THE EFFECT OF LOW TEMPERATURE
ON
THE PHYSICO-CHEMICAL TREATMENT
OF
DOMESTIC WASTEWATER

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DOMESTIC WASTEWATER

BY

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements for
the Degree
Master of Engineering

McMaster University
Hamilton, Ontario
December, 1975

Master of Engineering (1975)
(Chemical Engineering)

McMaster University
Hamilton, Ontario

Title	:	The Effect of Low Temperature on the Physico-Chemical Treatment of Domestic Wastewater.
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Supervisor	:	Dr. A. Benedek
Number of Pages	:	325
Abstract	:	

The effect of low temperature on the physico-chemical treatment (PCT) of domestic wastewater is examined with special emphasis placed on activated carbon adsorption. PCT is a recent processing scheme, wherein wastewater goes through sedimentation, precipitation, deep bed filtration and adsorption. In PCT, activated carbon adsorption takes the place of conventional biological treatment for organic removal.

Both batch studies using powdered activated carbon (PAC) and continuous flow studies with granular activated carbon (GAC) on a pure compound, sodium dodecyl sulfate (SDS) and domestic wastewater from the Dundas, Ontario Water Pollution Control Plant were investigated.

Theoretical analysis and batch feasibility studies indicate that the effect of low temperature on coagulation, flocculation and sedimentation were quite easily handled within established design parameters. Batch studies on PAC treatment show that the carbon floc is easily separable from wastewater with the aid of a small dosage of polyelectrolyte and high effluent quality is obtainable at temperatures ranging from $2^0 - 25^0$C.

Granular activated carbon was evaluated first on a pure compound, SDS. Batch isotherms and kinetics were also conducted at the same time to determine parameters needed for continuous flow modelling. Results derived from this phase of the study indicate that the activation energy from column studies is quite low (approximately 3.0 kcal/mole). Close match is obtained between the theoretical model (a modification of Thomas' reaction kinetics) and experimental data.

Finally PCT pilot plant studies on domestic wastewater were carried out, at 5^0C and 25^0C. Soluble organic carbon removal was in excess of that predicted by purely adsorption type phenomenon. This is attributed to microbial activity inside the carbon columns. Greater soluble organic removal was seen at 25^0C than at 5^0C. Denitrification inside the carbon columns was found to be quite significant, again with stronger denitrifying activity at 25^0C than at 5^0C. Microbiological investigation of the carbon from the exhausted columns revealed over 10^9 cells/cm^3 of GAC bed volume from the lead column at 25^{0}C. Denitrifiers were also detected in the carbon. Iodine numbers were determined on used carbon, which indicated the exhaustion of activated carbon capacity. Organic removal, however, continued undiminished, due to bacterial activity.

The study culminated with the development of a theoretical model incorporating bacterial activity. The results of column effluent profile, however, indicated great discrepancy between theoretical predictions and experimental observations. This was attributed to simplistic assumptions utilized in solving the fixed bed problem.

ACKNOWLEDGEMENTS

At the culmination of this work, which spanned a period of two years, I would like to express my sincere appreciation to Dr. A. Benedek, who initiated the project, and was a source of constant encouragement, advice and criticism.

At the same time, I would like to take the opportunity of recognizing the contribution of others associated with this project.

To Mr. A. Najak for helping with the batch studies and overall assistance;

To Mr. J. Bancsi for his assistance throughout the project;

To Messrs. T. Ho, A. Shaidle and D. Hughes for their help in both the lab and pilot plant studies;

To Ms. P. Usenik for assistance in TOC analysis;

To Mrs. A. Latozek for conducting the micro-biological investigations;

To employees of the Dundas Water Pollution Control Centre for their co-operation during the pilot plant studies;

To Mrs. H. Martin for typing the manuscript.

Acknowledgement is also made of the non-technical staff of the Wastewater Research Group.

The project enjoyed support from the Department of the Environment of the Federal Government.

TABLE OF CONTENTS

Appendix

LIST OF TABLES

Table No. Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The Northern portions of Canada, occupying vast stretches of land areas, are the subject of increasing attention today. Beneath the barren surfaces lie one of the world's richest oil and mineral deposits and this great economic potential is spurring unprecedented industrial growth. Concomitant with this activity, serious environmental problems threatening the naturally evolved fragile ecological balance have arisen. Furthermore, a high incidence of enteric infections stemming from inadequate methods of sewage disposal has been cited (Alter, 1972).

The availability of effective facilities for wastewater collection, treatment and disposal is, therefore, imperative in the further development of the North.

1.1 NORTHERN CONDITIONS

The climatic conditions prevailing in the North determine to a large extent the manner of waste water treatment. By definition, the mean temperature for the warmest month in the Arctic regions is no greater than 50°F, and for the coldest month is no greater than 15°F. Table 1 lists typical communities, their locations and characteristic temperatures. The population density is very low in the Arctic, with only 250,000 people in Alaska, and 24,000 in Canada. This factor plays an important role in providing adequate treatment. Due to the scarcity and dearness of water, the sewage flows are generally low and their strength high, as shown in Table 2 and 3, respectively. Average flows and concentrations in the Arctic tend to be misleading, as they do not take into account the high fluctuations which occur in small, thinly populated bases and camp sites.

TABLE 1

Typical High Latitude Communities

Station	Latitude	Mean Jan. Temp. °F	Mean July Temp. °F	Mean Annual Temp. °F
ALASKA				
Anchorage	61° 13 N	11.2	57.6	-36
Fairbanks	64° 51 N	-11.6	60.0	-66
Juneau	58° 18 N	27.5	56.6	-15
Nome	64° 30 N	3.4	49.8	-47
Barrow	71° 23 N	-17.0	40.2	-56
CANADA				
Chesterfield Inlet	63° 45 N	26.5	47.2	-17
Fort Good Hope	66° 25 N	-22.0	59.6	-79
Hebron	58° 12 N	- 5.7	47.1	-42

(From Alter, 1972)

TABLE 2

Approximate Volume of Sewage Generated at Selected Cold Region Installations in Gallons per Capita per Day

Thule AB, Greenland	80
Camp Century, Greenland	50
Fort Churchill, Canada (Air Force Base)	60
Barrow, Alaska (DEWLine Station)	30
Barter Island, Alaska (DEWLine Station)	25
College, Alaska	70
Fairbanks, Alaska	80
Island Homes, Fairbanks, Alaska	35
Average	55

(From Alter, 1972)

TABLE 3

Raw Sewage Characteristics

Location	Biochemical oxygen demand*
Site A - North Slope Alaska	380 to 484
Site B - North Slope Alaska	740
Site E - North Slope Alaska	500 to 1100
Site L - North Slope Alaska	600
Fairbanks, Alaska	260
College, Alaska	280
Ketchikan, Alaska**	30
Juneau, Alaska**	40
Anchorage, Alaska	165
U.S.	180

* Expressed in parts per million

** Water distribution system is kept from freezing by wasting water, thus sewage flows are high and strengths are low.

(From Alter, 1972)

The conditions thus found in the North demand a very rugged and stable method of treatment capable of dealing with intermittent operations and periods of low and high loadings.

1.2 CURRENT METHODS OF TREATMENT

In most Northern communities, there is no satisfactory system of sewage treatment available. Oil drums, box and can are the common methods of disposal in small and remote settlements. Slightly less primitive methods such as septic tanks have met with limited success, as disease-causing bacteria still persist in effluents. Chemical toilets as an alternative to the pail receptacle never became widely accepted due mostly to high chemical costs.

Some unconventional methods such as waste collection with oil followed by incineration (Logan, 1961) have been proposed. Their feasibility, however, is quite doubtful. Alter (1969) suggested freezing as a possible method of treatment. The mechanisms which might actually operate for this type of treatment are ill-defined at this stage and need further investigation.

The small number of treatment plants which do exist are inadequate for present purposes. Among these the biological mode of treatment predominates. Lagoons are commonly found as a stop-gap measure built usually for holding purposes. Dawson (1969) found that stabilization lagoons under extreme winter conditions could provide BOD and solids removal rates approximately equivalent to primary waste treatment. Efficiencies in the winter are in some cases notably lower than those in the summer (Pick _et al_, 1970).

Activated sludge plants have been built in larger centres such as Yellowknife. Among existing plants extended aeration systems are particularly common as they provide additional detention time for stabilizing organic wastes. BOD removals of over 80% are generally reported to be obtainable from activated sludge systems.

1.3 PROBLEMS AND ALTERNATIVES

Foremost amongst the factors affecting sewage treatment plant design and operation in the North is the cold, which exceeds that of the more populous Southern belt in both magnitude and duration. Biological systems which have been used extensively to date have many inherent shortcomings in their applications to cold climates. Most significantly these systems tend to be unreliable at low temperatures due to decreased biological rates. Problems arise in maintaining a stable bacterial population which are usually sensitive to temperature fluctuations. Proposals such as spiking biological systems with psychrophilic micro-organisms to degrade organic wastes have yet to prove their applicability as an alternative (Morrison, 1972). Operating problems in biological systems utilizing aeration for oxygen transfer are unique in cold climates. Freezing of rotors has been reported extensively in literature resulting in operating problems and anaerobic conditions.

Faced with these inherent disadvantages of biological systems, the need for developing and exploring alternative methods of treatment becomes crucial. The logical choice in the search for new techniques would be to adapt proven, reliable, nonbiological methods of treatment being currently used in milder climates to the climatic conditions existing in the North.

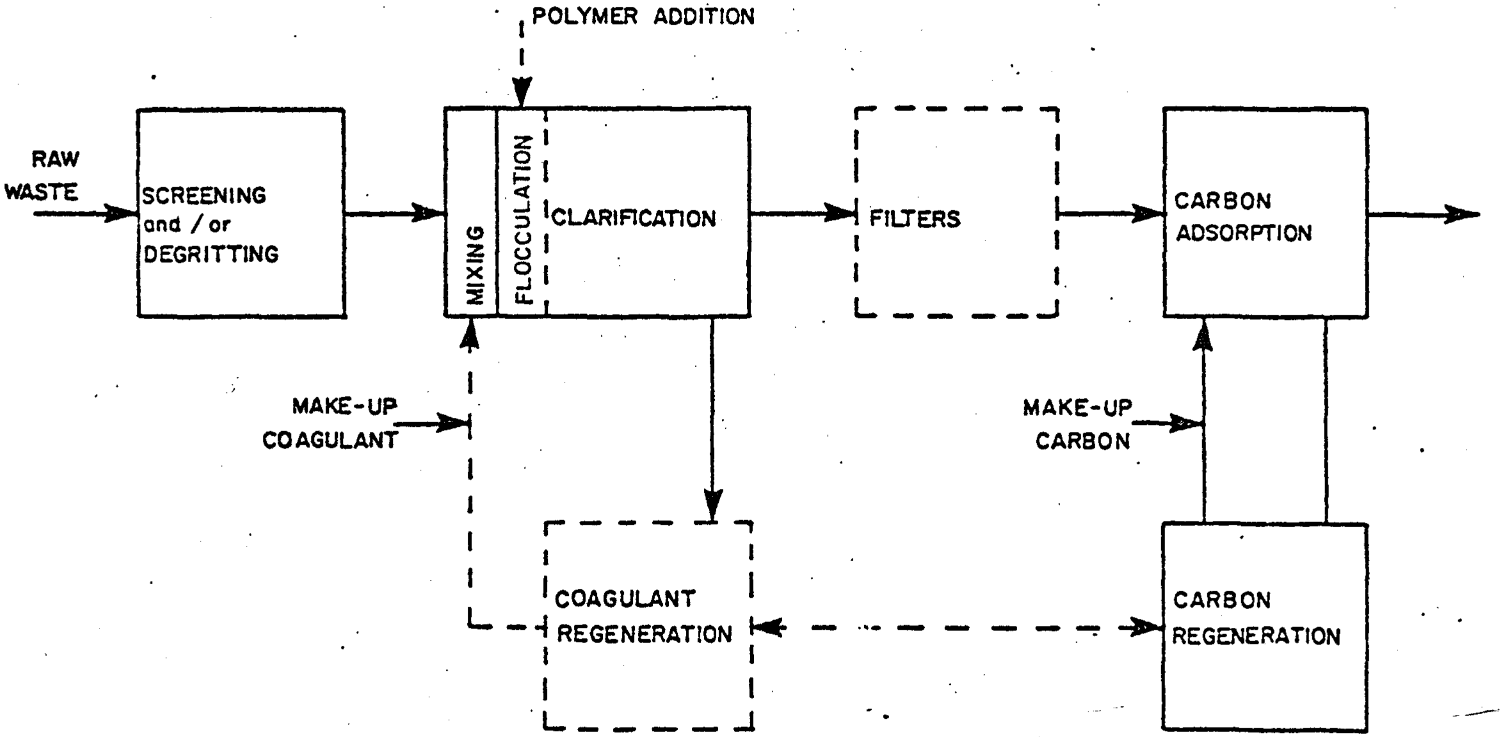
1.4 PHYSICAL/CHEMICAL TREATMENT

In the whole panorama of modern technological systems available, physico-chemical treatment (PCT) appears to be a most promising candidate for selection. A typical flow sheet of a PCT system is shown in Figure 1. Raw waste enters into the plant and conventional pre-treatment is provided to separate large solid particles from the flow. Metallic coagulants such as alum, ferric chloride or lime are then added at points of high turbulence to ensure good mixing. Polymeric flocculants are next added to produce larger and better settling flocs, which settle in the primary sedimentation tank.

The primary effluent is then treated to remove soluble contaminants by contacting with either Granular Activated Carbon (GAC) or Powdered Activated Carbon (PAC). In the case of PAC contacting an additional unit operation has to be provided, namely, the separation by sedimentation of the PAC particles from the sewage. Sand filtration

FIGURE 1

GENERALIZED FLOW SCHEME FOR PHYSICO-CHEMICAL TREATMENT



before or after carbon adsorption are options which are widely incorporated into PCT to provide even better quality effluent. The unique feature to note is the relative lack of dependence on biological removal steps.

The PCT system as we know it today may seem like a new and fresh approach to waste water treatment, but the individual unit operations which comprise it have been used for centuries. Chemical treatment enjoyed wide popularity in Europe until 1910, but soon lost its utility due to the development of activated sludge systems. Similarly, carbon adsorption as a separate unit operation has been used to decolorize sugars, purify water (by removal of taste and odour causing compounds) and recover metals from wastes. Adsorbents, however, found their widest use in gaseous systems where the molecular forces of attraction are stronger. In liquids the adsorbent has to compete with the solvent in capturing the solute.

With increasingly tough pollution problems plaguing the United States, a fresh look was cast in search of alternative technologies. Originally, activated carbon adsorption was examined for the removal of refractory materials, such as chlorinated hydrocarbons, dead cellular fragments, humic acids, etc., and alkyl benzene sulfonate (ABS), a surface active agent which created a nuisance by foaming. Later on it was shown that activated carbon had not only an excellent affinity for refractory compounds, but was generally non-specific in its adsorptive properties. Except for low and high molecular weight compounds, carbon could effectively remove most soluble organics. Since the cost of granular carbon is higher it was reserved for polishing purposes only.

Weber (1970) showed however, that it was possible to remove dissolved organics from primary effluents by contacting with activated carbon. Equal or better quality effluents were obtained on a remarkably consistent basis compared to a conventional activated sludge unit. The decisive advantage which tipped the balance in favour of PCT was that phosphates were being removed at no additional expenditure.

Many outstanding problems still remain in the application of PCT, such as long term regeneration effects, the role of biological activity on carbon surfaces, etc. In spite of this, over 40 municipalities and industries have adopted PCT. The largest one being designed is the 60 MGD Sewage Treatment Plant in Niagara Falls, N.Y. The popularity of PCT has been enhanced considerably because cost estimates show it to be comparable to conventional activated sludge (CAS) units. Based on data published by Smith (1968), it was shown by Weber (1970) that for plants larger than 1 MGD, the capital cost for PCT is less than CAS. Operating costs are, however, greater for PCT on a volume treated basis, with the difference decreasing with larger plant capacities. If cost comparison is based on improvement of water quality, then the process economics would definitely favour PCT. Total plant costs of the PCT system have been quoted in the range of 28¢/1000 gallons for 10 MGD to 10-15¢/1000 for 100 MGD (Kugelman and Cohen, 1973). These costs include amortization, operation and maintenance costs.

With PCT being accepted as an attractive alternative, both from the point of view of performance and economics, some manufacturers have been exploring the possibility of PCT treatment in the Arctic. Several such small package plants have been installed in Alaska to serve small population centers like hospitals, schools, hotels, etc. (Smith, 1973). Prototype installations were set up near Prudhoe Bay as reparted by Coutts (1972). In spite of many operational problems, an overall COD removal of 95% was achieved.

1.5 REASONS FOR PCT

In summary then, the PCT system is believed to be a promising process for Northern applications because of the following advantages:

1) PCT of domestic wastewater has been proven to be competitive with conventional activated sludge processes and shown to deliver equal or better overall removal of contaminants.
2) PCT is relatively unaffected by shock organic loadings or hydraulic fluctuations.

3) Besides removing soluble organics, PCT systems also remove phosphates, toxic compounds, heavy metals, without extra expenditure.

4) Since water is a precious commodity in the Canadian North, (costing sometimes up to $1/gallon), economics dictate that wastewater should be put to partial re-use by slight upgrading of the quality of secondary effluent. PCT can deliver re-usable water for non-drinking purposes from wastewater.

5) Experienced operators are very hard to come by in the Canadian North (Clark et al, 1972). PCT systems can by easily automated, requiring little maintenance.

6) The operations envisaged in the North are of an intermittent nature. Biological systems require at least three weeks to a month before they have a well-adjusted biomass to degrade the waste. PCT plants possess a unique advantage of going on-line without significant delay.

Although PCT has these advantages, some disadvantages to its application in the North do exist. This mostly relates to the operating cost of chemicals used for coagulation, flocculation and adsorption. Transportation costs are high, especially for remote areas. An added disadvantage with PCT systems is that design and operating experience is inadequate. A relative independence of temperature is an unknown that could make the advantages significantly outweigh the disadvantages. Theoretically, lower temperatures reduce rates and efficiencies of physical operations. Up to this time however, there have not been any investigation of the effect of low temperatures on PCT efficiency. Once the fundamentals are grasped, then sound engineering principles can be set for PCT systems in the North.

1.6 THESIS STRUCTURE

The work presented in this thesis has been divided into three phases for convenience to the reader. This organizational structure was designed to enable the reader to fully comprehend each study before proceeding to the next. As a result of this sub-division, some overlap might occur from chapter to chapter.

The three major aspects of the thesis are: (1) the effect of temperature on unit operations comprising PCT, (2) modelling theories for batch and fixed bed adsorption systems and (3) role of biological activity in carbon beds. In chapter 2 a literature survey is presented focusing on these three topics. The experimental sections are included for each part separately in latter chapters. The literature survey in chapter 2 is presented together to avoid duplication.

Chapter 3 presents the results and conclusions of a batch feasibility study on the effect of temperature on the unit operations of PCT using powdered activated carbon. Columnar adsorption is quite complicated and, therefore, a separate study described in Chapter 4 was undertaken to study temperature effects in columns. Due to the complexity of modelling carbon columns, at first a synthetic, single compound wastewater was used. In Chapter 5 the results of a pilot PCT plant on Dundas raw sewage are presented with attention focused on the operation of the activated carbon columns. In the last chapter, the conclusions gathered from this research are summarized and recommendations for future investigations are presented.

CHAPTER 2

LITERATURE SURVEY AND THEORY

2.1 EFFECT OF TEMPERATURE ON UNIT OPERATIONS OF PCT

In the first part of the literature survey, the theoretical effect of temperature on fluid properties and the unit operations which make up PCT will be surveyed as background to further studies.

2.1.1 FLUID PROPERTIES

a) Viscosity

Viscosity plays an important role in the temperature dependence of settling rates. Its' behaviour has been studied extensively for many years. Hazen (1904) demonstrated that for water a simple relationship can be derived.

$$\mu = 0.01309 \frac{60}{T + 10} \qquad (1)$$

where T - temperature in ^{o}F

μ - absolute viscosity in poise

Bingham (1922) tabulated data on viscosity of water, which is shown below for the relevant range of $0-30^{o}C$.

Temperature ^{o}C	μ Centipoise
0	1.792
5	1.519
10	1.308
15	1.140
20	1.005
25	0.894
30	0.801

When plotted as in Figure 2, it can be seen that over a narrow range an inverse relationship between viscosity and temperature can be safely assumed.

b) Density

The mass density, ζ, of pure liquid water at atmospheric pressure is equal to 1.0 gram per cm^3 at 4°C. At the ordinary pressures and temperatures encountered in sanitary engineering, water is for all practical purposes an incompressible fluid. The changes in density as a function of temperature are also negligible for our present purposes.

c) Diffusivity

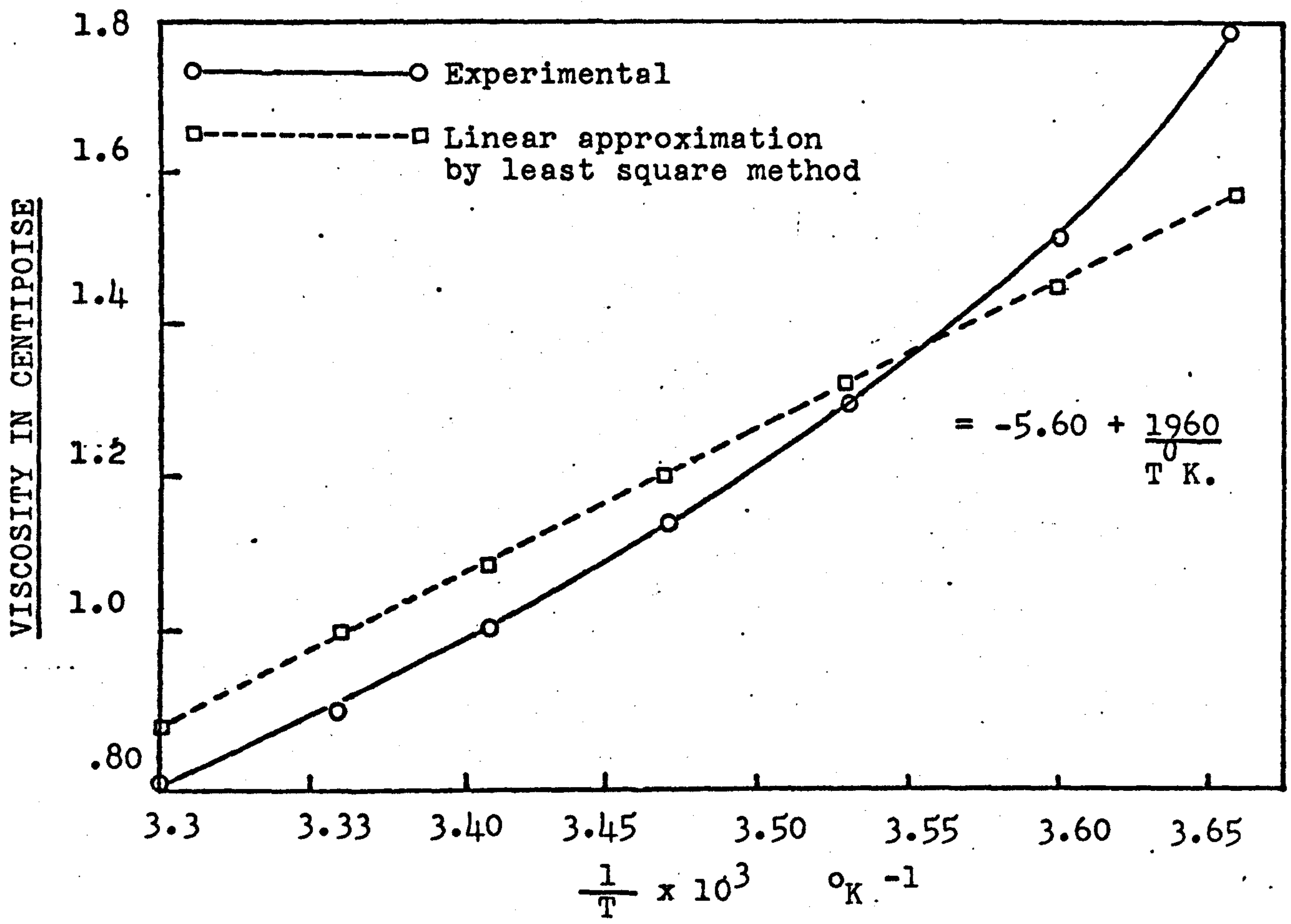
In most of the unit operations we are dealing with, mass transfer by diffusion is significant. Hence the temperature dependence of diffusivity needs to be determined. Estimates of the diffusivity cannot be made accurately owing to the inadequate development of liquid structure theory. For dilute solutions of non-electrolytes, the semi-empirical correlation of Wilke and Change (1955) is widely used.

$$D = 7.4 \times 10^{-8} \frac{(XM)^{0.5}}{V^{0.6}} \frac{T}{\mu} \qquad (2)$$

where D = diffusivity of solute in solvent - cm^2/sec

FIGURE 2

VISCOSITY OF WATER AS A FUNCTION OF INVERSE TEMPERATURE



M = molecular weight of solvent

X = association factor for solvent = 2.6 for water

V = solute molal volume at normal boiling point - cm^3/gm mole

T = absolute temperature - ^{o}K

μ = absolute viscosity - centipoise

Since viscosity was shown earlier to have an inverse relationship, diffusivity is expected to vary as the square of the temperature. For a temperature increase from 0^{o} to $30^{o}C$, the change in diffusivity will be no more than 23%.

d) Miscellaneous

Temperature affects the solubility of metallic coagulants. Concentrated feed stock would have to be kept heated to prevent precipitation. Alum has a solubility of 28.8% by weight at $30^{o}C$ and decreases to 23.8% at $0^{o}C$ (Krenaun, 1908). Ferric chloride exhibits similar behaviour (Roozeboon, 1892). Lime, however, is more soluble at lower temperatures (Bassett, 1934).

Flocculant effectiveness generally declines with decreasing temperatures (Hoerner, 1973).

2.1.2 FLOCCULATION

Intraparticle contact, the process of collision and aggregation is an important step towards obtaining a clarified effluent. A poorly flocculated sewage usually results in the loss of many small flocs over the effluent weir.

Intraparticle contact occurs principally by several means. First, by Brownian motion and second, by bulk fluid motion. The first is termed perikinetic flocculation and occurs due to the random movement of molecules caused by thermal energy. The rate of perikinetic flocculation is described by the following equation (Swift and Friedlander, 1964).

$$J_{pk} = \frac{dN^o}{dt} = -\frac{4\eta\bar{k}T(N^0)^2}{3\mu} \qquad (3)$$

where J_{pk} = rate of perikinetic flocculation
N^o = total concentration of particles in suspension at time t
η = collision efficiency factor
$\bar{k}$ = Boltzman's constant

Intraparticle contact through fluid motion is known as orthokinetic floccalution; its rate is given by the following equation derived by Overbeek (1952) as quoted by O'Melia (1972).

$$J_{ok} = \frac{dN^o}{dt} = -\frac{2}{3}\mu G d^3 (N^o)^2 \qquad (4)$$

where J_{ok} = rate of orthokinetic flocculation
d = diameter of colloidal particles
G = velocity gradient

The velocity gradient is dependent upon the power which is dissipated within the water and is defined as

$$G = \left(\frac{P}{V\mu}\right)^{\frac{1}{2}} \qquad (5)$$

where P = power input to fluid
V = volume of vessel

The relative significance of the two processes is very much dependent on particle size. For colloidal particles which are 0.1 micron in diameter, a velocity gradient of 1000 sec^{-1} is required for fluid motion to be as significant as Brownian diffusion in producing particle contact. Taking into account the viscosity, the overall temperature dependence of the rate of perikinetic flocculation will approach second order, whereas the rate of orthokinetic flocculation is less seriously affected. J_{ok} is almost proportional to the inverse square root of the temperature.

Since orthokinetic flocculation most probably prevails in sewage treatment plants owing to the relatively large size suspended particles and large scale fluid motion, the kinetics of the coagulation-flocculation step are a weak function of temperature and, therefore, our study was concentrated on the settlability of the flocs.

2.1.3 SEDIMENTATION

The law for frictional drag, which determines the settling velocity of a particle was first proposed by Newton and is usually expressed as

$$f_D = C_D A_p \frac{\zeta V_t^2}{2} \qquad (6)$$

where f_D = drag force

C_D = dimensionless drag coefficient

A_P = projected area of the body, in the direction of motion

V_t = relative velocity between falling particles and fluid

The general equation for the settling velocity of spheres of diameter d_p in terms of the drag coefficient can be obtained by equating the force due to gravity to the drag at steady state or terminal conditions as shown below.

$$V_t = \left(\frac{4}{3}\,\frac{g}{C_D}\,\frac{(\zeta_1-\zeta)}{\zeta}\,d_p\right)^{0.5} \qquad (7)$$

where g = gravitational constant
ζ_1 = mass density of sphere
d_p = particle diameter

The settling velocity thus depends on the drag coefficient which in turn has been correlated to the Reynolds number. A general equation for the settling velocity can be written as follows.

$$V_t = \left[\frac{4g\,d_p^{\,1+n}(\zeta_1-\zeta)}{3b'\,\mu^n\,\zeta^{1-n}}\right]^{1/(2-n)} \qquad (8)$$

where b', n are constants whose values are defined as the following:

Range		b'	n
Stokes Law	$N_{Re} < 2$	24	1.0
Intermediate	$2 < N_{Re} < 50$	18.5	0.6
Newton's Law	$500 < N_{Re} < 200{,}000$	0.44	0.0

For the laminar range a negative first order relationship between settling velocity and viscosity is seen. In the intermediate range, the order of viscosity dependence is -0.42, and finally for the Newton's Law region the terminal velocity is independent of viscosity.

The effect of low temperature on settling rates has been documented by various researchers. Howland (1953) stated that by raising the temperature from 70° to 80°F, removal could be increased by 13%. Thomas (1950) on the other hand noticed no pronounced deleterious effects of cold on process efficiency. He suggested that slower settling rates were offset by somewhat larger particles occurring at low temperatures.

Finally, thermal stratification can also occur due to differences in fluid temperatures causing density currents which hinder settling and create short circuiting.

2.1.4 POROUS MEDIA FILTRATION

In water treatment, sand filtration is used extensively for removal of turbidity and other colloidal particles. In wastewater treatment, sand filtration can be utilized to remove impurities which might otherwise clog up the activated carbon column. The head loss through a sand filter as given by the Carman-Kozeny equation is

$$\frac{h_f}{L} = \frac{72\,\mu\,V_s}{\zeta\,g\,\varepsilon^3}\,\frac{(1-\varepsilon)^2}{\psi_s^2\,d_p^2} \qquad (9)$$

where h_f = total head loss

L = length of bed

V_s = superficial fluid velocity

ε = bed porosity

ψ_s = particle sphericity

As can be seen from the equation, the head loss is greater at lower temperatures, because of higher fluid viscosity.

2.1.5 ADSORPTION

Adsorption involves the interphase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces.

In the system of our concern, dissolved organics are adsorbed on to the large surface area which exists inside the carbon particles. Most of this surface area is available in the narrow micropores of size 20 Å or less (Rankin, 1973) which are burnt into the particle during activation. Adsorption from solution on to a solid primarily results from two forces which are characteristic of a solute-solvent-solid system. First, the lyophobic nature of the solute provides a driving force for adsorption, second, the high affinity of the solute for the solid surface is another force which can cause adsorption. This latter force can be differentiated into three types; ionic attraction, Van der Waals attraction and chemical interaction.

Adsorption of the first type is basically ion exchange, where ions of one substance concentrate at a surface as a result of electrical attraction to charged sites at the surface. Van der Waals forces generally gives rise to "physical"adsorption, characterized by low heats of adsorption (2-4 Kcal/mole). Due to this weak bonding the molecule is free to move about and hence the adsorption reaction is reversible. Chemisorption involves heats of adsorption comparable to chemical reactions of the order of 50-100 Kcal/mole. The reaction is regarded as irreversible as the solute is bonded strongly.

Most adsorption phenomena are a combination of the three forms, although one of the three is usually dominant.

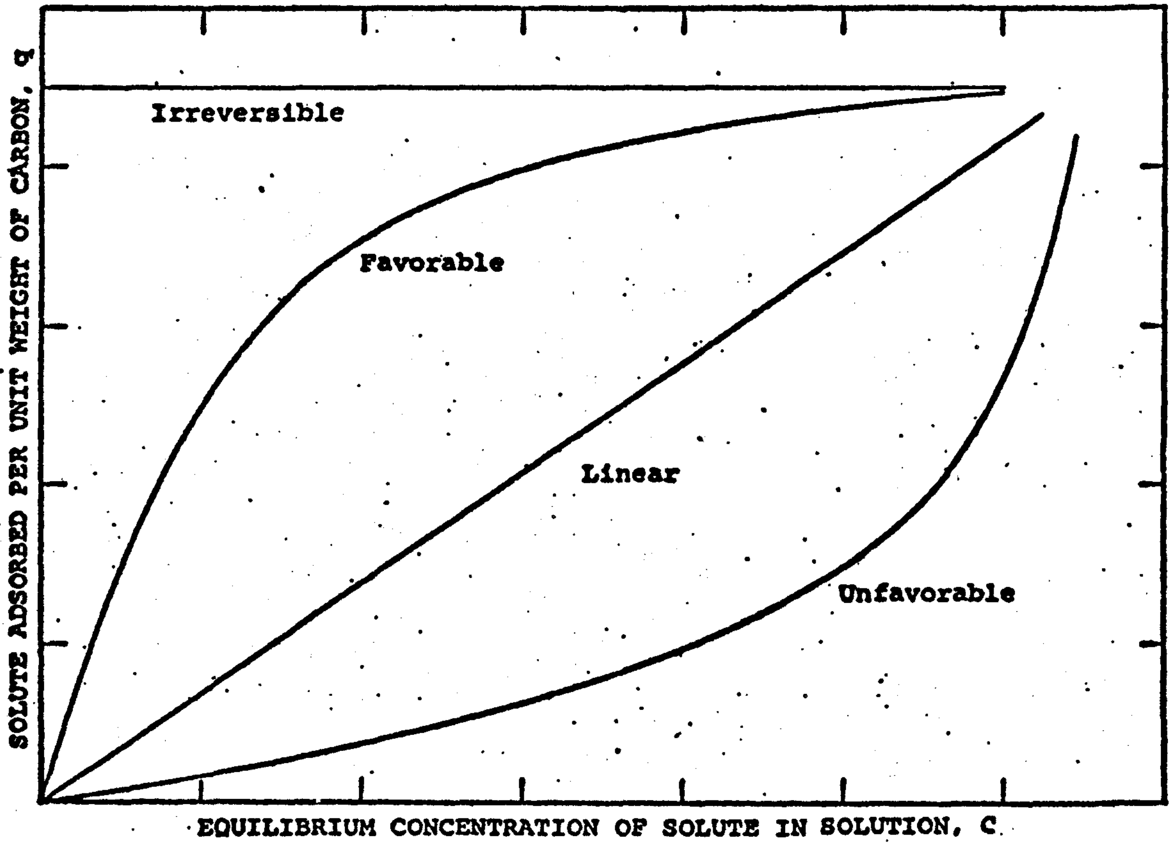
a) Equilibria

In the solid-liquid system, solute is concentrated at the surface of the solid until such time that there is a dynamic equilibrium between the solute concentration at the surface and that remaining in solution. The distribution ratio which relates the amount of solute adsorbed, q, to the liquid phase concentration, c, describes the adsorption equilibria, and is also referred to as an isotherm.

The shape of the equilibrium plot is of great significance in fixed bed processes, and can be classified into four categories as shown in Figure 3. In the irreversible case, the solid phase concentration remains constant. Linear isotherms assume a constant relationship with fluid phase concentration. In most situations, however, the solute either favors the liquid or the solid phase as the concentration increases; the favorable and unfavorable equilibria are two such examples.

FIGURE 3

BASIC TYPES OF POSSIBLE ADSORPTION ISOTHERMS



b) Theoretical Equilibria Relationships

Adsorption theory of liquids being not fully developed, is frequently based on empirical relationships. The Freundlich isotherm represents an early empirical, qualitative attempt to fit adsorption data to the form

$$q = KC^{1/n} \qquad (10)$$

where q = average solid concentration
C = fluid concentration
K,n = empirical constants

K is an approximate indicator of sorption capacity and can be shown to vary as follows:

$$K \propto RTn^{b} \; e^{\Delta H/RT} \qquad (11)$$

Although the Freundlich equation arose empirically, it can be derived from Langmuir's equation by the assumption of a logarithmic distribution of heats of adsorption with surface coverage (Adamson, 1967). The Freundlich isotherm is commonly used to represent multi-component systems such as wastewater.

Another very common correlation is Langmuir's isotherm. The important assumptions in its derivation are:

i) surface homogeneity
ii) no interactions between adsorbed molecules
iii) monomolecular coverage

Taking a kinetic approach, the forward and reverse reactions are equated and the equilibrium loading obtained.

$$q = \frac{Q^{o}bC}{1+bC} \qquad (12)$$

where Q^{o} = monolayer adsorption capacity

b = velocity constant

For the estimation of the two parameters, Q^{o} and b, from experimental data, the Langmuir isotherm is frequently linearized, using forms such as:

$$\frac{C}{Q} = \frac{1}{bQ^{o}} + \frac{C}{Q^{o}} \qquad (13)$$

and

$$\frac{1}{Q} = \frac{1}{Q^{o}} + \left(\frac{1}{bQ^{o}}\right)\left(\frac{1}{C}\right) \qquad (14)$$

b in turn can be shown to be equal to (Adamson, 1967)

$$b = \frac{K_0}{f_1} \cdot \left(\frac{2\pi MRT}{N}\right)^{0.5} e^{-v/RT} \qquad (15)$$

where K_o = frequency factor

f_1 = steric factor

M = molecular weight of adsorbate

N = number of molecules striking surface per unit time and area

v = activation energy of the solid-solute complex

An approximately Arrhenius type relationship over a narrow temperature range can be seen from above equation. The temperature dependence of adsorption equilibria in solid-gas systems have been investigated extensively, as opposed to the solid-liquid systems. The solubility of the solute is an additional factor complicating analysis in solid-liquid systems. Although adsorption is an exothermic process, it does not necessarily follow that an increase in temperature causes a decrease in adsorption. Bartell et al (1951) working with n-butyl alcohol, a substance having a negative solubility temperature coefficient showed that at lower concentrations adsorption decreases with increasing temperature and vice versa.

Weber and Morris (1964) studied the effect of temperature on adsorption of alkyl benzene sulfonate and calculated heats of adsorption for this system. These were of the order of -1.4 Kcal/mole indicating a weak temperature effect.

Snoeyink and Weber (1969) described equilibrium studies of phenol sorption on carbon at 11° and 37°C. Slightly greater adsorption at 37°C was noted. Similar trends were observed for p-nitrophenol adsorption. The authors concluded that temperature affects on equilibrium capacity were difficult to interpret as complex interactions between sorbate, solvent and sorbent are involved.

Jere (1973) conducted batch equilibria studies using dextrose and urea as adsorbates, and determined the effect of carbon oxidation on adsorption capacities. For the range 0° - 49°C, Jere noted that for both dextrose and urea, the amounts adsorbed at equilibrium decreased with increase in temperature. Since dextrose and urea are both representative of substances commonly found in domestic wastewaters, the results hint at the possible behaviour of sewage. The concentrations used were, however, much higher than those encountered in domestic wastewaters.

2.2 THEORETICAL MODELLING OF A CONTINUOUS FLOW ACTIVATED CARBON- SINGLE SOLUTE SYSTEM

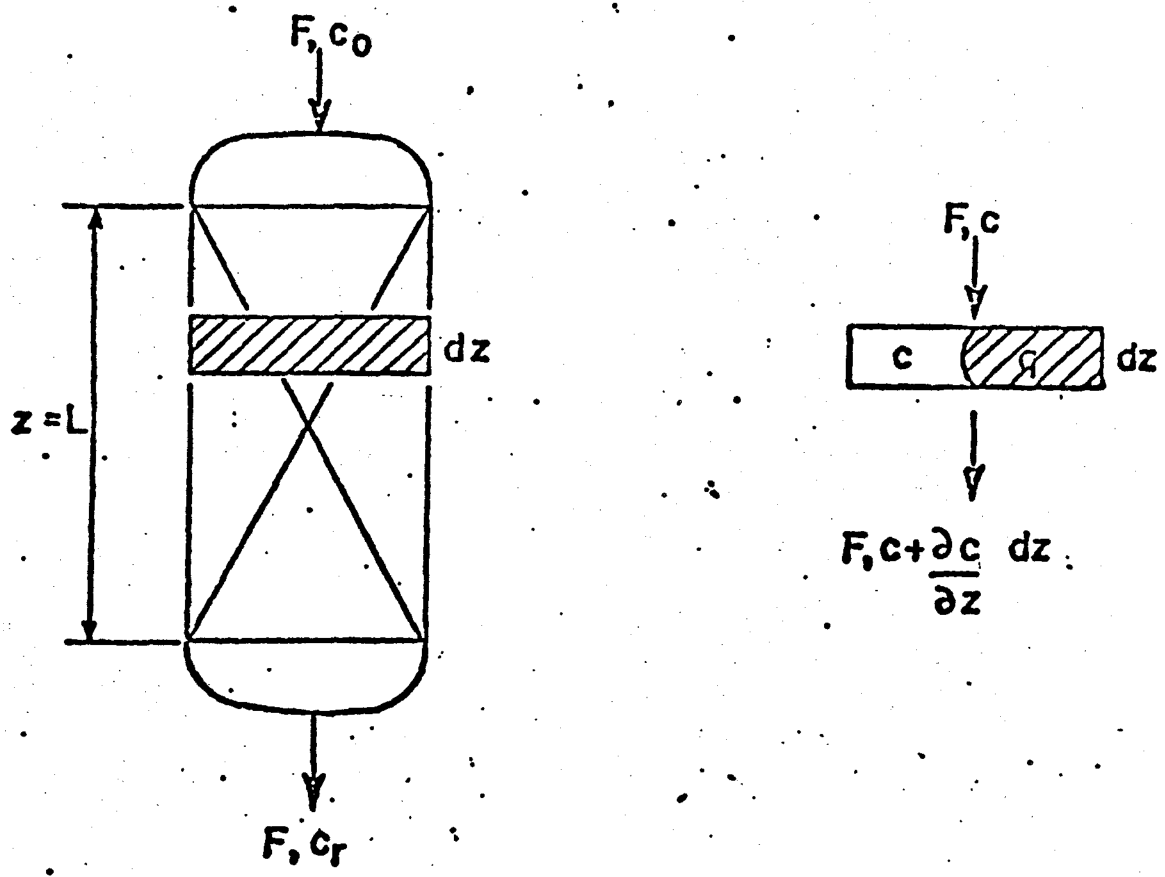
The theory describing the adsorption of a single component in a continuous flow system will be outlined, and the method used to predict column effluent concentrations from batch data is put forth in this section.

2.2.1 FIXED BED PROCESS

The system of interest is shown in Figure 4 where a single component solution is contacted with activated carbon particles in a packed bed. As the solution of a certain solute concentration enters the column, the solute will be removed from the liquid phase and adsorbed on to the solid phase. Initially this process will be accomplished by the first layer of particles. If the solute in the solution is followed down the length of the stationary bed, further and further layers down the column will continuously remove the remaining solute in solution. The effluent concentration theoretically will depend, therefore, on the non-adsorbable fraction introduced in the feed as well as on the length of the column.

FIGURE 4

COLUMN DYNAMICS AND THE DIFFERENTIAL SECTION BALANCE



The above discussion concerns itself with the solute concentration in the liquid phase. But, if the solute uptake is monitored at a fixed point along the column a different view is obtained. Initially the solid phase concentration will be negligible, but as adsorption takes place, the particle will get more and more saturated until the feed concentration matches the effluent concentration. At this point equilibrium is obtained, the adsorptive capacity of the bed is exhausted and the removal process stops until carbon is regenerated.

A typical plot of the fluid concentration against time, called the breakthrough curve, or the concentration history profile is illustrated in Figure 5. The sharpness of the profile is a measure of the equilibrium and kinetics of the system.

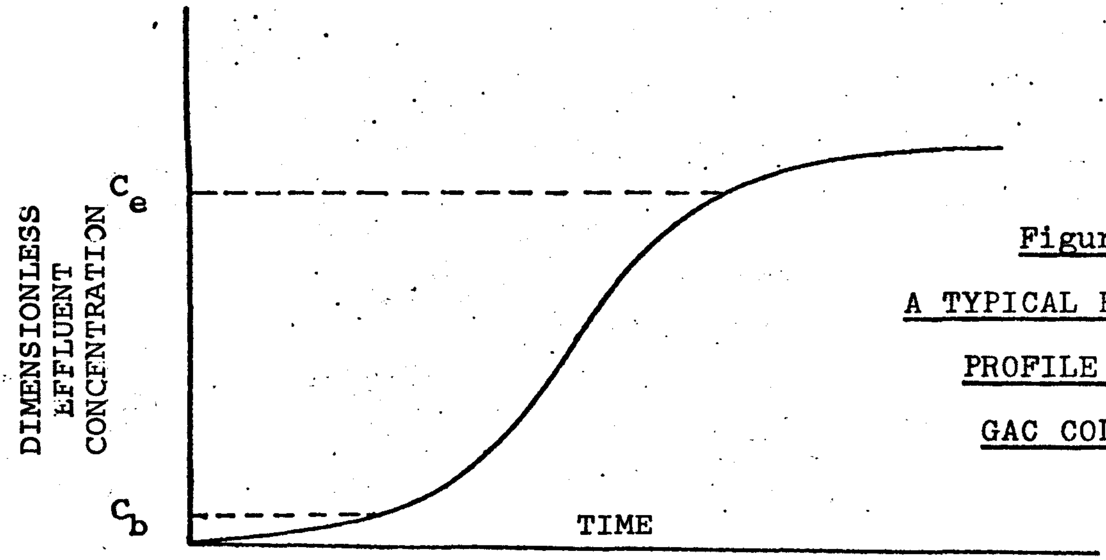


Figure 5

A TYPICAL EFFLUENT PROFILE FROM GAC COLUMN

Amundson (1952) showed that uniform distribution across the radial direction is a reasonable assumption. Plug flow or no axial dispersion is also assumed, even though some short circuiting due to irregularity in the shape of particles is expected. With these assumptions, a basic mass conservation equation, for a thin section of the column, Δz , can be written.

$$\begin{array}{c} \text{mass of solute} \\ \text{in incoming} \\ \text{liquid} \end{array} - \begin{array}{c} \text{mass of solute} \\ \text{in outgoing} \\ \text{liquid} \end{array} - \begin{array}{c} \text{amount consumed} \\ \text{by chemical} \\ \text{reaction} \end{array} = \begin{array}{c} \text{amount} \\ \text{adsorbed} \\ \text{in solid} \\ \text{phase} \end{array} + \begin{array}{c} \text{accumu-} \\ \text{lation} \\ \text{in} \\ \text{liquid} \\ \text{phase} \end{array}$$

$$FC - F\left(C + \frac{\partial C}{\partial z}\,\Delta z\right) - \varepsilon RA\,\Delta z = \zeta_b\,\frac{\partial q}{\partial t}\,A\Delta z + \varepsilon\,\frac{\partial C}{\partial t}\,A\Delta z \qquad (16)$$

where F = volumetric flow rate

C = solute concentration in liquid phase

x = length along the column

R = reaction rate per unit liquid volume

ζ_b = density of carbon particles based on bed volume

A = cross-sectional area of bed

Rearranging, one obtains

$$\frac{F}{A}\left(\frac{\partial C}{\partial z}\right) + \varepsilon\left(\frac{\partial C}{\partial t}\right) + \zeta_b\left(\frac{\partial q}{\partial t}\right) + \varepsilon R = 0 \qquad (17)$$

The third term in Equation 17 represents an averaged solid accumulation term over the entire particle. In order to integrate Equation 17 and derive the breakthrough curve, the adsorption uptake rate, $(\partial q/\partial t)$, must be known. The simpler the relationship between q and C, the easier the mathematical solution. In order to proceed further, it is very important to have a grasp of the mechanisms governing uptake rates, so that, with appropriate simplifications, Equation 17 can be solved.

2.2.2 ADSORPTION KINETICS

In the absence of any other steps, the uptake rate should be proportional to bulk fluid phase concentration and the number of vacant sites available for adsorption. In a majority of practical cases, however, the kinetics are governed by the mass transfer steps, which can be classified into four types.

i) external film diffusion
ii) fluid phase internal pore diffusion
iii) surface diffusion
iv) adsorption

a) Film Resistance

In this case, the resistance to mass transfer is offered by a thin imaginary film between the bulk fluid phase and the external surface of the adsorbent particle. Solute has to diffuse through this boundary to be adsorbed on the surface. The driving force will be the concentration gradient across this film. The concentration at the external surface of the particle can be assumed to be in equilibrium with the solute concentration in the solid phase. Thus the rate of adsorption is given by

$$\frac{\partial q}{\partial t} = K_f a \left(\frac{\varepsilon}{\zeta_b}\right) (C - C_s) \qquad (18)$$

where K_f = external film mass transfer coefficient

a = mass transfer area

C_s = fluid concentration at surface of particle

In the mass transfer systems normally encountered in chemical engineering, K_f is correlated with a mass transfer factor, J_D, which is based on analogy to heat transfer.

The correlation of Wilke and Hougen (1945) is suggested by Vermeulen (1958) for estimating K_f, i.e.,

$$K_f = 1.82\ v \left(\frac{d_p v \varepsilon}{\nu} \right)^{-0.51} \left(\frac{\mu}{\zeta D_f} \right)^{-0.67} \qquad (19)$$

where v = velocity

ν = kinematic viscosity

D_f = bulk fluid diffusivity

The correlation chosen, however, is developed by Wilson and Geankoplis (1966) and is of the form

$$K_f = 1.09\ (N_{Re})^{-.67}\ (N_{sc})^{-.67}\ v/\varepsilon \qquad (20)$$

where

$$N_{Re} = \frac{d_p v}{\nu(1-\varepsilon)} \quad \text{modified Reynolds number} \qquad (21)$$

$$N_{Sc} = \frac{\nu}{D_f} \qquad (22)$$

b) Internal Diffusion

This mechanism operates in the case of porous adsorbents, determining the mass transfer rate from the exterior surface of the adsorbent to the interior adsorption sites. Two types of internal diffusion mechanisms can operate, with one being primary.

i) Fluid Phase Pore Diffusion:

The solute remains in the liquid phase until adsorbed inside the particle. The driving force for the solute is the concentration gradient in the voids of the particle. Assuming a spherical particle with movement of solute directed radially and using Fick's second law, as outlined by Kasten and Amundson (1952) one obtains:

$$\zeta_p \frac{\partial q_i}{\partial t} + \alpha \frac{\partial c_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{pore}\, r^2 \frac{\partial c_i}{\partial r} \right) \qquad (23)$$

where q_i = point concentration of solute in solid phase

c_i = point concentration of solute in liquid phase

D_{pore} = fluid phase pore diffusivity

α = intraparticle porosity

r = radial direction in the particle

The first term accounts for accumulation in the solid phase, the second for accumulation in the fluid phase and the third represents the net outflow through a differential radial volume.

Wheeler (1955) suggested the following approximation for calculating fluid phase pore diffusivity:

$$D_{pore} = \frac{1}{2} D_f \alpha \qquad (24)$$

ii) Surface Diffusion:

In this case, the solute travels along the walls of the voids to the interior of the particle. Assuming the solid to be homogenous and the diffusional path to be radially directed, an expression for the mass transfer rate with surface diffusion controlling can be written in a manner similar to fluid phase pore diffusion.

$$\frac{\partial q_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s \, r^2 \, \frac{\partial q_i}{\partial r} \right) \qquad (25)$$

where D_s = solid phase pore diffusion coefficient

If the diffusivity, D_s, is assumed to be constant, i.e., independent of time and concentration, then

$$\frac{\partial q_i}{\partial t} = D_s \left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right) \qquad (26)$$

The average concentration, q, for the entire particle is given by

$$q = \frac{3}{R_p^3} \int_0^{R_p} q_i \, r^2 \, dr \qquad (27)$$

where R_p = particle radius

In typical problems, the estimation of D_s is made by trial and error. The uptake rate predicted by a chosen D_s, is matched to the experimentally derived uptake rate as a test for the correct value of D_s. Finite difference methods are commonly used to estimate D_s from batch adsorption kinetics (Weber and Rumer, 1965).

The method chosen to evaluate D_s, is the technique proposed by Tien (1962) which not only involves little computer time, but, more significantly, is applicable to generalized equilibrium relationships. For a non-flow, finite bath, well agitated system equation 26, along with the following equations, are used to define the problem of diffusion into initially empty spherical particles.

$$C = C_0, \quad q = 0 \qquad \text{for } 0<r<a \text{ at } t = 0 \tag{28}$$

$$q = \alpha(C) \qquad \text{at } r = a,\ t>0 \tag{29}$$

$$V \frac{\partial C}{\partial t} = KD_s \frac{\partial q}{\partial r}\Big)_{r=a} \qquad t>0 \tag{30}$$

Solutions to the second order partial differential equation have been given by Carslaw and Jaeger (1948) and others for the case of α being a linear function of C. For a non-linear adsorption isotherm, however, an analytical solution is not obtainable.

Tien's method involves using batch kinetic and adsorption equilibria data to obtain q_s, the solid phase concentration at the particle surface. This is approximated by a polynomial expression of degree m,

$$q_s(t) = \sum_{i=0}^{m} P_i t^i \tag{31}$$

Knowing $q_s(t)$, $q_i(t)$ is obtained and integrated over the particle volume to get q as in Equation 27. The fractional approach to equilibrium is given by

$$\frac{q}{q_s} = 1-6\phi_1(t)\left(\frac{a^2}{Dt}\right)\left(-\left(\frac{1}{2}\right)\left(\frac{1}{3!}\right)\frac{1}{5} + A_2\frac{1}{12\pi^2}\right) + 6\phi_2(t)\left(\frac{a^2}{Dt}\right)^2\left(\left(\frac{1}{2}\right)\frac{1}{5!}\frac{1}{7} - A_2\left(\frac{1}{3!}\right)\frac{1}{5\pi^2} + \frac{A_4}{3\pi^4}\right) + \cdots\cdots\cdots\cdots +$$
$$(-1)^m\phi_m(t)\left(\frac{a^2}{Dt}\right)^m \sum_{i=0}^{m}\frac{(-1)^{m+i}A_{2i}}{(2(m-i)+3)(2\pi)^{2i}\,(2(m-i)+1)!} \tag{32}$$
$$-6\sum_{n=1}^{\infty}\left(P_0 - P_1(t)\left(\frac{a^2}{Dt}\right)\frac{1}{n^2\pi^2} + \cdots\cdots\cdots + (-1)^m m!\,P_m t^m\left(\frac{a^2}{Dt}\right)^m\left(\frac{1}{n^2\pi^2}\right)^m\right)\frac{e^{-(Dt/a^2)n^2\pi^2}}{n^2\pi^2}$$

where $\Phi_1(t) = \left(\sum_{i=1}^{m} iP_i t^i\right)/\left(\sum_{i=0}^{m} P_i t^i\right)$

$$\Phi_m(t) = m!P_m t^m \Big/ \left(\sum_{i=0}^{m} P_i t^i\right)$$

A series of theoretical q/q_s can be plotted with (a^2/Dt) as the parameter and compared with the experimentally derived curve. At the intersection points (refer to Figure 6) a unique value of D_s can be obtained as both $(\frac{a^2}{Dt})$ and t are known.

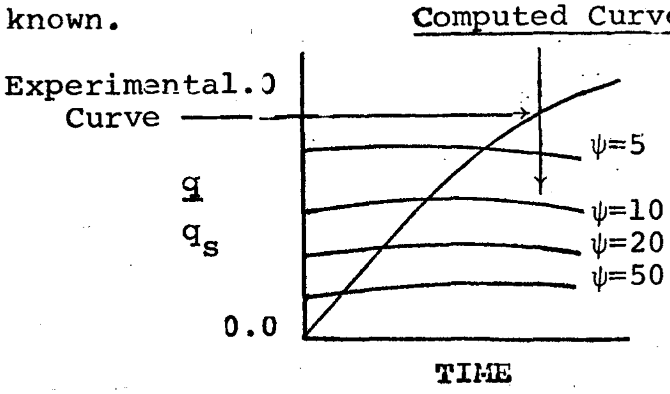


FIGURE 6
TIEN'S METHOD FOR CALCULATING SURFACE DIFFUSIVITY

For a third order polynomial fit to equation 31, Meier (1972) has derived an explicit solution for q/q_s, correcting some algebraic mistakes made by Tien.

$$\frac{q}{q_s} = (1 - \frac{\psi}{15 \sum_{i=0}^{3} P_i t^i} (3P_3 t^3 + 2P_2 t^2 + P_1 t) \tag{33}$$

$$+ \frac{\psi^2}{315 \sum_{i=0}^{3} P_i t^i} (12P_3 t^3 + 4P_2 t^2) - \frac{\psi^3}{1575 \sum_{i=0}^{3} P_i t^i} (6P_3 t^3)$$

$$-(6/(\sum_{i=0}^{3} P_i t^i)(\sum_{n=1}^{\infty} \frac{1}{n^2\pi^2} \exp(-n^2\pi^2/4)(\sum_{i=0}^{3} (-1)^i \; i! P_i t^i (\frac{\psi}{n^2\pi^2})^i)))$$

where $\psi = \frac{a^2}{Dt}$

c) Surface Reaction Kinetics

In the general case for reversible adsorption of a single solute

$$\frac{\partial q_i}{\partial t} = K_1 C_L C_S - K_2 q_i \tag{34}$$

where C_L = fluid concentration
C_S = vacant sites
K_1 = forward rate constant
K_2 = desorption rate constant

In this work, the adsorption process is assumed to be extremely rapid as compared to the diffusional resistances. The validity of this statement has been documented by the data of Vassiliov (1962) and others.

2.2.3 REVIEW OF ANALYTICAL SOLUTIONS TO FIXED-BED ADSORPTION EQUATIONS

The solution to the general fixed bed problem has been under intense investigation. For our present purposes, the reaction term R in equation 17 is set equal to zero. Chapter 5 includes a theory section which incorporates the effect of R in more detail.

The analytical solution depends strongly on two key aspects:

(i) The choice of the rate limiting step.
(ii) The nature of adsorption equilibria.

In earlier periods of investigation, many researchers restricted the solution by assuming only one resistance as being primary. Initially, this was due to lack of high speed computer facilities, which can today solve the more complex problems numerically. Thomas (1951), Rosen (1952) and Kasten et al (1952), for example, have presented solutions based on the assumption that intra-particle diffusion is the rate limiting step. Several investigators have attempted solutions by combining two resistances in series. Rosen (1954) obtained an exact solution in the form of an infinite integral suitable for numerical integration for the case of film diffusion in series with solid phase pore diffusion. Masamune and Smith (1965) presented and summarized solutions for a general case of film resistance, intraparticle diffusion and surface kinetics in an intregral form.

Unfortunately, however, all these solutions are only valid for linear isotherms, which are rarely encountered in wastewater systems.

The reaction kinetics model of Thomas (1948) uses a different approach from the above mentioned investigations and, therefore, allows the use of a generalized isotherm of the Langmuir type. This method involves the representation of mass transfer resistances by pseudo-kinetic rates and the combination of these rates into a general rate coefficient. Hiester and Vermeulen (1952) carried forward the Thomas solution for packed bed adsorbers. They also noted that

Thomas's method is the most general, as all other solutions can be referred back to Thomas's dimensionless relationships. A shortcoming in the Hiester and Vermeulen derivation has been the assumption of a linear driving force for solid phase pore diffusion of the type suggested by Gluckeauf and Coates (1947). Vermeulen (1953) later postulated a quadratic driving potential to account for the concentration gradient. Allen _et al_ (1967) chose an exponential concentration difference for ease in process design calculations.

Stuart (1967) considered the representation of solid phase pore diffusion by an equation of the following type

$$\frac{\partial q}{\partial t} = K\ f(q_s, q) \qquad (35)$$

as entirely wrong from a fundamental standpoint, since diffusional transfer should be predicated on diffusion equations, and not pseudo-kinetic rate approximations. Stuart and Camp (1967) presented a comparison of the diffusional and kinetic models for a linear isotherm and showed that the diffusional model is more accurate. Stuart (1967) advanced the work further by handling the case of general non-linear equilibria relations.

For reference purposes, the derivation of Thomas reaction-kinetics solution, as modified by Keinath and Weber (1968), is included in Appendix 5.

2.3 BIOLOGICAL ACTIVITY INSIDE ACTIVATED CARBON BEDS

In this third and final section of the literature review, an attempt will be made to explain the role of biological activity in activated carbon (AC) beds. The difficulties which have arisen and the experience which has been gained to date in the operation of AC systems for treatment of domestic wastewater are described. The possible mechanisms which are responsible for organic substrate removal are discussed. Denitrification inside AC beds, a recently observed phenomenon is also studied. Finally, the effect of low temperatures on biochemical reaction rates is elucidated.

2.3.1 LITERATURE REVIEW

In the early stages of application of AC to domestic wastewaters an associated phenomenon of biological growth was observed by many researchers. Controversy arose over whether biological activity was detrimental to effluent quality.

Bishop et al (1967), based on pilot plant runs, noted that output turbidity from carbon beds increased markedly, along with residual TOC in effluents. The explanation put forth was that the bed began to function as a partially anaerobic biological filter, producing particulate waste products which broke through the column. They concluded that biological growth would be harmful to final effluent quality. Predisinfection was suggested to curtail biological activity in AC columns.

Parkhurst _et al_ (1967) describing the performance of Pomona Water Reclamation Plant attributed higher overall COD removals to biological decomposition as opposed to pure adsorption. Proof of biological enhancement was found in the drop of nitrate levels, inability to exhaust carbon's capacity and reductions in dissolved oxyden. English _et al_ (1971) reporting on the same plant noted that the carbon's capacity dropped after each regeneration cycle, indicating the buildup of non-degradable organics inside the pores of the carbon.

The role of biological activity inside carbon beds was studied by Weber _et al_ (1970) in the operation of a pilot plant at Ewing-Lawrence,

Parallel studies were conducted using expanded and packed bed reactors to determine performance. Over a four month period no practical difference was discernable, with close to 60% removals by weight obtained in each of the two lead columns. Weber _et al_ (1970) noted that such high organic loadings could be only due to biological activity.

Expanded bed adsorbers possessed greater operational advantages, as none of the four columns required cleaning or maintenance over the entire four month period. Conversely, even with a highly clarified effluent, head loss in packed bed adsorbers increased steadily, requiring increased pumping pressures and eventual backwashing. The lead column was more frequently backwashed than the preceeding columns due to higher buildup of solids. Periodic anaerobic biological activity in the carbon columns was encountered, as evidenced by occurrence of H_2S odor in the effluent. Addition of hypochlorite was moderately effective in reducing H_2S odor. Aeration of primary effluent led to formation of bigger biological flocs and quicker plugging and fouling in packed beds.

Rodman (1971) reported that spent GAC could be regenerated biologically by an upflow aerated column. A pilot plant study treating textile wastes showed the efficacy of this concept.

Bishop et al (1972) questioned the desirability of biological activity in adsorption systems. The development of anaerobic conditions had to be balanced with the advantage of removing hydrophilic and poorly adsorbed organics. Growth of biological slimes in sand filter, and fouling of ion exchangers in PCT plant were described. Overall soluble organic removal decreased with time and was attributed to biological activity.

The merits of biological growth are still being debated. The controversy may only be resolved when a strong theoretical foundation is postulated, which explains the inter-relationship between the carbon and the micro-organism.

2.3.2 SUBSTRATE REMOVAL MECHANISMS

Interest in the effect of solid surfaces on microbial growth has existed for over decades now. More recently investigations have been carried out with surfaces such as activated carbon particles in wastewaters.

Kalinske (1972) suggested that GAC would be excellent as a growth site due to its high surface to volume ratio. Furthermore selective adsorption of oxygen from aqueous solution was expected. Thus he postulated that since the three ingredients - bacteria, oxygen and substrate - are brought together in such close proximity, the removal rates are bound to be enhanced. This follows from the first order concentration dependence of removal rates in the growth limiting region. Kalinske conducted experiments in order to establish that GAC acts solely as a surface, and that physical adsorption is insignificant. His claim that biological enhancement was achieved is difficult to interpret in view of the fact that he chose glucose, a highly degradable but poorly adsorbed compound as his substrate.

Besik (1973) operated an adsorption bio-oxidation reactor on raw sewage. The author also expected increased reaction rates due to increased concentrations of organics, microbes and oxygen. Based on BOD loading data, Besik claimed that the MLSS-GAC upflow bed performed better than conventional activated sludge systems. There appear to be, however, many unexamined questions in connection with this claim.

Scaramelli and Digiano (1973) used bench scale continuous flow biological reactors to study the effect of PAC dosage on organic removals. Two possible mechanisms were suggested to be verified by experimental investigations. The first one was essentially Kalinske's mechanism, which if valid, would result in both increased substrate removals and microbial populations.

On the other hand, if physical adsorption played a greater role, then substrate removal would be enhanced, but not microbial growth. Results of two parallel reactors showed that PAC caused no significant increase in oxygen uptake rates. Microbial growth was essentially unchanged leading to the conclusion that substrate removal was primarily due to adsorption. The authors cautioned, however, that only two parameters were used as indicators of biological activity, and suggested further respirometric studies.

Perrotti and Rodman (1973) used aerobic batch reactors containing GAC or sand in the presence of activated sludge. A synthetic feed made up of glucose and phenol was used. The authors noted a synergistic effect of AC on the biological process. Perrotti and Rodman advanced the hypothesis that since bacteria cannot penetrate the pores of the carbon, the adsorbed substrate could be degraded by reaction with extracellular enzymes which diffuse into the pores. The rate of regeneration would, therefore, be dependent on the concentration of these enzymes. The role of exo-enzymatic reactions is speculative, as the mechanism which governs enzymatic production is ill understood.

Weber _et_ _al_ (1972) theorized that bacteria not only degrade the organic materials on the surface, but also the adsorbed material on the pores. Studies were undertaken to evaluate the effect of aerobic and anaerobic conditions on GAC column performance. Overall performance in terms of TOC removal was not greatly different, although the aerobic columns always performed better. Comparisons between the aerobic and a non-porous anthracite carbon system, showed the latter to perform less well. Weber concluded that in situ regeneration enabled the surface of the carbon particle to continue to adsorb, thus extending the life of the bed. It was proposed that surface regeneration activity appeared to be anaerobic for the following reasons:

(i) No significant difference in capacity observed for aerobic system as opposed to anaerobic system.

(ii) No sludge accummulation seen.

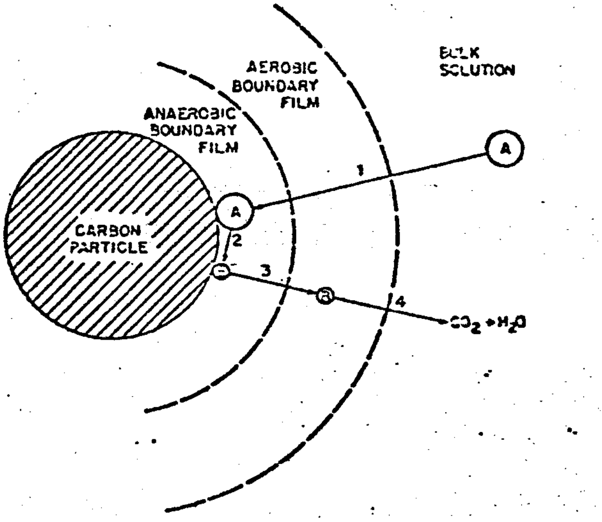
(iii) Sludge scoured had appearance of an anaerobic residue.

(iv) Oxygen utilization much less than theoretically required for aerobic mode of regeneration.

A schematic interpretation of in situ biological regeneration is presented below in Figure 7.

FIGURE 7

A POSSIBLE MECHANISM FOR BIOLOGICAL REGENERATION



EVENT SEQUENCE:

1. DIFFUSION OF LARGE ADSORBING ORGANIC MOLECULE Ⓐ TO SURFACE OF CARBON.
2. ANAEROBIC DEGRADATION OF LARGE MOLECULE Ⓐ TO SMALL MOLECULE ⊖
3. DIFFUSION OF SMALL NON-ADSORBING ORGANIC MOLECULE ⊖ AWAY FROM SURFACE OF CARBON.
4. AEROBIC DEGRADATION OF SMALL MOLECULE ⊖ TO CO_2 AND H_2O

The interpretation is entirely speculative, as no alcohols or low molecular weight compounds were ever monitored.

Hals (1974) studied the inter-relationship of micro-organisms and PAC in batch systems. Oxygen uptake rates and TOC removals were monitored as a function of time for various substrates. The data showed that little, if any, bio-regeneration took place for domestic sewage, although some regeneration appeared to exist for phenol. The substrate concentration effect on solid surfaces, which is envisaged by other authors, was not manifested. Hals concluded that the experimental conditions of his batch reactor limited the findings of his study.

Currently, a clear picture of regeneration mechanism does not exist. The purpose of this thesis is not to develop an alternative mechanism, but to understand the effect of temperature on gross removals in both batch and continuous systems. The theory provided in this section will help to explain the observed effects in Chapter 5.

2.3.3 DENITRIFICATION IN INERT MEDIA COLUMNS

In the course of studies involving soluble organics removal by carbon adsorption, a reduction in nitrate and dissolved oxygen levels were noticed. Initially, this was categorized as a side effect, but recently serious investigation has started to evaluate nutrient removal possibilities.

Biological denitrification is technically an anaerobic process, wherein the nitrate ion acts as an hydrogen ion acceptor in the electron transport chain. In aerobic systems this role is normally played by oxygen. Some bacterial species can maintain their metabolism by using nitrate ion as an alternate source and in the process reducing nitrates to nitrogen gas, as represented by the following equation:

$$4NO_3^- + 4H^+ + 5CH_2O \leftarrow 5CO_2 + 2N_2 + 7H_2O \qquad (36)$$

Most of the denitrifying organisms are facultative anaerobes, commonly found in wastewater treatment plants. Some genera are <u>Pseudomonas</u>, <u>Achromobacter</u>, <u>Bacillus</u> and <u>Micrococcus</u>. The existence of these genera points to a significant denitrifying potential, but does not indicate that actual reduction in nitrates is taking place. The presence of a suitable environment is more crucial in denitrification.

English <u>et al</u> (1974) conducted preliminary evaluation on two parallel beds, one sand and the other GAC. Potassium nitrate was added to supplement the feed. Initially limited denitrification was observed in both columns, and was attributed to the lack of an organic carbon source. Methanol was added to provide a readily available energy source. Denitrification was enhanced following methanol addition, with nitrate removals of over 80% in both columns. Pilot scale studies also indicated equally effective denitrification on sand or carbon media, with greater than 90% nitrate reductions in less than 10 minutes of contact time. Biological growth associated with denitrification caused significantly higher head losses. Bacterial counts in the effluents revealed large numbers of Pseudomonas.

Weber et al (1970) noted that nitrate levels as high as 15 mg/l NO_3 as N in the primary effluents were reduced to an average of less than 0.5 mg/l NO_3 as N during the adsorption stage.

Plastic media anaerobic filters have been used as well for denitrification purposes. Tamblyn (1969) noted that the role of the media is to provide a solid support for bacterial growth. The solids are retained in the filter for a time longer than the hydraulic retention time.

Sutton (1973) studied the continuous biological denitrification of wastewater using stirred tank reactors as well as packed columns. Nitrogen removal performance of the column reactors was found to be a function of detention time and surface area available for biological growth. Unit removal rates were noted to be independent of influent nitrogen concentrations.

2.3.4 EFFECT OF TEMPERATURE ON BIOCHEMICAL RATES

Temperature is a major variable influencing reaction rates of substrate utilization in biological systems. The total temperature span within which the organisms can grow is a narrow one, extending from about -5° to $80^{\circ}C$ (Stanier et al, 1970). The lower temperature limit is set by the freezing point of aqueous solutions. Micro-organisms are classified into three types, based on their optimum growth temperature. Psychrophiles and mesophiles, which are of interest in this study, cover the average ranges $5^\circ - 15^\circ C$ and $20^\circ - 35^\circ C$ respectively. Temperature variations can act as a selection mechanism, bringing about changes in the microbial make-up of a system. This can result in different reaction rates as differing species have independent metabolic pathways.

For single substrate, pure culture, systems temperature affects the rate of substrate removal in two ways. Mass transfer by diffusion of substrate from bulk solution to the surface of the bacterial cell can affect reaction rates. The temperature dependence of diffusivity is expressed by a Wilke-Chang type of correlation as Equation 2.

The effect of temperature on the rate of substrate utilization is commonly assumed to be primarily a thermochemical phenomenon (Busch, 1971). This assumption is set on the premise that oxidation of organic material by micro-organisms involves a series of enzymatic reactions that follow the law of thermodynamics and rate theory (Gunsalus and Stanier, 1962). An empirical relationship commonly used for chemical reactions was suggested by Arrhenius in 1889 (Ingraham, 1962).

$$K = Ae^{-E_a/RT} \qquad (37)$$

where K = reaction velocity

A = constant

E_a = activation energy

R = universal gas constant

T = absolute temperature

Streeter and Phelps (1925) developed an empirical equation for the effect of temperature on biochemical oxygen demand (B.O.D.) of polluted water.

$$\frac{K_2}{K_1} = \theta^{(T_2 - T_1)} \qquad (38)$$

where θ = thermal coefficient

The thermal coefficient is analogous to the activation energy as a measurement of temperature sensitivity of the reaction rate.

Typical activation energies range from a few thousand calories per mole up to 40,000 calories per mole (Johnson et al, 1954). Arrhenius estimated E_a to be 9.08 Kcal/mole for sucrose hydrolysis by invertase. Stephenson (1949) calculated an E_a of 14.2 Kcal/mole for growth rates of E. Coli. Other researchers usually report biological rates having activation energy of the order of 8-15 Kcal/mole (David and Goos, 1972, Fair et al, 1968).

Dawson (1971) studied the variation of unit denitrification rates with temperature of a single culture batch system and reported E_a value of 16.8 Kcal/mole. Stensel (1971) using mixed culture of denitrifiers, calculated E_a value of 10 Kcal/mole.

Little data is obtainable on temperature effects in packed columns. Conditions are expected to differ as diffusion plays an important role in the overall reaction rate. Sutton (1973) employed packed columns for denitrification and estimated an activation energy of 11.1 Kcal/mole in 5° - 25°C range. For stirred tank reactors having sludge ages 3 - 6 days, the E_a value was 15 - 16 Kcal/mole.

Definite conclusions are hard to form on the reasons for the lower temperature dependence in columns than the stirred reactors, and needs further investigation. In general denitrification rates do not appear to have a higher temperature dependence than other biological systems.

CHAPTER 3

FEASIBILITY OF PHYSICO-CHEMICAL TREATMENT OF DOMESTIC WASTEWATER USING POWDERED ACTIVATED CARBON

3.1 INTRODUCTION

A preliminary batch scale feasibility study was conducted to assess the effect of temperature on the unit operations which comprise PCT. This step was considered to be necessary before pilot scale continuous flow systems could be studied, as the batch study phase pointed out the areas of greatest concern for further temperature effect studies.

At the present time, there are several package PCT plants being installed in the North. Almost all of these plants have opted for a columnar contacting scheme. In view of the fact that recent developments make powdered carbon regeneration technology, economically and technically feasible, Shell (1974) indicated that powdered carbon presented an attractive alternative to GAC with the following advantages:-

i) 8-12¢ per lb. for PAC as compared to 34-45¢ per lb. for GAC

ii) faster reaction rates.

iii) easier to transport in slurry form.

iv) lower pumping costs.

An added advantage of PAC is that it can be incorporated into existing treatment plants.

Based on theoretical considerations discussed in Chapter 2.1., attention was paid to the settling step and carbon adsorption step as these were felt to be the most sensitive to temperature. Ho et al (1972), as part of this project, had made initial studies using Aqua Nuchar A (PAC) to study batch adsorption at low temperatures. These studies are included in this Chapter as they provide data which are useful in the analysis of results.

Some of the objectives set out for the study are listed below:-

i) To evaluate feasibility of PCT of raw sewage with PAC at low temperatures.

ii) To obtain the magnitude of temperature effect on settling rates, and to compare it with theoretical predictions.

iii) To estimate effects on carbon adsorption kinetics of low temperatures.

3.2 EXPERIMENTAL

In order to investigate the effect of temperature, this study was divided into two parts. During the first part the temperature dependence on chemical floc settling or primary treatment was evaluated. The second part concentrated on the effect of temperature on carbon adsorption.

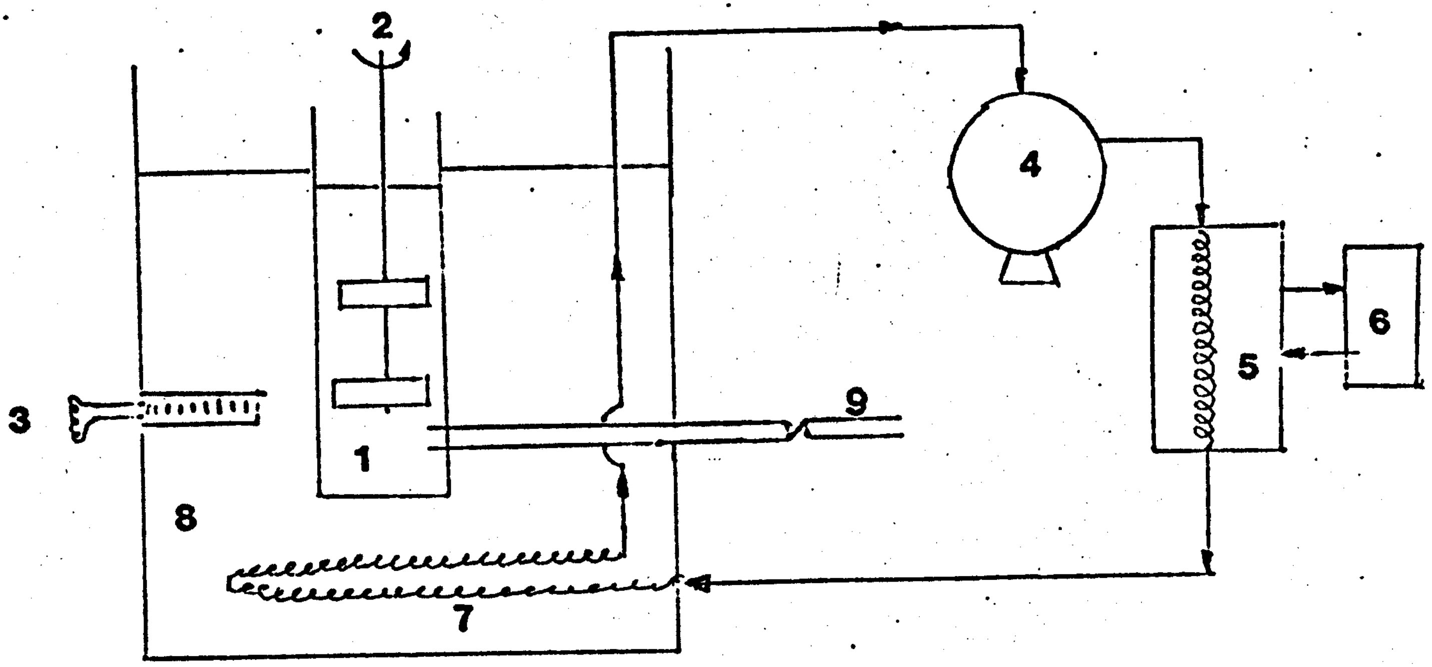
3.2.1 COAGULATION AND SETTLING STUDIES

Settling tests on raw sewage were conducted at three temperatures, 2°, 13°, $25^\circ C$, the range normally encountered in wastewater treatment. The apparatus used, was the modified jar tester of Bancsi and Benedek (1973a). Raw sewage was collected after the bar screen from the Dundas, Ontario, Water Pollution Control Centre. The sewage was largely domestic in nature, coming from a community with a population of 18,000.

3.4 litres of raw sewage was placed in the test jar, which was then immersed in a constant temperature bath. The details of the entire arrangement are included in Figure 8. After the sewage in the jar had reached the same temperature as that of the bath, 160 mg/l of alum (as $Al_2(SO_4)_3 \cdot 16H_2O$) was added and the liquid mixed for 5 minutes at a stirring rate of 90 RPM. Following the coagulation step, a polymer dosage of 0.8 mg/l Percol 730 (Allied Colloid Company) was introduced and the high stirring rate maintained for one minute to allow intraparticle contact to take place. These dosages are based on extensive studies carried out at McMaster University on Dundas domestic wastewater (Bancsi et al, 1973 b). Stirring speed was reduced to 30 RPM so as to avoid shearing the developing flocs. Fifteen minutes later the stirring was stopped completely and the flocs allowed to settle freely. Samples were taken during the settling period and analysed for their total phosphates content. This analysis was performed using a Technicon AutoAnalyzer Method No. 3-68W.

FIGURE 8

SCHEMATIC VIEW OF BATCH JAR TESTER WITH TEMPERATURE CONTROL



LEGEND

1) SEWAGE
2) FLOCCULATION PADDLE
3) THERMOREGULATOR
4) PUMP
5) REFRIGERANT BATH
6) COMPRESSOR
7) COPPER COIL
8) COOLING MEDIUM
9) SAMPLING OUTLET

3.2.2 CARBON TREATMENT STEP

The effluent after chemical treatment was contacted with 400 mg/l of HydroDarco H (Atlas Chemical) powdered activated carbon. HydroDarco H was chosen as it is relatively inexpensive and its relatively high density enables it to settle better.

The primary treated effluent was allowed an hour of contact with PAC, to allow equilibrium to be established. A polymer dosage of 1.6 mg/l Percol 728 (Allied Colloid) was next added to help separate the carbon particles from sewage. The polymer-carbon floc was allowed to settle quiescently following fifteen minutes of slow stirring. Samples were taken during settling and analyzed for their inorganic and total organic content using the Beckman 915 Total Organic Carbon Analyzer.

Two polymers Dow C-31 and Percol 728 were selected for comparative studies in their effectiveness to flocculate carbon particles. The former polymer was chosen as it was recommended by Garland and Beebe (1970) based on their evaluation of flocculants for Darco S-51. Percol 728 (P728) was chosen as an alternat higher molecular weight cationic polymer. Two jars containing 400 mg/l of HydroDarco H in distilled water were prepared and 2 mg/l each of the two selected polymers were added.

The particular dosage of 1.6 mg/l Percol 728 was obtained from an optimization study using a series of six jar test runs, with P728 concentrations ranging from 0 to 2 mg/l. Effectiveness in flocculation of carbon particles was measured after an hour of settling, by a Hellige Turbidimeter Model 8000.

3.2.3 ADSORPTION ISOTHERMS AND KINETICS.

The method used by Ho et al (1972) is described here. Known weights of adsorbent were added to 250 ml Erlenmeyer flasks containing 100 ml of wastewater. The carbon dosages ran from as low as 50 mg/l to as high as 4000 mg/l. Contact between the carbon particles and the solution was achieved by placing the samples in a constant temperature shaking bath (Research Specialities Company Model 2156) operated at a speed of 150 strokes per minute.

Raw sewage was pre-treated by first coagulation and flocculation, and then filtration through .1μ membrane filters. This last step was carried out to remove suspended matter interfering with adsorption and to delay the onset of biological growth. After equilibrium had been reached, the PAC was removed from solution by filtering through .1μ membrane filters, and the filtrate analyzed for TOC.

Batch kinetics were conducted by contacting adsorbate with PAC in a two litre jar agitated by a magnetic stirrer. 10 ml samples were withdrawn from the jar as a function of time and analyzed for TOC. Since with PAC, the reaction rate is initially very rapid, more samples were withdrawn at the beginning of the run, and the experiment terminated when there was no further drop in soluble organic concentration.

The procedures used in preparing carbon for the adsorption study, and the precautions used in analysis of filtrates are described in Appendix 1.

3.3 DISCUSSION OF RESULTS

3.3.1 Chemical Floc Settling

The results of the batch coagulation and settling study at the three temperatures are shown in Figure 9. The initial phosphate level was around 5.4 mg/l as P, which is a typical value for total phosphates in raw Dundas sewage. The total phosphate content in the settling floc was monitored as a function of time; according to independent studies (Bancsi, 1973 a) conducted on Dundas sewage at McMaster University, this curve is representative of suspended solids settling. The phosphate floc is enmeshed with the settling solids and thus can be used for determining particle concentrations remaining in suspension. Based on the residual phosphate concentration curves of Figure 9 all flocs settle well, although the low temperature flocs seems to take longer. Final residual phosphate concentration of 0.2 - 0.4 mg/l as P, can be obtained (about 94 - 96% P removal) over the temperature range of 2° - 25°C. In order to evaluate the temperature dependence of settling flocs, the phosphate values are replotted in terms of settled fraction of removable particles, as drawn in Figure 10. The detailed procedures are explained in Table 25 of Appendix 3. As can be seen from Figure 10 the initial settling rate is very high and gradually tapers down, with a distinct trend noticeable as the temperature is lowered.

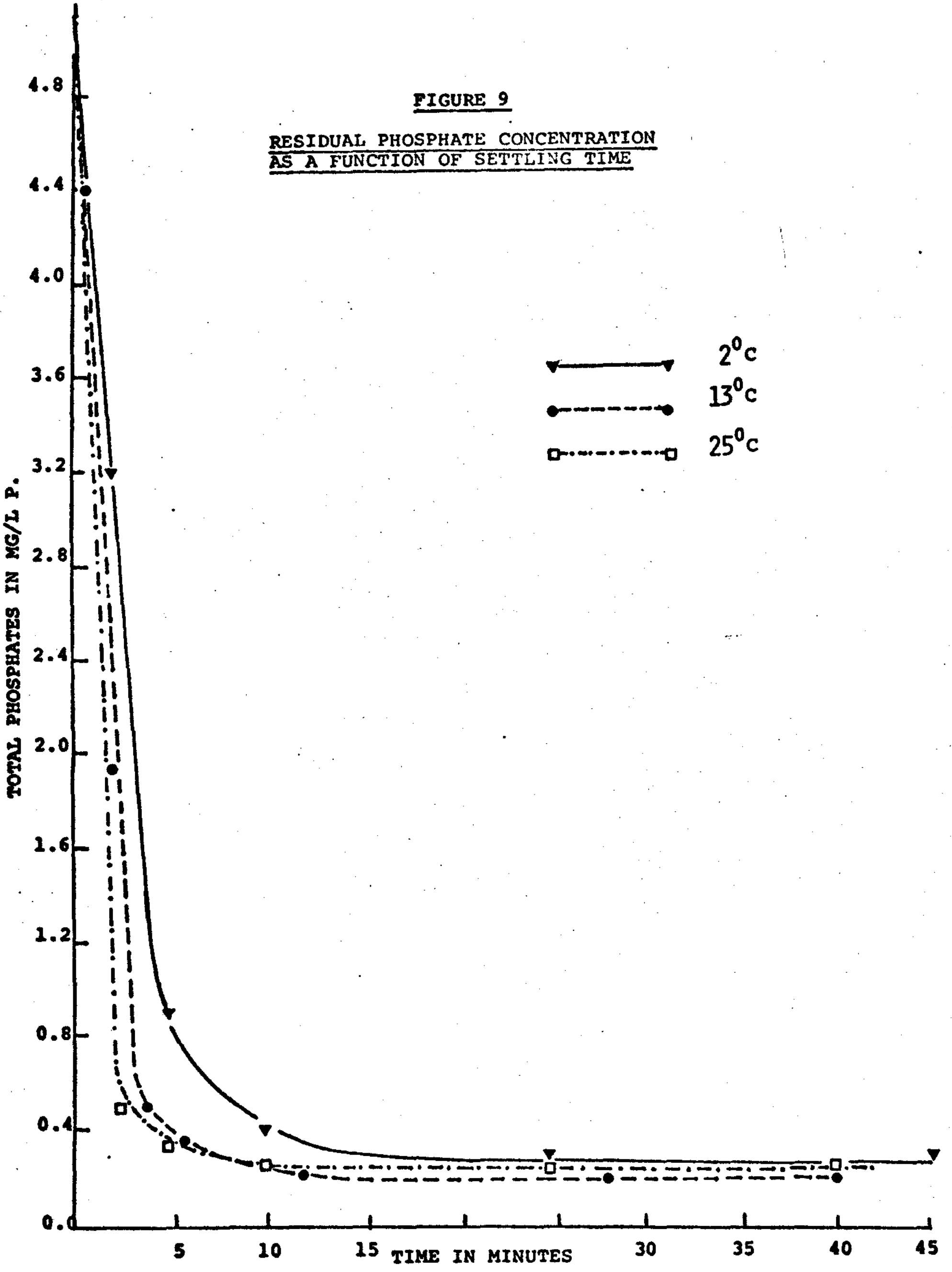
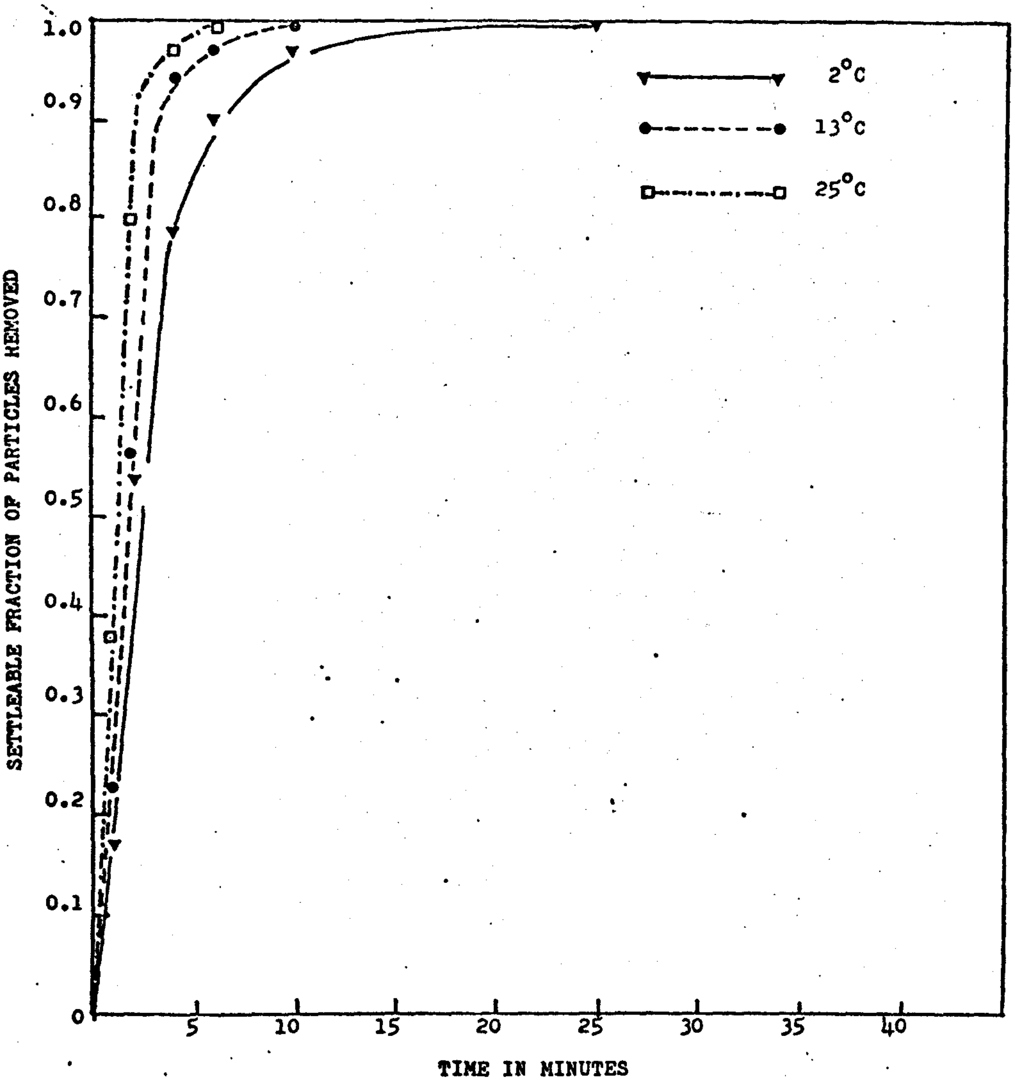


FIGURE 9

RESIDUAL PHOSPHATE CONCENTRATION AS A FUNCTION OF SETTLING TIME

FIGURE 10

SETTLEABLE FRACTION OF PHOSPHATE FLOCS REMOVED AS A FUNCTION OF TIME



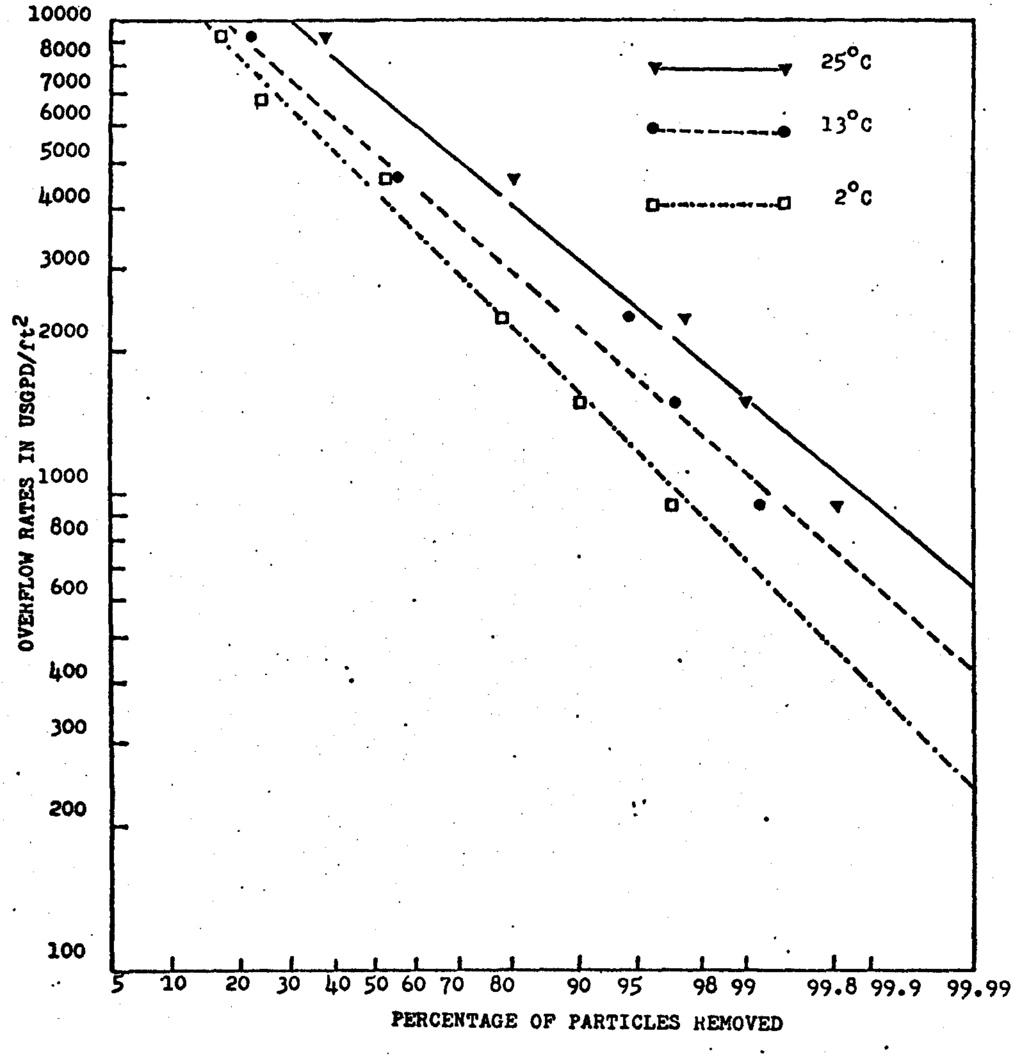
Using Hazen-Camp ideal sedimentation tank theory, overflow rates were calculated. Camp (1946) noted that certain assumptions had to be made to compare quiescent settling with actual tank settling. Short-circuiting, eddies due to turbulence, bed-load movement or scour, faster flocculation, convection currents and other phenomena affects performance of an actual basin, and the removal from an ideal basin may be more or less depending upon the relative magnitude of the disturbing factors. Other assumptions involved in Camp's ideal sedimentation tank theory are that initial concentration of particles is uniform throughout the column and that during settling the particles settle discretely and do not influence each other.

The overflow rate was, therefore, calculated on the basis of time the particle took to reach a certain depth in quiescent basin. The details of the procedures can be found in Table 30 of Appendix 3.

Figure 11 depicts the overflow rates plotted against percentage of particles settled at the three temperatures. The distribution of settling particles turns out to be a log normal distribution as the settling velocity plots linearly on a log probability paper. Irani and Callis (1963) derived the log-normal particle size distribution for a system with particles growing in size with time. In flocculant systems, particles grow in size as they fall, and hence can be described by a log-normal distribution. From Figure 11, it is important

FIGURE 11

DISTRIBUTION OF PARTICLE SETTLING VELOCITIES



to note that at conventional overflow rates of 600 GPD/ft^2, 99% of all particles would settle at temperatures down to 2°C. In Ontario, a criteria of 1 ppm as residual P, 80% of the time has been set for effluents discharging into the Great Lakes under the Canada-United States Agreement (1972). Using this criteria, Figure 12 shows how the settling velocity changes to achieve that treatment level, when the temperature varies from 2° to 25°C.

Verification of the theoretical behavior of settling velocities was conducted by calculating the overflow rates of 50% of settleable particles at the three temperatures. This is shown in Table 4, alongside with the values of viscosity of water.

If the following relationship between velocity rates and viscosity is assumed:-

$$V_t = A\mu^{-n}$$

where V_t = overflow rate

μ = absolute viscosity

A, n = empirical constants

The data in Table 4 can be plotted on log-log scale, as in Figure 13, to estimate the magnitude of n. The slope of the line in Figure 13 calculated from a least square method is -.78. In Chapter 2, n = -1 for the laminar range and is -.43 for the transition range. If the particle Reynold's number is in between these ranges then an intermediate value of n would be seen. This was ascertained by assuming a typical floc diameter of 110μ (Camp, 1968). The calculation is shown as following:-

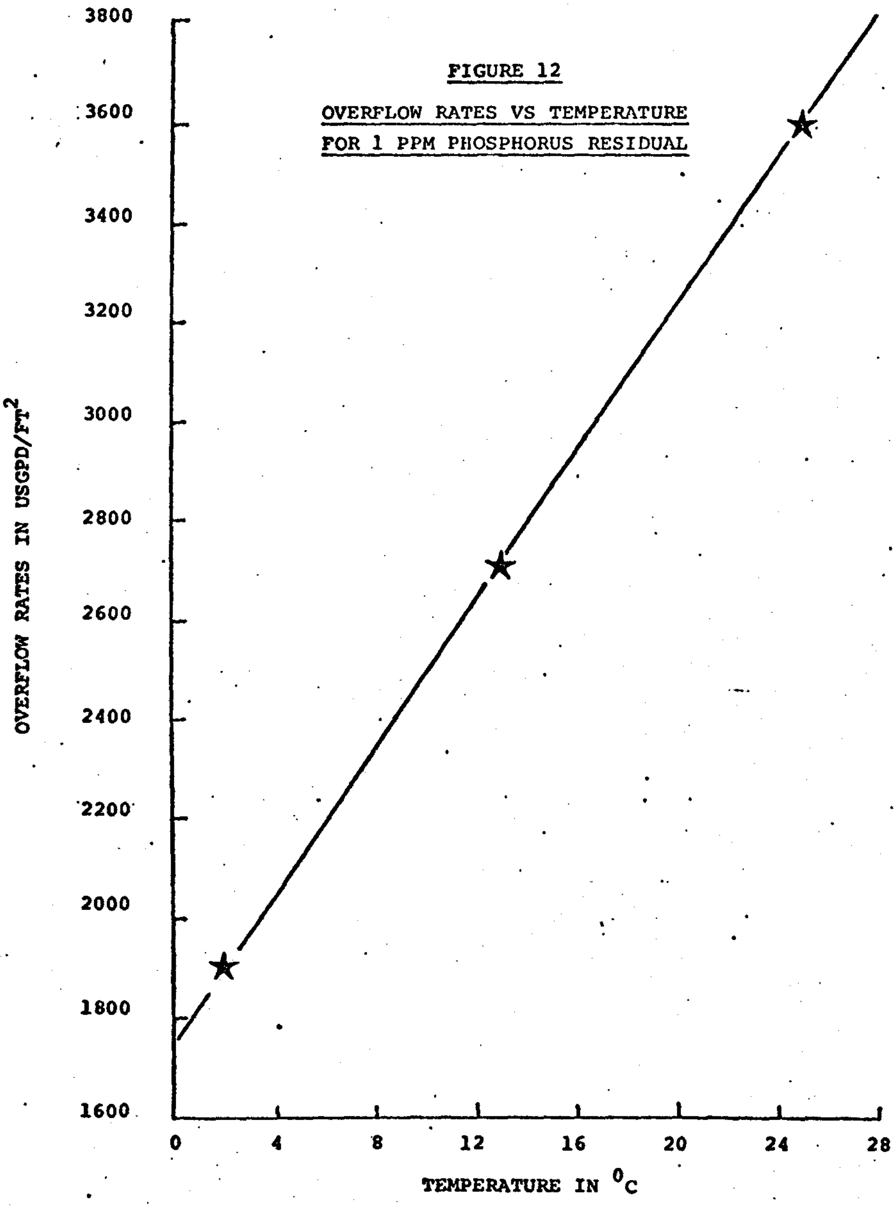


FIGURE 12

OVERFLOW RATES VS TEMPERATURE FOR 1 PPM PHOSPHORUS RESIDUAL

TABLE 4

VISCOSITY AND TEMPERATURE VERSUS OVERFLOW RATES FOR 50% PHOSPHATE REMOVAL

TEMPERATURE in ^0C	VISCOSITY in cp	OVERFLOW RATES in USGPD/ft^2
2	1.673	4400
13	1.203	5600
25	0.894	7200

$LOG_{10}\ V_t$	$LOG_{10}\ \mu$
3.644	.224
3.748	.080
3.857	-.049

$LOG\ V_t = LOG\ A + n\ LOG\ \mu$

using the least squares method to estimate the value of n

$$n = \frac{\left(\sum_{i=1}^{3} \log \mu_i \sum_{i=1}^{3} \log V_{ti} - 3 \sum_{i=1}^{3} \log \mu_i \log V_{ti} \right)}{\left(\left(\sum_{i=1}^{3} \log \mu_i \right)^2 - 3 \sum_{i=1}^{3} \log \mu_i^2 \right)}$$

$$= \frac{(.255)(11.25) - 3(.927)}{(.255)^2 - 3(.059)} = - \frac{.087}{.112} = -0.78$$

1) Perry's Chemical Engineers Handbook, 4th Ed, 1963, McGraw-Hill.

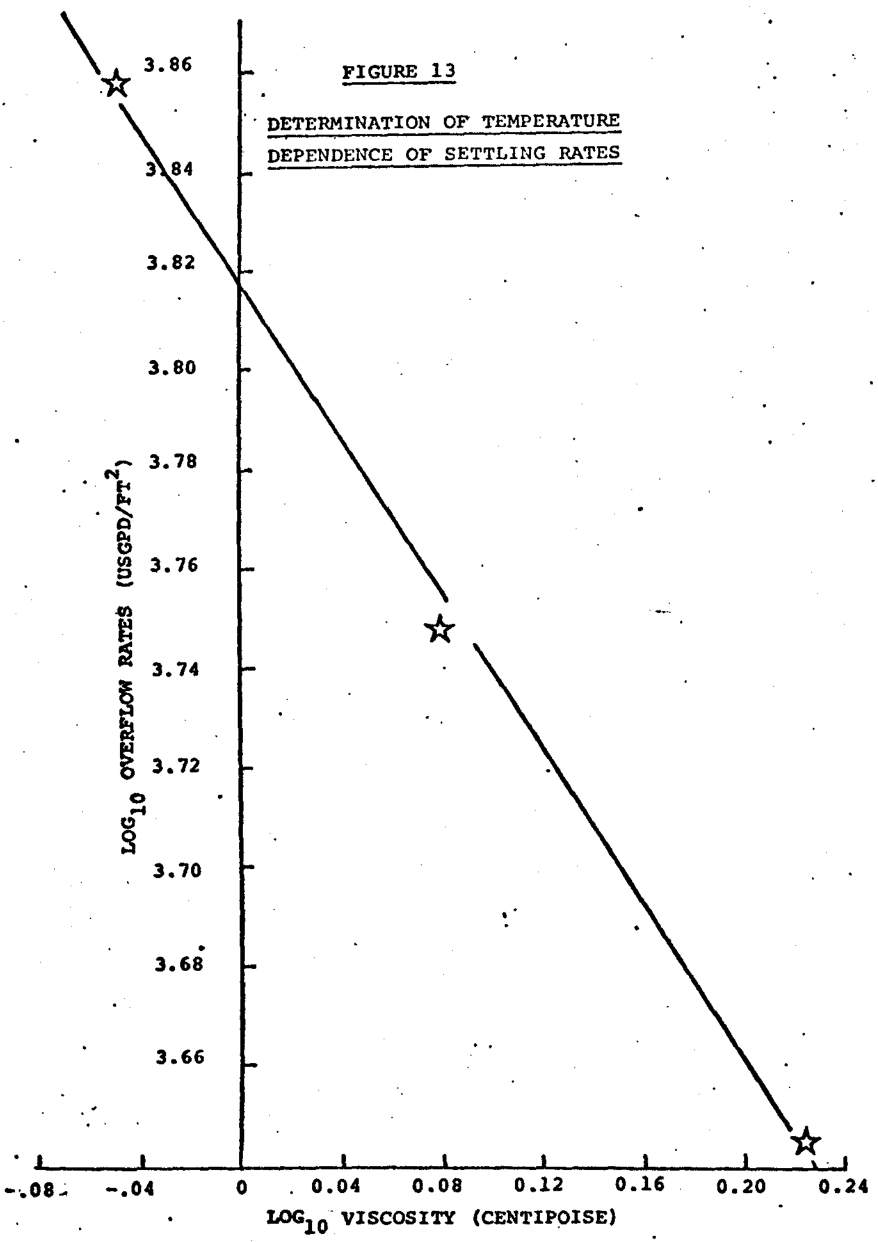


FIGURE 13

DETERMINATION OF TEMPERATURE DEPENDENCE OF SETTLING RATES

$$d_p = 1.1 \times 10^{-2} \text{cm}$$

$$\zeta_1 = 1.05 \text{ gm/cm}^3$$

$$v_t = 7200 \text{ USGPD/ft}^2 = 20.3 \text{ cm/min}$$

$$\mu = 0.894 \text{ cp} = 8.94 \times 10^{-3} \text{gm/cm sec}$$

$$N_{Re} = \frac{d_p \zeta_1 v_t}{\mu} = 1.1\text{x}10^{-2}\text{cm} \times 1.05\frac{\text{gm}}{\text{cm}^3} \times 20.3\frac{\text{cm}}{\text{min}} \times \frac{\text{min/60 sec}}{8.94\text{x}10^{-3}\text{gm/cm sec}}$$

$$= .44$$

The value of n therefore obtained seems plausible as the Reynolds number calculated is in the Stokes or possibly transitory region.

In view of the inherent experimental errors in such experiments, the particles can be assumed to fall in the Stokes' Law region for purposes of design procedures and calculations.

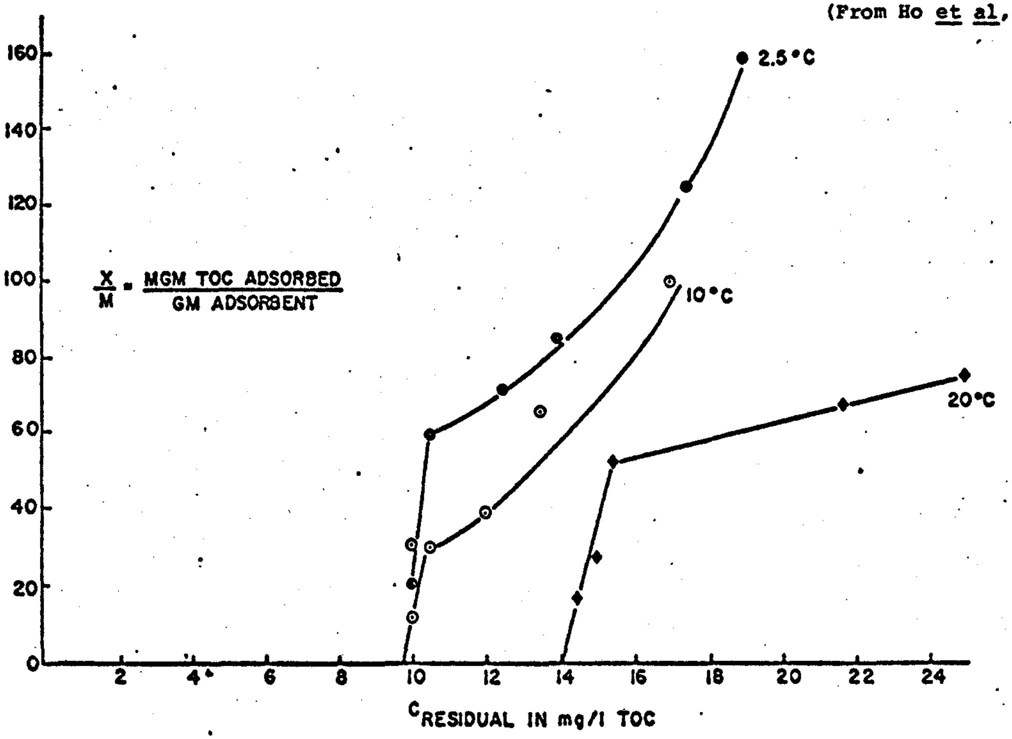
3.3.2 POWDERED CARBON ADSORPTION

Powdered activated carbon was contacted with coagulated and membrane filtered sewage and the isotherms obtained are shown in Figure 14, where the equilibrium loading on the carbon is plotted against the residual concentration in mg/l TOC. These are typical isotherms obtained from the study conducted by the Ho *et al* (1972) on Dundas sewage. Three temperatures were investigated and it is seen that the loading is generally higher at lower temperatures, for example at 16 mg/l residual TOC, loading increases 40% from 2°C to 20°C. In practice this is not always the case, the difference is usually less, as adsorption is not strongly temperature dependent.

FIGURE 14

EQUILIBRIA STUDIES ON AQUA NUCHAR A/RAW SEWAGE SYSTEM

(From Ho *et al*, 1972)



Another point to note is the presence of a clear breakpoint with sewage isotherms. Beyond this point, the carbon dosage required to bring about a further drop in residual concentration increases markedly. Also there is a certain fraction of sewage which is non-adsorbable, and remains in solution regardless of the carbon dosage.

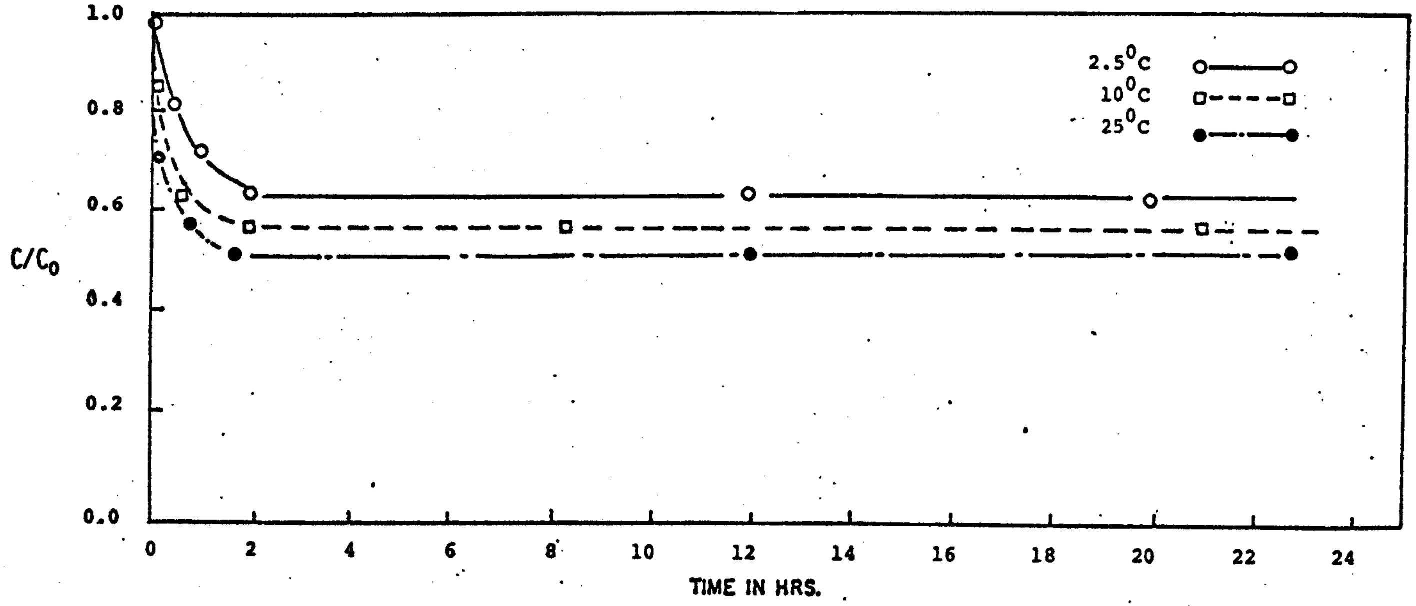
In Figure 15, results of the batch kinetic study are presented. A very rapid decrease in TOC is seen, after which not much appreciable change in TOC occurs. This is in concurrence with the observed behaviour with powdered carbons which have smaller particle size enabling faster diffusion into the pore structure. The temperature dependence of adsorption kinetics follows theoretical predictions, in that kinetics are adversely affected by decreasing temperature. The results are not very satisfactory, however, due to the errors involved in sampling at very short contact times, the initial stages of adsorption are the most crucial, and it is in this region where most of the error occurs. Qualitatively, one notes relatively little effects arising from temperature variations.

3.3.3. PAC SETTLING

PAC can be added to sewage, if and only if it can be separated or settled again. The flocculating properties of two polymers Dow C-31 and Percol 728 were evaluated. The former proved to be a poor flocculant contrary to what was

FIGURE 15

KINETICS OF POWDERED ACTIVATED CARBON ADSORPTION
WITH COAGULATED RAW SEWAGE



recommended by Beebe (1973). The results of this evaluation are presented below:-

	Percol 728	Dow C-31
Initial Turbidity in APHA units	16.0	22.0
Final turbidity	6.0	13.0
	(Very clear supernatant after 40 mins. of quiescent settling. Big flocs formed).	(Dark suspension little flocculation observed).

Percol 728 yielded promising results and an optimum polymer dosage was obtained through a series of six jar tests. The results are shown in Figure 16. The chosen dosage of 1.6 mg/l gave a clear supernatant and large flocs (.1 mm diameter) which settled rapidly. This dosage can be reduced further in continuous systems where a part of the settled powdered carbon sludge is recycled. Also, with bacterial growth taking place on the surfaces of the carbon particles, the floc size will be increased, leading to faster settling.

The separation of carbon particles from sewage turned out to be relatively easy as shown in Figure 17. Over 90% of the particles settle in 10 minutes; a clear supernatant is obtained after 25 minutes of quiescent settling. Results for 13°C are somewhat unrepresentative of settling, and are due mostly to poor sampling. Overflow rates were calculated from the results in Figure 17 and are shown in Table 5.

FIGURE 16

SETTLING TEST TO DETERMINE OPTIMUM DOSAGE OF POLYMER FOR PAC FLOCCULATION IN DISTILLED WATER

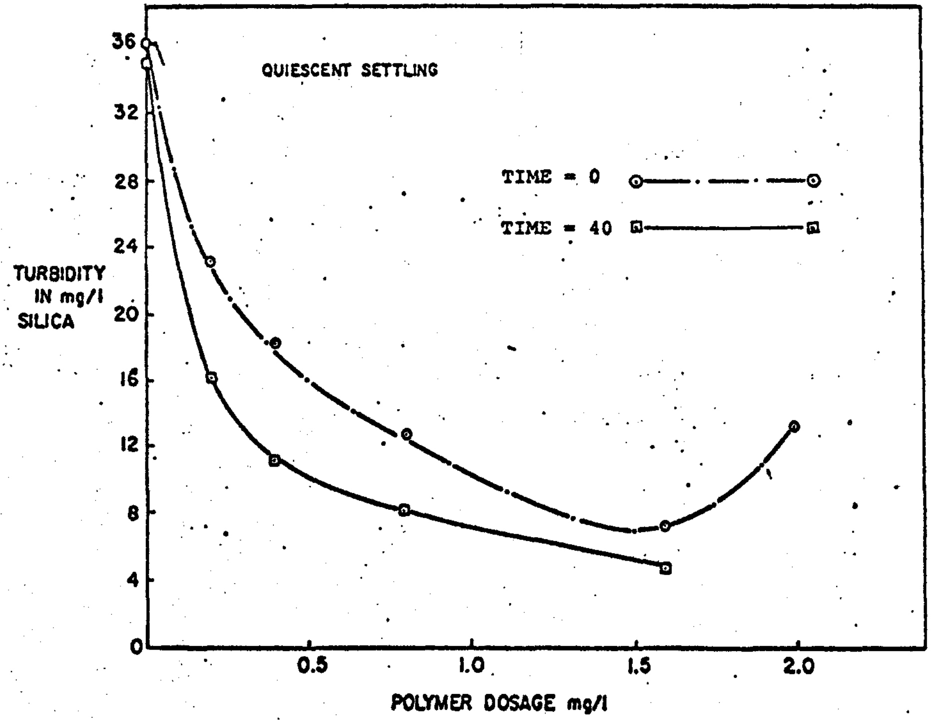


FIGURE 17

UNFILTERED TOC AFTER POWDERED CARBON ADSORPTION SETTLING AS A FUNCTION OF TIME

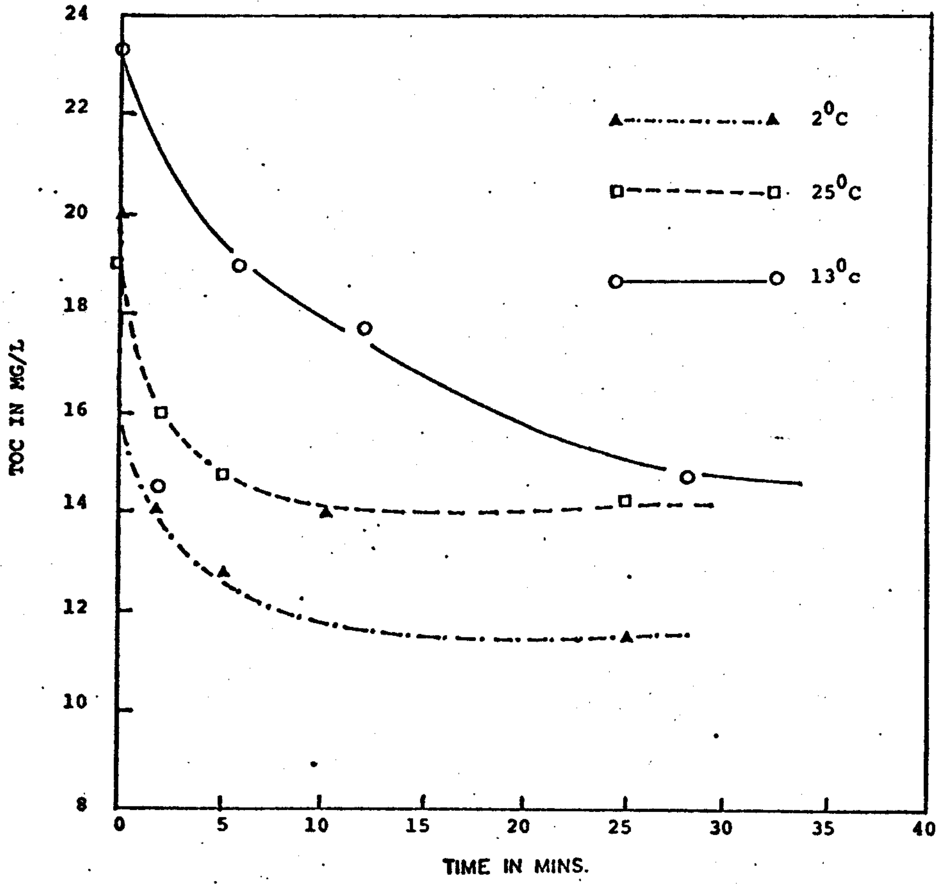


TABLE 5

UNFILTERED TOC REMOVAL AS A FUNCTION OF TIME

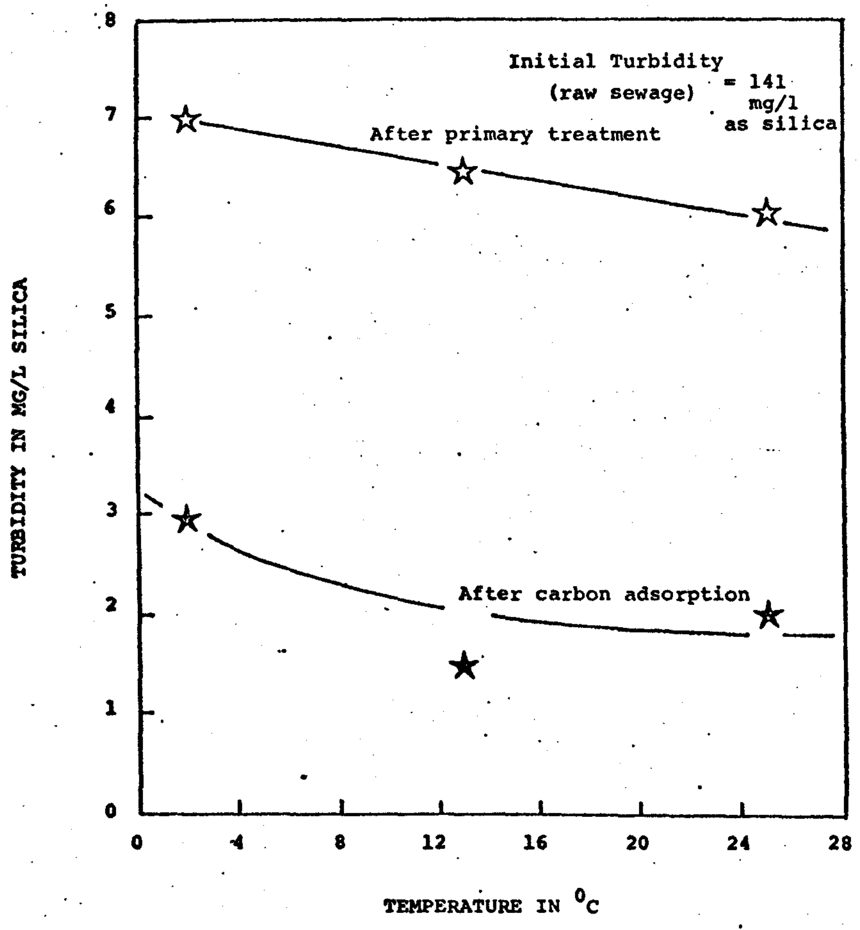
TIME in mins	OVERFLOW RATES in USGPD/ft^2	% OF PARTICLES REMOVED		
		TEMPERATURE		
		2^0C	13^0C	25^0C
0.0	0.0	0.000	0.000	0.000
1.0	7900.0	0.530	0.105	0.490
2.0	3950.0	0.660	0.233	0.612
4.0	1975.0	0.811	0.407	0.796
6.0	1317.0	0.884	0.500	0.878
0.0	790.0	0.960	0.629	0.980
25.0	316.0	1.000	0.954	1.000
40.0	197.0	1.000	1.000	1.000

A conventional clarifier with overflow rates in the range of 600 - 800 USGPD/ft^2 would provide adequate time for removal of over 95% of carbon particles for temperatures ranging from 2° to 25°C. Effluent quality after PAC adsorption based on our results is espected to be 10 to 15 mg/l TOC, quite independent of temperature. As a comparison, typical TOC values from a secondary biological system on this same sewage is in the 10 - 15 mg/l TOC, for filtered effluents (Murphy, 1974).

The final effluent produced from batch feasibility studies had very little turbidity as shown in Figure 18, no colour and no odour at the three temperatures.

FIGURE 18

SEWAGE TURBIDITY AFTER PRIMARY TREATMENT AND CARBON ADSORPTION AT THREE TEMPERATURES



3.4 CONCLUSIONS

1) Chemical coagulation was influenced by temperature, but this effect was small in view of the excellent settleability of chemical flocs. The order of dependence of overflow rate on viscosity was found to be -0.78.

2) Powdered carbon separation and settling was found to present little difficulty when a flocculant was used. Percol 728 appeared quite effective for this purpose; much more so than Dow C-31.

3) PAC adsorption kinetics are little affected by low temperature. Further investigation needs to be carried out to determine how significantly temperature affects adsorption capacity.

4) In general, physico-chemical systems using PAC can operate well at low temperatures and can deliver high quality effluents.

CHAPTER 4

TEMPERATURE EFFECTS ON THE COLUMNAR KINETICS OF SINGLE SOLUTE SYSTEMS

4.1 INTRODUCTION

Preliminary investigations in Chapter 3 revealed that batch PCT of raw sewage was feasible at low temperature. Although temperature effects turned out to be insignificant for batch adsorption kinetics, the sensitivity to temperature variations in continuous flow systems should be explored.

For continuous wastewater treatment, fixed bed arrangements using granular carbons are far more popular than powdered carbon systems. With granular carbon columnar processes the effluent concentration profile is of prime importance in design and operation. To better understand temperature effects from a theoretical view point, pure component systems are necessary as multi-component systems bring with them the problems of selective adsorption and complex boundary conditions, which render theoretical modelling difficult.

The pure compound chosen for theoretical modelling studies was sodium dodecyl sulfate (SDS), a major part of the linear alkyl commercial detergents. SDS is biodegradable and, because of its detergent origin, commonly found in sewage. SDS can form a mixture of colloidal and soluble solids in the concentration range of our interest. The solute particles join their hydrophobic tails to form an associated colloid. Colloidal particles arise once the critical micelle concentration is exceeded and since sewage feed to carbon columns is often a mixture of soluble and colloidal materials, we considered the existence of such colloids an advantage.

Thomas's reaction - kinetic model as modified by Keinath and Weber (1968) was used to predict effluent concentration profile for SDS-GAC system. The model was chosen as it is mathematically simple and requires parameter values which are easily obtainable from batch experiments.

The objectives set for this phase of study were:-

(i) To evaluate temperature sensitivity of columnar kinetics.

(ii) To theoretically model continuous flow columnar systems based on data obtained from agitated non-flow systems.

(iii) To assess the validity and shortcomings of proposed theoretical models.

4.2 EXPERIMENTAL

The experimental investigations were conducted in two parts, the batch system study and the continuous flow system study. Filtrasorb 400 (Calgon Corp.) was selected as the granular carbon for the study, as it has been used extensively in wastewater treatment and is known to have a large surface area with a pore size distribution suited for adsorption of molecules in sewage. Rankin and Benedek (1973) have characterized some of the physical properties (size, porosity, etc.) of Filtrasorb 400, which was used in this study.

4.2.1 BATCH ADSORPTION EQUILIBRIA

A one litre volume of a 250 mg/l freshly prepared SDS solution was contacted with Filtrasorb 400 for forty-eight hours to establish equilibrium. A set of nine such vessels were utilized for each isotherm run at each of the three temperatures studied, 2°, 13° and 25°C. Eight had carbon dosages ranging from 450 mg/l to 4000 mg/l and the last contained no carbon and served as a control blank (to account for possible bacterial action). The flasks were sterilized before use in dry oven at 350°C for an hour to minimize contamination of SDS solution. This precaution was deemed necessary as SDS is readily biodegradable.

In all cases, carbon was added only after the contents of the vessels had come to the temperature maintained in the bath. The details of the temperature controlling mechanism are elaborated in Chapter 3.2.

Batch vessels were agitated by magnetic stirrers. After the prescribed contact period, the flasks were withdrawn from the bath and filtered through .1μ membrane filters. Fifty ml of filtrate was collected and colorimetrically analyzed for SDS content.

4.2.2 BATCH ADSORPTION KINETICS

A two litre flask containing 250 mg/l of a SDS solution was placed in a constant temperature bath. Five grams of Filtrasorb 400 were added once the contents of the vessel had assumed the temperature of the bath. The vessel was agitated by means of a magnetic stirrer. Ten ml samples for analysis, were withdrawn progressively, with time to monitor the kinetics of the reaction. As in the equilibria studies, the kinetics were also conducted at three temperatures, 2°, 13°, 25°C.

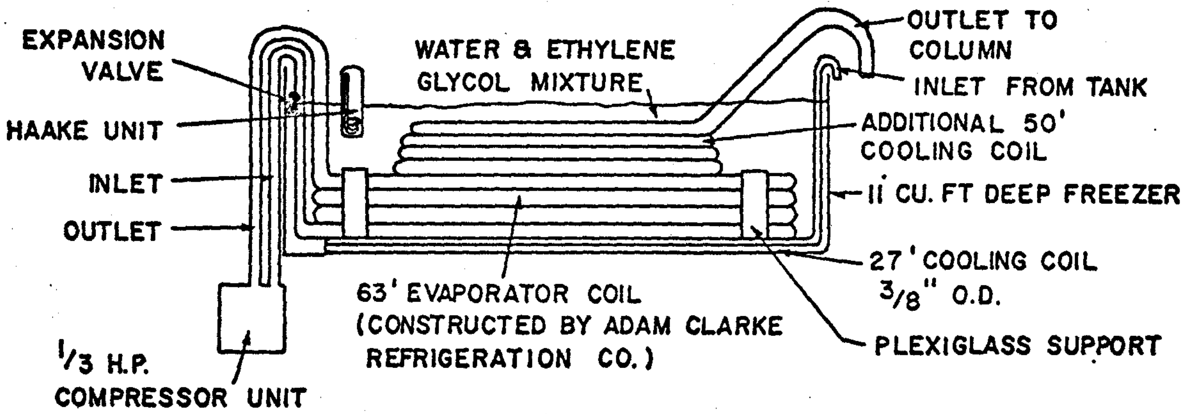
4.2.3 CONTINUOUS FLOW COLUMNAR KINETICS

A small pilot plant consisting of pumps, cooling system and 10 ft. long, 2 in. diameter Lucite columns, in series, were used to study columnar kinetics. The columns were filled with Filtrasorb 400 (12 x 40 mesh) as a slurry. Initially tap water was used to fluidize the beds and drive off the fine carbon particles at the top, and the height of the carbon in each bed adjusted to 5 ft.

Feed to the columns was prepared in a 75 gallon polyethylene container, with SDS concentration made up to 250 mg/l. By the use of a centrifugal pump, the feed was circulated through a cooling chamber, as shown in Figure 19. The cooled solution was then fed to the carbon column in a downflow mode at a flow rate of 4 USGPM/ft ^{2} and a pressure of 16 - 20 psig. Temperatures along the length of the columns were monitored by thermocouples inserted in the beds. Two-inch thick Fiberglass

FIGURE 19

REFRIGERATION UNIT



insulation was placed around each column. Periodic samples were obtained from outlets located along the bed (Figure 20) for subsequent analysis.

Similar procedure for all three temperatures was used except at 25°C when the cooling chamber was not utilized. Feed was pumped directly from the plastic container, which had an immersion heater placed in it for temperature control. The pilot plant apparatus is shown schematically in Figure 21.

4.2.4 ANALYTICAL METHODS

(i) Total Organic Carbon (TOC)

The organic carbon fraction of the samples were measured using the Beckman Model 915, Total Organic Carbon (TOC) Analyser. TOC measurements can be used to estimate SDS concentrations by using its molecular formula, $C_{12}H_{25}OSO_3Na$. The SDS/TOC concentration ratio is simply 288/144 or 2.0. TOC analysis was used for columnar runs, as it gives immediate results, and is a helpful operational tool. TOC has the added advantage that the samples do not require dilution to be in the range of measurement.

(ii) Color Development

The usual method for SDS analysis, as recommended by the Standard Methods 13th Edition (1971) is the methylene blue chloroform extraction method. Due to

FIGURE 20

COLUMN

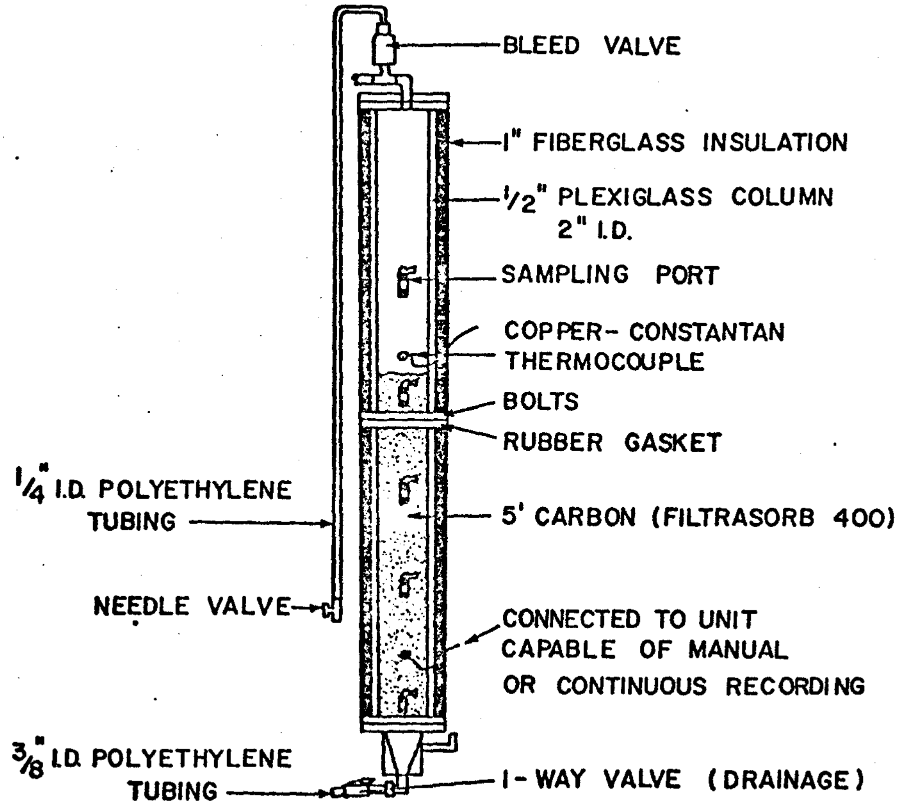
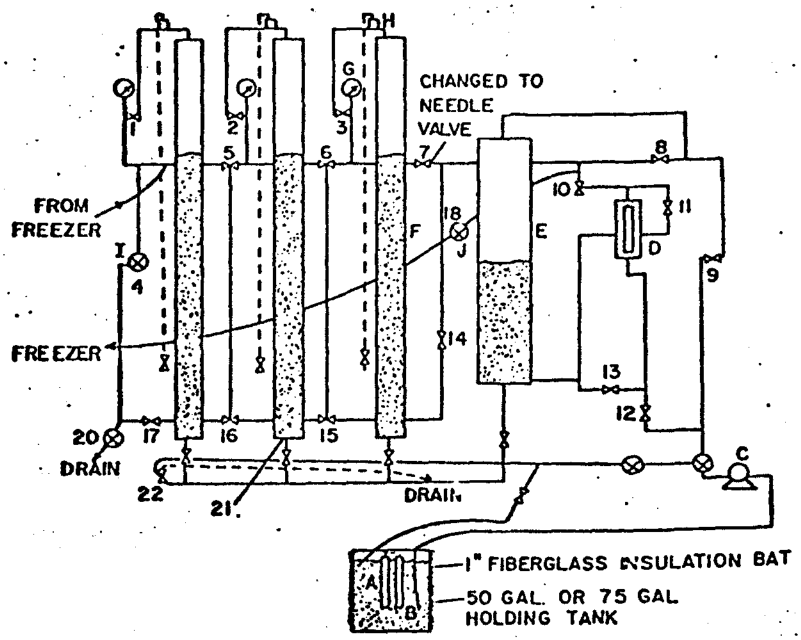


FIGURE 21

SCHEMATIC VIEW OF ACTIVATED CARBON COLUMNS



A. 1000W IMMERSION HEATER
B. THERMOREGULATOR (-35°C – 50°C)
C. PUMP + MOTOR (CAPACITY = 9 l/min)
D. ROTAMETER (CAPACITY = 1 l/min)
E. SANDFILTER (10 in.)
F. CARBON COLUMN (2" I.D.) (10' height)
G. PRESSURE GAUGE (100 psig)
H. BLEED OFF VALVE (1/8")
I. EXIT PRESSURE NEEDLE VALVE (1/2" GATE VALVE)
J. NEEDLE VALVE (1/2")

the sheer number of samples collected in the batch runs, the slightly faster and equally accurate technique of Moore and Kolbeson (1956) was employed. Methyl green dye formed a complex with SDS, which was extracted with benzene, and the absorbance of the benzene solution measured at 615 µ using a Beckman spectrophotometer, Model DB-2. The SDS concentration is obtained from a previously determined calibration of absorbance versus surfactant concentration, as shown in Figure 22.

4.3 DISCUSSION OF RESULTS.

4.3.1 BATCH ADSORPTION EQUILIBRIA

The residual SDS concentration was analyzed, using the colorimetric technique described previously, and the adsorption loading on the carbon calculated by the following method:-

$$q = \frac{V\,(C_o - C)}{M} \tag{39}$$

where q = loading in mg SDS/gm adsorbent.

V = solution volume in litre.

C_o = initial adsorbate concentration in mg/l.

C = residual adsorbate concentration in mg/l.

M = mass of adsorbent in grams.

The resulting isotherms for all three temperatures are plotted together in Figure 23. Langmuir type isotherms are chosen to approximate the data. The loading increases with

FIGURE 22

SDS CALIBRATION USING COLORIMETRIC TECHNIQUE

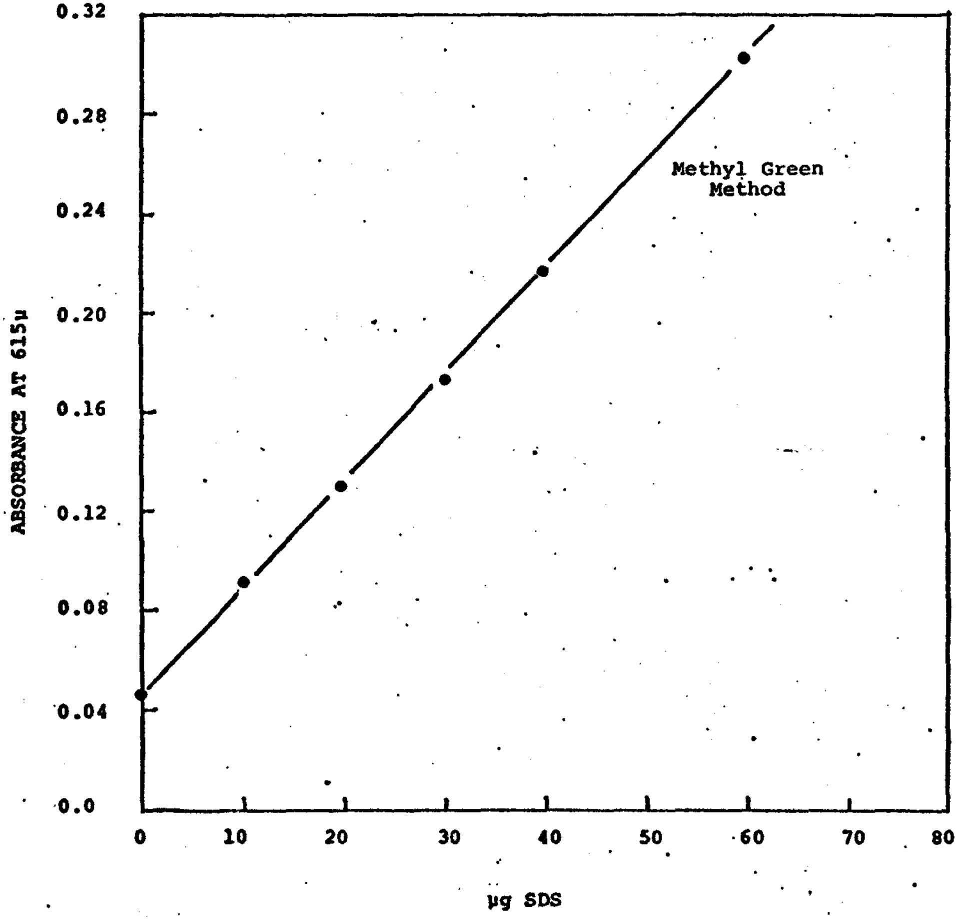
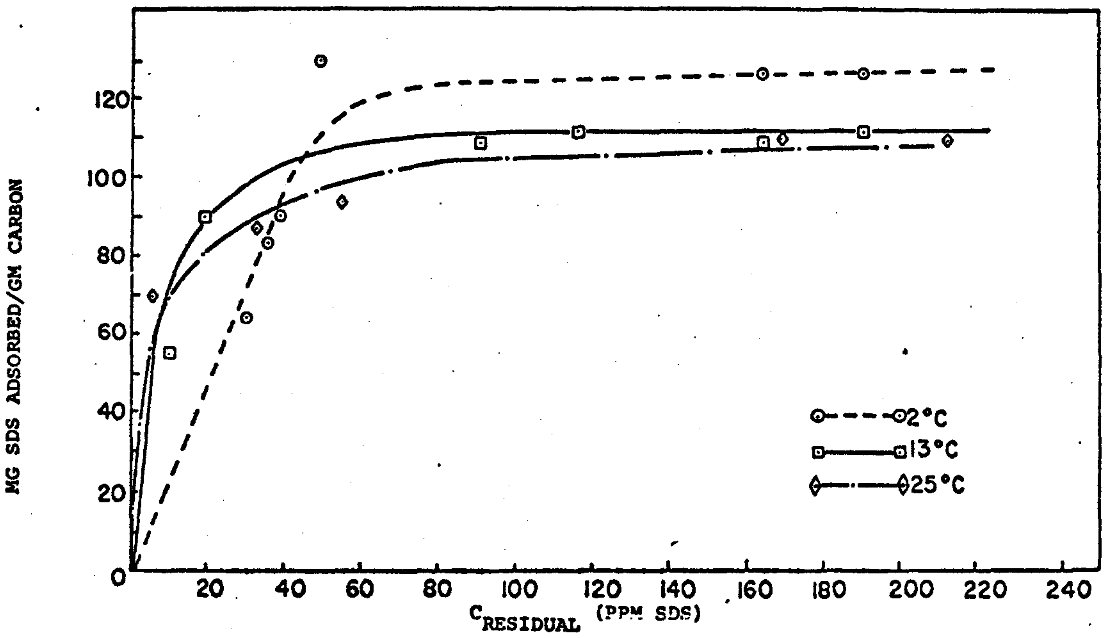


FIGURE 23

EQUILIBRIA STUDIES OF FILTRASORB 400/SDS SYSTEM

INITIAL CONCENTRATION = 250 MG/L



decreasing temperature, as predicted theoretically. The isotherms, shown in Figure 23, were plotted using reparametrized forms to obtain the Langmuir's constants Q^o and b (see Equations 13 and 14). Figure 24 is a plot of 1/C vs. 1/Q and Figure 25 is a plot of C/Q vs. C. The intercepts and the slopes are used to calculate Q^o and b as shown in Table 6. The straight lines shown in Figures 24 and 25 are drawn, using the least squares method with the extreme points omitted to avoid biasing the results.

An eye fitted curve was also used on the basis that Q^o is the saturation loading asymptotically approached at maximum solubility and b is the tangent to the Langmuir curve at low concentrations. The values obtained by eye method were compared with other sets of data in Table 6 and the C/Q vs. C linearization method was chosen to be the most consistent and reliable. The sensitivity of the mathematical model (for predicting effluent concentration profiles) to the Langmuir's constants Q^o and b was tested later on, using the data of Table 6.

An estimation of the magnitude of the heat of adsorption was made based on the monolayer saturation capacity at the three temperatures, as shown in Table 7. Heat of adsorption calculated is of the order of -1.8 Kcal/mole close to that quoted by Weber and Morris (1964) for Alkyl Benzene Sulphonates. The negative sign indicates the reaction is exothermic and the low ΔH values indicates "physical" adsorption involving weak bonds.

FIGURE 24

LINEARIZATION OF LANGMUIR'S ISOTHERM

BY $\frac{1}{C}$ VS $\frac{1}{Q}$ PLOT

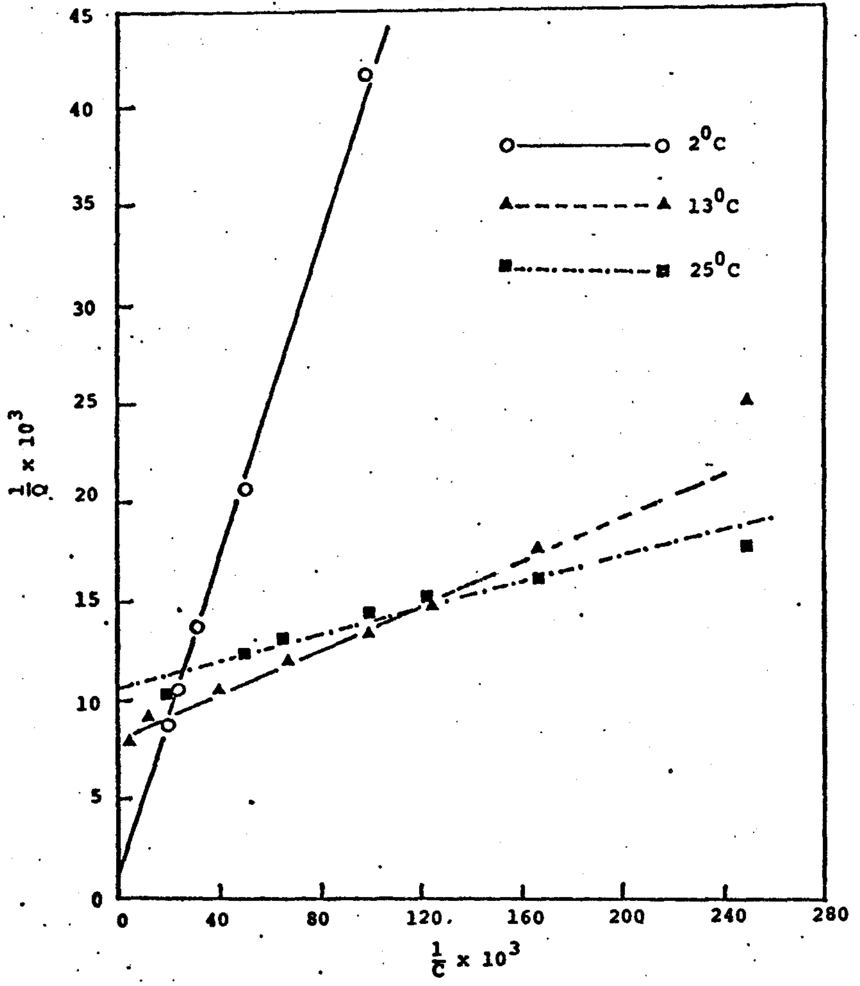


FIGURE 25

LINEARIZATION OF LANGMUIR'S ISOTHERM BY $\frac{C}{Q_e}$ VS C PLOT

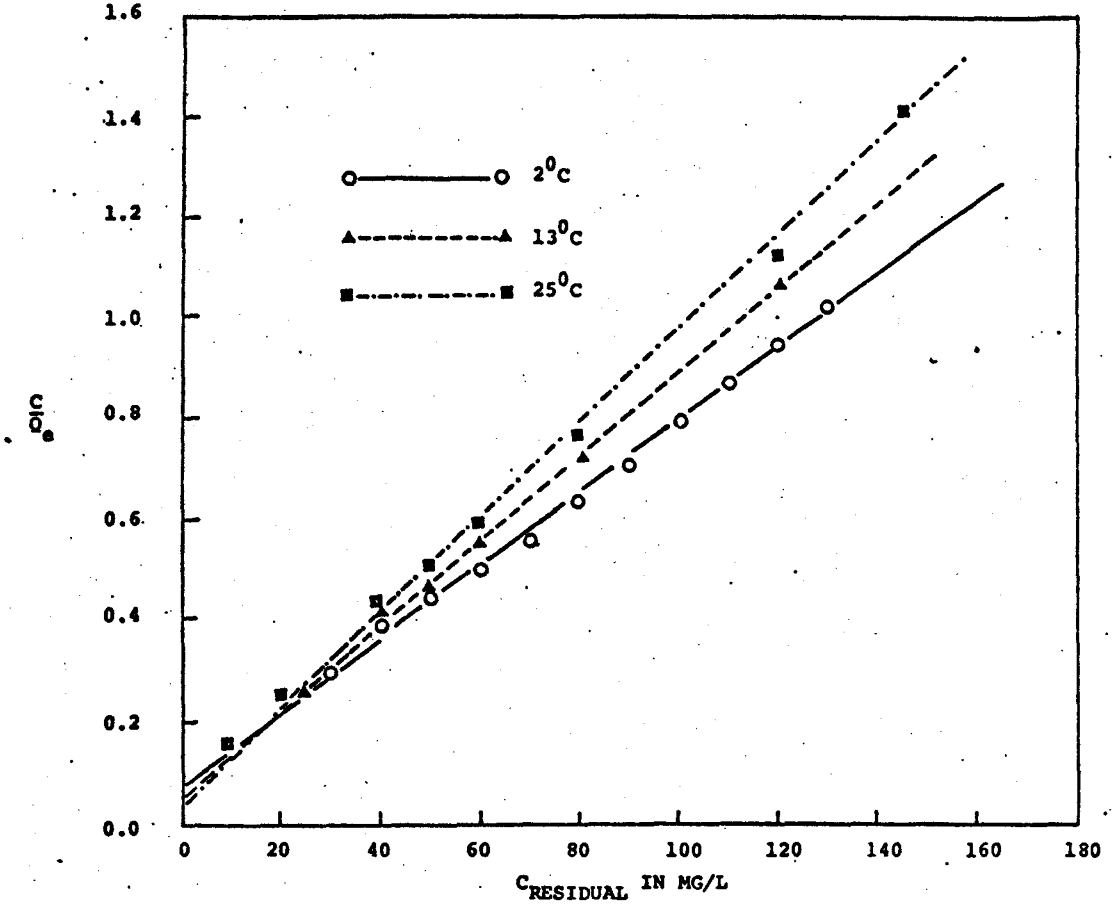


TABLE 6

VALUES OF LANGMUIR'S CONSTANTS ESTIMATED USING THREE METHODS

From C/Q vs. C graph

TEMPERATURE in ^{0}C	b (1/mg)	Q^{0} (mg/g)
2.0	0.0934	137.5
13.0	0.1230	120.0
25.0	0.1610	107.1

From 1/C vs. 1/Q graph

TEMPERATURE in ^{0}C	b (1/mg)	Q^{0} (mg/g)
2.0	0.0070	400.0
13.0	0.1510	121.2
25.0	0.3080	97.5

From " eye " method

TEMPERATURE in ^{0}C	b (1/mg)	Q^{0} (mg/g)
2.0	0.0189	127.0
13.0	0.0894	112.0
25.0	0.2800	107.0

TABLE 7

CALCULATION OF HEAT OF ADSORPTION FOR SDS/GAC SYSTEM

TEMPERATURE in ^{0}C	MONOLAYER ADSORPTION LOADING in mg/gms
2	137.5
13	120.0
25	107.1

Using least squares method to estimate ΔH

Temperature coefficient = -898

$$\Delta H = -898 \times \frac{1.98}{1000}\,\frac{\text{kcal}}{\text{mole}} \quad = -\ 1.78\ \text{kcal/mole.}$$

4.3.2 BATCH ADSORPTION KINETICS

The residual SDS concentration was analyzed and plotted as dimensionless concentration ratio versus time at all three temperatures as shown in Figure 26. It is evident that the relatively rapid initial rate of adsorption decreases markedly within a couple of hours or so to give a gradual approach to an equilibrium condition which is attained after about forty-eight hours. The second feature to note in Figure 26 is that the rate of adsorption is considerably slowed down at lower temperatures, as expected theoretically.

The pattern exhibited by the rate curves of Figure 26, can be most readily accounted for if it is assumed that the rate of adsorption is controlled by the rate of diffusion of solute in the pores within the carbon particle. Theoretical treatments of intraparticle diffusion yield complex solutions, although a functional relationship where the uptake rate varies approximately linearly with the half-power of time, $t^{\frac{1}{2}}$ rather than t has been used by researchers to obtain pseudo-rate constants (Weber and Morris, 1963). In Figure 27, the data from Figure 26 are plotted on a square root of time scale and slopes are calculated for all three temperatures. The temperature dependence as indicated by the activation energy, E_a, noted in Table 8 at 2.3 kcal/mole is considerably lower than expected. The assumed relationship fits the data well at 13° and 25°C but some deviations from linearity are evident at 2°C.

FIGURE 26

KINETICS OF GRANULAR ACTIVATED CARBON ADSORPTION OF SDS

VOLUME OF SOLUTION = 2150 mls.

WEIGHT OF CARBON = 5 grams.

INITIAL CONCENTRATION OF SDS = 250 mg/l

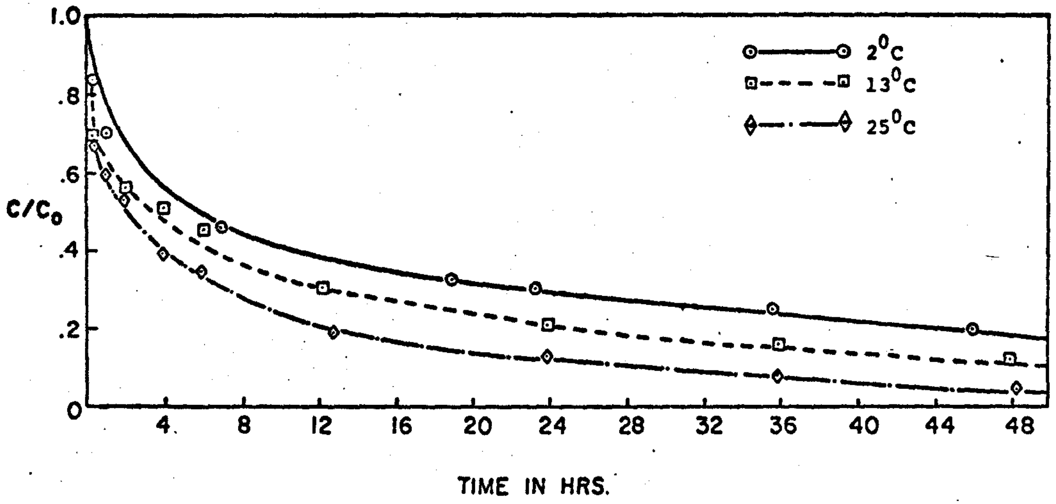


FIGURE 27

RATE OF ADSORPTION OF SDS BY GRANULAR CARBON
PLOTTED ON $T^{1/2}$ SCALE

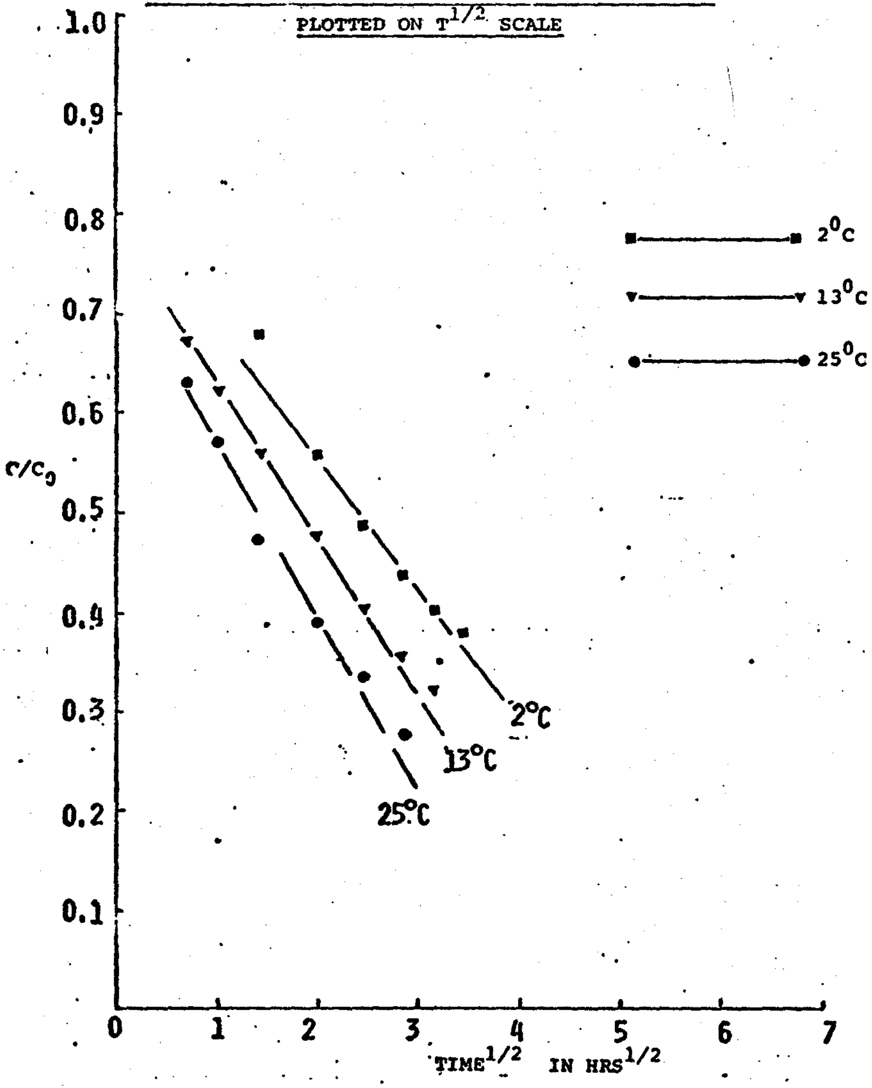


TABLE 8

RATES OF ADSORPTION FOR THE SDS/GAC SYSTEM

TEMPERATURE in ^0C	PSEUDO-REACTION RATE in $hr^{-1/2}$
2	0.130
13	0.158
25	0.180

$\kappa = Ae^{-E_a/RT}$

E_a = 2.3 kcal/mole.

4.3.3 DETERMINATION OF SOLID PHASE PORE DIFFUSION COEFFICIENTS

From the batch isotherm and kinetic data gathered at the three temperatures, it is now possible to estimate the solid phase pore diffusion coefficient using Tien's method, as outlined in Chapter 2.2.2. Kinetic data is tabulated from Figure 26 for 2°C in Columns I and II of Table 9. Concentration at a particular time is computed by multiplying Column II with initial concentration. The average uptake of the particle as a function of time is shown in Column IV and is simply the loading based on bulk concentration. By assuming mass transfer resistance due to film phase diffusion to be negligible, the concentration in the bulk solution can be considered essentially equivalent to that at the surface of the particle. The uptake rate at the particle surface, therefore, will be governed by the concentration in the bulk phase. The Q_s values in Column V are calculated from the equilibrium relations at 2°C in Figure 23 using concentrations tabulated in Column III. The ratio of the average and surface loadings as it approaches equilibrium is shown in Column VI. Similar calculations were made for 13°C and 25°C and are included in Appendix 3, as Tables 31 and 32, respectively.

The next step in Tien's method is to approximate the surface uptake as a polynomial function of time. Least squares technique was used to represent Q_s as a third order expression in time. The details of this procedure are included in Appendix 6. Using Equation 33, the fractional uptake profiles can be derived as a function of time. By varying ψ values $(a^2/D_s t)$

TABLE 9

CALCULATION OF SOLID PHASE PORE DIFFUSION COEFFICIENT
FOR SDS/GAC SYSTEM

TEMPERATURE = 2^{0}C

COL I TIME in hrs	COL II C/C_0	COL III C	COL IV Q_{av}	COL V Q_s	COL VI Q_{av}/Q_s
0.5	0.820	164.0	15.05	126.5	0.119
1.0	0.741	148.2	21.65	126.3	0.171
2.0	0.647	129.4	29.51	126.0	0.234
3.0	0.586	117.2	34.61	125.6	0.275
4.0	0.540	108.0	38.46	125.4	0.307
6.0	0.469	93.8	44.39	124.7	0.356
8.0	0.424	84.8	48.15	124.0	0.388
12.0	0.369	73.8	52.75	123.0	0.429
24.0	0.294	58.8	59.02	118.8	0.497
36.0	0.231	46.2	64.29	108.5	0.592
48.0	0.173	34.6	69.14	83.0	0.833

a whole family of curves are generated using the polynomial approximation, as shown in Figure 28 for 2°C. The experimental fractional uptake curve is superimposed on the theoretically generated curves. The intersection points uniquely define the solid phase pore diffusion coefficient if the adsorbent particle diameter is known. Rankin (1973) experimentally determined the average diameter of Filtrasorb 400 particles to be 0.90mm. Table 10 shows the calculated values for ψ values ranging from 20 to 240. Figures 62 and 63, as well as Tables 33 and 34, are included in Appendix 3 and 4 for 13°C and 25°C respectively. At all three temperatures, it is seen that diffusivity decreases as a function of time, as in Figure 29. This variation is attributed to the attrition of carbon particles under strong agitation, which reduces the effective particle diameter. Tien's derivation assumes that the solid phase pore diffusion coefficient is independent of concentration, which may not be strictly valid. Mathematical solutions to the diffusion problem in spherical particles are very complicated when diffusivity is itself a variable. To solve Equation 25 which defines this case, a pre-knowledge of the D_s variation in time is required. This can be handled by deriving an empirical correlation of particle diameter with time from batch experiments. The changing particle diameter can in turn be related to the solid phase pore diffusion coefficient. In order to obtain any kind of solution to Equation 25, a simple correlation

FIGURE 28

EXPERIMENTAL VS THEORETICAL FRACTIONAL UPTAKE CURVES FOR SDS/GAC SYSTEM AT 2^0C

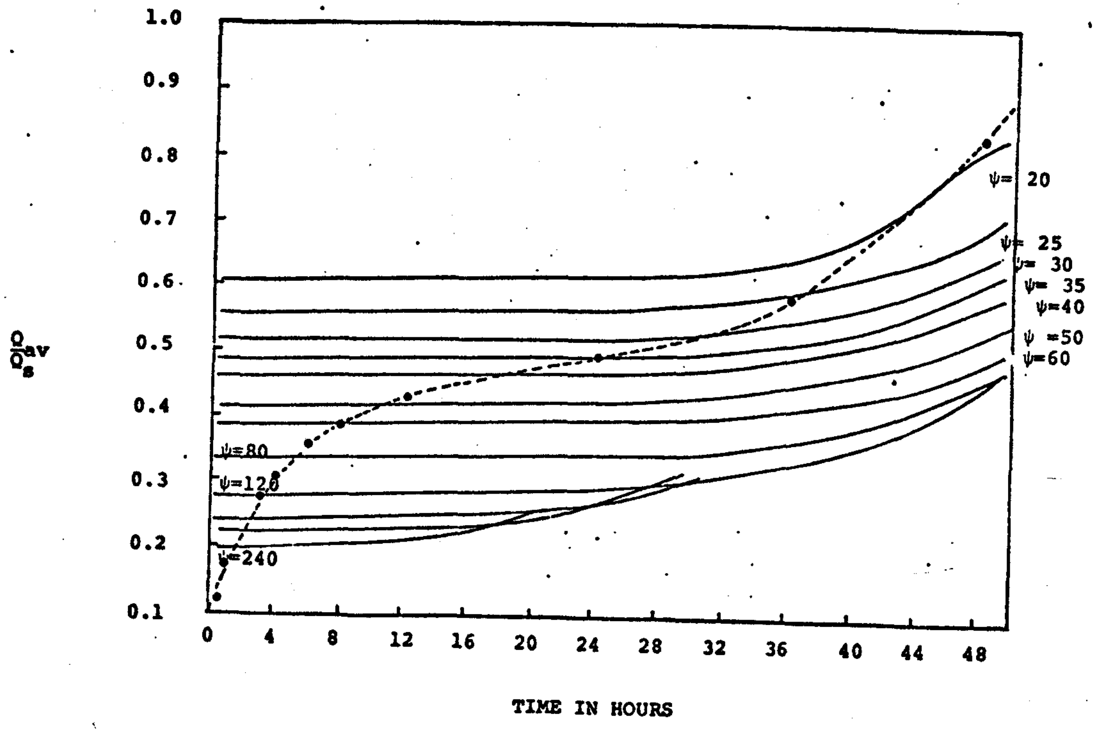


TABLE 10

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME

SDS/GAC SYSTEM

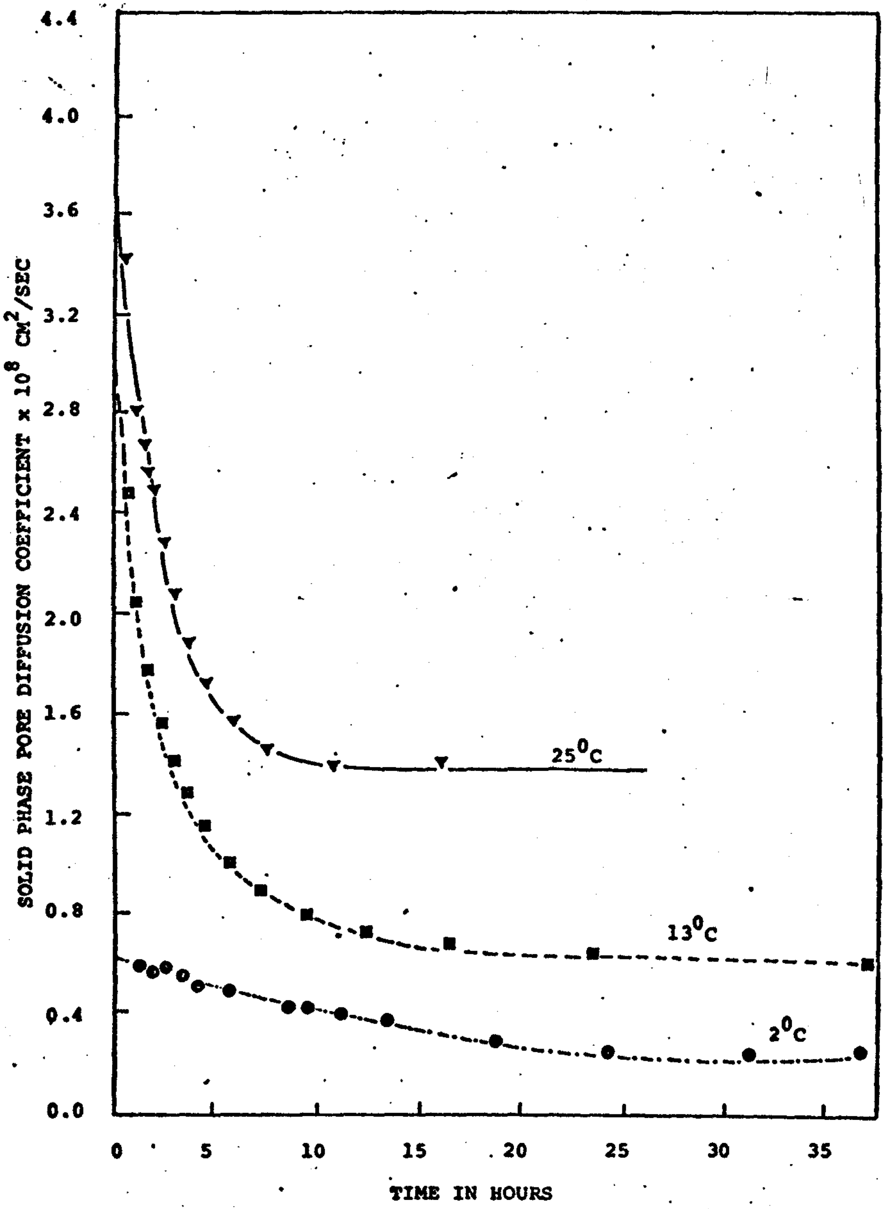
TEMPERATURE = 2^0C

TIME in hrs	ψ	$D_s \times 10^8$ cm^2/sec
47.00	20.0	0.239
36.80	25.0	0.245
31.20	30.0	0.240
24.50	35.0	0.262
19.00	40.0	0.296
13.50	45.0	0.370
11.30	50.0	0.398
9.70	55.0	0.422
8.80	60.0	0.426
5.78	80.0	0.486
4.38	100.0	0.514
3.37	120.0	0.558
2.45	160.0	0.575
2.00	200.0	0.564
1.60	240.0	0.585

Particle diameter = 0.09 cm

FIGURE 29

SOLID PHASE PORE DIFFUSIVITY AS A FUNCTION OF TIME



of the type $D_s = D_{s0}(1+Kt)$ would have to be attempted. An experiment was conducted to measure attrition in batch vessels due to stirring. After forty-eight hours of agitation, the particle diameter had been reduced from 0.09 cm to 0.054 cm. Using the corrected particle diameter, however, increased the variation of D_s with time indicating a strong inconsistency in Tien's method for calculating solid phase pore diffusivities. For the purposes of obtaining a reasonable approximation to the D_s values an alternate method was adopted. In Figure 29 the graph is extrapolated to time values equal to zero where particle attrition hasn't begun. These values are tabulated at all three temperatures in Table II. It is seen that the diffusion coefficients increase with increasing temperatures as expected from Wilke-Chang type correlations. A comparison of the bulk fluid diffusion values with the solid phase pore diffusivities reveals that intraparticle transport is about 100-400 times slower than bulk molecular diffusion. The temperature dependence for both types of diffusion is estimated using least squares method, as in Figure 30. The slope of the best fit line is the temperature coefficient from which an activation energy of 13.2 Kcal/mole was calculated for solid phase pore diffusion. A much lower value of 5 Kcal/mole was obtained for molecular diffusion.

FIGURE 30

ARRHENIUS TYPE PLOT FOR SOLID PHASE PORE DIFFUSIVITY TEMPERATURE DEPENDENCE

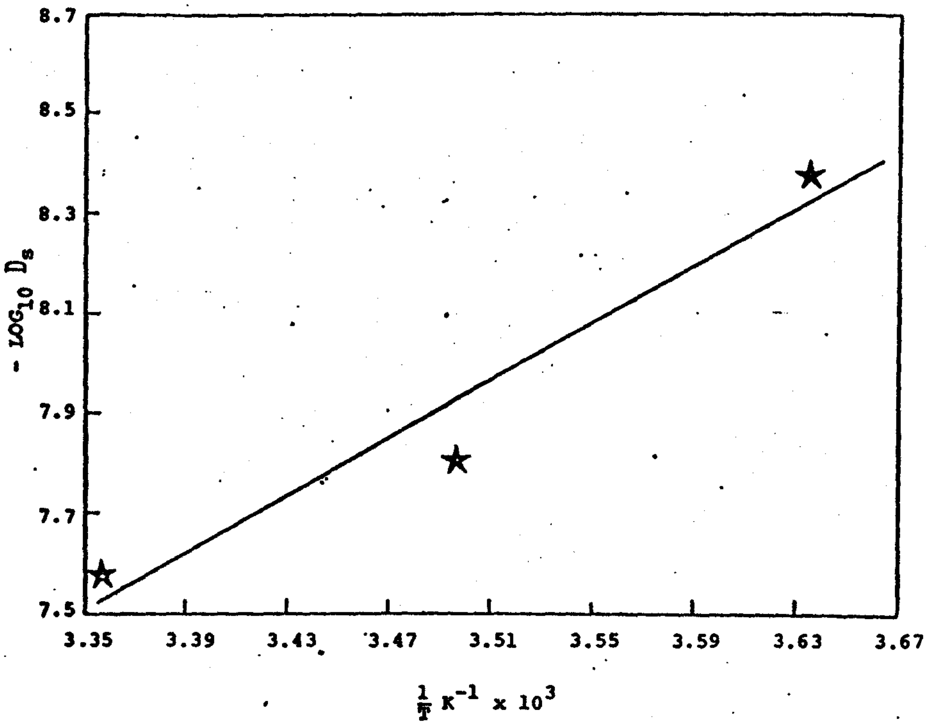


TABLE 11

COMPARISON OF SOLID PHASE PORE DIFFUSION COEFFICIENT AND BULK FLUID DIFFUSION COEFFICIENTS FOR SDS/GAC SYSTEM

Temperature in °C	Solid Phase Pore Diffusivity $\times 10^8$ in cm^2/sec	Bulk fluid Diffusivity $\times 10^6$ in cm^2/sec
2	0.64	2.50
13	2.70	3.61
25	3.76	5.06

Temperature coefficient = 6693 for solid phase pore diffusion

Temperature coefficient = 2533 for fluid diffusion

$$E_a = (\text{Temp. coeff.})\ (R)$$

$$= 6693 \times \frac{1.98}{1000}\ \frac{\text{kcal}}{\text{mole}} = 13.25\ \text{kcal/mole}$$

for solid phase pore diffusion

For fluid diffusion

$$E_a = 2533 \times \frac{1.98}{1000}\ \frac{\text{kcal}}{\text{mole}} = 5.02\ \text{kcal/mole}$$

4.3.4 COMPARISON OF THEORETICAL AND EXPERIMENTAL COLUMNAR KINETICS

Continuous flow column operations were conducted until equilibrium was established at three temperatures, 4°, 13° and 25°C. Due to variations in flow rate and initial solute concentration the results are plotted in terms of the mass of SDS applied to each adsorber.

SDS although presenting difficulties in analytical measurements, yielded consistent results. Some filtering action was expected to occur in columnar work with SDS due to its micellar nature. Increased loadings, however, were not discernible. The SDS concentration at which micelle starts to form is around 10^{-2}M or 2880 mg/l. The highest concentrations used during experimental study was 250 mg/l. Hence extensive micelle formation was not anticipated.

As shown in Figure 31, column kinetics are relatively insensitive, however, the observed temperature dependence confirms qualitatively the theory that low temperature slightly increases the saturation capacity, but decreases breakthrough time. Batch results showed similar trends where adsorptive capacity increases at low temperature, but rate of adsorption was affected adversely. The cumulative amount of SDS removed is calculated in Tables 35, 36, 37 for 4°, 13° and 25°C , respectively in Appendix 3. Figure 32 indicates again the insensitivity of loadings to temperature. Initially the

FIGURE 31

SDS CONCENTRATION RATIO VS ADSORBATE FED PROFILE

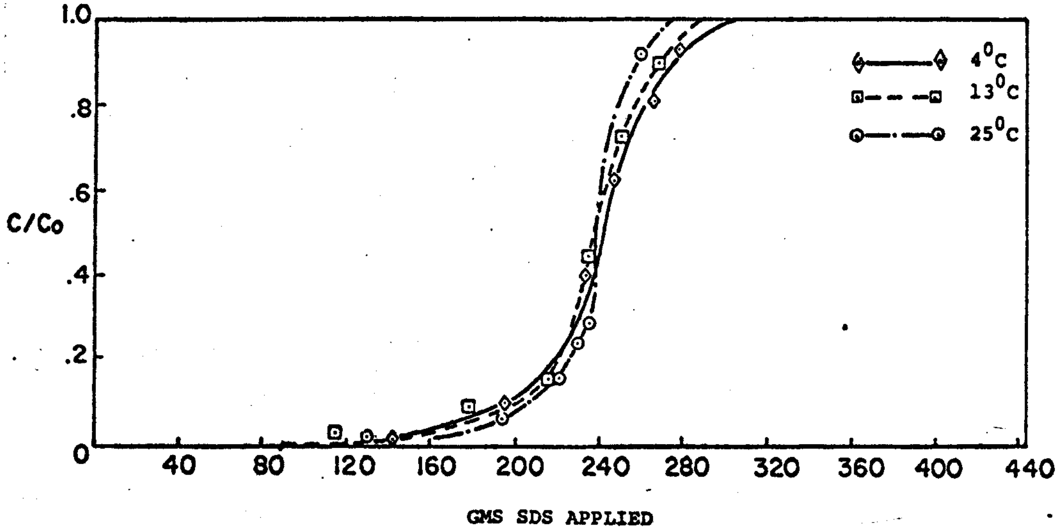
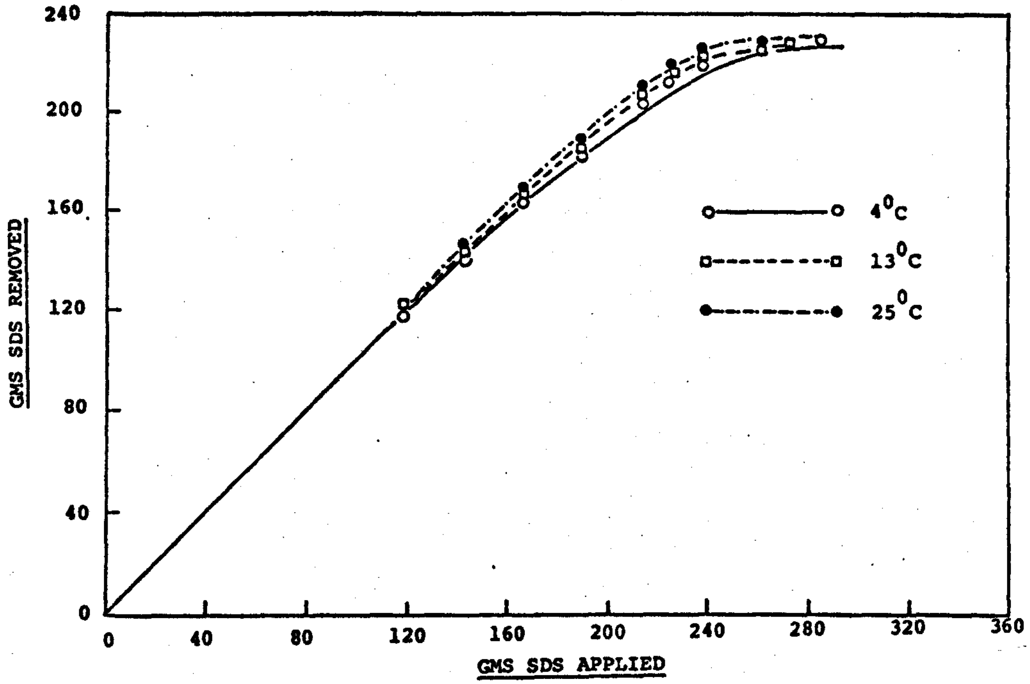


FIGURE 32

CUMULATIVE SDS ADSORBED VS SDS APPLIED



column removes the SDS completely, but rapidly reaches its saturation value. The loading values obtained are comparable to those attained in batch studies.

In an activated carbon column three zones can be distinguished. The equilibrium zone in the front where no mass transfer is taking place, the mass transfer zone (MTZ) in the middle where a concentration gradient exists between bulk liquid phase concentration and solid phase concentration and thirdly the unused zone where again no mass transfer is occurring. Breakthrough occurs when the leading edge of the mass transfer zone reaches the boundary of the bed. The S-shape curve obtained in Figure 31 is, therefore, the dynamic behaviour of the mass transfer zone as a function of time at a fixed point along the bed. The length of the MTZ is an indication of the difficulty of separation of contaminants from water. At low temperatures due to the adverse effect on kinetics, the mass transfer resistances are increased, which means that a longer residence time or height of MTZ is required to achieve the same separation efficiency. The actual MTZ is calculated on the basis of time required for the stoichiometric wave to exit from the column. This is between the breakthrough and the exhaustion points. The former is defined as the point where the pollutant concentration reaches the allowable discharge limit and the latter as the point where the column must be regenerated. Table 12 shows the variation in MTZ height with temperature. With the completion of the batch study phase and the derivation of the necessary input parameters,

TABLE 12

EFFECT OF TEMPERATURE ON EXPERIMENTALLY DERIVED MASS TRANSFER ZONE HEIGHTS

TEMPERATURE in ^{0}C	MTZ HEIGHT in cms
4	43.5
13	36.7
25	29.9

a theoretical modelling of adsorbers became possible. The reaction kinetics model, originally proposed by Thomas (1950), was used. An algorithm is shown in Table 13 describing, in brief, the step by step calculation. A detailed computer program describing the theoretical model is included in Appendix 6.

The predicted profiles calculated for the three temperatures are shown in Figure 33. The effect of temperature on theoretically derived columnar kinetics is much more pronounced than expected, based on experimental results. The results at 13° and 25°C seem reasonable, but at 2°C an instability in the model is noted. The extent of deviation from experimental results can be assessed by calculating the height of mass transfer zone as shown in Table 14. The values of 13°C and 25°C are comparable to that in Table 12, where as at 2°C an error of over 55% is seen.

The theoretical column capacities and the heat of adsorption calculated from those values are shown in Table 15.

The discrepancy obtained between the theoretical and experimental profiles was felt to depend upon the choice of parameter values utilized for modelling purposes. The sensitivity of the model to solid phase pore diffusivities and the Langmuir's constants, Q^o and b, were determined at all three temperatures. Table 16 shows the set of conditions which

TABLE 13

ALGORITHM USED FOR KEINATH AND WEBER MODEL

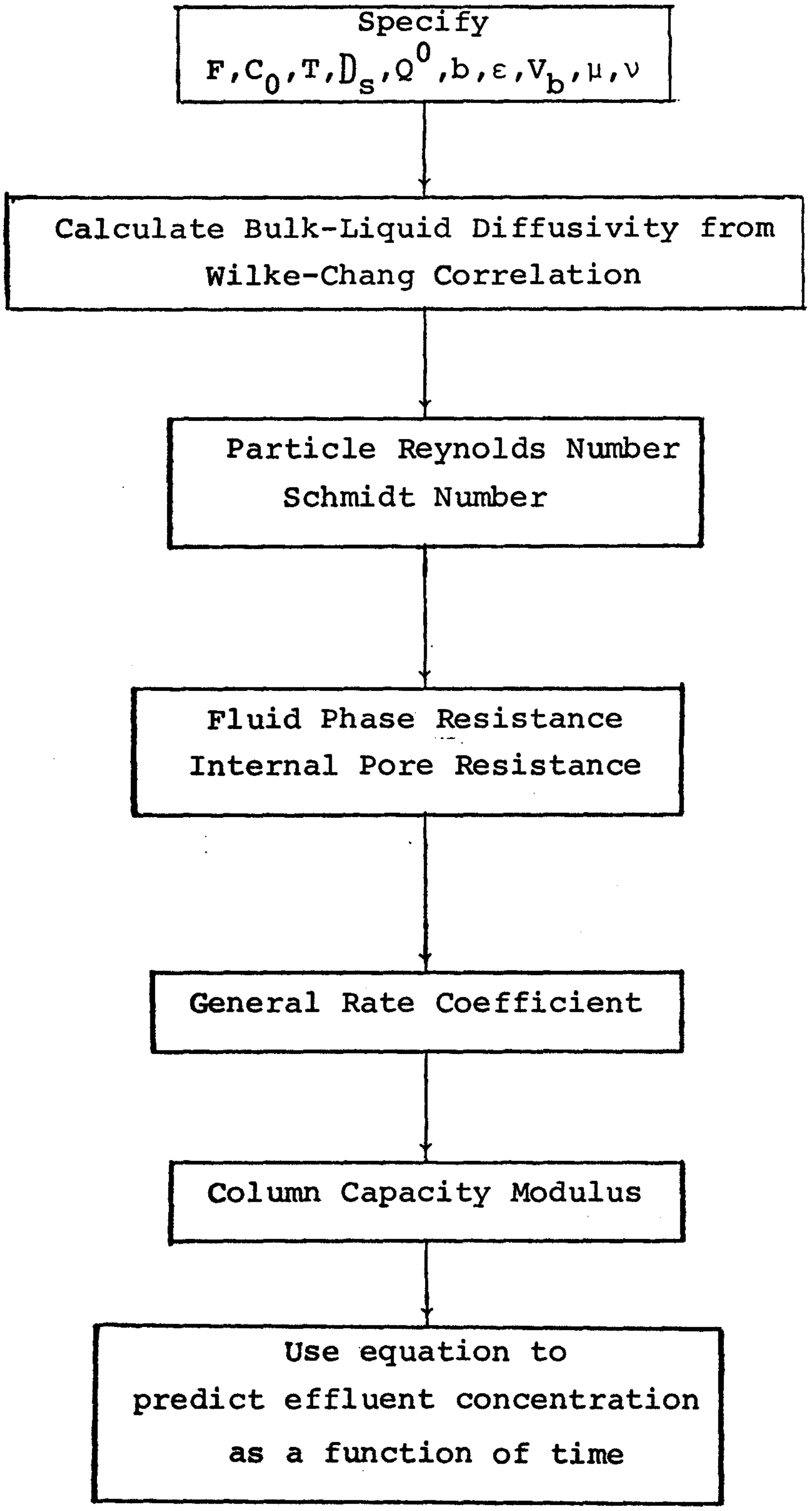


FIGURE 33

THEORETICAL EFFLUENT CONCENTRATION PROFILES GAC/SDS SYSTEM

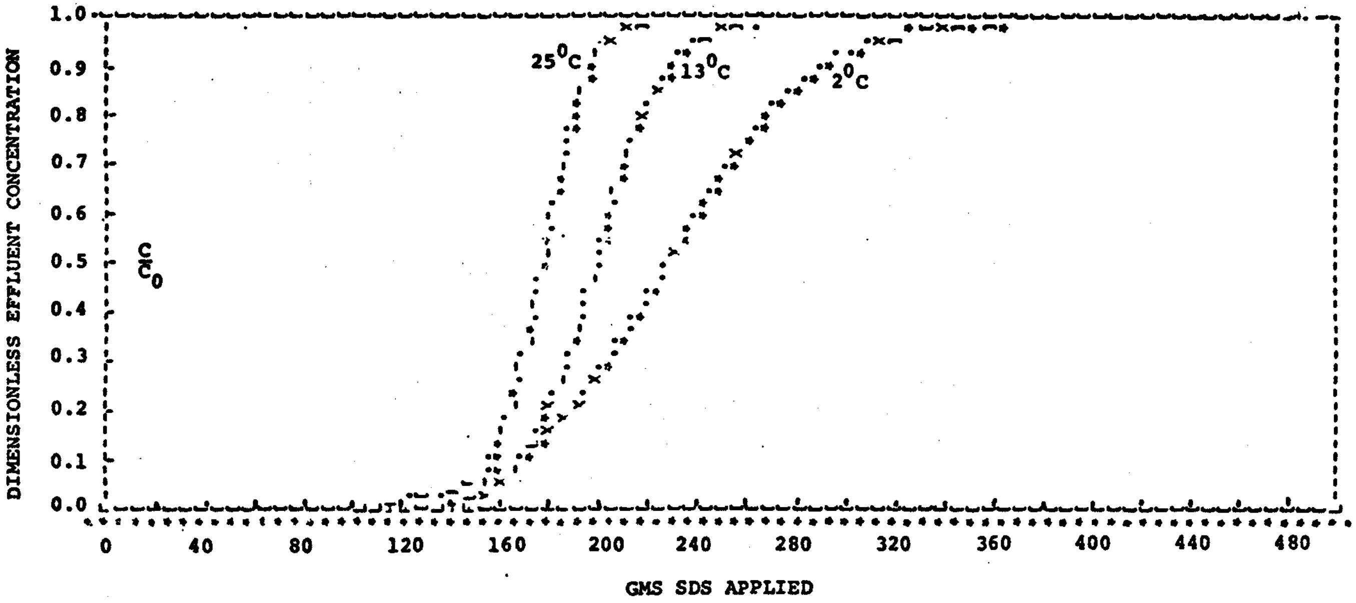


TABLE 14

CALCULATION OF MTZ HEIGHTS FOR THEORETICAL PREDICTIONS OF COLUMN EFFLUENT

TEMPERATURE in ^{0}C	MTZ HEIGHT in cms
2	67.2
13	41.4
25	30.8

Sample Calculation at 2^{0}C

Mass of SDS passed at breakthrough = 204 gms ($C/C_0 = 0.1$)

Mass of SDS passed at exhaustion = 364 gms ($C/C_0 = 0.9$)

Fraction of column where mass transfer is occuring

$$= \frac{364 - 204}{364} = 0.44$$

Total height of column = 5ft = 152.4 cm

Height of MTZ = 0.44 x 152.4 = 67.2

TABLE 15

HEAT OF ADSORPTION CALCULATED FROM THEORETICAL COLUMN EFFLUENT CONCENTRATION PROFILES

TEMPERATURE in ^{0}C	AMOUNT OF SDS REMOVED FROM COLUMN in gms	LOADING mg SDS/gm GAC
2	280.0	134.0
13	243.3	116.5
25	219.3	105.0

Weight of carbon in column = 2085 grams

Temperature coefficient from least squares analysis = -872

$$\Delta H = -\ 872 \times \frac{1.98}{1000} \times \frac{\text{kcal}}{\text{mole}} = -\ 1.73 \text{ kcal/mole.}$$

TABLE 16

LIST OF PARAMETER VALUES USED FOR SENSITIVITY TESTS

	Run No	Temperature in ^0C	$D_s \times 10^8$ cm^2/sec	b 1/mg	Ω^0 mg/g
	1A	2.0	0.640	0.0934	137.5
	1B	2.0	0.425	0.0934	137.5
	1C	2.0	0.230	0.0934	137.5
	2A	13.0	2.700	0.1230	120.0
	2B	13.0	1.560	0.1230	120.0
	2C	13.0	0.590	0.1230	120.0
	3A	25.0	3.760	0.1610	107.1
	3B	25.0	2.680	0.1610	107.1
	3C	25.0	1.370	0.1610	107.1
Base Conditions	4A	2.0	0.640	0.0934	137.5
	4B	13.0	2.700	0.1230	120.0
	4C	25.0	3.760	0.1610	107.1
	5A	2.0	0.640	0.0934	137.5
	5B	2.0	0.640	0.0934	127.0
	6A	2.0	0.640	0.0934	137.5
	6B	2.0	0.640	0.0189	137.5
	7A	13.0	2.700	0.1230	120.0
	7B	13.0	2.700	0.1230	112.0
	8A	13.0	2.700	0.1230	120.0
	8B	13.0	2.700	0.0894	120.0
	9A	25.0	3.760	0.1610	107.1
	9B	25.0	3.760	0.1610	107.0
	10A	25.0	3.760	0.1610	107.1
	10B	25.0	3.760	0.2800	107.1

were evaluated. In Runs 1a-c, 2a-c, 3a-c, the effect of D_s on the columnar kinetics was evaluated at 2°, 13° and 25°C respectively. Three values of D_s at each temperature were picked from Figure 29 and the profiles at 2°, 13° and 25°C are shown in Appendix 4 in Figures 64, 65 and 66, respectively. The pronounced effect occurs at 2°C, whereas at 13° and 25°C, the profiles are relatively independent of D_s values. In Table 17 a comparison of the two major contributing resistances to mass transfer is presented. At lower temperatures the solid phase pore diffusion is slow enough to be significant in affecting the total resistance and, therefore, the general rate coefficient. With increasing temperature it is seen that film resistance becomes the rate-controlling step. It is crucial, therefore, to have an accurate estimate of solid phase pore diffusivities at low temperatures due to greater sensitivity of the model to this parameter.

Since two methods were used to derive Langmuir's constants, Q^o and b, an attempt was made in Runs 5-10 to see how significantly these variables affect the effluent concentration profile at all three temperatures. Runs 5a, b, 7a, b and 9a, b are plotted in Figures 67, 68 and 69 in Appendix 4. An increase in Q^o simply changes the final loading on the column. The S-shape profile is not seriously affected. At 2°C the effect is again the strongest. The effect of b, Langmuir's velocity constant is more interesting, as it is directly related

TABLE 17

COMPARISON OF FILM AND SOLID PHASE PORE DIFFUSION RESISTANCES

TEMPERATURE in ^0C	FILM DIFFUSION RESISTANCE in secs	SOLID PHASE PORE DIFFUSION RESISTANCE in secs
2	36.9	27.9
13	28.8	7.72
25	22.9	3.64

to columnar kinetics through the general rate coefficient. Run 6, 8, 10 are shown in Figures 70 to 72 in Appendix 4. The most pronounced effect of b on general rate coefficient and the profile shape occurs at 2°C, as seen from Table 18. At the other two temperatures an over fifty per cent increase or decrease in value of b produces no overall change in shape of predicted profiles.

An estimate of the activation energy predicted theoretically can be made by assuming an Arrhenius type temperature behaviour for the general rate coefficients. Table 19 shows the computation and a value of 6.3 kcal/mole was derived using least squares analysis.

To estimate temperature dependence of experimentally derived column effluent profiles, a backcalculating method was used. Essentially a trial and error search was carried out to obtain that value of κ, the general rate coefficient, which then defined a certain S-curve, having a mass transfer zone height equivalent to that experimentally obtained. An initial κ value was specified, and the MTZ height calculated. This was compared to an observed value of MTZ.

If the absolute difference was greater than a specified tolerance, the search was started again with a new κ value based on the previous values. The program terminated when the calculated MTZ height matched the observed value within a tolerance limit. Details of the procedure are included in Appendix 6.

TABLE 18

EFFECT OF 'b' ON GENERAL RATE COEFFICIENTS

TEMPERATURE : 2^0C

b 1/mg	GENERAL RATE COEFFICIENT in sec^{-1}
.0189	.0263
.0934	.0297

TEMPERATURE : 13^0C

b 1/mg	GENERAL RATE COEFFICIENT in sec^{-1}
.1230	.0531
.0894	.0526

TEMPERATURE : 25^0C

b 1/mg	GENERAL RATE COEFFICIENT in sec^{-1}
.1610	.0722
.2800	.0734

The estimated rate coefficients from experimentally derived column effluent concentration profiles are tabulated in Table 19 as well. Theoretical and expermental κ values are quite close at 13° and 25°C, with greatest discrepancy at 2°C, as expected. A relatively low activation energy of 3 kcal/mole is estimated indicating low temperature sensitivity of activated carbon adsorption.

TABLE 19

COMPARISON OF THEORETICAL AND EXPERIMENTAL GENERAL RATE COEFFICIENTS FOR SDS/GAC SYSTEM

TEMPERATURE in ^{0}C	GENERAL RATE COEFFICIENT in sec^{-1} From Theoretical Model	GENERAL RATE COEFFICIENT in sec^{-1} From Experimental Estimate
2	.0297	.0497
13	.0531	.0608
25	.0720	.0768

Assuming Arrhenius type relationship

$$\kappa = Ae^{-E_a/RT}$$

Using least squares analysis

Temperature coefficient = 3174 for theoretical model

Temperature coefficient = 1556 for experimental model

E_a = 6.28 kcal/mole from theoretical prediction

E_a = 3.08 kcal/mole from experimental data

4.4 SUMMARY AND CONCLUSIONS

1. Batch agitated systems, as well as continuous flow systems, indicate a low order temperature dependence effect.

Heat of adsorption from batch isotherms was calculated to be -1.8 kcal/mole indicating weak, "physical" type of bonding. The effect of temperature on columnar kinetics was evaluated using the general rate coefficient and the mass transfer zone height concept. The activation energy computed from experimental columnar work was 3.1 kcal/mole.

2. Generally, theoretical modelling of column effluent concentrations proved to be adequate, except at 2°C. A good match is obtained for mass transfer zone heights. A reasonable agreement between predicted and experimentally determined general rate coefficients is also obtained. Heats of adsorption and activation energies predicted theoretically, yield acceptable values when compared to experimental data.

3. The inadequate match obtained at 2°C between theoretical and experimental column profile is attributed to a low D_s value obtained from Tien's method. The ratio of intraparticle diffusion resistance to film diffusion resistance is significantly higher at 2°C. Hence, the general rate coefficient is more sensitive to D_s than at other temperatures. One reason for the low D_s value obtained in Figure 29 is obviously the experimental data, in particular the batch isotherm at 2°C.

4. Tien's method for estimating solid phase pore diffusion coefficients, although remarkably simple and applicable to generalized adsorption isotherm, possesses serious disadvantages. Meier (1972) has noted in using Tien's method that a wide variation is seen in D_s values with time. Since a constant D_s value is assumed to solve the partial differential equations governing the batch adsorption system, the entire solution is rendered theoretically invalid.

CHAPTER 5

THE EFFECT OF LOW TEMPERATURE ON CONTINUOUS PHYSICO-CHEMICAL TREATMENT OF DOMESTIC WASTEWATER

5.1 INTRODUCTION

The batch feasibility study undertaken in Chapter 3 and the continuous column operations on a pure compound presented in Chapter 4 showed that temperature had a relatively weak effect on both adsorption equilibria and kinetics.

Single solute systems, however, are not necessarily representative of complex systems, such as domestic wastewater. The need, therefore, arises to study the effect of low temperature on domestic sewages directly.

For the purposes of rigorous comparison, one should treat the types of sewages anticipated in the Arctic conditions, which as illustrated in Chapter 1.1, are significantly more concentrated and of a more fluctuating nature than those found in Southern Ontario. Due to practical constraints, the Dundas Water Pollution Control Centre was chosen as the location for the pilot PCT plant.

Even though the sewage strength is comparatively low, valuable information can still be gained on the magnitude of the temperature effect in columnar operations.

Up to this point, the project had almost exclusively dealt with physical and chemical removal mechanisms. With the presence of bacteria in wastewaters, the availability of organic carbon and nutrients, and a detention time far greater than the hydraulic contact time, biological growth was expected to manifest itself. This phenomenon, as reported by earlier researchers, considerably enhances the adsorptive life of the carbon, although it complicates the analysis of the overall performance of the bed.

An attempt is made, albeitly, of a preliminary nature to model carbon adsorbers where not only pure adsorption is taking place, but also biological degradation and renewal of carbon surfaces by bacterial action. Batch studies were conducted to determine reaction rates and oxygen uptake requirements, in order to understand columnar behaviour. Microbiological studies on exhausted carbon were carried out to obtain a picture of the fauna inside carbon beds, and derive some quantitative measurements for modelling purposes.

Some of the objectives of the present phase of the study are listed below:-

i) To show feasibility of PCT of domestic wastewater at low temperatures, using continuous flow granular activated carbon beds.

ii) To observe and compare the extent of enhancement of removal capacities of GAC at low and high temperatures.

iii) To study the phenomenon of denitrification inside columnar beds and evaluate its temperature dependence.

iv) To develop a general theory, which explains the complex inter-relationship between adsorption and microbial activity based on observed facts.

v) To obtain batch data on adsorption equilibria, kinetics, reaction rates in aerobic and anaerobic environments, oxygen uptake rates, at both low and high temperatures.

vi) To gain a microbiological perspective on the nature and type of predominant bacterial species, in activated carbon beds.

5.2 THEORY

MODELLING OF FIXED-BED REACTORS IN THE PRESENCE OF BACTERIAL ACTIVITY

Consider the fixed-bed problem, as shown in Figure 34. Fluid enters at the bottom of the column at a velocity of U_s cm/min. and a contaminant concentration of C mg/l. The liquid phase volume fraction of the bed is ε and the length of the fixed bed reactor is L cm. To determine the set of equations governing the relationships between the fluid and the bed, a mass transfer balance is made across a control element of arbitrary thickness Δz . Since bacterial action is incorporated in this model, three distinct phases are noted. The solute (pollutant) exists not only in the bulk fluid phase, but also in the bacterial film phase, which surrounds the carbon particles, and lastly inside the adsorbent or solid phase. The material balance, which is, therefore, expressed in equation 40, accounts in a general way for the distribution of solute within the control volume, with axial dispersion neglected.

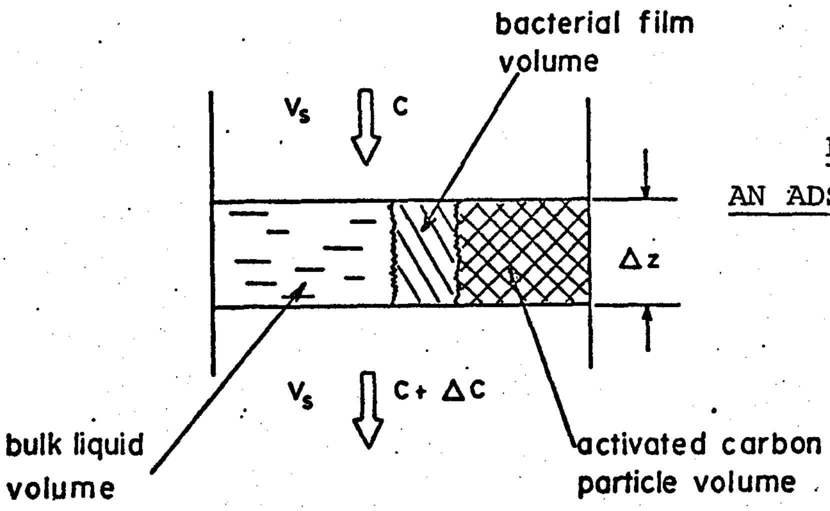


FIGURE 34

AN ADSORBER SEGMENT

(V_s = superficial column velocity, C = solute concentration in fluid phase, Δz = incremental bed height, ΔC = change in C over Δz).

$$U_sAC - U_sA(C+\frac{\Delta C}{\Delta z}\Delta z) - R_1(\varepsilon A\Delta z) - \frac{6}{d_p}(1-\varepsilon-\frac{6\delta}{d_p}(1-\varepsilon))R_fA\Delta z$$

$$-R_s(1-\varepsilon-\frac{6\delta}{d_p}(1-\varepsilon))A\Delta z = \varepsilon A\Delta z\frac{\Delta C}{\Delta t} + \frac{6\delta}{d_p}(1-\varepsilon-\frac{6\delta}{d_p}(1-\varepsilon))A\Delta z\frac{\Delta C_f}{\Delta t}$$

$$+\zeta_bA\Delta z(\Delta\bar{q}/\Delta t) \qquad (40)$$

where ε = Liquid phase volume fraction of column

A = Columnar cross-sectional area

d_p = Particle diameter

δ = Bacterial film thickness

R_1 = Bacterial reaction rate in fluid phase per unit volume of fluid

R_f = Film phase degradation rate per unit surface area of carbon particles

R_s = Bacterial reaction rate inside solid particle per unit volume

C_f = Solute concentration in film phase (variable with film thickness)

$\bar{q}$ = Average solute concentration in solid phase

Δt = Time increment

The first term in equation 40 is simply the total solute input, the second term is what exits from the control volume after having been changed by ΔC. $\varepsilon A\Delta z$ is the void volume (or liquid volume), hence the third term represents the solute lost due to bacterial oxidation in the liquid phase. The surface area for bacterial growth is calculated by assuming a spherically shaped carbon particle. Since the surface to volume ratio for a sphere is (6/dp) and solid volume is $(1-\varepsilon)A\Delta z$ (including the bacterial film and the AC particle), the fourth term in equation 40 corresponds to the solute in the bacterial film phase.

The solute degraded inside the carbon particles is given by the fifth term. Besides degradation, accumulation also occurs in the three phases. The sixth term represents the solute accumulation in the liquid phase. The volume of the bacterial film is estimated by assuming a spherical shell.

Volume ratio of film to particle is given by;-

$$\left(\frac{4}{3}\pi\left(\frac{d_p}{2}+\delta\right)^3-\frac{4}{3}\pi\left(\frac{d_p}{2}\right)^3\right)/\left(\frac{4}{3}\pi\left(\frac{d_p}{2}\right)^3\right)$$

$$= 6\frac{\delta}{d_p} + 12\frac{\delta^2}{d_p^2} + 8\frac{\delta^3}{d_p^3}$$

Assuming $\frac{\delta}{d_p}$ is less than 0.01 the higher order terms are neglected and accumulation in bacterial film phase estimated by the seventh term. Finally, the solid phase accumulation is given based on the average loading over the entire particle.

To proceed further in solving Equation 40, certain simplifying assumptions have to be made:-

i) Due to the small relative numbers of bacteria in the bulk liquid (after sand filtration) versus the number of bacteria in the film around the particles and the relatively short residence time available for significant degradation to take place in the bulk liquid phase in the column, the third term in Equation 40 is neglected altogether.

ii) Solid phase degradation has been postulated by various researchers. The author is of the opinion that this is, at best, insignificant in the degradation mechanism. Strong theoretical evidence points towards the inability of bacteria to penetrate the porous structure of the carbon. Enzymatic breakdown would, therefore, have to be the method by which degradation takes place inside the carbon particle. The nature of this mechanism is speculative and will be raised in later sections.

iii) A further assumption made is that accumulation of solute inside the bacterial film does not occur. In this model, any material, which is not degraded inside the film, is assumed to pass onto the carbon particle.

The simplified equation thus assumes the following form after dividing by $A\Delta z$

$$-U_s\frac{\partial C}{\partial z} - \frac{6}{d_p}\left(1-\varepsilon-\frac{6\delta}{d_p}(1-\varepsilon)\right)R_f = \varepsilon\frac{\partial C}{\partial t} + \zeta_b\frac{\partial \bar{q}}{\partial t} \qquad (41)$$

An additional equation can be derived from a radial shell balance in the bacterial film, as shown in Figure 35. The accumulation in the film is equal to mass transport flux, minus the degradation inside the film.

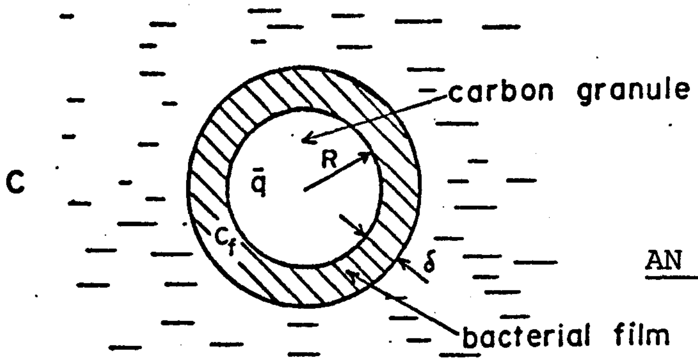


FIGURE 35

AN ACTIVATED CARBON GRANULE

δ = bacterial film thickness, R = carbon granule radius, C_f = solute concentration in film phase, $\bar{q}$ = average solute concentration in solid phase

thus:

$$\frac{\partial C_f}{\partial t} = D\nabla^2 C_f - \frac{R_f}{\delta} \qquad (42)$$

If we neglect the curvature of the shell (thin film on a relatively large sphere) and consider one dimensional mass transfer in the radial direction only, we get at steady state.

$$D\frac{\partial^2 C_f}{\partial r^2} = \frac{R_f}{\partial} \, , \qquad = K_0 \qquad (43)$$

Integrating Equation 43 yields

$$\frac{\partial C_f}{\partial r} = \frac{K_0 r}{D} + a_1 \qquad (44)$$

Further integration leads to

$$C_f = \frac{K_0}{D}\frac{r^2}{2} + a_1 r + a_2 \qquad (45)$$

The boundary conditions used to derive the constants a_1, a_2 in Equation 45, are obtained by assuming that the bacterial film resistance is the rate controlling mechanism.

Hence at $r = R + \partial$, $C_f = C$

at $r = R$, $C_f = C_s$

$$\therefore \quad C = \frac{K_0}{D}\frac{(R + \partial)^2}{2} + a_1(R + \partial) + a_2$$

$$C_s = \frac{K_0}{D}\frac{R^2}{2} + a_1 R + a_2$$

Solving for a_1

$$a_1 = \frac{1}{\partial}\left(C - C_s - \frac{K_0}{2D}\left(2R\partial + \partial^2 \right) \right) \tag{46}$$

The solute accumulation in the solid particle occurs through diffusion at $r = R$

$$\therefore \quad A_p\, D \left.\frac{\partial C_f}{\partial r}\right|_{r = R} = \zeta_b \frac{\partial \bar{q}}{\partial t} \tag{47}$$

From Equation 44

$$\left.\frac{\partial C_f}{\partial r}\right|_{r = R} = \frac{K_0}{D} R + a_1 \tag{48}$$

$$\therefore \quad \frac{\partial \bar{q}}{\partial t} = \frac{A_p D}{\zeta_b}\left(\frac{K_0}{D}R + \frac{1}{\delta}\left(C - C_s - \frac{K_0}{2D}(2R\delta + \delta^2)\right) \right)$$

$$= \frac{A_p D}{\zeta_b \delta}\left(C - C_s - \frac{K_0 \delta^2}{2D} \right) \tag{49}$$

The other Equations relating the variables are:-

$$Q_s = f\,(C_s) \tag{50}$$

which is the equilibria relationship between liquid phase concentration and solid phase concentration at the surface of the particle.

Also a kinetic type, first order relation is assumed for pore diffusion:-

$$\frac{\partial \bar{q}}{\partial t} = k_p a_p \, (q_s - \bar{q}) \qquad (51)$$

Where $k_p a_p$ intra-particle mass transfer rate

Equations 41, 49, 50, 51 are the set of four independent equations, which define the problem involving four variables C, C_s, Q, Q_s and is theoretically solvable provided the physical parameters are known.

An algaebraic substitution is made by change of variables

$$\lambda = \zeta_b z/U_s$$

$$\theta = t - \frac{z\varepsilon}{U_s}$$

using fundamental properties of partial diffentials

$$\frac{\partial C}{\partial z} = (\frac{\partial \lambda}{\partial z})(\frac{\partial C}{\partial \lambda})_\theta + (\frac{\partial \theta}{\partial z})(\frac{\partial C}{\partial \theta})_\lambda$$

$$= \frac{\zeta_b}{U_s}(\frac{\partial C}{\partial \lambda})_\theta - \frac{\varepsilon}{U_s}(\frac{\partial C}{\partial \theta})_\lambda$$

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \lambda}\frac{\partial \lambda}{\partial t} + \frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial t} = 0 + \frac{\partial C}{\partial \theta} = \frac{\partial C}{\partial \theta}$$

Similarly

$$\frac{\partial \bar{q}}{\partial t} = \frac{\partial \bar{q}}{\partial \theta}$$

Re-arranging Equation 41 using the new variables one obtains

$$(\frac{\partial q}{\partial \theta})_\lambda + (\frac{\partial C}{\partial \lambda})_\theta + \frac{6(1-\varepsilon)(1-6\,\frac{\delta}{d_p})R_f}{d_p \zeta_b} \qquad (52)$$

Equation 49 becomes

$$\left(\frac{\partial \bar{q}}{\partial \theta}\right) = \frac{A_p D}{\delta \zeta_b} \left(C - C_s - \frac{K_0 \delta^2}{2D} \right) \tag{53}$$

Equation 50 remains unchanged and equation 51 is represented by the following:-

$$\left(\frac{\partial \bar{q}}{\partial \theta}\right) = k_p a_p \left(q_s - \bar{q} \right) \tag{54}$$

The whole problem is next rendered dimensionless by introducing reduced variables:-

$y = \bar{q}/q_\infty$	reduced solid phase concentration
$x = C/C_0$	reduced fluid phase concentration
$x_s = C_s/C_0$	reduced fluid phase concentration at the surface
$y_s = q_s/q_\infty$	reduced solid phase concentration at the surface
$\xi = z/L$	reduced distance along the column
$\tau = \theta U_s/L\varepsilon$	reduced time
$q_\infty =$	loading at saturation
$C_0 =$	solute concentration at q_∞

Equation 53 is transformed to:-

$$\frac{\partial (\bar{q}/q_\infty)\; q_\infty}{\partial \left(\frac{\theta U_s}{L\varepsilon}\right) \frac{L\varepsilon}{U_s}} = \frac{A_p D C_0}{\delta \zeta_b} \left(\frac{C}{C_0} - \frac{C_s}{C_0} - \frac{K_0 \delta^2}{2 D C_0} \right)$$

or

$$\frac{\partial y}{\partial \tau} = K_2 \left(x - x_s - K_1 \right) \tag{55}$$

where $$K_1 = \frac{K_0\delta^2}{2DC_0}$$

and $$K_2 = \frac{A_p D L\varepsilon C_0}{\delta\zeta_b q_\infty U_s}$$

Equation 54 is reduced to:-

$$\frac{\partial(\bar{q}/q_\infty)q_\infty}{\partial\left(\frac{\theta U_s}{L\varepsilon}\right)\frac{L\varepsilon}{U_s}} = k_p a_p q_\infty (q_s/q_\infty - \bar{q}/q_\infty)$$

or $$\frac{\partial y}{\partial\tau} = K_3\,(\,y_s - y\,) \tag{56}$$

where $$K_3 = k_p a_p \frac{L\varepsilon}{U_s}$$

Equation 50 assumes the following form

$$y_s = f(x_s) \tag{57}$$

Finally, equation 52 is transformed in the following manner:-

$$\frac{\partial(\bar{q}/q_\infty)q_\infty}{\partial\left(\frac{\theta U_s}{L\varepsilon}\right)\frac{L\varepsilon}{U_s}} = -\frac{\partial(C/C_0)C_0}{\partial\left(\frac{\lambda U_s}{\zeta_b L}\right)\frac{\zeta_b L}{U_s}} - K_4$$

or $$\frac{\partial y}{\partial\tau} = -K_5\frac{\partial x}{\partial\xi} - K_6 \tag{58}$$

where $$K_4 = \frac{6(1-\varepsilon)(1-6\frac{\delta}{d_p})R_f}{d_p\zeta_b}\;,\; K_5 = \frac{\varepsilon C_0}{\zeta_b q_\infty}\;,\; K_6 = \frac{L\varepsilon}{U_s q_\infty}K_4$$

The problem now reduces to solving the equations 55, 56, 57 and 58.

The solution is obtained through numerical integration using explicit forward finite difference approximations to the differential equations.

The equations are re-arranged as:-

$$\frac{\partial y}{\partial \tau} = K_3(f(x_s) - y) \qquad (59)$$

$$x_s = (x - K_1) - \frac{1}{K_2} \frac{\partial y}{\partial \tau} \qquad (60)$$

and

$$-K_5 \frac{\partial x}{\partial \xi} = \frac{\partial y}{\partial \tau} + K_6 \qquad (61)$$

A simplified algorithm is included in Appendix 6, illustrating the method used to solve the above system of simultaneous differential equations.

5.3 EXPERIMENTAL

The details of the pilot plant operation, batch studies, the microbiological investigations and the analytical techniques used are presented in this section.

5.3.1 PILOT PLANT OPERATION

The pilot plant was located in the basement of the Dundas Water Pollution Control Centre. 300 litres of screened and degritted raw sewage was collected daily by syphoning into a 350 litre polyethylene tank. The tank was equipped with a 4 baffle paddle connected to a 1/6 HP motor. The width of each baffle was 2 inches and the ratio of the area spanned by the paddle to the tank was 0.23. The paddle height was adjusted so that the bottom edge of the paddle was a 1/4 of the tank height above the base. 57 gms of alum ($Al_2(SO_4)_3 \cdot 16H_2O$) was dissolved in 1 litre of water and added to 300 litres of the collected sewage to yield an alum dosage of 190 mg/l. The contents of the tank were stirred for 5 minutes at the maximum power output of the motor which gave a stirring rate of 31 RPM. Following the mixing of alum, 30 mls of a freshly prepared 3000 mg/l polymer solution of Percol 730 were added to the sewage tank to yield a flocculant dosage of 0.3 mg/l. The maximum stirring speed was maintained for a duration of 1 minute to allow the polymer to mix rapidly. After this period, the stirring rate was reduced to a 1/4 of the maximum motor power output which gave a stirring rate of 7 RPM. Slow stirring was used to prevent floc shearing and enabling the particles to flocculate. After 14 minutes of slow mixing, the motor was shut off and the flocs allowed to settle quiescently for the next 40 minutes. The clarified effluent (supernatant) was pumped through a sand filter (4"i.d. Lucite column, 10" sand depth (sand obtained from Burlington Water Pollution Control Center)) at a flow rate of 4 USGPM/ft^2 and collected in another 350 litre polyethylene tank. The sand filter was backwashed daily before use at a flow rate of 10 USGPM/ft^2.

Following sand filtration the sewage was fed to two parallel sets of granular carbon adsorbers. Equal flow rate of 1 USGPM/ft^2 was acheived through both sets of adsorbers by a dual head Masterflex pump (Model No. WZ1R031). Through the first set of columns sewage was fed at 5^{0}C, by passing through a refrigeration chamber described in Figure 19, whereas the second set of columns received sewage which had been circulated through a water bath maintained at 25^{0}C, by a Haake temperature controller (Model ED$_e$ 60626).

Each set of adsorbers consisted of three identical 2" i.d. Lucite columns, 10 ft high. The lead column was packed with 2 ft and the other two columns were filled with 5 ft of Filtrasorb 400. In the low temperature adsorbers, 2" thick tubular glass fibre insulation were put around each column. The feed between each column was recooled in the refrigeration chamber.

Both sets of adsorbers were operated in an upflow mode due to the pressure drops expected from bacterial growth. Backwashing of carbon columns was infrequent, depending on build up of solids inside columnar beds.

A schematic of the entire pilot plant is shown in Figure 36. The PCT pilot plant had therefore a daily batch coagulation, flocculation, sedimentation and sand filtration step, whereas the carbon adsorption was continuous.

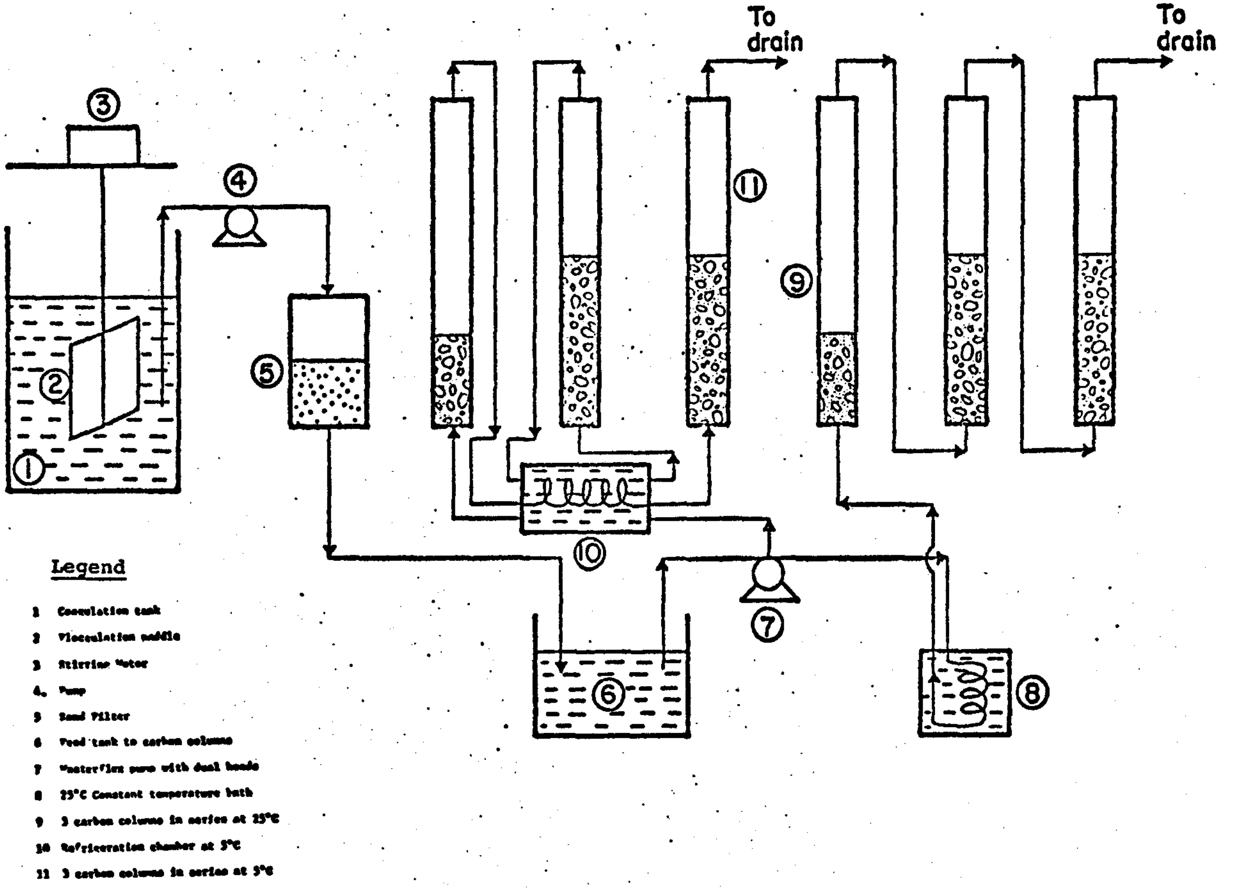
For an initial period coagulation was not necessary, as alum was already being added upstream as part of the research activities associated with the Canada-Ontario Agreement Phosphate Removal Program. During this phase sewage was collected at the end of the primary clarifier to allow for coagulation and sedimentation.

To study denitrification inside the carbon columns it was felt that the nitrate content of fresh sewage was too low. Thus 40 mg/l of sodium nitrate as NO_3^- were added daily to the carbon column feed.

Daily samples were collected of the feed to the carbon columns and the effluent from each bed. These were either analyzed immediately or refrigerated for later analysis.

FIGURE 36

SCHEMATIC VIEW OF DUNDAS PILOT PCT PLANT



5.3.2 BATCH REACTORS STUDY

Lab studies were run to obtain data which would enable estimation of parameters for modelling purposes.

5.3.2.1 Adsorption Isotherms

100 ml of .45μ membrane filtered sewage was contacted with granular activated carbon (Filtrasorb 400) in 250 ml vessels. The carbon dosages varied from 50 mg/l to 4000 mg/l. Agitation was achieved through magnetic stirrers. A set of vessels were used for two temperature runs at 5° and 25°C. One of the nine vessels contained no carbon and was used as a blank. The vessels were placed in a water bath for temperature control, as described in Chapter 4. After twenty-four hours of contact, the flasks were removed and carbon filtered out of the solution by a .1μ membrane filter. The filtrate was analyzed for TOC using an ultra-violet oxidation technique, described in Appendix 1.

5.3.2.2 Adsorption Kinetics

A two litre vessel was filled with .45μ membrane filtered sewage and placed in a constant temperature water bath on top of a magnetic plate.

5 gms of carbon (Filtrasorb 400) were added and the system well-agitated. 10 mls of solution were withdrawn as a function of time, and filtrate analysed for TOC. Kinetics were conducted at two temperatures, 5° and 25°C.

5.3.2.3 Regeneration Studies

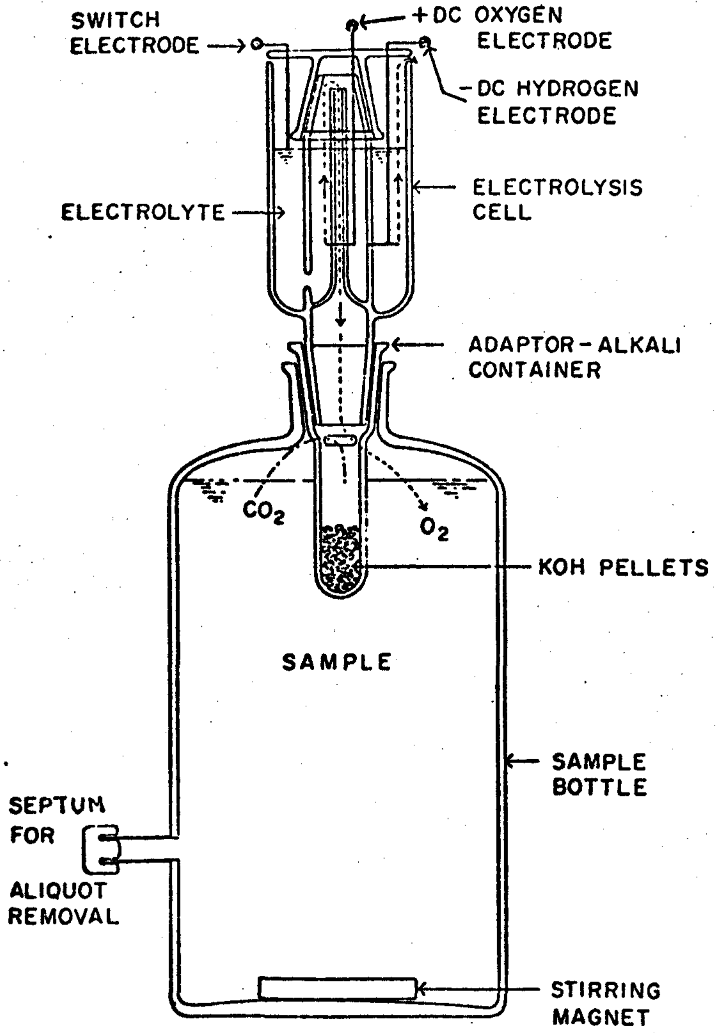
Twenty litres of fresh, sand filtered sewage was collected from Dundas Pilot Plant facility and filtered through .45µ membrane filters to remove bacteria.

Two 4 litre volume flasks were filled with the above sewage and the rest refrigerated. The two flasks were kept in separate constant temperature baths, one at 5°C and the other at 25°C. After temperature stabilization, 2 gms of Filtrasorb 400 were added to both flasks and the carbon allowed to adsorb to its maximum capacity. Following forty-eight hours of contact, the carbon was collected on a Whatman No.1 filter paper and drained. A portion of the collected carbon was used to measure moisture content by drying in an oven.

Two 1 litre reactors were next prepared containing the .45µ filtered sewage refrigerated earlier. To one reactor, a 10 ml activated sludge seed was added. The other reactor contained no seed, except for accidental bacterial contamination, which might have occurred. Both reactors were then contacted with 10 gms of the saturated wet carbon collected earlier. Iron, Calcium, Magnesium in small quantities, as well as phosphate buffer, were introduced to provide a suitable environment for bacterial growth. The two reactors were part of an electrolytic BOD respirometer (Oceanography International Corp. Model No. 6356), as shown in Figure 37. Oxygen is produced by an electric current, and the amount of oxygen produced monitored continuously. Oxygen uptake rates and TOC removal

FIGURE 37

SCHEMATIC DIAGRAM SHOWING THE BASIC OPERATION OF THE ELECTROLYSIS SYSTEM FOR MEASURING BOD



were observed, as it was felt that biological regeneration of carbon surface would occur. The carbon adsorption and substrate removal was allowed to continue until no further oxygen was being consumed.

This procedure was carried out at two temperatures, 5° and 25°C. At 5°C the cells were submerged in a separate water bath, the 25°C temperature was obtained with the respirometer's bath. After the establishment of equilibrium, the carbons were removed and their respective adsorptive capacities measured by the iodine number tests.

A portion of the carbon from regeneration studies was then used for isotherm studies for comparison purposes. One set of equilibria runs were conducted with regenerated carbon and the other with carbon which had no bacterial growth on it. Sewage collected earlier and preserved with mercuric sulfate was used during these runs.

Similar experiments were run at both 5° and 25°C. Further details on the regeneration studies are given by Najak and Benedek (1974).

5.3.3 STUDY ON CARBON FROM EXHAUSTED COLUMN

After nearly complete exhaustion, the pilot plant was shut down, and carbon samples were removed from each of the three columns of the two sets of adsorbers.

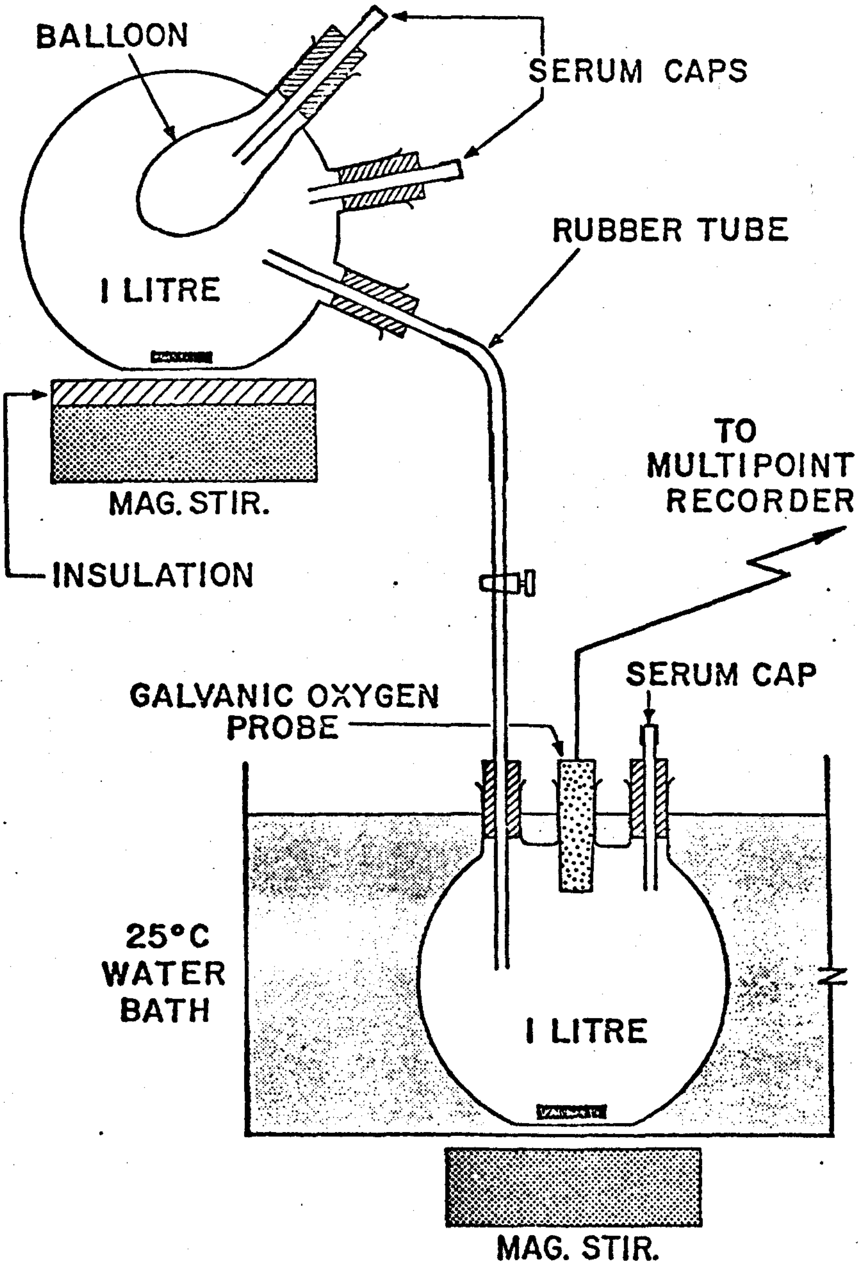
The carbon from the lead column was used to obtain some rough estimate of removal rates at the two temperatures, 5° and 25°C.

Two 1 litre round bottom flasks were filled with concentrated, sand filtered sewage and kept in a constant temperature room at 25°C. One reactor was maintained anaerobic by stripping out the dissolved oxygen (DO) with nitrogen, and the other was aerated with pure oxygen to DO levels of 20-30 mg/l.

An oxygen probe was fitted to the aerobic reactor and DO level monitored continuously with a Honeywell Multi-point Chart Recorder, as shown in Figure 38. Five grams of carbon from the lead column of 25°C adsorbers was added to both the anaerobic and aerobic reactors. Samples were taken periodically and analysed for TOC. Duplicate studies were run at 5°C using carbon from the 5°C lead column. All necessary nutrients and buffer were present in the reactors, based on Standard Methods (1973) BOD nutrient recommendations. Since the exhausted carbon presumably contained large numbers of bacteria, it was expected that regeneration would occur. The reactors were, therefore, allowed to run for close to ten days. After no further oxygen uptake was observed, the carbon was removed and iodine number tests were conducted for subsequent comparison to the iodine numbers obtained from exhausted carbon, which had not been further regenerated in batch reactors.

FIGURE 38

SCHEMATIC OF BATCH BIOLOGICAL REACTORS



5.3.4 MICROBIOLOGICAL INVESTIGATIONS

The carbon from the lead and last columns at both temperatures were examined for presence of bacterial activity.

Direct microscopic examination was carried out by observing small amount of the smallest carbon particles under Olympus phase-contrast microscope, using x100 and x400 magnifications.

Cultural investigations of the number of bacteria in the columns was embarked upon next. The lead and the last columns at 25°C were denoted as H_1 and H_3, respectively. Similarly, the lead and last columns at 5°C were denoted as L_1 and L_3, respectively. 2.5 gram portions of drained activated carbon from H_1, H_3, L_1, L_3 columns were mixed with 250 ml of sterilized buffered water (Standard Methods, p650) and macerated at the highest speed in a blender (Futura Waring 500) for ten minutes. The slurries obtained were then diluted ten-fold in a similar buffered water and used for:-

1. Determination of total viable count
2. Determination of MPN of denitrifiers

Tryptone-glucose-yeast extract agar (Difco - Bacto plate count agar) was used for viable counts determinations. Incubation temperature for H_1, H_3 samples was 26 - 27°C for a period of nine days. Similarly, for L_1, L_3 the samples were incubated at 5°C for thirty-three days.

For the determination of denitrifiers, NO_3 broth liquid was used. Ten-fold dilutions of AC slurries were used to inoculate the above medium in duplicates. Incubation time for H_1, H_3 samples was five days at a temperature of 26.5 ± 0.5°C. L_1, L_3 samples were incubated at 5°C for a total incubation time of twenty-seven days.

Further tests were performed for taxonomic purposes, which included:-

1. Gram staining
2. Oxidase Test (Kovacs, 1956)
3. Oxidative versus fermentative medium growth (Hugh and Leifson, 1953).

5.3.5 ANALYTICAL PROCEDURES

Samples collected from the carbon columns were usually analyzed for the following chemical parameters:-

PARAMETER	ANALYTICAL TECHNIQUE
Total organic carbon	Automated U.V. Oxidation
Soluble organic carbon (.1μ filtered)	Technique developed at McMaster
Nitrates + Nitrites	Technicon Auto Analyzer
B.O.D.	Standard Methods
Turbidity	Helige Turbidimeter
pH	Orion pH electrode
Dissolved oxygen	Winkler Test (Montgomery Modification)

The details of these analytical procedures are included in Appendix 1.

5.4 DISCUSSION OF RESULTS

5.4.1 ORGANIC REMOVAL IN THE PILOT PCT PLANT

Samples were taken twice daily, from both sets of parallel adsorbers and the raw data on feed and effluent TOC's from selected locations are shown in Tables 39 and 41 for 5° and 25°C, respectively, in Appendix 3. A precursory glance at the data indicates a wide fluctuation in the strength of the incoming feed and, secondly, a similar, but less pronounced, variation in the effluent concentrations. The major reason for the variation is that the sewage was collected daily between 9 - 12 A.M. each morning, and there are considerable variations in wastewater strength during this period. Furthermore, the tests were conducted during the winter months when molten snow can infiltrate into the sewer systems and thereby dilute the sewage. The differences in volumes passed each day arises from two reasons. First, the wear of the plastic tube in the pump causes disparities in pumping rates and, second, the time interval is not necessarily twenty-four hours between each daily collection.

The results when plotted as C/C_o versus TOC fed as a function of bed distance, as shown in Figures 39 and 40, for low and high temperature columns, respectively, indicate a fairly consistent pattern. After the initial start-up, the first and second columns remove almost all of the removable organics. The final 5 ft of the carbon serves little purpose as the effluent remains essentially unchanged.

FIGURE 39

DIMENSIONLESS EFFLUENT CONCENTRATION vs TOC APPLIED AS A FUNCTION OF BED DEPTH FOR LOW TEMPERATURE COLUMN

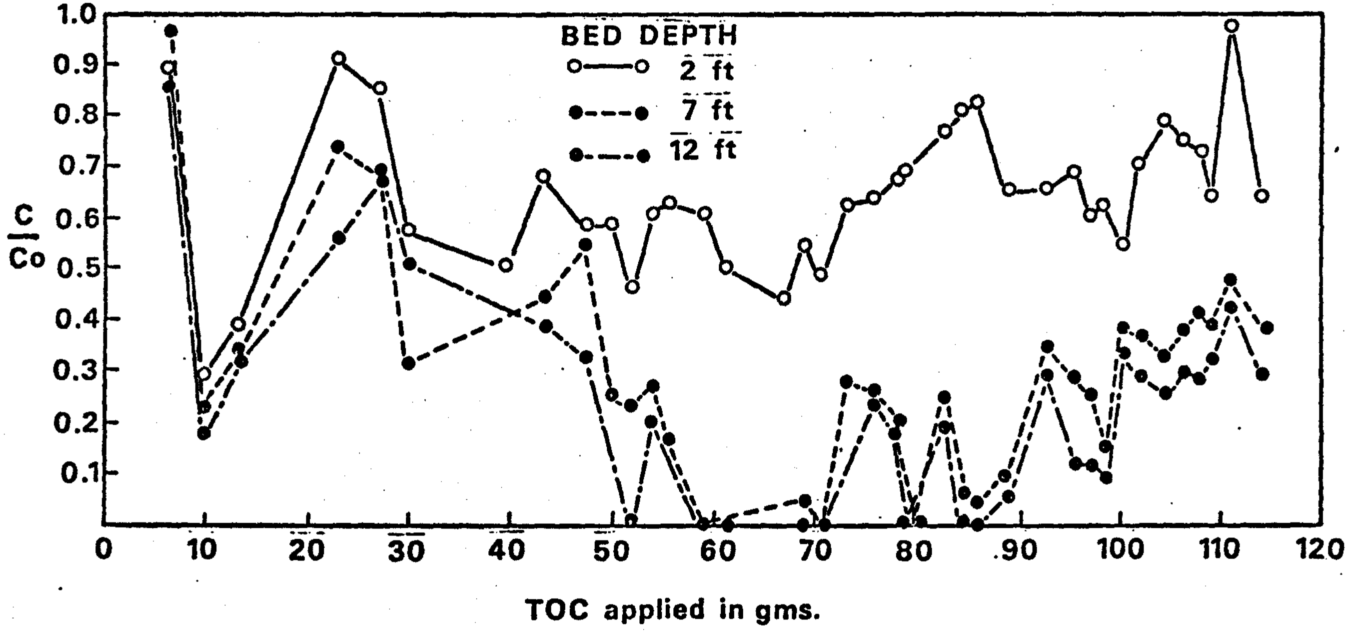
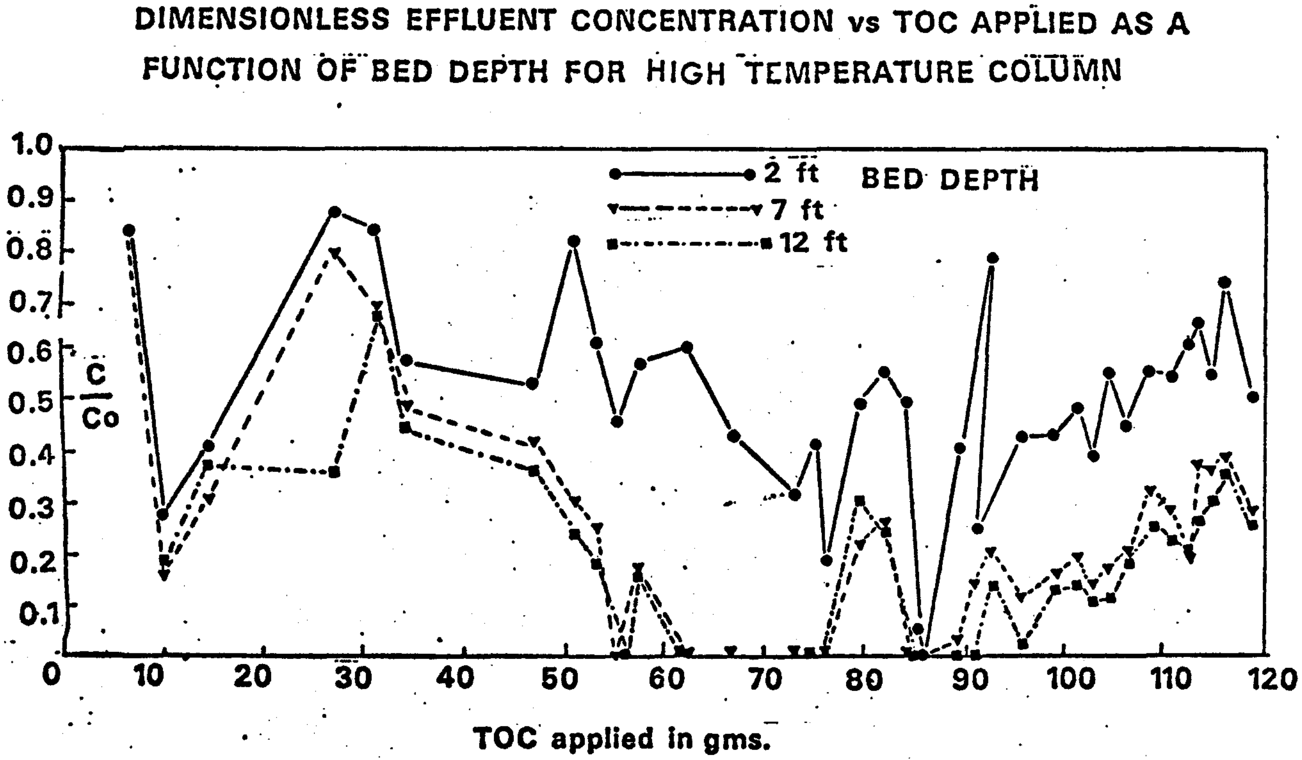


FIGURE 40



DIMENSIONLESS EFFLUENT CONCENTRATION vs TOC APPLIED AS A FUNCTION OF BED DEPTH FOR HIGH TEMPERATURE COLUMN
2 ft
7 ft
12 ft
BED DEPTH
C/Co
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
100
110
120
TOC applied in gms.

From Figures 39 and 40, the differences in effluent quality are difficult to distinguish. Effluents from the lead columns are compared as in Figure 41. Unfortunately, the significance of temperature cannot be determined from such a plot due to the fluctuations in feed concentrations. A slightly better representation can be obtained in Figure 42, where the feed and final effluents are shown. The average feed strength is about 20 mg/l TOC and the final effluent after an initial start-up period assumes a fairly consistent low value, averaging around 4 mg/l TOC from both temperature columns. A slight deterioration in the effluent quality is noticed after 100 grams of TOC have been applied (two months of operation). This can be interpreted as a sign of the onset of exhaustion. Some of the peaks, which occur in Figure 42 for the effluent concentration profiles, are attributed to backwashing and start-up after temporary breakdown. From this particular graph, however, it is still impossible to make any comments regarding the effectiveness of one set of columns over the other, and their possible removal rates. Further analysis, therefore, was carried out by comparing for both temperatures the overall removal by lead columns as a function of cumulative TOC input, as depicted in Figure 43. This method dampens the effect of daily strength variations.

Initially, the overall removal capacity of the lead columns are indistinguishable, but with time the differences become significant, and the rate and extent of removal becomes higher at 25°C than 5°C. This is probably linked to biological activity

FIGURE 41

DIMENSIONLESS EFFLUENT CONCENTRATION VS TOC APPLIED

LEAD COLUMNS

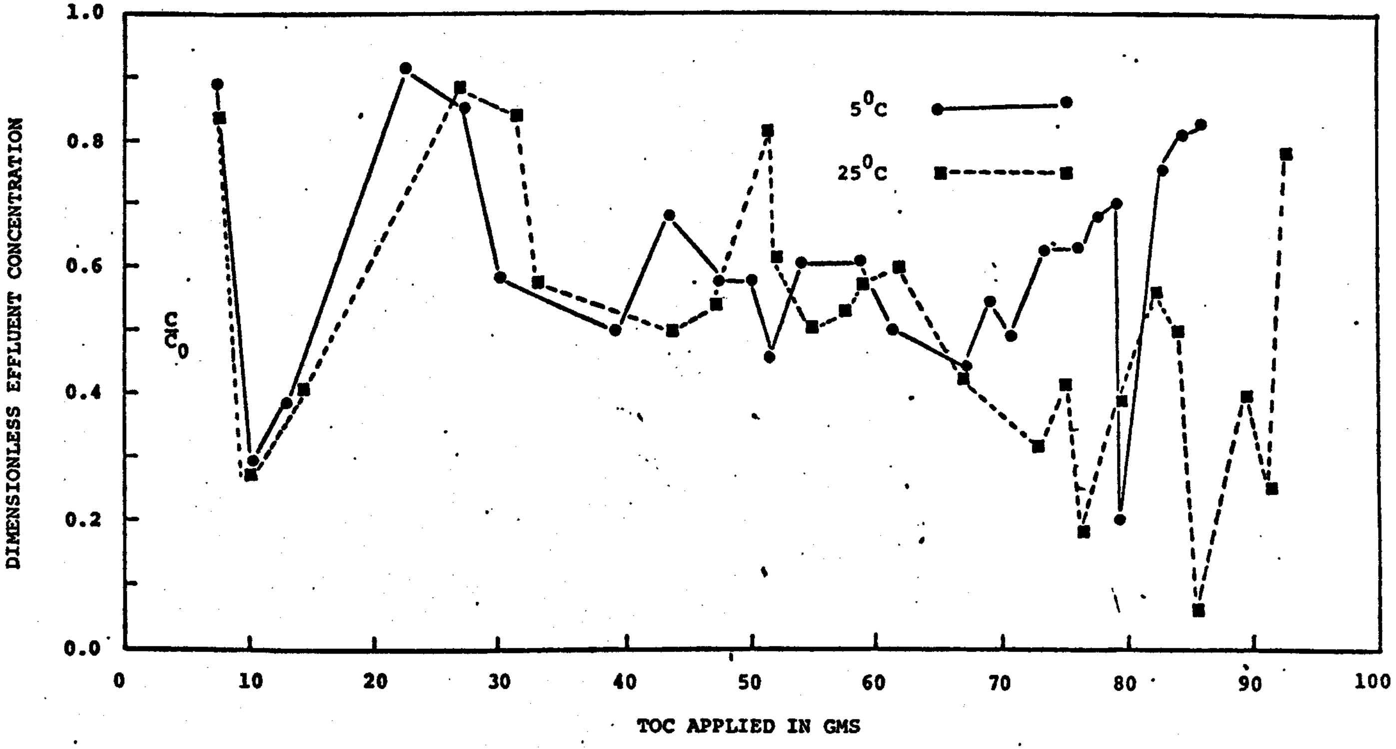


FIGURE 42

FEED AND FINAL EFFLUENTS VS TOC APPLIED

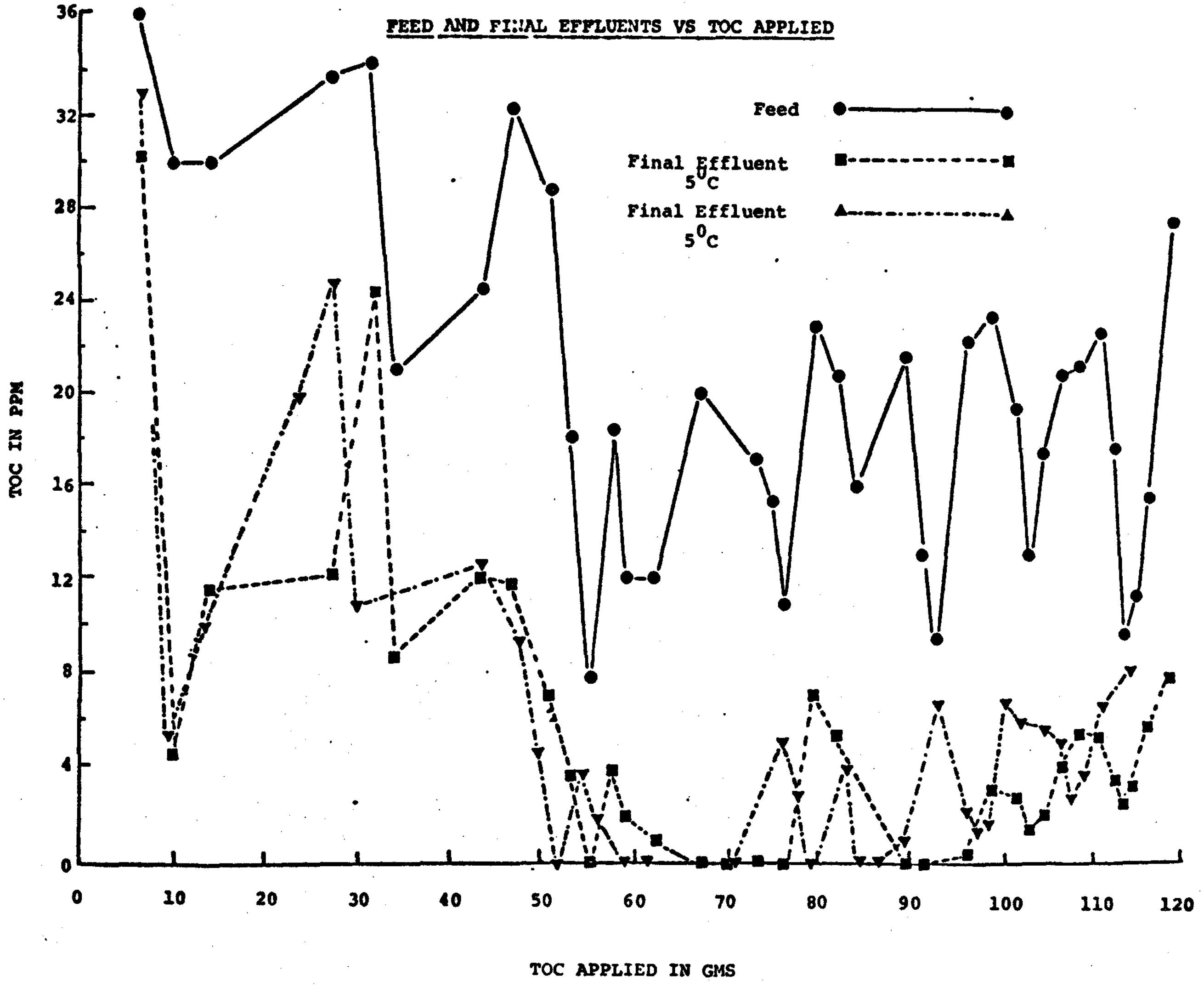
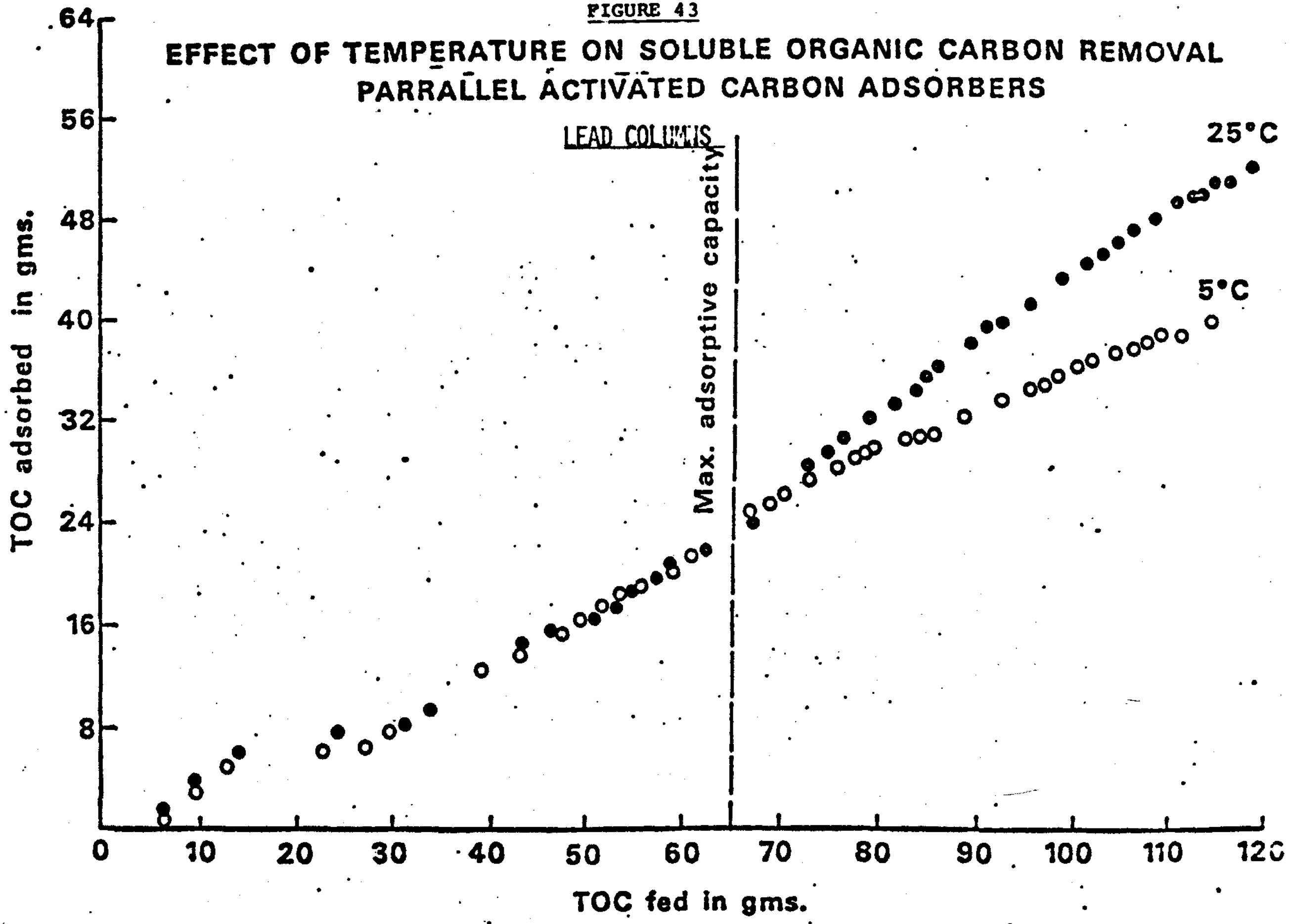


FIGURE 43

EFFECT OF TEMPERATURE ON SOLUBLE ORGANIC CARBON REMOVAL
PARRALLEL ACTIVATED CARBON ADSORBERS



which inevitably appears in activated carbon columns (see Section 2.3). Since bio-oxidation rates are greater at 25°C than at 5°C, it follows, therefore, that bacterial activity would be greater in the 25°C column. The direct evidence for greater microbial activity at higher temperatures is presented in a later section dealing with microbiological investigations.

The effect of column height on removal was also determined for both temperatures using the cumulative TOC removal method, as shown in Figures 44 and 45, for 5° and 25°C, respectively. As noted previously from the plots in Figures 39 and 40, the last column is contributing very little to organic removal. The bulk of TOC is removed at both temperatures in the lead column, which is only 2 ft in height, with the middle column acting as a polishing bed. The lack of removal in the third column can be explained on the basis of the low TOC concentration and the corresponding decrease in the driving force for separation. Also, the organics entering the last column may be largely of a non-adsorbable nature. Furthermore, a lower bacterial population was indicated from microbiological investigations, which would reinforce our conclusions on the low removal rates from the last column.

The results on rate and capacity derived from Figure 43, 44 and 45 are compiled in Table 20. Close to 80% overall TOC removal (final effluent) was obtained from the 25°C set of columns, with the removal at 5°C, similar, but a bit lower.

FIGURE 44

CUMULATIVE TOC REMOVAL vs TOC APPLIED AS A FUNCTION OF BED DEPTH FOR LOW TEMPERATURE COLUMN

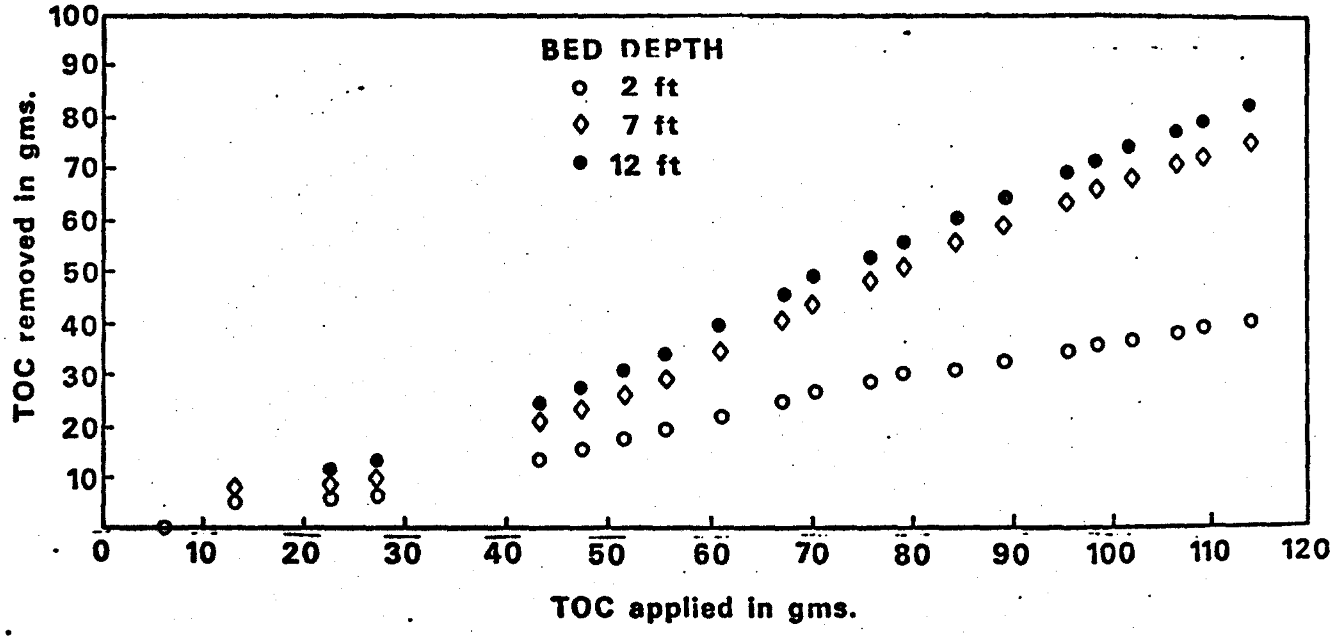


FIGURE 45

CUMULATIVE TOC REMOVAL VS TOC APPLIED AS A FUNCTION OF BED DEPTH FOR HIGH TEMPERATURE COLUMN

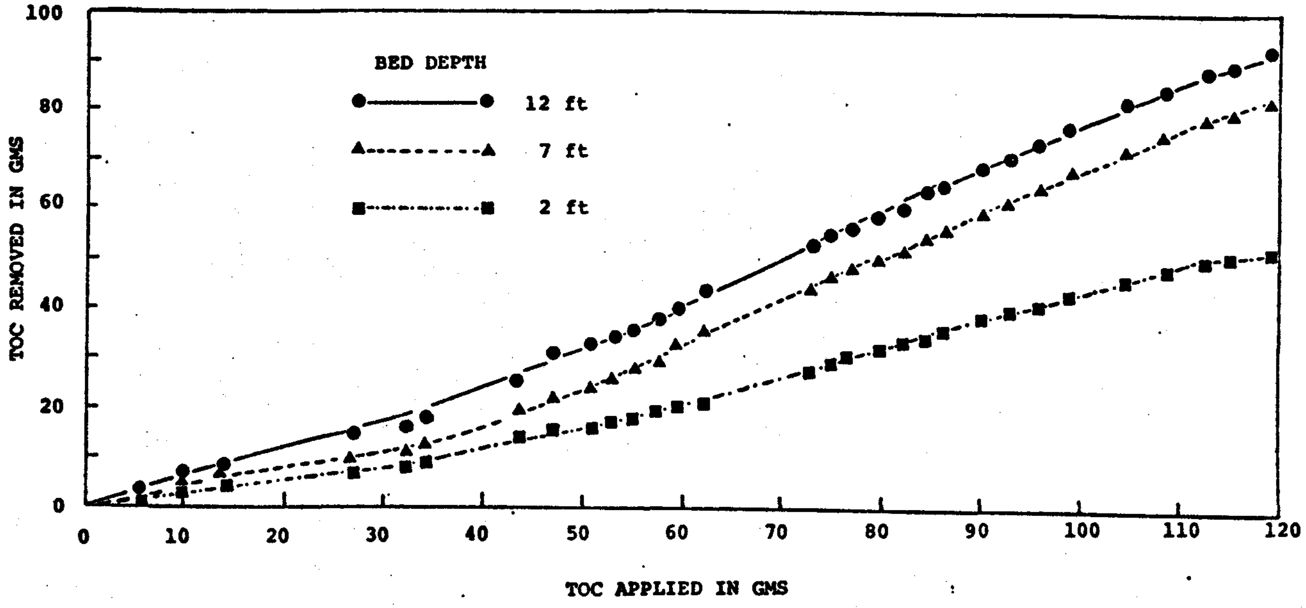


TABLE 20

COMPARISON OF RATES AND OVERALL REMOVAL FROM SET OF COLUMNS AT 5°C AND 25°C

	Lead Column		Middle Column		Last Column	
	5°C	25°C	5°C	25°C	5°C	25°C
$\frac{\text{(gm TOC removed)}}{\text{(gm TOC applied to each column)}}$	.350	.441	.480	.447	.185	.277
$\frac{\text{(gm TOC removed)}}{\text{(cumulative TOC applied)}}$	.350	.441	.662	.691	.724	.777
$\frac{\text{mg TOC removed}}{\text{gm adsorbent}}$	49.5	64.5	17.7	14.6	3.5	5.0
$\frac{\text{gm TOC removed}}{\text{hr-cm}^2\text{ surface area}}$	9.05×10^{-7}	11.85×10^{-7}	3.23×10^{-7}	2.68×10^{-7}	$.65 \times 10^{-7}$	$.92 \times 10^{-7}$

About 50% of the TOC removal occurs in the lead columns at both temperatures. The carbon effectiveness or loading is much greater in the lead columns due to the fact that the bed height is 2 ft compared to 5 ft in the remaining two columns. Loadings in the case of the lead columns are much higher at 25°C than 5°C. Batch isotherms discussed later in Chapter 5.4.3 indicate a maximum loading of 30-40mg TOC adsorbed/gram carbon. From this it is seen, therefore, that the life of the carbon beds are prolonged by at least 60% at 25°C, in comparison with batch "pure" adsorption capacities. In Figure 43, the dotted line indicates the approximate maximum adsorptive capacity of the carbon.

The undiminished removal after this point indicates that the rest of the removal is probably due to biological action. TOC removal rates are calculated per unit surface area, and an activation energy of 2.2 kcal/mole is estimated. This activation energy is much less than the typical values of 8 - 15 kcal/mole mentioned in Chapter 2.3.4 for biological reaction rates. From published work of previous researchers, carbon beds are known to also remove colloidal and suspended solids, thus contributing to higher observed removal. A comparison of the filtered and unfiltered results, however, indicated that the feed and effluents were predominantly smaller than .45μ material (usually defined in sanitary engineering as "soluble"). Filtration was, therefore, dismissed entirely.

This is not surprising since after alum coagulation, polyelectrolyte flocculation, settling and sand filtration, the sewage should be essentially "soluble".

BOD_5 values were measured for the feed and column effluents and the results, as shown in Table 21, indicate an average sewage BOD strength of 20 mg/l and an average of 2 mg/l BOD for final effluents from both sets of columns. The BOD/TOC ratio is thus calculated to be approximately 1.0. Theoretically, the ratio should be approximately or greater than 2.67, if the sewage is entirely oxidizable in five days. Normally, only 60-70% of organics show up by five days in BOD tests susceptible to biological attack. A BOD/TOC ratio of 1.0 indicates that close to 40% of sewage fed to the carbon columns is difficult to degrade in the BOD bottle. The 90% removal, which is achieved in the carbon beds, can be either attributed to adsorption or biochemical degradation in the absence of any specific knowledge on the distribution of soluble TOC into:-

1) Degradable, non-adsorbable
11) Adsorbable, non-degradable
111) Non-degradable, non-adsorbable fractions

Other parameters, such as turbidity and pH, were monitored from the columns. Generally, the effluents were clear and had turbidity values ranging from 8 to 10 mg/l silica. Fears of sloughing and bacterial end-products tending to make the effluent turbid proved to be unwarranted. The pH of the feed and effluents varied between 6 and 7 with no noticeable temperature effects.

TABLE 21

B.O.D. VALUES OF FEED AND EFFLUENT OF PILOT PCT PLANT

DATE	AVERAGE B.O.D$_5$ IN MG/L				
	Feed	L_1	L_3	H_1	H_3
22.1.74	4.80	-	4.0	-	4.7
23.1.74	27.6	-	3.2	-	2.3
25.1.74	22.0	-	3.3	-	2.5
26.1.74	20.5	-	1.3	-	2.5
27.1.74	6.1	-	>0.5	-	0.8
29.1.74	14.1	-	2.0	-	0.9
31.1.74	14.6	-	0.9	-	1.4
1.2.74	16.4	-	0.8	-	0.6
2.2.74	13.6	8.4	1.7	6.0	1.3
3.2.74	6.7	3.4	1.05	2.6	2.0
4.2.74	6.2	3.1	0.90	2.40	0.9
5.2.74	18.1	8.9	0.4	3.3	0.1
6.2.74	21.9	8.5	3.5	6.9	2.3

- not measured

5.4.2 DENITRIFICATION

Nitrates and nitrites were monitored in the feed and lead column effluents at both temperatures and results are plotted in Figure 46 as cumulative nitrates removed versus nitrates applied. Some nitrates were present in the sewage amounting to about 3.5 mg/l or less as $NO_3^-+NO_2^-$-N. Later an additional dose of nitrate was added to check column removal capacities. Prior to nitrate supplementation, particularly at 25°C, essentially all the nitrates in the feed were removed. Once addition began, effluent nitrates levels increased, indicating there was insufficient organic substrate available for nitrate removal. The theoretical requirement of organic carbon for dissimilative nitrate reduction has been expressed using methanol as substrate source to be 1.9 mg CH_3OH per mg $NO_3^-+NO_2^-$-N. As TOC, this ratio works out to be slightly more than 0.70. The carbon available to nitrogen fed ratio, for both the columns over a cumulative period from 18th January to 4th February, 1974 has been calculated to be 1.58 and 1.61 gm TOC/gm $NO_3^-+NO_2^-$-N for 25°C and 5°C columns respectively. If, however, it is assumed that all the carbon which is adsorbed is sequestered and not available for denitrification then considerably lower ratios of 0.8 and 1.11 are found for 25°C and 5°C, respectively. Higher overall removal at 25°C is again to be noted from Figure 46 as expected from theoretical temperature dependence of biochemical reaction rates. Evidence of larger amount of denitrifiers present in the high temperature column was obtained in the microbiological studies discussed in a later section.

FIGURE 46

DENITRIFICATION AS A FUNCTION OF TEMPERATURE IN ACTIVATED CARBON ADSORBERS

LEAD COLUMNS

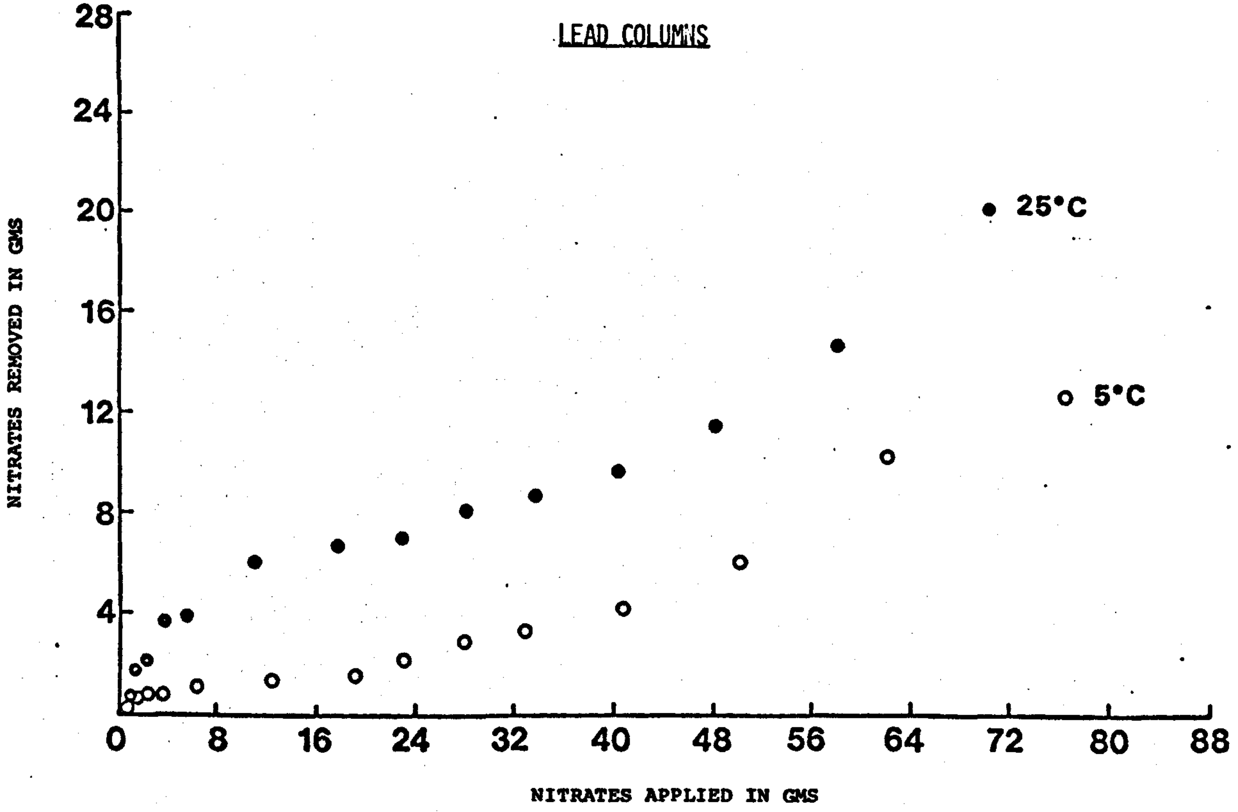


Table 22 depicts the quantitative results on rate and removal capacity obtained from Figure 46. Nitrate removal at $25^{\circ}C$ is slightly less than 30% and at $5^{\circ}C$ less than 20% from the lead column. The loading per gram of carbon is quite attractive, indicating possible economic feasibility of GAC as denitrification media. The rates obtained by Sutton (1973) on plastic media and Jeris (1974) on GAC fluidized bed show that the present denitrification rates are 1/4th to 1/10th lower, respectively.

The values derived from the pilot PCT plant are only preliminary, but still serve to show that activation energy as low as 4.7 kcal/mole can be obtained. Sutton (1974) reported biological denitrification rates of 11.1 kcal/mole for packed columns using plastic media.

Dissolved oxygen (DO) measurements of the feed and two effluents from the lead and the final columns are shown in Table 23. Typically the feed had a DO value of 6.0 mg/l and 2 - 3 mg/l for the lead column effluents. A significant drop in the DO level is seen after the lead columns. More oxygen seems to have been consumed at high temperature than at low temperature. The DO level, however, remains high enough to preclude the existence of bulk anaerobic conditions inside the lead columns. Other considerations, such as presence of nitrate in the feed and the possibility of some methane production lead us to conclude that the conditions inside the beds most likely remained aerobic (except for anaerobic pockets as discussion below). High DO values have been measured in final

TABLE 22

COMPARISON OF DENITRIFICATION RATES AND REMOVAL CAPACITIES OF PILOT PCT PLANT

	Temperature	
	$5^{o}C$	$25^{o}C$
GMS Nitrates removed / gm Nitrates applied	0.174	0.289
MG Nitrates Removed / GM Adsorbent	15.5	25.1
GMS Nitrates Reduced / $hr\text{-}cm^2$ (surface area)		
Present GAC Columns	9.09×10^{-7}	16.1×10^{-7}
BURL Saddles Plastic Media (Sutton, 1973)	28.6×10^{-7}	93.9×10^{-7}
GAC Fluidized Bed (Jeris, 1974)		157×10^{-7}

TABLE 23

DISSOLVED OXYGEN MEASUREMENTS ON EFFLUENTS FROM PILOT PCT PLANT

DATE	DISSOLVED OXYGEN IN MG/L				
	Feed	L_1	L_3	H_1	H_3
25.1.74	6.4	2.3	-	2.70	-
26.1.74	5.6	3.05	-	2.75	-
31.1.74	5.4	3.20	8.80	2.58	3.40
1.2.74	5.6	2.30	10.4	2.15	5.6
2.2.74	5.6	3.3	2.70	2.5	5.5
3.2.74	8.6	5.6	2.6	1.9	6.9
4.2.74	6.2	5.8	3.1	1.5	4.6
5.2.74	5.4	3.0	4.3	3.5	6.7
6.2.74	5.0	2.1	3.9	1.6	8.9

- not measured

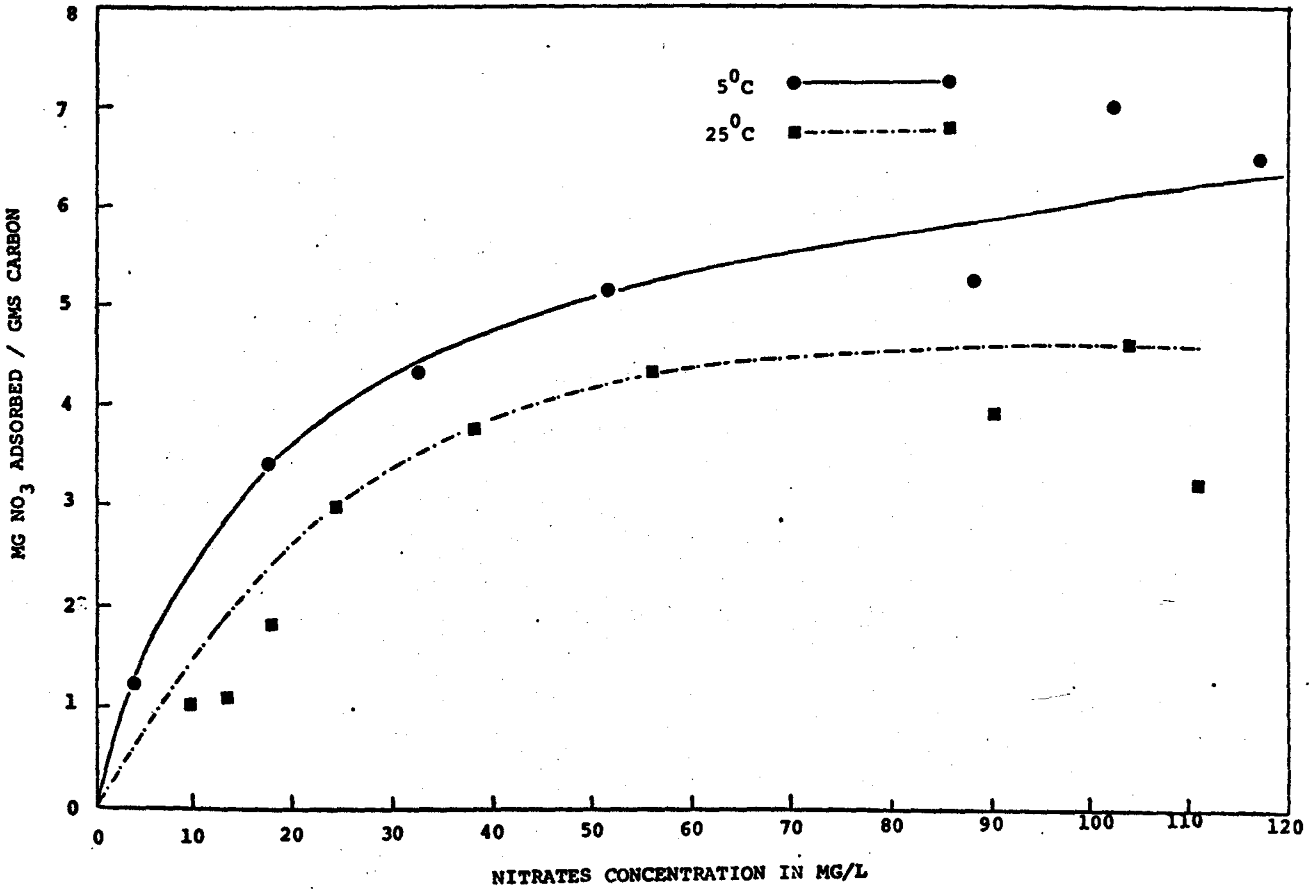
effluents, however, due to partially empty tubing ahead of the sampling point, the results are meaningless. H_2S was absent at all times.

Theoretically, an anaerobic environment is an imperative for cultivating denitrifiers. The results obtained, so far, do not explain this situation. Some removal must, of course, be attributed to adsorption itself by GAC. Batch isotherms were run at 5° and 25°C and results shown in Figure 47 confirm this. At 5°C therefore, if 5 - 6 mg Nitrates/gm carbon are removed per gram of GAC, this still does not account for the other 10 mg/gm carbon. Subtracting the removal due to adsorption indicates a much greater temperature dependence than before. It should be noted though that the carbon was most likely saturated with nitrates before data on nitrate removal was collected.

An explanation for aerobic denitrification is that although aerobic conditions prevail inside the beds, anaerobic pockets can exist, as profuse bacterial growth inside the beds can cause solids build-up, which tends to block the passage of flow creating channelling and dead pockets. Furthermore, even in aerobic areas, anaerobic zones can occur in the bacterial film near the activated carbon surface where oxygen mass transfer is rate limiting and adequate substrate exists for anoxic growth.

FIGURE 47

NITRATE ADSORPTION ISOTHERMS WITH GRANULAR ACTIVATED CARBON



5.4.3 CARBON REGENERATION STUDIES

Batch studies were conducted simultaneously with the pilot PCT plant, in an attempt to obtain some rate removal data in controlled lab conditions.

Batch adsorption isotherms run at 5°C and 25°C are shown in Figure 48. Loadings obtained are about half that calculated from columnar studies. In the absence of bacterial activity in batch experiments, the loadings are seen to be higher at lower temperatures as expected theoretically.

Saturated carbon was regenerated for periods lasting up to ten days and its adsorptive capacity evaluated by isotherm tests. Results at 5° and 25°C are presented in Figures 49 and 50, respectively. In both cases some rejuvenation occurs. Iodine numbers, which are a measure of adsorption capacities, also indicate partial biological regeneration at both temperatures as shown in Table 24.

5.4.4 STUDIES ON EXHAUSTED CARBON FROM PILOT PCT PLANT

An attempt was made to obtain reaction rates for carbon as it existed inside the columns. It was hoped that this carbon sample would be more representative than virgin carbon, which was utilized in the regeneration studies.

FIGURE 48

SEWAGE ADSORPTION ISOTHERMS USING VIRGIN FILTRASORB 400 CARBON

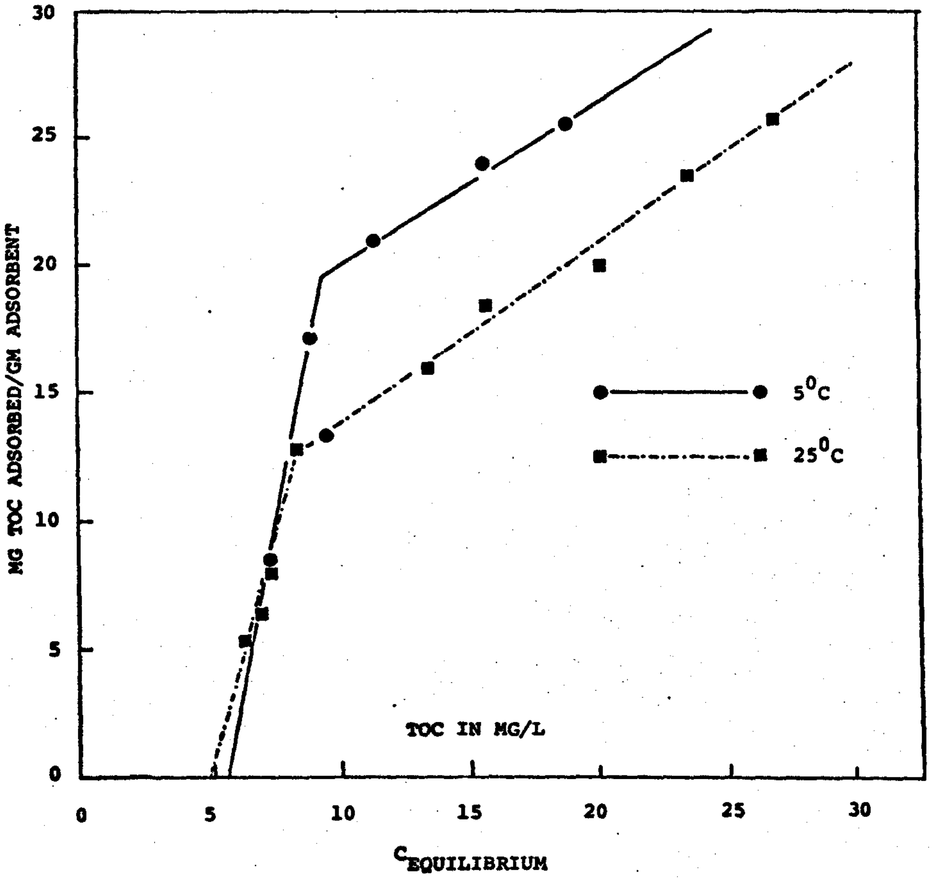


FIGURE 49

COMPARISON OF SEWAGE ADSORPTION ISOTHERMS USING FRESH AND REGENERATED CARBON AT 5^0C

BATCH STUDIES

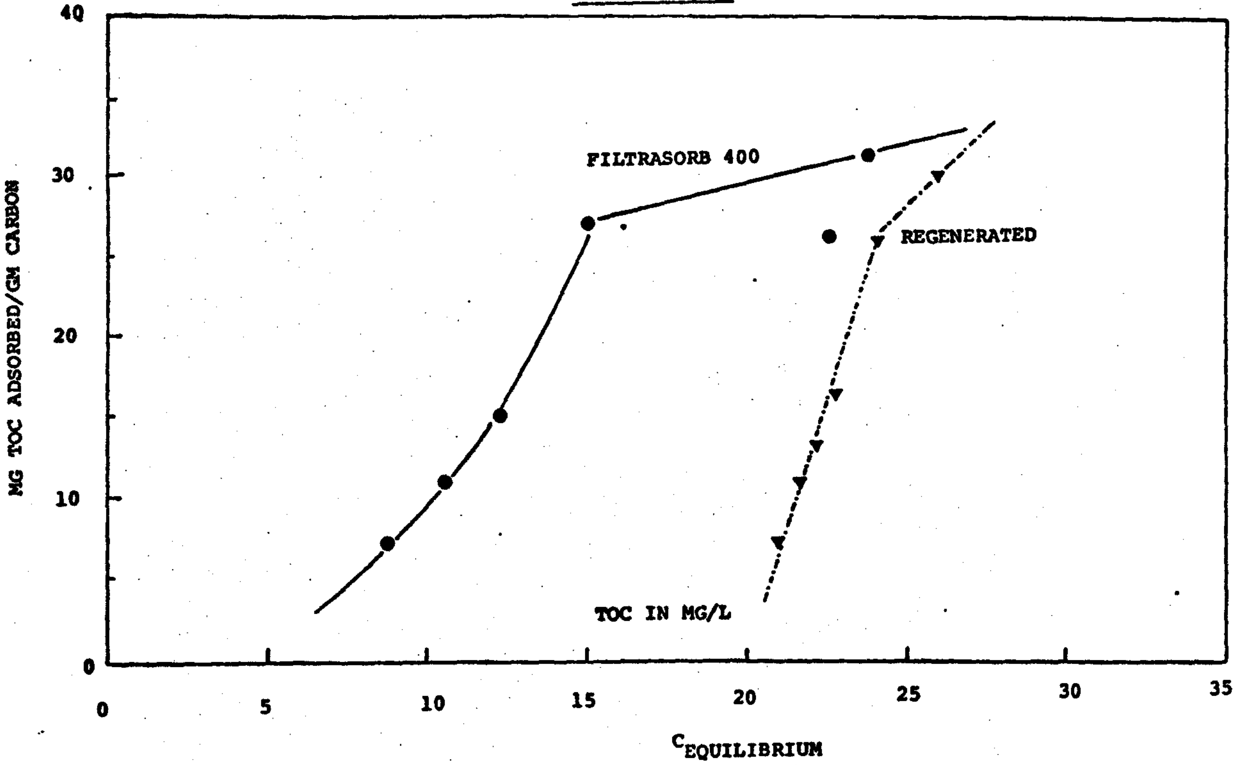


FIGURE 50

COMPARISON OF SEWAGE ADSORPTION ISOTHERMS USING FRESH AND REGENERATED CARBON AT 25^{0}C BATCH STUDIES

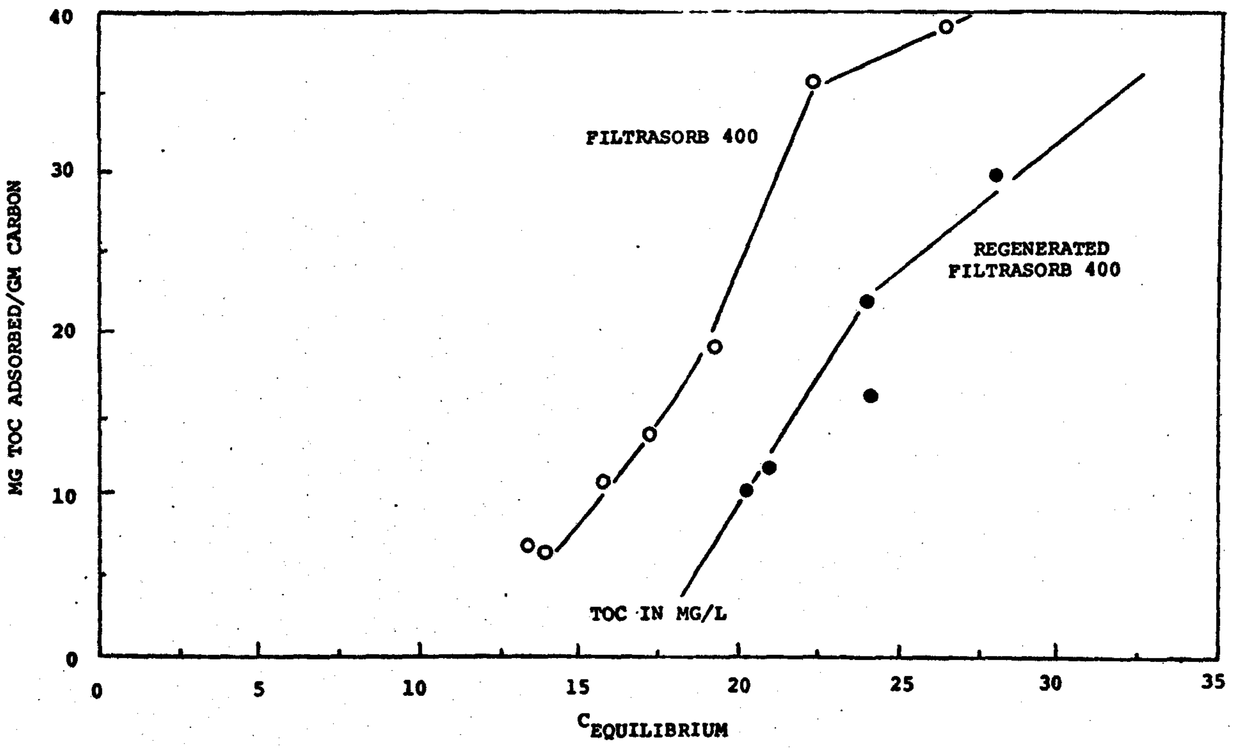


TABLE 24

COMPARISON OF IODINE NUMBERS FOR FRESH AND REGENERATED CARBONS

	IODINE NUMBER
FRESH FILTRASORB 400 (THRU 200 MESH)	1207
25^{0}C REGENERATED	938
5^{0}C REGENERATED	721
UNREGENERATED (ONCE SATURATED)	605

Regeneration on .2μ filtered raw sewage for 11 days

Batch isotherms were run firstly on carbon from both temperature columns. Results in Figure 51 show that the carbons in their present state are by and large exhausted, as indicated by the low loading values. The high temperature column shows a slightly higher remaining adsorption potential and again substantiates the findings in the columnar study. In Figure 52, a comparison of the adsorption isotherms from exhausted carbons is shown along with the fresh carbons at both 5° and 25°C. This shows quite conclusively that the carbon in the columns had reached their exhaustion point.

Batch aerobic reactors were set up in which the respective carbon samples were left and allowed to regenerate. Progress of the reactors were monitored and TOC removals, as well as oxygen uptakes, shown in Figure 53. At 25°C, one can see a much greater oxygen utilization rate indicating strong biological activity. Correspondingly organic substrate concentration drops with time due to both adsorption and biological degradation. At 5°C, even after ten days, substantial bacterial activity does not develop, as seen from low oxygen consumption. To compare quantitatively the extent of regeneration of these samples, Iodine numbers are provided in Table 25. Interestingly, regeneration is higher aerobically than anaerobically, and increases with temperature. But still Table 25 shows that after ten days or so of regeneration, only a maximum increase of 20% in loading capacities is achieved. Biological rejuvenation of carbon, as a technique for regenerating exhausted carbon, thus has some drawbacks in that over a period of time, the adsorption sites on the carbon get exhausted with non-regenerable material.

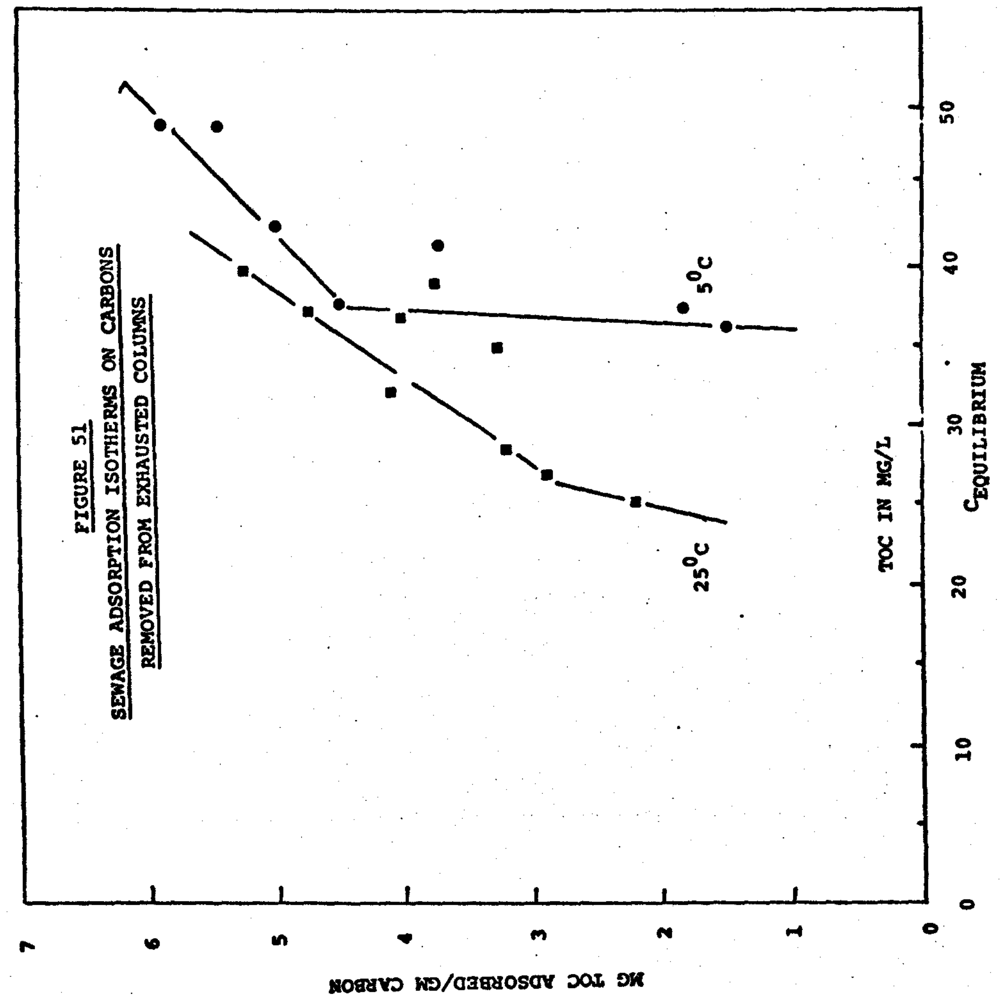


FIGURE 51

SEWAGE ADSORPTION ISOTHERMS ON CARBONS REMOVED FROM EXHAUSTED COLUMNS

FIGURE 52

COMPARISON OF ADSORPTION ISOTHERMS USING VIRGIN AND REGENERATED CARBON (FROM EXHAUSTED COLUMN)

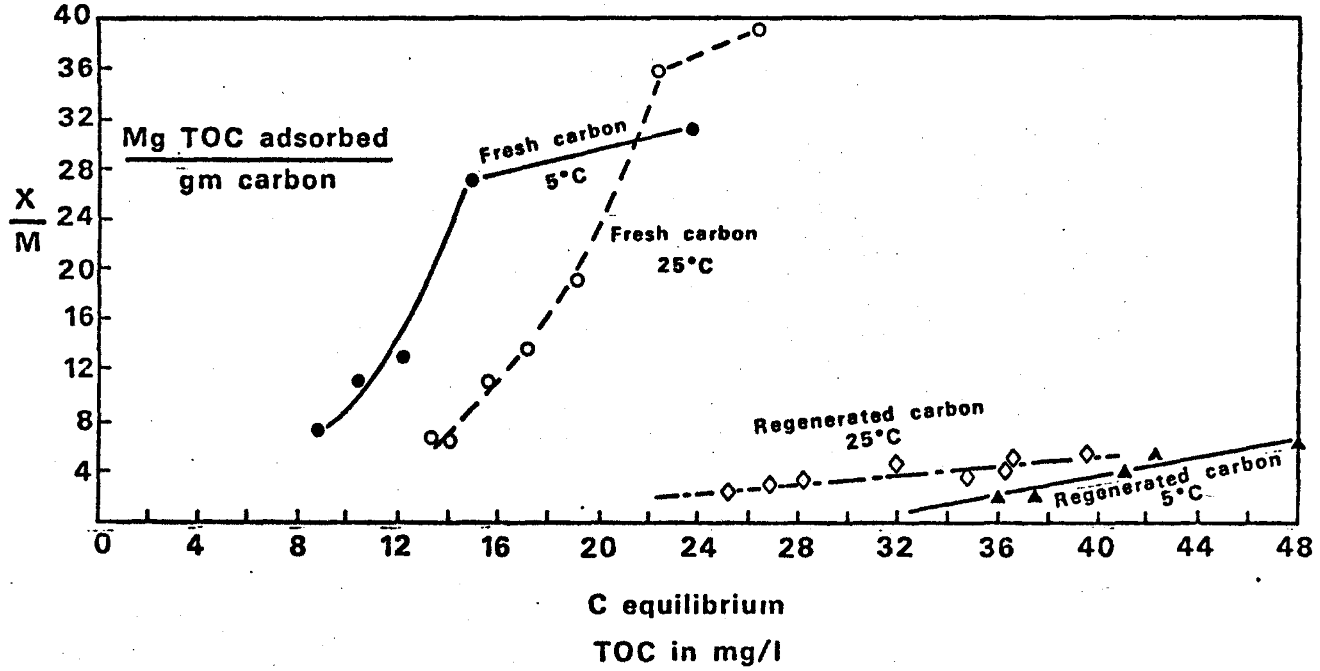


FIGURE 53

OXYGEN UPTAKE AND TOC REMOVAL IN BATCH AEROBIC REACTORS ON EXHAUSTED CARBON

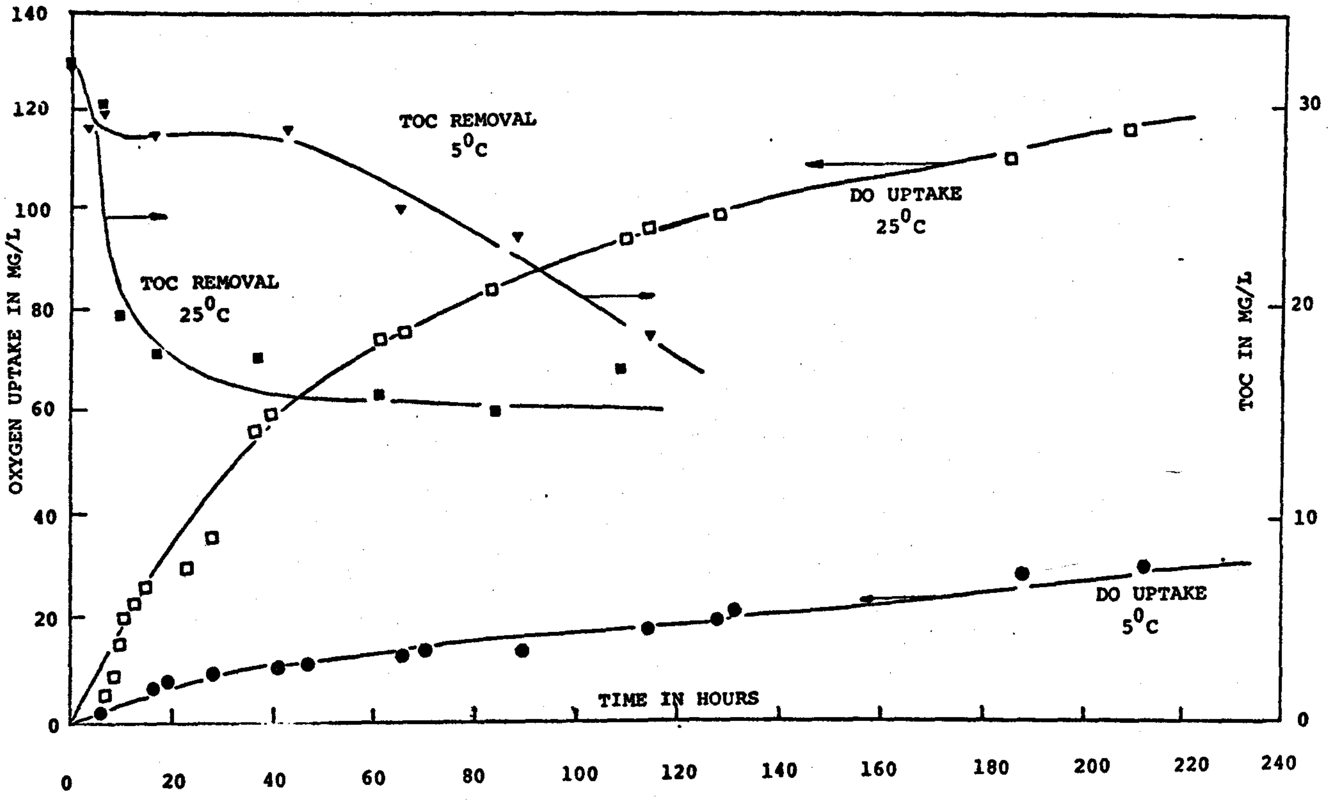


TABLE 25

COMPARISON OF IODINE NUMBERS OF EXHAUSTED CARBONS FROM LEAD COLUMNS

Carbon Type	Iodine Number
25°C column (as is)	600
5°C column (sample as is)	544
25°C aerobic reactor regenerated carbon	732
25°C anaerobic reactor regenerated carbon	650
5°C aerobic reactor regenerated carbon	616
5°C anaerobic reactor regenerated carbon	591

Based on these particular set of values, it would be safe to say that the carbon columns were nearly exhausted due to build-up of non-regenerable solids in the beds.

5.4.5 MICROBIOLOGICAL INVESTIGATIONS

Direct microscopic examination of the carbon removed from the columns indicated the following(see Latoszek & Benedek, 1975 for details).

1. Lead Column

High Temperature:	Nematoda worms along with extensive zoogleal bacterial mass growing on carbon particles.

2. Final Column

High Temperature:	Higher forms of micro-organisms were not detected. Less bacterial growth observed than on lead column.

3. Lead Column

Low Temperature:	Minute Amoebae and flagellata detected. Sphaerotilus like bacteria and large amount of free suspended rods observed; some of which were motile.

4. Final Column

Low Temperature:	Higher forms of micro-organisms not detected. Lesser bacterial presence noted in specimem.

Besides visual examination, total viable cell counts were obtained as shown in Table 26.

TABLE 26

TOTAL VIABLE CELL COUNT
OF SPECIMENS FROM EXHAUSTED CARBONS

VIABLE CELL COUNTS		
	5° C	25° C
	cells per gram wet carbon	
Lead Column	$.23 \times 10^9$	1.06×10^9
Last Column	10.7×10^6	56×10^6

The greater number of cells at 25°C than at 5°C confirm the importance of bio-oxidation and its enhancement of carbon bed life. More growth in the lead column is also reasonable as more of the substrate is available there.

An interesting point to note is that the density of bacteria in the lead columns is comparable in magnitude to that which occurs in activated sludge systems, as shown in Table 27. Weddle and Jenkins (1971) estimated that 20% of the volatile suspended solids (VSS) in activated sludge are the viable organisms and suggested 10^{-12} gm/cell to be a close estimate of the dry cell weight. Assuming a typical VSS concentration of 2000 mg/l, a value of 0.4×10^9 cells/cm^3 was derived for the bacterial density in the aeration tank of an activated sludge plant. Hawkes (1965) also quotes a similar maximum value for bacterial populations in activated sludge systems.

MPN determinations of denitrifiers led to indefinite results as all dilutions gave positive reaction with gas production. Therefore, exact determination of MPN was impossible for these three samples. The minimum number of denitrifiers, however, would be 11×10^6 cells per gram of wet AC at 25°C in the first column.

Taxonomic investigation of the bacterial population in H_1 and L_1 columns was conducted by Latoszek and Benedek (1975).

Using the tests mentioned in Section 5.3.4, isolates were differentiated on the generic level following the determinative scheme proposed by Shewan <u>et al</u> (1960).

TABLE 27

COMPARISON OF BACTERIAL DENSITY IN SOLID MEDIA AND ACTIVATED SLUDGE SYSTEMS

BACTERIAL DENSITY	
	# cells/cm^3
GRANULAR CARBON (FROM PRESENT PLANT)	1.0 x 10^9 (based on column volume)
HAWKES (1963) MIXED LIQUOR	2.2 x 10^9 - max
WEDDLE and JENKINS (1971) ACTIVATED SLUDGE	0.4 x 10^9 (typical)

The strains isolated from the H_1 and L_1 columns were classified as shown in Table 28. Of the thirteen strains belonging to the genus Pseudomonas isolated from the H_1 column, all but one produced alkaline reaction in O/F medium. Five of the strains from the H_1 columns were also denitrifiers. Four of the eight Pseudomonas strains isolated from the L_1 column produced alkaline reaction in O/F medium and showed denitrification ability.

In our taxonomy investigation, flagella staining or electro-microscopic determinations were not performed. According to Shewan et al (1960), however, the oxidase test of Kovacs is invaluable for the determination of Enterobacteriaceae. The taxonomy of the isolated bacterial strains from the columns is similar to the main bacterial groups characteristic of activated sludge and bacteria beds (Hawkes (1963), Benedict and Carlson (1971). It is interesting to note that in an earlier investigation of an activated carbon sample from EPA's Pomona, California pilot plant, similar groups of bacteria were isolated (Latoszek and Benedek, 1973).

Many species of the genus Pseudomonas as well as the Flavobacterium - Cytophaga group possess denitrification ability. From the twenty-one strains of Pseudomonas spp isolated in this study, ten are denitrifiers. Also, two isolates belonging to Flavobacterium-Cytophaga group show this ability.

TABLE 28

TAXONOMIC DISTRIBUTION OF MICRO-ORGANISMS FROM COLUMNS

TAXONOMIC DISTRIBUTION OF MICRO-ORGANISMS FROM COLUMNS

NUMBER OF STRAINS	GENERA
21	Pseudomonas
13	Flavobacterium
3	Achromobacter
2	Arthrobacter

ALSO

- NEMOTODA
- AMOEBAE
- FLAGELLATA
- SPHAEROTILUS

5.5 THEORETICAL MODELLING OF CARBON ADSORBERS IN THE PRESENCE OF BACTERIAL ACTION

To use the model developed in Chapter 5.2 certain physical parameters had to be first estimated from literature as well as experimental data.

5.5.1 SOLID PHASE PORE DIFFUSION COEFFICIENT OF SEWAGE

This was estimated at both 5°C and 25°C using the method outlined by Tien (1960). The batch adsorption isotherms on sewage, shown in Figure 48 for 5°C and 25°C, along with the batch kinetics illustrated in Figure 73 in Appendix 4 were used. The fractional uptake curves are plotted in Figures 74 and 75 in Appendix 4 using the data from Tables 49 and 50 for 25°C and 5°C, respectively. The intersection points from Figures 74 and 75 are determined in Tables 51 and 52 for 25°C and 5°C, respectively, and a constant D_s value taken as time approaches zero in Figures 76 and 77 for 25°C and 5°C, respectively. The solid phase pore diffusion coefficient values derived from this procedure are 8.0×10^{-9} and 5.9×10^{-9} cm^2/sec at 25°C and 5°C, respectively.

5.5.2 BULK LIQUID DIFFUSIVITY

Wilke-Chang's equation is used to estimate diffusivity of sewage organics in water. Robertson (1972) quotes an average molecular weight of 160 for sewage, which is used in Wilke-Chang correlation with an empirical formula of $C_6H_6O_4$ to estimate molecular volume.

Thus at 25°C, using Equation 2:-

$$D_{liq} = \frac{7.4 \times 10^{-8} \times 298.0K \times (2.6 \times 18g/mole)^{0.5}}{0.894cp \times (140.6cm^3/gmole)^{0.6}} = 0.83 \times 10^{-5}\ cm^2/sec$$

At 5°C, viscosity = 1.519 cp and

$$D_{liq} = 0.83 \times 10^{-5} \times \frac{273}{298} \times \frac{0.894}{1.519} = 0.46 \times 10^{-5}\ cm^2/\ sec$$

Tomlinson (1966) calculated that the diffusivity of molecules in bacterial films is about $2/3^{rds}$ that of the bulk liquid.

Hence at 25°C $D_{film} = 0.83 \times \frac{2}{3} \times 10^{-5}$

$= 5.5 \times 10^{-6}\ cm^2/sec$

And at 5°C $D_{film} = 3.0 \times 10^{-6}\ cm^2/sec.$

5.5.3 BACTERIAL FILM THICKNESS

An estimate of this is presented here based on the viable cell count derived in the microbiological studies.

Thus e.g. at 25°C

Number of cells per gram of wet carbon $= 10^9$

Moisture per cent in wet carbon = 30%

Number of cells/gm carbon $= \frac{10^9}{.7} = 1.43 \times 10^9$

Particle density $= 1.35\ \frac{gm}{cm^3}$

Average particle diameter = 0.09 cm

Volume per particle $= \pi \frac{d_p^3}{6} = 364 \times 10^{-6}\ cm^3$

Number of particles per gram of carbon $= \frac{cm^3}{1.35\ gm} \times \frac{particles}{364 \times 10^{-6}\ cm^3}$

= 2035 particles/gram.

$$\frac{\text{Number of cells}}{\text{Carbon Particle}} = \frac{1.43 \times 10^{9}}{2035} = 7.03 \times 10^{5}$$

Assume bacterial cell diameter $= 2\mu$

$= 2 \times 10^{-4}$ cm

Volume of bacteria per cell $= \frac{\pi d_p^3}{6} = \frac{\pi}{6} \times 8 \times 10^{-12}$

$= 41.9 \times 10^{-13}\ \text{cm}^3$

Volume per particle of carbon $= 7.03 \times 10^{5} \times 41.9 \times 10^{-13}$

$= 2.9 \times 10^{-6}\ \text{cm}^3$

Assuming the bacterial film forms a spherical shell

Volume of shell $= 4\pi r^2 \phi\, dr$

Where dr = Film thickness
r = Carbon particle radius
ϕ = Packing factor

A value of 0.7 for the packing factor is estimated by assuming the cells are packed with their centre to centre distance being 3μ

$$\delta \text{ (or dr)} = \frac{2.9 \times 10^{-6}\ \text{cm}^3}{\pi \times (.09)^2\ \text{cm}^2 \times 0.7} = 1.9\mu$$

A value of 10^9 viable cells/gm of carbon was used to estimate the bacterial film thickness. However, not all the organisms which are present in a sample respond to cell count medium and as a result an accurate estimate of the film thickness cannot be made . The purpose of this above calculation is to approximate the minimum film thickness required to account for the noted high bacterial densities.

Tomlinson (1960), for example, reports 20μ as the film thickness where oxygen becomes rate limiting. The bacterial film thickness is of importance in modelling, but due to lack of experimental data available a value of 20μ was chosen in conformance with the literature on solids supported growth.

5.5.4 FILM REACTION RATES

This parameter was estimated from the aerobic reactor kinetics data presented in Figure 53. The initial slope was taken to represent the rate and the surface area of carbon was estimated from the weight introduced in the reactor. A value of 9.75×10^{-10} gm TOC degraded/sec- cm^2 surface area was obtained at 25°C. By assuming an activation energy of 10 kcal/mole, an estimate of 2.92×10^{-10} gm/cm^2- sec was made of the reaction rate at 5°C.

5.5.5 NORMALIZATION OF ADSORPTION ISOTHERMS

The 25°C and 5°C sewage isotherms, shown in Figure 48, were normalized by dividing q or the TOC adsorbed by q_∞ the loading at saturation. The TOC concentration was normalized by subtracting the non-adsorbable fraction, which was assumed to be degradable. The graph presented in Figure 78 in Appendix 4 was broken into two straight line segments, each being defined by two coefficients calculated by the least squares method.

5.5.6 PREDICTED RESULTS FROM THEORETICAL MODEL.

The model proposed in Section 5.2 could now be solved once these parameters had been estimated. Only the lead column or the first 60 cm of the carbon bed was modelled as most of our experimental data (from pilot plant) was gathered over this section of the adsorbers. A copy of the computer program, written to solve the set of equations 59,60,61 is included in Appendix 6. The solutions converged rapidly to stable values and in no case took longer than 125 seconds on the McMaster University CDC 6400 System.

Figures 54 and 55 show the dimensionless effluent concentration profiles from the adsorbers plotted against the cumulative amount of TOC applied to the columns at 25°C and 5°C, respectively. At 25°C, it can be seen that according to the model, the effluent even at a bed depth (Z/L) of 0.2, never reaches the influent value. At $Z/L = 1.0$ or the final effluent end the model predicts $C/C_0 = 0.0$ or complete removal. Intermediate values of C/C_0 are obtained along the column. The breakthrough curves are very sharp and indicate that the initial removal is due to adsorption onto the pores of the carbon granules, followed by constant removal due to biological degradation.

FIGURE 54

DIMENSIONLESS EFFLUENT CONCENTRATION PROFILES
PREDICTED BY THEORETICAL MODEL
25°C

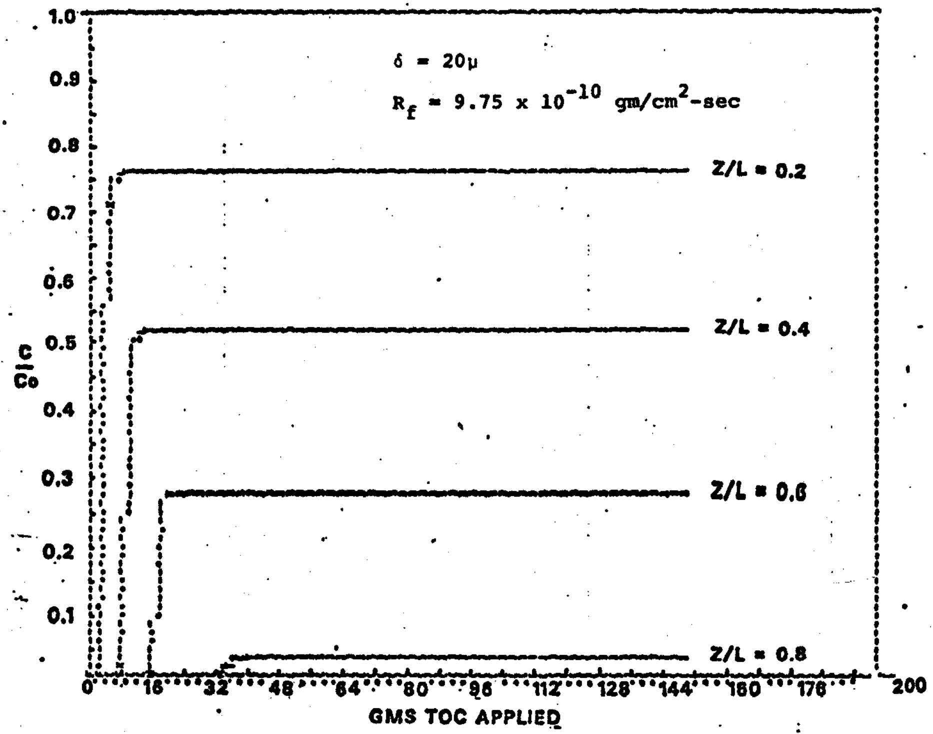
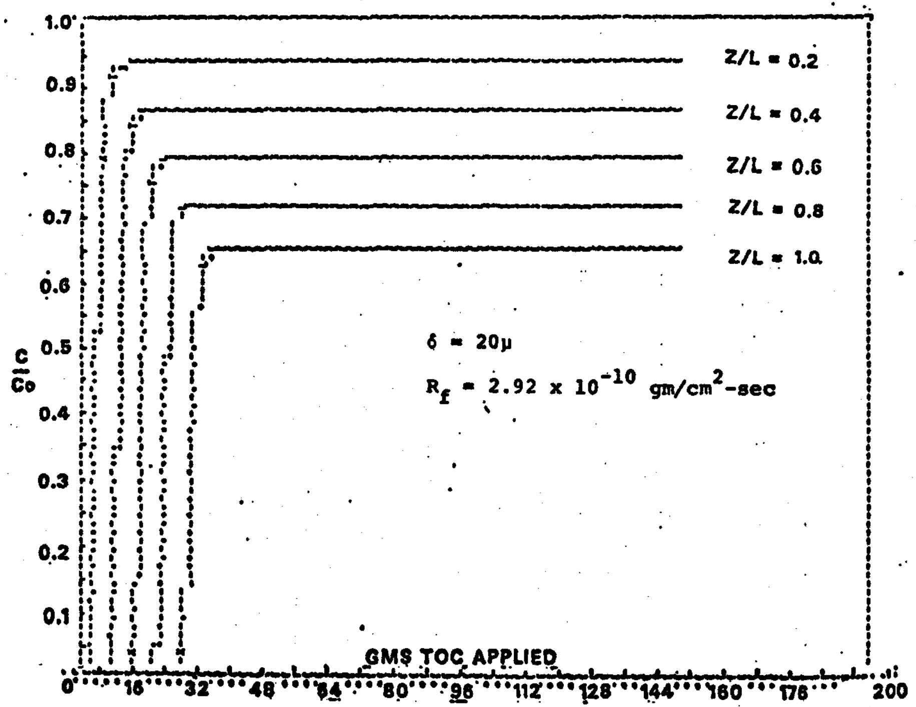


FIGURE 55

DIMENSIONLESS EFFLUENT CONCENTRATION PROFILES
PREDICTED BY THEORETICAL MODEL
5°C



At 5°C, in Figure 55, a different picture is obtained. At Z/L = 0.2 the effluent closely reaches the influent value, whereas at Z/L =1.0, the C/C_0 value equals about 0.65. The sharpness of the breakthrough curves once again indicates rapid initial adsorption followed by prolonged bio-oxidation. Poorer performance in TOC removal at 5°C than 25°C results from the differences in bacterial reaction rates in the model.

Figure 56 and 57 depict the build-up of solute inside the carbon particle vs. TOC applied as a function of bed depth at 25°C and 5°C, respectively. The two plots closely parallel the C/C_0 plots shown earlier. The steep rise in the profiles indicates that the pores get filled up very rapidly, although not completely exhausted. At 25°C at Z/L = 1.0 the carbon remains virgin according to the model, i.e. the bacterial film removes all the TOC before it reaches the carbon, thus prolonging the life of the bed indefinitely. At 5°C , in Figure 57, the build-up of solute is much more and even at Z/L = 1.0, the Y value is 0.83 indicating substantial exhaustion of the carbon.

Figures 58 and 59 show the TOC removed from the entire column vs. the TOC applied at 25°C and 5°C, respectively. Drawn on the plots are also the experimental curves (extrapolated) obtained from the pilot plant. At 25°C, the theoretical model

FIGURE 56

BUILD-UP OF AVERAGE SOLUTE CONTENT IN SOLID AS PREDICTED BY THEORETICAL MODEL

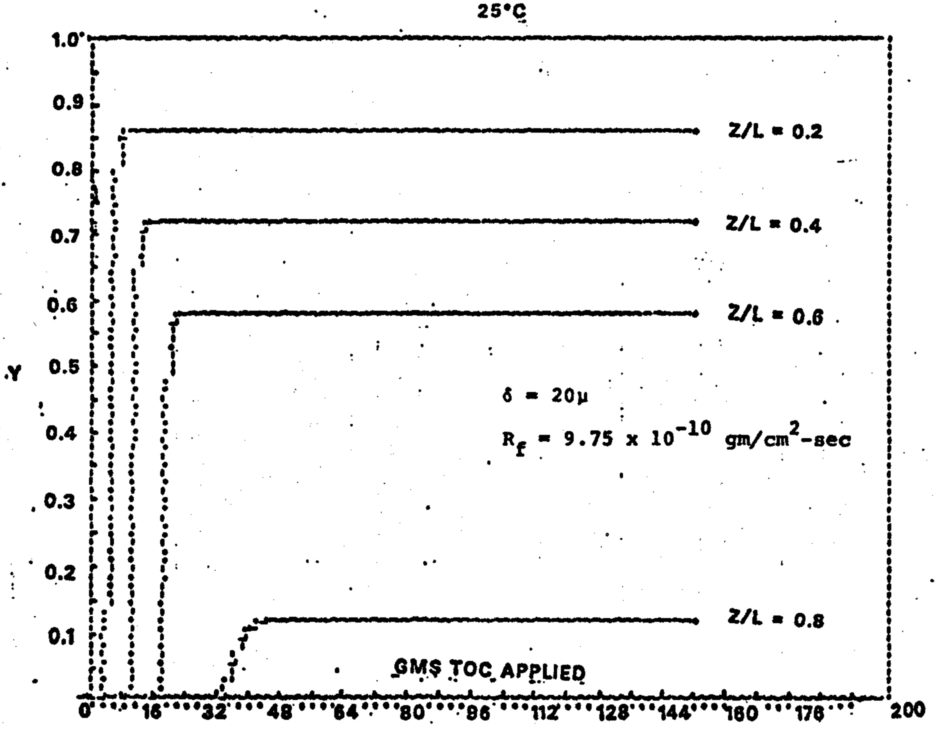


FIGURE 57

BUILD-UP OF AVERAGE SOLUTE CONTENT IN SOLID AS PREDICTED BY THEORETICAL MODEL

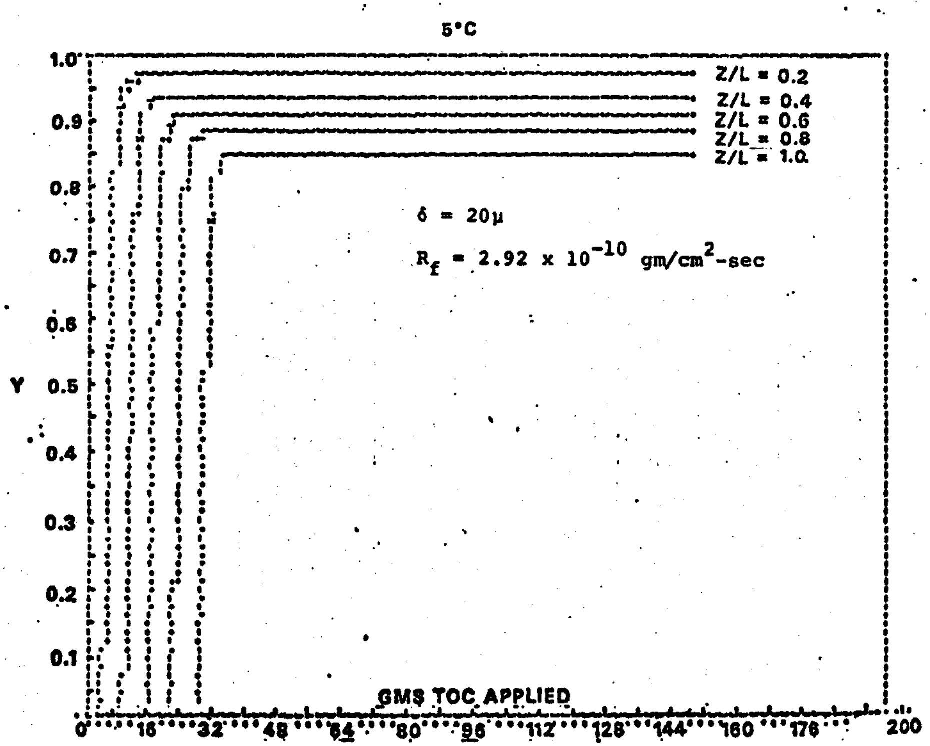


FIGURE 58

GMS TOC REMOVED vs GMS TOC APPLIED
AS PREDICTED BY THEORETICAL MODEL
25°C

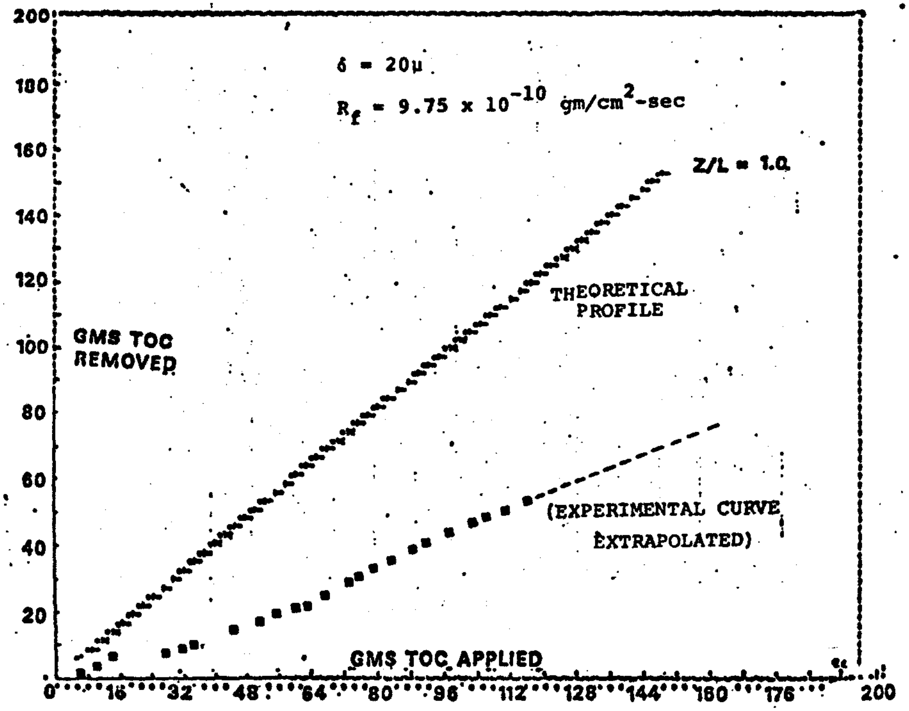
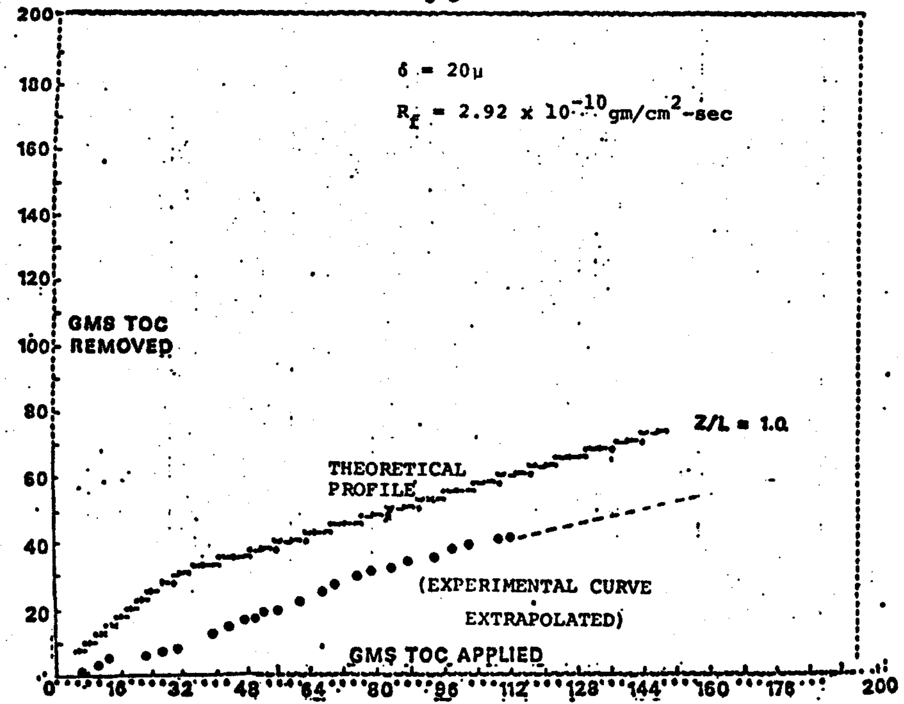


FIGURE 59

GMS TOC REMOVED vs GMS TOC APPLIED
AS PREDICTED BY THEORETICAL MODEL
5°C



predicts complete removal, which is in contradiction with our experimental observations where leakage of soluble organics was measured in the effluent. At 5°C in Figure 59, a much closer agreement to the experimental curve is predicted by the theoretical model. This is fortuitous as we happened to choose an R_f value in the right "ball park". Note that even at 5°C, the model predicts continued removal.

The dependence of these results on the R_f and δ values (chosen somewhat arbitarily) was next investigated. Table 53 in Appendix 4 shows a list of the parameters varied. Figures 79 and 80 in Appendix 4 are plots of cumulative TOC removal from the effluent end (Z/L = 1.0) vs. applied TOC at 25°C and 5°C, respectively. At 25°C, three profiles are shown for film reaction rates 9.75, 7.0 and 4.45 $(gm/cm^2\text{-sec}) \times 10^{10}$. The R_f values were varied in an attempt to duplicate the experimental curve which was obtained (which is shown in an extrapolated form on Figure 79, as well). One way of matching a theoretical profile to the experimental curve used, was to backcalculate the R_f value required to give the same slope as the experimental curve. Thus, 4.45×10^{-10} gm/cm^2-sec was estimated to be the value which would give the same slope or TOC removal rate as the experimentally derived curve.

Comparing these two curves, one sees little agreement in the initial period, with the two curves becoming closer as biological growth develops in the latter portion of the operation.

The large discrepancy between the TOC removal curve of $R_f = 9.75 \times 10^{-10}$ gm/cm^2 and the experimental curve can be attributed to the crude estimation made of the film reaction rate in our reactors. At 5°C, similarly, three profiles for R_f values of 2.92, 2.53 and 2.0 (gm/cm^2 - sec) x 10^{10} are shown. Much closer agreement is seen between the curve $R_f = 2.0 \times 10^{-10}$ and the experimental curve. The TOC removal also seems to be less sensitive to R_f values at 5°C, as seen from the small difference between 2.0×10^{-10} and 2.92×10^{-10} in Figure 80. Thus column performance is not only better at higher temperature, but also more strongly dependent on biological action.

Figure 81 and 82 are attached in Appendix 4 to show the effect of changing R_f value on C/C_0 and Y, respectively, at 25°C. Thus, by reducing the R_f value by 50% from 9.75×10^{-10} to 4.45×10^{-10} gm/cm^2 - sec, we get final effluent concentration of 0.45 and Y or solute build-up of 0.65. The effect of varying the film reaction rate is quite dramatic and underlines the predominance of biological removal over physico-chemical phenomenon.

Finally, the sensitivity of our model to the bacterial film thickness was tested.

Figure 83 in Appendix 4 shows a plot of TOC removal vs. TOC applied at 5°C for δ values of 5μ , 20μ and 40μ with the same R_f value of 2.53×10^{10} gm/cm^2 - sec. Higher TOC removal is seen to occur with smaller film thickness, although the effect is not very significant (17% more removal for an eight-fold drop in δ). This observed effect can be explained by the fact that faster diffusion occurs through the film when the film thickness is smaller.

The solutions obtained over-predict the bacterial action at both 25°C and 5°C. As figures 56 and 57 suggest, the carbon pores are very slowly exhausted. Based on iodine numbers and isotherms on regenerated carbons from the columns, the carbon had reached exhaustion at the end of the run. One similarity between theoretical and experimental results exists though. It was observed from the pilot plant run, as shown in Figure 43, that TOC removal did not stop, which agrees with the theoretical model.

The discrepancy between the experimental and theoretical results arises from the assumptions made and the input data utilized to mathematically define and solve the fixed-bed problem. It was assumed that the non-adsorbable fraction is completely degraded, and that the adsorbable fraction is vulnerable to biological decomposition (based on the work of Bertrandy (1974) on the same sewage). This may not necessarily be the case as obviously documented in the pilot PCT plant studies where TOC leakages did occur. With a more specific knowledge on the input parameters and the nature of organics in domestic wastewater in our model (e.g. reaction rates, film thickness) more reliable results can be assured. This is not a simple task, however, due to the complexity and great variations in domestic sewage.

In spite of the disagreement between pilot plant and mathematical model results, the model predictions have certain significant implications. Thus, the model implies that for the ideal use of a biodegradable and adsorbable feed, bioactivity would keep the column in operation indefinitely with an extremely high volumetric removal rate.

The model was developed specifically to explain adsorber behaviour in the presence of bacterial activity, and was only the first attempt to that end.

5.6 CONCLUSIONS

From the pilot PCT plant study and its associated investigations, the following conclusions can be drawn:-

1) Physical-Chemical treatment using granular activated carbon columns was shown to be capable of delivering high quality effluents continuously at 5°C and 25°C.

2) Microbiological studies indicated that there is extensive bacterial life in the carbon beds at both temperatures; although it proliferates more at the higher temperature. Greater bacterial numbers at 25°C than at 5°C partially explain why a higher rate and overall removal is seen in the 25°C column. Bacterial densities in the adsorbers were found to be similar to those reported in the mixed liquor of an activated sludge plant.

3) Denitrification occurs to a significant extent inside beds which were measured to be aerobic. It is postulated that this is made possible by anaerobic pockets created by localized flow

conditions. Denitrifiers were found to exist in significant quantities inside the beds, giving concrete evidence of denitrifying potential. Denitrification rates were found to be 1/4th to 1/10th less than those obtained in plastic media and GAC fluidized beds. Rates are still high enough considering the fact that excess organic substrate was not available in the pilot plant.

4) The rate and extent of organic removal seems to be governed by biological rather than physico-chemical phenomenon. The results indicate that although low temperature deteriorates the performance of the bed, sufficient bio-oxidation still occurs to make cold climate operation feasible.

5) Theoretical modelling indicates that bacterial action can prolong the life of the carbon indefinitely with extremely low activated carbon exhaustion rates.

6) Theoretical modelling procedures developed to account for bacterial reaction inside carbon beds, were found to be inadequate due to simplistic assumptions on the nature of sewage organics. Lack of physical parameter values needed to solve the problem also to some extent contributed towards the discrepancy between experimental observations and theoretical predictions.

CHAPTER 6

GENERAL SUMMARY AND RECOMMENDATIONS

6.1 SUMMARY AND CONCLUSIONS

The objective of evaluating the effect of low temperature on the Physical-Chemical treatment of domestic wastewater was divided into three separate phases, each one evaluating a different aspect of the problem.

Starting with the batch feasibility study of PCT using powdered activated carbon, it was shown that adsorption was the most temperature sensitive operation of PCT. Coagulation and flocculation were neglected on the basis of theoretical evaluation, and settling was observed to exhibit temperature dependence in the range 2 - 25°C. However, adequate overflow rates (above 600 GPM/ft^2) at low temperatures were obtained for over ninety per cent removal of suspended solids, indicating that settling is not a crucial variable.

Batch tests showed that PAC could be easily separated to yield high quality effluents at temperatures as low as 2°C.

For the time being, however, granular activated carbon is a more attractive choice, chiefly because of its regenerability which has been demonstrated to be economically and technically feasible. For this reason, one has to understand temperature effects on columnar behaviour.

Theoretical models for multi-component systems are very complex, hence a simple compound, Sodium Dodecyl Sulfate was chosen for the temperature effects study. Results at 4°, 13° and 25°C indicated a very low order of temperature dependence (3.2 kcal/mole, as estimated from general rate coefficients). A close match was obtained between the theoretical model (which was a modified version of Thomas' reaction kinetics solution) and experimental effluent concentration profiles, with the exception of the 2°C run. This discrepancy was attributed to the low values of D_s, the solid phase pore diffusivity, which results from Tien's method at 2°C. Generally, it was noted from the pure compound study that low temperature would cause mild adverse effect on adsorption kinetics.

A continuous flow PCT facility was set up and the long term effects of low temperature on carbon beds, especially with respect to biological activity, were studied. It was found that bacterial life plays a very important part in the enhancement of the life of the carbon beds, even at 5°C. Nevertheless, the carbon does get exhausted inspite of external bio-oxidation due to the build-up of solids in the carbon pores. A secondary phenomenon of denitrification was noted to occur simultaneously with soluble organic carbon removal. Although aerobic conditions prevailed inside the beds, it was hypothesized that denitrification could take place due to localized flow conditions.

Microbiological investigation of the carbon removed from the column after final shutdown revealed that over 1.4 x 10^9 cells per gram of GAC were present in the lead column at 25°C. Lower microbial numbers at 5°C partially explain why organic removal is lower at 5°C in the bed. Significant numbers of denitrifiers were also determined to be present in the carbon beds.

A theoretical model, which was developed to explain columnar kinetics in the presence of bacterial activity, was a limited success as the model at both 25°C and 5°C overpredicted the performance of the adsorbers in terms of TOC removal. This flaw was attributed to the inherent assumptions built into the model. The non-adsorbable fraction of domestic wastewater was assumed to be degradable, which was not the case, as seen from the leakages which occurred in the carbon columns. One point of significant agreement between the theoretical and experimental results was that continued TOC removal was indicated, in spite of carbon exhaustion.

The pilot PCT plant demonstrated quite successfully that high quality effluents could be delivered at temperatures as low as 5°C.

6.2 RECOMMENDATIONS

1) Continuous flow studies should be conducted using PAC at low temperature on a pilot scale. Bacterial enhancement is claimed to be higher in PAC due to its smaller size. Settling and re-cycling of microbial PAC flocs should be evaluated.

2) As bacterial life is ubiquitous inside carbon columns, it becomes necessary to make mass balances on carbon, nitrogen and oxygen within the sytem. It is important to know just how much of the TOC is removed by adsorption and what serves as substrate for bacterial consumption and the rest assimilated. Radioactive isotopes could be used as tracers to chart the behaviour of carbon atoms.

3) To further understand theoretical concepts, GAC study should be repeated using a single component soluble substrate, which is simultaneously well adsorbed and biologically oxidized inside carbon beds, e.g. Phenol. This could serve to demonstrate whether the theoretical model developed in this study was valid when the non-adsorbable fraction of the substrate was subsequently degraded.

4) Stuart's (1967) model using a diffusion type relation for the intra-particle mass transfer should be further investigated. It is felt that this approach is superior to kinetic type approximations.

5) As the quality of sewage is different in the North, some studies should be carried out to evaluate the feasibility of PCT on typical domestic wastewaters expected in the Arctic.

ABBREVIATIONS AND SYMBOLS

Abbreviations

ABS - alkyl benzene sulfate.

AC - activated carbon.

APHA - American Public Health Association.

B.O.D. - biochemical oxygen demand.

CAS - conventional activated sludge.

C.O.D. - chemical oxygen demand.

DO - dissolved oxygen.

GAC - granular activated carbon.

GPD - gallons per day.

H1 - lead column at 25°C.

H3 - last column at 25°C.

L1 - lead column at 5°C.

L3 - last column at 5°C.

MGD - million gallons per day.

mg/l - milligrams per liter.

MLSS - mixed liquor suspended solids.

MPN - most probable number.

MTZ - mass transfer zone.

$NO_2^= + NO_3^- - N$ - nitrites plus nitrates measured as nitrogen.

$NO_3^- - N$ - nitrates measured as N.

N_{Re} - Reynolds number.

N_{Sc} - Schmidt number.

as P - measured as phosphorus.

Abbreviations

P728 - Percol 728.
PAC - powdered activated carbon.
PCT - physico - chemical treatment.
ppm - parts per million.
psig - pressure per square inch, gauge.
RPM - revolutions per minute.
SDS - sodium dodecyl sulfate.
TOC - total organic carbon.
USGPD - U.S. gallons per day.
U.V. - ultra violet.

Symbols

(Note that symbols used in the computer program may differ slightly from those noted here. Symbols used in the computer programs are defined in the programs themselves, as in Appendix 6. A symbol is used at times to define different variables, which may cause come confusion. The reader should in that event search for the definition inside the thesis whereever the symbol was first introduced).

a - interfacial mass transfer area.
a - particle radius .
a_1, a_2 - constants used in bacterial film model.
A - bed cross-sectional area.
A^o - angstroms.
A_p - projected area of the body.
b - velocity constant in Langmuir's equation.
b' - constant in terminal velocity equation.

Symbols

C - solute concentration in bulk phase.

C_D - dimensionless drag coefficient.

C_f - solute concentration in film phase.

C_i - point concentration of solute in solid phase.

C_o - initial solute concentration.

C_s - solute concentration in fluid phase at particle surface.

C_s - concentration of vacant sites.

d - diameter of particle.

d_p - diameter of particle.

E_a - activation energy.

f_1 - steric factor.

f_D - drag force.

F - volumetric feed flow rate.

g - gravitational constant.

G - velocity gradient.

h_f/L - head loss per unit length of bed.

J_D - mass transfer factor based on analogy to heat transfer.

J_{ok} - rate of orthokinetic flocculation.

J_{pk} - rate of perikinetic flocculation.

$\bar{k}$ - Boltzman's constant.

K - empirical constant used in Freundlich's equation.

also - reaction velocity.

K_o - frequency factor.

Symbols

K_1 - forward rate constant.

K_2 - desorption rate constant.

K_f - external film mass transfer coefficient.

$k_p a_p$ - intra-particle mass transfer rate.

M - molecular weight of solvent in Wilke-Chang equation.

n - empirical constant in Freundlich's equation.

also - constant in terminal velocity equation.

N^o - total concentration of particles in suspension at time t.

P - power input to fluid.

q - average solute concentration in solid phase.

$\bar{q}$ - average solute concentration in solid phase.

q - adsorption loading at saturation.

q_i - point concentration in solid at particle surface.

q/q_s - fractional adsorption uptake.

Q^o - monolayer adsorptive capacity.

r - radial direction in the particle.

R - particle radius, universal gas constant.

\- reaction rate per unit volume.

R_f - film phase degradation rate per unit surface area.

R_l - bacterial reaction rate in fluid phase per unit fluid volume.

R_p - particle radius.

R_s - bacterial reaction rate inside solid particle per unit volume.

Symbols

T - absolute and relative temperature.

U_s - columnar velocity.

V - velocity.

also - solute molal volume at normal boiling point.

V - vessel volume.

V_s - superficial fluid velocity.

V_t - overflow rates.

also - relative velocity of particle with respect to the fluid.

x - reduced fluid phase concentration.

x_s - reduced fluid phase concentration at the particle surface.

X - association factor for solvent.

y - reduced solid phase concentration.

y_s - reduced solid phase concentration at the particle surface.

Greek symbols

α - intraparticle porosity.

δ - bacterial film thickness.

ε - liquid volume void fraction in bed.

D - solute diffusivity in bulk phase.

D_f - bulk fluid diffusivity.

D_{pore} - fluid phase pore diffusivity.

D_s - solid phase pore diffusion coefficient.

ζ - mass density.

ζ_1 - mass density of sphere.

ζ_b - bed porosity.

Greek symbols

θ - thermal coefficient.

ψ - dimensionless parameter used in Tien's model.

ψ_s - particle sphericity.

κ - general rate coefficient.

η - collision efficiency factor.

μ - microns.

also - viscosity.

ξ - reduced distance along the column.

ν - kinematic viscosity.

τ - reduced time.

ΔH - heat of adsorption.

Δt - time increment.

Δz - differential height in a fixed-bed.

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APPENDIX I

ANALYTICAL TECHNIQUES

The samples collected from pilot plant were usually analyzed for the following parameters.

A1.1 Turbidity

This was measured to see whether bacterial action caused any increase in turbidity due to sloughing of end-products. An Hellige turbidimeter (Model No.8000) was used, along with a calibration giving results in mg/l of silica.

A1.2 pH

An Orion specific ion electrode and meter (Model No 401) was used to measure pH.

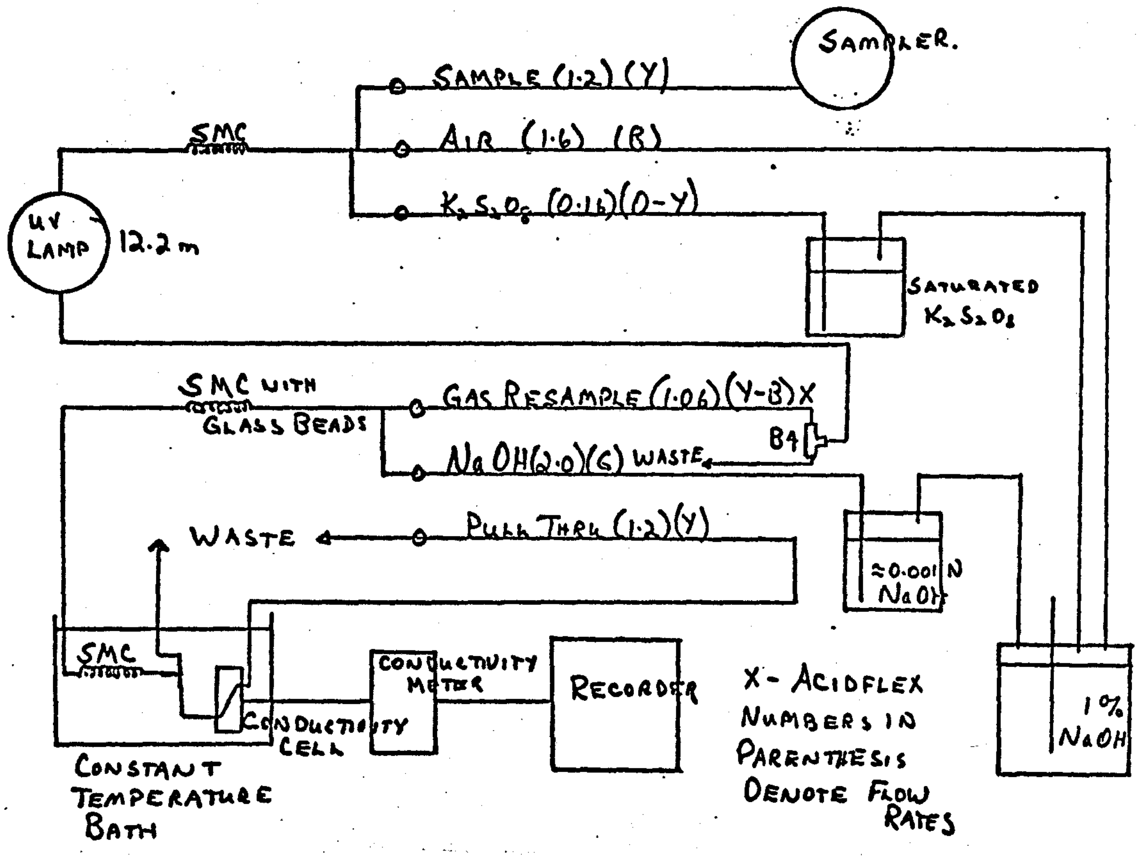
A1.3 Total Organic Carbon

To each 10 ml sample, one drop of concentrated sulfuric acid was added to bring pH down to 4.3. Inorganics were purged as carbon dioxide by stripping for five minutes with nitrogen gas. If the TOC of sample was known to be over 30 mg/l, dilution was undertaken to bring concentration to a measurable range.

An automated wet UV oxidation method as devised by Addie and Murphy (1973) was used at a sampling rate of 20/hr with two water rinses between each sample. A flow diagram of the process is included as Figure 60. Peaks obtained were converted to TOC values through a standard calibration curve. Daily calbrations were carried out using urea solutions.

FIGURE 60

TOTAL CARBON IN WATER AND WASTEWATER 0-30 MG/L



A1.4 Soluble Organic Carbon

TOC values represent a mixture of colloidal and soluble organic compounds present in wastewater. Often, we are interested in knowing exclusively the soluble organic content of the sewage. The sample is, therefore, filtered through a .1μ membrane, and the filtrate yields the soluble organic carbon.

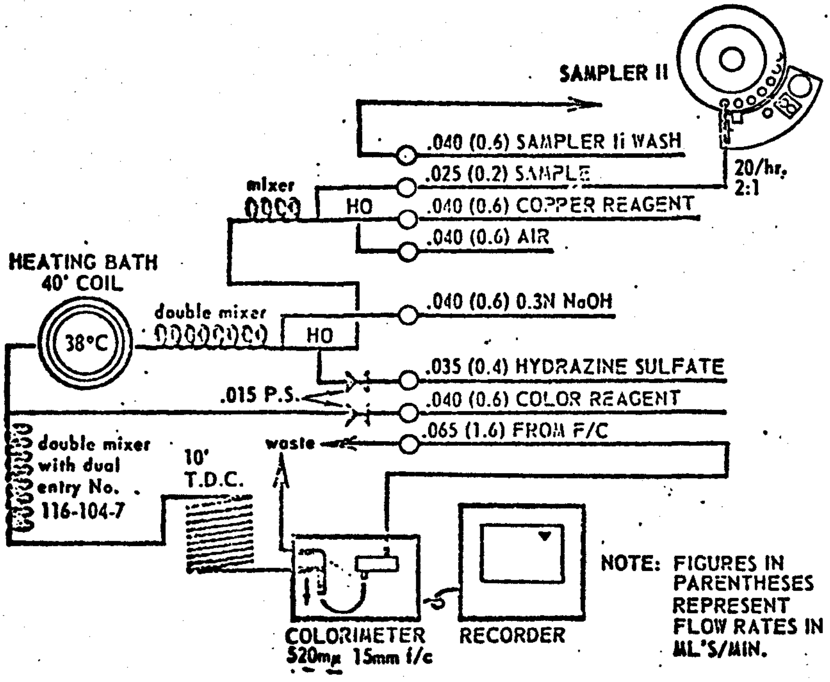
A1.5 Nitrates & Nitrites

The process of denitrification involes the conversion of nitrates and nitrites to nitrogen gas. The dissolved NO_3^- & $NO_2^=$ -N content in sewages was measured by an automated procedure No 33-69W outlined in Technicon Manual. The procedure is based originally on the development of Kamphake (1967) where the nitrates are reduced to nitrites by an alkaline solution of hydrazine sulfate containing a copper catalyst. The stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-napthylethylenediamine dihydrochloride to form a soluble dye which is measured colorimetrically at wavelength of 520μ .

The sampling rate is 20 litre/hour with a distilled water wash between alternate samples. Applicable range for the method is 0.05-10mg/1 $NO_3^- + NO_2^=$ - N. Standard calibration curves were obtained by using accurately prepared potassium nitrate solutions. A schematic flow chart is included as Figure 61.

FIGURE 61

TECHNICON METHOD FOR ANALYSIS OF NITRATE + NITRITE IN WATER AND WASTEWATER (RANGE 0-2.0 PPM)



A1.6 Dissolved Oxygen

Dissolved oxygen content in the sewage along the carbon columns was measured by the Winkler Test (Montgomery - Sodium Azide Modification) as recommended by Standard Methods (1971). The method is suitable if analysis is carried out immediately on the sample, as temperature variations can result in DO changes.

A1.7 Biochemical Oxygen Demand (BOD)

BOD tests were run on samples collected from pilot plant facility, using the dilution technique. The dissolved oxygen depletion was measured by an oxygen probe (with an attached stirrer) and a YSI meter (Model No 54 RC) giving readings directly in DO mg/l.

Sewage was aerated before the test, nutrients and buffer added, initial DO taken, sealed and incubated for five days after which the five day BOD was calculated. At times dilutions were unnecessary since the effluents had so little BOD. Sand filtered sewage was usually diluted in 1:2 and 1:5 ratios. No seed was added, since sewage already contains large numbers of acclimated bacteria.

A1.8 Chemical Oxygen Demand (COD)

A few COD tests were run on the samples from pilot plant runs using an automated procedure developed in the Technicon Manual.

The method was not found to be suitable for the COD concentration of our interest.

A1.9 Iodine Numbers

The iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration of the residual filtrate is 0.02 N. The procedure followed was as outlined by Culp and Culp (1971).

A1.10 Temperature Measurements

Copper constantan thermo-couples were inserted into the columns with the bare ends soldered. A reference electrode was submerged in an ice bath at 0°C, and the voltage generated due to the temperature gradient measured by a Honeywell Potentiometer (Model No. 2733). Standard calibration charts were used to convert voltage to temperature values.

APPENDIX II

ANALYTICAL DIFFICULTIES

A2.1 TOC Measurements

Hals (1974) has documented extensively the difficulties which arise in TOC measurements. His recommendations were followed rigorously to obtain accurate and precise determinations of TOC.

A2.2 Filter Wash-Off

A great disadvantage in the use of TOC as a parameter for the measurement of contaminant concentration is that it is a non-specific parameter. It measures any organic substance which leaches into the sample solution. Membrane filters can cause errors in measurements as they contribute TOC to the filtrate during filtration (Hals, 1974). Throughout the experiment, all membrane filters were rinsed under vacuum with 500 ml distilled water, before use. The initial 10 - 20 ml portion of the filtrate was discarded and analysis carried out on the remainder.

Another possible contribution to leaching can come from powdered carbon itself, if it passes through the filter. Researchers at McMaster University have shown (Hals, 1974) that .1μ filters completely prevents PAC from filtering through.

A2.3 Carbon Preparation Procedures

Activated carbon was washed and dried thoroughly to drive off any organic or inorganic residues, which might otherwise remain on the carbon and subsequently contaminate the solution.

Washing and drying were accomplished by following the step by step procedure detailed below:-

1) Fill up 2 litre beaker with 200 gm dry carbon.
2) Introduce 1500 ml distilled water.
3) Boil vigorously for two hours to expel gas bubbles.
4) Let contents settle and pour off supernatant.
5) Refill with 1500 ml distilled water.
6) Mix thoroughly.
7) Filter through Whatman #1 filter paper.
8) Dry in oven at 103°C for 24 hours.
9) Store in dessicator until used.

This procedure prevents moisture and dust particles from altering weight and quality of carbons.

APPENDIX III

TABLES AND CALCULATIONS

TABLE 29

SAMPLE CALCULATION OF SETTLEABLE FRACTION OF PARTICLES

Initial Phosphate concentration = 5.5 mg/l

Temperature = 2°C.

Time = 5 min.

Phosphate concentration in solution = 1.0 mg/l as P

Final residual concentration = 0.30 mg/l

% of Settleable Particles removed up to time of 5 min. $= \frac{5.5 - 1.0}{5.5 - .30} \times 100$

$= 86.5\%$

TABLE 30

CALCULATION OF OVERFLOW RATES

Volume of sewage in jar = 3400 cm^3

Cross-sectional area of jar = 100 cm^2

Initial height of liquid = $\frac{3400}{100}$ = 34 cm

Location of sampling outlet from base = 3" = 7.62 cm

Therefore the distance the particles fall = 34 - 7.62 = 26.38 cm

Overflow flux = Superficial linear velocity x Time

$$= 26.38\,\text{cm} \times 1440 \frac{\text{min}}{\text{day}} \times \frac{\text{ft}^2}{\text{ft}^2} \times 7.481 \frac{\text{U.S.Gal}}{\text{ft}^3} \times \frac{\text{ft}}{30.48\ \text{cm}}$$

$$= 9323 \frac{\text{U.S. Gal}}{\text{ft}^2} \quad \frac{\text{min}}{\text{day}}$$

Sampling Time min.	Overflow Rates USGPD/ft^2
0	∞
1	9323
2	4661
4	2331
6	1554
10	932
25	373
40	233

This table was used in all the settling curves as the initial liquid volume was the same.

TABLE 31

CALCULATION OF SOLID PHASE PORE DIFFUSION COEFFICIENT FOR SDS/GAC SYSTEM

TEMPERATURE = 13^{0}C

COL I TIME in hrs	COL II C/C_0	COL III C	COL IV Q_{av}	COL V Q_s	COL VI Q_{av}/Q_s
0.5	0.700	154.0	27.60	112.0	0.246
1.0	0.618	136.0	35.10	111.9	0.314
2.0	0.550	121.0	41.40	111.5	0.371
3.0	0.503	110.7	45.70	111.4	0.410
4.0	0.476	104.7	48.20	111.2	0.433
6.0	0.440	96.8	51.50	111.0	0.464
8.0	0.400	88.0	55.20	110.8	0.498
12.0	0.330	72.6	61.60	110.4	0.558
24.0	0.202	44.4	73.40	105.0	0.699
36.0	0.140	30.8	75.10	99.0	0.798
48.0	0.105	23.1	82.30	93.5	0.880

TABLE 32

CALCULATION OF SOLID PHASE PORE DIFFUSION COEFFICIENT FOR SDS/GAC SYSTEM

TEMPERATURE = 25^{0}C

COL I TIME in hrs	COL II C/C_0	COL III C	COL IV Q_{av}	COL V Q_s	COL VI Q_{av}/Q_s
0.5	0.650	133.6	30.20	107.0	0.282
1.0	0.581	119.4	36.20	106.8	0.339
2.0	0.501	103.0	43.00	106.0	0.406
3.0	0.435	89.4	48.80	105.0	0.465
4.0	0.389	80.0	52.70	104.0	0.507
6.0	0.320	65.8	58.70	102.0	0.575
8.0	0.270	55.5	63.00	99.5	0.633
12.0	0.201	41.3	69.00	95.0	0.726
24.0	0.109	22.4	76.90	83.5	0.920

TABLE 33

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME SDS/GAC SYSTEM

TEMPERATURE = 25^0C

Time in hrs	ψ	$D_s \times 10^8$ cm^2/sec
37.50	10.0	0.600
23.50	15.0	0.638
16.60	20.0	0.678
12.40	25.0	0.726
9.50	30.0	0.789
7.20	35.0	0.893
5.60	40.0	1.004
4.40	45.0	1.136
3.50	50.0	1.286
2.90	55.0	1.411
2.40	60.0	1.563
1.60	80.0	1.760
1.10	100.0	2.042
0.65	140.0	2.480

TABLE 34

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME SDS/GAC SYSTEM

TEMPERATURE = $25^{0}C$

Time in hrs	ψ	$D_s \times 10^8$ cm^2/sec
16.00	10.0	1.406
10.70	15.0	1.402
7.70	20.0	1.461
5.70	25.0	1.579
4.35	30.0	1.724
3.40	35.0	1.891
2.70	40.0	2.083
2.20	45.0	2.273
1.80	50.0	2.500
1.60	55.0	2.557
1.40	60.0	2.679
1.00	80.0	2.810
0.55	120.0	3.420

TABLE 35

SDS REMOVAL AND EFFLUENT CONCENTRATION RATIO VERSUS SDS APPLIED FOR EXPERIMENTAL COLUMNAR KINETICS

TEMPERATURE = 4^0C

Amount of SDS applied in gms (cumulative)	C/C_0 Effluent Ratio	Amount of SDS removed in gms (cumulative)
118.5	0.000	118.50
142.2	0.023	141.70
165.9	0.052	164.20
189.6	0.095	185.65
213.3	0.177	205.16
225.2	0.267	213.88
237.0	0.407	220.88
248.9	0.651	225.03
260.7	0.791	227.50
272.6	0.884	228.88
284.4	0.942	229.56

Weight of carbon in columns = Area x Particle Density x (1 - Void Fraction)

Void Fraction = 0.5 (from experiments)

$$\text{Weight of Carbon} = \frac{\pi}{4} \times \frac{1}{6^2}\text{ft}^2 \times 5\text{ft} \times 1.35\frac{\text{gms}}{\text{cm}^3} \times (30.5)^3\frac{\text{cm}^3}{\text{ft}^3} \times (1 - 0.5)$$

= 2085 grams.

$$\text{Loading} = \frac{229.56 \text{ gms SDS}}{2085 \text{ gms Carbon}} = 110.1 \ \frac{\text{mg SDS}}{\text{gm Carbon}}$$

TABLE 36

SDS REMOVAL AND EFFLUENT CONCENTRATION RATIO VERSUS SDS APPLIED FOR EXPERIMENTAL COLUMNAR KINETICS

TEMPERATURE = 13^0C

Amount of SDS applied in gms (cumulative)	C/C_0 Effluent Ratio	Amount of SDS removed in gms (cumulative)
118.5	0.000	118.50
142.2	0.017	141.80
165.9	0.035	164.70
189.6	0.084	186.40
213.3	0.157	206.40
225.2	0.256	215.20
237.0	0.477	221.40
248.9	0.709	224.90
260.7	0.849	226.60
272.6	0.930	227.50
284.4	0.977	227.70

Loading = 109.2 mgs SDS/gms Carbon

TABLE 37

SDS REMOVAL AND EFFLUENT CONCENTRATION RATIO VERSUS SDS APPLIED FOR EXPERIMENTAL COLUMNAR KINETICS

TEMPERATURE = 25^{0}C

Amount of SDS applied in gms (cumulative)	C/C_0 Effluent Ratio	Amount of SDS removed in gms (cumulative)
142.2	0.000	142.20
165.9	0.021	165.30
189.6	0.050	187.60
213.3	0.118	208.10
225.2	0.175	217.60
237.0	0.300	225.30
243.0	0.600	227.10
248.9	0.700	228.20
254.8	0.750	228.90
260.7	0.790	229.40
272.6	0.850	229.50

Loading = 110.0 mgs SDS/gms Carbon

TABLE 38

EFFECT OF D_s ON GENERAL RATE COEFFICIENTS AND MTZ HEIGHTS

TEMPERATURE = 2^0C

$D_s \times 10^8$ cm^2/sec	General Rate Coefficient sec^{-1}	MTZ Height cms
0.640	0.0297	67.2
0.425	0.0244	77.4
0.230	0.0168	88.5

TEMPERATURE = 13^0C

$D_s \times 10^8$ cm^2/sec	General Rate Coefficient sec^{-1}	MTZ Height cms
2.700	0.0531	41.4
1.560	0.0460	46.3
0.590	0.0303	65.0

TEMPERATURE = 25^0C

$D_s \times 10^8$ cm^2/sec	General Rate Coefficient sec^{-1}	MTZ Height cms
3.760	0.0722	30.8
2.680	0.0684	33.0
1.370	0.0583	51.0

TABLE 39

RAW DATA FROM LOW TEMPERATURE COLUMN UNFILTERED TOC

Date	Concentration in mg/l TOC				Volume passed in litre
	Feed	L_1	L_2	L_3	
4.12.73	38.6	34.4	37.4	33.0	165.0
5.12.73	30.0	8.8	6.8	5.4	118.0
6.12.73	30.0	11.6	10.0	10.0	104.0
12.12.73	35.4	32.2	26.1	19.8	275.0
13.12.73	36.4	30.9	24.8	24.8	121.5
14.12.73	21.6	12.5	6.7	11.0	122.5
15.12.73	25.0	12.5	-	-	382.0
20.12.73	32.4	22.0	14.4	12.6	121.0
23.12.73	29.3	17.0	16.0	9.4	142.6
24.12.73	18.2	10.6	4.5	4.5	121.0
26.12.73	7.8	3.6	1.8	-	250.0
27.12.73	18.9	11.4	5.0	3.8	131.0
28.12.73	12.2	7.6	2.0	2.0	130.0
30.12.73	12.2	7.4	-	-	260.0
1.1.74	20.0	10.0	-	-	110.0
4.1.74	17.2	7.6	-	-	354.0
5.1.74	15.4	8.4	0.6	-	119.0
6.1.74	11.0	5.4	-	-	128.5
9.1.74	22.8	14.2	6.2	11.4	130.0
10.1.74	20.8	13.2	5.2	5.2	118.0
11.1.74	15.8	10.6	3.0	3.0	117.0
13.1.74	6.6	4.6	-	-	169.0
15.1.74	4.0	0.8	-	-	103.0
18.1.74	21.5	16.4	5.2	4.0	171.0
19.1.74	13.0	10.5	0.8	-	121.0
22.1.74	9.4	7.7	0.4	-	161.0
23.1.74	22.2	14.4	2.1	1.1	134.0

TABLE 39 CONTD.

Date	Concentration in mg/l TOC				Volume passed in litres
	Feed	L_1	L_2	L_3	
F	21.1	17.4	8.8	6.8	**
25.1.74	23.5	15.4	8.0	6.8	199.5
F	23.6	16.5	8.5	6.9	**
26.1.74	19.4	13.4	5.5	2.3	142.8
F	19.0	13.4	5.5	4.0	**
27.1.74	13.1	7.9	3.3	1.5	112.9
F	12.7	6.8	3.3	1.4	**
29.1.74	17.4	10.8	2.6	1.7	77.4
F	16.5	10.3	3.5	2.0	**
30.1.74	20.8	11.4	7.8	6.8	90.0
F	20.2	10.3	5.5	6.0	**
31.1.74	21.3	15.0	7.7	6.0	75.4
F	20.8	14.6	7.2	6.2	**
1.2.74	22.7	17.9	7.2	5.7	116.0
F	22.6	16.6	7.8	5.7	**
2.2.74	17.7	13.3	6.6	5.2	117.9
F	17.2	11.9	6.8	5.7	**
3.2.74	9.6	7.0	4.0	2.7	119.5
F	10.4	7.6	4.2	3.0	**
4.2.74	11.3	7.2	4.4	3.6	136.3
F	11.8	8.2	-	3.6	**
5.2.74	15.6	15.3	7.4	6.6	118.5
F	20.3	15.2	6.9	6.2	**
6.2.74	27.6	17.6	10.4	8.2	115.1
F	-	18.5	11.2	9.5	**

F - Filtered TOC

TABLE 40

DIMENSIONLESS EFFLUENT CONCENTRATION FROM LOW TEMPERATURE COLUMN AS A FUNCTION OF TIME

Date	C/C_0		
	Packed bed height in ft		
	2	7	12
4.12.73	0.891	0.969	0.855
5.12.73	0.293	0.227	0.180
6.12.73	0.387	0.333	0.333
12.12.73	0.910	0.737	0.559
13.12.73	0.849	0.681	0.681
14.12.73	0.579	0.310	0.509
15.12.73	0.500	-	-
20.12.73	0.679	0.444	0.389
23.12.73	0.580	0.546	0.321
24.12.73	0.582	0.247	0.247
26.12.73	0.462	0.231	0.000
27.12.73	0.603	0.265	0.201
28.12.73	0.623	0.164	0.164
30.12.73	0.607	0.000	0.000
1.1.74	0.500	0.000	0.000
4.1.74	0.442	0.000	0.000
5.1.74	0.545	0.039	0.000
6.1.74	0.491	0.000	0.000
9.1.74	0.623	0.272	0.500
10.1.74	0.635	0.250	0.250
11.1.74	0.671	0.190	0.190
13.1.74	0.697	0.000	0.000
15.1.74	0.200	0.000	0.000
18.1.74	0.763	0.242	0.186
19.1.74	0.808	0.062	0.000
22.1.74	0.819	0.043	0.000
23.1.74	0.649	0.095	0.050
25.1.74	0.655	0.340	0.289
26.1.74	0.691	0.284	0.119
27.1.74	0.603	0.252	0.115
29.1.74	0.621	0.149	0.098
30.1.74	0.548	0.375	0.327
31.1.74	0.704	0.362	0.282
1.2.74	0.789	0.317	0.251
2.2.74	0.751	0.373	0.294
3.2.74	0.729	0.417	0.281
4.2.74	0.637	0.389	0.319
5.2.74	0.981	0.474	0.423
6.2.74	0.638	0.377	0.297

(-) not measured

TABLE 41

RAW DATA FROM HIGH TEMPERATURE COLUMN UNFILTERED TOC

Date	Concentration in mg/l TOC				Volume passed in litre
	Feed	H_1	H_2	H_3	
4.12.73	38.6	32.2	31.5	30.4	165.0
5.12.73	30.0	8.2	4.6	5.1	118.0
6.12.73	30.0	12.2	9.2	11.2	141.0
12.12.73	35.4	31.0	28.0	12.6	360.0
13.12.73	36.4	30.5	24.8	24.8	121.5
14.12.73	21.6	12.5	10.6	9.7	122.5
15.12.73	25.0	-	-	-	191.0
16.12.73	25.0	-	-	-	191.0
20.12.73	32.4	17.4	13.6	11.8	101.5
23.12.73	29.3	24.0	8.8	7.0	142.6
24.12.73	18.2	11.2	4.5	3.4	121.0
26.12.73	7.8	3.6	-	-	250.0
27.12.73	18.9	10.0	3.8	3.8	131.0
28.12.73	12.2	7.0	2.0	2.0	130.0
30.12.73	12.2	7.4	-	-	260.0
1.1.74	20.0	8.5	-	-	237.0
4.1.74	17.2	5.4	-	-	354.0
5.1.74	15.4	6.4	-	-	128.0
6.1.74	11.0	2.0	-	-	123.0
9.1.74	22.8	11.3	5.0	7.0	130.0
10.1.74	20.8	11.6	5.4	5.4	125.0
11.1.74	15.8	7.8	-	-	138.0
13.1.74	6.6	0.4	-	-	179.0
15.1.74	4.0	-	-	-	135.0
18.1.74	21.5	8.8	0.6	-	171.0
19.1.74	13.0	3.2	1.8	-	121.0
22.1.74	9.4	7.4	1.9	1.3	161.0

TABLE 41 CONTD.

Date	Concentration in mg/l TOC				Volume passed in litre
	Feed	H_1	H_2	H_3	
23.1.74	22.2	9.6	2.6	0.4	138.0
F	21.1	16.6	6.4	1.5	**
24.1.74	9.6	-	-	-	-
25.1.74	23.5	10.2	3.8	3.1	129.1
F	23.6	10.0	5.2	2.8	**
26.1.74	19.4	9.4	3.8	2.7	140.0
F	19.0	8.6	3.2	2.1	**
27.1.74	13.1	5.2	1.8	1.4	112.9
F	12.7	3.9	0.8	0.6	**
29.1.74	17.4	9.7	3.0	2.0	96.75
F	16.5	8.6	3.2	1.7	**
30.1.74	20.8	9.5	4.2	4.0	90.0
F	20.2	8.0	4.0	3.2	**
31.1.74	21.3	11.9	7.0	5.4	90.45
F	20.8	10.7	7.0	5.0	**
1.2.74	22.7	12.4	6.5	5.3	98.6
F	22.6	11.4	6.3	5.1	**
2.2.74	17.7	10.9	3.4	3.5	99.16
F	17.2	10.2	7.2	4.5	**
3.2.74	9.6	6.3	3.6	2.5	100.8
F	10.4	5.3	4.4	2.5	**
4.2.74	11.3	6.3	4.1	3.4	113.4
F	11.8	6.0	5.0	3.1	**
5.2.74	15.6	11.5	6.2	5.7	98.7
F	20.3	10.8	6.9	6.2	**
6.2.74	27.6	14.0	7.8	7.6	91.5
F	-	8.8	8.2	-	**

F - Filtered TOC

TABLE 42

DIMENSIONLESS EFFLUENT CONCENTRATION FROM HIGH TEMPERATURE COLUMN AS A FUNCTION OF TIME

Date	C/C_0		
	Packed bed height in ft		
	2	7	12
4.12.73	0.834	0.816	0.788
5.12.73	0.273	0.153	0.170
6.12.73	0.407	0.307	0.373
12.12.73	0.876	0.791	0.356
13.12.73	0.838	0.681	0.681
14.12.73	0.579	0.491	0.449
15.12.73	-	-	-
16.12.73	-	-	-
20.12.73	0.537	0.420	0.364
23.12.73	0.819	0.300	0.239
24.12.73	0.615	0.247	0.187
26.12.73	0.462	0.000	0.000
28.12.73	0.574	0.164	0.164
30.12.73	0.607	0.000	0.000
1.2.74	0.425	0.000	0.000
4.2.74	0.314	0.000	0.000
5.2.74	0.416	0.000	0.000
6.2.74	0.182	0.000	0.000
9.2.74	0.496	0.219	0.307
10.1.74	0.558	0.260	0.260
11.1.74	0.494	0.000	0.000
13.1.74	0.061	0.000	0.000
15.1.74	0.000	0.000	0.000
18.1.74	0.409	0.028	0.000
19.1.74	0.246	0.138	0.000
22.1.74	0.787	0.202	0.138
23.1.74	0.432	0.117	0.018
24.1.74	-	-	-
25.1.74	0.434	0.162	0.132
26.1.74	0.485	0.196	0.139
27.1.74	0.397	0.137	0.107
29.1.74	0.557	0.172	0.115
30.1.74	0.457	0.202	0.192
31.1.74	0.559	0.329	0.254
1.2.74	0.546	0.286	0.233
2.2.74	0.616	0.192	0.198
3.2.74	0.656	0.375	0.260
4.2.74	0.558	0.363	0.301
5.2.74	0.737	0.397	0.365
6.2.74	0.576	0.283	0.275

(-) not measured

TABLE 43

CUMULATIVE SOLUBLE ORGANIC CARBON REMOVAL FROM PILOT PLANT AT LOW TEMPERATURE

Date	Cumulative volume in litres	Gm TOC applied	Cumulative feed in gms	Gm TOC removed lead column	Cumulative TOC removal in gms	Gm TOC removed by 2nd column	Cumulative TOC removal from 2 lead columns	Gm TOC removed by 3rd column	Cumulative TOC removed entire column
4.12.73	165.0	6.36	6.36	0.69	0.69	0.000	0.694	0.231	0.925
5.12.73	283.0	3.54	9.90	2.50	3.19	0.236	3.430	0.165	3.826
6.12.73	367.0	3.12	13.02	1.91	5.10	0.166	5.506	0.000	5.902
12.12.73	662.0	9.75	22.77	0.88	5.98	1.678	8.064	1.733	10.193
13.12.73	783.5	4.43	27.20	0.67	6.65	0.741	9.475	0.000	11.600
14.12.73	905.0	2.64	29.84	1.09	7.74	0.711	11.270	*****	13.400
16.12.73	1287.0	9.55	39.39	4.78	12.52	0.000	0.000	0.000	0.000
20.12.73	1408.0	3.92	43.31	1.26	13.78	3.823	21.139	0.505	24.173
23.12.73	1551.6	4.18	47.49	1.76	15.54	0.143	23.042	0.541	27.017
24.12.73	1672.6	2.20	49.69	0.92	16.46	0.738	24.700	0.000	28.675
26.12.73	1922.6	1.95	51.64	1.05	17.51	0.450	26.200	0.450	30.625
27.12.73	2053.0	2.48	54.12	0.98	18.49	0.838	28.018	0.157	32.600
28.12.73	2183.0	1.57	55.69	0.59	19.08	0.728	29.336	0.000	33.918
30.12.73	2443.0	3.14	58.83	1.21	20.29	1.924	32.470	0.000	37.052
1.1.74	2553.0	2.20	61.03	1.10	21.39	1.100	34.670	0.000	39.252
4.1.74	2907.0	6.10	67.13	3.40	24.79	2.690	40.760	0.000	45.342
5.1.74	3026.0	1.83	68.96	0.83	25.62	0.928	42.518	0.000	47.100
6.1.74	3154.5	1.41	70.37	0.72	26.34	0.654	43.932	0.000	48.514
9.1.74	3284.5	2.97	73.34	1.11	27.45	1.040	46.082	0.000	50.664
10.1.74	3402.0	2.46	75.80	0.90	28.35	0.944	47.926	0.000	52.508
11.1.74	3519.0	1.85	77.65	0.61	28.96	0.889	49.425	0.000	54.007
13.1.74	3688.0	1.12	78.77	0.34	29.30	0.777	50.542	0.000	55.124
15.1.74	3791.0	0.41	79.18	0.33	29.63	0.082	50.954	0.000	55.536
18.1.74	3962.0	3.68	82.86	0.87	30.50	1.915	53.739	0.205	58.526
19.1.74	4083.0	1.57	84.42	0.30	30.80	1.174	55.213	0.097	60.097
22.1.74	4244.0	1.51	85.94	0.27	31.07	1.175	56.658	0.064	61.606
23.1.74	4378.0	2.97	88.91	1.04	32.42	1.648	59.346	0.134	64.428
25.1.74	4577.5	3.16	92.69	1.09	33.51	1.032	61.468	0.167	66.717
26.1.74	4720.3	2.77	95.46	0.86	34.37	1.128	63.456	0.457	69.162
27.1.74	4833.2	1.48	96.94	0.59	34.96	0.519	64.565	0.203	70.474
29.1.74	4910.6	1.35	98.29	0.51	35.47	0.635	65.710	0.070	71.689
30.1.74	5000.6	1.87	100.16	0.85	36.32	0.324	66.884	0.090	72.953
31.1.74	5076.0	1.61	101.77	0.48	36.80	0.550	67.914	0.120	74.111
1.2.74	5192.0	2.63	104.40	0.54	37.34	1.241	69.715	0.174	76.086
2.2.74	5309.9	2.09	106.49	0.52	37.86	0.750	71.025	0.165	77.541
3.2.74	5424.4	1.15	107.64	0.31	38.17	0.359	71.694	0.155	78.365
4.2.74	5565.7	1.44	109.18	0.58	38.75	0.382	72.636	0.104	79.411
5.2.74	5684.1	1.85	111.03	0.99	39.74	0.936	73.612	0.095	[illegible]
6.2.74	5744.2	3.18	114.21	1.19	35.44	0.829	75.591	0.253	[illegible]

TABLE 44

CUMULATIVE SOLUBLE ORGANIC CARBON REMOVAL FROM PILOT PLANT AT HIGH TEMPERATURE

Date	Cumulative volume in litres	Gm TOC applied	Cumulative feed in gms	Gm TOC removed lead column	Cumulative TOC removal in gms	Gm TOC removed by 2nd column	Cumulative TOC removal from 2 lead columns	Gm TOC removed by 3rd column	Cumulative TOC removed from entire column
4.12.73	165.0	6.36	6.36	1.05	1.05	0.116	1.166	0.182	1.348
5.12.73	283.0	3.54	9.90	2.58	3.63	0.425	4.171	0.000	4.353
6.12.73	424.0	4.23	14.13	2.51	6.14	0.423	7.104	0.000	7.284
12.12.73	784.0	....	26.85	1.58	7.72	1.020	9.704	5.544	15.490
13.12.73	905.5	4.43	31.28	0.72	8.44	0.653	11.177	0.000	16.903
14.12.73	1020.0	2.64	33.92	1.12	9.56	0.233	12.530	0.110	18.366
16.12.73	1410.0	9.55	43.47	4.78	14.34	1.837	19.147	0.670	25.853
20.12.73	1515.0	3.29	46.76	1.53	15.87	2.168	22.845	1.543	31.454
22.12.73	1654.1	4.18	50.94	0.75	16.62	0.811	24.406	0.133	33.188
24.12.73	1775.0	2.20	53.14	0.85	17.47	0.900	26.156	0.000	34.938
26.12.73	2025.0	1.95	55.09	1.05	18.52	0.812	28.018	0.000	36.800
27.12.73	2150.0	2.48	57.57	1.17	19.69	0.650	29.838	0.000	38.620
28.12.73	2266.0	1.57	59.14	0.67	20.36	1.924	32.432	0.000	41.214
30.12.73	2546.0	3.14	62.28	1.24	21.60	2.015	35.687	0.000	44.469
1.1.74	2783.0	4.74	67.02	2.72	24.32	0.000	0.000	0.000	0.000
4.1.74	3137.0	6.10	73.12	4.15	28.51	1.912	44.509	0.000	53.291
5.1.74	3265.0	1.47	75.09	1.15	29.66	0.419	46.478	0.000	55.260
6.1.74	3386.0	1.41	76.50	1.15	30.81	0.246	47.874	0.000	56.656
8.1.74	3518.0	2.96	79.46	1.49	32.30	0.819	50.183	0.000	[illegible]
10.1.74	3643.0	2.60	82.06	1.15	33.45	0.775	52.108	0.000	60.890
11.1.74	3761.0	2.18	84.24	1.09	34.54	1.076	54.274	0.000	63.056
13.1.74	3960.0	1.18	85.42	1.11	35.65	0.072	55.456	0.000	64.238
15.1.74	4095.0	0.54	85.96	0.54	36.19	0.000	55.996	0.000	64.778
18.1.74	4260.0	3.68	89.64	2.08	38.27	1.402	59.478	0.000	68.260
19.1.74	4387.0	1.57	91.21	1.18	39.45	0.169	60.827	0.000	69.609
22.1.74	4548.0	1.51	92.72	0.32	39.77	0.886	62.033	0.097	70.912
23.1.74	4666.0	3.06	95.78	1.74	41.51	0.966	64.739	0.304	73.922
25.1.74	4880.1	3.03	98.81	1.71	43.22	0.826	67.275	0.090	76.548
26.1.74	5020.1	2.72	101.53	1.40	44.62	0.784	69.459	0.154	78.886
27.1.74	5160.1	1.48	103.01	0.89	45.51	0.384	70.733	0.045	80.205
29.1.74	5256.9	1.68	104.69	0.74	46.25	0.648	72.121	0.097	81.650
30.1.74	5346.4	1.87	106.56	1.02	47.27	0.477	73.618	0.018	83.205
31.1.74	5437.4	1.93	108.50	0.85	48.12	0.443	74.911	0.217	84.715
1.2.74	5536.0	2.24	110.74	1.02	49.14	0.582	76.513	0.118	86.435
2.2.74	5635.1	1.76	112.50	0.68	49.82	0.744	77.937	0.000	87.859
3.2.74	5736.0	0.97	113.47	0.33	50.15	0.272	78.539	0.111	88.572
4.2.74	[illegible]	[illegible]	114.75	0.57	50.72	[illegible]	79.356	0.079	89.471
5.2.74	5946.1	1.54	116.29	0.40	51.12	0.563	80.242	0.049	90.443
6.2.74	6035.0	2.52	118.81	1.24	52.36	0.547	82.044	0.010	[illegible]

TABLE 45

RAW DATA FOR NITRATE REMOVAL FROM PILOT PCT PLANT AT LOW TEMPERATURE

	Nitrate + Nitrite Concentration in mg/l				Volume passed in litres
Date	Feed	L_1	L_2	L_3	
18.1.74	5.18	4.12	1.95	1.99	171.0
19.1.74	-	1.95	1.95	0.64	121.0
22.1.74	4.34	3.99	1.42	0.09	161.0
23.1.74	9.83	8.51	2.08	0.04	134.0
25.1.74	15.2	14.1	5.1	0.15	199.5
26.1.74	42.0	40.25	37.0	1.25	192.8
27.1.74	56.0	52.5	47.5	5.5	112.9
29.1.74	53.0	46.1	31.0	43.0	77.4
30.1.74	56.5	48.5	51.0	34.5	90.0
31.1.74	62.0	55.25	51.3	40.5	75.4
1.2.74	68.25	61.75	63.75	47.0	116.0
2.2.74	80.0	64.5	64.5	52.0	117.9
3.2.74	100.0	65.0	64.5	53.0	119.5
4.2.74	105.0	87.5	90.0	60.0	136.3

TABLE 46

CUMULATIVE NITRATE REMOVAL AT LOW TEMPERATURE FROM PILOT PCT PLANT

Date	Gms NO_3+NO_2 fed	Cumulative nitrate fed	Gms NO_3+NO_2 removed from lead columns	Cumulative nitrates removed in gms
18.1.74	0.89	0.89	0.180	0.180
19.1.74	0.61	1.50	0.37	0.550
22.1.74	0.70	2.22	0.06	0.610
23.1.74	1.32	3.54	0.180	0.790
25.1.74	3.03	6.57	0.22	1.01
26.1.74	6.00	12.57	0.25	1.26
27.1.74	6.32	18.89	0.40	1.660
29.1.74	4.10	22.99	0.53	2.190
30.1.74	5.09	28.08	0.72	2.91
31.1.74	4.67	32.75	0.51	3.42
1.2.74	7.92	40.67	0.75	4.17
2.2.74	9.43	50.10	1.83	6.00
3.2.74	11.95	62.05	4.18	10.18
4.2.74	14.31	72.36	2.39	12.57

TABLE 47

RAW DATA FOR NITRATE REMOVAL FROM PILOT PCT PLANT AT HIGH TEMPERATURE

Date	Nitrate + Nitrite Concentration in mg/l				Volume passed in litres
	Feed	H_1	H_2	H_3	
18.1.74	5.18	0.18	0.18	0.18	171.0
19.1.74	-	0.09	0.04	0.00	121.0
22.1.74	4.34	0.75	0.09	0.09	161.0
23.1.74	9.83	0.04	0.04	0.04	138.0
25.1.74	15.2	11.6	6.15	0.15	129.1
26.1.74	42.0	26.3	25.5	15.0	140.0
27.1.74	56.0	51.0	44.5	26.5	112.9
29.1.74	53.0	49.5	46.5	17.5	96.8
30.1.74	56.5	43.5	39.5	49.5	90.0
31.1.74	62.0	56.0	49.5	38.5	90.5
1.2.74	68.25	58.5	53.5	35.0	98.6
2.2.74	80.0	61.5	55.0	41.3	99.2
3.2.74	100.0	68.5	64.5	47.5	100.8
4.2.74	105.0	55.0	32.5	45.0	113.4

TABLE 48

CUMULATIVE NITRATE REMOVAL AT HIGH TEMPERATURE FROM PILOT PCT PLANT

Date	Gms NO_3+NO_2 fed	Cumulative nitrates fed in gms	NO_3+NO_2 removed from lead columns	Cumulative nitrates removed in gms
18.1.74	0.89	0.89	0.86	0.86
19.1.74	0.61	1.50	0.590	1.450
22.1.74	0.70	2.20	0.580	2.03
23.1.74	1.360	3.56	1.35	3.380
25.1.74	1.960	5.520	0.460	3.840
26.1.74	5.880	11.40	2.20	6.040
27.1.74	6.32	17.72	0.560	6.60
29.1.74	5.13	22.85	0.340	6.940
30.1.74	5.09	27.94	1.17	8.11
31.1.74	5.61	33.55	0.54	8.65
1.2.74	6.73	40.28	0.960	9.610
2.2.74	7.93	48.21	1.83	11.44
3.2.74	10.08	58.29	3.18	14.62
4.2.74	11.90	70.19	5.67	20.29

TABLE 49

CALCULATION OF SOLID PHASE PORE DIFFUSION COEFFICIENT OF SEWAGE/FILTRASORB 400 SYSTEM AT 25^{0}C

Initial Concentration C_0 = 25 mg/l TOC

COL I	COL II	COL III	COL IV	COL V	COL VI
Time in hrs	C/C_0	C mg/l	q_{av} mg TOC/gm Carbon	q_s mg TOC/gm Carbon	q_{av}/q_s
0.2	0.900	22.500	1.00	22.75	0.044
0.4	0.810	20.250	1.90	21.25	0.089
1.0	0.646	16.150	3.54	18.20	0.195
2.0	0.510	12.750	4.90	16.10	0.304
4.0	0.390	9.750	6.10	13.60	0.449
6.0	0.338	8.450	6.62	12.70	0.521
8.0	0.320	8.000	6.80	11.50	0.591
14.0	0.309	7.725	6.91	10.25	0.674
18.0	0.309	7.725	6.91	10.00	0.691
24.0	0.301	7.525	6.99	9.75	0.717

TABLE 50

CALCULATION OF SOLID PHASE PORE DIFFUSION COEFFICIENT OF SEWAGE/FILTRASORB 400 SYSTEM AT 5^{0}C

COL I Time in hrs	COL II C/C_0	COL III C mg/l	COL IV q_{av} mg TOC/gm Carbon	COL V q_s mg TOC/gm Carbon	COL VI q_{av}/q_s
0.2	0.950	23.750	0.50	28.75	0.0174
0.4	0.890	22.250	1.10	27.75	0.0396
0.6	0.740	18.500	2.60	25.50	0.1020
1.0	0.620	15.500	3.80	23.75	0.1600
2.0	0.500	12.500	5.00	21.50	0.2320
4.0	0.400	10.000	6.00	20.00	0.3000
6.0	0.340	8.500	6.60	16.00	0.4120
8.0	0.325	8.120	6.75	13.75	0.4910
15.0	0.315	7.880	6.85	12.00	0.5710
24.0	0.310	7.750	6.90	11.00	0.6260

TABLE 51

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME

SEWAGE/GAC SYSTEM

TEMPERATURE = 25^{0}C

Time in hours	ψ	$D_s \times 10^8$ cm^2/sec
14.90	20.0	0.755
12.10	25.0	0.745
9.80	30.0	0.765
7.90	35.0	0.814
6.60	40.0	0.853
5.70	45.0	0.875
4.50	55.0	0.910
3.15	80.0	0.894
2.55	100.0	0.883

e.g.

$$D_s = \frac{a^2}{\psi t} \doteq \frac{81 \times 10^{-4} \text{ cm}^2}{\psi \times t \times 3600 \text{ sec}} = \frac{225}{\psi t} \times 10^8 \text{ cm}^2/\text{sec}$$

TABLE 52

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME SEWAGE/GAC SYSTEM

TEMPERATURE = 5^0C

Time in hours	ψ	$D_s \times 10^8$ cm^2/sec
2.62	155.0	0.554
3.10	135.0	0.537
3.70	115.0	0.529
4.61	95.0	0.514
5.64	80.0	0.499
6.60	70.0	0.486
7.78	60.0	0.482
9.80	50.0	0.459
12.62	40.0	0.445
17.63	30.0	0.425

TABLE 53

LIST OF R_f, δ VALUES USED FOR THEORETICAL MODEL

PROGRAM NUMBER	R_f x 10^{10} gm/cm^2-sec	TEMPERATURE in ^{0}C	δ in μ
1	2.92	5	20
2	9.75	25	20
3	2.53	5	20
4	4.45	25	20
5	2.00	5	20
6	7.00	25	20
7	2.53	5	5
8	2.53	5	40
9	2.92	5	20

(In sensitivity analysis convergence test of ($Y - Y_s$) to 10^{-10} was used).

APPENDIX IV

ILLUSTRATIONS

FIGURE 62

EXPERIMENTAL VS THEORETICAL FRACTIONAL UPTAKE CURVES FOR SDS/GAC SYSTEM AT 13^{0}C

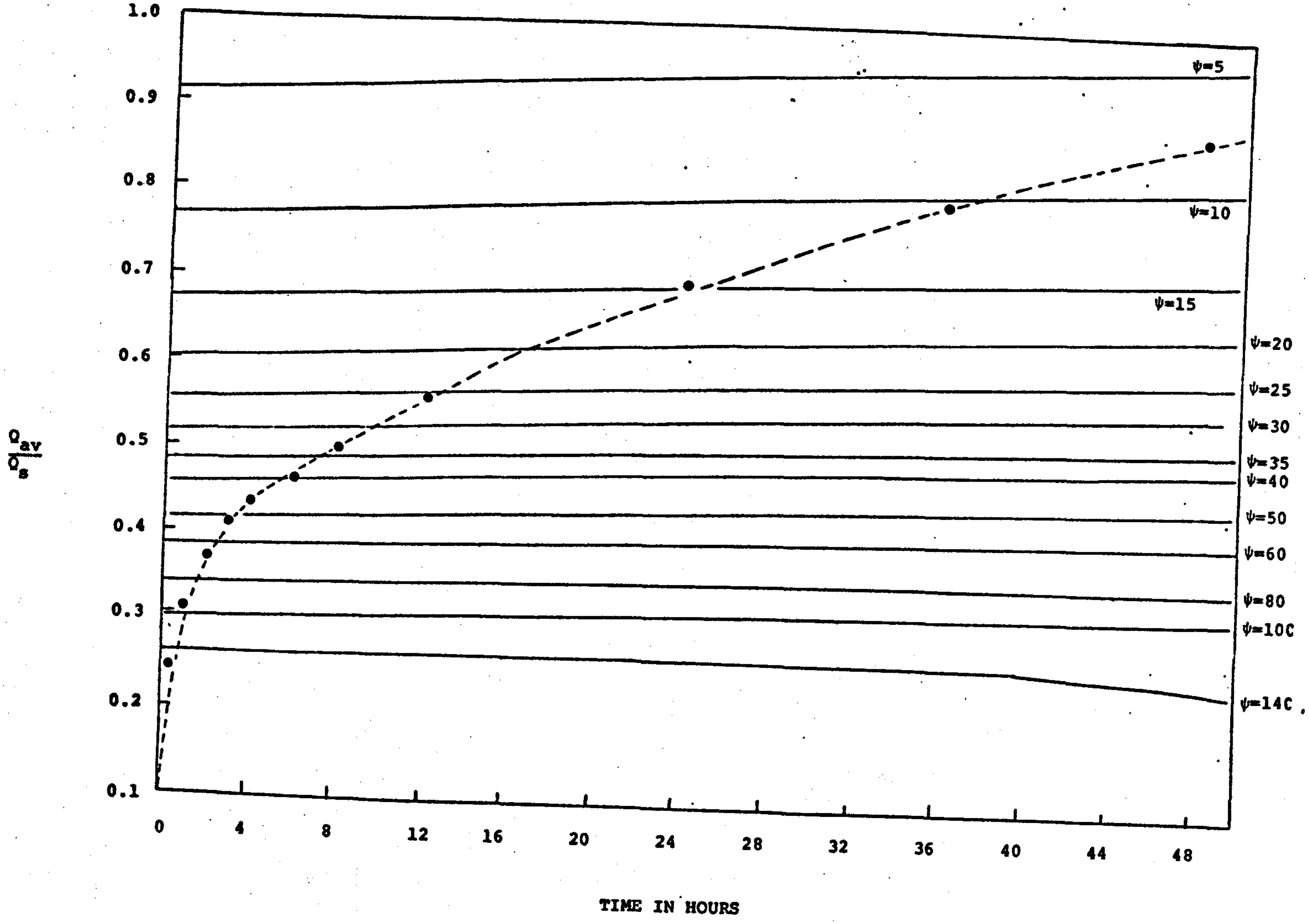


FIGURE 63

EXPERIMENTAL VS THEORETICAL FRACTIONAL UPTAKE CURVES SDS/GAC SYSTEM AT 25^{0}C

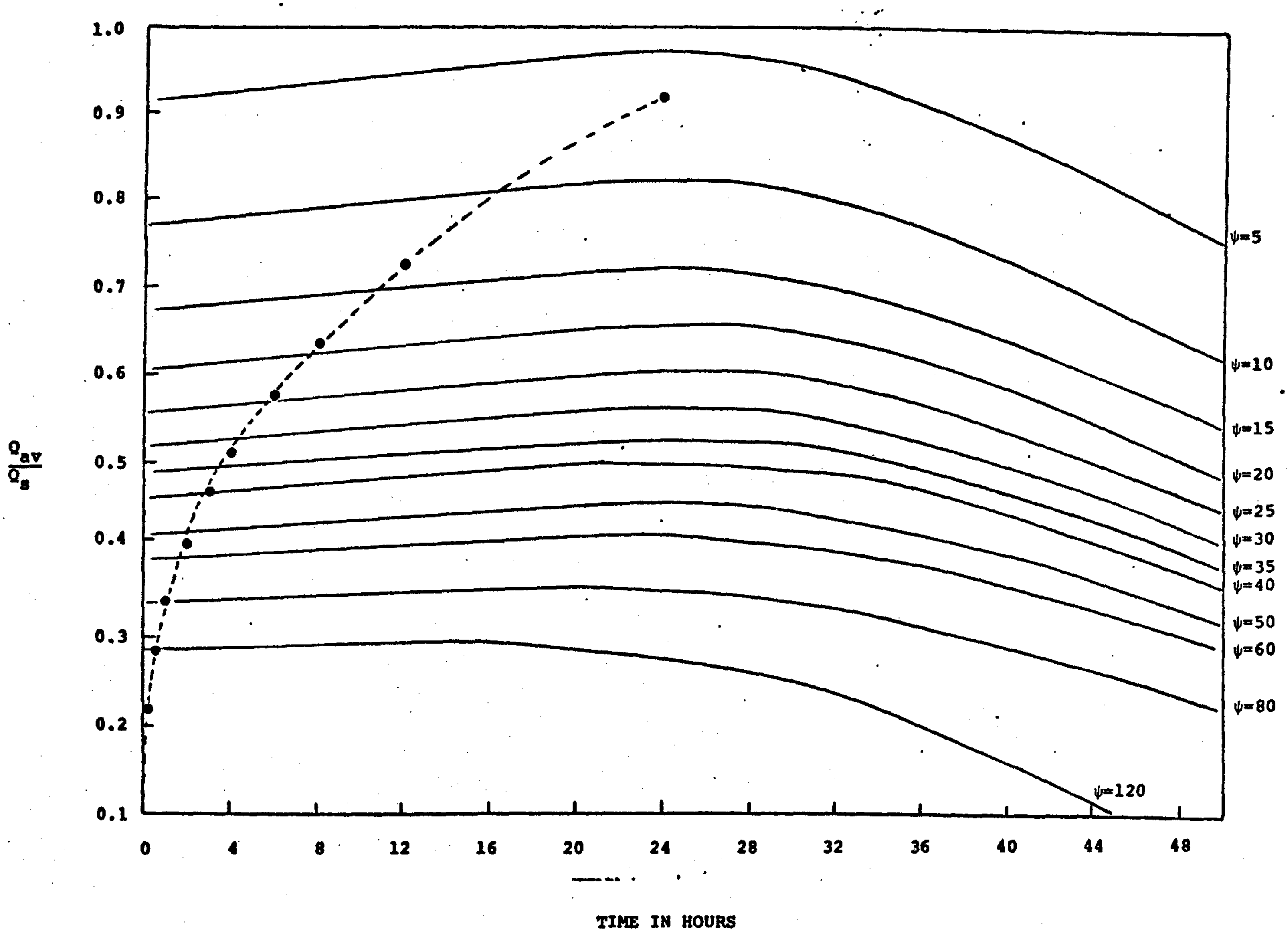


FIGURE 64

EFFECT OF D_s ON THEORETICAL EFFLUENT CONCENTRATION PROFILES

FOR SDS/GAC SYSTEM

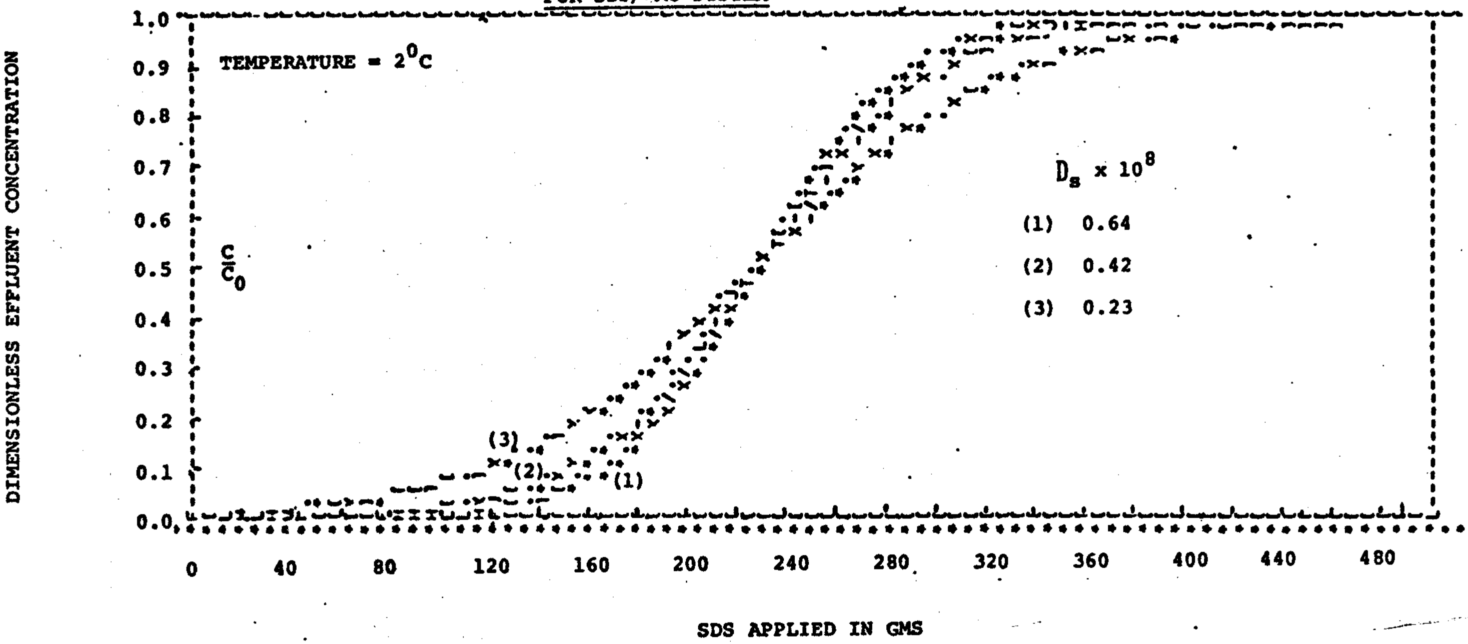


FIGURE 65

EFFECT OF D_s ON THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

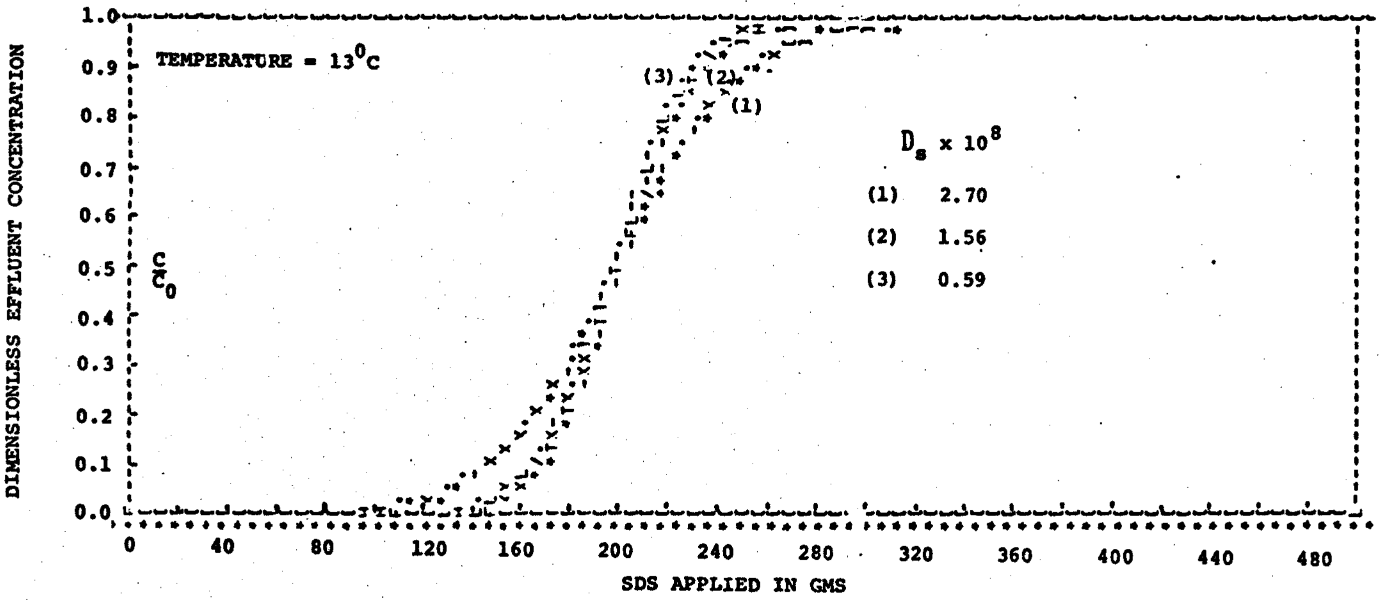


FIGURE 66

EFFECT OF D_s ON THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

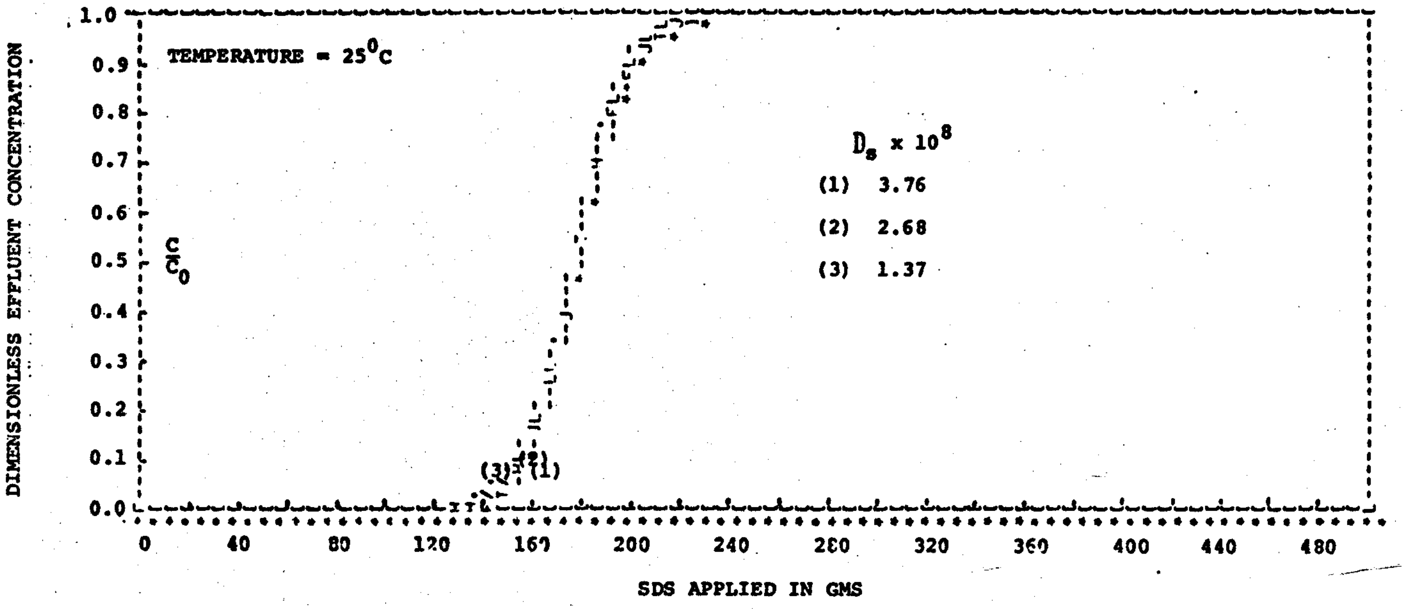


FIGURE 67

EFFECT OF Q^0 ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

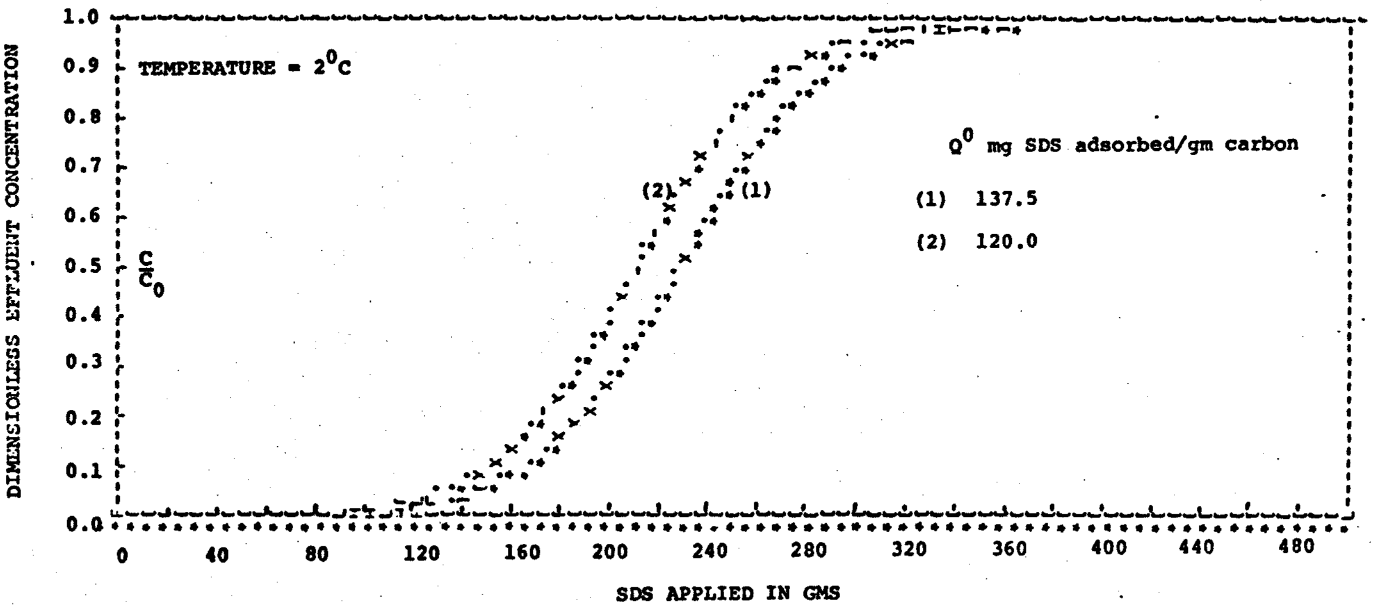


FIGURE 68

EFFECT OF Q^0 ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

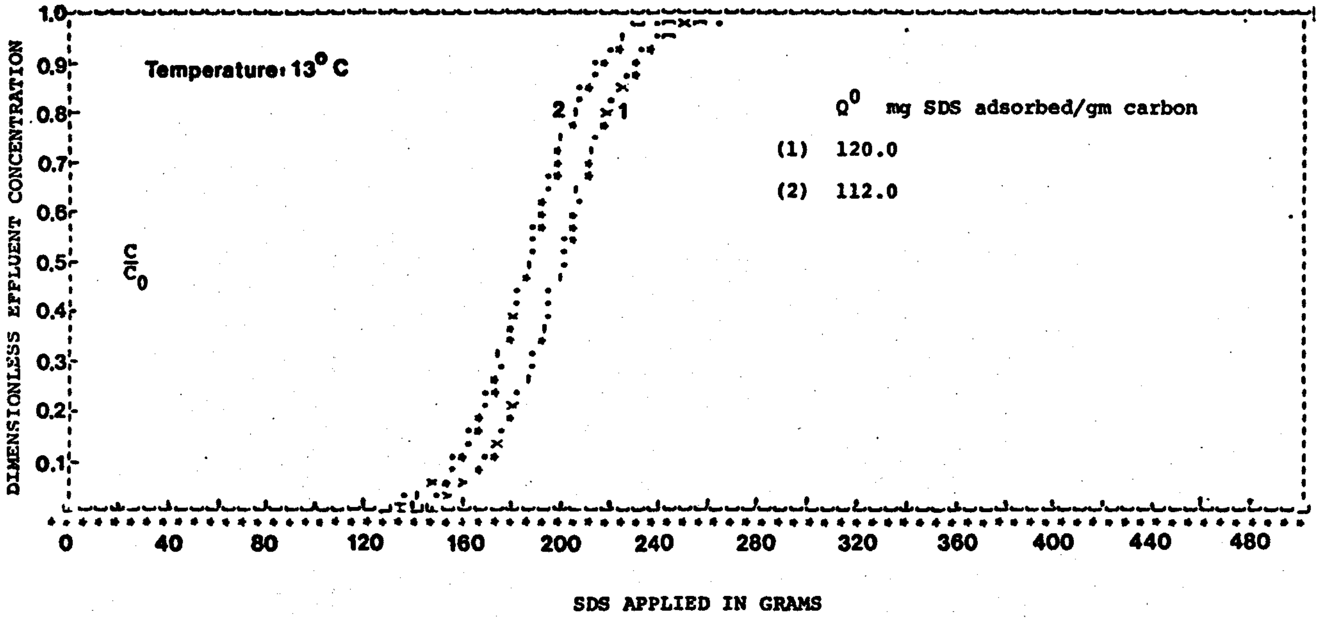


FIGURE 69

EFFECT OF Q^0 ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

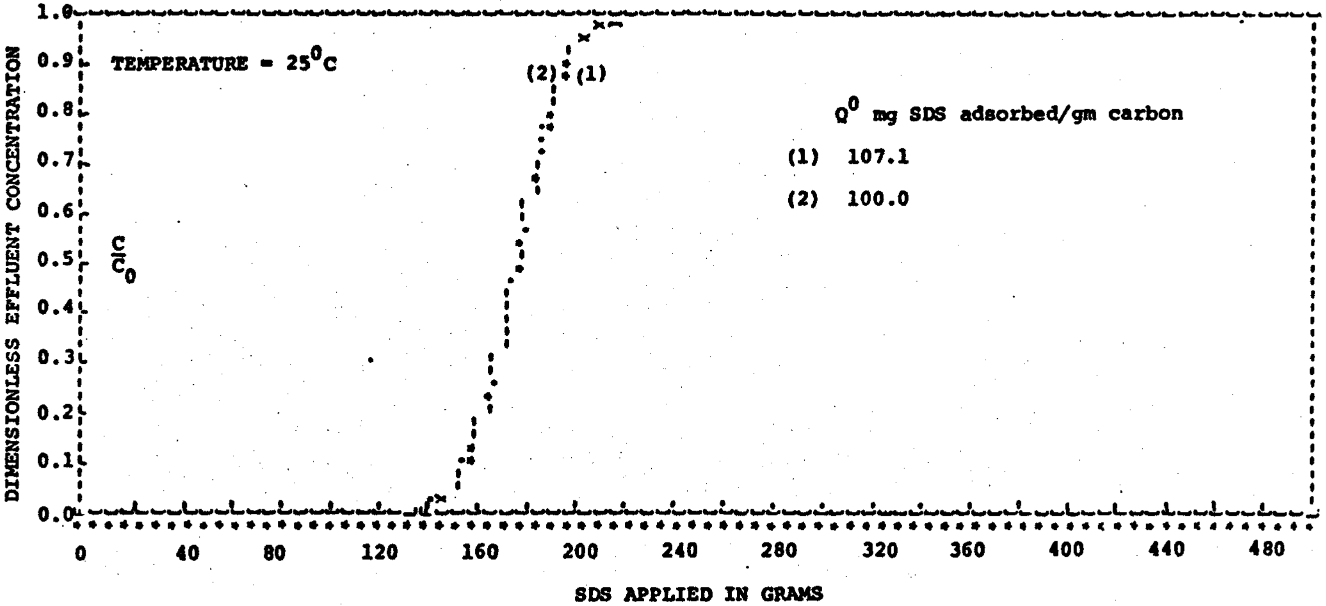


FIGURE 70

EFFECT OF VELOCITY CONSTANT 'b' ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

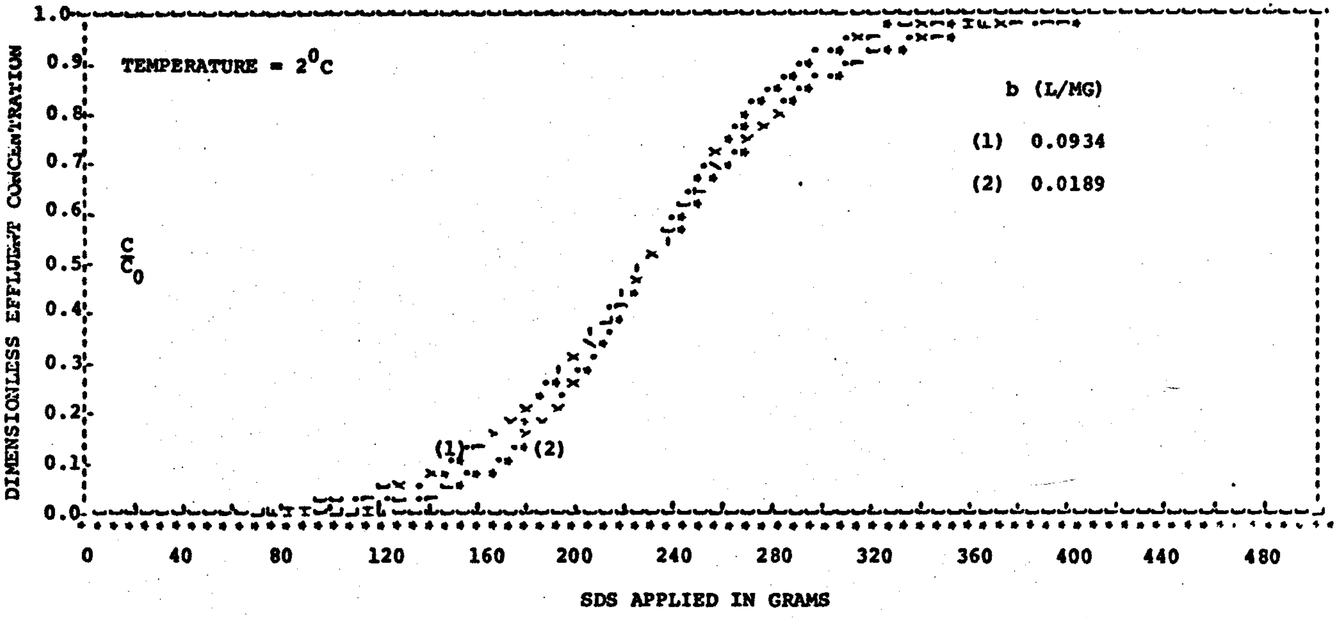


FIGURE 71

EFFECT OF VELOCITY CONSTANT 'b' ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

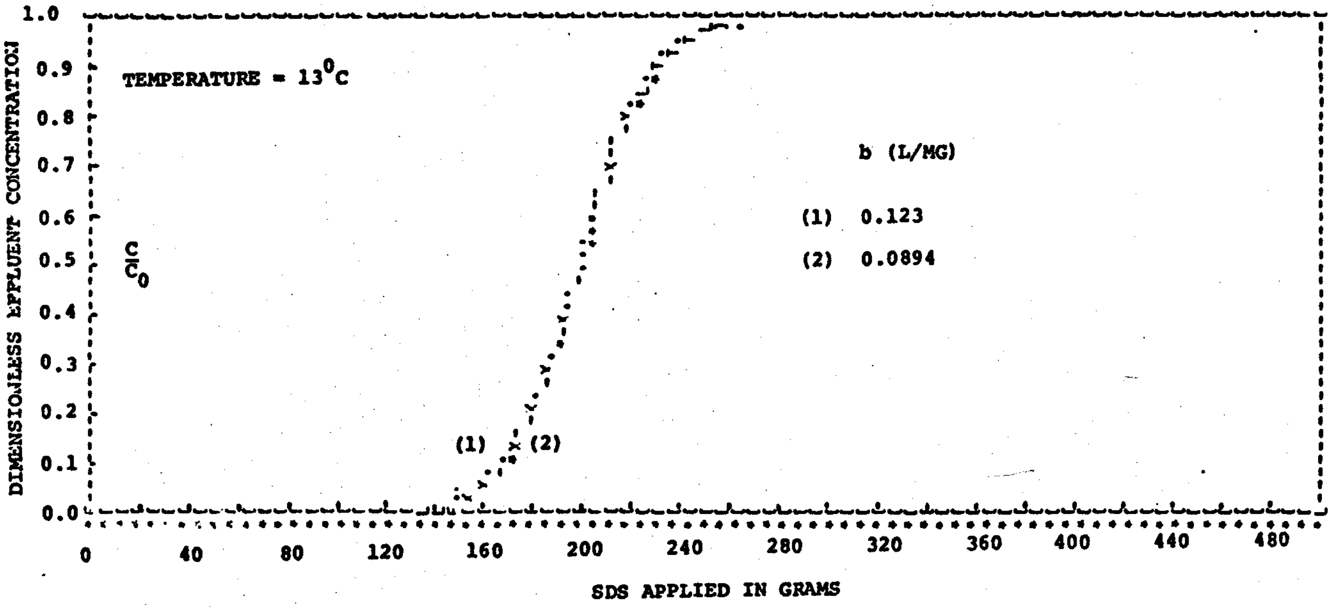


FIGURE 72

EFFECT OF VELOCITY CONSTANT 'b' ON THE THEORETICAL EFFLUENT CONCENTRATION PROFILES FOR SDS/GAC SYSTEM

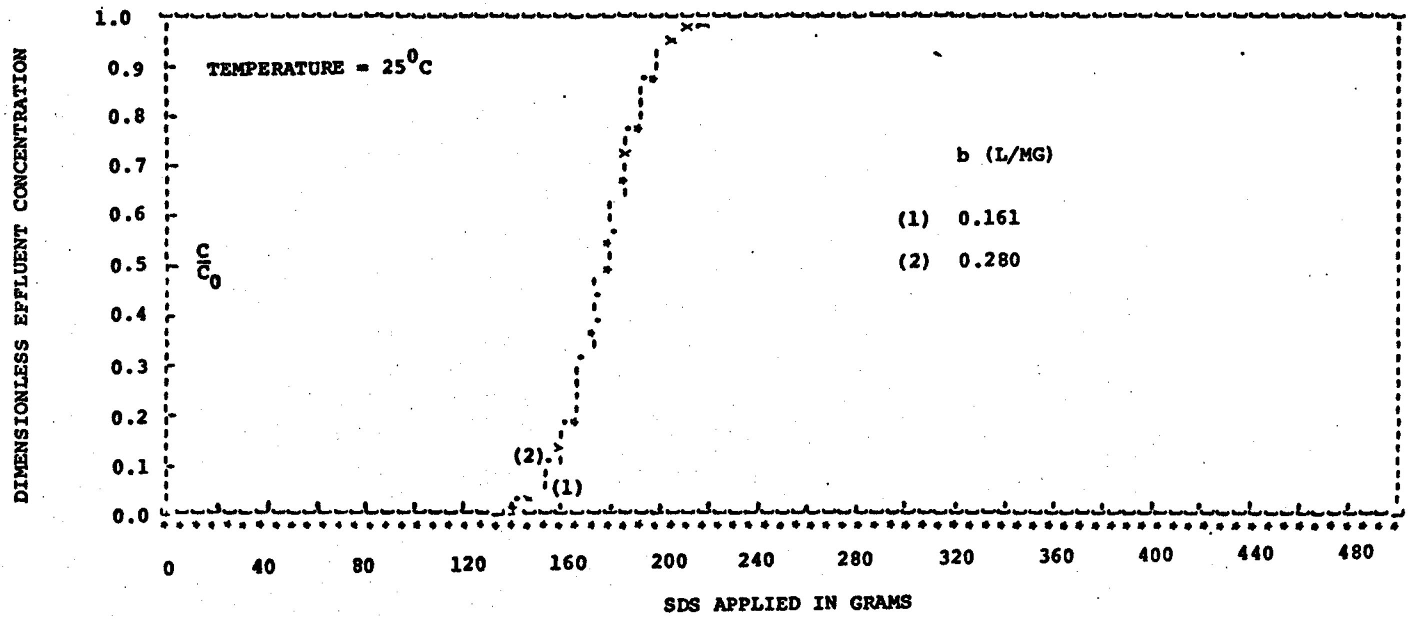


FIGURE 73

BATCH ADSORPTION KINETICS FOR SEWAGE/GAC SYSTEM

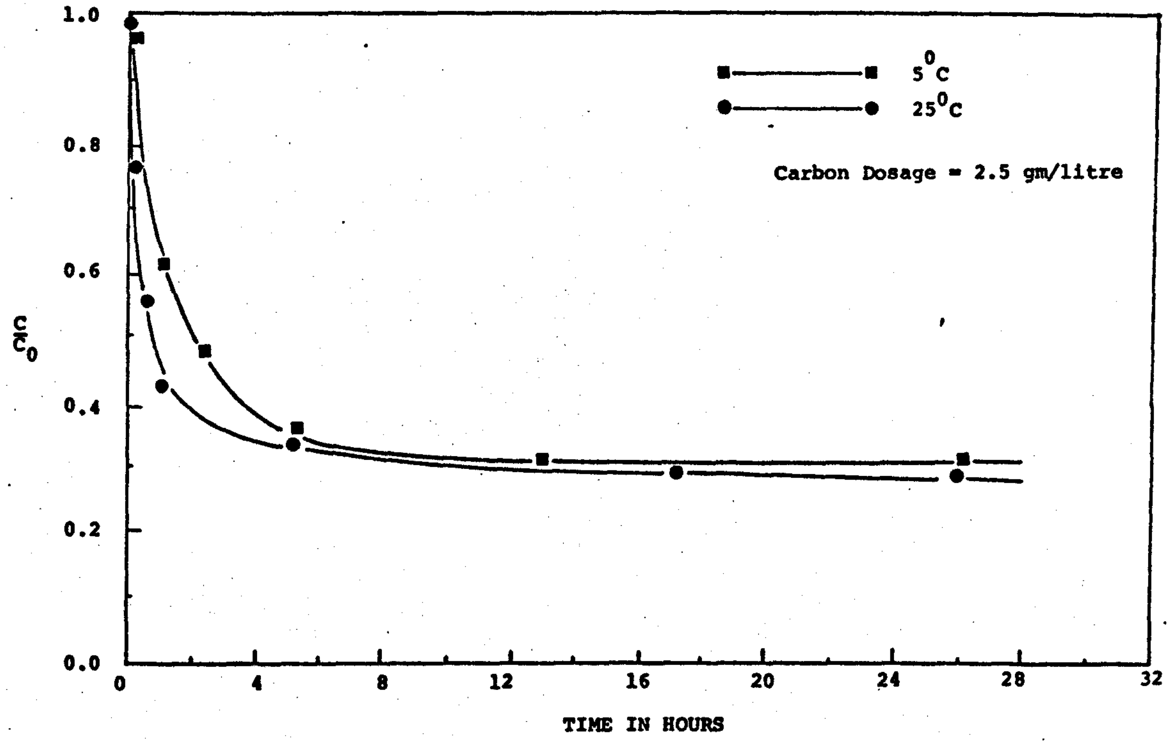


FIGURE 74

EXPERIMENTAL AND THEORETICAL FRACTIONAL UPTAKE CURVES FOR SEWAGE/GAC SYSTEM

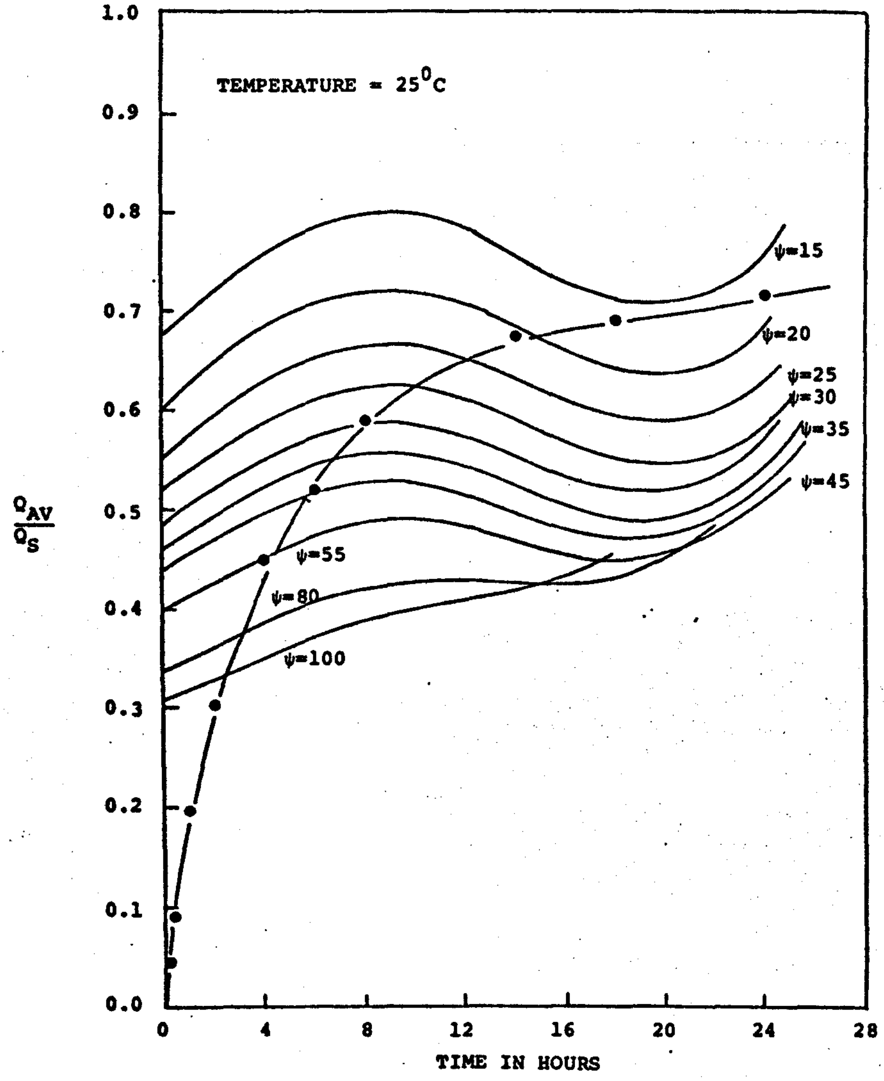


FIGURE 75

EXPERIMENTAL AND THEORETICAL FRACTIONAL UPTAKE CURVES FOR SEWAGE/GAC SYSTEM

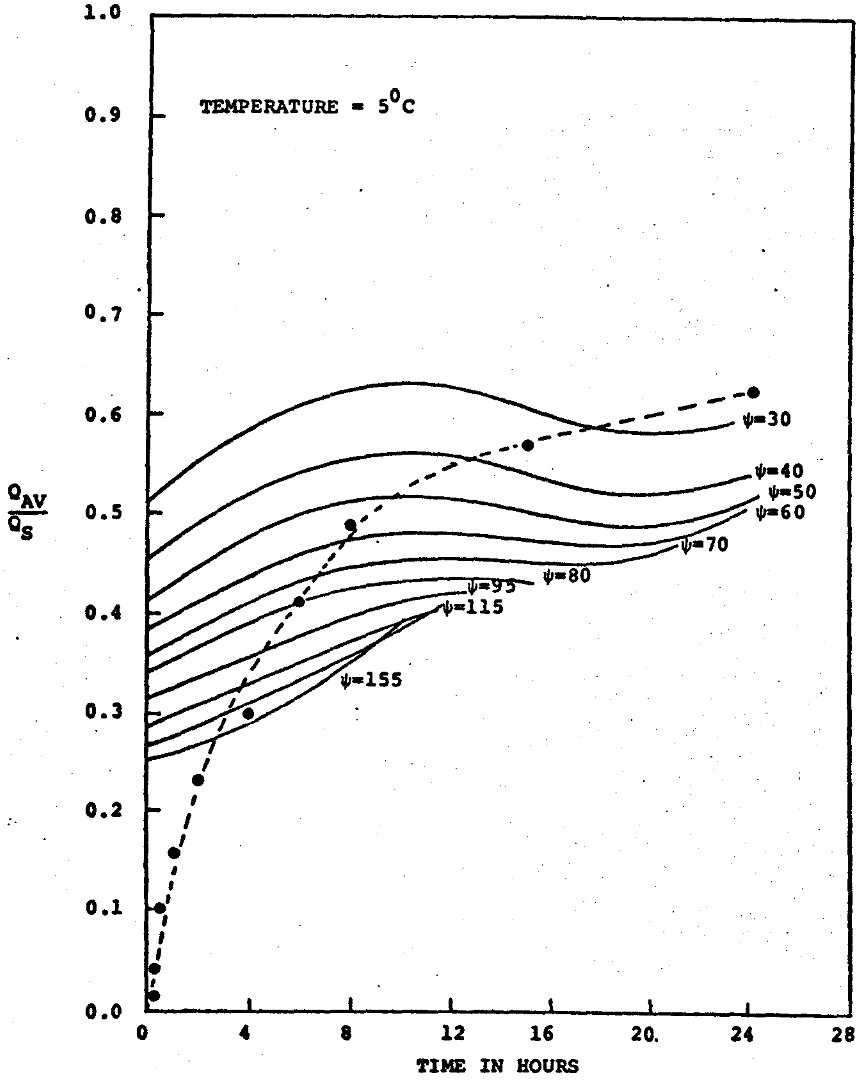


FIGURE 76

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME FOR SEWAGE/GAC SYSTEM AT 25^{0}C

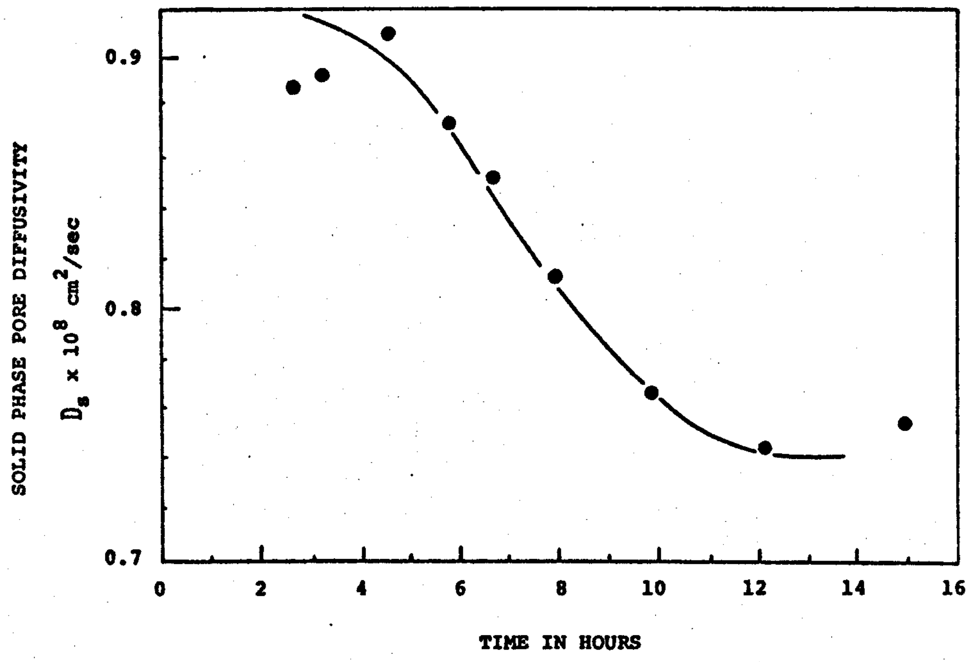


FIGURE 77

SOLID PHASE PORE DIFFUSION COEFFICIENT AS A FUNCTION OF TIME

FOR SEWAGE/GAC SYSTEM AT 5^0C

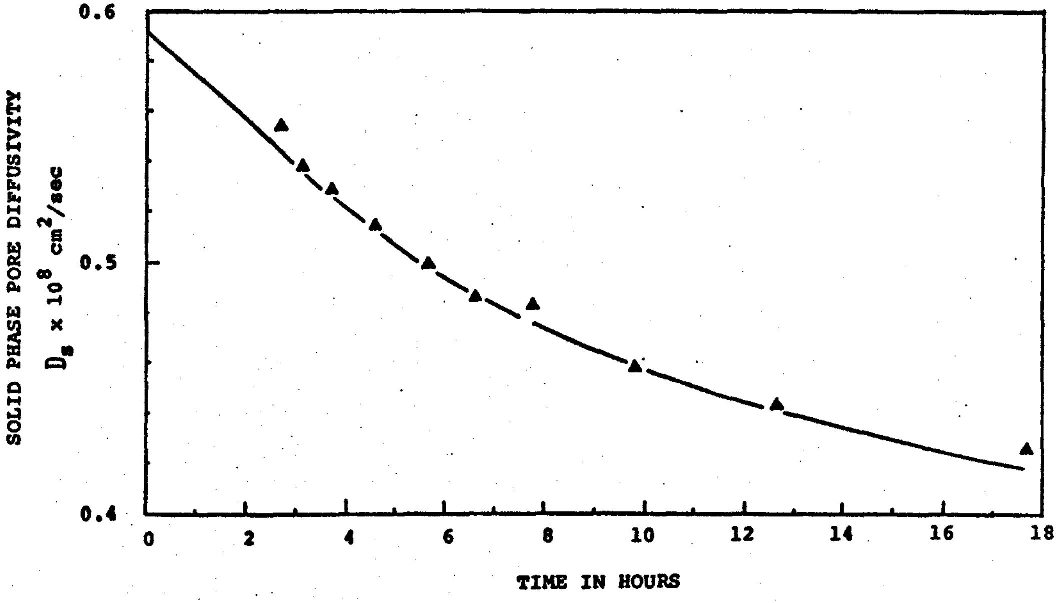


FIGURE 78

BATCH ADSORPTION ISOTHERM IN NORMALIZED COORDINATES

FOR SEWAGE/GAC SYSTEM

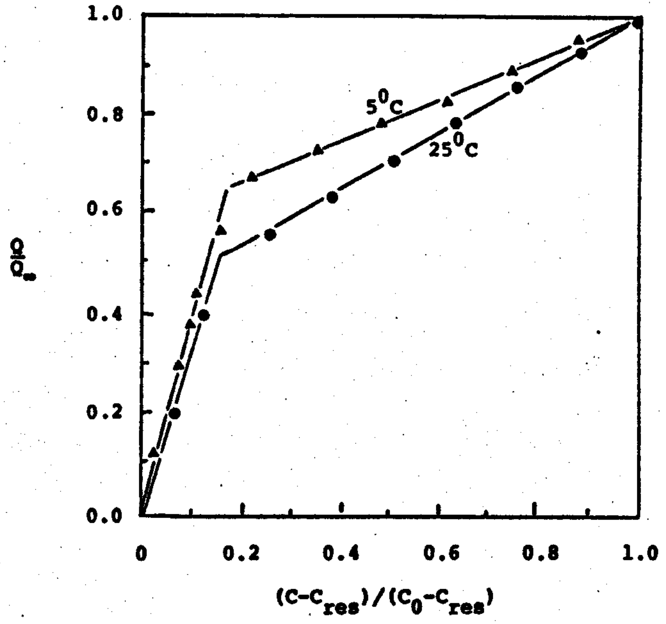


FIGURE 79

GMS TOC REMOVED VS GMS TOC APPLIED
AS PREDICTED BY THEORETICAL MODEL

25°C

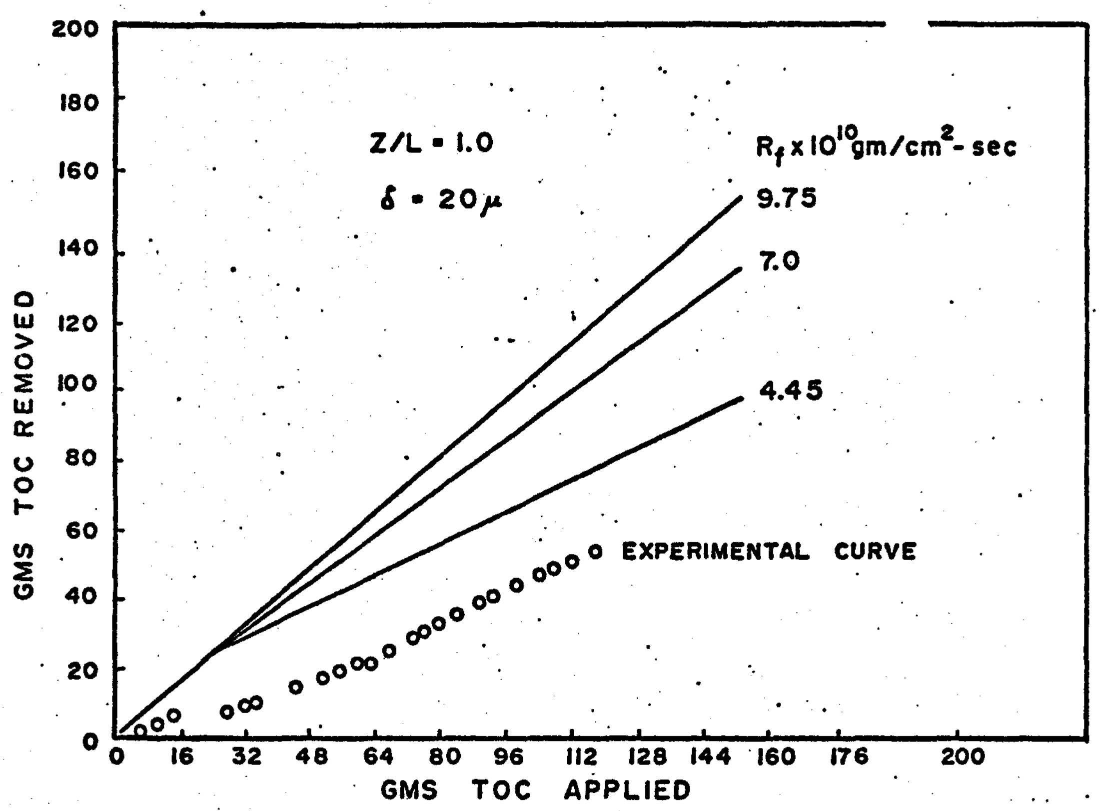


FIGURE 80

GMS TOC REMOVED VS GMS TOC APPLIED AS PREDICTED BY THEORETICAL MODEL

5°C

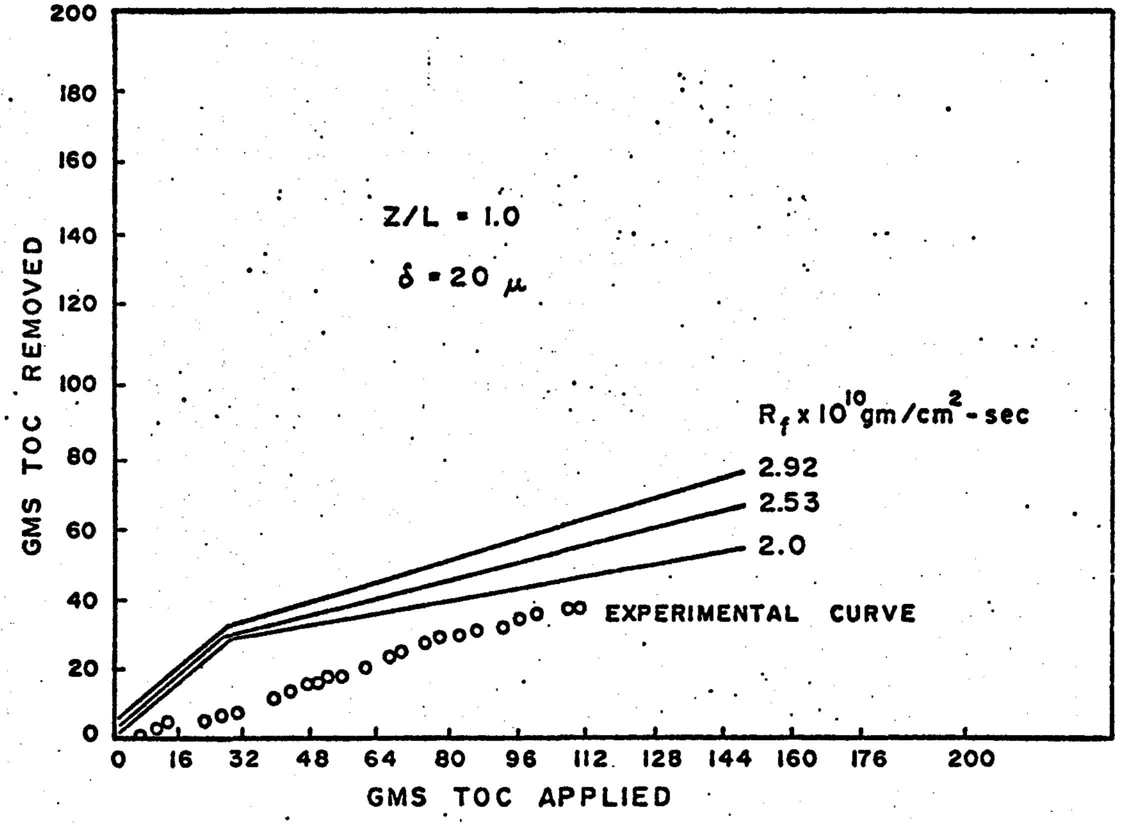


FIGURE 81

DIMENSIONLESS EFFLUENT CONCENTRATION PROFILES
PREDICTED BY THEORETICAL MODEL
25°C

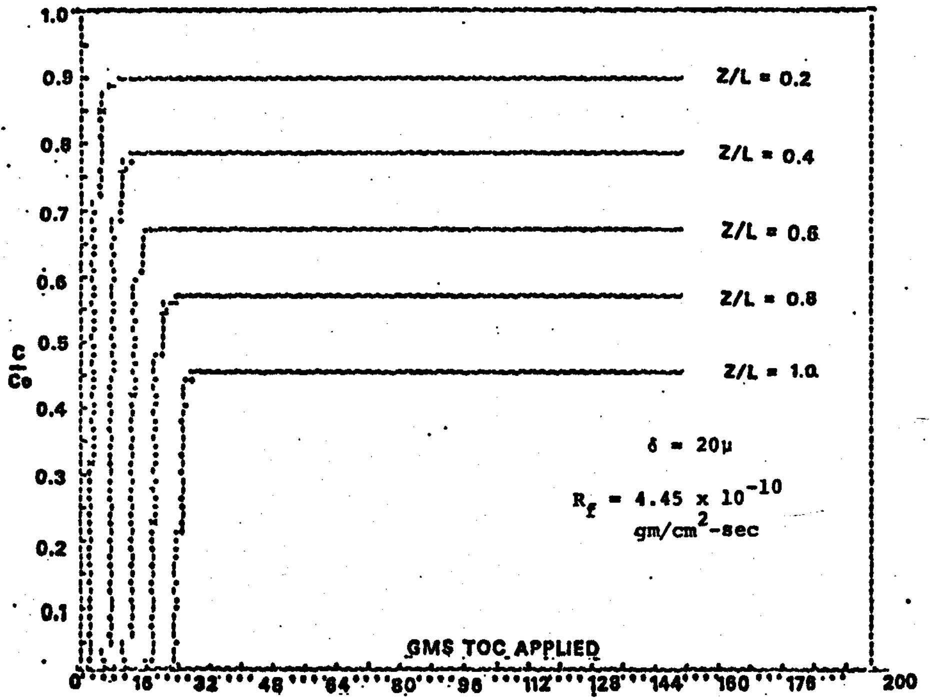


FIGURE 82

BUILD-UP OF AVERAGE SOLUTE CONTENT IN SOLID AS PREDICTED BY THEORETICAL MODEL

25°C

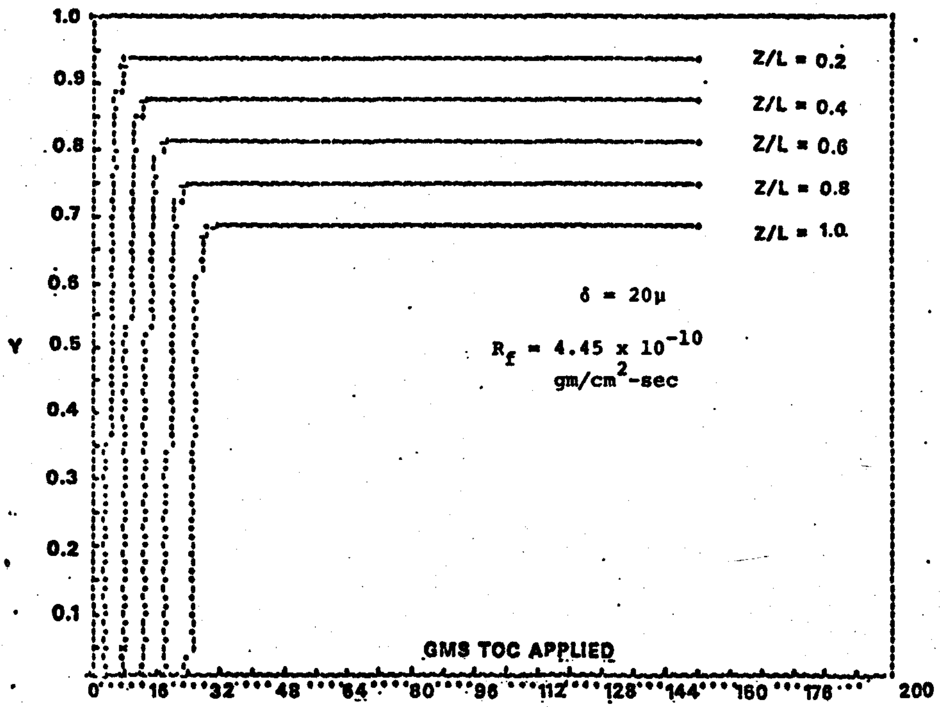


FIGURE 83

ADSORBER PERFORMANCE AS A FUNCTION OF BACTERIAL FILM THICKNESS AS PREDICTED BY THEORETICAL MODEL

5°C

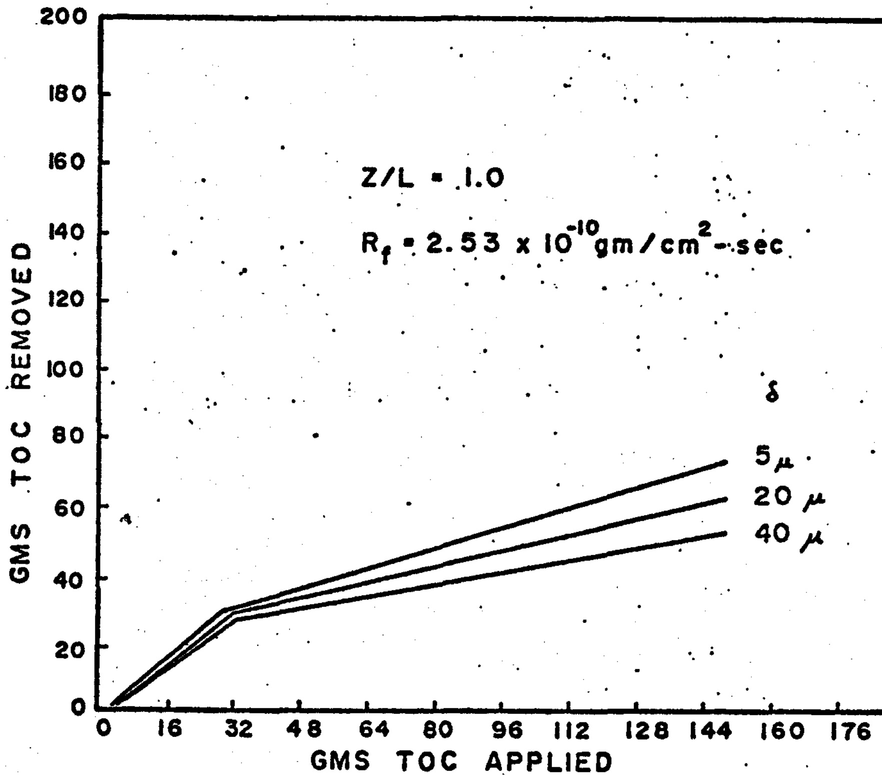


FIGURE 84

TYPICAL NITRATES CALIBRATION CURVE USING AUTOANALYZER METHOD

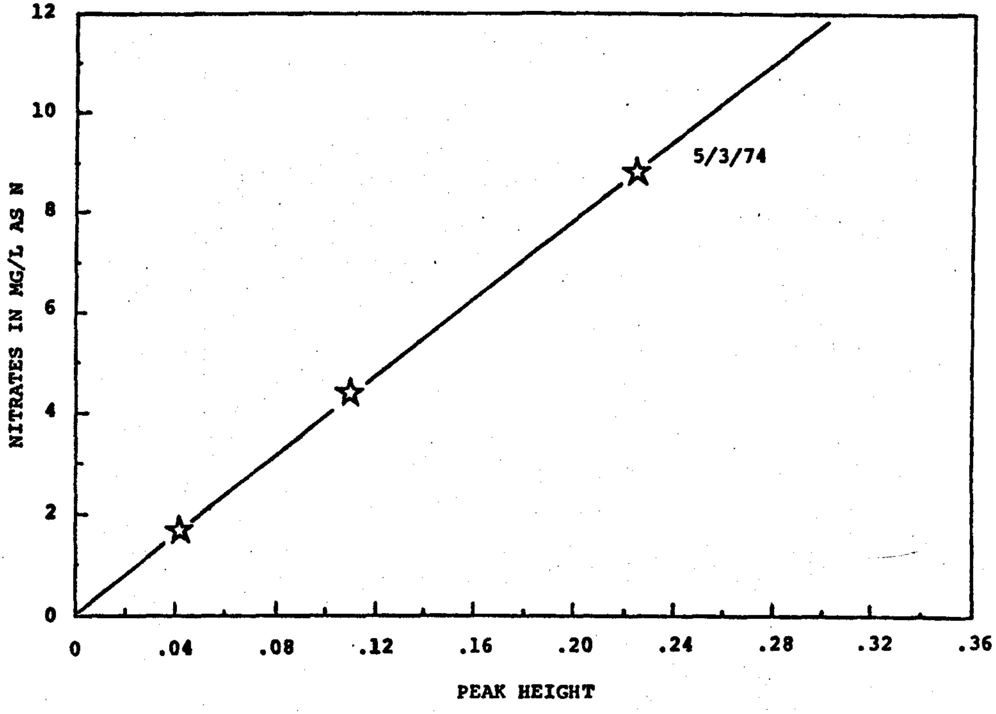
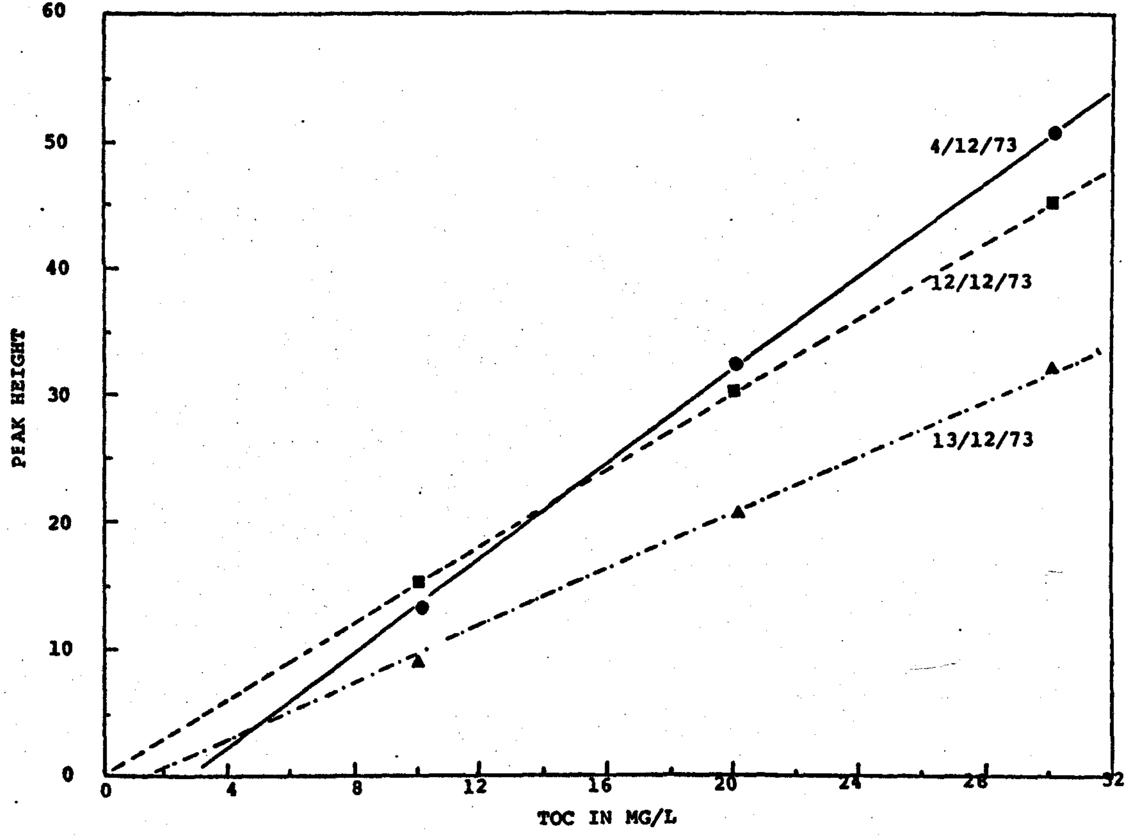


FIGURE 85

TYPICAL TOC CALIBRATION CURVES USING AUTOANALYZER METHOD



APPENDIX V

THEORETICAL DERIVATIONS

Thomas' Reaction Kinetics Model

Starting from the basic mass balance relationship for the fixed bed process

$$-\left(\frac{\partial C}{\partial V_b}\right)_V = \zeta_\varepsilon\left(\frac{\partial q}{\partial V}\right)_{V_b} + \varepsilon\left(\frac{\partial C}{\partial V}\right)_{V_b} \tag{62}$$

Using a property of partial differentials

$$-\left(\frac{\partial C}{\partial V_b}\right)_{V-V_b\varepsilon} = \zeta_\varepsilon\left(\frac{\partial q}{\partial (V-V_b\varepsilon)}\right)_{V_b} \tag{63}$$

Assuming a Langmuir type isotherm, the rate of sorption is written

$$\frac{\partial q}{\partial \tau} = \kappa\left(C(Q^0 - q) - \left(\frac{1}{b}\right)q \right) \tag{64}$$

q_∞ the saturation capacity is defined as $\dfrac{Q^0 bC_0}{1+bC_0}$

Equilibrium modulus r is defined as $\dfrac{1}{1+bC_0}$

and solution-capacity modulus is defined as $t = \kappa(\frac{1}{b} + C_0)\tau$

D_g dimensionless coefficient defining the limiting distribution of solute between the solution and adsorbent phases.

$$D_g = \frac{q_\infty \zeta_\varepsilon}{C_0 \varepsilon}$$

The fixed bed problem can then be reduced to the rate equation and conservation of mass equation which are respectively

$$\left(\frac{\partial (q/q_\infty)}{\partial t}\right)_{V_b} = \frac{C}{C_0}\left(1-\frac{q}{q_\infty}\right) - r\frac{q}{q_\infty}\left(1 - \frac{C}{C_0} \right) \tag{65}$$

$$-(\partial(C/C_0)/\partial S_c)_t = (\partial(q/q_\infty)/\partial t)_{S_c} \tag{66}$$

These equations have been integrated subject to appropriate boundary conditions by Thomas (1944) and modified by Hiester and Vermeulen (1952). An explicit analytical solution for the concentration ratio of effluent to influent is given by

Keinath and Weber (1968)-as follows:

$$\frac{C}{C_0} = \left(\frac{\sqrt{\pi}\{1-\mathrm{erf}(\sqrt{rt}-\sqrt{s})\}\exp(\sqrt{rt}-\sqrt{s})^2 - (1/(\sqrt{rt}+\sqrt[4]{rst}))}{\sqrt{\pi}\{1-\mathrm{erf}(\sqrt{rs}-\sqrt{t})\}\exp(\sqrt{rs}-\sqrt{t})^2 + (1/(\sqrt{t}+\sqrt[4]{rst}))} + 1 \right)^{-1} \quad (67)$$

This equation enables one to evaluate the quantity (C/C_0) numerically for any specified combinations of the parameters r,s,t.

The general rate coefficient is given by in the case of external and internal solid phase diffusion controlling ;

$$\frac{1}{\kappa} = \frac{1}{\kappa_f} + \frac{1}{\kappa_s} \quad (68)$$

κ_f is calculated by comparing the mass transfer to a reaction type kinetic approach;

$$\kappa_f = 2k_f\alpha/(r^0+1) \quad (69)$$

$$\kappa_s = 2k_s\alpha\zeta D_g/(r^0+1) \quad (70)$$

APPENDIX VI

COMPUTER PROGRAMS

TIEN'S METHOD
FOR
CALCULATING SURFACE DIFFUSION COEFFICIENT
SAMPLE CALCULATION SHOWN
FOR
SDS/GAC SYSTEM AT 25°C.

```
      PROGRAM [illegible] (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION [illegible]
      DIMENSION [illegible]
      DIMENSION D(66)
      DIMENSION B(10),E(10),SB(10),T(10)
      DIMENSION XBAR(11),STD(11),COE(11),SUMSQ(11),ISAVE(11)
      DIMENSION ANS(10)
      DIMENSION QS(50),TIME(50),QAV(50)
      DIMENSION P(300)
 1    FORMAT(A4,A2,I5,I2,I1)
 2    FORMAT(2F10.4)
 3    FORMAT(27H1POLYNOMIAL REGRESSION.....,A4,A2/)
 4    FORMAT(23H0NUMBER OF OBSERVATIONS,I6//)
 5    FORMAT(32H0POLYNOMIAL REGRESSION OF DEGREE,I3)
 6    FORMAT(12H0 INTERCEPT,E20.7)
 7    FORMAT(26H0 REGRESSION COEFFICIENTS/(6E20.7))
 8    FORMAT(1H0/24X,24HANALYSIS OF VARIANCE FOR,I4,19H DEGREE POLYNOMI
     1AL/)
 9    FORMAT(1H0,5X,19HSOURCE OF VARIATION,7X,9HDEGREE OF,7X,6HSUM OF,9X
     *,4HMEAN,10X,1HF,9X,20HIMPROVEMENT IN TERMS/33X,7HFREEDOM,8X,7HSQUA
     $RES,7X,6HSQUARE,7X,5HVALUE,9X,17HOF SUM OF SQUARES)
 10   FORMAT(21H0 DUE TO REGRESSION,12X,I6,F17.5,F14.5,F13.5,F20.5)
 11   FORMAT(32H  DEVIATION ABOUT REGRESSION   ,I6,F17.5,F14.5)
 12   FORMAT(8X,5HTOTAL,19X,I6,F17.5///)
 13   FORMAT(17H  NO IMPROVEMENT)
 14   FORMAT(1H1//27X,18HTABLE OF RESIDUALS//16H OBSERVATION NO.,5X,7HX
     1VALUE,7X,7HY VALUE,7X,10HY ESTIMATE,7X,8HRESIDUAL/)
 15   FORMAT(1H ,3X,I6,F18.5,F14.5,F17.5,F15.5)
      READ(5,1)PR,PR1,N,M,NPLOT
      WRITE(6,3) PR,PR1
      WRITE(6,4) N
      L=N*M
      DO 110 I=1,N
      J=L+I
      READ (5,2) X(I),X(J)
      TIME(I)=X(I)
 110  QS(I)=X(J)
      CALL GDATA (N,M,X,XBAR,STD,D,SUMSQ)
      MM=M+1
      SUM=0.0
      NT=N-1
      DO 200 I=1,M
      ISAVE(I)=I
      CALL ORDER (MM,D,MM,I,ISAVE,DI,E)
      CALL MINV (DI,I,DET,B,T)
      CALL MULTR (N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,SB,T,ANS)
      WRITE (6,5) I
      IF(ANS(7)) 140,130,130
 130  SUMIP=ANS(4)-SUM
      IF(SUMIP) 140,140,150
 140  WRITE (6,13)
      GO TO 210
 150  WRITE (6,6) ANS(1)
      WRITE (6,7) (B(J),J=1,I)
      IF(I.EQ.3) GO TO 101
      GO TO 102
 101  P0=ANS(1)

      P1=B(1)
      P2=B(2)
      P3=B(3)
 102  CONTINUE
      WRITE (6,8) I
      WRITE (6,9)
      SUM=ANS(4)
      WRITE(6,10) I,ANS(4),ANS(6),ANS(10),SUMIP
      NI=ANS(8)
      WRITE (6,11) NI,ANS(7),ANS(9)
      WRITE (6,12) NT,SUMSQ(MM)
      COE(1)=ANS(1)
      DO 160 J=1,I
 160  COE(J+1)=B(J)
      LA=1
 200  CONTINUE
 210  IF(NPLOT) 100,100,220
 220  NP3=N*M
      DO 230 I=1,N.
      NP3=NP3+1
      P(NP3)=COE(1)
      L=I
      DO 230 J=1,LA
      P(NP3)=P(NP3)+X(L)*COE(J+1)
 230  L=L+N
      N2=N
      L=N*M
      DO 240 I=1,N
      P(I)=X(I)
      N2=N2+1
      L=L+1
 240  P(N2)=X(L)
      WRITE(6,3) PR,PR1
      WRITE(6,5) LA
      WRITE(6,14)
      NP2=N
      NP3=N+N
      DO 250 I=1,N
      NP2=NP2+1
      NP3=NP3+1
      RESID=P(NP2)-P(NP3)
 250  WRITE(6,15) I,P(I),P(NP2),P(NP3),RESID
 100  CONTINUE
      DO 45 I=1,N
      READ(5,46) QAV(I)
 46   FORMAT(F10.4)
 45   CONTINUE
      CALL PLOT(0.0,0.0,-25)
      XSCALE=2.0
      YSCALE=.025
      Y=0.
      [illegible]
      [illegible]
      [illegible]
      [illegible]
      [illegible]
      CALL PLTIN (XSCALE,YSCALE,V,4,XMIN,XMAX,YMIN,YMAX)
```

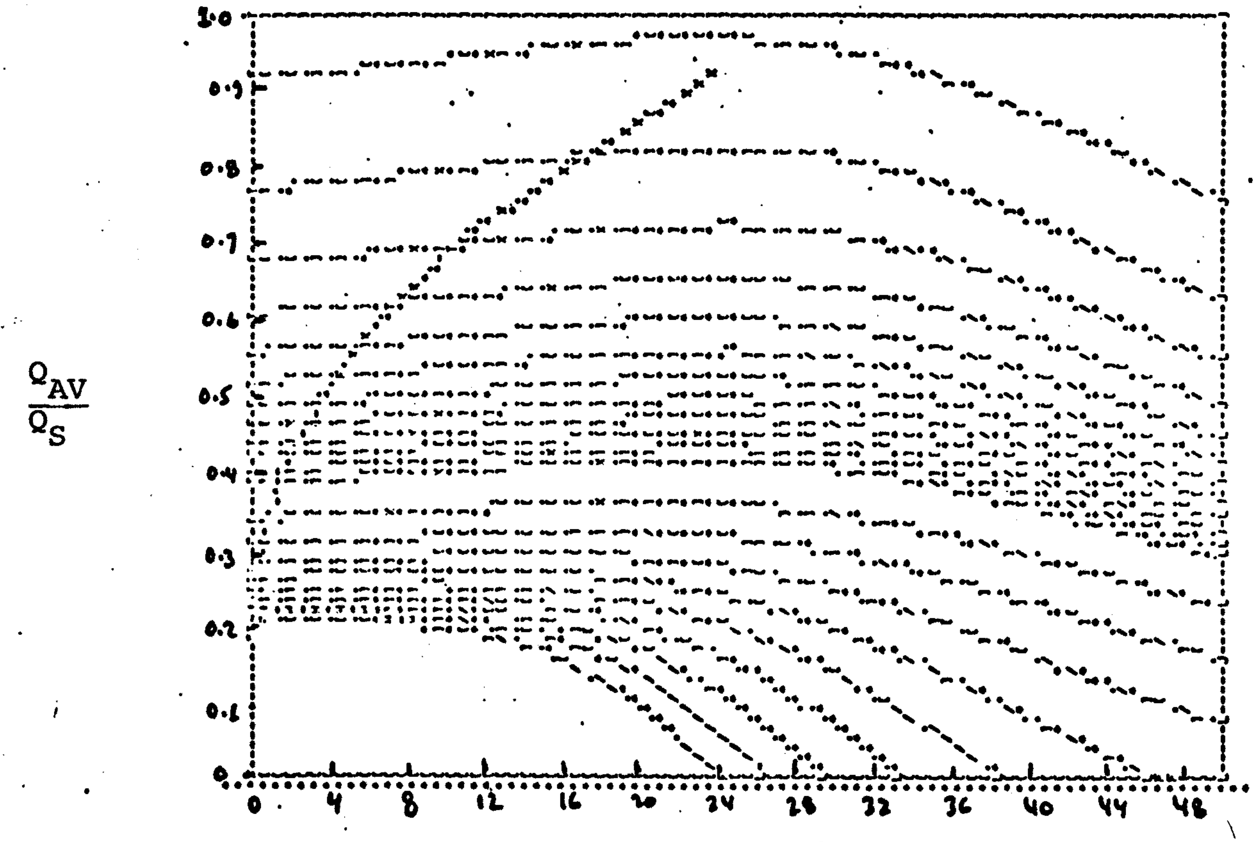
```
      CALL PLOT([illegible])
      CALL PLOT([illegible])
      CALL PLOT(15.,[illegible],2)
      CALL PLOT(1.0,20.0,2)
      CALL PLOT([illegible],2)
      DO 24 I=1,21
      IF(I.GT.12) GO TO 333
      PHI=5*I
      GO TO 334
333   PHI=60.+(I-12)*20
334   CONTINUE
      WRITE(6,58)PHI
58    FORMAT(//,20X,≠PHI=≠,F10.3,///,6X,≠Z=≠,11X,≠CONS≠,11X,≠GAMMA1≠,9X,
     $≠GAMMA2≠,6X,≠GAMMA3≠,10X,≠Y1≠,11X,≠Y2≠,11X,≠Y3≠,10X,≠Y4≠,8X,≠QAVS≠
     ,)
      PISQ=3.1416*3.1416
      U1=0.0
      U2=0.0
      U3=0.0
      U4=0.0
      DO 26 K=1,7
      U1=U1+(EXP(-(K*K*PISQ/PHI)))/(K**2*PISQ)
      U2=U2+(EXP(-(K*K*PISQ/PHI)))/(K**4*PISQ**2)
      U3=U3+(EXP(-(K*K*PISQ/PHI)))/(K**6*PISQ**3)
      U4=U4+(EXP(-(K*K*PISQ/PHI)))/(K**8*PISQ**4)
26    CONTINUE
      DO 25 J=1,11
      Z=5*(J-1)
      CONS=P0+P1*Z+P2*Z*Z+P3*Z*Z*Z
      GAMMA1=(P1*Z+2*P2*Z*Z+3*P3*Z*Z*Z)/CONS
      GAMMA2=(4*P2*Z*Z+12*P3*Z*Z*Z)/CONS
      GAMMA3=(6*P3*Z*Z*Z)/CONS
      Y1=(GAMMA1*PHI)/15.0
      Y2=(GAMMA2*PHI*PHI)/315.0
      Y3=(GAMMA3*PHI*PHI*PHI)/1575.0
      Y4=6*(P1*U1-P1*Z*PHI*U2+2*P2*Z*Z*PHI*PHI*U3-6*P3*Z*Z*Z*PHI*PHI*PHI
     $*U4)/CONS
      QAVS=1.0-Y1+Y2-Y3-Y4
      WRITE(6,57)Z,CONS,GAMMA1,GAMMA2,GAMMA3,Y1,Y2,Y3,Y4,QAVS
57    FORMAT(//,2X,F6.1,7X,F6.1,8X,F8.3,8X,F8.3,6X,F8.3,7X,F8.3,5X,F8.4,
     *6X,F7.3,3X,F7.3,3X,F8.4)
      XP=(Z-V)/XSCALE
      YP=(QAVS-W)/YSCALE
      CALL PLOT(XP,YP,2)
25    CONTINUE
      CALL PLOT(3.0,0.0,-3)
24    CONTINUE
      DO 27 I=1,9
      ATY=QAV(I)/QS(I)
      ATX=TIME(I)
      XAT=(ATX-V)/XSCALE
      YAT=(ATY-W)/YSCALE
      CALL PLOT(XAT,YAT,2)
27    CONTINUE
      CALL PLOT(XAT,YAT,999)
      STOP
      END
```

```
POLYNOMIAL REGRESSION....SDS25C

NUMBER OF OBSERVATIONS

POLYNOMIAL REGRESSION OF DEGREE  1

  INTERCEPT          .1078561E+03

  REGRESSION COEFFICIENTS
      -.1023221E+01

                        ANALYSIS OF VARIANCE FOR   1  DEGREE POLYNOMIAL

     SOURCE OF VARIATION        DEGREE OF       SUM OF        MEAN          F            IMPROVEMENT IN TERMS
                                 FREEDOM        SQUARES       SQUARE       VALUE         OF SUM OF SQUARES

  DUE TO REGRESSION                 1          464.39474    464.39474   4388.06584            464.39474
  DEVIATION ABOUT REGRESSION        7             .74082       .10583
        TOTAL                       8          465.13555


POLYNOMIAL REGRESSION OF DEGREE  2

  INTERCEPT          .1079759E+03

  REGRESSION COEFFICIENTS
      -.1066117E+01        .1784089E-02

                        ANALYSIS OF VARIANCE FOR   2  DEGREE POLYNOMIAL

     SOURCE OF VARIATION        DEGREE OF       SUM OF        MEAN          F            IMPROVEMENT IN TERMS
                                 FREEDOM        SQUARES       SQUARE       VALUE         OF SUM OF SQUARES

  DUE TO REGRESSION                 2          464.46324    232.23162   2072.52015               .06850
  DEVIATION ABOUT REGRESSION        6             .67232       .11205
        TOTAL                       8          465.13556


POLYNOMIAL REGRESSION OF DEGREE  3

  INTERCEPT          .1074952E+03

  REGRESSION COEFFICIENTS
      -.7165439E+00       -.4324797E-01        .1310490E-02

                        ANALYSIS OF VARIANCE FOR   3  DEGREE POLYNOMIAL



     SOURCE OF VARIATION        DEGREE OF       SUM OF        MEAN          F            IMPROVEMENT IN TERMS
                                 FREEDOM        SQUARES       SQUARE       VALUE         OF SUM OF SQUARES

  DUE TO REGRESSION                 3          465.06697    155.02232  11301.60536               .60373
  DEVIATION ABOUT REGRESSION        5             .06859       .01372
        TOTAL                       8          465.13555


POLYNOMIAL REGRESSION OF DEGREE  4

  INTERCEPT          .1073428E+03

  REGRESSION COEFFICIENTS
      -.5289261E+00       -.9267553E-01        .5443958E-02       -.9953913E-04

                        ANALYSIS OF VARIANCE FOR   4  DEGREE POLYNOMIAL

     SOURCE OF VARIATION        DEGREE OF       SUM OF        MEAN          F            IMPROVEMENT IN TERMS
                                 FREEDOM        SQUARES       SQUARE       VALUE         OF SUM OF SQUARES

  DUE TO REGRESSION                 4          465.09884    116.27471  12669.00731               .03187
  DEVIATION ABOUT REGRESSION        4             .03671       .00918
        TOTAL                       8          465.13555
```

```
              PHI=      5.000

    Z=         CONS        GAMMA1        GAMMA2        GAMMA3         Y1          Y2          Y3         Y4        QAVS

    0.0        107.5        0.000         0.000         0.000        0.000      0.0000       0.000       .085      .9155

    5.0        103.0        -.051         -.023          .016        -.017      -.0019        .001       .089      .9253

   10.0         97.3        -.122         -.016          .091        -.041      -.0013        .006       .094      .9393

   15.0         91.4        -.185          .155          .294        -.062       .0123        .023       .097      .9544

   20.0         86.3        -.232          .656          .725        -.067       .0520        .058       .096      .9661

   25.0          [illegible] -.237      1.457         1.49[illegible] -.042    .1319        .117       .088      .9581

   30.0         82.5     [illegible]    [illegible]    2.475         .024     [illegible]   .2[illegible]4  .073  .9544

   35.0         85.6         .439         5.349         3.937         .146       .4285        .312       .049      .9214

   40.0         93.5     [illegible]      7.803         5.392         .301       .6193        .427       .019      .8717

   45.0     [illegible]  [illegible]   [illegible]   [illegible]      .47[illegible] .8[illegible]24 .531  -.011   .8130

   50.0     [illegible]  [illegible]   [illegible]      7.727         .496       .9555        .612      -.038      .7547
```

```
                PHI=    10.000
  Z=        CONS      GAMMA1     GAMMA2     GAMMA3       Y1        Y2         Y3       Y4       QAVS
  0.0      107.5      0.000      0.000      0.000      0.000    0.0000      0.000     .230     .7705
  5.0      103.0      -.051      -.023       .010      -.034    -.0073       .006     .240     .7503
 10.0       97.3      -.122      -.016       .081      -.081    -.0051       .051     .231     .7942
 15.0       91.4      -.185       .155       .290      -.124     .0491       .184     .179     .8094
 20.0       86.3      -.202       .656       .728      -.135     .2081       .463     .059     .8216
 25.0       83.0      -.127      1.657      1.480      -.085     .5261       .940    -.154     .8248
 30.0       82.5       .083      3.261      2.575       .055    1.0353      1.635    -.467     .8130
 35.0       85.6       .438      5.399      3.937       .292    1.7141      2.500    -.861     .7827
 40.0       93.5       .904      7.803      5.382       .603    2.4772      3.417   -1.279     .7361
 45.0      107.1      1.469     10.110      6.691       .939    3.2096      4.248   -1.658     .6806
 50.0      127.4      1.879     12.039      7.717      1.253    3.8218      4.900   -1.956     .6249
                PHI=    15.000
  Z=        CONS      GAMMA1     GAMMA2     GAMMA3       Y1        Y2         Y3       Y4       QAVS
  0.0      107.5      0.000      0.000      0.000      0.000    0.0000      0.000     .326     .6740
  5.0      103.0      -.051      -.023       .010      -.051    -.0164       .020     .331     .6831
 10.0       97.3      -.122      -.016       .081      -.122    -.0115       .173     .241     .6960
 15.0       91.4      -.185       .155       .290      -.185     .1105       .622    -.036     .7100
 20.0       86.3      -.202       .656       .728      -.202     .4683      1.561    -.612     .7214
 25.0       83.0      -.127      1.657      1.480      -.127    1.1837      3.171   -1.585     .7246
 30.0       82.5       .083      3.261      2.575       .083    2.3293      5.517   -2.984     .7142
 35.0       85.6       .438      5.399      3.937       .438    3.8568      8.437   -4.705     .6869
 40.0       93.5       .904      7.803      5.382       .904    5.5737     11.532   -6.537     .6447
 45.0      107.1      1.469     10.110      6.691      1.469    7.2215     14.337   -8.118     .5942
 50.0      127.4      1.879     12.039      7.717      1.879    8.5992     16.537   -9.361     .5434
                PHI=    20.000
  Z=        CONS      GAMMA1     GAMMA2     GAMMA3       Y1        Y2         Y3       Y4       QAVS
  0.0      107.5      0.000      0.000      0.000      0.030    0.0000      0.000     .393     .6069
  5.0      103.0      -.051      -.023       .010      -.058    -.0291       .048     .375     .6153
 10.0       97.3      -.122      -.016       .081      -.163    -.0205       .410     .105     .6272
 15.0       91.4      -.185       .155       .290      -.247     .1965      1.474    -.671     .6403
 20.0       86.3      -.202       .656       .728      -.276     .8325      3.700   -2.249     .6508
 25.0       83.0      -.127      1.657      1.480      -.169    2.1344      7.516   -4.896     .6539
 30.0       82.5       .083      3.261      2.575  [illegible] [illegible] 13.077   -8.691     .6445
 35.0       85.6       .438      5.399      3.937       .584    6.8565     19.999  -13.346     .6195
 40.0       93.5       .904      7.803      5.382      1.206    9.9089     27.335  -18.213     .5807
 45.0      107.1      1.469     10.110      6.691      1.878   12.8382     33.984  -22.558     .5342
 50.0      127.4      1.879     12.039      7.717  [illegible] [illegible] 39.193  -25.995     .4874
                PHI=    30.000
  Z=        CONS      GAMMA1     GAMMA2     GAMMA3       Y1        Y2         Y3       Y4       QAVS
  0.0      107.5      0.000      0.000      0.000      0.000    0.0000      0.000     .482     .5180
  5.0      103.0      -.051      -.023       .010      -.102    -.0654       .164     .348     .5254
 10.0       97.3      -.122      -.016       .081      -.244    -.0462      1.385    -.723     .5359
 15.0       91.4      -.185       .155       .290      -.371     .4422      4.975   -3.710     .5473
 20.0       86.3      -.202       .656       .728      -.405    1.8731     12.488   -9.767     .5565
 25.0       83.0      -.127      1.657      1.480      -.254    4.7349     25.367  -19.937     .5592
 30.0       82.5       .083      3.261      2.575       .165    9.3173     44.136  -34.535     .5509
 35.0       85.6       .438      5.399      3.937       .876   15.4271     67.495  -52.473     .5289
 40.0       93.5       .904      7.803      5.382      1.809   22.2950     92.257  -71.265     .4949
 45.0      107.1      1.469     10.110      6.691      2.817   28.8860    114.696  -88.082     .4541
 50.0      127.4      1.879     12.039      7.717      3.759   34.3966    132.297 [illegible]1.072 .4131
```

```
                PHI=   45.00

  Z=        CONS       GAMMA1      GAMMA2      GAMMA3        Y1        Y2          Y3        Y4        QAVS
  0.0      107.5        0.000       0.000       0.000      0.000     0.0000      0.000      .562     .4380
  5.0      103.0        -.051       -.023        .010      -.153     -.1472       .552      .009     .444
 10.0       97.3        -.122       -.016        .081      -.366     -.1039      4.675    -3.866     .453
 15.0       91.4        -.105        .155        .290      -.556      .9949     16.791   -14.703     .463
 20.0       86.3        -.202        .656        .728      -.607     4.2145     42.147   -36.796     .470
 25.0       83.0        -.127       1.657       1.480      -.381    10.6535     85.612   -74.050     .472
 30.0       82.5         .083       3.261       2.575       .248    20.9640    148.959   *27.707     .464
 35.0       85.6         .438       5.399       3.937      1.315    34.7110    227.796   *93.845     .444
 40.0       93.5         .904       7.933       5.382      2.713    50.1637    311.367   *63.331     .414
 45.0      107.1        1.469      10.110       6.691      4.226    64.9935    387.100   *25.711     .370
 50.0      127.4        1.879      12.339       7.717      5.636    77.3924    446.501   *74.089     .342

                PHI=   100.000

  Z=        CONS       GAMMA1      GAMMA2      GAMMA3        Y1        Y2          Y3        Y4        QAVS
  0.0      107.5        0.000       0.000       0.000      0.000     0.0000      0.000      .691     .3085
  5.0      103.0        -.051       -.023        .010      -.340     -.7271      6.359    -5.759     .3130
 10.0       97.3        -.122       -.016        .081      -.816     -.5133     51.360   -50.319     .3187
 15.0       91.4        -.105        .155        .290     -1.235     4.9231    194.265   *77.440     .3236
 20.0       86.3        -.202        .656        .728     -1.349    20.0123    462.524   *39.656     .3245
 25.0       83.0        -.127       1.657       1.480      -.867    52.4[illegible]  939.501   *25.342     .3180
 30.0       82.5         .083       3.261       2.575       .551   103.5904    *34.664   *30.930     .3660
 35.0       85.6         .438       5.399       3.937      2.922   171.4123    *99.819   *30.601     .2724
```



THOMAS REACTION KINETIC MODEL
FOR
PREDICTING EFFLUENT CONCENTRATION PROFILES
ALONG WITH SAMPLE CALCULATIONS
FOR SDS/GAC SYSTEM
AT
2°, 13° and 25°C.

```
        PROGRAM TST         73/73    OPT=0   TRACE                    FTN 4.0+P355       05/26/74  15.31.40.        PAGE      1

                        PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
                  C
                  C
                  C
                  C
                  C
                  C
                  C
                  C
                  C*****************************************************************
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C     NOMENCLATURE                                                *
                  C     ------------                                                *
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C     F      FLOW RATE THROUGH COLUMNS.                           *
                  C                                                                 *
                  C     E      POROSITY OF BED.                                     *
                  C                                                                 *
                  C     PDIA   ADSORBENT PARTICLE DIAMETER.                         *
                  C                                                                 *
                  C     KVIS   KINEMATIC VISCOSITY OF WATER.                        *
                  C                                                                 *
                  C     TEMP   TEMPERATURE OF FEED.                                 *
                  C                                                                 *
                  C     X      ASSOCIATION FACTOR FOR WATER IN WILKE-CHANG EQUATION.*
                  C                                                                 *
                  C     U      ABSOLUTE VISCOSITY OF WATER.                         *
                  C                                                                 *
                  C     M      MOLECULAR WEIGHT OF WATER.                           *
                  C                                                                 *
                  C     VB     SOLUTE VOLUME AT NORMAL BOILING POINT.               *
                  C                                                                 *
                  C     DP     SOLID PHASE PORE DIFFUSION COEFFICIENT.              *
                  C                                                                 *
                  C     RHO    DENSITY OF BED                                       *
                  C                                                                 *
                  C     C0     FEED CONCENTRATION.                                  *
                  C                                                                 *
                  C     B      LANGMUIR*S VELOCITY CONSTANT.                        *
                  C                                                                 *
                  C     Q0     LANGMUIR*S MONOLAYER CAPACITY.                       *
                  C                                                                 *
                  C     DLIQ   BULK LIQUID DIFFUSIVITY.                             *
                  C                                                                 *
                  C     A      INTERFACIAL PARTICLE VOLUME.                         *
                  C                                                                 *
                  C     AREA   CROSS-SECTIONAL AREA OF BED.                         *
                  C                                                                 *
                  C     VBED   EMPTY BED VOLUMES.                                   *
                  C                                                                 *

        GRAM TST            73/73    OPT=0   TRACE                    FTN 4.0+P355       05/26/74  15.31.40.        PAGE      2

                  C     VEL    SUPERFICIAL EMPTY BED VELOCITY.                      *
                  C                                                                 *
                  C     NSC    SCHMIDT NUMBER                                       *
                  C                                                                 *
                  C     NRE    REYNOLDS NUMBER OF PARTICLE.                         *
                  C                                                                 *
                  C     KF     FLUID PHASE MASS TRANSFER RATES.                     *
                  C                                                                 *
                  C     KPAP   SOLID PHASE DIFFUSION.                               *
                  C                                                                 *
                  C     DG     DIMENSIONLESS RATIO OF SOLID PHASE CAPACITY TO LIQUID PHASE.
                  C                                                                 *
                  C     R      EQUILIBRIUM MODULUS.                                 *
                  C                                                                 *
                  C     K      GENERAL RATE COEFFICIENTS.                           *
                  C                                                                 *
                  C     S COLUMN CAPACITY MODULUS.                                  *
                  C                                                                 *
                  C     TAU    TIME IN SECONDS.                                     *
                  C                                                                 *
                  C     GLAS   AMOUNT OF LAS APPLIED.                               *
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C                                                                 *
                  C*****************************************************************
                  C
                  C
                  C
                  C
                  C
                  C
```

```
C
      REAL KVIS,KF,K,KPAP,M,NSC,NRE,KP
      NI=1
      NM=3
   66 IF(NI.EQ.NM) GO TO 67
      READ(5,2)KVIS,TEMP,U,DP,DO,CO,B
    2 FORMAT(F9.5,/,F6.1,/,F8.5,/,F6.3,/,F8.4,/,F9.3,/,F9.5)
      GREM=0.0
      F=5.5
      E=0.5
      PDIA=0.09
      X=2.6
      M=18.0
      VO=305.3
      DP=DP/(10.0**7.0)
      RHO=1.475
      CO=CO/(10.0**6.0)
      B=B*10.0**6.0
      DLIQ=(7.4*10.0**(-8)*TEMP*SQRT(X*M))/(U*(VO**0.6))
      A=6*(1.0-E)/PDIA
      PI=3.1416
      AREA=PI*5.08*5.08/4.0
      VBED=AREA*5.0*30.48
```

```
      VEL=F/AREA
      NSC=(KVIS/DLIQ)**(-0.6666)
      NRE=((VEL*PDIA)/(KVIS*(1.0-E)))**(-0.6666)
      KF=1.09*NSC*NRE*VEL/E
      KPAP=60.0*DP/(PDIA*PDIA)
      KP=KPAP/3
      DG=(DO*RHO)/(CO*E)
      R=1.0/(1.0+B*CO)
      H1=1.0/(KF*A)
      H2=1.0/(KPAP*DG)
      K=2.0/((R+1.0)*(H1+H2))
      S=K*VBED*E/F
      WRITE(6,20)KVIS,TEMP,U,DP,DO,CO,B
   20 FORMAT(////,10X,*FLOW RATE IN CM3/SEC=5.5*,/,10X,*VOID FRACTION=0.
     $55*,/,10X,*PARTICLE DIAMETER CM =0.09 *,/,10X,*KINEMATIC VISCOSITY
     *IN CM2/SEC=*,F9.5,/,10X,*TEMPERATURE IN DK=*,F6.1,/,10X,*ABSOLUTE V
     1ISCOSITY IN CENTIPOISE=*,F8.5,/,10X,*PORE DIFFUSIVITY IN CM2/SEC=*
     5,E12.4,/,10X,*EQUILIBRIUM LOADING IN GM LAS/GM CARBON=*,F6.3,/,10X
     2,*PARTICLE DENSITY IN GM/CM3=1.35*,/,10X,*INFLUENT CONCENTRATION O
     1F LAS IN GM/CM3=*,E12.4,/,10X,*LANGMUIR VELOCITY CONSTANT IN CM3/G
     4M=*,F12.4)
      WRITE(6,30)DLIQ,A,AREA,VBED,VEL,NSC,NRE
   30 FORMAT(/,10X,*BULK LIQUID DIFFUSIVITY IN CM2/SEC=*,E10.4,/,10X,*IN
     *TERFACIAL PARTICLE AREA IN 1/CM=*,F6.2,/,10X,*COLUMNAR AREA IN CM2
     *=*,F7.3,/,10X,*VOLUME OF CARBON BED IN CM3=*,F8.2,/,10X,*SUPERFICI
     *AL LIQUID VELOCITY IN CM/SEC=*,F8.3,/,10X,*SCHMIDT NUMBER**-2/3=*,
     *F9.6,/,10X,*REYNOLDS NUMBER**-2/3=*,F9.4)
      WRITE(6,40)KF,KPAP,DG,R,K,S
   40 FORMAT(/,10X,*FLUID PHASE DIFFUSION RATE IN CM/SEC=*,F10.7,/,10X,*
     *PORE DIFFUSION RATE COEFFICIENT IN 1/SEC=*,F10.7,/,10X,*RATIO OF S
     *OLID PHASE TO FLUID PHASE=*,F12.4,/,10X,*EQUILIBRIUM MODULUS=*,F10
     9.5,/,10X,*GENERAL RATE COEFFICIENT IN SEC-1=*,F12.4,/,10X,*COLUMN
     3CAPACITY MODULUS=*,F12.4)
      WRITE(6,12)
   12 FORMAT(////////////,12X,*TIME IN HOURS  *,12X,*DIMENSIONLESS CONCE
     $NTRATION RATIO*,12X,*GRAMS LAS PASSED*,12X,*GRAMS LAS REMOVED*)
      IF(NI.EQ.1) GO TO 69
      GO TO 70
   69 CONTINUE
      CALL PLOT(0.0,0.0,-20)
      XSCALE=25.0
      YSCALE=0.1
      V=0.0
      W=0.0
      XMIN=0.0
      YMIN=0.0
      XMAX=625.0
      YMAX=1.0
      CALL PLTIN(XSCALE,YSCALE,V,W,XMIN,XMAX,YMIN,YMAX)
      CALL PLOT(0.0,0.0,3)
      CALL PLOT(25.0,0.0,2)
      CALL PLOT(25.0,10.0,2)
      CALL PLOT(0.0,10.0,2)
      CALL PLOT(0.0,0.0,2)
   70 CONTINUE
      DO 10 I=1,50
      TAU=I*10000.0
```

```
      T=K*TAU/S
      X1=SQRT(S)
      X2=SQRT(T)
      X3=X1-X2
      X4=SQRT(0.3*T)
      X5=SQRT(X4)
      X6=1.0/(X1+X5)
      X7=SQRT(R*S)
      X8=SQRT(T)
      X9=X7-X8
      X10=1.0/(X9+X5)
      X11=ERF(X3)
      X12=X3*X3
      X13=EXP(X12)
      PI=SQRT(PI)
      X14=(PI*(1.0-X11)*X13)-X6
      X15=ERF(X9)
      X16=X9*X9
      X17=EXP(X15)
      X18=(PI*(1.0-X15)*X17)+X10
      X19=(X14/X18)+1.0
      X20=1.0/X19
      GLAS=TAU*F*CO
      GREM=GREM+CO*(1.0-X20)*10000.*F
      TAU=TAU/3600.0
      Y50=X20/YSCALE
      X50=GLAS/XSCALE
      CALL PLOT(X50,Y50,2)
      WRITE(6,11)TAU,X20,GLAS,GREM
   11 FORMAT(//,12X,F9.2,29X,F9.4,29X,F9.3,20X,F9.3)
   10 CONTINUE
      CALL PLOT(0.0,0.0,-3)
      NI=NI+1
      GO TO 66
   67 CONTINUE
      CALL PLOT(0.0,0.0,999)
      STOP
      END
```

```
FLOW RATE IN CM3/SEC=5.5
VOID FRACTION=0.5
PARTICLE DIAMETER CM =0.39
KINEMATIC VISCOSITY IN CM2/SEC=    .01680
TEMPERATURE IN OK= 275.0
ABSOLUTE VISCOSITY IN CENTIPOISE= 1.67280
PORE DIFFUSIVITY IN CM2/SEC=    .6400E-08
EQUILIBRIUM LOADING IN GM LAS/GM CARBON=  .138
PARTICLE DENSITY IN GM/CM3=1.35
INFLUENT CONCENTRATION OF LAS IN GM/CM3=    .2450E-03
LANGMUIR VELOCITY CONSTANT IN CM3/GM=    .9340E+05

BULK LIQUID DIFFUSIVITY IN CM2/SEC= .2496E-05
INTERFACIAL PARTICLE AREA IN 1/CM= 33.33
COLUMNAR AREA IN CM2= 20.268
VOLUME OF CARBON BED IN CM3= 3099.93
SUPERFICIAL LIQUID VELOCITY IN CM/SEC=    .271
SCHMIDT NUMBER**-2/3=  .02917
REYNOLDS NUMBER**-2/3=     .4969

FLUID PHASE DIFFUSION RATE IN CM/SEC=  .0008153
PORE DIFFUSION RATE COEFFICIENT IN 1/SEC=  .0000474
RATIO OF SOLID PHASE TO FLUID PHASE=  757.5531
EQUILIBRIUM MODULUS=        .04197
GENERAL RATE COEFFICIENT IN SEC-1=     .0297
COLUMN CAPACITY MODULUS=         9.3393
```

2°C

```
TIME IN HOURS        DIMENSIONLESS CONCENTRATION RATIO        GRAMS SDS PASSED        GRAMS SDS REMOVED
    2.78                     .0004                              13.475                  13.470
    5.56                     .0004                              26.950                  26.937
    8.33                     .0019                              40.425                  40.400
   11.11                     [illegible]                        53.900                  53.856
   13.89                     .0121                              67.375                  67.303
   16.67                     .0331                              80.850                  80.737
   19.44                     .0145                              94.325                  94.151
   22.22                     .0166                             107.800                 107.536
   25.00                     .0397                             121.275                 120.851
   27.78                     .0141                             134.750                 134.165
   30.56                     .0205                             148.225                 147.364
   33.33                     .0296                             161.700                 160.439
   36.11                     .0426                             175.175                 173.340
   38.89                     .0616                             188.650                 185.993
   41.67                     .0964                             202.125                 198.333
   44.44                     .1211                             215.600                 210.146
   47.22                     .1672                             229.075                 221.368
   50.00                     .2262                             242.550                 231.795
   52.78                     .2986                             256.025                 241.246
   55.56                     .3427                             269.500                 249.555
   58.33                     .4744                             282.975                 256.647
   61.11                     .5679                             296.450                 262.470
   63.89                     .6568                             309.925                 267.094
   66.67                     .7359                             323.400                 270.653
   69.44                     .8322                             336.875                 273.318
   72.22                     .8552                             350.350                 275.270
   75.00                     .8956                             363.825                 276.673
   77.78                     .9260                             377.300                 277.670
   80.56                     .9480                             390.775                 278.371
   83.33                     .9637                             404.250                 278.860
   86.11                     .9748                             417.725                 279.230
   88.89                     .9925                             431.200                 279.435
   91.67                     .9579                             444.675                 279.598
   94.44                     .9917                             458.150                 279.710
   97.22                     .9943                             471.425                 279.737
  100.00                     .9961                             485.100                 279.849
  102.78                     .9973                             499.575                 279.877
  105.56                     .9981                             512.050                 279.902
  108.33                     .9987                             525.525                 279.919
  111.11                     .9991                             539.000                 279.931
```

```
FLOW RATE IN CM3/SEC=5.5
VOID FRACTION=0.5
PARTICLE DIAMETER CM =.023
KINEMATIC VISCOSITY IN CM2/SEC=   .01210
TEMPERATURE IN K= 286.0
ABSOLUTE VISCOSITY IN CENTIPOISE= 1.20290
PORE DIFFUSIVITY IN CM2/SEC=    .2713E-07
EQUILIBRIUM LOADING IN GM LAS/GM CARBON=  .120
PARTICLE DENSITY IN GM/CM3=1.35
INFLUENT CONCENTRATION OF LAS IN GM/CM3=   .2500E-03
LANGMUIR VELOCITY CONSTANT IN CM3/GM=   .1233E+06

BULK LIQUID DIFFUSIVITY IN CM2/SEC= .3611E-05
INTERFACIAL PARTICLE AREA IN 1/CM= 33.33
COLUMNAR AREA IN CM2= 20.294
VOLUME OF CARBON BED IN CM3= 3038.90
SUPERFICIAL LIQUID VELOCITY IN CM/SEC=    .271
SCHMIDT NUMBER**-2/3=  .004469
REYNOLDS NUMBER**-2/3=    .3945

FLUID PHASE DIFFUSION RATE IN CM/SEC=  .0013426
PORE DIFFUSION RATE COEFFICIENT IN 1/SEC=  .0002003
RATIO OF SOLID PHASE TO FLUID PHASE=  649.0000
EQUILIBRIUM MODULUS=     .03152
GENERAL RATE COEFFICIENT IN SEC-1=     .0531
COLUMN CAPACITY MODULUS=     14.9215
```

13°C

```
TIME IN HOURS      DIMENSIONLESS CONCENTRATION RATIO      GRAMS SDS PASSED      GRAMS SDS REMOVED

    2.78                     .0000                             13.750                13.750
    5.56                     .0000                             27.500                27.500
    8.33                     .0000                             41.250                41.250
   11.11                     .0000                             55.000                55.000
   13.89                     .0000                             68.750                68.749
   16.67                     .0001                             82.500                82.498
   19.44                     .0001                             96.250                96.247
   22.22                     .0003                            110.000               109.992
   25.00                     .0007                            123.750               123.733
   27.78                     .0015                            137.500               137.463
   30.56                     .0033                            151.250               151.168
   33.33                     .0072                            165.000               164.816
   36.11                     .0150                            178.750               178.350
   38.89                     .0345                            192.500               191.626
   41.67                     .0732                            206.250               204.369
   44.44                     .1455                            220.000               216.074
   47.22                     .2784                            233.750               225.930
   50.00                     .4511                            247.500               233.400
   52.78                     .6544                            261.250               238.153
   55.56                     .8273                            275.000               240.803
   58.33                     [illegible]                      288.750               242.142
   61.11                     .9335                            302.500               242.751
   63.89                     .9784                            316.250               243.077
   66.67                     .9901                            330.000               243.213
   [illegible]               .9955                            343.750               243.275
   72.22                     .9980                            357.500               243.303
   75.00                     .9991                            371.250               243.315
   77.78                     .9996                            385.000               243.321
   80.56                     .9998                            398.750               243.323
   83.33                     .9999                            412.500               243.325
   86.11                    1.0000                            426.250               243.325
   88.89                    1.0000                            440.000               243.325
   91.67                    1.0000                            453.750               243.325
```

```
FLOW RATE IN CM3/SEC=5.5
VOID FRACTION=0.5
PARTICLE DIAMETER CM =0.09
KINEMATIC VISCOSITY IN CM2/SEC=   .00895
TEMPERATURE IN K= 298.
ABSOLUTE VISCOSITY IN CENTIPOISE=  .89370
PORE DIFFUSIVITY IN CM2/SEC=    .3763E-07
EQUILIBRIUM LOADING IN GM LAS/GM CARBON=  .107
PARTICLE DENSITY IN GM/CM3=1.35
 INFLUENT CONCENTRATION OF LAS IN GM/CM3=   .1470E-03
LANGMUIR VELOCITY CONSTANT IN CM3/GM=   .1610E+05

BULK LIQUID DIFFUSIVITY IN CM2/SEC= .5054E-05
INTERFACIAL PARTICLE AREA IN 1/CM= 33.33
COLUMNAR AREA IN CM2= 20.258
VOLUME OF CARBON BED IN CM3= 3089.90
SUPERFICIAL LIQUID VELOCITY IN CM/SEC=    .271
SCHMIDT NUMBER**-2/3=  .006844
REYNOLDS NUMBER**-2/3=     .3226

FLUID PHASE DIFFUSION RATE IN CM/SEC=  .0013363
PORE DIFFUSION RATE COEFFICIENT IN 1/SEC=  .002785
RATIO OF SOLID PHASE TO FLUID PHASE=  983.5716
EQUILIBRIUM MODULUS=    .24054
GENERAL RATE COEFFICIENT IN SEC-1=     .0722
COLUMN CAPACITY MODULUS=     20.2791
```

25°C

TIME IN HOURS	DIMENSIONLESS CONCENTRATION RATIO	GRAMS SDS PASSED	GRAMS LAS REMOVED
2.78	[illegible]	[illegible]	8.085
5.56	.0000	16.170	16.170
8.33	[illegible]	24.255	24.255
11.11	[illegible]	32.340	32.340
13.89	.0000	40.425	40.425
16.67	.0000	48.510	48.510
19.44	.0000	56.595	56.595
22.22	.0000	64.680	64.680
25.00	.0000	72.765	72.765
27.78	.0000	80.850	80.850
30.56	.0000	88.935	88.935
33.33	.0000	97.020	97.020
36.11	.0000	105.105	105.104
38.89	.0001	113.190	113.189
41.67	.0001	121.275	121.273
44.44	.0003	129.360	129.356
47.22	.0006	137.445	137.436
50.00	.0011	145.530	145.512
52.78	.0023	153.615	153.578
55.56	.0046	161.700	161.626
58.33	.0093	169.785	169.635
61.11	.0187	177.870	177.569
63.89	.0372	185.955	185.353
66.67	.0724	194.040	192.852
69.44	.1364	202.125	199.834
72.22	.2422	210.210	205.961
75.00	.3326	218.295	210.872
77.78	.5666	226.380	214.376
80.56	.7256	234.465	216.595
83.33	.8425	242.550	217.868
86.11	.9154	250.635	218.552
88.89	.9363	258.720	218.936
91.67	.9779	266.805	219.084
94.44	.9890	274.890	219.174
97.22	.9945	282.975	219.218
100.00	.9973	291.060	219.240
102.78	.9987	299.145	219.251
105.56	.9993	307.230	219.256
108.33	.9997	315.315	219.259
111.11	.9998	323.400	219.260

PROGRAM FOR ESTIMATING GENERAL RATE COEFFICIENT BY COMPARISON OF MASS TRANSFER ZONE HEIGHTS FOR SDS/GAC SYSTEM.

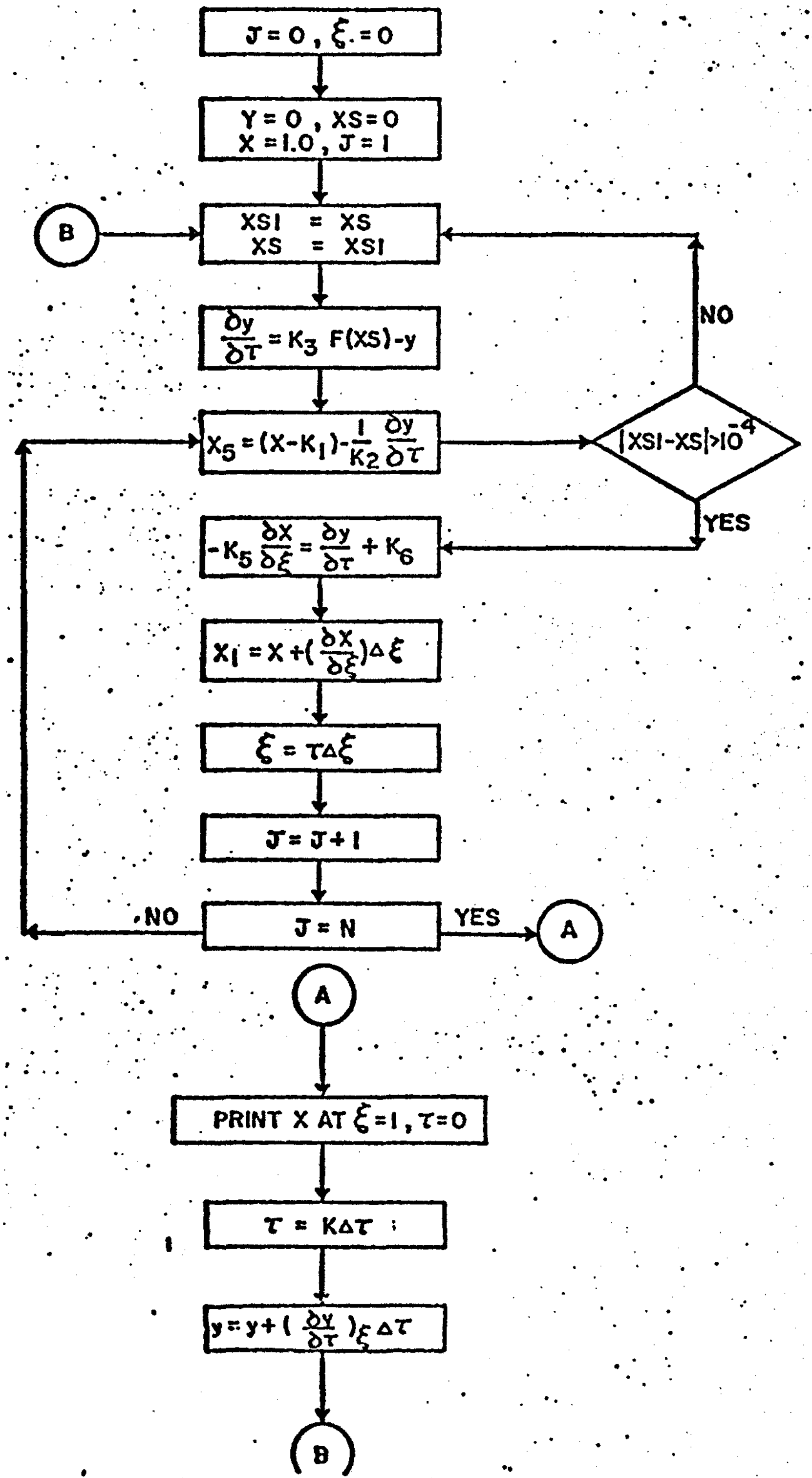
```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION TAU(100),X20(100),GLAS(100)
      DIMENSION GREM(100)
      REAL KVIS,KF,K,KPAP,M,NSC,NRE,MTZONE,K1,K2
      M1=0
      NM=3
68    IF(M1.EQ.NM) GO TO 67
      READ(5,2)KVIS,TEMP,U,DP,Q0,C0,B,MTZONE
2     FORMAT(F9.5,/,F6.1,/,F8.5,/,F5.3,/,F8.4,/,F7.2,/,F9.5,/,F9.3)
      N=50
      GREM(1)=0.0
      F=5.5
      E=0.5
      PDIA=0.09
      X=2.6
      M=19.0
      V0=345.3
      DP=DP/(10.0**7.0)
      RHO=0.675
      C0=C0/(10.0**6.0)
      B=B*10.0**6.0
      ICOUNT=0
      DLIQ=(7.4*10.0**(-8)*TEMP*SQRT(X*M))/(U*(V0**0.6))
      A=6*(1.0-E)/PDIA
      PI=3.1416
      AREA=PI*5.08*5.08/4.0
      VBED=AREA*5.0*30.48
      VEL=F/AREA
      NSC=(KVIS/DLIQ)**(-0.6666)
      NRE=((VEL*PDIA)/(KVIS*(1.0-E)))**(-0.6666)
      KF=1.09*NSC*NRE*VEL/E
      KPAP=60.0*DP/(PDIA*PDIA)
      DG=(Q0*RHO)/(C0*E)
      R=1.0/(1.0+B*C0)
      H1=1.0/(KF*A)
      H2=1.0/(KPAP*DG)
      K=2.0/((R+1.0)*(H1+H2))
      WRITE(6,20)KVIS,TEMP,U,DP,Q0,C0,B
20    FORMAT(////,10X,≠FLOW RATE IN CM3/SEC=5.5≠,/,10X,≠VOID FRACTION=0.
     335≠,/,10X,≠PARTICLE DIAMETER IN= 0.09 ≠,/,10X,≠KINEMATIC VISCOSITY
     +IN CM2/SEC=≠,F9.5,/,10X,≠TEMPERATURE IN DK=≠,F6.1,/,10X,≠ABSOLUTE V
     $ISCOSITY IN CENTIPOISE=≠,F8.5,/,10X,≠PORE DIFFUSIVITY IN CM2/SEC=≠
     5,E12.4,/,10X,≠EQUILIBRIUM LOADING IN GM LAS/GM CARBON=≠,F6.3,/,10X
     2,≠PARTICLE DENSITY IN GM/CM3=1.35≠,/,10X,≠INFLUENT CONCENTRATION O
     1F LAS IN GM/CM3=≠,E12.4,/,10X,≠LANGMUIR VELOCITY CONSTANT IN CM3/G
     4M=≠,E12.4)
      WRITE(6,30)DLIQ,A,AREA,VBED,VEL,NSC,NRE
30    FORMAT(/,10X,≠BULK LIQUID DIFFUSIVITY IN CM2/SEC=≠,E10.4,/,10X,≠IN
     *TERFACIAL PARTICLE AREA IN 1/CM=≠,F6.2,/,10X,≠COLUMNAR AREA IN CM2
     *=≠,F7.3,/,10X,≠VOLUME OF CARBON BED IN CM3=≠,F8.3,/,10X,≠SUPERFICI
     *AL LIQUID VELOCITY IN CM/SEC=≠,F8.5,/,10X,≠SCHMIDT NUMBER**-2/3=≠,
     *F8.4,/,10X,≠REYNOLDS NUMBER**-2/3=≠,F8.4)
      WRITE(6,40)KF,KPAP,DG,R,MTZONE
40    FORMAT(/,10X,≠FLUID PHASE DIFFUSION RATE IN CM/SEC=≠,F10.7,/,10X,≠
     *PORE DIFFUSION RATE CO-EFFICIENT IN 1/SEC=≠,F10.7,/,10X,≠RATIO OF S
     *OLID PHASE TO FLUID PHASE=≠,F10.4,/,10X,≠EQUILIBRIUM MODULUS=≠,F1
     *0.5,/,10X,≠HEIGHT OF MASS TRANSFER ZONE IN CMS =≠,F9.3)

107   S=K*VBED*R/F
      L=0
      LC=0
      DO 10 I=1,N
      TAU(I)=[illegible]
      T=K*TAU(I)/R
      X1=SQRT(R*T)
      X2=SQRT(S)
      X3=X1-X2
      X4=SQRT(R*S*T)
      X5=SQRT(X4)
      X6=1.0/(X1+X5)
      X7=SQRT(R*S)
      X8=SQRT(T)
      X9=X7-X8
      X10=1.0/(X8+X5)
      X11=ERF(X3)
      X12=X3*X3
      X13=EXP(X12)
      PI=SQRT(PI)
      X14=(PI*(1.0-X11)*X13)-X6
      X15=ERF(X9)
      X16=X9*X9
      X17=EXP(X16)
      X18=(PI*(1.0-X15)*X17)+X10
      X19=(X14/X18)+1.0
      X20(I)=1.0/X19
      GLAS(I)=TAU(I)*F*C0
      GREM(I+1)=GREM(I)+C0*(1.0-X20(I))*F*10000.0
      IF(X20(I).GE.0.1000) GO TO 101
      GO TO 104
101   L=L+1
      IF(L.GT.1) GO TO 102
      TA=TAU(I-1)+(((0.1-X20(I-1))/(X20(I)-X20(I-1)))*(TAU(I)-TAU(I-1)))
      GO TO 104
102   IF(X20(I).GE.0.9000) GO TO 103
      GO TO 104
103   LC=LC+1
      IF(LC.GT.1) GO TO 104
      TE=TAU(I-1)+(((0.9-X20(I-1))/(X20(I)-X20(I-1)))*(TAU(I)-TAU(I-1)))
104   CONTINUE
10    CONTINUE
      TD=TE-TA
      MT=TD*5.0*30.48/TE
      TOL1=(MT-MTZONE)
      IF(ABS(TOL1).LT.0.001) GO TO 105
      IF(TOL1.LT.0.0) GO TO 106
      IF(ICOUNT.EQ.0) GO TO 110
      K2=K
      K=(K1+K2)/2.0
      GO TO 107
110   K2=K
      K=2.0*K
      GO TO 107
106   ICOUNT=ICOUNT+1
      K1=K
      K=(K1+K2)/2.0

      GO TO 107
105   WRITE(6,200)K,S
200   FORMAT(/,10X,≠GENERAL RATE COEFFICIENT IN SEC-1=≠,F10.4,/,10X,≠COL
     $UMN CAPACITY MODULUS=≠,F12.4)
      WRITE(6,12)
12    FORMAT(////////////,12X,≠TIME IN HOURS  ≠,12X,≠DIMENSIONLESS CONCE
     $NTRATION RATIO≠,12X,≠GRAMS LAS PASSED≠,12X,≠GRAMS LAS REMOVED≠)
      IF(M1.EQ.0) GO TO 69
      GO TO 70
69    CONTINUE
      CALL PLOT(0.0,0.0,-20)
      XSCALE=25.0
      YSCALE=0.1
      V=0.0
      H=0.0
      XMIN=0.0
      YMIN=0.0
      XMAX=625.0
      YMAX=1.0
      CALL PLTIN(XSCALE,YSCALE,V,H,XMIN,XMAX,YMIN,YMAX)
      CALL PLOT(0.0,0.0,3)
      CALL PLOT(25.0,0.0,2)
      CALL PLOT(25.0,10.0,2)
      CALL PLOT(0.0,10.0,2)
      CALL PLOT(0.0,0.0,2)
70    CONTINUE
      DO 150 I=1,N
      TAU(I)=TAU(I)/3600.0
      Y5=X20(I)/YSCALE
      X5=GLAS(I)/XSCALE
      J=I+1
      CALL PLOT(X5,Y5,2)
      WRITE(6,11)TAU(I),X20(I),GLAS(I),GREM(J)
11    FORMAT(//,11X,F9.2,29X,F8.4,29X,F9.3,20X,F9.3)
150   CONTINUE
      CALL PLOT(0.0,0.0,-3)
      M1=M1+1
      GO TO 68
67    CONTINUE
      CALL PLOT(0.0,0.0,999)
      STOP
      END
```

SOLUTION TO FIXED-BED PROBLEM IN THE PRESENCE OF BACTERIAL ACTIVITY WITH SURFACE DIFFUSION STEP.

SAMPLE CALCULATION INCLUDED FOR 25^0C SOLUTION

TABLE 54

ALGORITHM FOR SOLUTION TO FIXED-BED PROBLEM WITH PRESENCE OF BACTERIAL ACTIVITY



```
C
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C*******************************************************************************
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C     NOMENCLATURE                                                             *
C     ------------                                                             *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C     FILMT   BACTERIAL FILM THICKNESS.                                        *
C                                                                              *
C     RF      REACTION RATE INSIDE BACTERIAL FILM PER UNIT SURFACE AREA.       *
C                                                                              *
C     DIFF    BULK SOLUTE DIFFUSIVITY INSIDE FILM.                             *
C                                                                              *
C     QC      MONOLAYER SATURATION LOADING ON CARBON.                          *
C                                                                              *
C     DP      SURFACE DIFFUSION COEFFICIENT.                                   *
C                                                                              *
C     A,B     LINEAR COEFFICIENTS USED TO APPROXIMATE ISOTHERM.                *
C                                                                              *
C     C,D     LINEAR COEFFICIENTS USED TO APPROXIMATE ISOTHERM.                *
C                                                                              *
C     XS2     TURNING POINT IN SEWAGE ISOTHERMS.                               *
C                                                                              *
C     DELL    BED LENGTH REDUCED PARAMETER.                                    *
C                                                                              *
C     DELT    LENGTH OF TIME STEP USED IN INTEGRATION.                         *
C                                                                              *
C     CF      INITIAL FEED CONCENTRATION.                                      *
C                                                                              *
C     CC      CONCENTRATION USED TO MAKE ISOTHERM DIMENSIONLESS.               *
C                                                                              *
C     XF      DIMENSIONLESS FEED CONCENTRATION.                                *
C                                                                              *
C     POR     POROSITY OF PARTICLES.                                           *
C                                                                              *
C     PDIA    PARTICLE DIAMETER.                                               *
C                                                                              *
C     FEED    VOLUMETRIC FLOW RATE IN CM3/SEC.                                 *
C                                                                              *
C     PAREA   INTERFACIAL PARTICLE AREA.                                       *
C                                                                              *
C     L       LENGTH OF CARBON BED IN CMS.                                     *
C                                                                              *
C     RHOB    BULK BED DENSITY.                                                *
C                                                                              *
C     VEL     SUPERFICIAL FLUID VELOCITY THROUGH BED.                          *
C                                                                              *
C     N       NUMBER OF TIME STEPS TO BE TAKEN.                                *
C                                                                              *
C     N1      NUMBER OF DIVISIONS OF COLUMN.                                   *
C                                                                              *
C     I,J     COUNTERS.                                                        *
C                                                                              *
C     JAM     COUNTER USED TO CONTROL PRINTOUT.                                *
C                                                                              *
C     XS      LIQUID PHASE CONCENTRATION AT SURFACE OF PARTICLE.               *
C                                                                              *
C     YS      SOLID PHASE CONCENTRATION AT EQUILIBRIUM WITH XS.                *
C                                                                              *
C     AFED    AMOUNT OF TOC APPLIED TO COLUMN.                                 *
C                                                                              *
C     ARMVD   CUMULATIVE TOC REMOVED FROM SOLUTION AS A FUNCTION OF TIME.      *
C                                                                              *
C     THRS    TIME IN HRS.                                                     *
C                                                                              *
C     XSCALE  SCALING FACTOR USED FOR X-AXIS IN PLOTTING.                      *
C                                                                              *
C     YSCALE  SCALING FACTOR USED FOR Y-AXIS IN PLOTTING.                      *
C                                                                              *
C     PLOT    SUBROUTINE USED TO PLOT X VS TIME AND AFED VS ARMVD.             *
C                                                                              *
C                                                                              *
C                                                                              *
C     ARRAYS                                                                   *
C     ------                                                                   *
C                                                                              *
C                                                                              *
C                                                                              *
C     X       LIQUID PHASE CONCENTRATION STORED IN ARRAYS AS A FUNCTION OF TIME*
C                                                                              *
C     Y       SOLID PHASE CONCENTRATION STORED IN ARRAYS AS A FUNCTION OF TIME.*
C                                                                              *
C     X1      LIQUID PHASE CONCENTRATION AT BED POSITION (J+1).                *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C                                                                              *
C*******************************************************************************
C
C
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```

```
C
      DIMENSION Y(1300),X(1300),X1(1300)
      REAL K0,K1,K2,K3,K4,K5,K6,DELT,DELL,CF,C0,KPAP,FILMT,PDIA
      REAL RF,POR,DIFF,PAREA,L,RHOB,Q0,VEL,DP,ARMVD,[illegible]
      REAL YS,XS
      REAL K7,K8,K9,K10,K11
      INTEGER N,N1,I,J
      READ(5,1)N,N1,CF,C0
1     FORMAT(I4,/,I3,/,2F10.4)
      READ(5,31)FILMT,RF,DIFF,Q0,DP
31    FORMAT(5F15.6)
      READ(5,32)A,B,C,D,XS2
32    FORMAT(5F15.5)
      READ(5,621)TEMP1
621   FORMAT(F5.1)
      DELL=0.01
      DELT=10.0
      DELT1=DELT
      CF=CF/(10.0**6.0)
      C0=C0/(10.0**6.0)
      XF=CF/C0
      DO 2 I=1,N
2     X(I)=XF
      Y(I)=0.0
      POR=0.35
      PDIA=0.09
      RF=RF/(10.0**9.0)
      FEED=1.417
      TOL10=1.0/(10.0**7.0)
      ARMVD=0.0
      K0=RF*(1.0-6.0*FILMT/PDIA)/FILMT
      DIFF=DIFF/(10.0**5.0)
      K1=K0*FILMT*FILMT/(2.0*DIFF*C0)
      PAREA=6.0*(1.0-POR)/PDIA
      NO=5
      L=60.0
      RHOB=0.675
      VEL=0.070
      K2=(PAREA*DIFF*L*POR*C0)/(FILMT*RHOB*Q0*VEL)
      DP=DP/(10.0**9.0)
      KPAP=(60.0*DP)/(PDIA*PDIA)
      K3=(KPAP*L*POR)/VEL
      K4=(6.0*(1.0-POR)*(1.0-6*FILMT/PDIA)*RF)/(PDIA*RHOB)
      K5=(POR*C0)/(RHOB*Q0)
      K6=(K4*L*POR)/(VEL*Q0)
      K7=K3*DELT
      K8=K2*DELT
      K9=K6*DELL/K5
      K10=DELL/(DELT*K5)
      K11=(L*POR*DELT)/(VEL*3600.0)
      CALL PLOT(0.0,0.0,-20)
      XSCALE=6.0
      YSCALE=0.05
      V=0.0
      H=0.0

      XMIN=0.0
      YMIN=0.0
      YMAX=1.00
      XMAX=200.0
      CALL PLTIN(XSCALE,YSCALE,V,H,XMIN,XMAX,YMIN,YMAX)
      CALL PLOT(0.0,0.0,3)
      CALL PLOT(25.0,0.0,2)
      CALL PLOT(25.0,20.0,2)
      CALL PLOT(0.0,20.0,2)
      CALL PLOT(0.0,0.0,2)
      CALL PLOT(50.0,0.0,3)
      CALL PLOT(75.0,0.0,2)
      CALL PLOT(75.0,20.0,2)
      CALL PLOT(50.0,20.0,2)
      CALL PLOT(50.0,0.0,2)
      A1=A
      B1=B
      C1=C
      D1=D
      J=1
      JAM=1
11    IF(J.GT.N1) GO TO 4
      IF(JAM.EQ.NO) GO TO 95
      GO TO 96
95    WRITE(6,51)J
51    FORMAT(//,60X,≠J=≠,I3)
      WRITE(6,75)
75    FORMAT(///,15X,≠X≠,18X,≠Y≠,18X,≠YS≠,18X,≠XS≠,20X,≠I≠,16X,≠TIME IN
     $HRS≠)
96    CONTINUE
      MCM=0
      A=A1
      B=B1
      C=0.0
      D=0.0
      I=1
5     IF(I.GT.N) GO TO 6
      IF(X(I).EQ.0.0) GO TO 76
      GO TO 79
76    X1(I)=0.0
      Y(I+1)=0.0
      I=I+1
      GO TO 5
79    CONTINUE
190   XS=((X(I)-K1)+(K7/K8)*(Y(I)-A-C))/(1.0+(K7/K8)*(B+D))
      IF(MCM.NE.0) GO TO 185
      IF(XS.GT.XS2) GO TO 186
      GO TO 185
186   A=0.0
      B=0.0
      C=C1
      D=D1
      MCM=1
      GO TO 190
185   CONTINUE
      IF(XS.LT.0.0) XS=0.0
      YS=A+B*XS+C+D*XS
```

```
      Y(I+1)=Y(I)+K7*(YS-Y(I))
      X1(I)=X(I)-K9-(Y(I+1)-Y(I))*K10
      IF(X1(I).LT.0.0) X1(I)=0.0
      IF(JAM.EQ.NO) GO TO 93
      GO TO 94
93    CONTINUE
      THRS=K11*I
      WRITE(6,33)X(I),Y(I),YS,X0,I,THRS
33    FORMAT(//,10X,F10.6,9X,F10.8,10X,F10.6,10X,F10.6,10X,I4,17X,F9.2)
94    CONTINUE
      IF(YS.GT.0.050) GO TO 101
      I=I+1
      GO TO 5
101   IF(ABS(YS-Y(I)).LT.TOL10) GO TO 67
      I=I+1
      GO TO 5
67    DO 68 JACK=I,N
      Y(JACK+1)=Y(JACK)
      X1(JACK)=X(JACK)-K9
68    CONTINUE
6     CONTINUE
      DO 58 I=1,N
58    X(I)=X1(I)
      IF(J.EQ.20) GO TO 110
      IF(J.EQ.40) GO TO 110
      IF(J.EQ.60) GO TO 110
      IF(J.EQ.80) GO TO 110
      IF(J.EQ.100) GO TO 110
      GO TO 217
110   DO 111 I=1,N
      TIME=K11*I*3600.0
      X5=(FEED*CF*TIME)/XSCALE
      Y5=X(I)/YSCALE
      CALL PLOT(X5,Y5,2)
111   CONTINUE
      CALL PLOT(50.0,0.0,3)
      DO 313 I=1,N
      TIME=K11*I*3600.0
      X8=(FEED*CF*TIME)/XSCALE+50.0
      Y8=Y(I)/YSCALE
      CALL PLOT(X8,Y8,2)
313   CONTINUE
      CALL PLOT(0.0,0.0,-3)
217   J=J+1
      IF(JAM.EQ.NO) JAM=0
      JAM=JAM+1
      GO TO 11
4     CONTINUE
      WRITE(6,13)
13    FORMAT(////////////////////////////////////,40X,≠RESULTING EFFLUENT
     $PROFILES FROM GAC COLUMNS WITH BACTERIAL ACTIVITY≠,/,40X,≠--------
     $---------------------------------------------------------≠)
      WRITE(6,29)FILMT,RF,DP,Q0,DIFF
29    FORMAT(/////,20X,≠BACTERIAL FILM THICKNESS IN CMS =≠,F10.6,/,20X,≠
     $FILM REACTION RATE IN GMS/CM2-SEC =≠,E10.3,/,20X,≠SURFACE DIFFUSIV
     $ITY IN CM2/SEC =≠,E10.3,/,20X,≠SATURATION LOADING IN GMS TOC/GMS C
     +ARBON =≠,F8.4,/,20X,≠LIQUID PHASE DIFFUSIVITY IN CM2/SEC =≠,E10.3)

      WRITE(6,45)C0,POR,PDIA,FEED,L
45    FORMAT(20X,≠INFLUENT CONCENTRATION IN GMS/CM3 TOC =≠,E10.3,/,20X,≠
     $POROSITY OF BED =≠,F8.4,/,20X,≠PARTICLE DIAMETER IN CMS =≠,F8.5,/,
     $20X,≠FLOW RATE IN CM3/SEC =≠,F8.4,/,20X,≠LENGTH OF BED IN CMS =≠,F
     =8.3)
      WRITE(6,46)VEL,RHOB,DELL,DELT1
46    FORMAT(20X,≠SUPERFICIAL VELOCITY IN CM/SEC =≠,F8.4,/,20X,≠BULK BED
     $ DENSITY IN GMS/CM3 =≠,F8.4,/,20X,≠LENGTH STEP SIZE =≠,F8.4,/,20X,
     $≠INITIAL TIME STEP SIZE =≠,F10.3)
      WRITE(6,622)TEMP1
622   FORMAT(20X,≠TEMPERATURE IN CENTIGRADES = ≠,F5.1)
      WRITE(6,343)A,B,C,D,XS2
343   FORMAT(20X,≠A=≠,F8.3,/,20X,≠B=≠,F8.3,/,20X,≠C≠,F8.3,/,20X,≠D=≠,F8.
     $3,/,20X,≠XS2=≠,F8.3)
      WRITE(6,14)K0,K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11
14    FORMAT(////////////////////,20X,≠K0=≠,F12.7,/,20X,≠K1=≠,F12.7,/,20X,
     $≠K2=≠,F12.7,/,20X,≠K3=≠,F12.7,/,20X,≠K4=≠,F12.7,/,20X,≠K5=≠,F12.7,
     A/,20X,≠K6=≠,F12.7,/,20X,≠K7=≠,F12.7,/,20X,≠K8=≠,F12.7,/,20X,≠K9=≠,
     9F12.7,/,20X,≠K10=≠,F12.7,/,20X,≠K11=≠,F12.7)
      WRITE(6,15)
15    FORMAT(//////////////,20X,≠TIME PAST≠,25X,≠TOC APPLIED≠,25X,≠TOC REMO
     $VED≠,/,20X,≠IN HRS≠,29X,≠IN GMS≠,30X,≠IN GMS≠)
      XSCALE=6.0
      YSCALE=10.0

      CALL PLOT(100.0,0.0,3)
      CALL PLOT(125.0,0.0,2)
      CALL PLOT(125.0,20.0,2)
      CALL PLOT(100.0,20.0,2)
      CALL PLOT(100.0,0.0,2)
      DO 12 I=1,N
      TIME=K11*I*3600.0
      AFED=FEED*CF*TIME
      X6=AFED/XSCALE+100.0
      ARMVD=ARMVD+(1.0-X(I))*C0*FEED*K11*3600.0
      Y6=ARMVD/YSCALE
      TIME=TIME/3600.0
      WRITE(6,16)TIME,AFED,ARMVD
16    FORMAT(/,19X,F7.2,28X,F8.3,28X,F8.3)
      CALL PLOT(X6,Y6,2)
12    CONTINUE
      CALL PLOT(0.0,0.0,-3)
      CALL PLOT(0.0,0.0,999)
      STOP
      END
```

J= 5

X	Y	YS	XS	I	TIME IN MIN
.20791036	0.00000000	.18217332	.04023040	1	1.19
.24521534	.03423814	.24199746	.06142068	2	2.38
.28251117	.07328370	.30532591	.07794566	3	3.57
.33564043	.11693124	.38624784	.09603224	4	4.76
.38635693	.16754552	.47304272	.12306166	5	5.95
.45819037	.22455359	.57987732	.14717691	6	7.14
.52661370	.29166133	.66456323	.19309364	7	8.33
.57470460	.36181856	.69934142	.27022496	8	9.52
.62867443	.42536419	.73126938	.35442672	9	10.71
.66503674	.48285495	.75931036	.42235022	10	11.90
.70363425	.53481395	.78439291	.46368004	11	13.10
.73762723	.58171652	.80881601	.51623392	12	14.29
.76652124	.62402104	.82685163	.56690093	13	15.48
.79256237	.66214031	.84474259	.63031724	14	16.67
.81554979	.69645795	.86071346	.66336552	15	17.86
.83563420	.72732699	.87495469	.70432665	16	19.05
.85372074	.75507162	.88765505	.72492713	17	20.24
.86951059	.77998889	.89897349	.76240591	18	21.43
.88342543	.80235044	.90905572	[illegible]	19	22.62
.89569091	.82240426	.91843276	.80603304	20	23.81
.90649976	.84637635	.92602231	.82027014	21	25.00
.91602263	.85047235	.93331663	.84557105	22	26.19
.92441041	.87447913	.93945368	.86135055	23	27.38
.93179672	.88376622	.94506320	.87402054	24	28.57
.93829961	.89528729	.95006170	.88676613	25	29.76
.94482344	.90558148	.95449628	.89795785	26	30.95
.94986046	.91477429	.95843307	.90713036	27	32.14
.95349211	.92297952	.96192894	.91504220	28	33.33
.95735034	.93029954	.96583018	.92010779	29	34.52
.96081865	.93682674	.96778135	.92938050	30	35.71
.96383338	.94284415	.97022435	.93501594	31	36.90
.96648389	.94782672	.97230269	.94107711	32	38.10
.96881223	.95244169	.97429893	.94573549	33	39.29
.97085912	.95654946	.97599658	.94907101	34	40.48
.97265750	.96028420	.97750312	.95352028	35	41.67
.97423723	.96345480	.97883139	.95676737	36	42.86
.97562482	.96634463	.98003979	.95963453	37	44.05
.97684323	.96891281	.98105260	.96217177	38	45.24
.97791311	.97119432	.98197517	.96441646	39	46.43
.97885226	.97322043	.98279115	.96640183	40	47.62
.97967636	.97501912	.98351269	.96815735	41	48.81
.98039996	.97661537	.98415355	.96970337	42	50.00
.98103469	.97803151	.98471436	.97106163	43	51.19
.98159155	.97928745	.98521245	.97229165	44	52.38
.98208002	.98040397	.98565251	.97330376	45	53.57
.98250843	.98138793	.98604117	.97420042	46	54.76
.98288411	.98226244	.98638437	.97514446	47	55.95
.98321351	.98303713	.98668736	.97598165	48	57.14
.98350220	.98372312	.98695476	.97653132	49	58.33
.98375541	.98433047	.98719377	.97716651	50	59.52

J= 20

X	Y	YS	XS	I	TIME IN HRS
.00154034	0.00000000	0.00000000	0.00000000	14	16.67
.00335216	0.00000000	0.00000000	0.00000000	15	17.86
.00558134	0.00000000	.00125659	.00031653	16	19.05
.00821153	.00023616	.00379494	.00096216	17	20.24
.01143053	.00090424	.00718576	.00162360	18	21.43
.01512213	.00208477	.01139927	.00249322	19	22.62
.01967232	.00383530	.01642115	.00426933	20	23.81
.02472460	.00627582	.02322545	.00569478	21	25.00
.03167094	.00946127	.03130259	.00796065	22	26.19
.03784394	.01357733	.04060273	.01030475	23	27.38
.04662459	.01865601	.05237614	.01329395	24	28.57
.05561017	.02499363	.06531207	.01657667	25	29.76
.06763511	.03257393	.08192202	.02079239	26	30.95
.07982721	.04184581	.09999376	.02537313	27	32.14
.09576969	.05277393	.12269700	.03144137	28	33.33
.11227760	.06591503	.14761658	.03746624	29	34.52
.13316799	.08126973	.17616526	.04521561	30	35.71
.15552635	.09947994	.21223502	.05356051	31	36.90
.18254472	.12667085	.25277523	[illegible]	32	38.10
.21291105	.14549027	.29912176	.07751361	33	39.29
.24732197	.17436972	.35220595	.09935139	34	40.48
.28876928	.20779239	.41510624	.11535742	35	41.67
.33174934	.24675461	.48365943	.12275620	36	42.86
.38873303	.29127768	.56903156	.14442425	37	44.05
.44037356	.34347777	.65555371	.16633371	38	45.24
.48716415	.40212936	.68396348	.23332719	39	46.43
.52955503	.45539628	.71070489	.25439145	40	47.62
.56795431	.50313447	.73494377	.26336883	41	48.81
.60273373	.54665990	.73691214	.41631765	42	50.00
.63422942	.58620645	.77682365	.46525715	43	51.19
.66274735	.62202982	.79486055	.50514376	44	52.38
.68856532	.65451102	.81120547	.54631342	45	53.57
.71193540	.68335963	.82681303	.58434054	46	54.76
.73308660	.71065665	.83942631	.61750626	47	55.95
.75222670	.73485717	.85157519	.64714159	48	57.14
.76954421	.75679275	.86257757	.67311137	49	58.33
.78521610	.77667356	.87254045	.69815255	50	59.52
.79937936	.79469346	.88156093	.72029459	51	60.71
.81219430	.81101066	.88972715	.73996872	52	61.90
.82378121	.82540916	.89711906	.75745392	53	63.10
.83425652	.83921091	.90360924	.77423173	54	64.29
.84372534	.85213513	.90980351	.78805232	55	65.48
.85226338	.86234788	.91534161	.80229162	56	66.67
.86001593	.87230733	.92029770	.81434363	57	67.86
.86700248	.88132046	.92476392	.82945772	58	69.05
.87331366	.88949315	.92803585	.83512373	59	70.24
.87961352	.89600736	.93258293	.84434459	60	71.43
.88416128	.90290360	.93561471	.85211366	61	72.62
.88840846	.90903331	.93801651	.85940756	62	73.81
.89260445	.91512270	.94152643	.86633164	63	75.00
.89679135	.92040499	.94397375	.87138040	64	76.19
.90020882	.92507433	.94616923	.87734066	65	77.38

.90329239	.92803765	.94818929	.88221239	66	78.57
.90607423	.93231163	.94999025	.88660883	67	79.76
.90858345	.93563922	.95162852	.89058035	68	80.95
.91084641	.93884094	.95310278	.89416734	69	82.14
.91288692	.94135085	.95443412	.89740682	70	83.33
.91472657	.94381617	.95563023	[illegible]	71	84.52
.91636465	.94603759	[illegible]	[illegible]	72	85.71
.91787934	.94804549	.95770113	[illegible]	73	86.90
.91927615	.94986313	.95858528	[illegible]	74	88.10
.92043955	.95145991	.95938315	.90944364	75	89.29
.92153261	.95298146	.96010303	.91119368	76	90.48
.92251710	.95431986	.96075247	.91277974	77	91.67
.92340368	.95552070	.96133027	.91420564	78	92.86
.92420135	.95662060	.96186059	.91549346	79	94.05
.92492055	.95760651	.96234299	.91664962	80	95.24
.92556743	.95849667	.96277252	.91769471	81	96.43
.92614957	.95930026	.96315974	.91863083	82	97.62
.92667343	.96002560	.96350875	.91948660	83	98.81
.92714467	.96068021	.96382328	.92025129	84	100.00
.92756860	.96127091	.96410670	.92094066	85	101.19
.92794988	.96180386	.96436205	.92156216	86	102.38
.92829275	.96228403	.96459207	.92212163	87	103.57
.92860103	.96271828	.96479925	.92262551	88	104.76
.92887817	.96310937	.96498582	.92307586	89	105.95
.92912728	.96346283	.96515382	.92348261	90	107.14
.92935115	.96377998	.96530507	.92385661	91	108.33
.92955232	.96406660	.96544121	.92418767	92	109.52
.92973305	.96432494	.96556375	.92448661	93	110.71
.92989541	.96455776	.96567432	.92475431	94	111.90
.93004123	.96476754	.96577324	.92499373	95	113.10
.93017218	.96495655	.96586251	.92521291	96	114.29
.93028976	.96512081	.96594280	[illegible]	97	115.48
.93039533	.96528017	.96601502	.92558099	98	116.67
.93049038	.96541427	.96607996	[illegible]	99	117.86
.93057513	.96554263	.96613835	[illegible]	100	119.05
.93065145	.96565459	.96619085	[illegible]	101	120.24

J= 22

X	Y	YS	XS	I	TIME IN HRS
.00154604	0.00000000	0.00000000	0.00000000	14	16.67
.00335216	0.00000000	0.00000000	0.00000000	15	17.86
.00558134	0.00000000	.00128659	.00031693	16	19.05
.00821193	.00023616	.00379698	[illegible]	17	20.24
.01143053	.00090424	.00718576	[illegible]	18	21.43
.01512213	.00230477	.01139927	.00229322	19	22.62
.01967232	.00383530	.01642115	.00426933	20	23.81
.02472465	.00627582	.02322545	.00759476	21	25.00
.03187634	.00946127	.03130259	[illegible]	22	26.19
.03784394	.01357733	.04063273	[illegible]	23	27.38
.04662459	.01865601	.05237614	.01329395	24	28.57
.05561017	.02499363	.06531207	.01637667	25	29.76
.06763511	.03257393	.08192202	.02079236	26	30.95

.07982721	.64104581	.09999376	.62537313	27	[illegible]
.09570309	.65277393	.12269730	.63144137	28	33.33
.11227763	.66591563	.14761658	.63746624	29	[illegible]
.13316719	.68126973	.17616526	.64521561	30	[illegible]
.15552035	.69947994	.20223502	[illegible]	31	[illegible]
.18254472	.12667085	.25277323	[illegible]	32	[illegible]
.21291165	.14549027	.29912170	.07591341	33	[illegible]
.24732197	.17436972	.35220995	.08939339	34	[illegible]
.28676928	.20779239	.41510424	.10535742	35	[illegible]
.33174934	.24675461	.48365943	.12275620	36	[illegible]
.38873303	.29127768	.56903156	.14442425	37	[illegible]
.44037390	.34347777	.65555371	.16635371	38	[illegible]
.48716415	.40212936	.64396348	.23932719	39	[illegible]
.52955503	.45539628	.71070489	.30439145	40	[illegible]
.56795451	.50313447	.73494377	.36336383	41	[illegible]
.60273379	.54669994	.75691214	.41632785	42	[illegible]
.63422942	.56620645	.77682305	.46525765	43	[illegible]
.66274735	.62202982	.79488095	.50914376	44	[illegible]
.68856532	.65451102	.81120547	.54631642	45	[illegible]
.71193540	.68395963	.82601303	.58434054	46	[illegible]
.73308600	.71065665	.83942631	.61730026	47	[illegible]
.75222070	.73485717	.85157519	.64714159	48	[illegible]
.76954413	.75679275	.86257757	.67391127	49	[illegible]
.78521010	.77667358	.87254045	.69815155	50	[illegible]
.79537930	.79469040	.88156093	.72009559	51	[illegible]
.81219433	.81101066	.88972715	.73996072	52	[illegible]
.82376121	.82540916	.89711966	.75785142	53	[illegible]
.83425052	.83921391	.90380924	.77423073	54	[illegible]
.84372534	.85135134	.90980351	.78839632	55	[illegible]
.85220301	.86234768	.91534101	.80229162	56	[illegible]
.86601593	.87230733	.92029770	.82143363	57	[illegible]
.86700249	.88132040	.92478392	.82505772	58	[illegible]
.87331300	.88549315	.92883365	.83312373	59	[illegible]
.87901352	.89688708	.93250290	.84410559	60	[illegible]
.88416120	.90358360	.93581471	.85211166	61	[illegible]
.88860040	.90563931	.93881651	.85941755	62	[illegible]
.89300449	.91512278	.94152643	.86632164	63	[illegible]
.89679135	.92018499	.94397575	.87138040	64	[illegible]
.90026032	.92457493	.94616923	.87734606	65	[illegible]
.90329239	.92863765	.94816929	.88221639	66	[illegible]
.90687423	.93231163	.94998025	.88606301	67	[illegible]
.90850343	.93563522	.95162852	.89050035	68	[illegible]
.91084041	.93864094	.95310228	.89416734	69	[illegible]
.91288632	.94135685	.95443412	.89743062	70	[illegible]
.91472057	.94331017	.95563025	[illegible]	71	[illegible]
.91636403	.94603759	.95672000	[illegible]	72	[illegible]
.91787933	.94804549	.95770113	[illegible]	73	[illegible]
.91922615	.94986313	.95856520	[illegible]	74	[illegible]
.92043933	.95149991	.95938319	[illegible]	75	[illegible]
.92153201	.95298146	.96018303	.91115363	76	[illegible]
.92251710	.95431986	.96075247	.91277374	77	[illegible]
.92346303	.95552070	.96133027	.91464964	78	[illegible]
.92426135	.95662060	.96180053	.91549746	79	[illegible]
.92492033	.95760651	.96228295	.91630962	80	[illegible]

.92556743	.95849667	.96277252	.95709471	81	96.43
.92614937	.95930026	.96315374	.91303583	82	97.62
.92667341	.96002560	.96350475	.91394806	83	98.81
.92714467	.96066021	.96362328	.92025125	84	100.00
.92756806	.96127091	.96410070	.91934468	85	101.19
.92794966	.96188386	.96436205	.92150216	86	102.38

J= 56

X	Y	YS	XS	I	TIME IN HRS
.00148772	0.00000000	0.00000000	0.00000000	80	95.24
.00294507	0.00000000	0.00000000	0.00000000	81	96.43
.00496454	0.00000000	.00065142	.00016333	82	97.62
.00780676	.00012243	.00262581	.00066645	83	98.81
.00984648	.00059290	.00534984	.00135763	84	100.00
.01260211	.00148691	.00868378	.00220460	85	101.19
.01684748	.00283946	.01281310	.00325130	86	102.38
.02614204	.00471331	.01792044	.00454634	87	103.57
.02444201	.00719541	.02368359	.00631166	88	104.76
.03613531	.01029414	.03116956	.00791166	89	105.95
.03597230	.01421740	.03942195	.01030357	90	107.14
.04319566	.01895425	.04954285	.01257433	91	108.33
.05110225	.02470297	.06105655	.01549655	92	109.52
.06883435	.03153513	.07432496	.01886420	93	110.71
.07676204	.03957690	.08931434	.02267079	94	111.90
.08815401	.04907653	.10712229	.02721846	95	113.10
.09662431	.05998707	.12855447	.03262264	96	114.29
.11655730	.07267339	.15145804	.03844413	97	115.48
.12428372	.08764231	.17872508	.04536172	98	116.67
.14786511	.10476089	.20946705	.05316423	99	117.86
.16673234	.12443635	.24333471	.06176169	100	119.05
.19553030	.14678407	.28457466	.07222767	101	120.24
.22690743	.17287995	.32735629	.08308535	102	121.43
.25575190	.20174926	.38034942	.09600767	103	122.62
.29034202	.23542753	.43787871	.11113673	104	123.81
.33670925	.27347550	.50338613	.12776298	105	125.00
.37845217	.31668410	.57947879	.14707584	106	126.19
.42155277	.36637282	.65619795	.16654770	107	127.38
.46646359	.42658792	.68070855	.23142767	108	128.57
.49559295	.46548221	.70417760	.26025558	109	129.76
.52730902	.51359604	.72535945	.34604732	110	130.95
.55594565	.55338324	.74447755	.38056336	111	132.14
.58186133	.58920271	.76173348	.42854462	112	133.33
.60514714	.62178794	.77730908	.46644546	113	134.52
.62622742	.65695167	.79136030	.50555499	114	135.71
.64526233	.67734001	.80425335	.53303127	115	136.90
.66245139	.70115569	.81551343	.55944569	116	138.10
.67797349	.72204607	.82589725	.58496252	117	139.29
.69159803	.74204484	.83519326	.60724652	118	140.48
.70464902	.75955083	.84362162	.62770963	119	141.67
.71688183	.77535080	.85123073	.64636349	120	142.86
.72648658	.78961141	.85816643	.66311967	121	144.05
.73573130	.80240300	.86432273	.67816063	122	145.24
.74415325	.81410118	.86993261	.69173305	123	146.43

.75175983	.82458831	.87455473	.70403584	124	147.62
.75863020	.83405475	.87952400	.71524355	125	148.81
.76483575	.84260008	.88364617	.72567316	126	150.00
.77044094	.85031414	.88736834	.73422954	127	151.19
.77550395	.85727798	.89072942	.74240734	128	152.38
.78007731	.86356472	.89376449	.74979155	129	153.57
.78420840	.86924036	.89650525	.75640647	130	154.76
.78794026	.87436443	.89898630	.76246248	131	155.95
.79131134	.87899365	.90121544	.76792278	132	157.14
.79435663	.88316750	.90323397	.77263266	133	158.33
.79955922	.89034384	.90672333	.78137380	135	160.71
.80183011	.89341834	.90819321	.78495161	136	161.90
.80386640	.89619452	.90953313	.78815047	137	163.10
.80569890	.89870133	.91074634	.79120953	138	164.29
.80735442	.90096497	.91184153	.79377562	139	165.48
.80885010	.90300907	.91283100	.79616249	140	166.67
.81020139	.90485497	.91372472	.79835659	141	167.86
.81142225	.90652192	.91453197	.80032210	142	169.05
.81252527	.90802730	.91526113	.80209521	143	170.24
.81352134	.90938686	.91591976	.80369772	144	171.43
.81442224	.91061459	.91651470	.80514325	145	172.62
.81523575	.91172343	.91705211	.80645281	146	173.81
.81597079	.91272488	.91753755	.80763395	147	175.00
.81663493	.91362936	.91797637	.80870091	148	176.19
.81723494	.91444627	.91837220	.80966473	149	177.38
.81777759	.91518409	.91873005	.81053546	150	178.57
.81826694	.91585351	.91905331	.81132193	151	179.76
.81870955	.91645243	.91934534	.81203245	152	180.95
.81910940	.91699612	.91960915	.81267433	153	182.14
.81947079	.91748726	.91984747	.81325415	154	183.33
.81979727	.91793076	.92006277	.81377505	155	184.52
.82009220	.91833146	.92025727	[illegible]	156	185.71
.82035073	.91869339	.92043299	.81467664	157	186.90
.82059902	.91902032	.92059173	.81506364	158	188.10
.82081722	.91931565	.92073514	.81541347	159	189.29
.82101362	.91958242	.92086470	.81572925	160	190.48
.82119146	.91982341	.92098175	.81601402	161	191.67
.82135137	.92004111	.92108750	.81627129	162	192.86
.82149693	.92023776	.92118363	.81650373	163	194.05
.82162602	.92041541	.92126934	.81671373	164	195.24
.82174041	.92057590	.92134732	.81690345	165	196.43
.82185337	.92072088	.92141776	.81707465	166	197.62
.82195031	.92085185	.92148141	.81722970	167	198.81
.82203733	.92097016	.92153491	.81736966	168	200.00
.82211022	.92107705	.92159065	.81749559	169	201.19
.82218749	.92117361	.92163778	.81760917	170	202.38
.82225136	.92126085	.92168018	.81771333	171	203.57
.82231000	.92133966	.92171844	.81780853	172	204.76
.82236242	.92141085	.92175309	.81789772	173	205.95
.82241021	.92147517	.92178435	.81796879	174	207.14
.82245331	.92153324	.92181259	.81803556	175	208.33
.82249176	.92158577	.92183811	.81809756	176	209.52
.82252677	.92163319	.92186116	.81815367	177	210.71
.82255640	.92167604	.92188198	.81820433	178	211.90

J= 75

X	Y	YS	XS	I	TIME IN HRS
.00113736	0.00000000	0.00000000	0.00000000	140	166.67
.00246027	0.00000000	0.00000000	0.00000000	141	167.86
.00409633	0.00000000	0.00000000	0.00000000	142	169.05
.00599403	0.00000000	.00162560	.00041259	143	170.24
.00803855	.00030551	.00368992	.00093653	144	171.43
.01070936	.00094156	.00657021	.00166757	145	172.62
.01352477	.00199939	.00990497	.00231395	146	173.81
.01686215	.00348514	.01403770	.00356267	147	175.00
.02069573	.00546635	.01859206	[illegible]	148	176.19
.02474553	.00801119	.02454592	[illegible]	149	177.38
.02989349	.01111943	.03159159	.00601017	150	178.57
.03526972	.01496639	.03937223	.00939455	151	179.76
.04148023	.01955355	.04847236	.01226455	152	180.95
.04869826	.02498839	.05912745	.01540657	153	182.14
.05684347	.03140437	.07065536	.01793283	154	183.33
.06552604	.03878106	.08443693	.02153222	155	184.52
.07531476	.04743664	.10028430	.02545463	156	185.71
.08621315	.05736800	.11770334	.02987455	157	186.90
.09939703	.06870722	.13825771	.03549479	158	188.10
.11239525	.08177829	.15938495	.04062542	159	189.29
.12902637	.09647018	.18621336	.04726227	160	190.48
.14647584	.11334137	.21485038	.05433256	161	191.67
.16466965	.13241968	.24582196	.06239136	162	192.86
.18858545	.15373227	.28366439	.07139564	163	194.05
.21113743	.17815126	.32277233	.08192343	164	195.24
.23912532	.20533197	.36881630	.09530521	165	196.43
.27614975	.23605604	.42030911	.10667744	166	197.62
.29883840	.27668441	.47273065	.11930643	167	198.81
.34158921	.30605627	.54166493	.13722562	168	200.00
.38133243	.35225992	.60955626	.15476971	169	201.19
.41670358	.40461530	.66219868	.16637148	170	202.38
.44849637	.44977637	.68472937	.24111468	171	203.57
.47708162	.49393261	.70437435	.25344043	172	204.76
.50278139	.53359506	.72316815	.33471464	173	205.95
.52588770	.56922239	.73951362	.37440570	174	207.14
.54666314	.60122633	.75429427	.41022937	175	208.33
.56534335	.62597647	.76740650	.44215153	176	209.52
.58214326	.65580459	.77927155	.47122433	177	210.71
.59724427	.67590854	.78993525	.49716606	178	211.90
.61082647	.69965572	.79951959	.52046061	179	213.10
.62304303	.71858626	.80813412	.54144355	180	214.29
.63462492	.73541552	.81587727	.56128534	181	215.48
.64390353	.75653722	.82243744	.57722364	182	216.67
.65278648	.76412507	.82509402	.59244267	183	217.86
.66677856	.77633511	.83471035	.61612736	184	219.05
.66796646	.78738745	.83977449	.61842342	185	220.24
.67443078	.79716792	.84432033	.62549412	186	221.43
.68824563	.80682953	.84848666	.63943627	187	222.62
.68547635	.81399374	.85208366	.64437193	188	223.81

.6901817[illegible]	.62115170	.85536437	[illegible]	189	225.00
.6944146[illegible]	.62758527	.85835470	.66503674	190	226.19
.69822203	.63336737	.86132554	.67023014	191	227.38
.70164856	.63856584	.86342716	.67537655	192	228.57
.70473063	.64323619	.86556064	.68023119	193	229.76
.70750431	.64743632	.86752836	.68535354	194	230.95
.70999926	.65121408	.86927552	.69020018	195	232.14
.71224432	.65460449	.87084627	.69402906	196	233.33
.71426453	.65766016	.87225896	.69746765	197	234.52
.71608241	.66040381	.87352954	.70[illegible]5848	198	235.71
.71771826	.66287361	.87467234	.70333963	199	236.90
.71919042	.66508859	.87570026	.70584064	200	238.10
.72051527	.66708291	.87662487	.70808971	201	239.29
.72170753	.66887619	.87743659	.71011336	202	240.48
.72278075	.67048876	.87820478	.71193377	203	241.67
.72374654	.67193886	.87887785	.71357141	204	242.86
.72461586	.67324297	.87948338	.71504466	205	244.05
.72539833	.67441576	.88002812	.71637013	206	245.24
.72610267	.67547353	.88051624	.71756263	207	246.43
.72673666	.67641918	.88095921	.71863356	208	247.62
.72730742	.67727242	.88135598	.71960354	209	248.81
.72782121	.67803987	.88171300	.72045556	210	250.00
.72828376	.67873618	.88203424	.72125120	211	251.19
.72870016	.67935114	.88232332	.72195455	212	252.38
.72907510	.67990972	.88258346	.72260749	213	253.57
.72941265	.68041221	.88281756	.72315726	214	254.76
.72971656	.68086426	.88302824	.72366568	215	255.95
.72999024	.68127395	.88321785	.72413162	216	257.14
.73023665	.68163685	.88338859	.72454023	217	258.33
.73045854	.68196605	.88354210	.72491394	218	259.52
.73065835	.68226224	.88368034	.72525031	219	260.71
.73083829	.68252876	.88380478	.72555038	220	261.90
.73100033	.68276657	.88391679	.72583161	221	263.10
.73114627	.68298436	.88401762	.72607694	222	264.29
.73127770	.68317455	.88410839	.72629779	223	265.48
.73139636	.68335330	.88419010	.72649663	224	266.67
.73150269	.68351057	.88426366	.72667558	225	267.86
.73159873	.68365210	.88432989	.72683672	226	269.05
.73168523	.68377946	.88438952	.72698184	227	270.24
.73176314	.68389413	.88444320	.72711242	228	271.43
.73183333	.68399732	.88449154	.72723063	229	272.62

J=100

X	Y	YS	Xs	I	TIME IN HRS
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.80183621	0.00000000	0.00000000	0.00000000	206	245.24
.80309784	0.00000000	0.00000000	0.00000000	207	246.43
.80471323	0.00000000	.00046036	.00012192	208	247.62
.80651190	.00009326	.00215049	.00034784	209	248.81
.80843927	.00047697	.00416232	.00130056	210	250.00
.81096710	.00117496	.00692700	.00175314	211	251.19
.81251032	.00225559	.01029041	.00256062	212	252.38
.81648742	.00372837	.01381913	.00330739	213	253.57

.01589039	.60562479	.01840606	.60407174	214	254.76
.02353982	.60812697	.02351972	.60573647	215	255.95
.02774903	.61093862	.02953438	.60749863	216	257.14
.03258044	.61443344	.03655008	.60927019	217	258.33
.03755017	.61859116	.04421394	.61122181	218	259.52
.04355817	.62340656	.05330074	.61352113	219	260.71
.05011033	.62902627	.06351717	.61612111	220	261.90
.05676076	.63550837	.07447651	.61893267	221	263.10
.06525102	.64233156	.09772054	.62226465	222	264.29
.07441453	.65126849	.10208042	.62597804	223	265.48
.08277443	.66081759	.11729583	.62977147	224	266.67
.09467445	.67143220	.13614153	.63455369	225	267.86
.10622737	.68359344	.15587306	.63956169	226	269.05
.11856764	.69717742	.17743845	.64502753	227	270.24
.13416173	.11225976	.20300052	.65102561	228	271.43
.14920025	.12931152	.22964763	.65820620	229	272.62
.16626397	.14816834	.25947552	.66585073	230	273.81
.18676600	.16908762	.29397315	.67401466	231	275.00
.20612926	.19255881	.32943804	.68301371	232	276.19
.22987695	.21828341	.37038007	.69400369	233	277.38
.25635342	.24646793	.41636639	.10507675	234	278.57
.28100743	.27872288	.46300097	.11751294	235	279.76
.31353355	.31335546	.51806208	.13109188	236	280.95
.34604015	.35197765	.57957644	.14716062	237	282.14
.37692443	.39475178	.64025169	.16250043	238	283.33
.40655093	.44669317	.66967042	.21457377	239	284.52
.43127020	.48368816	.68844080	.25324036	240	285.71
.45338916	.52233252	.70523539	.29138268	241	286.90
.47318150	.55070665	.72104344	.34701440	242	288.10
.49089352	.58744231	.73307051	.38022634	243	289.29
.50674349	.61492543	.74569029	.39591410	244	290.48
.52692784	.63953092	.75643478	.41505020	245	291.67
.53362209	.66147705	.76603574	.43904074	246	292.86
.54458312	.68112932	.77464324	.45995322	247	294.05
.55515120	.69873400	.78233432	.47667230	248	295.24
.56425213	.71442119	.78921475	.49541301	249	296.43
.57239795	.72847763	.79537016	.51034971	250	297.62
.57968921	.74104918	.80087714	.52376046	251	298.81
.58621578	.75229304	.80580414	.53577653	252	300.00
.59285634	.76234973	.81021238	.54653215	253	301.19
.59728791	.77134487	.81415601	.55609061	254	302.38
.60196975	.77939076	.81768576	.56460562	255	303.57
.60616113	.78658779	.82084367	.57236963	256	304.76
.60991354	.79302372	.82366943	.57924436	257	305.95
.61327357	.79878479	.82619038	.58539678	258	307.14
.61628036	.80393675	.82844031	.59080247	259	308.33
.61897411	.80854574	.83048596	.59542958	260	309.52
.62138553	.81266910	.83229825	.60023904	261	310.71
.62354476	.81635414	.83392319	.60416339	262	311.90
.62547825	.81965860	.83537184	.60771736	263	313.10
.62720965	.82261176	.83667110	.61087058	264	314.29
.62876015	.82525462	.83783401	.61376065	265	315.48
.63014068	.82761826	.83887492	.61624067	266	316.67
.63139222	.82973380	.83980465	.61850767	267	317.86
.63254593	.83162680	.84064309	.62053696	268	319.05

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.63350342      .83332088      .84138733      .62235354      269      320.24
.63439633      .83463686      .84205568      .62337375      270      321.43
.63519749      .83619354      .84265403      .62543559      271      322.62
.63591334      .83740773      .84318971      .62673456      272      323.81
.63655531      .83849435      .84366931      .62790566      273      325.00
.63713137      .83946692      .84409873      .62895462      274      326.19
.63764631      .84033740      .84448317      .62984655      275      327.38
.63816793      .84111654      .84482741      .63072362      276      328.57
.63852141      .84181395      .84513565      .63147360      277      329.76
.63889193      .84243622      .84541166      .63224517      278      330.95
.63922333      .84299764      .84565883      .63274655      279      332.14
.63952123      .84349726      .84588017      .63326508      280      333.33
.63978771      .84394512      .84607839      .63370737      281      334.52
.64002649      .84434603      .84625591      .63415329      282      335.71

.64269127      .84778264      .84778306      [illegible]    364      433.33
.64269132      .84778288      .84778311      [illegible]    365      434.52
.64269133      .84778293      .84778312      .63791514      366      435.71
.64269135      .84778296      .84778315      [illegible]    367      436.90
.64269136      .84778300      .84778316      .63791523      368      438.10
.64269139      .84778303      .84778317      .63791525      369      439.29
.64269143      .84778305      .84778319      .63791530      370      440.48
.64269143      .84778308      .84778319      .63791531      371      441.67
.64269145      .84778310      .84778323      .63791533      372      442.86
```

PREDICTING EFFLUENT PROFILES FROM GAC COLUMNS WITH BACTERIAL ACTIVITY

```
BACTERIAL FILM THICKNESS IN CMS =  .0[illegible]
FILM REACTION RATE IN GMS/CM2-SEC =  .[illegible]E-05
SURFACE DIFFUSIVITY IN CM2/SEC =  .592[illegible]-08
SATURATION LOADING IN GMS TOC/GMS CARBON =  .0295
LIQUID PHASE DIFFUSIVITY IN CM2/SEC =  .[illegible]E-05
INFLUENT CONCENTRATION IN GMS/CM3 TOC =  .[illegible]E-04
POROSITY OF BED =  .5000
PARTICLE DIAMETER IN CMS =  .09600
FLOW RATE IN CM3/SEC =  1.4173
LENGTH OF BED IN CMS =  60.000
SUPERFICIAL VELOCITY IN CM/SEC =  .0760
BULK BED DENSITY IN GMS/CM3 =  .6753
LENGTH STEP SIZE =  .0100
INITIAL TIME STEP SIZE =  10.000
TEMPERATURE IN CENTIGRADES =  5.0
A=  [illegible]
B=  [illegible]
C=  .300
D=  .411
XS2=  .108
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K0=  .0[illegible]61
K1=  [illegible]
K2=  .0[illegible]
K3=  .0167337
K4=  [illegible]
K5=  [illegible]
K6=  [illegible]
K7=  .1375305
K8=  .2173790
K9=  [illegible]52
K10=  [illegible]
K11=  [illegible]4702
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TIME PAST IN HRS	TQC APPLIED IN GMS	TQC REMOVED IN GMS
1.19	.121	.121
2.38	.243	.243
3.57	.364	.364
4.76	.486	.486
5.95	.607	.607
7.14	.729	.729
8.33	.850	.850
9.52	.972	.972
10.71	1.093	1.093
11.90	1.215	1.215
13.10	1.336	1.336
14.29	1.457	1.457
15.48	1.579	1.579
16.67	1.700	1.700
17.86	1.822	1.822
19.05	1.943	1.943
20.24	2.065	2.065
21.43	2.186	2.186
22.62	2.308	2.308
23.81	2.429	2.429
25.00	2.551	2.551
26.19	2.672	2.672
27.38	2.794	2.794
28.57	2.915	2.915
29.76	3.036	3.036
30.95	3.158	3.158
32.14	3.279	3.279
33.33	3.401	3.401
34.52	3.522	3.522
35.71	3.644	3.644
36.90	3.765	3.765
38.10	3.887	3.887
39.29	4.008	4.008
40.48	4.130	4.130
41.67	4.251	4.251
42.86	4.372	4.372
44.05	4.494	4.494
45.24	4.615	4.615
46.43	4.737	4.737
47.62	4.858	4.858
48.81	4.980	4.980
50.00	5.101	5.101
51.19	5.223	5.223
52.38	5.344	5.344
53.57	5.466	5.466
54.76	5.587	5.587
55.95	5.708	5.708
57.14	5.830	5.830
58.33	5.951	5.951
59.52	6.073	6.073
60.71	6.194	6.194
61.90	6.316	6.316
63.10	6.437	6.437
64.29	6.559	6.559
65.48	6.680	6.680
66.67	6.802	6.802
67.86	6.923	6.923
69.05	7.045	7.045
105.95	10.810	10.810
107.14	10.931	10.931
108.33	11.053	11.053
109.52	11.174	11.174
110.71	11.296	11.296
111.90	11.417	11.417
113.10	11.538	11.538
114.29	11.660	11.660
115.48	11.781	11.781
116.67	11.903	11.903
117.86	12.024	12.024
119.05	12.146	12.146
120.24	12.267	12.267
121.43	12.389	12.389
122.62	12.510	12.510
123.81	12.632	12.632
125.00	12.753	12.753
126.19	12.874	12.874
127.38		

128.57	13.117	13.117
129.76	13.239	13.239
130.95	13.360	13.360
132.14	13.482	13.482
133.33	13.603	13.603
134.52	13.725	13.725
135.71	13.846	13.846
136.90	13.968	13.968
138.10	14.089	14.089
139.29	14.210	14.210
140.48	14.332	14.332
141.67	14.453	14.453
178.57	18.219	18.219
179.76	18.340	18.340
180.95	18.461	18.461
182.14	18.583	18.583
183.33	18.704	18.704
184.52	18.826	18.826
185.71	18.947	18.947
186.90	19.069	19.069
188.10	19.190	19.190
189.29	19.312	19.312
190.48	19.433	19.433
191.67	19.555	19.555
192.86	19.676	19.676
194.05	19.798	19.798
195.24	19.919	19.919
196.43	20.040	20.040
197.62	20.162	20.162
198.81	20.283	20.283
200.00	20.405	20.405
201.19	20.526	20.526
202.38	20.648	20.648
203.57	20.769	20.769
204.76	20.891	20.891
205.95	21.012	21.012
207.14	21.134	21.134
208.33	21.255	21.255
209.52	21.376	21.376
210.71	21.498	21.498
211.90	21.619	21.619
213.10	21.741	21.741
214.29	21.862	21.862
251.19	25.627	[illegible]
252.38	25.749	[illegible]
253.57	25.870	[illegible]
254.76	25.992	[illegible]
255.95	26.113	[illegible]
257.14	26.235	[illegible]
258.33	26.356	26.345
259.52	26.478	[illegible]
260.71	26.599	[illegible]
261.90	26.721	[illegible]
263.10	26.842	[illegible]
264.29	26.963	[illegible]
265.48	27.085	[illegible]
266.67	27.206	[illegible]
267.86	27.328	[illegible]
269.05	27.449	[illegible]
270.24	27.571	[illegible]
271.43	27.692	[illegible]
272.62	27.814	[illegible]
273.81	27.935	[illegible]
275.00	28.057	[illegible]
276.19	28.178	[illegible]
277.38	28.300	28.132
278.57	28.421	[illegible]
279.76	28.542	[illegible]
280.95	28.664	[illegible]
282.14	28.785	[illegible]
283.33	28.907	[illegible]
284.52	29.028	[illegible]
285.71	29.150	[illegible]
286.90	29.271	[illegible]

759.52	77.490	46.532
760.71	77.611	46.575
761.90	77.733	46.620
763.10	77.854	46.664
764.29	77.975	46.708
765.48	78.097	46.752
766.67	78.218	46.796
767.86	78.340	46.840
769.05	78.461	46.883
770.24	78.583	46.927
771.43	78.704	46.971
772.62	78.826	47.015
773.81	78.947	47.059
775.00	79.069	47.103
776.19	79.190	47.147
777.38	79.312	47.191
778.57	79.433	47.235
779.76	79.554	47.279
780.95	79.676	47.323
782.14	79.797	47.366
783.33	79.919	47.410
784.52	80.040	47.454
785.71	80.162	47.498
786.90	80.283	47.542
788.10	80.405	47.586
789.29	80.526	47.630
790.48	80.648	47.674
791.67	80.769	47.718
792.86	80.890	47.762
794.05	81.012	47.806
795.24	81.133	47.849

1050.00	107.125	57.246
1051.19	107.247	57.290
1052.38	107.368	57.334
1053.57	107.490	57.376
1054.76	107.611	57.422
1055.95	107.732	57.466
1057.14	107.854	57.510
1058.33	107.975	57.553
1059.52	108.097	57.597
1060.71	108.218	57.641
1061.90	108.340	57.685
1063.10	108.461	57.729
1064.29	108.583	57.773
1065.48	108.704	57.817
1066.67	108.826	57.861
1067.86	108.947	57.905
1069.05	109.069	57.949
1070.24	109.190	57.993
1071.43	109.311	58.036
1072.62	109.433	58.080
1073.81	109.554	58.124
1075.00	109.676	58.168
1076.19	109.797	58.212
1077.38	109.919	58.256
1078.57	110.040	58.300
1079.76	110.162	58.344
1080.95	110.283	58.388
1082.14	110.405	58.432
1083.33	110.526	58.476
1084.52	110.647	58.519
1085.71	110.769	58.563

1413.10	144.170	70.589
1414.29	144.291	70.664
1415.48	144.413	70.725
1416.67	144.534	70.770
1417.86	144.655	70.814
1419.05	144.777	70.858
1420.24	144.898	70.902
1421.43	145.020	70.946
1422.62	145.141	70.990
1423.81	145.263	71.034
1425.00	145.384	71.078
1426.19	145.506	71.122
1427.38	145.627	71.165
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1444.05	147.328	71.[illegible]
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1448.81	147.813	71.956
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1451.19	148.056	72.[illegible]
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1453.57	148.299	72.161
1454.76	148.421	72.185
1455.95	148.542	72.219
1457.14	148.664	72.26[illegible]
1458.33	148.785	72.3[illegible]7
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1463.10	149.271	72.483
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1465.48	149.514	72.571
1466.67	149.635	72.[illegible]
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1471.43	150.121	72.7[illegible]
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1477.38	150.728	[illegible]
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1482.14	151.214	72.[illegible]
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1484.52	151.457	73.2[illegible]3
1485.71	151.579	73.[illegible]7
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1488.10	151.821	73.[illegible]5