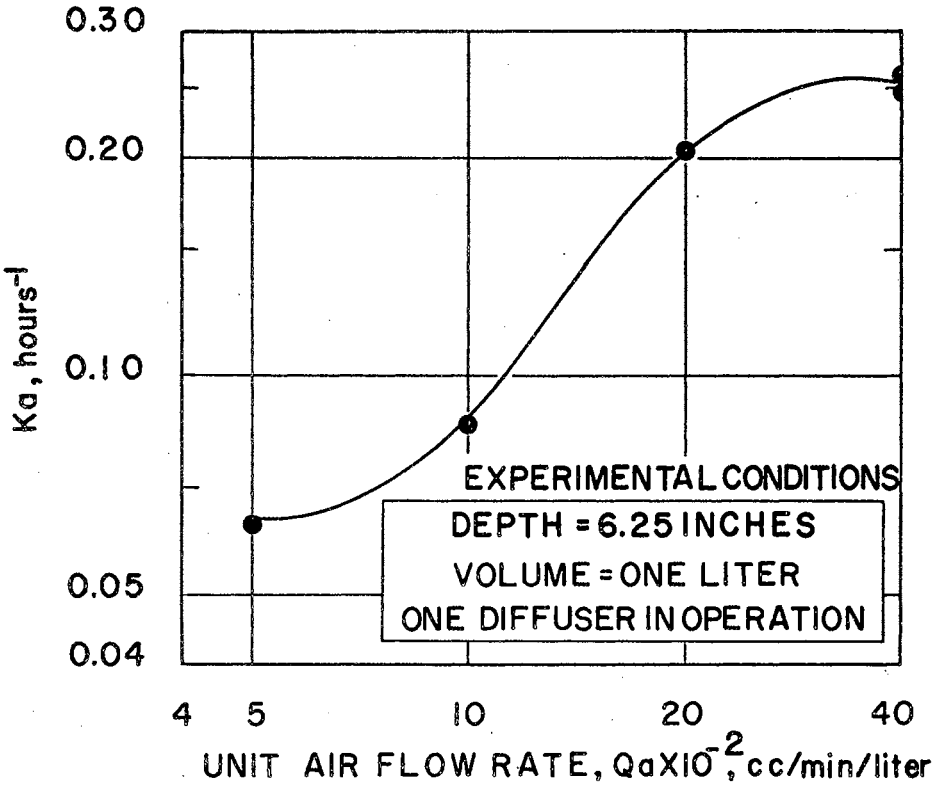


Figure 85 - Effect of unit airflow rate, Qa, on Ka for air stripping of methyl ethyl ketone under batch conditions (log-log plot).

Mixture of Acetone and Methyl Ethyl Ketone

It was observed from Figure 30 that removal of both acetone and MEK (analyzed by GLC independently) as well as removal of total COD of the mixture followed first order kinetics. The rate constant for the mixture, 0.15 hr^{-1} was approximately equal to the arithmetic average of the rate constants for acetone and MEK, i.e., $\left[(0.1317 + .20)/2 = 0.1658\ hr^{-1}\right]$. These values of the constants for acetone and MEK compared favorably with the first order rate constants (acetone = .1317 hr^{-1}; MEK = .2062 hr^{-1}) determined independently by the COD test. The fact that these compounds retained the same kinetic order and value for rate constants in the mixture shows that there was no interaction between the compounds in the mixture. Since acetone and MEK were mixed in approximately equal proportions, the rate constant of the mixture was approximately half of the sum of the values for each compound when it was the sole component in the system. The present results which showed that both acetone and MEK were stripped independently are in accordance with the results of Eckenfelder, Kleffman, and Walker (26) for aeration studies of solvent mixtures at 70°C and 200 cc/min/l airflow rate. This provided experimental evidence for the conclusions drawn by Eckenfelder, Kleffman, and Walker (26) on the stripping of the solvent mixture, especially of the acetone-MEK system, more convincingly in the sense that in the present research independent determinations of components of the mixture were possible by GLC analyses whereas the previous authors (26) used only COD as an analytical parameter to determine the course of removal in the mixed system as well as removal of the constituents of the system separately.

Propionaldehyde

Based on COD values, the removal of propionaldehyde did not conform to first order kinetics (for the entire course of the aeration period) at any of the airflow rates studied. However, under quiescent conditions first order kinetics was obeyed (Figure 35).

Gaudy, Engelbrecht, and Turner (29) reported that, at 25°C and at an airflow rate of 900 cc/min/l, removal of propionaldehyde followed first order kinetics. Using a specific test for the aldehyde group (30) it was possible for these authors to compare the rate of aldehyde removal with that of COD removal. For purposes of comparison with the results of previous workers, the run at an airflow rate of 1000 cc/min may be considered. As can be seen from Figure 33, the semilogarithmic plot of COD remaining at any time does not conform to first order kinetics when all of the plotted points are taken into consideration. The linearity of this plot ceases after two hours, whereas previous workers (29) reported a linear plot up to eight hours. This difference in findings with regard to the kinetics of propionaldehyde removal in the two cases may be traced to the differences in tank geometry, aeration device, and unit airflow rates. These workers (29) used the conventional aerator (rolling motion). The design specifications for their apparatus and for those used in the present study were described previously.

At an airflow rate of 2000 cc/min (Figure 32) when two analytical techniques were employed to follow the removal pattern of aldehyde, it was found from the GLC analyses that the aldehyde was removed more rapidly than the COD, and there was considerable divergence of the two curves beginning at the fourth hour. Based on GLC data, aldehyde

removal conformed to first order kinetics for about 97.6 per cent of the removal, and the kinetic constant was calculated to be 0.303 hr^{-1}. This constant for propionaldehyde is much higher than the stripping constants of the two ketones studied previously at this airflow rate under identical operational conditions. At all sampling points, GLC COD was lower than the total COD; the divergence was magnified as the run progressed. This result suggests the possibility that propionaldehyde was subject to autoxidation probably to the propionic acid level.

Even though the COD analysis of samples in the run at an airflow rate of 4000 cc/min was not accompanied by GLC analyses, the results of this run are consistent with the findings of the run at an airflow rate of 2000 cc/min. At the airflow rate of 4000 cc/min (Figure 31), the level of residual COD was more than double that at half this airflow rate (Figure 32). This is interpreted as an indication that at the higher airflow rate (4000 cc/min) there was an earlier onset of autoxidation to nonstrippable oxidation products. In other words, it would seem that the rate of autoxidation was greater at the airflow rate of 4000 cc/min than at 2000 cc/min, and the increase in rate of autoxidation is affected more than rate of stripping by increased airflow rate.

Butyraldehyde

On the basis of COD removal data, butyraldehyde did not conform to first order kinetics (for the entire aeration period) at any of the airflow rates employed. Gaudy, Engelbrecht, and Turner (29) also reported that butyraldehyde removal could not be characterized by first order kinetics at an airflow rate of 900 cc/min/l and at 25°C. Thus, regardless of the basic differences in tank geometry, mode and extent of aeration, the compound in both studies behaved in the same manner, i.e.,

nonconformity to first order kinetics. Both zero and first order kinetic profiles could be obtained with equal ease from either the arithmetic or semilogarithmic plots (Figure 44) for butyraldehyde stripping under quiescent conditions. The first order stripping constant calculated from the semilogarithmic plot (0.015 hr^{-1}) was higher than the corresponding value for propionaldehyde (0.0115 hr^{-1}) under identical conditions.

At an airflow rate of 4000 cc/min, the residual COD in the system was somewhat higher than in the system operated at 2000 cc/min of air. Based on results of GLC analyses for the latter experiment (airflow = 2000 cc/min), a straight line (semilogarithmit plot) was obtained up to two hours, which yielded a stripping constant of 0.514 hr^{-1} and provided evidence for the more rapid removal of aldehyde than of COD (stripping constant based on COD was 0.455 hr^{-1}). The divergence of the two curves (Figure 41, COD versus GLC) beginning from the 15-minute sample, indicated the presence of some compound or compounds in the samples in increasing proportions as aeration prceeded. The phenomenon of autoxidation was apparent, but the logical oxidation product, butyric acid, could not be detected using the Poly Pak-2 column, even at an attenuation of 4.

Butyraldehyde removal at an airflow rate of 500 cc/min exhibited first order kinetics for a considerable period of time, and the same trend with a higher rate constant was observed with the addition of disodium hydrogen phosphate. The solubility of butyraldehyde (3.7 gm/100 ml) might have been enhanced in the butyraldehyde-distilled water aeration liquor by the addition of the emulsifier.

Valeraldehyde

Removal of valeraldehyde was not in accordance with first order kinetics at the various rates of airflow employed in the present study. This result agrees with the previous results of Gaudy, Engelbrecht, and Turner (29) at an airflow rate of 900 cc/min/l. Valeraldehyde disappeared from the system faster than did the COD (Figure 50). The divergence between the two curves could not be attributed to the accumulation of valeric acid, a possible oxidation product of valeraldehyde.

Valeraldehyde was removed by air stripping more rapidly than the other aldehydes studied under batch conditions. No definite kinetic order could be established from the COD curve alone for the whole period of aeration; however, when both GLC and COD analyses were conducted concurrently on samples, it was found from the experiment at an airflow of 2000 cc/min (Figure 50) that aldehyde was removed faster than COD, and that the aldehyde removal pattern could be described by a first order rate constant. The divergence between the COD and GLC data at lower concentrations was attributed to the possible autoxidation product of valeraldehyde, valeric acid. However, valeric acid could not be detected by the GLC analysis; neither were propionic and butyric, the postulated autoxidation products due to air stripping respectively of propionaldehyde and butyraldehyde, detectible. However, in each case where both COD and aldehyde were measured, aldehyde removal was found to be faster than COD removal, experimentally supporting the explanation previously proposed by Gaudy, Engelbrecht, and Turner (29) for non-first order kinetics with these compounds on the basis of COD removal alone.

From GLC data which yielded a straight line up to two hours on the semilogarithmic plot (Figure 50), the slope was calculated to be

0.62 hr^{-1}, which was the highest rate constant (on the basis of GLC data) for all of the aldehydes subjected to stripping at an airflow rate of 2000 cc/min. This rate constant was even higher than the rate constants of the ketones at 4000 cc/min of air. On the basis of COD data, the stripping constant was calculated to be 0.5081 hr^{-1} (Figure 50). Stripping at 2000 cc/min of air did not materially alter the pH of the medium; the initial pH was 4.75, and the average during the experiment was in the same region, about 4.80. Disodium hydrogen phosphate at 60 mg/l slowed the COD removal pattern of valeraldehyde at an airflow rate of 500 cc/min (Figure 52). Valeraldehyde is slightly soluble in water. The added dosage of the phosphate compound apparently did not emulsify or disperse the valeraldehyde-distilled water mixture to render it more susceptible to stripping. In contrast to all quiescent state batch experiments with other aldehydes and ketones, a zero order kinetic plot was not feasible with valeraldehyde (Figure 53). However, with the possible exclusion of the initial COD value, a first order plot was obtained through the rest of the points. From the semilogarithmic plot the rate constant was found to be 0.0125 hr^{-1}. This value is lower than the corresponding value with butyraldehyde, and slightly higher than the value for propionaldehyde.

Since some of the compounds were stripped in accordance with first order kinetics while others were not, the stripping constants do not provide a ready basis for comparing the ease of removal of the compounds from solution by aeration. As a basis for comparison, the COD removal for each compound after two hours and after eight hours of aeration is listed for all airflow rates in Table V. For acetone and MEK (which were stripped in accordance with first order kinetics) the beneficial

TABLE V

COD REMOVAL (EXPRESSED AS PERCENT OF INITIAL COD) FOR VOLATILE KETONES AND ALDEHYDES AFTER TWO AND EIGHT HOURS OF AERATION AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS

Unit Airflow Rate cc/min/l	Acetone		Methyl Ethyl Ketone		Propionaldehyde		Butyraldehyde		Valeraldehyde	
	2 hrs	8 hrs	2 hrs	8 hrs	2 hrs	8 hrs	2 hrs	8 hrs	2 hrs	8 hrs
4000	66.2	98.0	71.4	98.5	71.6	79.5	89.5	93.7	94.5	95.0
2000	44.8	92.6	59.5	97.2	77.1	93.5	86.0	95.6	89.3	-
1000	30.4	84.4	30.9	80.1	50.25	84.2	60.0	90.0	76.6	96.4
500	18.9	66.5	26.2	68.5	39.2	79.8	50.0	90.0	65.5	93.7
0	3.98	12.62	2.82	12.07	4.76	13.75	4.18	20.9	12.5	26.8

effect of airflow rate is apparent at either the 2-hour or 8-hour sampling points. For propionaldehyde, which was subject to some degree of autoxidation to products less strippable than the original aldehyde, increasing airflow rate beyond 2000 cc/min retarded COD removal and the result may be interpreted as an indication that airflow rate had a greater effect on rate of autoxidation than on rate of stripping. However, butyraldehyde and valeraldehyde were so strippable that even though they were subject to autoxidation (to less strippable compounds), overall COD removal did increase with increasing airflow rate.

The results indicate that both the 3-carbon ketone, acetone, and the 4-carbon ketone, MEK, were removed solely by stripping with air. This conclusion is based upon the facts that both were removed in accordance with first order kinetics, there was concurrence of the COD and GLC data, and there was no depression in pH during aeration. On the other hand, the aldehydes (propionaldehyde, 3 carbons, butyraldehyde, 4 carbons, and valeraldehyde, 5 carbons) were subject to some degree of autoxidation. This conclusion is based upon the facts that they were not removed in strict accordance with first order kinetics, and there was some divergence of COD and GLC data. This finding is expected since aldehydes are much more readily oxidized than are ketones.

For both the aldehydes and the ketones, the removal rate was higher for compounds with the greater number of carbon atoms in the chain. Based upon GLC data, and considering only the early portion of each run during the studies at an airflow rate of 2000 cc/min, first order constants could be estimated. The values increased as the number of carbons increased, i.e., propionaldehyde, 0.303 hr^{-1}, butyraldehyde, 0.514 hr^{-1}, and valeraldehyde, 0.62 hr^{-1}. These values were higher

than those for the corresponding ketones tested at a comparable airflow rate. Using the COD data for stripping studies with the aldehydes, only a rough approximation of first order kinetic conditions could be obtained, since none of the aldehydes was removed in strict accordance with kinetics of the first order over the entire aeration period. The values plotted in Figure 86 represent the slopes for the best first order fit of the data (curves fitted by eye). As with ketones (see Figures 83 and 84), the rate constants increased at a decreasing rate as airflow was increased. The relationship between stripping rate and airflow could be taken as approximately linear up to an airflow rate of 2000 cc/min.

Phase II

B. Treatment of Strippable Compounds by the Activated Sludge Process (Batch Studies, Stripping Plus Metabolism)

Acetone

Acetone removal efficiency due to the joint action of physical stripping and biological utilization by acclimated organisms of sewage origin was increased at all airflow rates over the removal efficiencies observed for air stripping alone. It will be recalled that stripping of acetone at all airflow rates conformed to first order kinetics. Under the added influence of biological metabolism, certain deviations from this kinetic order (with respect to COD removal) were observed in some systems. With a dual removal mechanism in operation, COD was removed in accordance with first order kinetics to a point at or near the exhaustion of the added substrate (see Figure 17). From a semilogarithmic plot of COD remaining versus time for the data of Figure 17,

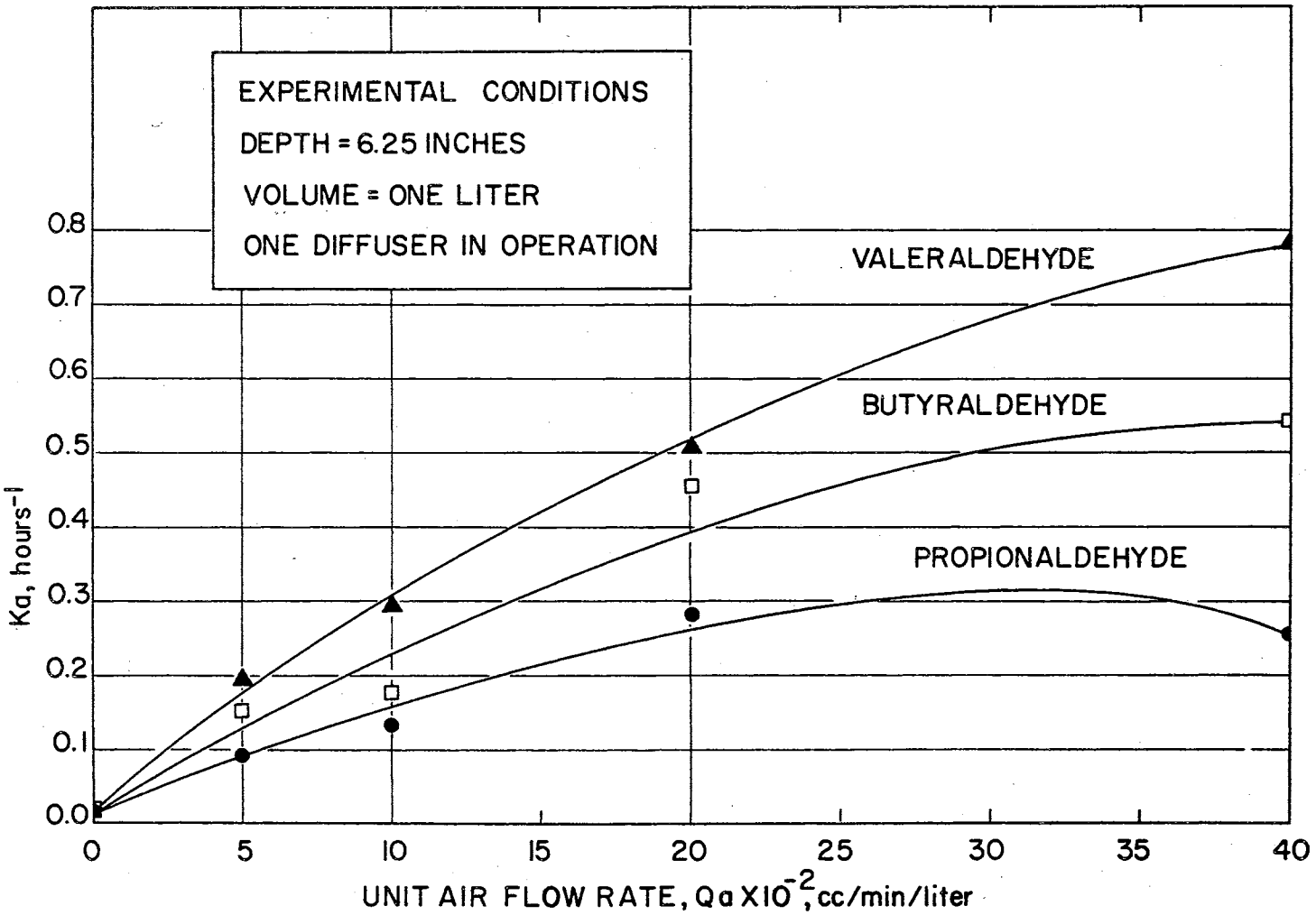


Figure 86 - Effect of unit airflow rate, Qa, on Ka for air stripping of propionaldehyde, butyraldehyde, and valeraldehyde under batch conditions.

the first order rate constant was calculated to be 0.2784 hr^{-1}, whereas the corresponding first order rate constant by stripping alone was 0.224 hr^{-1}. Thus at the high airflow rate (4000 cc/min) bacteria did not alter the mode of kinetics for COD removal nor did they increase the rate of COD removal to an appreciable extent. From an initial biological solids of 612 mg/l, the system showed a steady decline (except for a slight increase between 0.5-1 and 3-4 hours). This result indicated that for the most part, acetone removed by the cells was not channelled into synthesis. In the absence of Warburg data, wherefrom one might obtain the kinetic mode and magnitude for biological metabolism alone, it was assumed that biological removal rate was first order. The equation developed by Gaudy, Turner, and Pusztaszeri (3) was used; when both stripping and biological removal followed first order kinetics the overall removal according to these authors (3) could be predicted by the following equation:

$$C = C_o \cdot 10^{-(Ka + Kb_1)t}$$

where

C = substrate (COD, mg/l) at any time t

C_o = substrate (COD, mg/l) at zero time

Ka = first order stripping constant (hr^{-1}) using common logarithms

Kb_1 = first order biological constant (hr^{-1}) using common logarithms

t = time in hours

Using the above equation, the first order rate constant for biological metabolism was calculated to be 0.048 hr^{-1}. This value is low, but does not seem unrealistic. From actual determination in the Warburg apparatus, Gaudy, Turner, and Pusztaszeri (3) found the first order rate

constant of biological metabolism of acetone to be 0.0308 hr^{-1} with an initial solids concentration of approximately 300 mg/l of acclimated cells.

The observed difference between the total COD and the acetone COD indicated the presence of a significant amount of metabolic intermediates and/or end products; however, no specific compound other than the substrate (acetone) was detected.

In the experiment for dual removal at 2000 cc/min of air (Figure 18) the initial biological solids concentration was 640 mg/l. Unlike the previous experiment, the COD removal curve could not be fitted to first order removal kinetics. From the 0.5-hour sample until substrate exhaustion, a zero order rate constant of 123 mg/l/hr was calculated. Physical stripping of acetone at this airflow rate proceeded in accordance with the first order kinetics (rate constant = 0.142 hr^{-1}) without giving rise to autoxidation products. The compounds other than acetone in the system are therefore probably directly ascribable to the metabolic activity of the microorganisms present. It is interesting to note that even though the kinetic order of substrate removal was decidedly changed, the presence of the microorganisms significantly enhanced COD removal. This increase in COD removal efficiency at the 4000 and 2000 cc/min airflow rate was effected even though very little of the substrate was channelled into sludge synthesis. It is noted that there was some increase in biological solids concentration at the 2000 cc/min rate, but none at the 4000 cc/min airflow rate. This difference would seem attributable to the magnitude of physical stripping. In the system with 4000 cc/min of air (Figure 17), stripping proceeded so rapidly that little substrate was available for the cells. From an operational

standpoint, such a system might be desirable since sludge-handling facilities could be considerably reduced; however, the cost of supplying this high rate of airflow might be prohibitive. At an airflow rate of 2000 cc/min, less of the acetone was stripped, and more was available to the organisms for growth; hence, some increase in biological solids was registered.

At an airflow rate of 1000 cc/min, the first order rate constant for acetone removal by stripping alone was 0.105 hr^{-1}, and that by dual removal at an initial biological solids concentration of 1060 mg/l (Figure 19) was 0.3580 hr^{-1}. The presence of acclimated cells did not cause any shift in the order of kinetics of COD removal. Using the equation of Gaudy, Turner, and Pusztaszeri (3) the first order rate constant for biological removal of acetone was estimated to be 0.2568 hr^{-1}, which is fairly close to the value of 0.2530 arrived at by subtraction of the first order stripping constant from the first order dual removal constant. For the experiment shown in Figure 19, the COD was removed in 3.5 hours; however, in a similar run at this airflow rate (1000 cc/min) and with an initial biological solids concentration of 450 mg/l (results not plotted), acetone was eliminated from the medium only after 6.5 hours, and not much sludge synthesis was observed. Thus it appears that for effective sludge synthesis to occur, higher levels of initial biological solids concentrations are desirable.

A considerable amount of sludge synthesis was observed during the study at an airflow rate of 500 cc/min with an initial biological solids concentration of 928 mg/l (Figure 20). The slope of the line of best fit from a semilogarithmic plot of COD versus time yielded a first order rate constant of 0.2787 hr^{-1}, whereas the first order rate

constant from the stripping run at this airflow rate was 0.0628 hr^{-1}.

Methyl Ethyl Ketone

Under conditions of physical stripping alone, methyl ethyl ketone was stripped strictly in accordance with first order kinetics, and from GLC analysis at an airflow rate of 2000 cc/min there was no evidence of autoxidation of this compound. Joint removal by stripping and biological metabolism changed the kinetic order of MEK removal. COD removal curves in Figures 26, 27, and 28 can (after the first sampling point) be approximated with zero order kinetics; the curve for the experiment at 500 cc/min (Figure 29) can be fitted better by first order than by zero order kinetics. The magnitudes of the zero order rates were 355, 320, and 350 mg/l/hr for Figures 26, 27, and 28, respectively, and that of the first order rate in Figure 29 was 0.2441 hr^{-1}. It had been previously observed by Gaudy, Turner, and Pusztaszeri (3) that the COD removal curve for butanone (MEK) in an activated sludge aeration tank operated at various airflow rates could be described using an equation combining first order stripping and zero order biological rate constants which can be written as

$$C = C_o \cdot e^{-2.3Kat} + \frac{Kbo}{2.3Ka}\left(e^{-2.3Kat} - 1\right)$$

where Kbo = zero order biological constant, mg/l/hr, and other notations retain their meaning as previously defined.

Experimental data for the dual removal of MEK at an airflow rate of 500 cc/min (Figure 29) was employed with this equation in order to determine the apparent zero order rate constant for biological removal of butanone. The value obtained was 146 mg/l/hr. This value

is somewhat higher than the Kbo values determined by Gaudy, Turner, and Pusztaszeri (3). For roughly comparable initial biological solids concentrations they obtained values ranging from 70 to 110 mg/l/hr. However, considering the fact that heterogeneous populations were employed, the similarity of the results of the two studies on MEK is quite satisfactory.

Propionaldehyde

Treatment of propionaldehyde by stripping and biological metabolism always led to accumulation and subsequent utilization of monocarboxylic acids as intermediates. At times during the runs on propionaldehyde, acetic, propionic, isobutyric, butyric, and isovaleric acids were present in the filtrates. In experiments at all airflow rates studied, acetic and propionic acids were detected in the filtrates; all of the above-mentioned acids were present in the filtrates during the experiment conducted at an airflow rate of 2000 cc/min (Figure 37). Since propionic and acetic acids were the major products observed in the filtrates, it is interesting to tabulate certain key data concerning accumulation of these products during the experiments. The maximum concentration and its time of occurrence during experiments at various airflow rates are givn in Table VI. The maximum amounts of propionic and acetic acids in terms of their equivalent COD mg/l were expressed as the percentages of the initial COD, and COD corresponding to the point where maximum propionic and acetic acid were detected.

At an airflow rate of 4000 cc/min (Figure 36), acetic, propionic, and isovaleric acids were detected in the filtrates along with the substrate (propionaldehyde). Although both propionic and isovaleric acids attained their respective peak concentrations in the medium at the

TABLE VI

PROPIONIC AND ACETIC ACIDS AS INTERMEDIATES IN THE METABOLISM OF PROPIONALDEHYDE IN THE ACTIVATED SLUDGE AERATION TANK AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS

Unit Air-flow Rate cc/min/l	Fig. No.	Initial COD mg/l	Initial Solids mg/l	Parameters for Max. Propionic Acid: Pro. Acid COD mg/l	Time at Max. Value hrs.	COD at that Time	Propionic Acid as % of: Initial COD	Propionic Acid as % of: COD at Point	Parameters for Max. Acetic Acid: Acetic Acid COD mg/l	Time at Max. Value hrs.	COD at that Time	Acetic Acid as % of: Initial COD	Acetic Acid as % of: COD at Point
4000	36	1067	640	25.8	0.25	505	2.42	5.1	47.4	0.5	448	4.45	10.6
2000	37	1400	544	56.3	1.5	415	3.96	13.4	28.6	1.5	415	2.04	6.9
1000	38	1077	732	92.5	1.5	411	8.61	22.5	58.2	1.0	484	5.41	12.0
500	39	1141	644	208	1.0	638	18.2	32.4	206	1.0	638	18.05	32.2

same time, isovaleric acid was removed more rapidly than propionic, and acetic acid was still accumulating when the other two acids were being metabolized. Biological solids increased after the point of exhaustion of the original exogenous substrate, and most of the growth was attained at the expense of intermediate products not detected on the Poly Pak column. The biological solids concentration did not increase during the first one-half hour of aeration, but more than one-half of the COD was removed by a combination of stripping and microbial respiration. The cells were active during this early period, since isovaleric and propionic acids were detected in the medium. The greatest variety of intermediate products was detected during the experiment conducted at an airflow rate of 2000 cc/min (Figure 37). Propionic acid was present in the highest quantity. At 1.5 hours when the highest concentration of propionic acid was detected, it amounted to more than 13 per cent of COD remaining at that time (Table VI), butyric and isobutyric acids were detected in only two samples (one hour, and 2.5 hours, respectively).

Conversion of a 3-carbon aldehyde to a 3-carbon acid could possibly be the result of autoxidation, but the presence of 2-, 4-, and 5-carbon monocarboxylic acids definitely must be attributed to biological degradation of propionaldehyde. Very little is known about the production of such acids during aerobic metabolism of propionaldehyde. It is known that acetic acid can accumulate in the medium during rapid dissimilation of glucose by microorganisms (66) under aerobic conditions. From the results of the present study it would appear that the phenomenon is not one peculiar to carbohydrate metabolism.

The results in Figure 38 also indicated that most of the increase in biological solids concentration was attained at the expense of

metabolic intermediates. At 1.5 hours, the maximum amount of propionic acid was detected, and it amounted to 23 per cent of the COD in the system at that time (see Table VI). At an airflow rate of 500 cc/min (Figure 39), both acetic and propionic acids attained a peak at one hour, and the two taken together accounted for 64 per cent of the total COD in the system at that time (Table VI).

Removal of propionaldehyde by the dual mechanism of stripping and biological metabolism is more efficient and proceeds at a faster rate than removal by stripping alone at identical airflow rates. The divergence of the COD and GLC data as the experiment progressed during stripping studies led to the conclusion that autoxidation products were formed, although no such products were detected using the Poly Pak-2 column. The presence of a variety of acids in the medium, produced from propionaldehyde when microorganisms were present, showed that the dual mechanism, although more rapid, is one which is extremely complicated from a kinetic point of view. Even under conditions of stripping alone, no first order kinetic pattern of COD removal could be employed to describe the entire course of propionaldehyde removal. The assigning of any one kinetic order for a system under combined conditions of physical and biochemical reaction seems a fruitless endeavor. Under the combined removal mechanisms the apparent COD removal curves in some cases gave apparent first order kinetics (Figures 36 and 37), whereas in others (Figures 38 and 39) zero order kinetics seemed prevalent (within the limitations of the analytical techniques employed). In general, as a result of these studies, it is known that propionaldehyde is subject to stripping and to utilization by bacteria; metabolic products are accumulated in the medium and are subsequently utilized by

the bacteria (either by those which produced the product or by a satellite population). However, the kinetic nature of each of these occurrences is not adequately known. The presence of some intermediates was detected only for isolated sampling points. In the absence of more frequent sampling, the kinetic patterns of intermediate production and utilization and their contribution to the overall kinetics of the integrated system cannot be evaluated. If kinetics of all reactions were known, there might exist a possibility of predicting the kinetics of the overall reaction. Under the circumstances it would be unwise to attempt to predict the kinetic behavior of the observed system solely from statistical evaluation of COD removal curves. However, disregarding the kinetics of the individual reactions which constituted the apparent profile of the COD curve, it appears that under the combined action of stripping and biological metabolism the overall removal pattern of propionaldehyde still conformed to first order kinetics except at the lowest airflow rate (Figure 39) where removal kinetics could be said to be equally obeying first order (0.273 hr^{-1}) and zero order (226 mg/l COD/hr) kinetics.

Special mention should be made of the fact that at the two higher unit airflow rates (4000 and 2000 cc/min/l), on the average 54 per cent of the initial COD was removed in the first fifteen minutes and the initial COD point did not fall in the line of best fit (fitted by eye) through the rest of the points on a semilogarithmic plot. The kinetic constants for total COD removal, along with those for air stripping, are compiled in Table VII for propionaldehyde as well as for the other two aldehydes studied. With regard to propionaldehyde (as well as the other aldehydes), no explanation can be offered as to why

TABLE VII

COMPILATION OF RATE CONSTANTS FOR REMOVAL OF VOLATILE ALDEHYDES DUE TO STRIPPING AND STRIPPING COMBINED WITH BIOLOGICAL METABOLISM AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS AT 25°C

		Particulars of Air Stripping Experiments			Particulars of Stripping plus Biological Experiments					
Compound	Unit Air-flow rate cc/min/l	Fig. No.	Initial COD mg/l	Ka (hrs^{-1}) Base 10 1st Order	Fig. No.	Initial COD mg/l	Initial Biological Solids Concentration mg/l	K Total 1st Order (hr^{-1}) Base 10	Zero Order mg/l hr^{-1}	*Remarks refer to Stripping plus Biological Experiments Only
Propion-aldehyde	4000	31	1109	0.257	36	1067	640	0.322		52.3% initial COD removed in 15 min.
	2000	32	1070	0.285	37	1400	544	0.247		55.2% initial COD removed in 15 min.
	1000	33	1000	0.135	38	1077	732	0.288		
	500	34	991	0.092	39	1141	644	0.273	226	
Butyral-dehyde	4000	40	958	0.544	45	1059	772	0.371		50% initial COD removed in 15 min.
	2000	41	975	0.455	46	1095	514	0.348	278	46% initial COD removed in 15 min.
	1000	42	1000	0.176	47	952	672	0.375		
	500	43	1000	0.152	48	1009	760	0.264	210	33.4% initial COD removed in 15 min.
Valeral-dehyde	4000	49	1075	0.784	54	1182	952	0.580		66% initial COD removed in 12 min.
	2000	50	1170	0.508	55	1213	1044	0.499	298	60.5% initial COD removed in 15 min.
	1000	51	1060	0.294	56	1169	496	0.372	285	42.5% initial COD removed in 15 min.
	500	52	1105	0.199	57	1201	1552	0.387		56.4% initial COD removed in 15 min.

*Because of removal of a significant amount of initial COD in the first 12 or 15 minutes, the straight line of best fit (fitted by eye) on the semilogarithmic plot in each case does not pass through the initial point.

there was in most cases a substantial removal of COD during the first twelve or fifteen minutes. When one compares COD removal due to stripping alone with COD removal under combined stripping and biological action (e.g., compare Figures 31 and 36) it is seen that the rapid removal during the first fifteen minutes cannot be attributed solely to stripping. Also, examination of the biological solids data indicates that little or none of the COD was incorporated into the cells. A portion of the COD removal during this period may be attributed to microbial respiration, but it does not seem reasonable that all COD removal over and above that amount stripped could be due to bacterial respiration of the substrate. In all cases the GLC results at the first sampling point (either twelve or fifteen minutes) indicate that intermediate accumulation was well under way; therefore, it would seem that the cells began to act upon the aldehyde almost immediately upon contact. It may be possible that the cells produced some intermediate product which was even more volatile than the original exogenous substrate. This possibility is only a conjecture, and no adequate explanation for the result can be offered.

In general the residual COD when bacteria were present was lower than for the systems examined under sole stripping conditions. Such a result would be expected, since oxidized products not subject to stripping might be metabolized by the cells. It is also interesting to note that propionic acid at the point of its maximum concentration expressed as percent of COD at that time, increased with decreasing airflow rates. Similar calculations for acetic acid showed that its percentage of the COD remained unaffected for three airflow rates, 4000, 2000, and 1000 cc/min, but increased to 32 per cent at the lowest

airflow rate studied (500 cc/min). Acetic acid has been detected as an intermediate in studies by George (67) in the bioenengineering laboratories, using nonvolatile carbon sources, i.e., glucose, during temperature shocks from 25 to 57.5°C; also by Goel (68) in continuous flow reactor effluent at low nitrogen levels; by Krishnan (69) in continuous flow reactors during shock loading; and by Bustamante (70) using pure cultures.

Butyraldehyde

Removal of butyraldehyde by the dual mechanism of stripping and biological treatment was accompanied by release of propionic and butyric acids as intermediates in all experiments. For the experiment shown in Figure 46 a small amount of isovaleric acid was also detected. Also in this experiment (Figure 46) the amount of butyric acid was less than propionic acid, while in all others the amount of butyric acid was in excess of propionic acid, and in most cases (except Figure 45) butyric acid attained its peak concentration earlier than propionic acid. Acetic acid was not detected in the filtrates for any of the experiments. The immediate oxidation product of butyraldehyde is butyric acid, and it was the major intermediate detected. The maximum amount of butyric acid detected in each system was expressed as percent of the COD prevailing at that time, to determine whether there was any correlation between airflow rates, butyric acid production, and corresponding COD. These data are shown in Table VIII. Excluding the run at an airflow rate of 2000 cc/min (Figure 46), the average butyric acid production expressed as percent of the COD at the time of maximum butyric acid concentration amounted to 42 per cent, and was seemingly independent of airflow rate. From Figures 45 through 48 it appears that

TABLE VIII

BUTYRIC ACID AS INTERMEDIATE IN THE METABOLISM OF BUTYRALDEHYDE IN THE ACTIVATED SLUDGE AERATION TANK AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS

Unit Airflow Rate cc/min/l	Fig. No.	Initial COD mg/l	Initial Solids mg/l	Parameters for Maximum Butyric Acid				
				Butyric Acid COD mg/l	Time at Max. Value hrs	COD at that Time	Butyric Acid as % of Initial COD	Butyric Acid as % of COD at that Point
4000	45	1059	772	129	1.0	255	12.2	50.5
2000	46	1095	514	48.2	0.50	464	4.4	10.4
1000	47	951	672	132	0.25	396	13.8	33.2
500	48	1009	760	208	1.0	495	20.6	42

the released acidic intermediates which accumulated in the medium were later metabolized in two ways; sometimes concurrently with the remaining butyraldehyde, and at other times, sequentially after the butyraldehyde was exhausted.

As in the case of propionaldehyde, with regard to kinetic order and velocity constants, it is felt that no attempt can be (or should be) made to predict the course of purification on the basis of the COD removal data alone. Intermediates played a significant role in determining the shape of the COD removal curve, and apart from the intermediates detected, there appear to be other intermediates which were undetected by the analytical technique employed. However, using the COD profile alone, in all cases of dual removal of butyraldehyde, first order rate constants were obtained. At airflow rates of 2000 and 500 cc/min/l, the data could be fitted with equal facility to either zero order or first order kinetics; the zero order constants were 278 and 210 mg/l COD/hr, respectively. At 4000 and 2000 cc/min/l airflow, the first order dual removal constants 0.371 and 0.348 hr^{-1} are lower than their corresponding air stripping constants (0.544 and 0.455 hr^{-1}, respectively). This apparent anomaly is attributable to the fact that at these two high airflow rates, 50 and 46 per cent of the initial COD were removed in the first fifteen minutes, thus making the incorporation of the initial COD point impossible in the straight line profile through the rest of the points. The removal constants for stripping and biological metabolism, along with air stripping constants for butyraldehyde are given in Table VII. As in the case of propionaldehyde, there was an initial lag in solids production except for the experiment at an airflow rate of 500 cc/min (Figure 48). Most of the

COD removed during this period was undoubtedly removed due to stripping, and it appears that before utilizing butyraldehyde for growth, the organisms convert a large portion of butyraldehyde to butyric acid (or in one case, to propionic acid).

From the COD removal data in stripping runs, it was found that butyraldehyde did not strip in accordance with any established rate law for the entire period of substrate removal. It was felt that non-first order stripping was due to the possible autoxidation of butyraldehyde to butyric acid, although butyric acid was not detected by GLC analysis. Such a hypothesis was based on the increasing divergence between GLC and COD data from a stripping experiment conducted at an airflow rate of 2000 cc/min.

In all of the dual removal experiments concerning utilization of butyraldehyde, GLC analysis indicated that biological removal of butyraldehyde produced three, four and, at times, five carbon monocarboxylic acids, and that these were subsequently metabolized. It is important to note that these products were produced under aerobic conditions. Dissolved oxygen measurements were made during the experiment run at the lowest airflow rate (500 cc/min); the initial biological solids concentration for this experiment was rather high (760 mg/l). Dissolved oxygen concentrations in the range of 3.9 mg/l were observed; thus the acids were not the result of fermentative conditions. While it does seem possible that both fermentation and aerobic metabolism could proceed concurrently, it is significant to note that these acid products were subsequently used, i.e., they did not remain in the system as fermentation products as would be expected in a fermentation process. Thus, it is concluded that the accumulation of

these acids in the medium was not a result of oxygen deficiency.

Valeraldehyde

Removal of valeraldehyde in the activated sludge aeration tank was invariably associated with the production and subsequent metabolism of nonstrippable valeric acid along with lesser amounts of acetic, propionic, and butyric acids. At all airflow rates, valeric acid concentration attained its peak much earlier (see Table IX) than did butyric and propionic acids during removal of butyraldehyde (Table VIII), and propionaldehyde (Table VI), respectively. Acetic acid was detected only in the experiment conducted at an airflow of 4000 cc/min, and at the point of occurrence of its maximum concentration it accounted for only 4.4 per cent of the COD at that time. From Table IX it is seen that valeric acid at the point of its maximum occurrence accounted for 26 per cent of the COD in the system at that point during the run at an airflow rate of 4000 cc/min, and 25 per cent during the experiment at an airflow rate of 2000 cc/min.

For experiments run at an airflow rate of 1000 and 500 cc/min, valeric acid, at the point of its maximum concentration, accounted for 56 and 52 per cent, respectively, of the COD remaining at that time. Thus it would appear that the lower airflow rates permitted more of the original substrate to be converted, metabolically, to acids. The acid intermediates were metabolized while valeraldehyde was still present in the medium.

It will be recalled that valeraldehyde stripping at various airflow rates could not be fitted to first order kinetics when all observed COD points were taken into consideration. However, for practical purposes, the data could be approximated by a first order plot.

TABLE IX

VALERIC AND ACETIC ACIDS AS INTERMEDIATES IN THE METABOLISM OF VALERALDEHYDE IN THE ACTIVATED SLUDGE AERATION TANK AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS

				Parameters for Max. Valeric Acid					Parameters for Max. Acetic Acid				
							Val. Acid as % of					Acetic Acid as % of	
Unit Air-flow Rate cc/min/l	Fig. No.	Initial COD mg/l	Initial Solids mg/l	Valeric Acid COD mg/l	Time at Max. Value hrs	COD at that Time	Initial COD	COD at that Point	Acetic Acid COD mg/l	Time at Max. Value hrs	COD at that Time	Initial COD	COD at that Point
4000	54	1182	952	105	0.20	400	8.86	26.2	17.6	0.20	400	1.49	4.4
2000	55	1213	1044	72.6	0.75	288	6.00	25.2	-	-	-	-	-
1000	56	1169	496	266	0.75	475	22.8	56.0	-	-	-	-	-
500	57	1201	1552	270	0.50	516	22.4	52.1	-	-	-	-	-

Similarly (excluding the zero time COD values), the COD removal curve during the combined stripping and biological removal experiments could be fitted to a first order curve. The kinetic constants are tabulated in Table VII, along with the air stripping constants. In all cases of dual removal of valeraldehyde, on the average , 56 per cent of the initial COD was removed within twelve or fifteen minutes after the initiation of the experiments (see Table VII for percent of initial COD removed for each experiment).

Effect of Airflow Rate on Cell Yield

With nonvolatile substrates, e.g., glucose, the added carbon source is partitioned entirely into synthesis and respiration. Calculations of actual cell (or sludge) yields with volatile carbon sources in aerated systems are difficult because of stripping. However, in a practical sense, i.e., from a standpoint of determining the amount of sludge accumulation, the calculation of cell yield in the usual manner can offer a means of balancing the cost of extra aeration against the cost of sludge disposal. In general, it would be expected that the "cell yield" would decrease as airflow rate was increased. Such may not be always the case, for some compounds may be autoxidized to less volatile or nonvolatile compounds at higher airflow rates. In the present study cell yields were calculated without regard to stripping and the yields at the various airflow rates were compared. Yield was calculated as follows:

$$\text{Yield} = \frac{\text{increase in biological solids in a time interval}}{\text{decrease of substrate (COD) in the same time interval}}$$

Also, the percent of substrate removal or utilization was calculated as follows:

$$\frac{\text{substrate COD removed in a time interval} \times 100}{\text{substrate COD present at the beginning of the time interval}}$$

In all cases the time interval was from zero time to the point of maximum biological solids level (often coincident with the exhaustion of exogenous substrate) in the system. The cell yields and percentages of substrate utilization for all experiments are shown in Table X. For both acetone and methyl ethyl ketone, which were not subject to autoxidation, yield values exhibited an increasing trend with decreasing airflow rates. At an airflow rate of 4000 cc/min, yield calculations were not possible for acetone because biological solids did not increase.

Since dual removal was in general more efficient than the physical process of stripping alone at comparable airflow rates, in installations treating such kinds of waste it would be advisable to design the treatment facility on the basis of balancing airflow rate against sludge production for the desired degree of purification. It may be pointed out that whereas a relatively large capital investment is involved in the construction of sludge-handling facilities, an increased airflow rate contributes largely to operational rather than fixed costs. Therefore, investment writeoff and tax deduction schedules must be taken into account.

The yield values for the aldehydes (propionaldehyde, butyraldehyde, and valeraldehyde) also increased with decreasing airflow rate. For these substrates the increasing yield can be attributed to two factors. First, as with ketones, the slower stripping rate at the lower airflow rates permitted the microbial population to "capture" a greater proportion of the original carbon source. Secondly, the cells produced nonvolatile compounds from the original substrate, thus tending to

TABLE X

CELL YIELDS AND PERCENTAGES OF SUBSTRATE UTILIZATION DURING METABOLISM OF VOLATILE KETONES AND ALDEHYDES AT VARIOUS UNIT AIRFLOW RATES UNDER BATCH CONDITIONS

Airflow Rate cc/min/l	Acetone		Methyl Ethyl Ketone		Propionaldehyde		Butyraldehyde		Valeraldehyde	
	Yield	% Substrate Utilization	Yield	% Substrate Utilization	Yield	% Substrate Utilization	Yield	% Substrate Utilization	Yield	% Substrate Utilization
4000	-	96	.073	95.9	.085	88.8	.084	89.7	.045	91
2000	.148	97	.117	98.7	.11	96	.198	91.2	.101	91.1
1000	.364	92	.089	97.5	.162	91.6	.278	85.1	.155	93
500	.301	92.1	.326	94.1	.22	90.6	.328	84.6	.218	95

conserve more of the carbon source for eventual incorporation into the sludge mass. Thus even though the aldehydes were more volatile and could be stripped faster than the ketones, and even though biological growth was not noticeably more rapid on the aldehydes, the increase in cell yield with decreasing airflow rate was comparable to that observed with the ketones.

For all three aldehydes, the metabolic product produced in the greatest quantity was the corresponding acid. In general the maximum concentration of acid (equivalent COD, mg/l) and maximum intermediates (total COD-substrate COD) mg/l increased as airflow rate decreased. These latter values (shown in Table XI) and the sludge yield values are plotted for each compound at the various airflow rates employed in Figures 87, 88, and 89. The general trend mentioned above is apparent in all three figures; however, it is more strikingly evident in the case of the experiments with propionaldehyde (Figure 87).

Phase II

C. Treatment of Strippable Compounds by Stripping and Stripping Combined with Biological Metabolism in Continuous Flow Reactors

In some respects the continuous flow condition is more akin to field operations than the discontinuous (batch) study. Previously in this discussion the present results concerning batch studies were compared with studies by other workers (28)(29). Such comparison is not possible for the continuous flow studies because there was no reference found in the literature pertaining to results of continuous air stripping in a completely mixed reactor. Such studies are important when biological removal of strippable compounds is contemplated, since it is

TABLE XI

PRODUCTION OF MAXIMUM INTERMEDIATES (TOTAL COD-SUBSTRATE COD) WITH CHANGING UNIT AIRFLOW RATES FOR METABOLISM OF PROPIONALDEHYDE, BUTYRALDEHYDE, AND VALERALDEHYDE AS THE EXOGENOUS SUBSTRATES UNDER BATCH CONDITIONS

Unit Air-flow Rate cc/min/l	Propionaldehyde			Butyraldehyde			Valeraldehyde		
	Figure No.	Time (min)	Maximum Intermediates COD, mg/l	Figure No.	Time (min)	Maximum Intermediates COD, mg/l	Figure No.	Time (min)	Maximum Intermediates COD, mg/l
500	39	15	609	48	45	368	57	30	382
1000	38	15	456	47	30	426	56	45	408
2000	37	90	314	46	60	329	55	30	225
4000	36	60	304	45	30	219	54	24	198

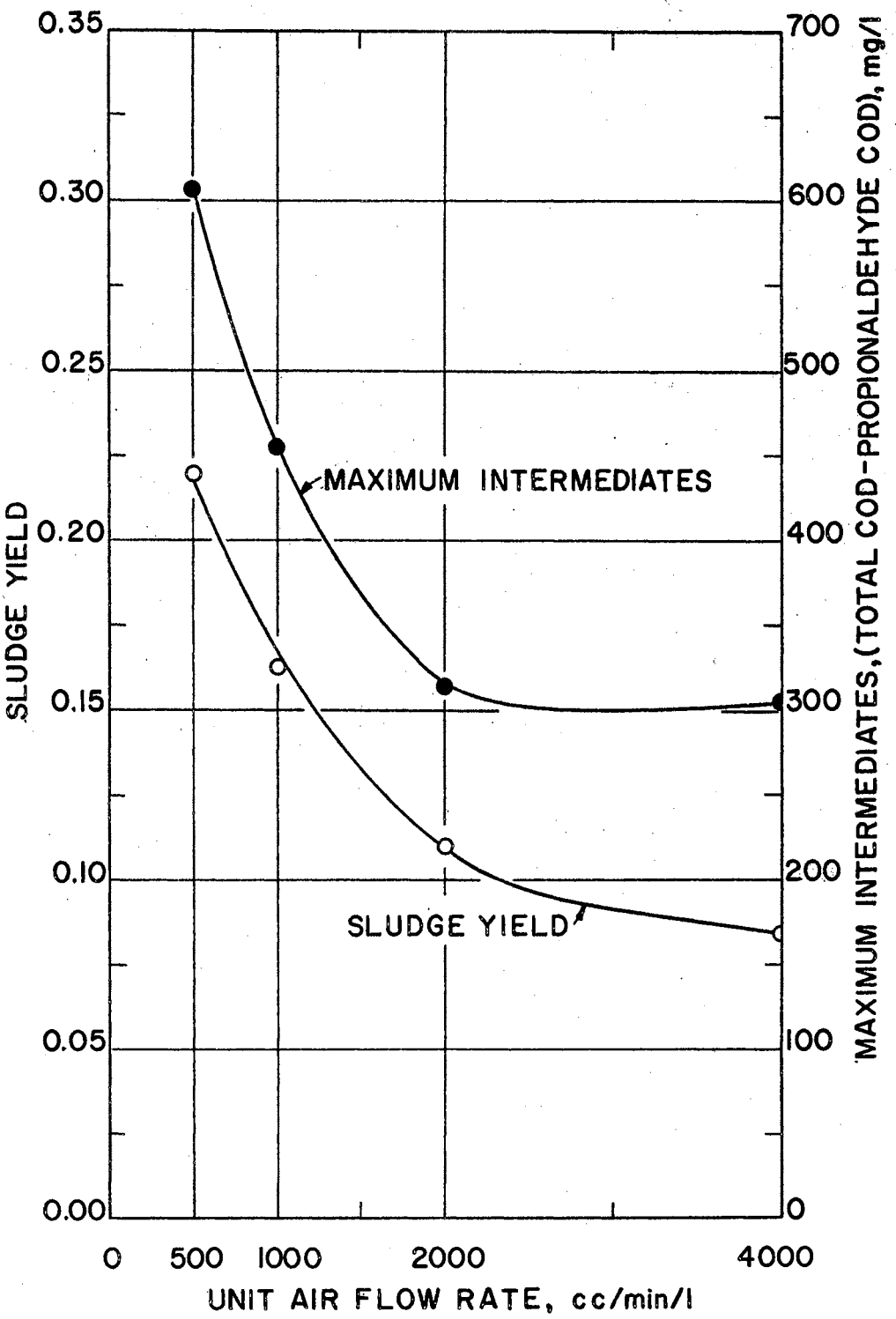


Figure 87 - Variation in sludge yield and production of maximum intermediates with changing unit airflow rates for propionaldehyde as the exogenous substrate.

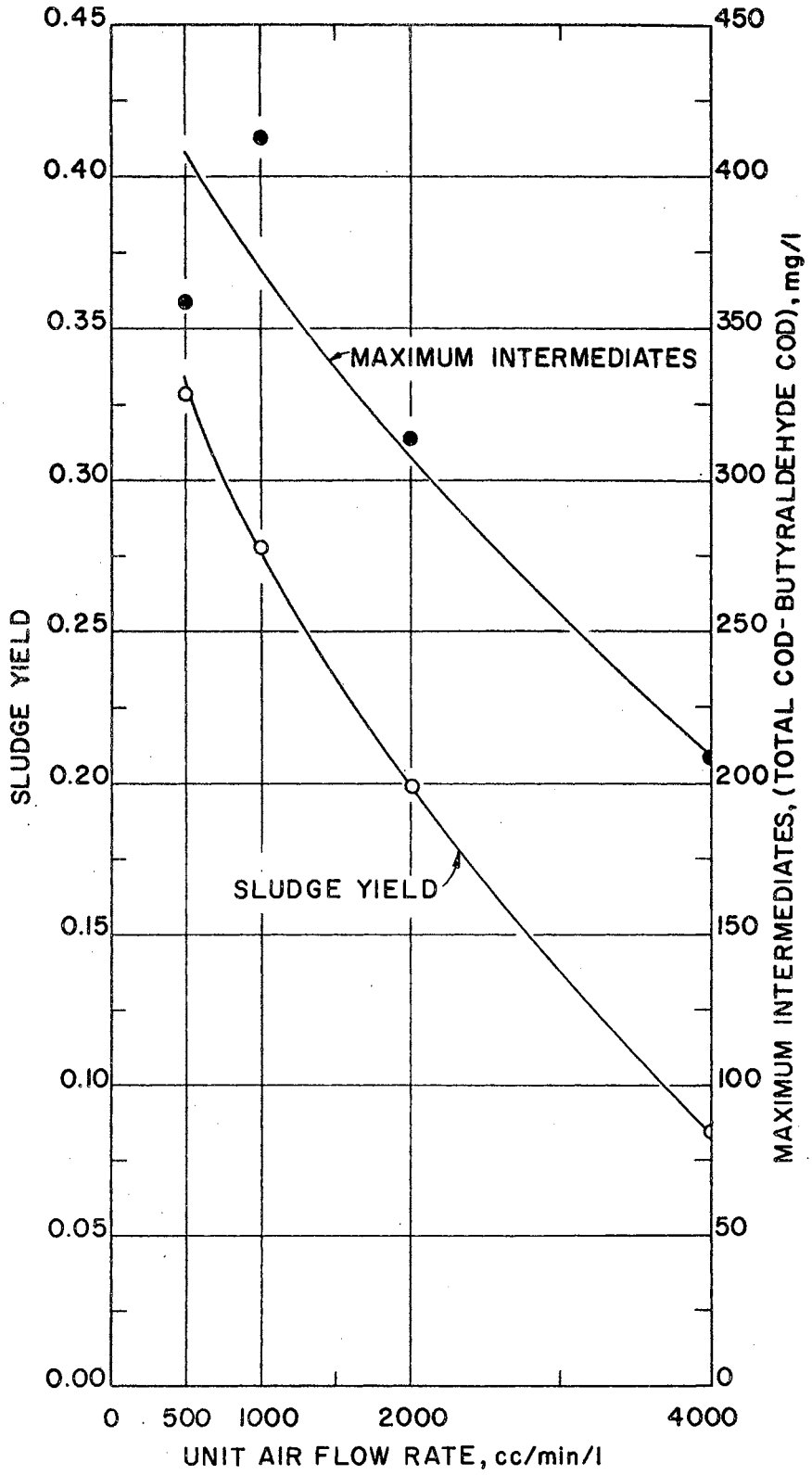


Figure 88 - Variation in sludge yield and production of maximum intermediates with changing unit airflow rates for butyraldehyde as the exogenous substrate.

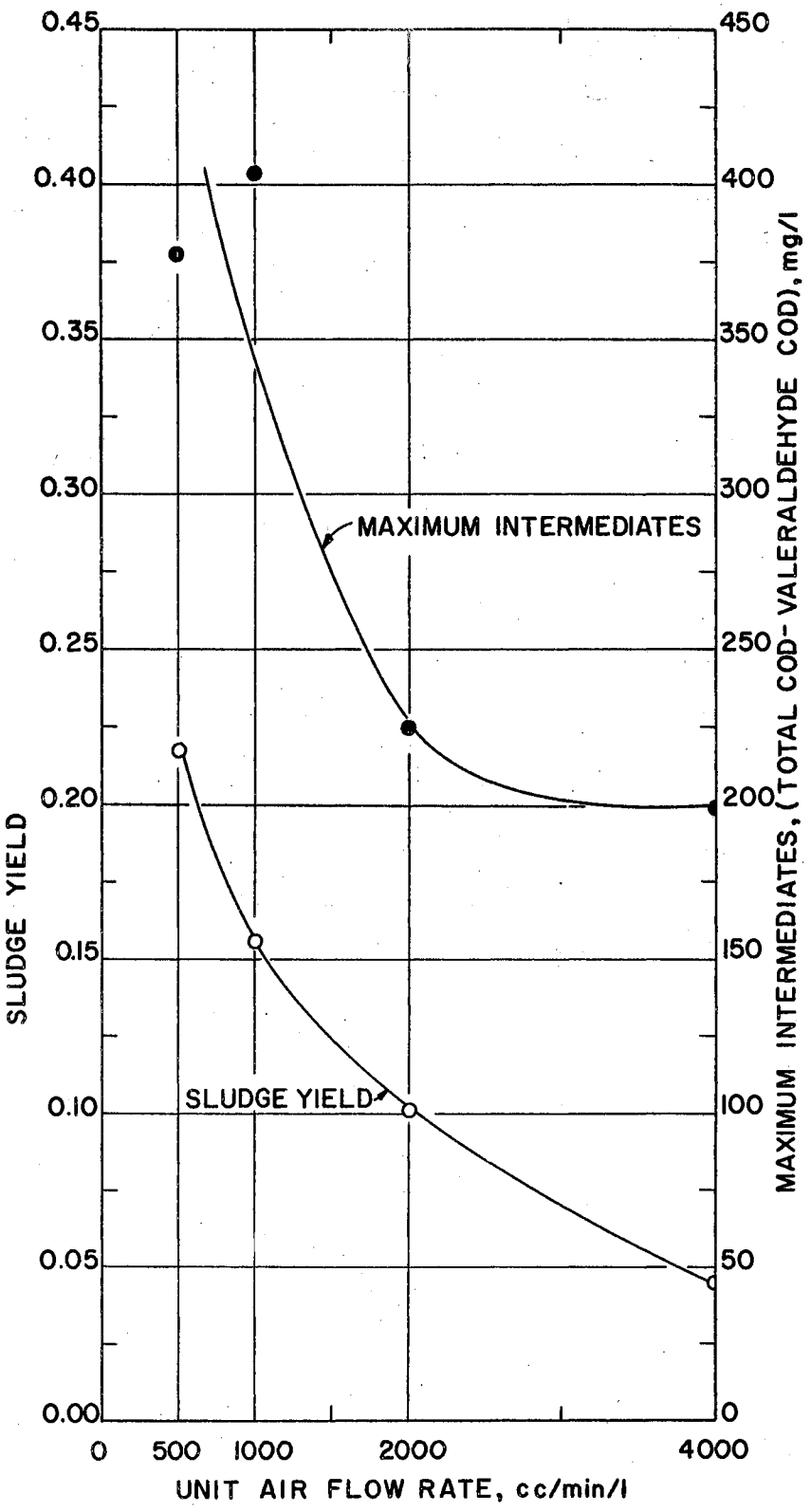


Figure 89 - Variation in sludge yield and production of maximum intermediates with changing unit airflow rates for valeraldehyde as the exogenous substrate.

essential to know whether a heterogeneous microbial population can flourish in an environment in which a significant portion of the food resource is being removed by another mechanism.

Certain similarities with regard to the two modes of operation (discontinuous and continuous) were observed; for example, during stripping of acetone no evidence for autoxidation was obtained in either the batch study at 4000 cc/min/l of air (Figure 12) or the continuous flow study at 4000 cc/min (Figure 58). Upon attainment of the steady state in the continuous flow reactor, the total COD values at different sampling points were in good agreement with the values obtained by GLC analysis. The pH of samples under both types of operation were neutral, which further substantiates the conclusion that acetone was not subject to autoxidation by air in the range of air supply employed.

A "dual" removal efficiency of 59.6 per cent was achieved for acetone at an airflow rate of 2000 cc/min in contrast to 47 per cent for stripping alone at the same airflow rate and approximately the same feed level of acetone COD (compare Figure 59 with Figure 62). The COD:N ratio was 9.3:1 in the feed for the results shown in Figure 62. The overall cell yield was (405/2325) = 0.174 for the continuous flow experiment. The actual yield would be somewhat higher than this value because a portion of the substrate was stripped. Assuming the percent removal by stripping to be the same as that in the straight stripping run, the yield would accrue to 0.805. In the absence of knowledge of the independent contribution of biological removal, precise yield values cannot be predicted. The overall yield is very low and overall treatment efficiency was also very low. From the high amount of

untreated acetone remaining in the effluent, it appears that the extent of air stripping under the specified rate of airflow is constant. Under such circumstances attainment of a higher degree of overall treatment efficiency would necessitate either an increase of airflow rate or maintenance of a higher solids level, or a combination of both. Results for the air stripping of methyl ethyl ketone under continuous flow operations were, in general, similar to those with acetone. Also, like acetone, there was no evidence for autoxidation of methyl ethyl ketone in either batch or in continuous flow studies (see Figures 22 and 65). In both the continuous flow and batch studies MEK was observed to be more readily stripped than acetone. Overall treatment efficiency under the dual removal mechanism at an airflow rate of 4000 cc/min was 79.5 per cent (Figure 68) as opposed to 65 per cent due to air stripping only at the same airflow rate (Figure 64). The overall yield for continuous flow operation was $\left(\frac{268}{1788-368}\right) = \frac{268}{1420} = 0.189$. The "dual" removal efficiency of 96.4 per cent (Figure 69) was approximately double that for air stripping (49.2 per cent, Figure 65) during the MEK experiment at an airflow rate of 2000 cc/min. For the experiment shown in Figure 69 the biological solids were grown in the continuous flow reactor from the beginning rather than being grown in batch and transferred to the continuous flow unit. As a result the wash-out of biological solids from the continuous flow reactor which had occurred in experiments shown in Figures 62 and 68 prior to attainment of a "steady-state" level was not discernible. The overall yield for this dual removal experiment was $\left(\frac{396}{581}\right) = 0.68$. In the two experiments shown in Figures 68 and 69 there was no evidence of intermediates or endproducts from the primary break down of MEK under the influence of stripping and biological metabolism.

This was observed also in case of all dual removal batch studies on MEK. Although certain amounts of metabolic intermediates may be present in the effluent, from the results shown in Figure 68 no intermediates were detected by GLC analysis on the filtrates using the Poly Pak-2 column. The percent stripping efficiency of propionaldehyde at an airflow rate of 2000 cc/min was higher than that at an airflow rate of 4000 cc/min providing presumptive evidence for the presence of nonstrippable autoxidation products at the higher airflow rate. Unfortunately, GLC analyses were not made on samples during the 4000 cc/min experiment; however, it was observed in the batch studies with propionaldehyde (also see Table V, page 182) that the percent removal efficiencies (at both the 2- and 8-hour samples) were higher at an airflow rate of 2000 cc/min than those at 4000 cc/min. Granted that the unit airflow rates in the aforesaid batch and continuous flow experiments are not comparable (2.5-fold increase of aeration volume in continuous flow reactor at the same total air supply rate), the trend with respect to removal efficiencies was consistent.

From GLC analyses on samples under batch conditions at an airflow of 2000 cc/min/l (Figure 32) and those for the continuous flow study at an airflow of 2000 cc/min (Figure 71), no acidic autoxidation products were detected. The propionaldehyde removal curve obtained from GLC analysis indicated slightly more rapid removal of the compound than did the removal curve plotted from total COD analysis (Figure 32).

From the semilogarithmic plots of the COD removal during propionaldehyde experiments at all airflow rates in batch study, it was observed that first order kinetics could not be applied for the entire course of propionaldehyde removal. This is in contrast with the

findings of Gaudy, Engelbrecht, and Turner (29), who observed first order removal at 25°C but not at 40°C. However, the difference in tank geometry and airflow rate may account for the slight difference in results at 25°C. In any case, it may be concluded that some degree of autoxidation can be evidenced for propionaldehyde during aeration at atmospheric pressure.

Dual removal (stripping plus biological) of propionaldehyde in the continuous flow reactor at an airflow of 2000 cc/min proceeded in two distinct phases with respect to biological solids concentration and filtrate COD (Figure 74). The overall yield for these two distinct states of operation were $0.284\left(\frac{153}{861-323}\right)$ and $0.49\left(\frac{356}{861-135}\right)$, respectively. However, the increasing trend in biological solids concentration after 100 hours of operation (Figure 74) was due largely to noncomplete mixing during this time. Indication that biological solids were retained in the aerator was obtained by the measurement of optical density of samples in the aerator and in the effluent line.

Metabolic intermediates and/or endproducts were more numerous during the dual removal of this compound in batch studies than in the continuous flow studies. In addition to propionic acid, which was the common intermediate in all the batch dual removal experiments, other monocarboxylic acids such as acetic, butyric, isobutyric, and isovaleric were present in the filtrates. However, in dual removal experiments with propionaldehyde in the continuous flow reactor, only propionic acid was detected, and this was present only during the initial stage of operation (Figure 74). It seems likely that in the batch studies conditions were more favorable for observing the buildup or accumulation of metabolic intermediates since the cells can grow at as rapid a growth

rate as the available substrate concentration will permit, whereas in the continuous flow reactor the growth was hydraulically-controlled at 1/8 hr^{-1}.

Continuous stripping of butyraldehyde at airflow rates of 4000 cc/min (Figure 75) and 2000 cc/min (Figure 76) showed that aldehyde COD values from GLC analysis of the samples were less than their corresponding total COD values, thus indicating that some autoxidation of the aldehyde occurred. These results agree with those of the batch studies. Based on the present data, the autoxidation of butyraldehyde during air stripping at normal temperature and atmospheric conditions seems to be a distinct possibility, but the occurrence of autoxidation cannot be firmly established in the absence of direct supporting evidence such as detection of the oxidation product.

In the continuous flow air stripping studies on valeraldehyde, the COD values were slightly higher than the steady state values for aldehyde COD as determined by GLC analysis. In the experiment in which the compound was dissolved in distilled water there was a drop in pH; the feed pH was 5.8, whereas the effluent pH was 4.5. Thus there was some indication that acidic products were formed; however, such products (valeric acid would be expected) were not detected by GLC analysis. In the presence of acclimated microorganisms, very high concentrations of valeric acid accumulated in the medium. Indeed, all of the COD in the effluent was attributable to valeric acid, the immediate oxidation product of valeraldehyde (see Figure 78). The acclimated population was grown up in a batch reactor over a fairly long period (61 days) and upon initiation of continuous flow operation (at D = 1/8 hr^{-1}) the solids concentration dropped from an initial value of over 1800 mg/l to

slightly over 400 mg/l during a 2-day period. Thereafter, the solids concentration averaged less than 500 mg/l throughout the period of continuous flow operation. The organisms could apparently dissimilate valeraldehyde, producing valeric acid faster than they could assimilate the oxidation product. The overall removal efficiency suffered because the cells trapped the carbon source in the form of a nonstrippable compound. The result was not due to lack of nitrogen (COD:N = 9.5:1) or to lack of dissolved oxygen in the medium. The pH was somewhat low (4-5) but the results shown in Figure 81, for an experiment in which a higher concentration of buffer was employed, also indicate erratic behavior of the microbial population, i.e., an increasing biological solids concentration (often an initial decrease) during which total effluent COD removal was good and no acids were detected followed by a period of decreasing solids concentration and a rapidly rising effluent COD which could be accounted for almost entirely by valeric and acetic acids. In view of the results it seems possible that the long aeration period of the batch experiments (23 hours) permitted metabolic reactions which were not possible in the continuous flow unit. First, it could be reasoned that the organisms which dissimilated the aldehyde could not grow rapidly on the acid or that at a growth rate of 1/8 hr^{-1} they were operated near their μ_m with respect to the acid. Second, it might be reasoned that a secondary population which could compete for the acids could not grow very well at a dilution rate of 1/8 hr^{-1}; thus much of the product of the dissimilation of the aldehyde was wasted in the effluent. In the batch system all organisms were retained in the system during the aeration period, and there was an opportunity for a symbiotic population to develop.

It seems possible that after prolonged acclimation under continuous flow conditions a population could evolve which would be able to metabolize, efficiently, all of the carbon source. It would have been useful to continue the continuous flow operation for a longer period of time to ascertain whether such would have been the case. It was felt that the continuous flow experiments which were run demonstrated that the biological populations which acted upon the aldehydes were rather delicately poised, and that activated sludge systems which are employed in the field to treat such wastes could be subject to rather wide fluctuations in treatment efficiency. This conclusion is a conservative one since in the continuous flow systems studied sludge recycle was not employed. Cell recycle might tend to stabilize the populations; however, it may be argued that return of cells which could not readily metabolize the acid oxidation products of aldehyde dissimilations would have little beneficial effect.

The fact that a continuous flow system could deliver rather good treatment efficiency when grown on volatile waste components even under conditions which would normally be considered to be adverse (shock loading) was shown in Figure 82. During these experiments the reactor was not completely mixed with respect to biological solids. In general solids were retained in the reactor and at times the solids concentration was subject to severe fluctuations. Since the solids concentration was high, the results might be somewhat similar to those expected if solids recycling had been practised, and in general it may be said that the high biological solids concentrations seemed to permit rather successful responses to the changes in substrates which were applied. The retention of solids in the reactor came about because of the large heavy

microbial floc. The airflow rate, 500 cc/min (200 cc/min/l) did not provide enough agitation to keep the reactor in a condition of complete mixing. Dissolved oxygen was not determined during this experiment, but there was at no time any discernible evidence for the existence of anaerobic conditions.

Prediction of Stripping in Continuous Flow Reactor from Batch Data

While the variations in experimental data and the complex nature of the reactions involved make it extremely difficult to attempt to predict COD removal in the continuous flow reactor from the results of batch studies, it would seem reasonable to expect that one could make such predictions from batch data when stripping is the sole COD removal mechanism. Since, in this case, steady state conditions were approximated, the rate of change in the concentration of strippable COD $\left(\frac{dS}{dt}\right)$ can be expressed as follows:

$$\frac{dS}{dt} = \underset{\text{(inflow)}}{DS_R} - \underset{\text{(outflow)}}{DS} - \underset{\text{(stripping)}}{KaS}$$

In the above equation D is the dilution rate (hr^{-1}), S_R is the COD concentration in the feed (mg/l), S is the COD concentration in the reactor or in the effluent (mg/l), and Ka is the stripping constant (hr^{-1}). Under steady state conditions $\frac{dS}{dt} = 0$, and steady state concentration of S is given as follows:

$$S = \frac{(D)S_R}{D+Ka}$$

If the value of S is known, the stripping constant Ka can be determined as follows:

$$Ka = \frac{(S_R - S)D}{S}$$

It can be seen that a convenient way to determine the predictability of the steady state concentration of S from batch data is to compare the Ka values obtained from batch and steady state data. In the present study only acetone and methyl ethyl ketone were stripped in accordance with first order kinetics, and a first order rate constant could be only approximated for the aldehydes. The Ka values from batch and continuous flow data for all compounds for the various unit airflow rates employed are given in Table XII. In all cases Ka (batch) is greater than Ka (continuous flow), and at first glance it would appear that batch data cannot be used to predict the results in continuous flow. It should also be noted that the unit airflow rate (rather than the total airflow rate) is used as a basis for comparison. In the batch and in the continuous flow studies the total airflow rates were the same; however, the volume of aeration liquor in batch was one liter whereas it was 2.5 liters in the continuous flow studies. Thus on the basis of unit airflow rate (cc/min/l) the experiments were not comparable. The Ka (batch) values for acetone were estimated at the unit airflow rates of the continuous flow studies using the graph shown in Figure 90. The Ka (batch) values at each airflow rate (cc/min/l or cc/min, since one liter volume of aeration liquor was employed) are plotted and Ka (batch) values at unit airflow rates employed in the continuous flow studies estimated from the curve drawn through the plotted data are shown in parentheses on the curve (Figure 90). These values are those listed for Ka (batch) in Table XII. The curves from which values of Ka (batch) for MEK, propionaldehyde, butyraldehyde,

TABLE XII

COMPARISON OF AIR STRIPPING CONSTANTS FOR STRIPPABLE ALDEHYDES AND KETONES UNDER BATCH AND CONTINUOUS FLOW OPERATIONS (DILUTION RATE = 1/8 hr^{-1}) AT VARIOUS UNIT AIRFLOW RATES

Unit Air-flow Rate cc/min/l	Acetone Ka		Methyl Ethyl Ketone Ka		Propionaldehyde Ka		Butyraldehyde Ka		Valeraldehyde Ka	
	Continuous Flow	Batch	Continuous Flow	Batch	Continuous Flow	Batch	Continuous Flow	Batch	Continuous Flow	Batch
1600	0.15	0.29	0.229	0.375	0.197	0.52	0.495	0.75		1.01
1600	0.186									
800	0.111	0.20	0.121	0.195	0.231	0.30	0.34	0.44	0.423	0.59
800			0.121		0.244					
400	0.072	0.12	0.108	0.105	0.128	0.18		0.25		0.34
200	0.032	0.07	0.065	0.06	0.086	0.10		0.15		0.20

Note: Ka (continuous flow) values are calculated from the predicting equation $Ka = \frac{(S_R - S)D}{S}$; expressed as hr^{-1} (base e)

Ka (batch) values are interpolated from plot of unit airflow rate versus Ka (hr^{-1}, base e) Figures 90, 91, and 92.

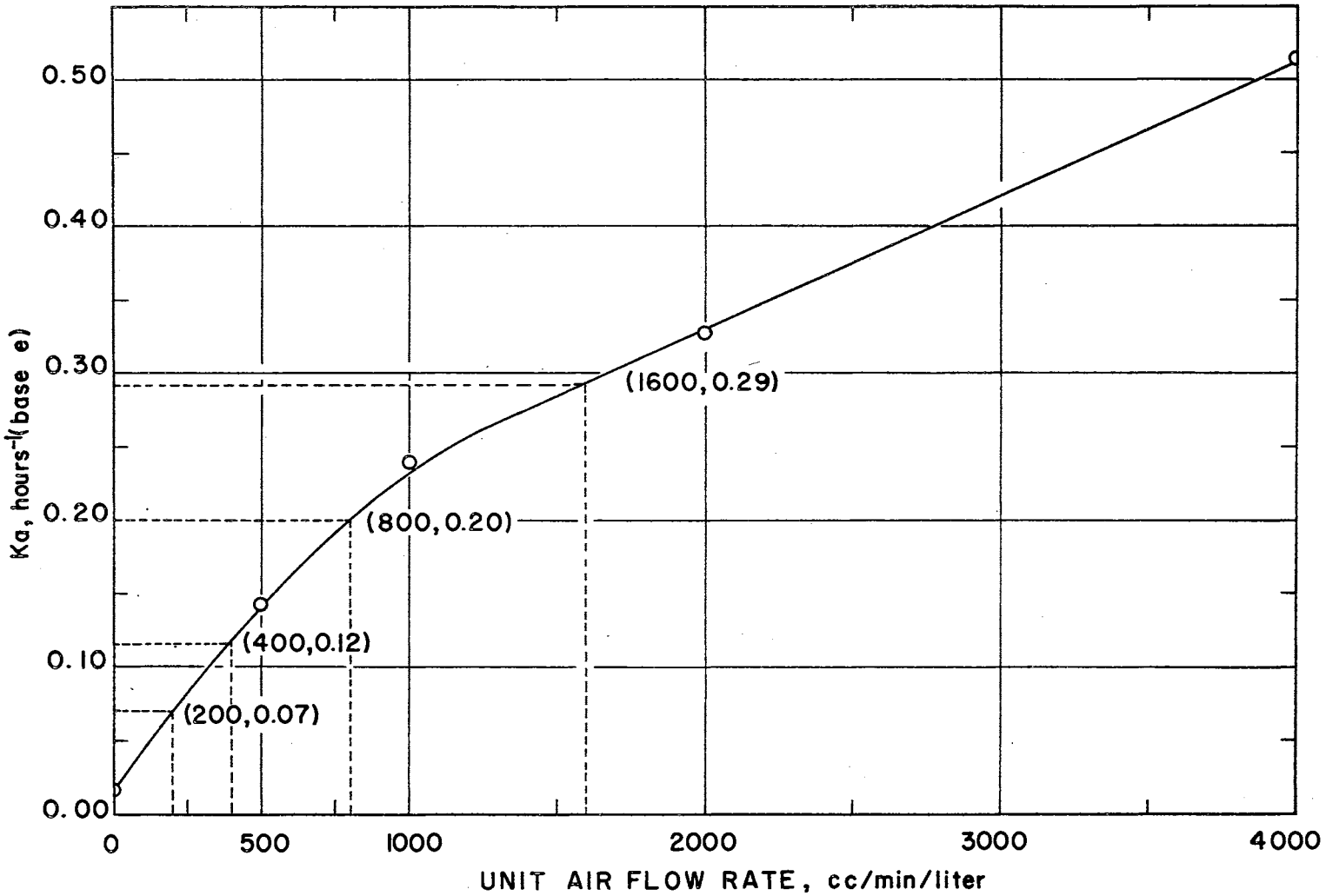


Figure 90 - Prediction of Ka (base e) for continuous flow reactor by interpolation from plot of Ka (base e) versus unit airflow rate (under batch conditions) for acetone.

and valeraldehyde were estimated are shown in Figures 91 and 92. Even though the Ka (batch) values for unit airflow rates comparable to those used in the continuous flow reactor could be only roughly estimated, it would be expected that there should be closer agreement between Ka (batch) and Ka (continuous flow). It may be discerned from Table XII that the values tended to converge (note acetone and MEK) as the unit airflow rate decreased. It had been previously found by Gaudy, Engelbrecht, and Turner (29) that such factors as tank geometry and depth affected Ka. These workers (28)(64) also felt there was a considerable need for caution in extrapolating data on stripping obtained in a one-liter volume to field conditions. While application of values obtained from a one-liter volume to a 2.5-liter volume of reaction liquor is an extrapolation of far less magnitude, it is seen that it did have a significant effect.

The fact that the difference in Ka (batch) and Ka (continuous flow) values at the same unit airflow rate was due to the difference in reactor volumes is demonstrated by the results of an experiment shown in Figure 93. The upper curve (on either the arithmetic or semilog plot) shows the course of acetone removal for a batch study in which the volume under air was the same as that during the continuous flow stripping studies, and the lower curve shows the course of acetone removal (COD) during a similar batch experiment in which the volume under air was the same as that during the batch stripping studies. The unit airflow rate was 500 cc/min/l in both cases. It is seen that the difference in Ka (batch) values from the data obtained at the two aeration volumes is approximately the same as the difference between Ka (batch) and Ka (continuous flow) shown in Table XII. Thus it seems clear that the

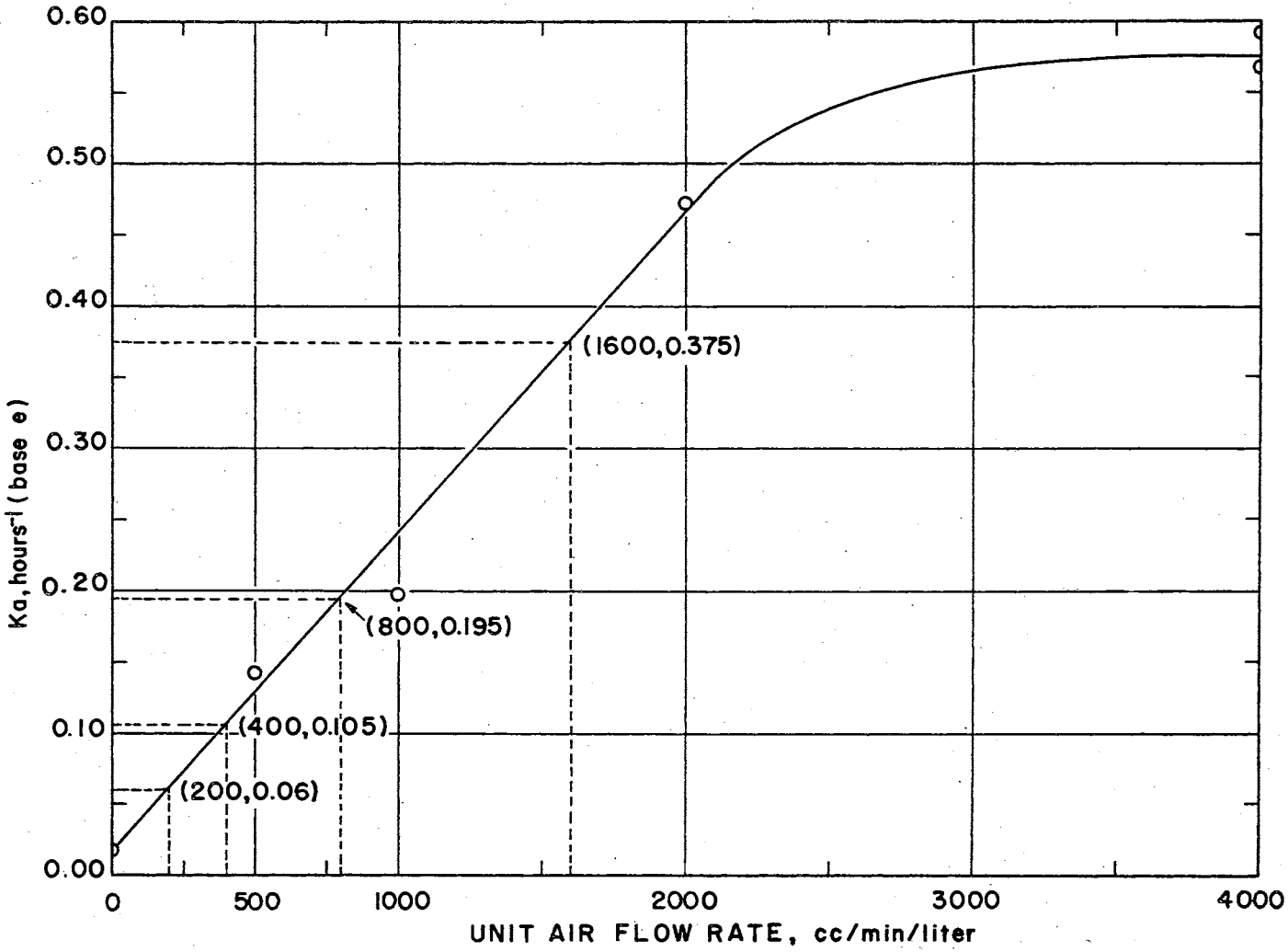


Figure 91 - Prediction of Ka (base e) for continuous flow reactor by interpolation from plot of Ka (base e) versus unit airflow rate (under batch conditions) for methyl ethyl ketone.

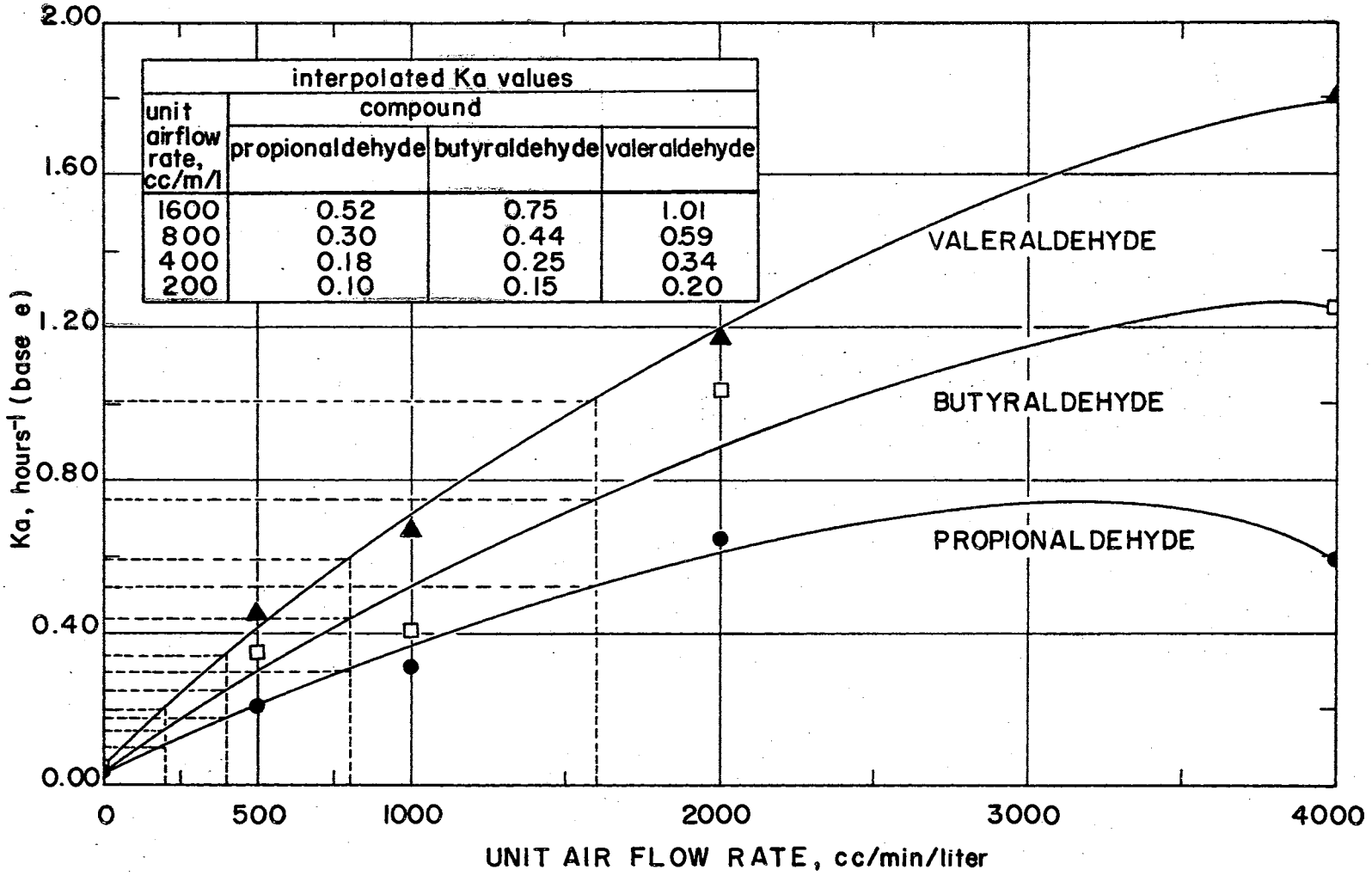


Figure 92 - Prediction of Ka (base e) for continuous flow reactor by interpolation from plot of Ka (base e) versus unit airflow rate (under batch conditions) for propionaldehyde, butyraldehyde, and valeraldehyde.

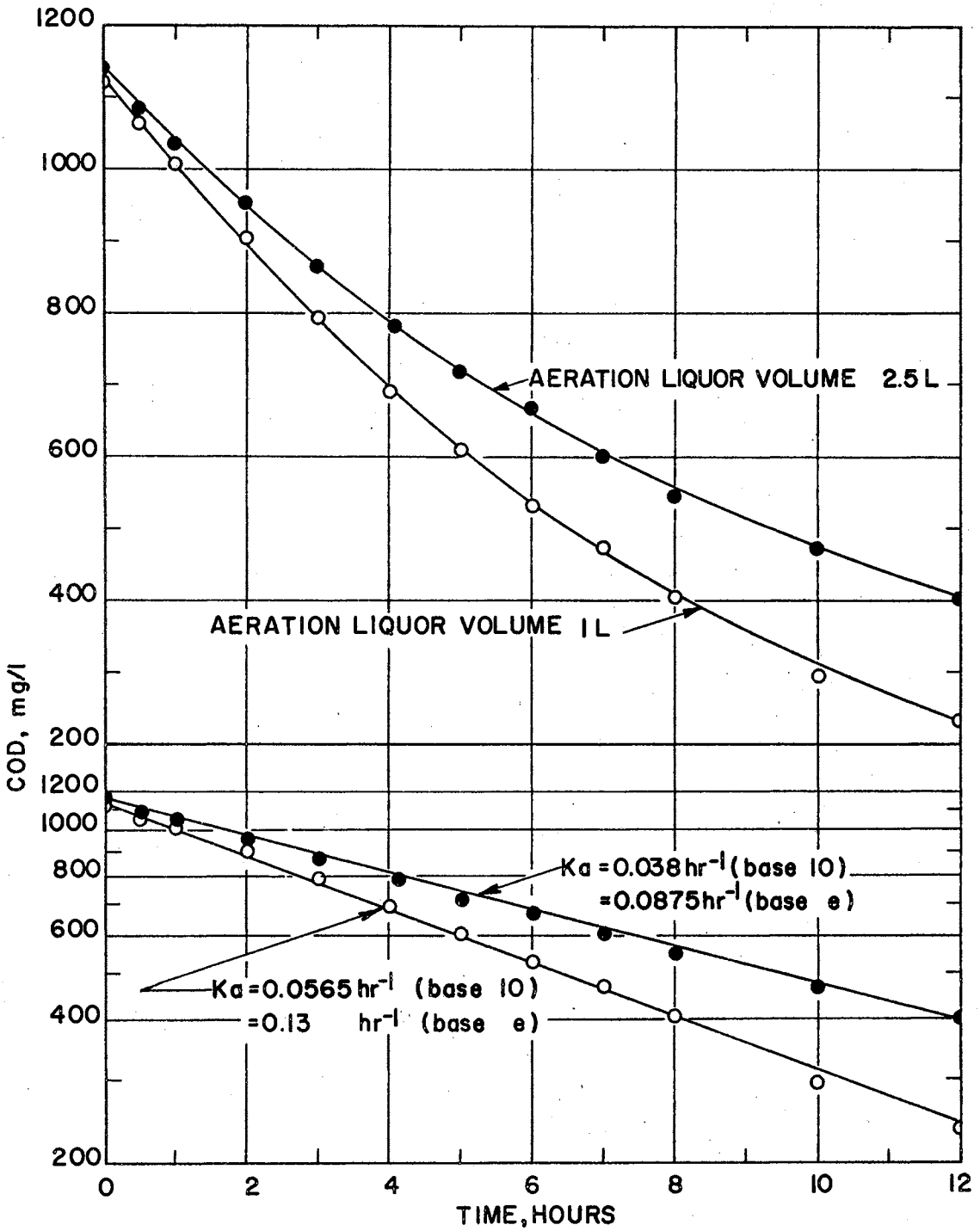


Figure 93 - Effect of aeration liquor volume on Ka of acetone at a unit airflow rate of 500 cc/min/l under batch conditions.

difference in Ka values is not due to an intrinsic difference in the stripping kinetics in batch and continuous flow reactors, but due to the reactor liquor volumes employed. It is interesting now to determine whether the Ka value for continuous flow at an airflow rate of 500 cc/min/l is the same as that obtained in batch (i.e., 0.0875 hr^{-1}) when the same reactor liquor volume was used. Continuous flow runs were not made at 500 cc/min/l; however, the Ka value can be estimated in the same way as was done for Ka (batch) values at other airflow rates. In Figure 94 the Ka (continuous flow) values determined at each unit airflow rate are plotted and the Ka at 500 cc/min/l is estimated from the curve through the observed values as 0.087 hr^{-1}. This value agrees extremely well with the value of 0.0875 hr^{-1} obtained from the batch data plotted in Figure 93. There appears to be little doubt that Ka values obtained in batch studies can be used to predict COD level under continuous flow steady state conditions, i.e., Ka (batch) = Ka (continuous flow) at comparable conditions of temperature, etc., but it is equally apparent that if unit airflow rate is the prime common parameter, the batch data should be obtained in the same reactor using the same volume of reaction liquor which is to be used under continuous flow operations.

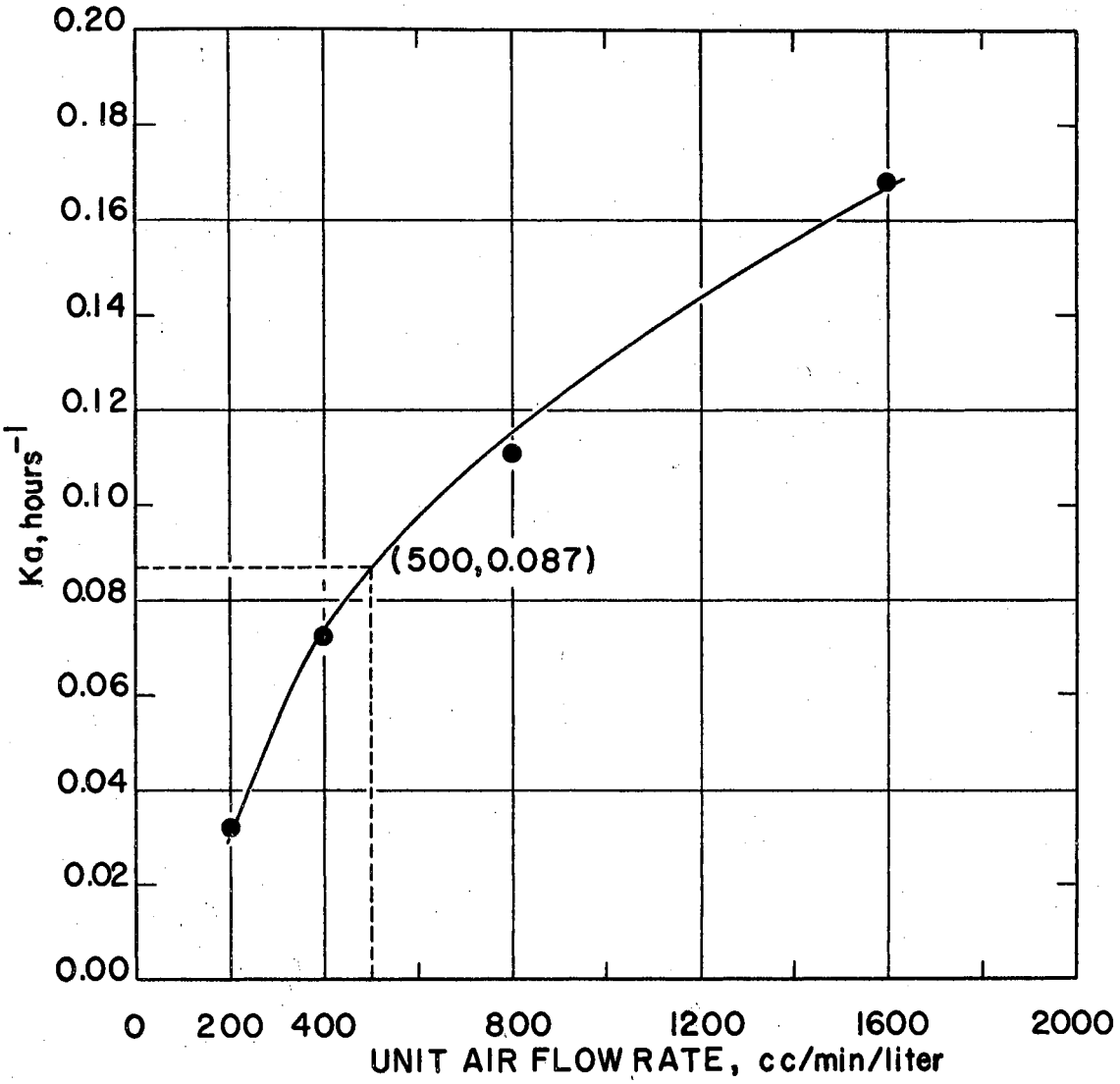


Figure 94 - Effect of unit airflow rate on Ka (calculated from predicting equation) for air stripping of acetone in a continuous flow reactor (dilution rate = 1/8 hr^{-1}).

CHAPTER VI

SUMMARY AND CONCLUSIONS

On the basis of the results herein presented, the following conclusions seem warranted:

1. The removal pattern of ketones due to stripping alone at 25°C and at various unit airflow rates obeys first order kinetics. These findings agree with results of Gaudy and Engelbrecht (64), and Engelbrecht, Gaudy, and Cederstrand (25) for acetone and methyl ethyl ketone. At identical unit airflow rates under batch conditions, elimination of methyl ethyl ketone is significantly more rapid than that of acetone. Removal of acetone and methyl ethyl ketone due to stripping and biological metabolism under batch conditions can be described adequately by the predicting equation formulated by Gaudy, Turner, and Pusztaszeri (3). Despite differences in operational parameters (unit airflow rate, tank geometry, biological solids concentrations, etc.), rate constants for biological metabolism calculated from the predicting equation (3) do not differ significantly from those experimentally determined by Gaudy, Turner, and Pusztaszeri (3) using the Warburg apparatus.

2. Acetone and methyl ethyl ketone retain the same kinetic mode and velocity constant when a mixture of the two in approximately equal initial concentrations is subject to physical stripping at the same airflow rate, as they exhibit when stripped independently, i.e., there is

no apparent interaction between these compounds during air stripping at 25°C. The overall removal of the composite waste (mixture) is dictated by the stripping characteristics of the least volatile component (in this case, acetone). These findings agree with the conclusions of Eckenfelder, Kleffman, and Walker (26).

3. Disodium hydrogen phosphate at a dosage of 60 mg/l enhanced the rate of removal of methyl ethyl ketone without altering first order stripping kinetics at a unit airflow rate of 500 cc/min/l. Very little enhancement of COD removal was observed in the acetone system with disodium hydrogen phosphate at a unit airflow rate of 500 cc/min/l until a period of six hours, beyond which COD removal was distinctly retarded. Order of kinetics, however, remained the same in both periods. Disodium hydrogen phosphate at the aforesaid dosage enhanced the rate of stripping of butyraldehyde only; whereas for propionaldehyde and valeraldehyde, disodium hydrogen phosphate at the same dosage and airflow rate distinctly slowed the COD removal rate.

4. Comparison of samples analyzed by gas liquid chromatography and by COD indicated no evidence for autoxidation of acetone and methyl ethyl ketone during stripping under batch conditions. Aldehyde COD removal based on gas liquid chromatographic analysis was more rapid than total COD removal (under batch conditions at a unit airflow rate of 2000 cc/min/l). Thus, for propionaldehyde, butyraldehyde, and valeraldehyde there was evidence for autoxidation. Direct confirmation of autoxidation of these aldehydes was not possible, since no peaks other than the respective aldehydes were detected by gas liquid chromatographic analysis. The first order stripping constants for aldehydes increased with increasing numbers of carbon atoms, i.e.,

propionaldehyde, 0.303 hr^{-1}; butyraldehyde, 0.514 hr^{-1}; and valeraldehyde, 0.62 hr^{-1}.

5. Using acclimated heterogeneous microbial populations of sewage origin, all the ketones and aldehydes studied could be treated more efficiently by the dual process (stripping and microbial metabolism) than by stripping alone under batch conditions. Ketones (acetone and methyl ethyl ketone) during dual removal did not exhibit any evidence for the presence of metabolic intermediates. Methyl ethyl ketone was removed more rapidly than was acetone. Dual removal of aldehydes, however, involved accumulation of metabolic intermediates and/or end-products and their subsequent utilization. In all cases, monocarboxylic organic acids with carbon numbers ranging from two to five, depending on the nature of the initial carbon source, were found in the medium. The sum of the equivalent COD for intermediate products detected did not equal the observed total COD. Thus not all metabolic products in medium were identified.

6. Aldehydes in general do not strip in strict adherence to first order kinetics for the entire course of aeration, under batch conditions, at various airflow rates. Nevertheless, first order rate constants for propionaldehyde, butyraldehyde, and valeraldehyde can be approximated (after a significant proportion of the initial COD is removed) from the straight line portion of a semilogarithmic plot of total COD remaining versus time. Stripping constants (Ka) for three and four carbon aldehydes which are higher than those for the corresponding (three and four carbon) ketones indicate that aldehydes are more susceptible to stripping than ketones.

7. Both sludge yield and maximum intermediate accumulation

(difference between total COD and substrate COD) decreased with increases in unit airflow rates during joint treatment (biological and stripping).

8. Significant portions of both aldehydes and ketones can be stripped in the aeration tank of a continuous flow reactor (at a dilution rate of 1/8 hr^{-1}). At a fixed airflow rate, percent stripping efficiencies for acetone (4000 cc/min), methyl ethyl ketone, propionaldehyde, and valeraldehyde (all at 2000 cc/min) are independent of initial feed concentration (COD, mg/l) of the respective compounds. Continuous stripping proceeds at steady state conditions quite readily. For a given volatile compound and given operational conditions (temperature, airflow rate, dilution rate), enhancement of treatment efficiency beyond this state is possible only by addition of an acclimated microbial population in the aeration tank of the continuous flow system.

9. There was no evidence for autoxidation during air stripping of acetone and methyl ethyl ketone in a continuous flow reactor. Steady state concentrations of aldehyde COD (from gas liquid chromatographic analysis) lower than total COD (strikingly apparent in the case of butyraldehyde and valeraldehyde) indicated the presence of certain autoxidation products.

10. Removal of ketones by combined stripping and biological metabolism can be effected more efficiently than sole stripping of the compounds in a continuous flow reactor. During combined stripping and biological treatment, neither of the ketone systems gave rise to any metabolic intermediates or endproducts. Thus with respect to metabolic intermediates, the heterogeneous populations developed under both batch and continuous culture conditions yield the same results.

11. For propionaldehyde and valeraldehyde, fewer monocarboxylic acids in the form of intermediary metabolites were detected under continuous flow conditions than under batch conditions. For valeraldehyde, all of the effluent COD was attributable to valeric acid. At the dilution rate employed, a high concentration of valeric acid was found in the effluent. It is possible that at lower dilution rates, the valeric acid would have been metabolized.

12. The activated sludge process can successfully withstand qualitative shock loads of aldehydes and ketones without impairment of overall treatment efficiency (range 81-95 per cent). During the entire course of shock load studies (over two months), no evidence for metabolic intermediates was detected; a leakage of a very small amount of untreated methyl ethyl ketone (66 mg/l COD) was observed in the effluent for two days after the system was shocked with methyl ethyl ketone.

13. The difference in Ka (stripping constant) values obtained under batch and continuous flow conditions is attributable to the difference in reactor liquor volumes employed under the two conditions and is not due to any intrinsic difference in the stripping kinetics under the two operational conditions. So long as the volume of aeration liquor (hence depth) and the unit airflow rate (cc/min/l) are the same and the same aeration tank is used (tank geometry not affecting the results), stripping constants obtained under batch operations are the same as those obtained under continuous flow conditions.

CHAPTER VII

SUGGESTIONS FOR FUTURE WORK

The results of the present research have indicated that the following additional studies would provide useful information pertinent to the treatment of volatile waste components.

1. Stripping experiments may be conducted using diffused oxygen rather than air to gain further insight into autoxidation of the aldehydes which did not conform to first order stripping kinetics and for which there was evidence of autoxidation.

2. Independent determinations of biological rate constants should be made for the aldehydes using the experimental protocol outlined by Gaudy, Turner, and Pusztaszeri (3) for their work on ketones.

3. Stripping experiments on mixtures of ketones and aldehydes similar to the batch experiment of the present study should be conducted in continuous flow reactors to determine whether the overall steady state removal efficiency for the mixture can be predicted from a knowledge of the stripping rates of the individual compounds in the mixture.

4. A series of quantitative and qualitative shock loading experiments should be undertaken in continuous flow activated sludge reactors to determine the magnitude of shock which can be successfully handled by the system.

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APPENDIX

Compound	Equivalent COD of Compound, mg/l = Concentration (mg/l) of Compound x Multiplying Factor
glucose	1.06
acetone	2.21
methyl ethyl ketone	2.44
propionaldehyde	2.21
butyraldehyde	2.44
valeraldehyde	2.60
acetic acid	1.06
propionic acid	1.51
isobutyric acid	1.82
butyric acid	1.82
isovaleric acid	2.03
valeric acid	2.03
hexanoic acid	2.20

VITA

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Doctor of Philosophy

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Professional Experience: Worked as Engineering Assistant in the Public Health Engineering Department of Rourkela Steel Project, Rourkela, India, from September, 1957, to June, 1958; Assistant Engineer, Public Health Engineering Deparment, Durgapur Steel Project, Durgapur, India, from June, 1958, to August, 1960; part-time Demonstrator in the Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Canada; Research Assistant, Gault Research Station, Mt. St. Hilaire, Quebec, Canada; Graduate Research Assistant, University of Illinois, Urbana; Graduate Teaching Assistant-Research Assistant, Civil Engineering Department, Oklahoma State University, Stillwater, Oklahoma.

Membership in Honorary and Professional Societies: Sigma Xi; Engineering Institute of Canada; American Society of Civil Engineers; American Association for the Advancement of Science; Société des Ingénieurs Civils de France; American Water Works Association; Chi Epsilon; Sigma Tau; Omicron Delta Kappa.

Special Mention: Winner of Canadian Commonwealth Scholarship for higher studies at McGill University, Montreal, Canada; represented India at the World University Conference in London, Ontario, Canada, 1961, from McGill University; listed in "Men of Science and Technology in India;" accepted for listing in "Who's Who in the South and Southwest" in the United States of America.