THE ADSORPTION OF BIORESIDUAL ORGANICS IN A FLUIDIZED BED BIOLOGICAL REACTOR

THE ADSORPTION OF BIORESIDUAL ORGANICS IN A FLUIDIZED BED BIOLOGICAL REACTOR

by

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ABSTRACT:

The adsorption of residual organic molecules generated during the metabolic activity of bacteria was investigated.

At first a number of potential adsorbants and ion exchange resins were selected with different average pore diameters and specific surface areas.

The adsorption (removal) capacity of these materials was evaluated through the determination of their adsorption isotherms on a residual organics solution, obtained from an activated sludge reactor, that operated with Phenol as a substrate.

On the basis of these isotherms Filtrasorb 400, an activated Carbon with 35A^{o} average pore diameter and 1200 m^2/g specific surface area, was selected as the best adsorbant. Subsequently a fluidized bed biological reactor was used to study the direct adsorption of the residual organics produced by the biofilms on the Filtrasorb 400 particles supporting the growth. A phenol solution was fed to the reactor and different

Oxygen to Phenol ratios were applied.

The adsorption of the residual organic molecules generated by the biological growth in a fluidized bed biological reactor proved feasible and independent of the Oxygen to Phenol ratio applied. The Phenol removal efficiency of the reactor was determined by the Oxygen supplied. The removal reached 100% whenever residual Oxygen was present in the effluent of the reactor (no Oxygen limitation).

Specific reaction rates higher than the ones reported in the literture were observed.

The removal of the residual organics resulted in a stable effluent pH.

The monitoring of the height of the expanded bed that developed biological growth is a parameter that can be used to monitor the total volume of biological films in the reactor. A volume yield factor can also be calculated.

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CHAPTER 1

1. INTRODUCTION

The treatment of the waste products of our society has been established as a vital necessity.

It is a matter of survival for humanity to realize that the quality of our environment cannot be altered without affecting our well-being and ultimately our existence. There have already been cases where the ecological balance has been upset, or cases which have produced fatal consequences (e.g. Minimata, Japan).

A few decades ago, conventional biological treatment of aqueous wastes was considered satisfactory. The environmental research of the last decade, however, has clearly shown that bio-treatment alone, is often insufficient. As a result, physical-chemical operations have been integrated in the biological treatment scheme in order to improve its efficiency. Addition of alum and polyelectrolytes as coagulating and flocculating agents is becoming quite common now and there are many recent tertiary treatment installations using activated carbon adsorption. There are also pure Physical-Chemical Treatment installations that utilize operations like coagulation sedimentation and adsorption "without" a biological step in between. They show a lot of advantages like high removal

efficiencies, and resistance to shock loadings, but they also require more sophisticated equipment and higher operating cost.

Our increasing awareness of the environmental problems, their complexity and interrelationships lead, and will probably continue to lead, to stricter standards for effluent quality. In order to meet the new requirements of treatment efficiency, and comply with the strict present and future standards we have to restudy our processes. We can either modify and optimize them, or if necessary, develop new and more efficient ones.

The present work was organized and carried out with this general framework in mind. Not all the organic molecules can be degraded biologically. In a waste stream there are usually constituents that are partially or completely non-degradable by the microbial population of a specific treatment plant. There are also organic compounds generated as by-products of the bacterial metabolism. All these compounds escape in the effluent of the bio-treatment plant as residual organics and impair its quality. Therefore, biological treatment alone is incomplete. On the other hand adsorption can handle organic compounds regardless of their biodegradability but adsorption columns exhaust very fast when a waste rich in organics is applied. Adsorption itself can remove "dissolved" pollutants by adsorbing them on the active sites of the adsorbing particles.

Adsorption and biological oxidation if used simultaneously can give a very high treatment efficiency. The biodegradable portion of the organic load will be removed by the biological mass and the residual organics will be adsorbed by the adsorbant.

Such a treatment scheme is already being used whenever adsorption columns polish secondary effluents. The presence of biodegradable organic molecules and nutrients in secondary effluents have been observed to stimulate biological growth on the particles of the adsorbant inside the adsorption columns. By encouraging this biological activity through the supply of Oxygen and micronutrients a biological population in the form of biofilms develops around the adsorbant particles. Thus the two steps of biological and adsorption treatment are expected to occur simultaneously, in a one-step process. For such a process it is very important to study the adsorption of the residual organics so that the best adsorbants can be selected for their removal. It is also important to monitor the biological growth since it is responsible for the removal of a big part of the T.O.C. applied, and its control is imperative for the proper functioning of such a process.

The objective of the present work is to select the best adsorbant for the removal of the residual organic molecules generated during the biological oxidation of a

waste, and second, the evaluation of the residual T.O.C. removal efficiency of this process through pilot plant runs.

CHAPTER 2

2.1.1 Adsorption Theory

Adsorption can be described as the concentration of a particular component of a bulk solution on a surface that contacts the solution, as a separate phase. The material that forms the surface area is named the adsorbant, and the particular component that adsorbs is called the adsorbate.

Adsorption is a molecular migration phenomenon. Due to the attraction forces that exist between the adsorbant and the adsorbate, molecules of the adsorbate migrate to the interface and they slowly form a film on the adsorbant's surface. This film can be unimolecular or multimolecular depending on the specific conditions.

Adsorption is therefore a function of the surface area of the adsorbant. Porous solids usually make the best adsorbants. The surface area of porous solids can be separated into two different categories:

i) the external surface area that can be viewed as plane;

ii) the curved surface area that consists of the surface of the walls of the pores and the interstices. Almost 99 per cent of the total "true" surface area belongs to the internal surface area (for most adsorbants).

It is obvious therefore that the porosity of an adsorbant and the parameters related to this property are of major importance. Mathematically adsorption can be described by the following Gibbs adsorption equation:

$$\Delta \sigma_{ab} = \left(-\sum_{i=1}^{n} \Gamma_i \Delta \mu_i\right) \qquad (1)$$

where σ_{ab} = the interfacial tension between the adsorbant and the solution

Γ_i = the surface concentration of the component i

μ_i = the chemical potential of i

For a binary solution at equilibrium the Gibbs-Duhem equations give:

$$\sum_{i=1}^{i=2} N_i \, d\mu_i = 0 \qquad \text{or} \qquad (2)$$

$$N_1 d\mu_1 = -N_2 d\mu_2 \qquad \text{or} \qquad (2a)$$

$$d\mu_1 = -\frac{N_2}{N_1} d\mu_2 \qquad (2b)$$

where N_i = the mole fraction of the component i in the solution.

Equation 2 simply states that the net change of the free enthalpy, at equilibrium, is zero

Combining equation 1 with equation 2 we have:

$$-\Delta_{\sigma ab} = \left[\Gamma_2 - (N_2/N_1)\,\Gamma_1 \right] d\mu_2 \qquad (3)$$

Since $(N_2/N_1)\,\Gamma_1$ is the concentration of component 2 that would exist on the surface of the bulk solution, if no adsorption had taken place, the term :

$$\left[\Gamma_2 - (N_2/N_1)\,\Gamma_1 \right] = \Gamma_2^e \qquad (4)$$

is the surface enrichment (Γ_2^e) for component 2.

Given that T is constant and

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad (5)$$

where μ_i° = standard chemical potential of component i

a_i activity of component i in the bulk solution

Then,

$$d\mu_i = d(RT \ln a_i) \qquad (5a)$$

and equation (3) can be written:

$$\Gamma_2^e = -\frac{\Delta_{6ab}}{d\mu_2}$$

or

$$\Gamma_2^e = -\frac{\Delta_{6ab}}{d(RT \ln a_i)}$$

or

$$\Gamma_2^e = -\frac{a_2}{RT}\left(\frac{\Delta_{6ab}}{da_2}\right)$$

or, approximately, assuming that the activity coefficient: $f = 1$

$$\Gamma_2^e = -\frac{C_2}{RT}\left(\frac{d\sigma_{ab}}{dC_2}\right) \qquad (6)$$

where C_2 = concentration of component 2 in the bulk solution.

This is the Gibbs adsorption equation that reveals the thermodynamical nature of the adsorption phenomena. Indeed increase of the Γ_2^e term necessitates a decrease of the value of the term $\left(\frac{d\sigma ab}{dC_2}\right)$. This behaviour means

that the adsorption phenomena favour the decrease of the interfacial tension of a system. The interfacial tension of a system, in turn, is a measure of the free surface energy of the system, therefore, adsorption favors the decrease of the free interfacial energy of a system, and consequently, adsorption is a spontaneous thermodynamic phenomenon. A number of researchers have verified experimentally the Gibbs adsorption equation (Chen, 1977; Skoulikidis, 1971). Two different types of adsorption phenomena can be considered, the physical adsorption and the chemical adsorption or chemisorption.

a) Physical Adsorption

This type of adsorption occurs as the result of Van der Waals attraction forces between the adsorbate and the adsorbant. The adsorbed molecules are not fixed on specific sites and are free to undergo transitional motion at the surface of the adsorbant. This type of adsorption is reversible and is characterized by heats of adsorption below 20K cal/mol and multiple adsorbed layers.

b) Chemical Adsorption

Chemical adsorption is the result of strong chemical bond forces among the adsorbant and the adsorbate molecules. The adsorbed molecules are

fixed on specific sites. The heats of adsorption are more than 20 Kcal/mol due to the high energy bonds. This form of adsorption is very rarely reversible and is usually associated with a monolayer formation by the adsorbate on the adsorbants surface.

In actual cases it is very difficult to distinguish between the different kinds of adsorption since both may occur simultaneously and therefore they give heats of adsorption that do not allow a positive classification by themselves.

In the cases of multilayer adsorption the first molar layer is usually considered to be chemisorbed (Skoulikidis, 1967).

The exact mechanism of the adsorption phenomenon is neither simple nor very clear.

None of the surface filling or the pore filling mechanisms, that have been proposed a long time ago, can describe the phenomenon completely.

A new mechanism, the concentration and adsorption mechanism (Chen, 1969) that is based on the surface curvature is a more accurate description of the adsorption phenomena. According to this mechanism, for each system there is a range of pore diameters within which the phase separation occurs in a series of a concentration - precipitation processes.

For the range:

$$3.3 \leq D/d \leq 6.1$$

where D - Adsorbates average molecular diameter

d pore diameter.

the solution inside the pores concentrates and becomes supersaturated and precipitation of the adsorbate in the pore occurs.

For D/d ratios outside the above range precipitation does not occur and an equilibrium is established by means of adsorption between the concentrated solution and the pore walls. Fig.2.1 gives a schematic diagram of a pore on an adsorbant particle as given by Davis et al (1972).

2.1.2 Behavior of an Adsorption System

The short explanation of adsorption that was given in the previous paragraph made clear the fact that adsorption phenomena result in a redistribution of the adsorbate between the adsorbants surface area and the bulk solution. There is an equilibrium concentration of adsorbate between the solution and adsorbant phases. The mathematical correlation between those two quantities, at a constant temperature is the equation that describes this equilibrium and is called adsorption isotherm.

A lot of work has been done in order to identify the equation that describes in general the adsorption

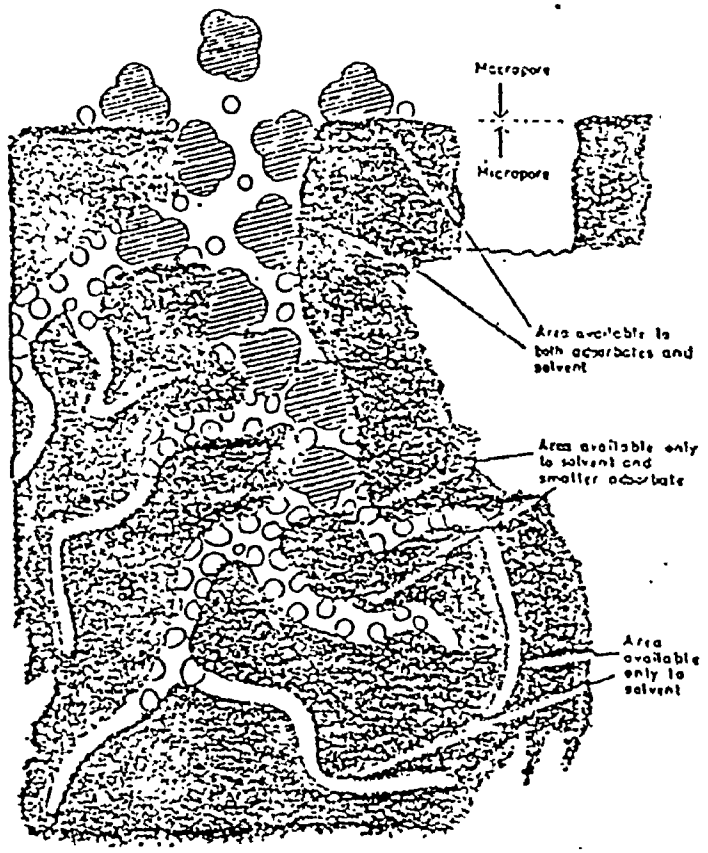


Fig.2.1 Schematic Presentation of Multisolute Adsorption.

Davies et al, (1972)

isotherms. Therefore there are many general mathematical formulations available. Not all the data in literature obey the various formuli, due to the diversity and complexity of adsorption phenomena. The usual adsorption isotherms have been classified by Brunauer, Emett, Teller into five types of adsorption isotherms. This is commonly known as the B.E.T. classification. The five types of adsorption isotherms are given in (Fig. 2.2). Each one of them corresponds to special adsorption mechanism. More details on each mechanism can be found in literature (Chen, 1969, Skoulikidis, 1967).

The Langmuir and Freundlich models are the important ones and can be linearized easily. The table that follows gives the mathematical formulation for the three most common adsorption isotherms equations.

Fig.2.2 Adsorption Isotherms

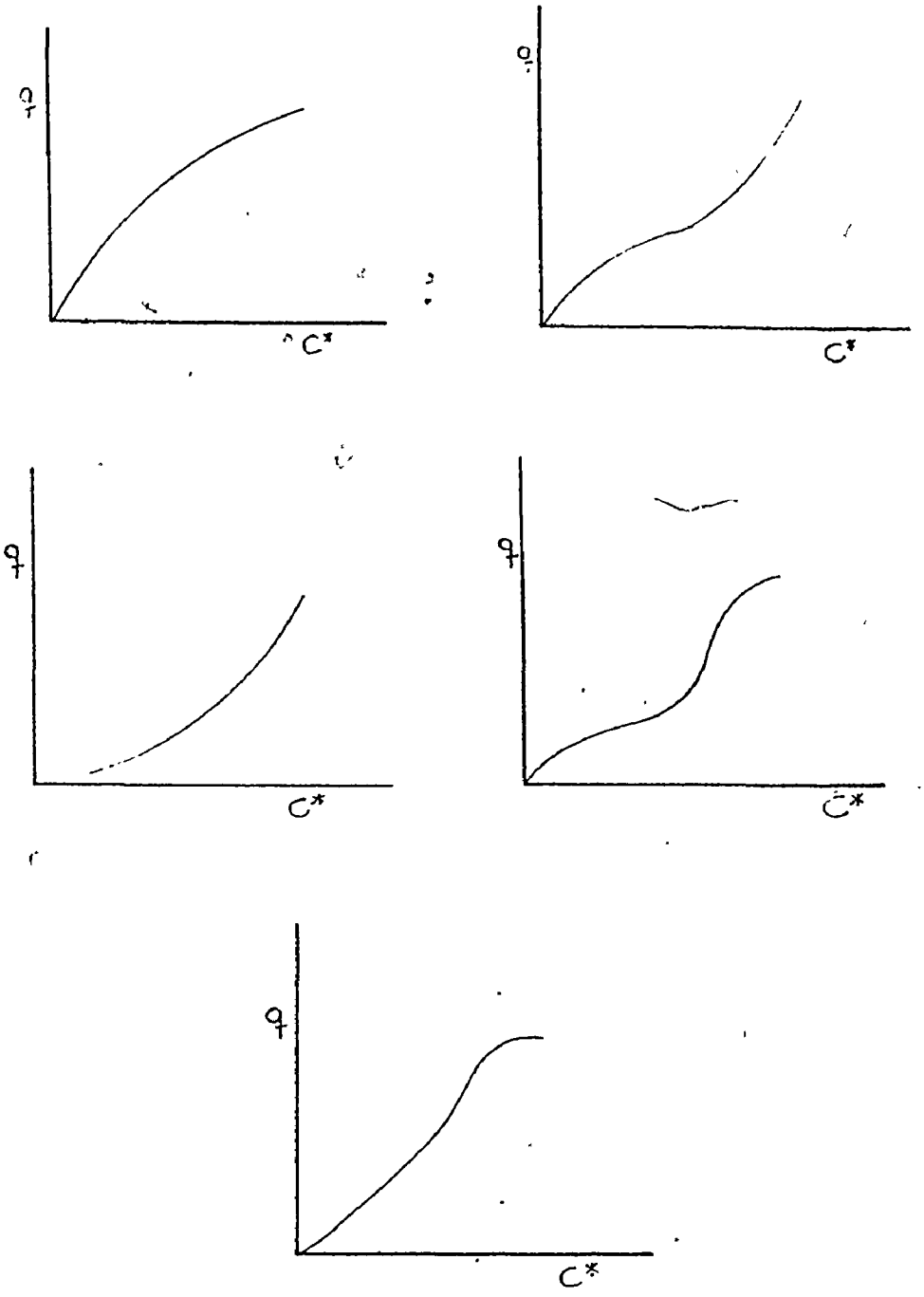


TABLE 2.1

Adsorption Isotherm Models in a Liquid-Solid System

Model	Equation	Assumptions
Langmuir (1918)	$Q = Q_o \frac{bC^*}{1+bC^*}$	1) Limiting adsorption loading Q_o refers to monolayer formation 2) Homogeneous adsorbant surface 3) No lateral interaction among adsorbed molecules
Freundlich (1926)	$Q = K\ C^{*\,1/n}$	1) Exponential distribution of surface sites energies
B.E.T. (1938)	$Q = \frac{Q_o B C^*}{(C_s - C^*)[1+(B-1)(C^*/C_s)]}$	1) Langmuir assumptions 2,3 2) Multilayer formation 3) The heats of adsorption of the 2nd, 3d, ... nth layers are equal

Where: Q_o, b, K, n, B, C_s, are constants. C^* is the equilibrium concentration of the solution after adsorption. Q is the loading of the adsorbate on the adsorbant.

2.2 Parameters Influencing Adsorption

Adsorption as a thermodynamic phenomenon is influenced by a number of parameters that relate to the bond between adsorbant and adsorbate as well as their individual properties either by themselves or in the adsorption system.

Temperature is a very important parameter that

influences the phenomenon in many ways, e.g., increasing temperature, increases the kinetic energy of the molecules as well as the entropy of the system and therefore weakens the bonds between the adsorbant and the adsorbate molecules. In other words, temperature increase is unfavorable for the phenomenon. The temperature changes influence the solvation of the solute (adsorbate) by the solvent, and since the overall phenomenon is isually exothermic, increase of the temperature decreases the adsorption capacity. The rate of adsorption is favored by temperature increases, because it results in a decrease of the solution viscosity and an increase in the mobility of the molecules of the adsorbate.

Another important parameter is the solubility of the adsorbate in the bulk solution. The more soluble the adsorbate, the more it will prefer the solution over the adsorbant. Solubility is a function of the nature of the adsorbate. The more lyophobic the adsorbate is, the less soluble it is and therefore, the more adsorbable it becomes. This correlation between lyophobic nature and adsorption is known as Lundelius rule. Weber (1972) has pointed out that many systems exist that do not obey the above rule. According to the concentration adsorption mechanism it can be also seen that low solubility favours adsorption. Indeed, low solubility results in a quicker and easier increase in the concentration of the solution inside the pores. Therefore, saturation-precipitation

occurs more easily and the whole phenomenon is favored.

The polarity of the adsorbed molecules influences adsorption as well. Solubility and solvated radius are functions of polarity, and they both affect adsorption significantly. A polar adsorbant will prefer the more polar phase and vice-versa. This is a generally followed rule in nature.

Another property of interest is the molecular radius of the adsorbate. It affects the solvated radius of the molecule and hence its adsorption and diffusivity. For molecules belonging to one specific class of chemical compounds (Weber-Morris, 1964) it has been noticed that the overall rate of adsorption decreases as the molecular radius increases. The adsorption capacity behaves in a more complex way as a function of molecular size (Weber, 1971, Benedek, 1974). There is not any definite result on the effect of molecular geometry on the adsorption phenomenon although some investigation has been done in this domaine.

On the other hand, the particle size of the adsorbant affects the rate and capacity of adsorption. The smaller particle size results in (a) shorter pore lengths and (b) greater number of pores accessible to the adsorbate molecules. In the case of pore diffusion controlled adsorption, all these factors affect favorably and

significantly the rate of adsorption and capacity of adsorbants. Smaller particle size also results in larger external surface areas.

Finally the true surface area and the pore volume are two of the most important parameters that influence the practical application of the adsorption phenomenon. It is actually the pore size distribution along with the specific surface area and specific pore volume that determines the applicability of a material as an adsorbant in a specific case (Chen, 1969, Benedek, 1974, Weber, 1971).

High specific surface areas and favorable pore size distribution result in high adsorption capacities. It is easily understood why the pore size distribution and the specific surface area are important parameters if we consider that only a narrow range of pore sizes are effective in the adsorption process, according to the adsorption-concentration mechanism (Chen, 1969) that was briefly described in section 2.1.1.

Along with the above described parameters some others play a role in the adsorption phenomena. They are parameters that are related to the qualities and the nature of the surface of the adsorbing material.

It is obvious therefore that adsorption is a very complicated phenomenon influenced by a large number of parameters. This explains the difficulties in deriving the

proper mathematical formulations for the general description of the adsorption isotherms, as well as the difficulties of applying successfully adsorption to industrial processes.

2.3 The Biological Degradation of Organic Substances

Biological waste treatment processes involve the utilization of the pollutants existing in a waste stream by a variety of living organisms. Because the wastewaters are normally non-sterile, there is with the feed a constant input of organisms that maintain the diversity of the population. This diversity is advantageous since it permits the utilization of wide varieties of pollutants that are available as substrates to the different species of microorganisms existing in the treatment systems. Most of the active organisms in a biological treatment reactor are bacteria.

Bacteria can directly metabolize only organic substances whose molecules are small enough to be transported through the cell membrane pores. Particulate or colloidal dimension matter has to be treated first by exoenzymes that cleave it by hydrolysis to smaller fractions. There are also some dissolved single molecules that may require extracellular enzymatic treatment prior to transportation in the cell and utilization.

It is obvious that this extracellular activity provides one more difficulty in the sequence of steps for

the substrate utilization, and may introduce in some cases a rate limiting step. Bacteria of interest in the waste treatment systems, are in general heterotrophic. This means that they require organic molecules in order to derive their energy and basic building blocks for their cellular constituents. In any process, natural selection will gradually select the most efficient species in utilizing a specific waste.

In general, bacterial action can be represented by the following qualitative equation:

$$\text{Substrate} \xrightarrow[\text{acceptors, nutrients}]{\text{cells, electron}} \text{more cells} + CO_2 + \text{reduced electron acceptors}$$

During bacterial metabolism, organic molecules are oxidized in order to provide energy to the cell. The cell using organic carbon atoms as the basic building block, plus the energy furnished by the oxidation process, synthesizes new cellular material necessary for growth and multiplication.

Along with the organic substrates bacteria also need a terminal electron acceptor, for the energy production (oxidation) cycle. The kind of terminal oxidant used is a very important characteristic of their function. Depending on whether they can use oxygen, or not, as the terminal electron acceptor they are named respectively aerobic or anaerobic. Between the two extremes there are a lot of bacterial

species that can grow with or without the presence of oxygen and are named facultative bacteria.

In addition to the organic substrate and the terminal electron acceptor, a large number of chemical elements are required for the support of the bacterial life. These elements, necessary at low concentrations, are called micro nutrients. Some of the most important ones are the following (Howe, 1970):

N, P, K, Na, Ca, Mg, Mn, Fe , S, Zn, Cu, Co, etc.

Most of the metallic elements are usually present in the carriage water in sufficient quantities and therefore they do not impose any growth limitation. Nitrogen and Phosphorus, though, need special attention because they are not always available in sufficient quantities. Their presence is necessary in amounts related to the net cell growth. The requirements of N and P are usually expressed in the form of ratios of the organic carbon content of the waste over the required N or P. These ratios are expressed as BOD_5:N and BOD_5:P respectively. Ratios of 17:1 to 32:1 have been cited for N and 90:1 to 150:1 for P (Bush, 1971). In general, the following ratios have been accepted widely in practice as adequate:

$$BOD_5:N:P = 100:5:1$$

It should be noted here that maximum cell synthesis nutrients requirements differ markedly from nutrients requirements

needed in a continuous reaction at less than maximum synthesis rate. Nutrient deficiency results in a rate limitation of the treatment process since the oxidation rate becomes dependant on nutrient concentration.

Finally along with all the above requirements, parameters like the temperature, the pH, the mixing or the uniformity of distribution of the food to the microorganisms are very important for a bio-system since they determine the physiological state of the system and ultimately the efficiency as a treatment system, examined from the engineering point of view.

2.4 Nature of the Residual Organics of Biological Treatment

Bacteria during the process of biological degradation of the different organic molecules produce additional biomass(bacteria) and generate a wide variety of metabolic by-products.

There is a balance between the synthesis and energy production cycles that depend on the environmental conditions of growth. This equilibrium may move towards one or the other cycle, but both of them always co-exist. This means that the by-products of the bacterial metabolism are always generated, and the only condition that may change is the rate of their production, and possibly their relative composition depending on the physiological state of

the cells.

Therefore, within a system that uses biological oxidation in order to treat a certain waste, we will observe the removal (partial or complete) of the biodegradable organics, the generation of the metabolic by-products and the production of new biomass. Any organic molecules that can not be metabolized by the active cells of the system, will remain in solution as biorefractory molecules and they will be found in the effluent of the plant.

Figure 2.3 gives a qualitative representation of

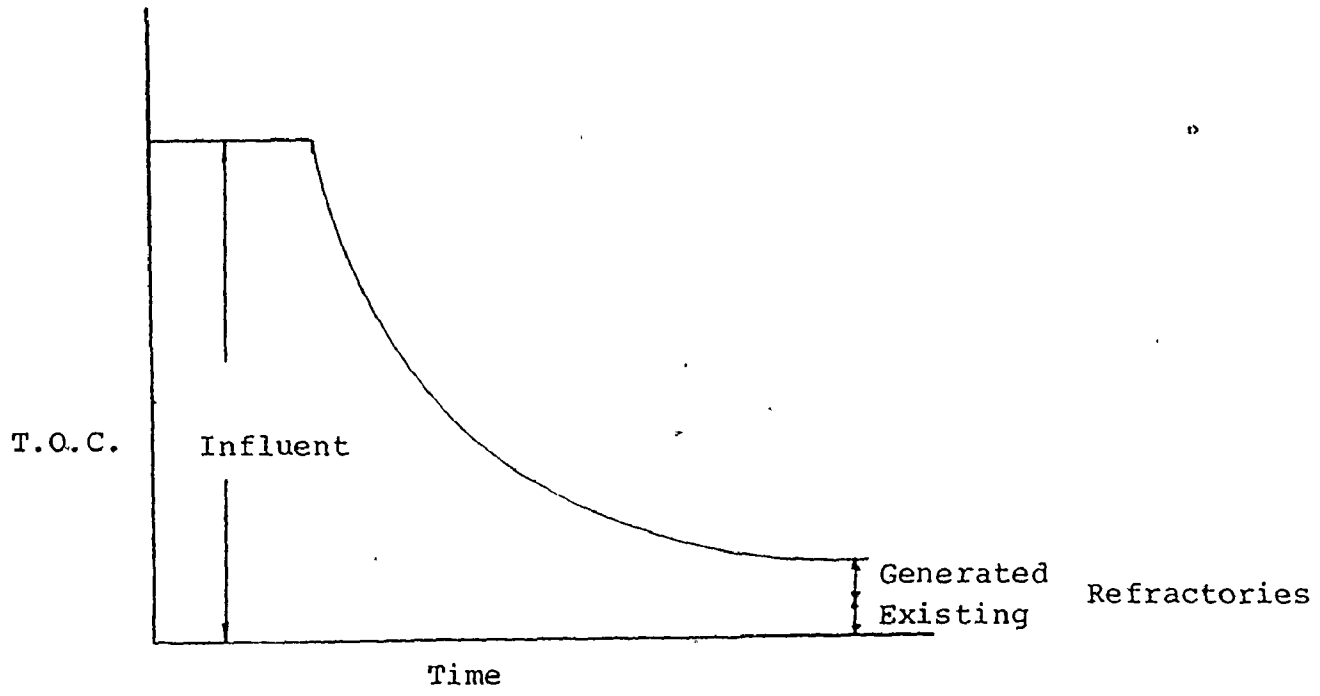


Fig.2.3 Qualitative Presentation of Biological TOC Removal

the removal of T.O.C. (Total Organic Carbon) during biological treatment. Recently a strong interest has been expressed on the nature and identity of the residual organics after biological treatment of wastes as:

i) They may prove to be toxic;

ii) Their presence acts as a limitation in meeting the low T.O.C. effluent requirements.

At this point, a distinction has to be made between the meaning of the terms biodegradable and biodegraded organic molecule. A compound is biodegradable when it can be broken down via intermediate metabolites by a microorganism or a group of them to CO_2 and H_2O. A compound may be biodegradable but may have not been biodegraded in a particular system to which it has been subjected. There is a variety of possible reasons for this phenomenon (Painter, 1972), for example: if the appropriate organisms are not present in the proper concentration or in the absence of necessary co-factors or presence of inhibitors, a very poor treatment efficiency will result. Hydraulic deficiency, the assymptotic nature of removal kinetics or the sequential removal of some compounds can also result to the incomplete oxidation of a chemical compound that is found consequently present in the effluent of the plant as a residual organic compound.

Some microbiologists are of the belief that every organic molecule is biodegradable provided it is exposed to the properly acclimated biota, under the proper condition of pH , temperature, concentration, co-factors, etc. Experience has proven that the organic compounds can be classified into three categories (Thom and Agg, 1975):

a) Easily Biodegraded Substances

In this group we find organic molecules like acetic acid, butyric acid, glycerol, lactic acid or urea. In general, these compounds are simple in structure containing, C, N, O only and can be utilized by the microorganisms in both the energy production and the synthesis cycles.

b) Resistant Substances

Molecules like D.D.T. or E.D.T.A. and branched A.B.S. belong to this category. Most, but not all of the compounds of this group are toxic. (Thom, 1971)

c) Substances that can be Removed Provided Suitable Acclimatization can be Achieved

Organic molecules like linear A.B.S., methanol, toluene, thiourea belong to this group. The acclimatization of microorganisms to the utilization of organic molecules of this group can be achieved by applying to them initially a low, constant concentration of the compounds, and by

increasing slowly this concentration later. It is important to note that the supply of the compound has to be kept constant since fluctuations of either the rate of supply or the concentration, can prevent adequate acclimatization.

In a treatment plant there is usually a large number of different substances entering with the carriage water, and they may belong to any of the above-mentioned three categories. Therefore the residual organics that the plant will have present in its effluent can be generated by any of the mentioned mechanisms. Thus they may be by-products of the cell metabolism, or intermediate compounds in the process of biological oxidation or even the compound itself, if for one reason or another it by-passes the treatment system.

Chudoba et al in 1969 came to the conclusion that on the average the C.O.D. of a secondary effluent treating biodegradable organics was 0.75% of the C.O.D. of the influent. Therefore every biodegradable compound gives rise to non-biodegradable molecules. Using sewage from Prague, Chudoba et al have shown that secondary effluent had an average of 15% of the C.O.D. value present in the influent. According to their previous work, 14.25% of the biorefractory matter was originally present in the sewage. On the other hand, Ricket and Hunter (1971), using the average oxidation number of the carbon of several

compounds concluded that the residual organics were predominantly of treatment origin. Both research groups although they disagreed on the origin of the biorefractories, verified the existence of refractories in secondary effluents.

The diversity and complexity of origin of residual organics result in a wide diversity of chemical compositions. Because most of the residual organics exist in low concentrations it is necessary to use very sensitive analytical techniques for their qualitative and quantitative determinations. Separation techniques for the separation of the different groups of organic molecules have been applied to assure zero interference among different molecules that coexist in solution. Work done at WPRL (Painter, 1972) on secondary effluents using a dialysis membrane for a gross separation, detected different groups of organic compounds (Table 2.2) as well as some individual molecules (Table 2.3).

Similar work in Israel (Rebhun-Manka, 1974) on secondary effluents again, revealed the presence of similar groups of organics but in different relative concentrations. The residual organics are considered by Rebhun and Manka as well as by other researchers as the factors that are responsible for undesirable qualities in water bodies, as colour, odor or taste. Special attention has been given to the so-called "humic substances". The analogy

TABLE 2.2

Composition of an Ultrafiltered Effluent from a Percolating Filter Treating Domestic Waste (Painter, 1973)

Constituent	Proportion of Total C.O.D.
Carbohydrates	4.0
Amino acids	0.2
Volatile acids	4.6
Non volatile acids	5.4
Neutral volatile compounds	11.8
Steroids	3.1
Tannins lignins	0.8
Anionic detergents	5.1
Non ionic detergents	3.2
Optical brightners	1.6
Organo chlorine compounds	0.5
Non-dialysable	<0.001
Polysaccharides	4.0
Proteins	1.7
Total Allocated	41.5

TABLE 2.3

Compounds Positively Identified
In Secondary Sewage Effluent

(Painter, 1973)

Compounds		Concentration (mg/l)
Glucose		
Fructoze		
Manoze		2 - 50
Allulose		
Xyloze		
Raffinose		
Formic Acid		10
Acetic Acid		20
Propionic Acid		5
Buturic Acid		10
Iso-Buturic Acid		10
Iso-Valeric Acid		50
Caproic Acid		10
Uric Acid		10
Pyrene		
Perylene	10 hydrocarbons in all	1
Benzpyrene		
D.D.T.		
B.H.C.		0.1 each
Dieldrin		

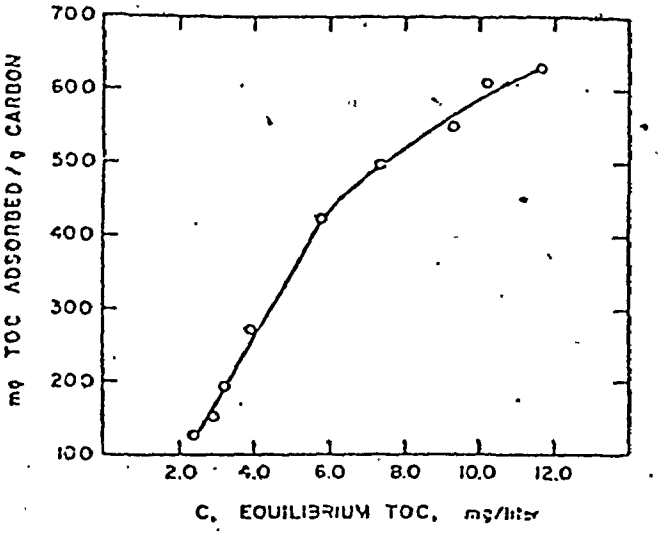
between the condition of humus formation in nature and those in a biological waste treatment plant led to the assumption that a considerable part of the residual organics consists of humic type compounds. Analysis performed on secondary effluents supported the assumption as the data of Table 2.4 shows. Also the data of chemical analysis of effluents shown on Table 2.5 (Bunch-Barth-Ettinger, 1961) present the same groups of organics like proteins carbohydrates lignins etc. It must be noted though that the term humic acids covers a large group of still unidentified molecules.

A different form of analysis (Hunter et al) classified (Table 2.6) the ether soluble organics of a secondary effluent according to their ionic charge. It is important to note that 54% of the total organics consisted of acidic substances.

The importance of the ionic fraction of the residual organics can be seen by the curves shown on Figure 2.4 (Helfgott-Hunter-Rickert, 1970) where it is obvious that the application of an ion exchange technique can remove a significant portion of the C.O.D. thus improving the quality of the effluent.

A more sensitive separation technique using high resolution ion exchange chromatography and ultra-violet (U.V.) analysis was applied by Katz et al (1972) to secondary effluents.

—RESIDUAL ORGANICS IN SECONDARY EFFLUENT AFTER CONTACT WITH POWDERED ACTIVATED CARBON



—ADSORPTION ISOTHERM FOR POWDERED ACTIVATED CARBON WITH CENTRIFUGED SECONDARY SEWAGE EFFLUENT

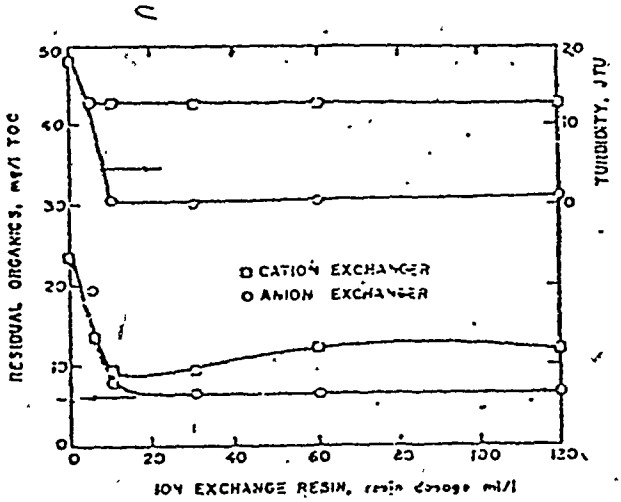


Fig.2.4 Residual organics Removal by Adsorption or Exchange (Helfgott et al. 1970)

TABLE 2.4

Organic Compunds in Secondary Effluents (Rebhun & Manka 1971)

Constituent	% of COD
Carbohydrates	13.7
Proteins	28.4
Anionic Surfactants	11.3
Tanins - Lignins	1.5
Humic Substances	36.6
Ether extractables	8.5

TABLE 2.5

Organic Compounds in Secondary Effluents (Bunch et al 1960)

Compound		Percent of Total C.O.D.
Ether Extractables		
i. Organic Acids	6.5	
ii. Neutral	2.7	
iii. Others	0.8	Total: 10
Proteins		10
Carbohydrates & Polysaccharides		
Non-Simple Sugars		5
Tannins - Lignins		5
Anionic Detergents		10
Unidentified		65
Average C.O.D. 100 mg/l		

TABLE 2.6

Ethyl-Ether Soluble Colloidal Organics
In Secondary Effluent (Helfgott et al 1970)

Compound	Concentration (mg/l)	% Total Conc.
Acids	10.7	54
Bases	2.1	11
Amphoterics	1.1	6
Neutrals	5.6	29

The results of this research correspond well with the results given by Manka et al, who identified the same sugars as individual molecules in Israel in secondary effluent.

The application of high resolution gas chromatography along with mass spectrometry is the latest, most sophisticated and sensitive analytical technique in the identification of residual organics. A large number of individual residual organic molecules have been identified by this technique (Manka et al, 1974). Tables 2.7 and 2.8 summarize the results of these analyses and there is good qualitative correlation with the results of other researchers.

Finally a recent effort to clarify the residual organics according to their Apparent Molecular Weight (AMW) through gel permeation (Sachdev et al, 1976) provided the data shown on Table 2.9, where a distribution over a wide range of AMW values can be seen.

Looking again at the data the literature has supplied on the identity of the residual organics, we can see that among the organics cited, groups of compounds (Table 2.10) such as carbohydrates or proteins, a variety of other soluble organic compounds are always present along with a large number of unidentified ones. (A significant part of the T.O.C. consists of acidic components.) The apparent

TABLE 2.7

Characterization of Ether Extractables In Secondary Effluent By GC-MS In Israel (Manka et al, 1974)

Fatty Acids

Nonanoic Acid
Decanoic Acid
Undecanoic Acid
Dodecanoic Acid
Tetradecanoic Acid
Pentadecanoic Acid
Palmitic Acid
Stearic Acid

No unsaturated acids have been identified in the secondary effluents. The presence of molecules with even numbers of carbon atoms are considered as a product of the bacterial oxidation of unsaturated acids during the treatment.

Hydrocarbons

- Alkanes $C_{17}H_{36}$ - $C_{35}H_{72}$ (19 compounds)

Alkyl Benzenes

Isopropyl Benzene Dodecyl Benzene

Higher Aromatics

Napthalene, Methyl Napthalene, Diphenyl, Diphenyl Methane, Dioctylpthalate, Phenol, Triethyl Phosphate

TABLE 2.8

Distribution of Organic Groups in Secondary Effluents
(Manka et al, 1970)

Organic Group	% of Total C.O.D.		
	High Rate Trickling Filter Municipal	Stabil. Pond	Extended Aeration
Proteins	21.6	21.1	23.1
Carbohydrates	5.9	7.8	4.6
Tannins Lignins	1.3	2.1	1.0
Anionic Detergents	16.6	12.2	16.0
Ether Extractables	13.4	11.9	16.3
Fulvic Acid	25.4	26.6	24.0
Humic Acid	12.5	14.7	6.1
Hymathomelanic Acid	7.7	6.7	4.8

TABLE 2.9

AMW Distribution of Organics in Secondary Effluent
(Sachdev et al, 1976)

Lake George Effluent		Clifton Knolls Effluent	
AMW Range	% of T.O.C.	AMW Range	% of T.O.C.
700	37.8	700	41.5
430	33.7	310	31.6
117	7.1	100	6.3
Not Defined	7.3	Not Defined	14.6
Not Defined	6.7	Not Defined	1.6
1500	20.4	1500	28.8
1200	17.4	750	12.7
5000	20.4	5000	28.8
Total	92.6		95.6

TABLE 2.10

Common Groups of Organic Compounds Identified in Secondary Effluents

Organic Group	Painter 1973 % T.O.C.	Rebhun-Manka 1971 % C.O.D.	Manka et al 1970 % C.O.D.	Bunch et al 1961 % C.O.D.
Carbohydrates	4.0	11.5	6.1	2.5
Organic Acids	10.2	40.3	45.8	6.5
Tannins - Lignins	0.8	1.7	1.4	5
Anionic Detergents	5.1	13.9	44.8	10
Proteins	1.7	22.3	14.9	10
Polysaccharides	4.0	--	--	2.5

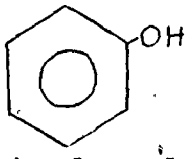
molecular weights of the residual organic molecules are distributed over a wide range of values.

Provided the proper adsorbant is selected, these groups of compounds are removable from the solution. Highly soluble ionic species could also be removed by an ion exchange resin.

Some tedious research is still necessary to reveal to us the identity of the constituents of the secondary effluents. The significance of this subject is great in view of the inevitable recycling of the waste waters and the presence of toxic compounds such as organochlorine compounds, D.D.T and benzpyrene among the residual organics.

2.5 Biological Degradation of Phenol

Phenol is an organic compound that consists of an aromatic ring and a hydroxyl group with the following configuration.

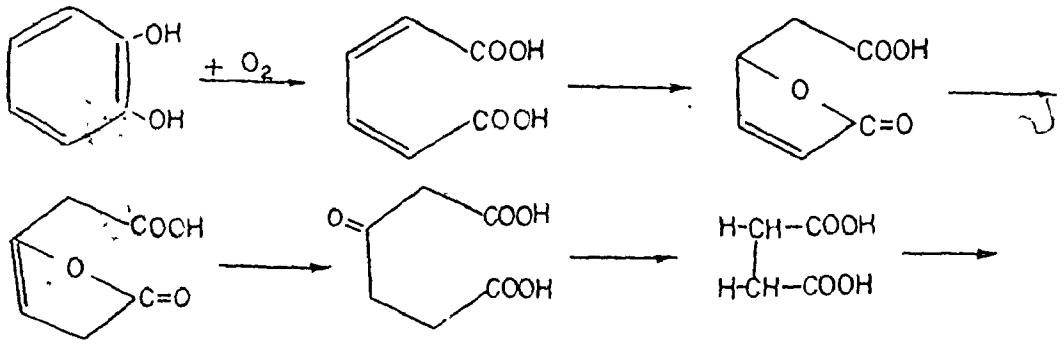


It can be ionized, and it is an easily biodegradable molecule. It is toxic to bacteria, but acclimatization occurs rapidly and easily. It is a strong poison for human beings and harmful even on skin contact. It is a common pollutant in a number of industrial effluents and the current limit of its concentration in final effluents in Ontario is

20 p.p.b.

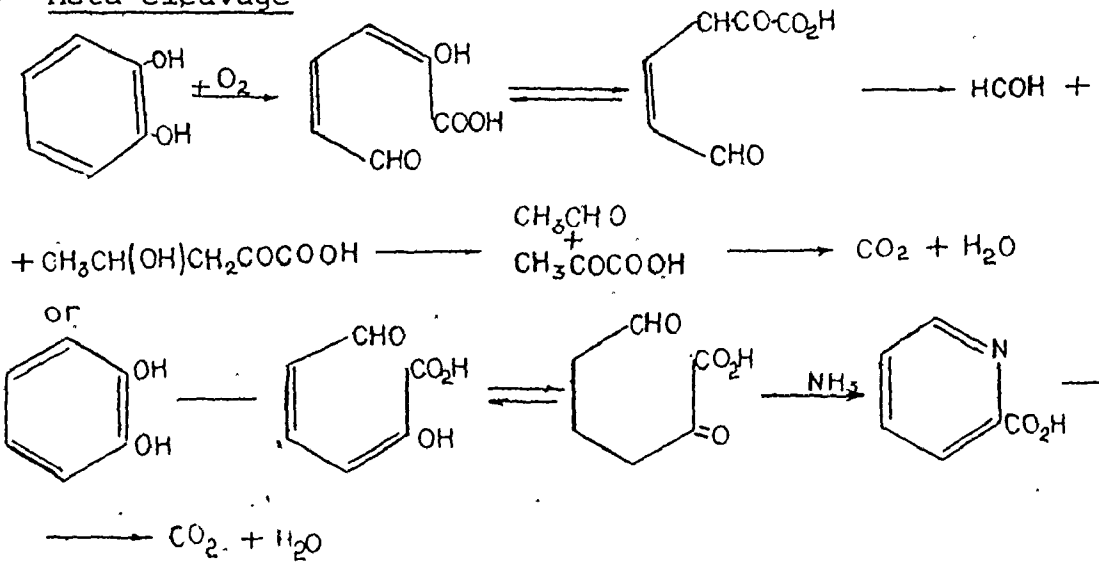
The metabolism of Phenol can follow a number of different ways, depending upon the enzymes that catalyze the reactions. The first step in the oxidation process is (McLaren, 1963) the insertion of an extra hydroxyl group in the ortho position. The extra oxygen alters the electronic structure and destabilizes the otherwise stable benzene ring. A fission process occurs that cleaves the formed catechol ring. This fission can be catalyzed by different enzymes and therefore can follow different pathways. Two of the possible ways are given below.

a) Ortho-Cleavage



$\longrightarrow CO_2 + H_2O$

b) Meta Cleavage



It is clear that along the possible degradation pathways there are a lot of intermediate organics of acidic nature.

2.6 Simultaneous Adsorption and Biological Oxidation

The use of activated carbon to improve water quality is now well established. A great number of contact systems have been developed for treating potable water and waste water. The volume of literature that has been gathered around this subject is voluminous, yet there are still a lot of aspects of the adsorption phenomenon that have to be clarified (see sections 2.1.1 and 2.1.2)by additional research.

Originally, the adsorption or filtration systems were designed and were thought to be functioning exclusively as physical-chemical systems. Research in the past decade , however, proved that active biological growth exists inside the contact columns most of the time , depending on the conditions inside the contact columns, and the nature of the waste.

2.6.1 Observation on Biological Activity in Operating Columns

In 1952 a study on rapid sand filters treating secondary effluents (Pettet et al, 1952) revealed a 3.3 to 3.7 mg/l drop of the dissolved oxygen level across the same beds indicating that active biological growth existed within the sand beds.

The growth of bacteria in contact columns was verified again by Ghosh et al (1967) in a study on the removal of iron from ground waters, where extensive backwashing and even chlorination of their influent could not eliminate the biological activity from the filters. Similar situation was experienced at the Pomona sewage treatment plant (Directo et al, 1974), during the 27 months of the pilot plant scale experiment performed there. The high concentration of soluble organics applied to the activated carbon particles stimulated biological growth within the adsorption columns. This activity resulted in enhanced organics removal, since organics were being removed by biological oxidation and adsorption as well. The biological growth could not be eliminated by backwashing or even by chlorination of the influent. Successful control of the biological sufides production was achieved by the addition of nitrates which are preferred over sulfates as terminal electron acceptors by the bacteria.

A study on the effect of low temperature on organic removal and denitrification in A.C. columns treating domestic waste water (Maqsood-Benedek, 1974) showed extensive bacterial activity in the carbon beds at low and high temperatures. Enhancement of the adsorption capacity of the columns was observed as well due to microbial degradation.

An approach to the utilization of biological activity on A.C. was attempted by Rodman et al (1971). The A.C. treating dye wastes,after exhaustion was "regenerated" in a separate reactor by an acclimatized aerobic biological culture,that was kept in suspension in a separate reactor. The carbon was then put again in adsorption columns. Biological activity continued inside the adsorption columns as well,since the carbon particles were seeded with bacteria acclimatized to the use of the waste.

In general the concentration of the substrates on the adsorption particles create an environment that is beneficial for biological growth (Johnson et al,1966). With this basic idea in mind,research has been conducted towards the addition of powdered activated carbon in the mixed liquor of activated sludge treatment plants. Recent reports on this subject (Wei & LeClair 1974, Ahlberg & Rupke,1974) were encouraging but not conclusive. In recent years ICI America and Du Pont de Neymour have experimented with the addition of powdered activated carbon to the mixed liquor of activated sludge plants (Flynn,1975).Du Pont has recently started up a plant based on this principle in their Deepwater ,New Jersey,plant. Zimpro has been promoting wet oxidation treatment for the combined carbon biomass sludge as carbon regeneration process, and several plants are in various stages of completion.

2.6.2. Rates of Biological Activity

Jeris et al (1974) operated a denitrification

fluidized bed biological reactor with encouraging results. Their fluidized bed demonstrated the capacity to handle very high hydraulic and nitrogen loadings with correspondingly low detention times. Denitrification rates up to 424 lb/day/1000ft^3 of reactor were experienced. The major operational problem was the control of the biological growth that results in continued bed expansion and finally bed wash out.

Similar behaviour was experienced by Jennings (1974) in a fluidized bed biological reactor utilizing glucose as substrate. Again, high degradation rates were experienced, and the major operational problem was the control of the bacterial growth. Due to increasing growth on the A.C. particles, the bed kept expanding and washed out of the contact columns.

In the work by Maqsood (1975) the specific reaction rate for the biological activty ranged between 6.53×10^{-10} g T.O.C./s cm^2 at 25^{o}C to 3.94×10^{-10} g T.O.C./s cm^2 at 5^{o}C.

The specific biological reaction rate for the Pomona P.C.T. plant mentioned in section 2.6.1, has been calculated by Peel (1975) to be 6.9×10^{-10} g T.O.C./s cm^2. In the same publication by Peel (1975), the specific reaction rate for the Ewing-Lawrence, N.J. bio-adsorption study, has been calculated to be equal to 4.99×10^{-10} g

T.O.C./s cm^2.

Recent parallel studies (Holladay et al, 1975) of a CSTR, packed bed bioreactor and a fluidized bed biological reactor treating a phenol waste proved that the three phase fluidized bed biological reactor had the highest degradation rates and the shortest retention times of all. Degradation rate of up to 8.6 g T.O.C./day/ reactor volume for 99% removal at 260 mg/l influent phenol concentration were experienced. The control of the biological growth and resulting bed expansion was achieved by continuous external regeneration of part of the bed. Residual T.O.C. escaped in the effluent and resulted in unstable effluent pH.

In all the above studies, activated carbon had been used as column packing material. Table 2.11 summarizes the above information. In the waste treatment processes the use of biological oxidation along with adsorption is capable of forming a high removal efficiency system, since each process is supplementing the other towards a high quality effluent. The adsorbant particles concentrate the substrates and adsorb the by-products (hopefully) of the metabolism of the biological film that develops around them. At the same time, the biological population removes the biodegradable soluble organics of the waste that would otherwise exhaust the adsorbant faster. This leads to higher rates and longer adsorbant life (Holladay et al, 1976).

TABLE 2. 11

Reaction Rates Reported in Literature

Researcher	Column Packing Material	Parameter Used	Reaction Rate
Jeris et al (1974)	Activated Carbon	Total Nitrogen	425 lb/day/1000ft^3 of Reactor-Volume
Maqsood (1975)	Activated Carbon	T.O.C.	6.53×10^{-10} g/s cm^2 at 25°C 3.94×10^{-10} g/s cm^2 at 5°C
Peel (1975)	Activated Carbon	T.O.C.	6.9×10^{-10} g/s cm^2 (Pomona) 4.99×10^{-10} g/s cm^2 (Ewing Lawrence)
Holladay et al (1976)	Coal	T.O.C.	8.6 g/day/reactor vol

2.7 Quantitative Monitoring of Growth

The assimilation of organic carbon by bacteria results in the growth of the thickness of the biological film around the adsorbant particles and thereby increases the overall diameter of the particles. At the same time, the apparent specific gravity of the particles decrease and the bed expands.

Knowledge of the yield of bacterial volume is critical for proper engineering of fluidized bed biological reactors. The parameter that is related to the overall hydraulically effective volume of the biological growth is the height of the expanded fluidized bed (L_e^t).

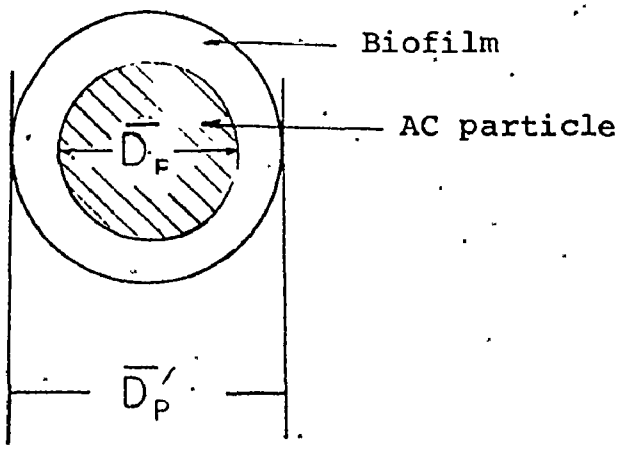


Fig.2.5 Fluidized Bed Particle

The following assumptions are necessary for the development of a system of equations that can provide an estimation of the total hydraulically effective volume of the biological growth around the bed particles.

(I) The virgin carbon particles are spherical, rigid and uniform with diameter $\overline{Dp}$

(II) The carbon particles that have developed biological film around them, also behave like rigid uniform spheres with diameter $\overline{Dp}'$.

(III) The growth is uniform along the length of the bed and has a constant density (Holladay et al, 1976)

The following equations hold:

$$U = \frac{Q}{A} \qquad (7)$$

Where U = Superficial velocity
Q = Flow rate
A = Cross sectional area of flow

$$U_f = \frac{U}{\epsilon_e^t} \qquad (8)$$

Where U_f = Fluidization velocity
ϵ_e^t = Porosity of expanded bed at time t

A force balance in a fluidized bed can be used to relate the bed void fraction to particle and fluid properties. Particulate fluidization is assumed :

$$150\frac{(1-\epsilon_e^t)}{\epsilon_e^{t3}}\frac{\mu U}{\overline{D}_p'^2} + 1.75\frac{\rho U^2}{\overline{D}_p'} = (\rho_s' - \rho)g \qquad (9a)$$

In most cases (Foust et al, 1964, Leva, 1969) and in the present case, the second term of equation 9a is neglected over the first term and the equation is written as follows:

$$\frac{150\,\mu\,U}{(\rho_s' - \rho)\,g\,\bar{D}_p'^{2}} = \frac{\varepsilon_e^{t\,3}}{1-\varepsilon_e^t} \qquad (9)$$

Where: ρ_s' = Average particle density

μ = Viscosity of liquid phase

ρ = Density of liquid phase

Combining equations 7 – 9 we have:

$$\frac{Q}{A} \leq \frac{\varepsilon_e^{t\,3}}{1-\varepsilon_e^t} \cdot \frac{(\rho_s' - \rho)\,g\,\bar{D}_p'^{2}}{150\,\mu} \qquad (10)$$

A mass balance for the expanded bed gives

$$L_e^t\,A\,(1-\varepsilon_e^t) = N\,\frac{\pi\,\bar{D}_p'^{3}}{6} \qquad (11)$$

Where: N = Number of carbon particles with developed growth

L_e^t = Length of expanded bed, with growth

The number of carbon particles can be calculated as equation 12 shows:

$$N = \frac{6\,M}{\pi\,\bar{D}_p'^{3}\,\rho_s'} \qquad (12)$$

Where: M = Total mass of virgin carbon that participates in growth.

Combining equations 10-11 we have:

$$\frac{Q}{A} = \frac{\left[\frac{6 L_e^t A - N\pi \overline{D_p'}^3}{6 L_e^t A}\right]^3}{\frac{N\pi \overline{D_p'}^3}{6 L_e^t A}} \cdot \frac{(\rho_s' - \rho) g \overline{D_p'}^2}{150 \mu} \qquad (10a)$$

Where: ρ_s' = is the apparent density of the particles that have developed biological film around them.

The new ρ_s' of the particles can be expressed as:

$$\rho_s' = \frac{\text{mass of carbon} + \text{mass of biofilm}}{\text{total volume}} \quad \text{or} \quad (13a)$$

$$\rho_s' = \frac{\left[\pi \overline{D_p}^3 \rho_c + \pi(\overline{D_p'}^3 - \overline{D_p}^3)\rho_b\right] 1/6}{1/6\, \pi \overline{D_p'}^3} \qquad (13b)$$

Where: ρ_c = Virgin carbon wetted particle density (1.35 g/cm^3)

Biomass: ρ_b = Assumed equal to 1 g/cm^3

or

$$\rho_s' = \frac{\overline{D_p}^3 \rho_c + \overline{D_p'}^3 - \overline{D_p}^3}{\overline{D_p'}^3} \quad \text{or}$$

$$\rho_s' - 1 = \frac{0.35\ \overline{D_p}^3}{\overline{D_p'}^3} \tag{13}$$

Combining 10a and 13 we have

$$\frac{Q}{A} = \frac{\left[6 L_e^t A - N\pi \overline{D_p'}^3\right]^3}{36\ L_e^{t2} A^2 N \pi\ \overline{D_p'}^4} \cdot \frac{9\ 0.35\ \overline{D_p}^3}{150\ \mu} \quad \text{or (10b)}$$

$$\left[\frac{Q\ .36\ L_e^{t2}\ A^2\ N \pi \mu\ 150}{0.35\ \overline{D_p}^3\ A\ g}\right]^{0.33} = \frac{6 L_e^t A - N\pi \overline{D_p'}^3}{\overline{D_p'}^{4/3}} \tag{10c}$$

Let Ω be equal to the left term of equation 10c above. (14)

Then 10c can be written again as follows:

$$N\pi \overline{D_p'}^3 + \Omega \overline{D_p'}^{1/3} - 6 L_e^t A = 0 \tag{15}$$

Equation 15 gives the $\overline{D_p'}$ as a function of time using as variable the L_e^t values.

Knowing the $\overline{D_p'}$ values we can calculate the total biomass volume around the particles as equation 16 shows:

$$V = N \frac{\pi \left(\overline{D_p'}^3 - \overline{D_p}^3\right)}{6} \tag{16}$$

Equation 14 can be rewritten as follows:

$$\eta = 21.57 (Q L_e^{t^2} N)^{0.33} \qquad (14a)$$

Where we have substituted

$$\mu = 0.9510^{-2} \text{ stokes } (24^{\circ} C)$$

$$\bar{D}_p = 0.1548 \text{ cm}$$

$$A = 80.12 \text{ cm}^2$$

$$g = 981 \text{ cm/sec}^2$$

Simultaneous solution of the three equations gives the average particle diameter of the bed particles, including the developed biological film, as well as the total volume of this growth.

The simultaneous numerical solution of the three equations has been done through the use of the simple computer program that is given in Appendix A.

CHAPTER 3

EXPERIMENTAL METHODS

The experimental part of the present work has been divided into two parts; the batch tests and the continuous tests.

The batch tests were performed in an effort to determine the best of a number of different adsorbants that would remove the residual organics resulting from the biological oxidation of Phenol. The continuous tests were performed in order to examine the direct adsorption of the bio-residuals on the selected adsorbant.

3.1 Batch Tests

3.1.1 Materials

Adsorbants

A number of different adsorbants and ion exchange resins were used for the batch tests. Activated Alumina Alcoa F-1, Amberlites XAD-4, XAD-7, XAD-8, WRL 200A ion exchange resin, IRA 458 ion exchange resin, and activated carbons Special A and Filtrasorb 400 were tested.

The table that follows gives a brief summary of their most important properties. More details are given in Appendix B.

Table 3.1

Properties of Adsorbants Tested

Adsorbants	Supplier	Spec. Surf. Area m^2/g	Pore Volume	Avg Pore Diameter	Specific Gravity g/cm^3	Total Exchange Capacity mg/g	Ionic Form
F-1 Activated Alumina	Alcoa	210	0.25 ml/g	40	3.3	--	--
XAD-4	Rohm Haas	450	0.50 ml/ml	50	1.08	--	--
XAD-7	Rohm Haas	URO	0.50 ml/ml	80	1.24	--	--
XAD-8	Rohm Haas	140	--	250	1.23	--	--
F-400 Activated Alumina	Calgon	1200	0.94 ml/g	35	--	--	--
Special A Activated Carbon	--	.91	0.33 ml/g	75	--	--	--
WRL 200 A i.e. Resin	WRL	--	--	--	--	0.35 eq/l	Anionic
IRA 458 i.e. Resin	Rohm Haas	--	--	--	--	1.25 mg/ml	Anionic

3.1.2 Equipment

1) Activated Sludge Reactor

The activated sludge reactor had a volume of 20 l, and a sludge age of 20 days. Phenol was fed once a day at C:N:P ration of 100:5:1. The reactor was reseeded every week with 1 l of return sludge from the Dundas Sewage Treatment Plant, and it was situated in a constant temperature room at 24°C.

The aeration system consisted of a number of diffusers at the bottom of the rectangular reactor.

2) Buchler Rotating Flash Evaporator (Model PTFE, 16N)

The residual organics solution taken out of the reactor described above, was concentrated in a Buchler rotating flash evaporator.

3) High Speed Lourde LRA 200 Centrifuge

The G value could be adjusted to any desired level up to 3×10^4 G. The time of centrifugation can also be selected and set.

4) Sartorious Membrane Filters (# 11306)

Cellulose membrane filters (0.45μ) were used to define the upper limit of soluble organics in the present experimental work.

5) Spectrophotometer

Bausch and Lomb Spectronic 20 spectrophotometer was used for the direct colorimetric analysis of Phenol at $\lambda = 510 \mu m$

6) Beckman 915, Carbon Analyser

A Beckman Model 915 T.O.C. analyser was used for the determination of the Total Organic Carbon of the samples (T.O.C.). It is equiped with separate channels for the determination of Total Carbon (T.C) and of Inorganic Carbon (I.C).A 20 µl sample volume was injected in each of the channels of the carbon analyser for the determination of the T.C. and I.C. concentration respectively.

7) Oscillating Constant Temperature Shakers (RSCO-2156)

Shakers manufactured by Research Specialties, equiped with a water bath temperature control were used for the adsorption studies. Each shaker can accommodate eighteen, 250 ml, Erlenmeyer flasks. The mixing conditions can also be adjusted by changing the oscillation speed.

8) pH Meter

A Fisher Accumet Model 230 pH/ION meter was used for all pH determinations. The same instrument along with a specific ion electrode was also used during the continuous runs, for the determinations of sulfide concentrations.

3.1.3 Procedures

a) Residual Organics Solution Preparation

First a mixed liquor sample was withdrawn from the activated sludge reactor. The sample was analysed for Phenol according to Standard Methods (1971). Since Phenol was still present in the solution, the sample was kept aerated separately and the Phenol concentration was monitored. When the Phenol concentration dropped to zero, the mixed liquor sample was centrifuged at 10000 G for 20 minutes to separate most of the bacteria.

The supernatant of the centrifugation was filtered through 0.45 μ Sartorius membrane filters. Each filter before use was washed with 250 ml of distilled, deionized water, and the first 20 ml of filtrate were discarded. This way, no change in the composition of the solution occurred, due to either leaching of organics from the filters or adsorption of organics on the filters (Hals, 1974).

After the filtration, the Phenol concentration of the filtrate was checked again and then the Total Organic Carbon of the filtrate was determined by the use of the Beckman Carbon Analyser. The T.O.C. of the sample was usually low (around 18 mg/l) and it was decided to increase this concentration to improve the accuracy of the isotherm tests through the use of the rotating flask evaporator.

Low temperature and reduced pressure (35°C and 50 torr) were applied resulting in a minimum alteration of the chemical composition of the solution (Brownstein and Murphy, 1972). During the increase of the concentration, no precipitate was formed. The initial pH of the residual organics solution was 3 and because the continuous runs would be performed at neutral pH, the residual organics solution was neutralized with NaOH. During the neutralization a precipitate was formed, and the T.O.C. dropped 30%. It was decided to perform two sets of batch tests, one on the original acidic pH and one after neutralization filtration and reconcentration. The solutions were stored at 4 °C.

b) Adsorbants Preparation

Each adsorbant was washed according to the instructions provided by the manufacturer. Absolute methanol was used for the Amberlites and distilled water for the activated carbons.

c) Isotherm Tests

Erlenmeyer flasks of 250 ml volume along with rubber stoppers were used for the isotherm determinations. Each flask contained a different weight of the adsorbant and 50 ml of the solution carrying the residual organics. A blank containing only 50 ml of the residual organics solution was included each time to determine every possible

biological activity or unusual reaction that might result in the removal of organic carbon from the solution.

Another (in some cases, more than one) blank sample containing a known weight of the adsorbant and 50 ml of distilled water was used to determine any organic carbon that might leach out of the adsorbant to the solution.

Whenever the later phenomenon was encountered, a linear correction was used to correct the equilibrium concentration of the organic carbon in the solution after adsorption.

A 26-hour shaking time was used for all the batch studies. Kinetic control through duplicate samples proved that equilibrium had been reached, as no further change in concentration was observed after 48 hours of shaking.

At the end of the 26 hour period, the flasks were taken off the shakers and the content of each flask was filtered through a 0.45 μ Sartorius membrane. Each filter before use was washed with 250 ml of distilled deionized water in order to eliminate the leaching organic carbon. The first 20 ml of the filtrate were discarded and the rest was collected inside 50 ml test tubes. Each tube was immediately sealed with parafilm and stored at $4^{o}C$.

All the analytical methods are based on Standard Methods (1971).

3.2 Continuous Tests

3.2.1 Materials

The following materials were used:

a) Activated Carbon

Filtrasorb 400 was sieved and the -12 +14 mesh fraction was retained. This was done in an effort to have in terms of size, as uniform a population of carbon particles as possible. The uniformity of the carbon particles,was also verified by fluidizing the bed with dilution water and by retaining in the reactor only the particles that remained below the bed-water interface.

b) Phenol

Liquified Phenol of reagent grade as supplied by the Fisher Co., was used.

c) Nutrients

Ammonium Chloride and Potassium Phosphate salts were used as Nitrogen and Phosphorus sources. The nutrients solution was added to the 350 l covered feed tank. The nutrients ratio used was

$$C : N : P = 100 : 5 : 1$$

d) Gaseous Oxygen

Oxygen supplied by Liquid Air in cylinders was used to adjust the D.O. level of the influent.

3.2.2 Equipment

3.2.2.1 Pilot Plant Schematics

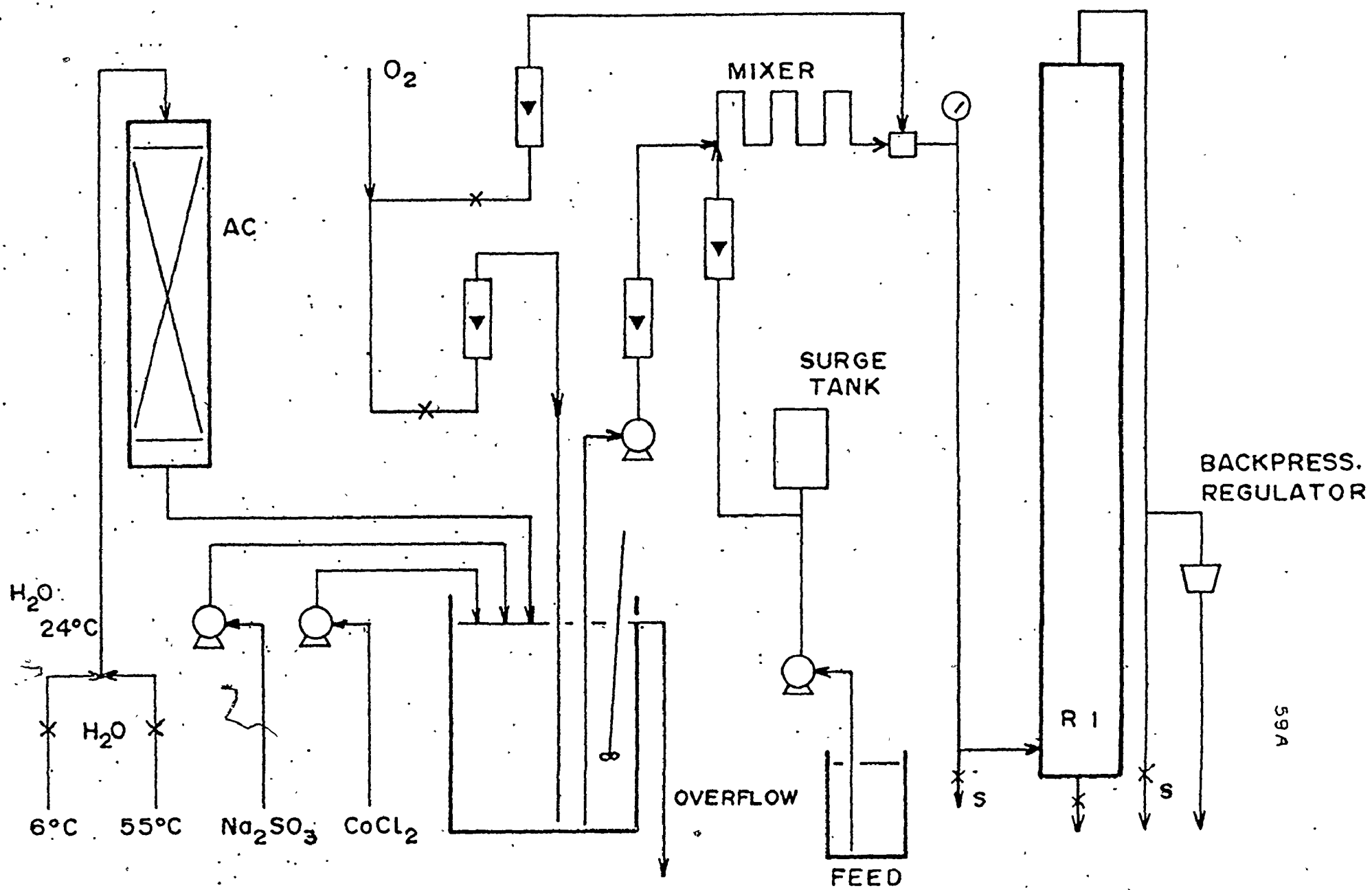
The schematics of the pilot plant are presented in Figure 3.1. It can be seen that after mixing hot and cold tap water to desired temperature, the dilution water passes through an Activated Carbon (Filtrasorb 400) column and goes to the overflow tank. The D.O. is adjusted and the dilution water is sent by the main pump to the in-line mixer, where it mixes with the concentrated feed solution. The resulting "waste" is supplied to the reactors. Two metering pumps could supply chemicals to the overflow tank. Another metering pump was supplying the concentrated feed solution.

More details on the structure of the pilot plant are available in Appendix D.

3.2.2.2 Instruments

A number of different instruments were used during the course of the continuous runs, either to monitor some parameters or to perform analysis. Again, the Beckman Carbon Analyser, the Spectrophotometer Spectronic 20, the Fisher Accumet 230 pH/ION meter, and the filtration system, that were described in 3.1.2 were used during the course of the continuous tests. The following instruments were also used during this part of the work.

Fig 3.1 Continuous Runs Experimental Set Up



1) YSI 51 Dissolved Oxygen Meter

Utilizing a probe that is actually a galvanic cell, this D.O. meter gives directly the D.O. concentration of a solution in mg/l . It was calibrated with air saturated distilled water samples of known temperature, and therefore of D.O. concentrations.

2) YSI 43-TD Telethermometer

Based on a thermocouple this telethermometer gives the temperature directly in degrees Centigrade or Farhenheit.

3) Dilution Water Pump

A Flotec RS-PI continuous rated, self-priming pump was used to supply the dilution water. The flow rate of the pump can be adjusted within a wide range of values and the flow delivered is satisfactorily constant.

4) Concentrated Feed Pump

An American Pumps, piston metering pump was used to supply the concentrated Phenol solution to an in-line mixer where it was diluted by the dilution water to create the waste of the desired strength.

5) Sulfide Specific Ion Electrode

An Orion 44-16A specific ion electrode, coupled with an Orion 9802-00 double junction reference electrode were used to monitor the presence of sulfide anions (S^{2-}) in the effluent of the system.

The presence of sulfide was used as the parameter that would indicate the presence of anaerobic conditions in the column. The selection of sulfide was made on the basis of its easy, accurate and reliable detection, and its positive association with the anaerobic activity of bacteria.

7) ARO Back Pressure Regulator

The ARO 27528-200 back pressure regulator was used at the outlet of the system, so that the whole system would always be under positive pressure with respect to the atmospheric pressure. This assured good flow through the sampling valves, regardless of the head losses through the bed or the filters.

8) Perplex 10200 Peristaltic Pump

Manufactured by L.K.B., it is a fixed flow rate pump (2 ml min^{-1}) that delivers consistent volume of liquids for long periodsof operation. It was used to supply the sulfite concentrated solution for the control of the concentration of the D.O. of the waste, before it was pumped in the reactors.

9) Sigmamotor AL-4E40, Kinetic Clamp Pump

This is a variable flow rate (0-35 ml min^{-1}) metering pump that was used to supply the $CoCl_2$ solution which acted as a catalyst in the sulfite to sulfate

oxidation reaction that controlled the D.O. of the waste stream going in the reactor.

10) Phillips PM 8010, Two Channel Recorder

This is a two channel recorder with variable voltage scale.

11) Electrolytic Respirometer

Designed and made in the Chemical Engineering Laboratories, it utilizes external recorders to register the time the electrolytic device produces Oxygen to compensate the consumption inside the 800 ml flask. A magnetic stirrer assures the uniformity and mixing of the environment inside the respirometer flask.

3.2.3 Procedure

After adjustment of the flow rates of the pumps and the preparation of the concentrated feed solution, a known mass of F-400 was put in the reactors.

Six liters of mixed liquor withdrawn from the activated sludge pilot plant, containing bacteria acclimated to Phenol were left to settle. The supernatant was removed since it contained residual T.O.C. that would exhaust the A.C. of the bed before the run would start. The settled bacteria were resuspended in dilution water, and the system was put into a closed loop operation, with this bacteria suspension for 15 minutes. Oxygen was supplied during this time.

The actual run commenced immediately after the seeding period. During the run samples of the influent and effluent were withdrawn for analysis. The flow rates were monitored every few hours. The D.O. consumption was also monitored. Each sample was immediately filtered through a 0.45 μ membrane filter. The samples were analysed for pH, Phenol concentration, T.C concentration and I.C. concentration. The height of the expanded bed (at the run flow rate) was also registered.

The determination of the concentration of Phenol in the effluent of the reactor by the direct photometric method, and the determination of the T.O.C. value of the same sample by the carbon analyser, allow the detection by difference of organics other than Phenol present in the effluent.

Seven continuous runs and a blank run were executed, at various Oxygen to Phenol ratios. The first three runs were executed at low Oxygen to Phenol ratios and the last four at high ratios. At the end of each of the last four runs, samples of the activated carbon that had formed the fluidized bed were withdrawn. The Phenol adsorption isotherm on this sample was determined. Comparison of this isotherm with the Phenol adsorption isotherm of virgin F-400 indicates whether other material had been adsorbed by the A.C. At the same time, a

respirometer study was performed on the spent carbon of the fluidized bed,to determine whether any biodegradable organics were present on the A.C. Before performing the isotherms, the excess biological growth was removed from the carbon particles. The excess growth was sheared off the carbon particles by bubbling air in a suspension of bed particles in reactor effluent,and decanting. Mercuric Chloride ($HgCl_2$) at a concentration of 33 mg/l was added to the adsorption flasks(Hals, 1975) to insure suppression of biological activity. The use of $HgCl_2$ was preferred over the use of heat,because Phenol is volatile and it may desorb from the activated carbon particles at elevated temperatures.

The exact dry weight of the carbon in the adsorption flasks was determined the same way as for XAD-4 during the batch tests (Appendix B).

Additional information on the continuous runs is given in Appendix D. Appendix C gives details on the analytical methods applied.

CHAPTER 4

RESULTS — DISCUSSION

4.1 Batch Tests

The results are summarized in Table 4.1.0 and are presented in detail in Appendix B. Table 4.1.0 presents the equilibrium concentration (Ceq mg/l) at zero loading (q = 0 mg/g), as well as the loadings at a C_{eq} of 10 mg/l and 20 mg/l.

Filtrasorb 400, an activated carbon with a specific surface area of 1200 m^2/g not only exhibited loadings at least one order of magnitude higher than the other adsorbants, but also reduced the equilibrium concentration at q = 0 mg/g to zero mg/l T.O.C. (Fig. 4.1.1) The high removal capacity of this adsorbant is due to the large specific surface area, and the low residual concentration is due to a favourable pore size distribution as well as to a surface heterogeneity that favor the adsorption of the different residual organics. Filtrasorb 400 was therefore the adsorbant that was selected for the second part of the present work, the continuous runs. The Phenol adsorption isotherm of the selected adsorbant was determined as well (Fig. 4.1.2).

All the other adsorbants showed a poorer behavior as can be seen in Table 4.1.0.Indeed, they showed high residual concentrations and low loadings.

TABLE 4.1.0

Comparison of Ceq and q Values for the Adsorbants Tested

Adsorbants	Ceq at q = 0 (mg/l)	q at Ceq = 10 (mg/i)	q at Ceq = 20 mg/l
XAD-4	23*	0*	0*
XAD-7	12, 5*	0, 0*	0.4, 1.2*
XAD-8	29*	0*	0*
IRA 458	30, 15*	0, 0*	0, 0.6*
Al_2O_3 F-1	10, 8*	0, 0.8*	1.5, 1.3*
WRL 200A	18	0	0.4
Special A	1	5	6
Filtrasorb 400	Ø	37	60

Star values refer to the original pH=3. Non star values to pH=6.7.

Ceq is the Total Organic Carbon (T.O.C) concentration of the solution after establishment of the equilibrium.

q is the loading of adsorbate per unit mass of adsorbant (mg/g).

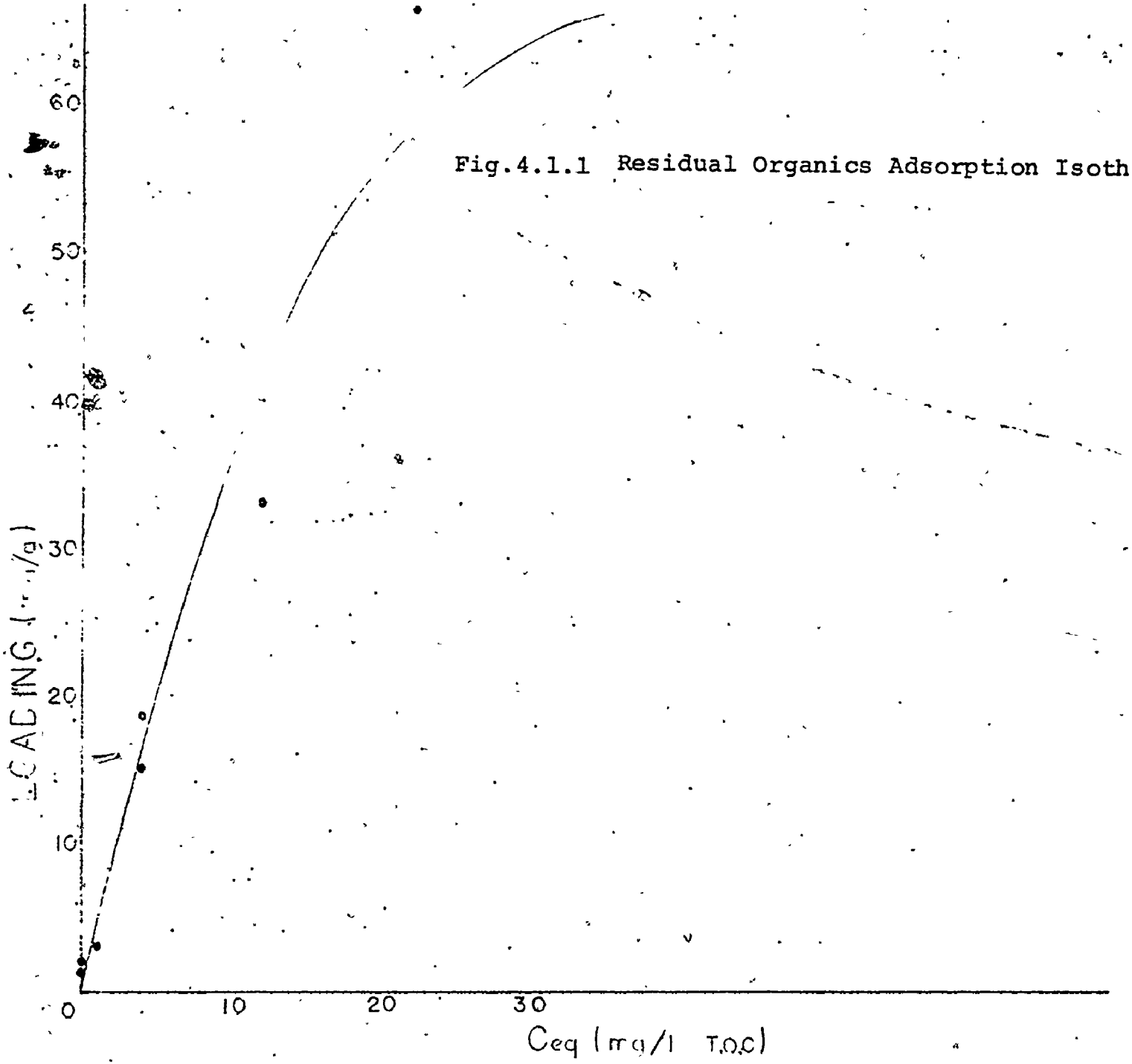
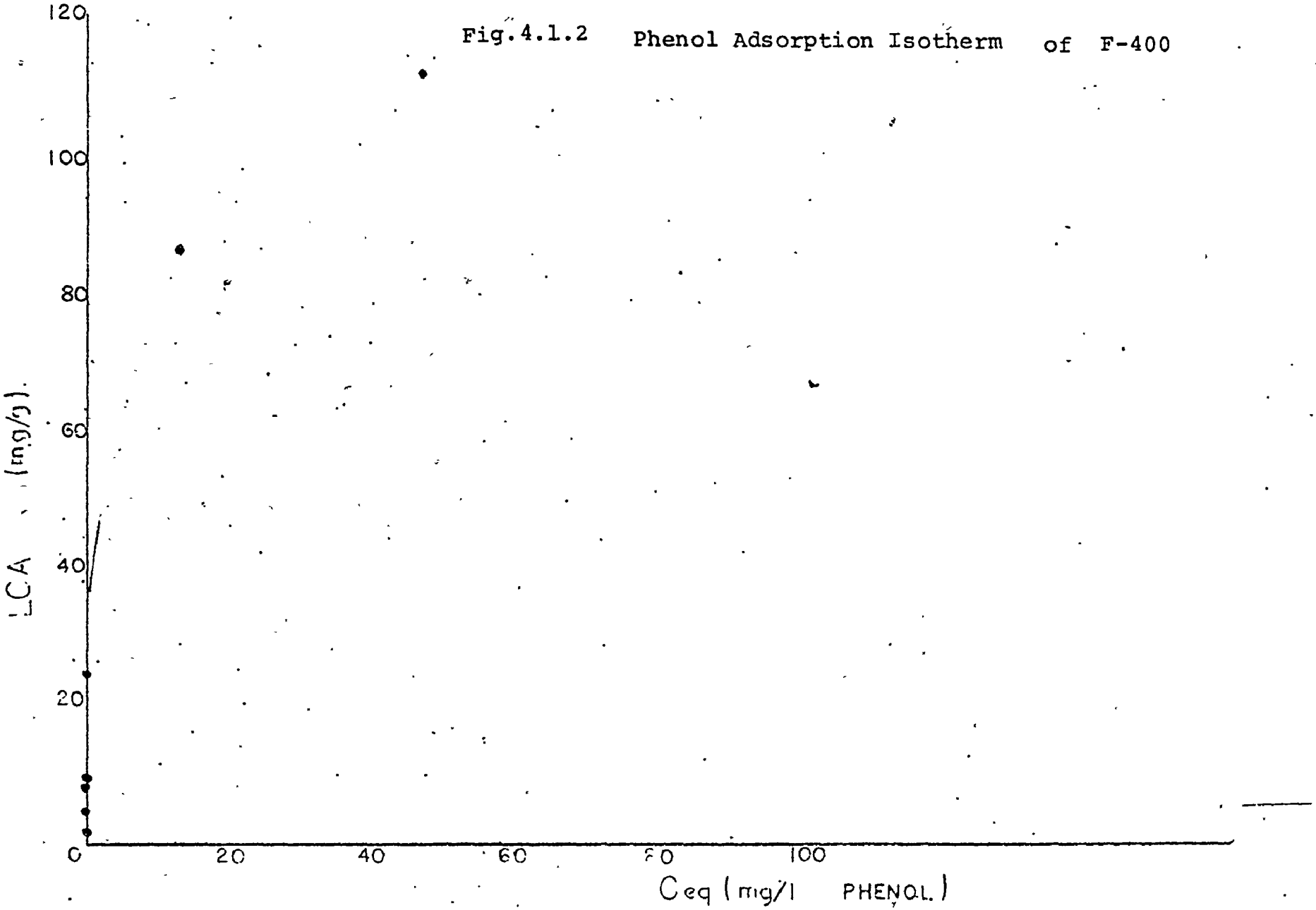


Fig.4.1.1 Residual Organics Adsorption Isotherm for F 400 at pH=6.7

Fig.4.1.2 Phenol Adsorption Isotherm of F-400



Amberlites XAD-4 and XAD-8 present unfavourable isotherms. The low dipole moment of XAD-4 is mainly responsible for this poor adsorptive behavior, since it does not favor the removal of soluble polar species that obviously (see section 2.4) predominate in terms of T.O.C contribution.

The very low specific surface area and the large average pore diameter of XAD-8 are responsible for the poor adsorptive behavior.

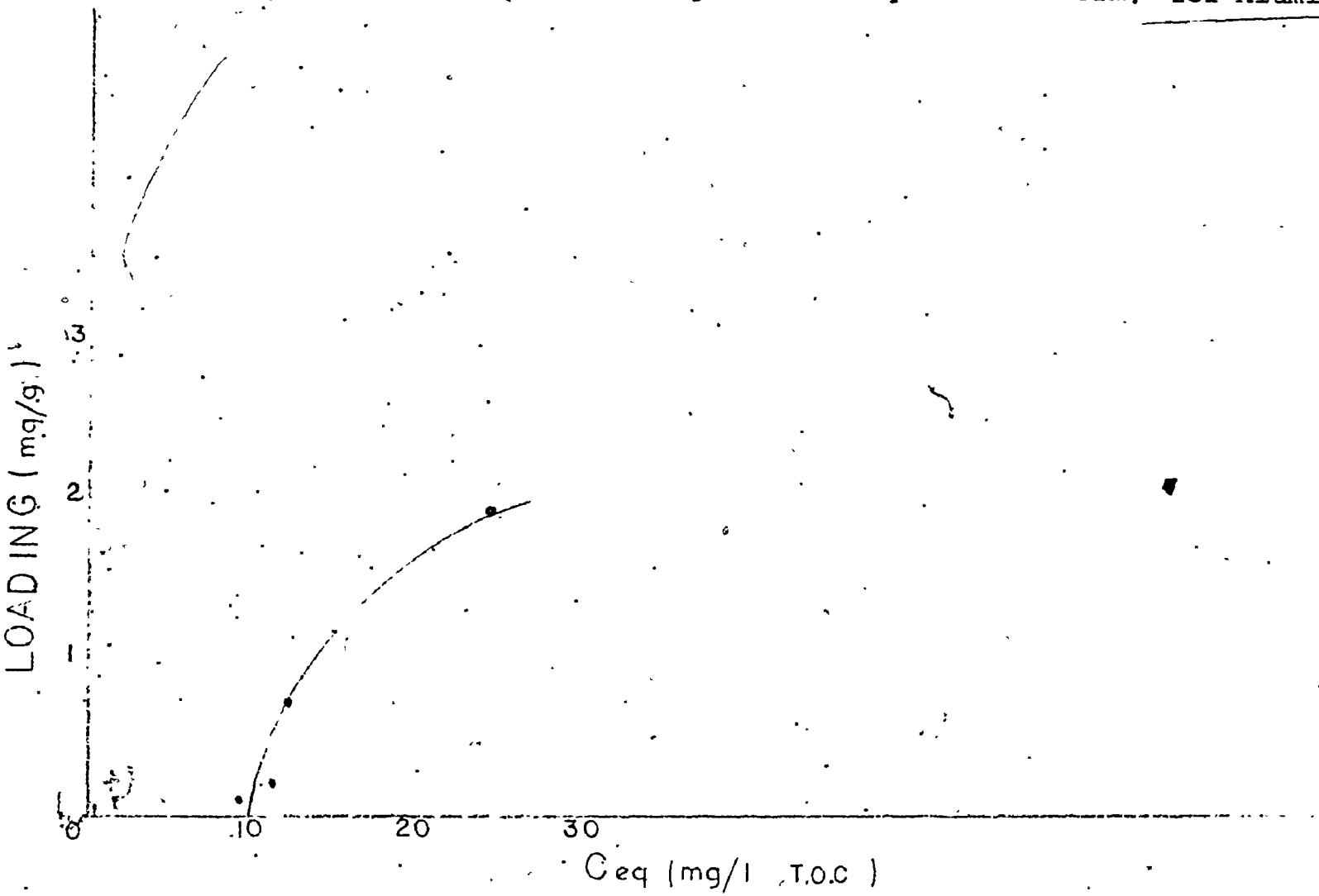
These two amberlites were not tested in a neutral pH range due to their poor apparent adsorptive potential.

XAD-7 presented a poor adsorptive capacity as well. Activated Alumina F-1 did not reduce the equilibrium concentration below 8-10 mg/l T.O.C. (Fig.4.1.3) For this particular adsorbant, an acid-base neutralization reaction can be the removal mechanism. This is supported by the fact that Al_2O_3 is an amphoteric molecule that forms Aluminum Hydroxide. In the presence of water it hydrates:

$$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3$$

This molecule can act as a base in the presence of acids, with three ionizable OH groups, or as an acid (H_3AlO_3) in the presence of bases. Due to the high affinity of the Activated Alumina for water the hydration and therefore the conversion of the oxide to hydroxide of , at least , the surface of the particles used in the

Fig.4.1.3 Residual Organics Adsorption Isotherm for Alumina at pH=6.7



adsorption studies is probable. This means that a very alkaline surface area contacted the solution of residual organics with the potential of precipitating by reaction organic anions on the Alumina particles.

The pH of the blank Alumina samples (9.2 to 9.6) as well as the pH change of the solution after contact with Alumina F-1 support this idea. (Appendix B.)

Although a large part of residual T.O.C. has been identified as originating from acidic components (see section 2.4), both anion exchange resins: IRA 458 and WRL 200A, exhibited very poor removals with high equilibrium residual concentrations at $q = 0$. This is probably due to unfavorable distribution factors and exchange coefficients among the fixed anions on the resins and the counterions in the residual organics solution.

Special A, an activated carbon with 75 A^{o} average pore diameter exhibited poor removal too. The very low specific surface area (91 m^2/g) is mainly responsible for this behavior. At $q = 0$ the equilibrium concentration was about 1 mg/1 T.O.C .

The effect of the PH of the solution on the isotherm was not significant.

CONTINUOUS RUNS RESULTS

4.2.1 General Comments

4.2.1.1 Parameter Selection

Table 4.2.1 gives an overall presentation of the seven continuous runs that were executed and gives the average values of the main parameters that characterize them.

Average influent Phenol concentration is somewhat different for each of the seven runs, yet they can be grouped into three concentration ranges: 50-56 mg/l, 15-18 mg/l and 34-35 mg/l ,with at least two continuous runs in each concentration range.

The 50-56 mg/l range of influent Phenol concentration was used in the first continuous runs. The selection was based on the fact that the response of the system to the influent Phenol concentration was still unknown, and such a value would indicate the need for stronger or weaker waste. The need to monitor Oxygen consumption necessitated predissolving Oxygen in the feed instead of direct addition to the reactor of gaseous Oxygen. The use of D.O. in turn limits the Oxygen supply ratio. The results of Run # 1 (R1), an early trial run, indicated that:

(a) The Dissolved Oxygen level in the influent should be increased, above the equilibrium value at the operating temperature (24°C). Such an increase would increase the Oxygen (in) to Phenol (in) ratio without the need for very low influent Phenol concentration. Such an increase had to be done through the use of pure gaseous Oxygen and a special system that insured Oxygen dissolution. (Appendix D1)

(b) Good biological growth could not be achieved in reactor 2 due mainly to Oxygen limitation. Therefore the second reactor was eliminated.

(c) The length of each continuous run depends on the height of the reactor available to the fluidized bed for expansion. The height available to the fluidized bed in the first reactor was insufficient. Thus it was decided to use less activated carbon (Lo) in each run, increase the column length by two feet and reduce the flow of the waste.

(d) A precipitate, believed to be a Calcium-Phosphate, was observed in the feed lines. The high concentration of nutrients, at the ratios of :

C : N : P = 100 : 20 : 5

was chosen mainly to insure buffering. In view of the precipitate formation, however, this ratio was reduced to

C : N : P = 100 : 5 : 1

in accordance with biological requirements (see section 2.3). The subsequent runs relied on the natural buffering capacity of dilution tap water (alkalinity = 100 mg/l as $CaCO_3$) (Stumm & Morgan ,1970)

The frequent feed interruptions during R1 due to precipitate formation practically limited its use to the indications noted above. No further processing of the acquired data was feasible.

The level of dissolved oxygen supply ranged from severe Oxygen deficiency (R3 anaerobic conditions) to oxygen in excess of the required (R5). Dissolved Oxygen concentrations below the equilibrium value were achieved (R3) by adding stoichiometrically to the dilution water Sodium Sulfite. The reaction is:

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-}$$

Table 4.2.1

Main Parameters of Continuous Runs

Run	Phenolin mg/l	TOC in mg/l	DO in mg/l	Carbon mass-g	L^{o}- cm	Q -l/min	Superficial Velocity cm/min.
1	56	43	11.5	1727	57.0	2.5	30.8
2	56	43	10-14.4	1246	10.5	2.5	30.8
3	50	37	18-4.5	835	10.3	2	24.7
4	15	11.5	17-27	800	13.8	2	24.7
5	18	12	26-38	800	13.5	2	24.7
6	35	27	42	802	13.5	2	24.7
7	34	26	39-45	800	13.5	2	24.7

The addition of $CoCl_2$ to the level of 1 mg/l was necessary to accelerate the kinetics of the above reaction, and to assure constant level of dissolved Oxygen supply.

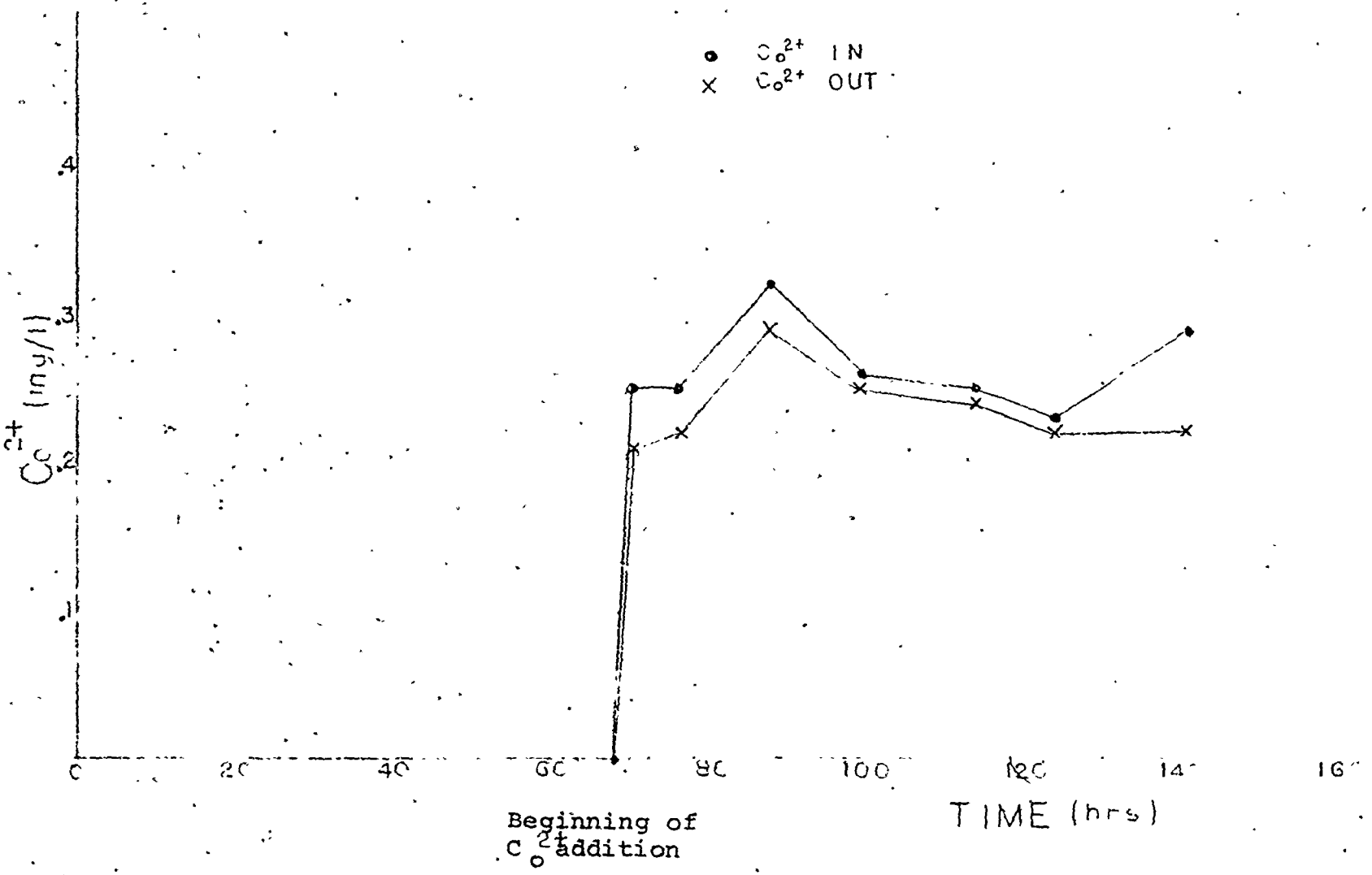
Each continuous run was stopped when the fluidized bed had expanded more than the available height inside the reactor, and started washing out along with the effluent. The wash-out phenomenon resulted from the increase of biological film thickness around the activated carbon particles, which resulted in a decrease of the average particle density. Hence the degree of fluidization, or apparent bed height, increased, until the column height was reached and wash out occurred.

Tables D.2.1 to D.2.7 in Appendix D2 summarize the main volume of data accumulated during the continuous runs.

4.2.1.2 The Use of S^{2-} as a Parameter for the Detection of Anaerobic Activity

Analysis of influent and effluent samples of R3 revealed a drop of Co^{2+} concentration across the fluidized bed (Fig. 4.2.1). Both adsorption of Co^{2+} on activated carbon (Netzer-Norman , 1972) and biological sulfide precipitations of heavy metals in anaerobic columns (Maruyama et al, 1974) have been reported in the literature.

Fig.4:2.1 C_o^{2+} Concentration Variation with Time . Run 3



Samples of bed particles (0.8g) were digested with 50 ml of concentrated HCl, and the filtrate was analyzed for Co^{2+} and S^{2-}. On the average 40 mg/l Co^{2+} and S^{2-} above the range of the specific probe (O,IM) were detected. These data support the hypothesis that precipitation of Co^{2+} by biologically generated sulfide, occurred inside the biological films. The precipitation of CoS explains the fact that S^{2-} was not detected in third run's effluent despite the fact that as early as t = 80 hrs, the biological growth macroscopically had changed to the characteristic black colour of anaerobic growth and the influent D.O. was reduced to 4.5 ppm. Sulfide, therefore, cannot be considered as a reliable parameter for the detection of anaerobic biological activity inside a contact column in the presence of heavy metals.

4.2.2 Fate of Residual Organics

Table 4.2.2 compares the effluent's organic carbon concentration (T.O.C.) and organic carbon from Phenol (O.C.P.). A difference between T.O.C. and O.C.P. indicates the presence of residual organics.

The effluent T.O.C. and O.C.P. as shown in Table 4.2.2 correspond within the experimental accuracy (Appendix C) of analytical methods applied.

Table 4.2,2

Effluent Parameters for Residual Organics Detection

Run #	Average Phenol Out mg/l	Average O.C.P. Out mg/l	Average T.O.C. Out mg/l	Average Residual Organic Carbon mg/l	Average pH of Influent	Average pH of Effluent
1	33	25	25	None Detected	7.8	7.8
2	45	34	34	None Detected	7.5	7.5
3	43	33	33	None Detected	7.4	7.4
4	5	4	4	None Detected	7.4	7.4
5	4	3	3	None Detected	7.4	7.4
6	16	12	12	None Detected	7.5	7.5
7	13	10	10	None Detected	7.5	7.5

The numbers shown in Table 4.2.2 are the closest integers (as shown in Appendix C, experimental accuracy is $\pm$ 1 mg/l) to the calculated average values. The residual organic molecules produced during the metabolic activity of the biota therefore had been adsorbed by the activated carbon particles that supported the growth. This is supported also by the work of Holladay et al (1976) who degraded Phenol in a fluidized coal bed bioreactor and observed the residual non-Phenol T.O.C. in the effluent, and pH instability. Both these facts indicate that residual organics were formed in their system and therefore are probably formed in the present system.

In the present system, the substitution of an activated carbon for coal explains the lack of these compounds in the effluent. The pH stability experienced in the present work (Table 4.2.2) is also attributed to the adsorption of residual organic molecules.

The presence of residual organics on the activated carbon particles was also verified indirectly through Phenol adsorption isotherms performed on the spent carbon showing biological growth. Samples of spent carbon were withdrawn at the end of the run. Details on the determination of the adsorption isotherms on the spent activated carbon particles

are available in Appendix D4. These isotherms are graphically presented in Appendix D4 in Fig. D4.1 to D.4.4. All the isotherms showed Phenol loadings lower than the loadings of the virgin activated carbon, thus supporting the hypothesis that part of the adsorption capacity of the activated carbon had been exhausted by the residual organics. The data from R4 and R5 are the most indicative ones, as no biodegradable organics (Phenol) were detected on the spent activated carbon (no Oxygen consumption in the respirometer, see Appendix D2), yet lower Phenol loadings were observed through the isotherms. The same applies for R6 and R7 where the Phenol being adsorbed on the carbon particles by the end of each run, (verified by the respirometer and the Phenol mass balances), plus the Phenol that was uptaken during the isotherm determination, resulted in total Phenol loadings somewhat lower than the virgin carbon.

The behavior of Phenol, T.O.C. and O.C.P. and D.O. (Dissolved Oxygen consumption) with time is presented separately for each run in Appendix D.2 and in Figures D.2.1 to D.2.7.

The adsorption of residual organics was not affected by the level of Dissolved Oxygen available to biological growth. Figure 4.2.2 refers to R3 where after t=66 hrs

anaerobic conditions prevailed (Table D.2.3). Figure 4.2.3 refers to Run 5 where Oxygen in excess of the required was supplied (Table D.2.5). Both figures show very good correlation of T.O.C. (out) and O.C.P. (out) values, and, therefore, indicate equally good residual organics removal regardless of the level of the Dissolved Oxygen supply.

Analysis of the feed dilution water showed that no detectable T.O.C. was contributed (due to pre-treatment, see section 3.2.1) by it, and therefore it did not interfere with the results.

At the end of seventh run the supply of Phenol was stopped and the run was continued with only water and D.O. as feed. No organic carbon was detected in the effluent as shown in Table 4.2.3. Thus adsorbed residual organics are either held irreversibly, or their desorption is below the detactable concentration limit. The Dissolved Oxygen consumption was probably due to the biological oxidation of previously adsorbed Phenol and to the endogenous respiration (autooxidation) of the declining biomass. Soon after the Phenol supply was stopped, the bed started contracting, thus showing a decrease in the average particle diameter, or biofilm thickness. Below a bed height of 120 cm, chanelling appeared in the reactor. The particles adhered together, the biomass serving as the adhesive

Table 4.2.3

Desorption Control Run

Time Hrs.	D.O. In mg/l	D.O. Out mg/l	Phenol In mg/l	Phenol Out mg/l	O.C.P. In mg/l	O.C.P. Out mg/l	T.O.C. In mg/l	T.O.C. Out mg/l	pH In	pH Out	D.O. mg/l	Temp. °C
29.5	41	11.5	0	0	0	0	0	0	7.3	7.3	29.5	24
27.	41	14.	0	0	0	0	0	0	7.3	7.3	27.	24
19.7	38.3	18.6	0	0	0	0	0	0	7.3	7.3	19.7	24
22.	39	17.	0	0	0	0	0	1	7.3	7.3	22.	24
19.	39	20.	0	0	0	0	0	0	7.3	7.3	19.	24
16.	39	23.	0	0	0	0	0	0	7.3	7.3	16.	24

Fig.4.2.2 Effluent T.O.C. and O.C.P. Variation with Time . Run 3

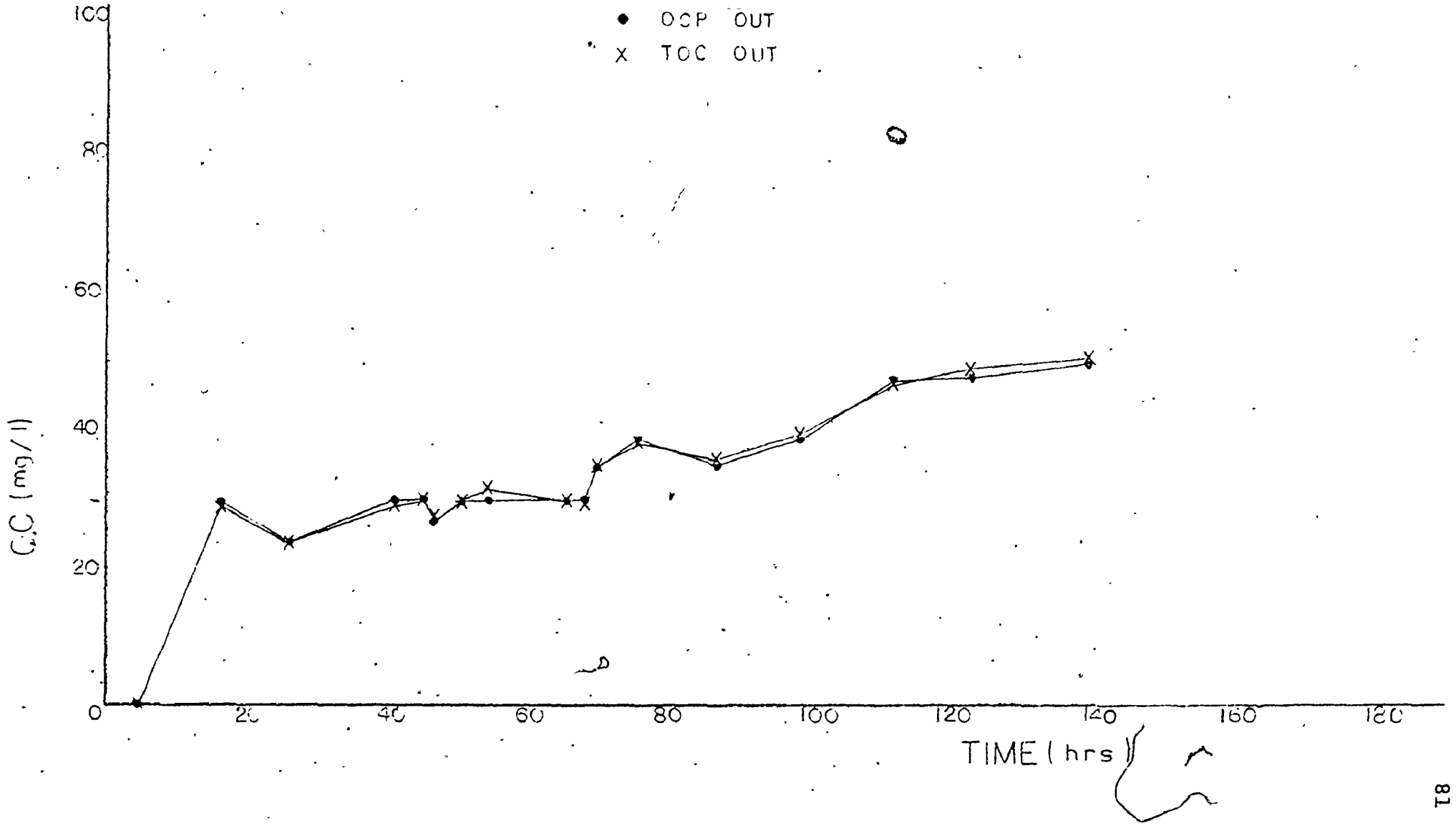
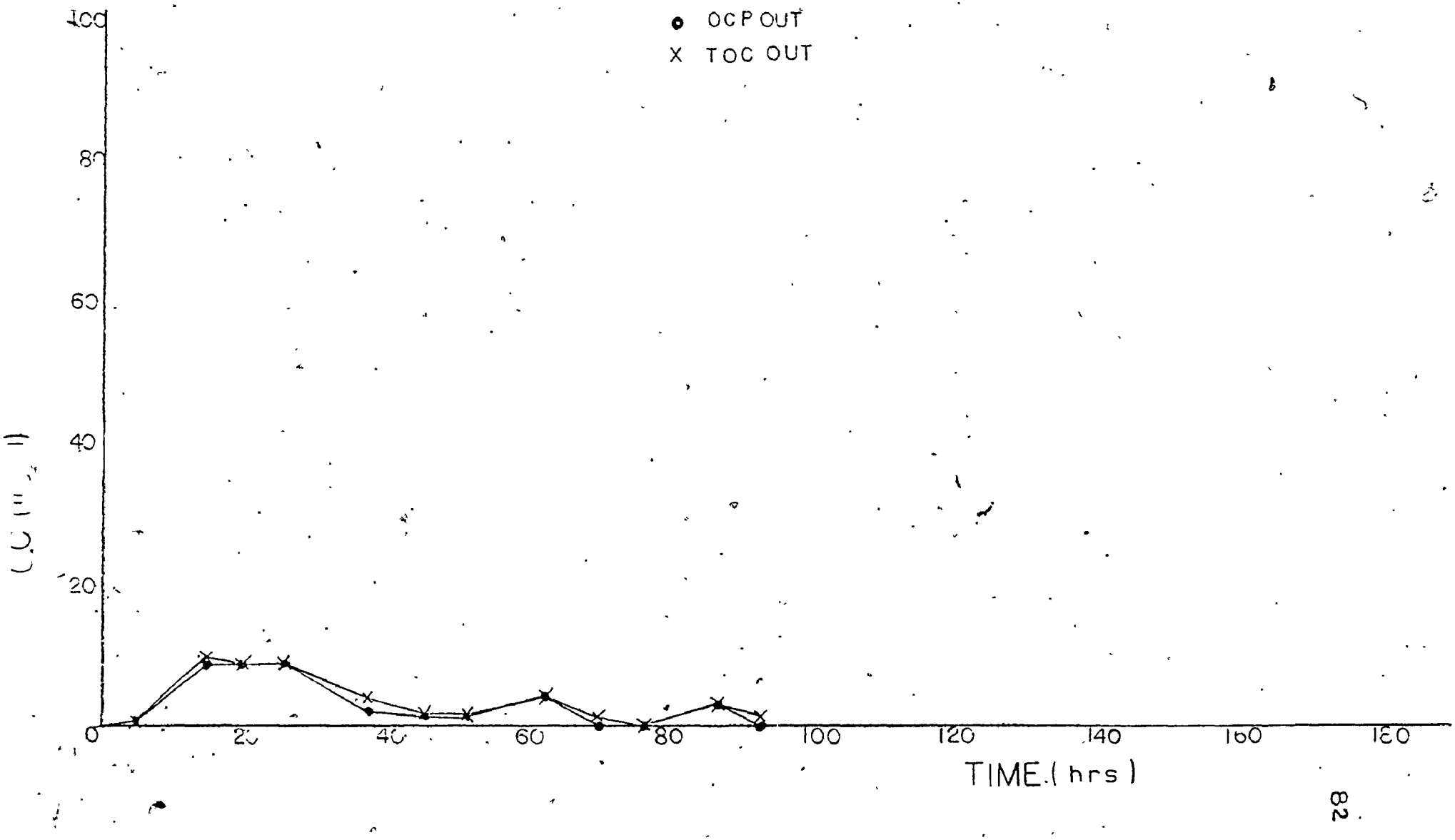


Fig.4.2.3 Effluent T.O.C. and O.C.P. Variation With Time , Run 5



medium, and the fluidized state of the bed ceased to exist. At that point the control run was discontinued.

4.2.3 Fate of Removed Phenol

4.2.3.1 Phenol Mass Balances

Mass balances for Phenol, across the reactor, are summarized in Table 4.2.4. They have the following general form:

(TOTAL PHENOL IN) - (TOTAL PHENOL OUT) = (TOTAL ACCUMULATED PHENOL) + (TOTAL BIODEGRADED PHENOL)

Total Phenol in and out, were calculated by using the average concentration and the absolute time between two samplings in the following way:

(TOTAL PHENOL)(IN OR OUT) = FLOW X TIME X AVERAGE CONCENTRATION (IN OR OUT)

The use of the average concentration between two samplings probably introduces an error as we do not know the exact behavior of concentration in between the two samplings. This approximation would be possible to avoid only if there were on line analytical equipment, monitoring continously in and out Phenol concentrations. Such an experimental set-up was not possible during the present work.

Table 4.2.4

Phenol Mass Balances

Run Number	Total Removed Phenol (g)	Total Biodegraded Phenol (g)	Total Phenol (g) Adsorbed on Part of Bed with Growth (by difference)	Total Phenol (g) Adsorbed on Part of Bed with Growth (by Respirometer)
2	124.4	113.2	10.2	--
3	127	86.9	40.2	--
4	160	160	0	0
5	151	151	0	0
6	236	189	47	42
7	180	152	28	22.3

The biodegraded mass of Phenol was evaluated through the Oxygen consumption values neglecting endogenous respiration (see section 4.2.3.1). It was assumed that since Phenol is an easily and completely biodegradable molecule, the Oxygen requirement for its biodegradation in the reactor is equal to the plateau of the BOD curve (Busch, 1971 Hals , 1974). This equivalent is 1.7 mg Oxygen per mg of biologically degraded Phenol (Hals , 1974).

Calculation of removed and biodegraded Phenol, allowed by difference the evaluation of adsorbed (accumulated) Phenol inside the reactor. The accumulated Phenol amounts were checked (for the last 4 runs) through respirometer studies, on the spent carbon. Details of the respirometer studies are available in Appendix D2. As part of the bed did not develop biological growth (Appendix D3) the values of accumulated Phenol given in Table 4.2.4 refer to the part of the bed that developed growth. Details on the evaluation of the mass balances are available in Appendix D2).

As Table 4.2.4 shows, the part of the bed that developed biological growth was by the end of the run biologically "regenerated" in terms of adsorbed Phenol. The results of the mass balances indicate that whenever the system was not oxygen limited (R4 and R5) the bioxidation

rate of Phenol was higher than the supply rate of substrate. That is why by the end of R4 and R5 the effluent concentration of Phenol was zero, and Phenol that was previously adsorbed (before the establishment of biological activity) during the first hours of operation had been biodegraded as well. The above results point out the fact that (in the case of no Oxygen or nutrient limitation) the adsorption capacity of the bed support medium can be considered available to the residual organics without competition from the substrate.

4.2.3.2 Mechanisms of Phenol Removal

Figures D.2.8 to D.2.14 in Appendix D2 present graphically the percent removal of Phenol as a function of time, for each one of the continuous runs. All removal curves present a common characteristic. The removal at the beginning of each run is 100%. It starts dropping quickly, reaches a minimum value, and then starts increasing again, depending on the level of available Dissolved Oxygen.

This common behavior of removal values leads to the hypothesis that two distinct mechanisms of Phenol removal operate in the reactor:

(a) during the first hours of operation, while biological growth has not developed yet inside the reactor, removal is due to the adsorption of Phenol on activated carbon. Therefore, the part of the removal curve that refers to the first hours of operation, is in the form of an adsorption breakthrough curve. This mechanism explains the complete (100%) Phenol removal observed at the beginning of all runs.

(b) As Phenol breaks through the bed, the biological population of the reactor starts developing on the activated carbon particles and starts utilizing Phenol as a substrate. Biological removal of Phenol takes place. The rate of growth of the biological population, and consequently the rate of biological degradation of Phenol, depend on the level of terminal electron acceptor available (D.O.). Whenever Dissolved Oxygen was not limiting (R5), biological oxidation replaced adsorption in a short period of time, and a low minimum removal value, (as the ones observed in

all other runs: R2, R4, R6, R7) was not experienced. On the other hand in the case of R3 where anaerobic conditions were imposed, removal due to bioxidation remained very low, proportional to the level of Dissolved Oxygen available, and overall Phenol removal never increased during the run. Phenol removal observed at the later stages of each run, was believed to be the result of biological oxidation. This hypothesis is also supported by the following facts:

(i) Phenol removed during the late stages of each run was proportional to the Dissolved Oxygen consumption. This proportionality is expressed by the ratio (ΔO.C.P.)/ (ΔD.O.) = K, which is approximately constant with respect to time. Values of K versus time are plotted in Figures D2.9 D2.14 in Appendix D2. Figure 4.2.6 that follows is a simultaneous plotting of K values for all continuous runs except the anaerobic run R3.

Figures 4.2.4 and 4.2.5 that follow are two samples of cumulative plots of cumulative removed T.O.C per gram of carbon versus cumulative applied T.O.C per gram of carbon.The slope of the curve is the average T.O.C removal.Figure 4.2.4 refers to R3 (Oxygen limited) and it can be seen that the

Fig.4.2.4 Cumulative Plotting of Removed Versus Applied TOC . Run 3

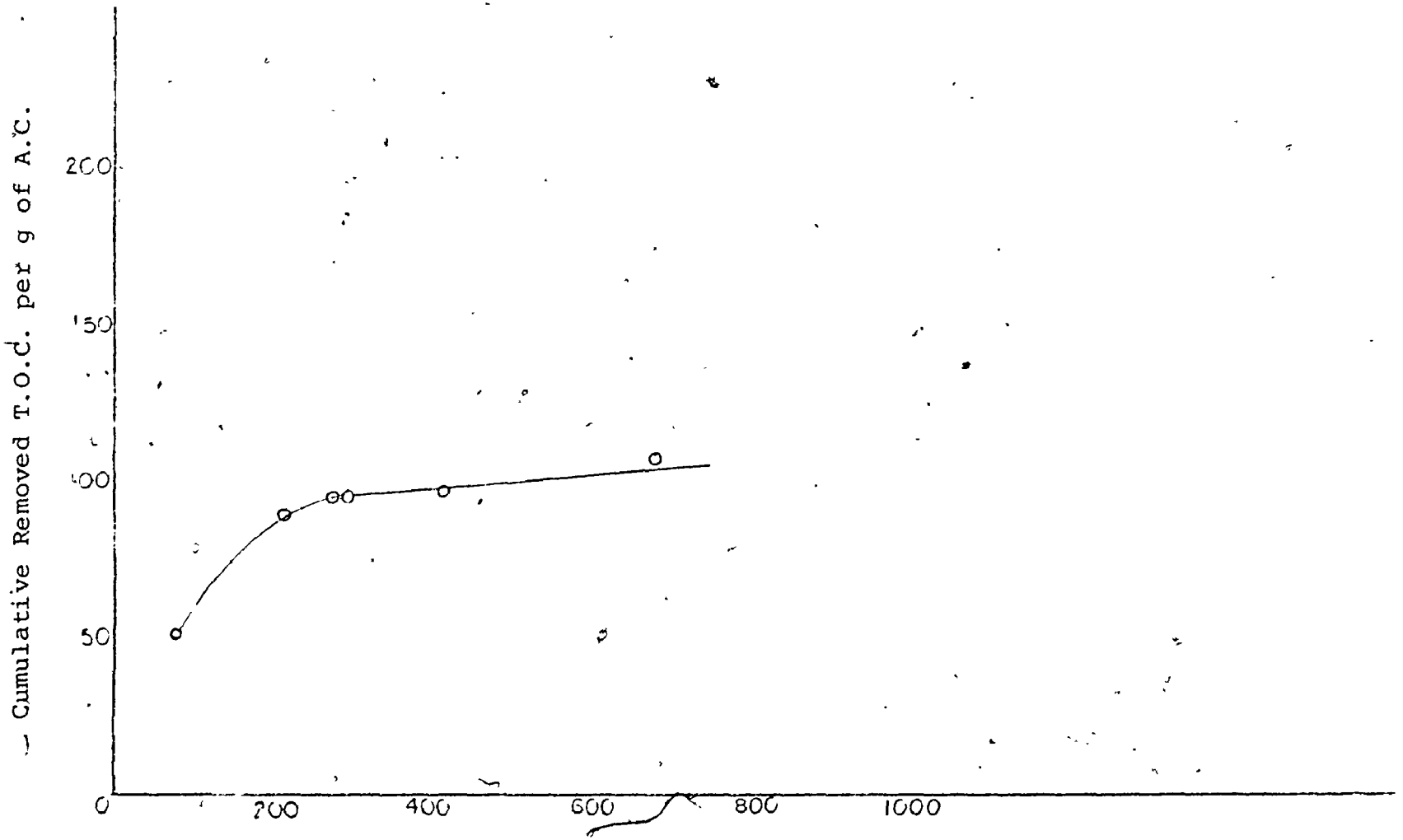


Fig.4.2.5 Cumulative Plotting of Removed Versus Applied TOC . Run 4

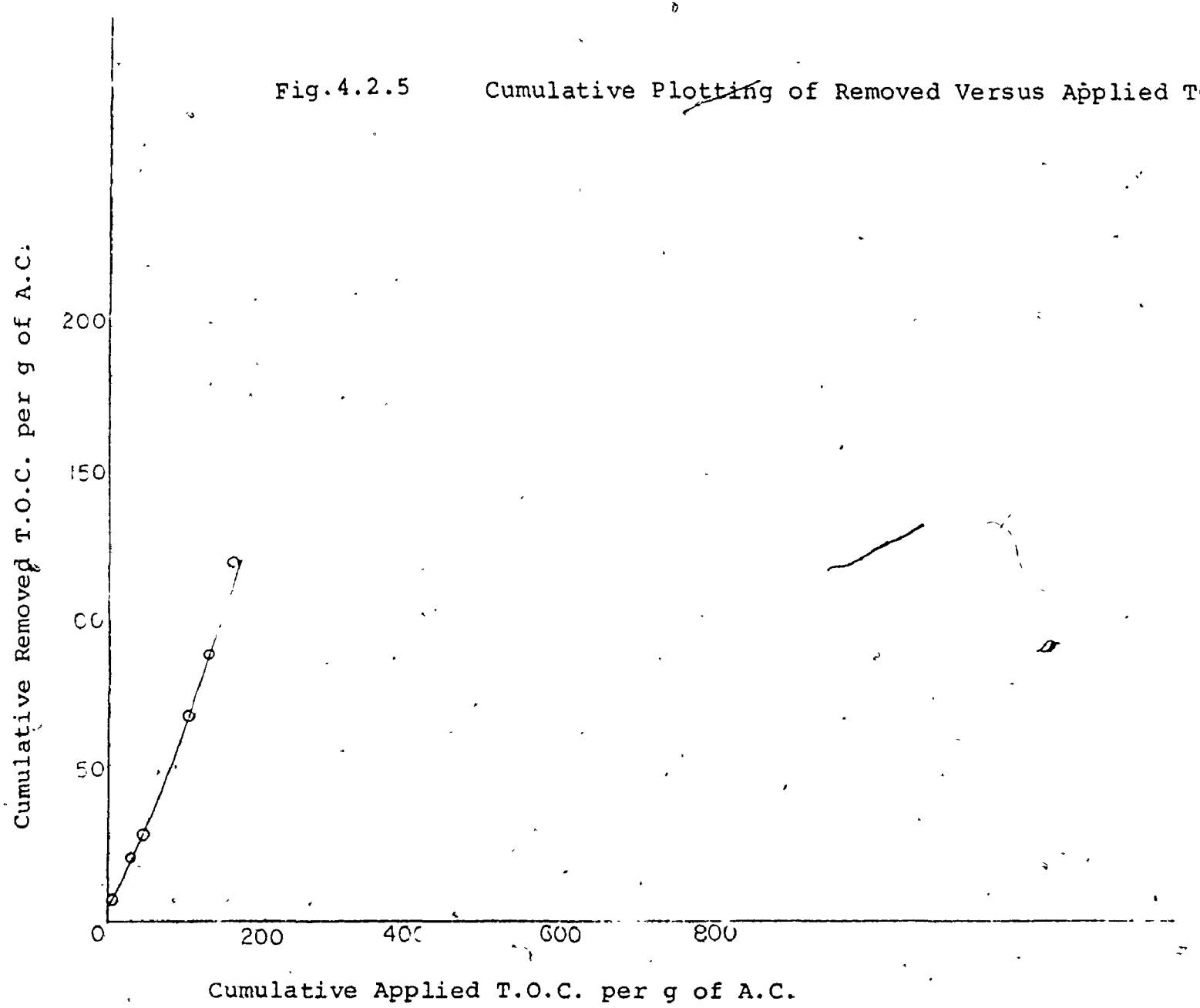
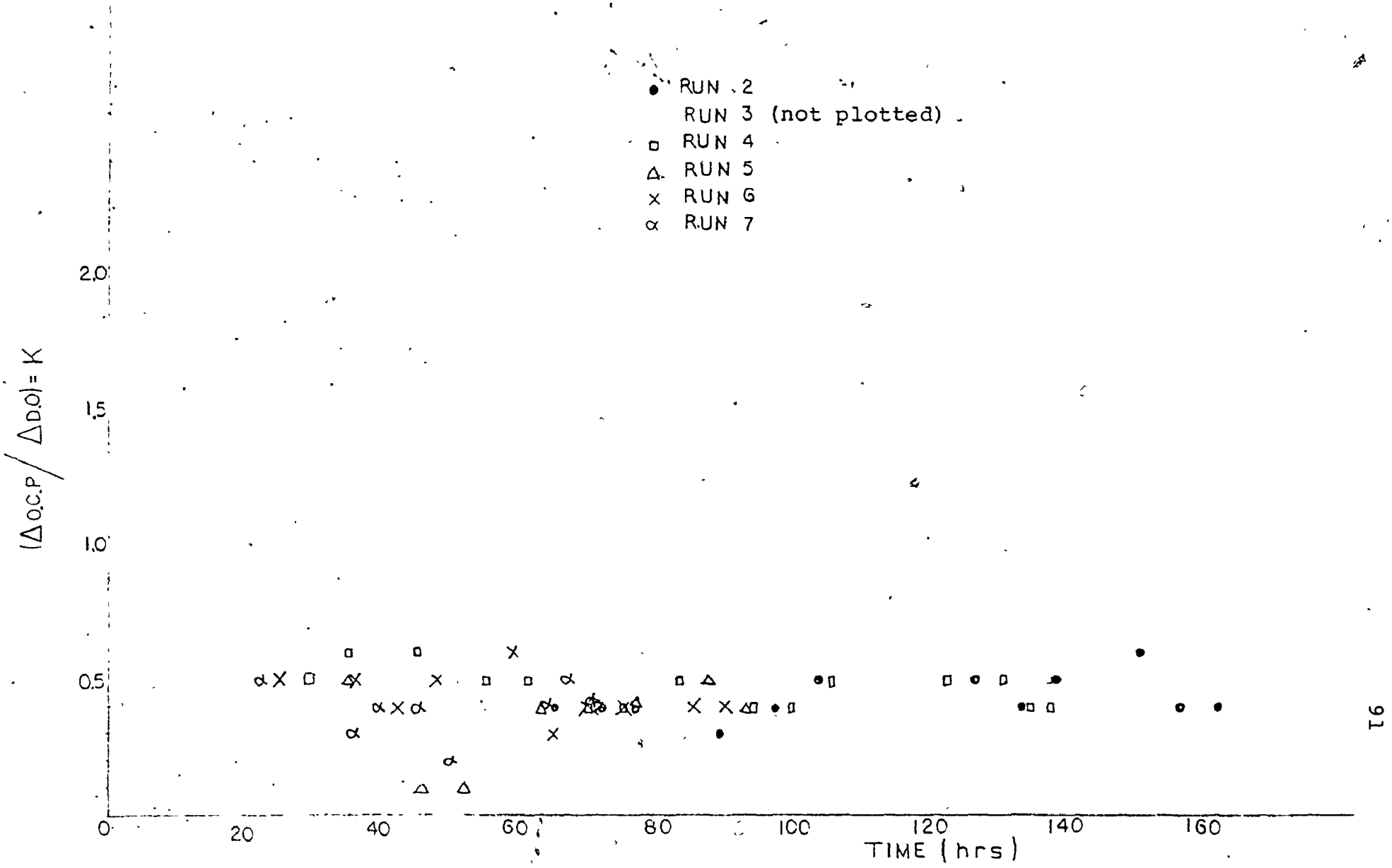


Fig.4.2.6 Simultaneous Plotting of △OCP / △DO=K for all Continuous Runs



quick establishment of good growth results in a change of removal during the run, and smooth transition from adsorptive (high) removal to biological (low) removal. Such change is not observed in other runs due mainly to higher biological removal rates. Additional plots for the rest of the runs are available in Appendix D2 (Fig. D2.15 to Fig. D2.18). The data of the cumulative curves are summarized in Table D.2.13 in Appendix D.2. The constant value of the ratio $(\triangle O.C.P.) / (\triangle D.O.) = K$ is significant as it also indicates that the endogenous respiration rate of the biological mass, in state of dynamic growth, can be, as an approximation, neglected.

Normally, Oxygen requirements are described by the following equation:

$$\frac{dCO_2}{dt} = a' \times \frac{dCs}{dt} + b' \times Cb \qquad (17)$$

Where dCO_2/dt = rate of Oxygen consumption

dCs/dt = rate of substrate removal

Cb = concentration of biomass

Rewriting equation 17 with the symbols used in the continuous runs, we obtain:

$$\frac{\Delta DO}{\Delta t} = a' \times \frac{\Delta O.C.P.}{\Delta t} + b' \times Cb \qquad (18)$$

But:

$$\frac{\Delta O.C.P.}{\Delta D.O.} = K \quad \text{or} \qquad (19)$$

$$\frac{\Delta D.O.}{\Delta t} = \frac{1}{K} \times \frac{\Delta O.C.P.}{\Delta t} \qquad (20)$$

Combining equations 18 and 20

$$a' = 1/K \qquad (21)$$

$$b' \simeq 0 \qquad (22)$$

4.2.4 Bioreaction Rates

Table 4.25 that follows summarizes the observed bioreaction rates in terms of specific T.O.C. removal rates. The last part of each run when biological growth was well developed and pseudo steady state was reached, has been used for the calculations. Comparing the values of Table 4.5 with rates reported in literature (see Section 2.6) we see that the T.O.C. removal rates experienced during the present work are at least one order of magnitude higher. These higher rates are probably due to the easily biodegradable low molecular weight substrate, as well as the supply of Oxygen, which was

Table 4.2.5

Specific TOC Removal Rates During Pseudo Steady State for Continuous Runs

Run	Period of Run (hrs)	Total Carbon Surface Area with Growth (cm^2)	TOC Removed in Time Period (g)	Specific Bioreaction Rate g TOC / s. cm^2
2	132.5-161	10040	29.4	2.8×10^{-8}
3	112.5-140	9407	1.26	1.3×10^{-9} *
4	122-137	9542	21.6	4.2×10^{-8}
5	71-93	9542	44.0	5.8×10^{-8}
6	70-89	18952	38.9	3.0×10^{-8}
7	63-69	19853	12.6	5.0×10^{-8}

* Anaerobic Conditions.

very low in other studies reported in literature. In support of the above hypothesis comes the fact that R3 that was severely Oxygen limited, presented specific T.O.C. removal rate one order of magnitude lower than the other runs.

The highest bioreaction rate was experienced at the highest Oxygen (in) to Phenol (in) ratio (R4), and the minimum bioreaction rate was experienced at the lowest Oxygen (in) to Phenol (in) ratio applied. (R3)

4.2.5 Biological Growth

4.2.5.1 General Comments

The main volume of data that refer to biological growth are tabulated in Tables D3.1 to D3.7 in Appendix D3. They present the expanded bed height (of the part of the bed that developed biological growth), L_e^t, the average particle diameter, $\bar{D}p'$, and the total hydraulically effective volume of biomass, MA, as a function of time. Only L_e^t is a measured parameter. $\bar{D}p'$ and MA have been calculated according to the method presented in section 2.7

Figures D3.2 and D3.5 show that the rate of increase of biological film diameter in R5 where a higher Oxygen (in) to Phenol (in) ratio was applied, is higher than the rate of increase of $\bar{D}p$ of R2 where a very low ratio was applied. Therefore the rate of growth is affected, as expected, by the

level of Dissolved Oxygen available to the biological population.

During R2 at t = 120 hrs (Figure D3.2), the fluidized bed started contracting, although all influent parameters were at the same level as before. This behavior was experienced again in R3 at t = 66 hrs (Figure D3.3) when the D.O. was reduced with the intention of turning the system anaerobic. Based on R3, the response of biological growth experienced in R2 is interpreted as a result of Oxygen deficiency and its effect on the density of the biological film. That is why an increase of the Dissolved Oxygen level in R2 (t=120.2 hrs) resulted in an immediate short expansion of the fluidized bed followed by the higher rate of bed expansion. Increase of the bed expansion rate with increase of Oxygen (in) to Phenol (in) ratio was also experienced in R4 at t = 120 hrs (Figure D3.4). The immediate response of the volume of the biological mass to the change of the Dissolved Oxygen (in) concentration supports the hypothesis of a change of density of the biological film according to the environmental conditions to which it is subjected; that hypothesis has also been suggested by others, e.g. Holladay et al (1976).

4.2.5.2 Quantitative Evaluation of Biological Growth

Direct evaluation of the exact dry mass of biological

growth inside a fluidized bed biological reactor is complicated when activated carbon is the supporting medium (Holladay et al, 1976).

The technique developed in the present work based on a number of assumptions listed in Section 2.7, can provide a satisfactory evaluation of the average particle diameter of the fluidized bed (including the biological film) and consequently the total hydraulically effective volume of biological growth. The accuracy of the calculated $\overline{Dp}'$ values can be verified in the following two ways:

i) $\overline{Dp}'$ values calculated at $t = 0$, when no biological films have yet developed on the activated carbon particles, should be equal to $\overline{Dp}$ (average diameter of virgin carbon particle).

ii) $\overline{Dp}'$ evaluated through the use of the system of equations for time t, can be checked with $\overline{Dp}'$ diameters measured on photographs of bed particles withdrawn from the reactor at time t. The pictures presented in Appendix D3 show particles withdrawn from the reactor at the end of each run.

Table 4.2.6 follows and summarizes the comparison of $\overline{Dp}'$ values calculated at $t = 0$, with $\overline{Dp}$ and compares $\overline{Dp}'$ values calculated for the end of each run with $\overline{Dp}'_p$ values measured from

Table 4.2.6

Calculated and "Actual" $\overline{Dp}'$ Values

Run	Calculated $\overline{Dp}'$ (cm) t = 0	Actual $\overline{Dp}$ (cm)	$\overline{Dp}'/\overline{Dp}$ (t=0)	Calculated $\overline{Dp}'$ (cm) End of Run	Actual * $\overline{Dp}'_p$ (cm) from Pictures	$\overline{Dp}'/\overline{Dp}'_p$
1	0.20	0.1545	1.25	0.32	--	—
2	0.19	0.1545	1.18	0.54	0.40	1.35 **
3	0.19	0.1545	1.18	0.52	—	--
4	0.21	0.1545	1.30	0.55	0.51	1.08
5	0.21	0.1545	1.30	0.55	0.49	1.11
6	0.21	0.1545	1.30	0.45	0.48	0.94
7	0.20	0.1545	1.25	0.43	0.43	1.00

* Average of the diameters shown in Photographs in Appendix D.3.

** Biological film not stained (hard to be seen clearly).

respective photographs.

4.2.5.3 Evaluation of Volume Yield

By plotting the cumulative removed T.O.C. per gram of activated carbon with growth (ΔT.O.C.) / (g. A.C) versus the cumulative increase in the total hydraulically effective volume of biomass per gram of activated carbon with growth (ΔMA) / (g A.C), a volume yield factor can be evaluated.

Figures D3.8 to D3.13 in Appendix D3 present the relation among ΔT.O.C / g A.C. (g/g) and ΔMA/ g A.C. (cm^3/g); Table D3.8 summarizes the plotted data. The data points on the graph can be separated into two distinct groups. The first group of data (at low values of both parameters) include the effect of adsorption on ΔT.O.C / g A.C and since good biological growth had not been established yet, MA / g A.C is low. The slope of the line that fits the first group of data is very low. The second group of data, clearly distinguished by their slope, refer to the later stages of each run, when pseudo steady state

was accomplished. The slope (W) of the (straight) line that fits these points expresses the ratio:

$$W = (\triangle MA \ / \ g\ A.C) \ / \ (\triangle T.O.C \ / \ g\ A.C) \quad \text{or}$$

$$W = (\triangle MA) \ / \ (\triangle T.O.C)$$

The units of W are cm^3/g and W expresses the increase in the hydraulically effective volume of biomass (cm^3), per gram of biologically removed (Section 4.2.3) T.O.C.

Table 4.2.7 summarizes W values for the continuous runs. The volume yield was not determined for R3, as the severe oxygen limitation resulted in low T.O.C. removal and growth.

Table 4.2.7

Volume Yield Values Observed During Continuous Runs

Run	2	3	4	5	6	7
W (cm^3/g)	0.8	-	1.3	2.0	2.1	2.9
DO (IN) mg/l	11.5	4.5	27	38	42	45

Variation of W values follows, as can be seen in Table 4.2.7 the variation of influent Dissolved Oxygen concentration. A graphic representation of the above correlation is presented in Figure 4.2.7.

The hypothesis that the variation of W values is a result of influent Dissolved Oxygen concentration variation is also supported by the observed effect of influent Dissolved Oxygen concentration on the density of the biological film (see section 4.2.5.1).

The volume yield values are independant of the T.O.C oxidized as the slope of the curve that represents the value of W, for each run, is constant (within the range studied). Calculated W values fall within the range of values from 0.8 to 2.9 cm^3 /g.

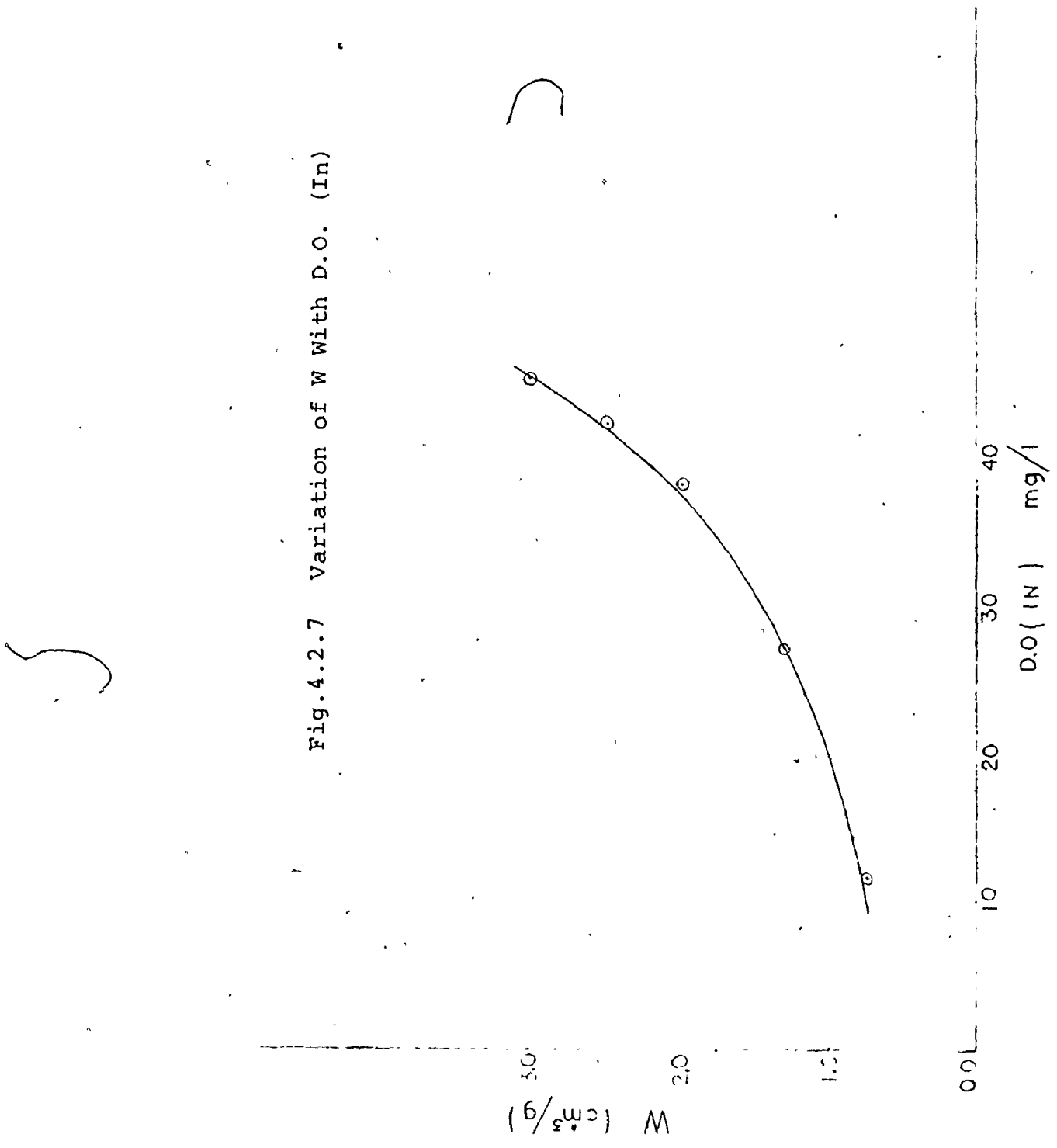


Fig.4.2.7 Variation of W With D.O. (In)

CHAPTER 5

Conclusions & Recommendations

The following conclusions can be derived from the present work:

1) Activated carbon appears to be the best adsorbant available for the adsorption of bioresidual organics.

2) The use of the proper adsorbant as the growth support medium in a fluidized bed biological reactor, results in the removal of the residual T.O.C. that is generated by the active microbial population of the reactor. The adsorption of the residual organic molecules did not exhibit dependence on the Oxygen to Phenol ratio applied.

3) The specific reaction rate was approximately 10^{-8} g T.O.C./ s cm^2 in this study. This value is an order of magnitude higher than values reported in literature.

4) It is possible to evaluate the average diameter of the particles of a fluidized bed biological reactor, and, therefore, the total volume of biological films by monitoring the height of the expanded bed in the reactor. The evaluated volume yield factor is affected by the quantity of Oxygen supplied and does not depend on the T.O.C oxidized. The calculated W values fall in the

range of 0.8 to 2.9 cm^3/g.

5) Sulfide is not always a reliable parameter for the detection of the presence of anaerobic activity in a fluidized bed biological reactor since it can be precipitated inside the biological film by heavy metals present in the waste.

It is recommended that further research on the same subject should be conducted with a system designed for continuous regeneration of part of the bed. This will enable longer runs that will allow time for the establishment of real steady state conditions.

The use of a number of different substrates (simple and complex) is suggested as well. The study of removal rates can be investigated by supplying Oxygen (air) in gaseous form in a three phase reactor.

APPENDIX A

Numerical Solution of the Equation of Section 2.7

The system of the three equations used for the calculation of the average particle diameter of the fluidized bed and the total volume of the biological growth around them, as a function of the expansion of the bed and ultimately as a function of time, has been solved by trial and error, with the help of a computer program. Equation 9 is a third order equation and its solution is obtained thrcugh the use of the Newton Raphson method.

The method locates the root of the equation given a initial guess, by successive approximations. Given an approximation X_k of the root, a closer approximation X_{k+1} can be calculated as follows:

$$X_{k+1} = X_k - \frac{f(x_k)}{f'(x_k)}$$

It is understood that the derivative of the equation, $f'(x)$, to be solved, must be expressed analytically.

Fig. A.1 explains how the method operates in order to locate the root of an equation $f(x) = 0$.

Certain conditions have to be satisfied so that the Newton Raphson method will converge and therefore will locate

the root of the equation.

a) $f'(x) = 0$

b) $f'(x)$ must now change sign within the region we are working

c) $x \in [a, b]$, $f(a)\,f(b) < 0$, $\left|\frac{f(a)}{f'(a)}\right| \leq |b - a|$

$\left|\frac{f(b)}{f'(b)}\right| \leq |b - a|$.

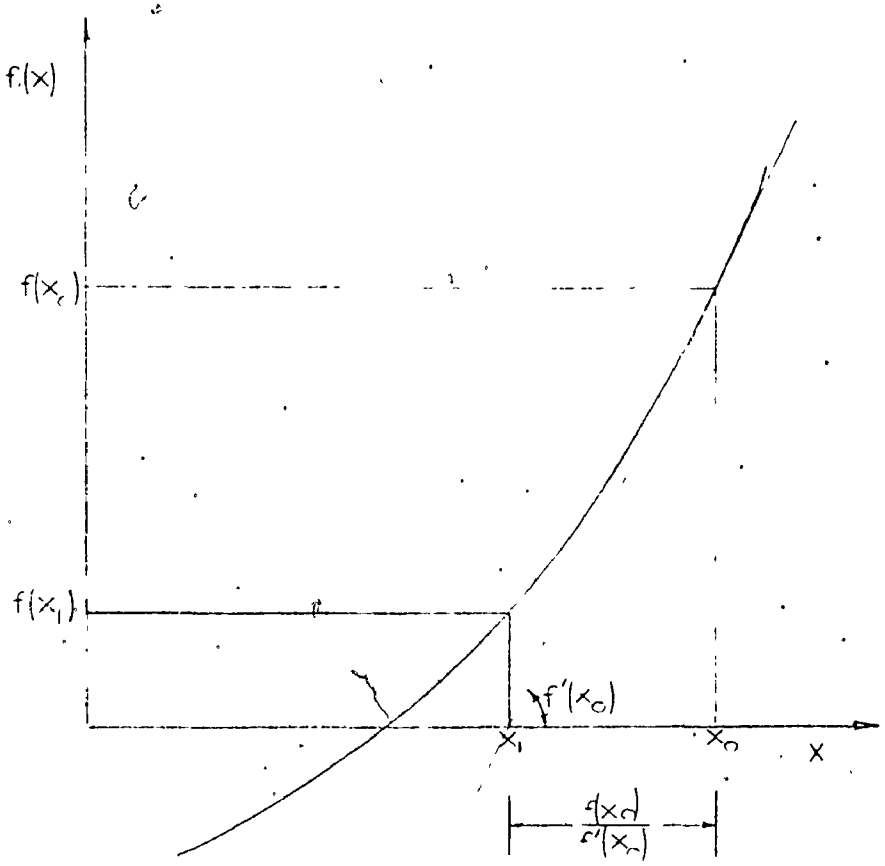


Fig.A.1 The Newton Raphson Method for Numerical Solution of Equations

These conditions simply make sure that the equation, at the range we are looking for a root, is monotonous and crosses the X axis.

The method is very fast, simple and efficient.

The program that was used is the following:

```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL LE,MA,LAMDA, NPI
      QU=33.33
      NPI=3.3000
      DVC=0.1545
      DO 50 I=1,4
      READ(5,100) LE
  100 FORMAT(F 6.2)
      LAMDA=21.57*((QU*NPI*(LE**2.0))**0.33)
      DP=0.3
   60 DPNEW=DP-(((NPI*3.14*(DP**3.0))+(LAMDA*(DP**1.33))-(6.0*LE*80.12))
     +/((9.42*NPI*(DP**2.0))+(1.33*LAMDA*(DP**0.33))))
      IF (ABS(DP-DPNEW) .LE. 0.000001) GO TO 20
      DP=DPNEW
      GO TO 60
   20 WRITE(6,30) I,DP
   30 FORMAT(1H0, I5, 3HDP=, F10.4)
      MA=NPI*0.5236*((DP**3.0)-DVC**3.0)
      WRITE(6,40) MA
   40 FORMAT(1H0,3HMA=, F 10.4)
   50 CONTINUE
      STOP
      END
```

The QU, NPI and DO statements change in each run according to the conditions of the run. The data shown in this program are from run 3 .

QU = Flow rate of the waste in lt/sec

NPI = Number of A.C. particles with a biological film around them

DVC = Average diameter of virgin A.C. particles (cm)

DP = $\bar{Dp}$

MA = Total volume of the biological growth in cm^3

APPENDIX B

Additional Data and Information on the Batch Tests

Adsorbants Characteristics

A number of different adsorbants and ion exchange resins were used for the batch tests. A brief description of each one is given below, and their important characteristics are given in separate tables.

1. Activated Alumina: Alcoa F-1

It is an inorganic adsorbant with very good physical properties especially resistance to attrition. This latter property is desirable for fluidized beds because it diminishes the losses due to the generation of fines by attrition. It is a strong adsorbant of water (Alcoa Tech Bulletin) and has been already studied as an adsorbant for removal of phosphates. (Gangoli-Thodos, 1973-74). Table B.1 summarizes its important properties.

2. Amberlites

They are synthetic polymetic adsorbants manufactured by the Rhom-Haas Company, and they are available with different dipole moments, average pore diameters and specific surface areas. Amberlites XAD-4, XAD-7, XAD-8. were selected in a series of increasing dipole moment and average pore diameter.

Table B1

-- Alumina Properties (Alcoa Technical Paper #10, 1960)

Chemical Analysis (%)

Al_2O_3	92
Na_2O	0.5
Fe_2O_3	0.12
SiO_2	0.09
Loss of Ignition 1100°C	6.8

Physical Properties

Form	Granular Opaque
Surface area m^2/g	210
Bulk placed density lb/ft_3	55
Bulk loose density lb/ft_3	50
Specific gravity g/cm^3	3.3
Crushing strength	55
Pore volume ml/g	0.25
Average pore diameter A°	40

i) Amberlite XAD-4

It is a polymeric adsorbant in the form of white insoluble beads. It is a completely non-ionic and hydrophobic polymer with macroreticular structure and aromatic surface nature. It is a polystyrene type polymer with mesh size 20 X 50. The most important physical-chemical characteristics of XAD-4 are given on Table B2.

ii) Amberlite XAD-7

Is also a polymeric adsorbant made of acrylic ester with a more hydrophilic nature than XAD-4. It has a macroreticular porosity and an aliphatic nature of surface. The dipole moment is higher than XAD-4 as well as its average pore size diameter (Table B-2).

iii) Amberlite XAD-8

It is a macroreticular polymeric adsorbant made of acrylic ester. It has the same dipole moment as XAD-7 but a considerably larger average pore size diameter (Table B2).

The pore size distribution of the three Amberlites used, as determined by Mercury porosimetry is given on Fig. B1 (Howe, 1972).

3) Cellulose Ion Exchange Resin (WRL-200A)

It is an anionic exchange resin based on cellulose with structure that resembles thin wood flakes of approximately

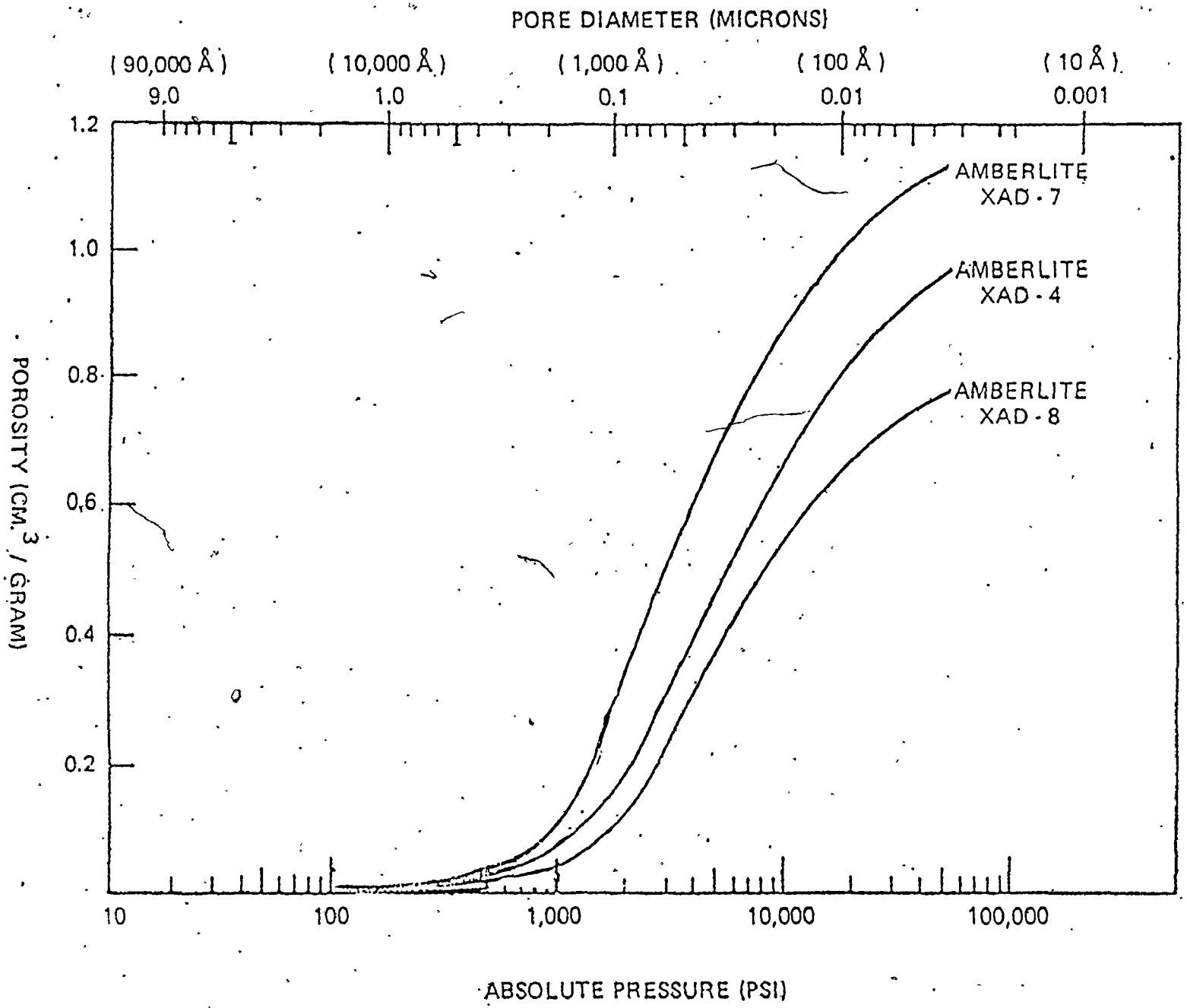
Table B2

Property	XAD-4	XAD-7	XAD-8
Form	Hard opaque beads	Hard opaque beads	Hard opaque beads
Average particle diameter	0.30-0.45 mm	0.30-0.45 mm	0.30-0.45 mm
True wet density	1.02g/cm^3	1.05g/cm^3	1.07g/cm^3
Scale total density	1.08g/cm^3	1.24g/cm^3	1.23g/cm^3
Bulk density	39lb/ft^3	41lb/ft^3	43lb/ft^3
Porosity of particles	0.50-0.55 ml/ml	0.50-0.55 ml/ml	-----
Specific surface area*	750m^2/g	450 m^2/g	140 m^2/g
Average pore diameter*	50A$^\circ$	80A$^\circ$	250A$^\circ$
Dipole moment	0.3	1.8	1.8
Porosity % of volume*	51	55	52

* Value determined on dry amberlite.

(Rhom-Haas Technical Bulletin # 141, Bulletins on each amberlite)

Fig.B.1 PORE DISTRIBUTIONS OF SOME AMBERLITE ADSORBENTS AS DETERMINED BY MERCURY INTRUSION



$4mm^2$ surface area. It has been manufactured for the removal of the humic type compounds. Its exchange capacity is 0.35 eq/l. Additional information on this resin is given in Table B6.

4. IRA-458 Ion Exchange Resin

Manufactured by the same company that provides the Amberlites, it is a strongly basic anion exchange resin. It is available in the chloride form, although a number of unknown other anions exist on the virgin resin due to the fact that during its production procedure, the resin is washed with tap water rich in anions.

The manufacturer supplies additional information on this ion exchange resin (Rohm Haas Technical Bulletin) the most important of which is listed in Table B3.

Table B3

Properties of IRA-458 Ion Exchange Resin

Ion form available	Mainly chloride
Apparent wet density (g/cm^3)	0.72
True wet density (g/cm^3)	1.08
Effective size (mm)	0.40-0.51
pH range	0-14
Maximum operating temp. (^oF)	100^o(OH) 170^o (Cl)
Total exchange capacity	1.25
Swelling %	10-15 ($Cl^- \rightarrow OH^-$)
Structure	Acrylic, non hydrophobic

Table B4

"Special A" Activated Carbon Properties (Rankin)

Base material	Clay and baked carbon surface
Pore volume	0.331 cm^3/g
Specific surface area	90.9 m^2/g
Average pore diameter	74.9 A^o
Form	Granular

Good mechanical strength

"Special A" Activated Carbon

This form of activated carbon is not available commercially yet, and has been synthesized for a previous study (Rankin, 1975). The important characteristic of this activated carbon in its higher mechanical strength and therefore its resistance to losses by attrition. It has a very low specific surface area (Table B.4). The pore size distribution of Special A is given in comparison with the pore size distribution of Filtrasorb 400 in Fig. B2.

Filtrasorb 400, Activated Carbon

The specifications of this widely used activated carbon are summarized in Table B5. The pore sizes of this carbon are distributed in a narrow range and it has shown very good loadings in a number of applications. The high specific surface area must be noted in contrast to the specific surface area of Special A.

Residual Organics Solution

It was obtained from a 20 l. activated sludge reactor that was operated at 24^{o}C, utilizing Phenol as the only carbon source. The reactor had been running for 4 months before the samples for the experimental work were withdrawn. The sludge age was about 20 days. The reactor was operated in a semi-batch form. The reactor was

Table B5

"Filtrasorb 400" Activated Carbon Properties (P.Rankin,1975)

Raw material source	Coal
Pore volume	0.44 cm^3/g
Average pore diameter	35A^o
Specific surface area (nitrogen)	1050-1200 m^2/g
% Ash	8.5% max.
Iodine number	1100
Molasses index	--
Form	Granular

Table B6

WRL-200 Ion Exchange Resin Properties (WRL Information Bulletin 1976)

Type: Anionic exchange on a cellulose matrix

Properties: Able to take up humic acids and high molecular weight anions

Capacity: 30g. humic acids/ l

Capacity: 30g DBS/l

Capacity: 30g Azeodyes/l

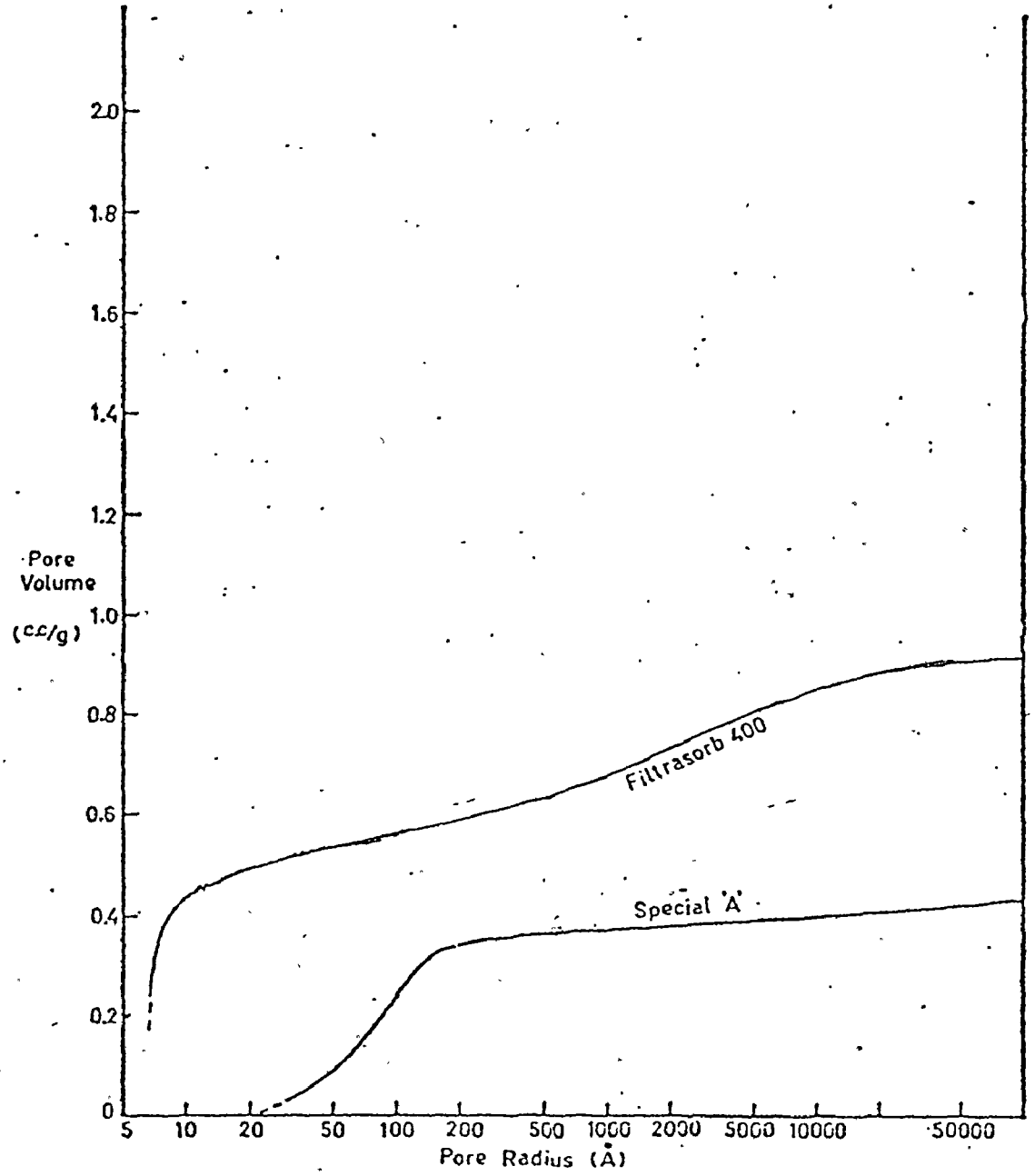
Ion exchange capacity: 0.35 eq /l

Volume weight: 0.24 kg/l

Recommended flow rate: 5-10 bed volumes/hr

Elution: by 5% Na_2CO_3 NaOH or NaCl

Fig.B.2 Overall Pore Volume Distribution for Activated Carbons Used (P.Rankin,1975)



reseeded with return sludge from a municipal sewage treatment plant every week.

B.2 Adsorbants Preparation

(a) Amberlites

These polymeric adsorbants were regenerated before their use for adsorption studies, according to the instructions provided by the manufacturer. Absolute methanol was used as the solvent for this purpose, and the methanol was, after the regeneration, eluted with water. The removal of methanol was done in successive batch washings with distilled deionized water, with the help of a magnetic stirrer.

Amberlite XAD-7, XAD-8, and the ion exchange resin IRA-458, were then dried under vacuum at 30^0C in the rotary flash evaporator so that no thermal damage would occur to adsorbants due to high drying temperatures, and also the exact dry mass of each adsorbant in each flask during the adsorption studies would be known. Because of the quick rehydration of the above adsorbants, along with the small quantities of hydrating water, and the relatively large sample volumes (50 ml), the change in volume of the samples during the adsorption studies was neglected.

Special care was taken with XAD-4 as its highly hydrophobic nature makes rehydration difficult. The XAD-4 particles after regeneration with methanol, then remained for 15 minutes in absolute methanol. This methanol is

then slowly eluted with distilled water. The complete elution of methanol was monitored through the T.O.C. of the elution water.

(b) WRA-200A, Ion Exchange Resin

It was available in regenerated form and hydrated form also. The same procedure as the one for XAD-4 was followed for the preparation of the samples for its isotherm determination. This ion exchange resin was also used at the particle size provided by the manufacturer. That is to say, small thin flakes of about 4 mm^2 surface area.

(c) Activated Alumina: Alcoa F-1

Due to the high adsorption capacity for water, of this adsorbant (ALCOA T.paper 10) that resulted in a complete distortion of the results during the first two efforts to determine its adsorption isotherm, it was decided to use the adsorbant in a hydrated form.

The Alumina particles were first reduced in size, and the -200+ 400 mesh fraction was retained. Then the F-1 alumina was regenerated in the same way that activated carbon was regenerated. Then it was boiled for 30 minutes with distilled water. The supernatant after the end of the 30 minutes was decanted and the process was repeated once again. At the end of the second boiling, the slurry was left to settle.

Subsequently, it was filtered so that most of

the water was removed. The same procedure as the one followed for XAD-4 and WRL-200A ion exchange resin was used for the preparation of samples of Al_2O_3 F-1 for its isotherm determination. (Appendix B3.)

(d) Activated Carbons Filtrasorb 400, Special A

The activated carbons were available in a pulverized form. The -200 + 400 mesh size was kept and it was regenerated according to the standard procedures. That is to say, boiling the carbon with distilled water for 30 minutes. Let is settle, decant the supernatant, and repeat the same process. At the end of the second boiling the carbon slurry was settled and the resulting cake was put in a 103°C oven where it was left to dry for 48 hours.

The XAD-7, XAD-8, IRA-458, Special A and Filtrasorb 400, regenerated dry adsorbants were kept in a desicator and were brought to room temperature before they were used.

B.3 Determination of Dry Weights for the Isotherms

During the batch adsorption tests some of the adsorbants, for the reasons explained in this appendix before, were used in their hydrated form. This means that the exact wet weight of the adsorbant in each flask was unknown. Since the exact dry weight of the adsorbant is

necessary for the calculation of the loadings, the water content of these adsorbants had to be determined.

This determination was done by taking exact known weights of the wet adsorbants, desiccating it at 103°C, for 24 hours and measuring the weight loss, that was obviously the water that had evaporated. The weight loss was then expressed as per cent of the initial weight.

Because it takes a period of time to weigh all the samples, that are necessary for an isotherm determination, and during that time the adsorbant loses some of its moisture to the environment, the samples were taken at the beginning, the middle and the end of the sample weighing procedure. The average of these determinations was used to describe the water content of the wet adsorbant that was inside the flasks.

XAD- 4 because of its hydrophobic nature presented a wider difference between the first and the last water content determination samples.

The results are presented in the form of a table that gives (Table B.7) the wet weight, the dry weight and the water content as a per cent of the dry mass of the adsorbant.

Table B.7

Water Content Determination of Samples Used in Isotherms

Adsorbant	Wet & Container (g)	Dry & Container (g)	Container (g)	Wet Weight (g)	Dry Weight (g)	Weight of H_2O (g)	H_2O as % of Dry Weight	Average of %
	3.0857	2.4787	1.3624	1.7233	1.1163	0.6070	54.5	
Al_2O_3	2.9367	2.3714	1.3618	1.5749	1.0096	0.5653	56.0	54.5
F-1	3.0031	2.4342	1.3651	1.6380	1.0691	0.5689	53.2	
PH Acidic	3.8306	2.9650	1.3684	2.4622	1.5966	0.8656	54.2	
	2.7145	2.0722	1.3681	1.3464	0.7041	0.6423	91.0	
XAD-4	2.3390	1.8770	1.3630	0.9760	0.5140	0.4620	89.9	89.5
	1.9170	1.8770	1.3696	0.5566	0.2965	0.2602	87.8	
Al_2O_3	2.2720	1.9335	1.3676	0.9044	0.5654	0.3390	59.9	
	3.8540	2.9250	1.3626	2.4914	1.5624	0.9290	59.9	59.5
PH Neutral	2.4695	2.0605	1.3691	1.1004	0.6914	0.4090	59.2	
	1.9067	1.4783	1.3623	0.5444	0.1160	0.4284	369.3	
WRL 200A	1.7042	1.4462	1.3723	0.3319	0.0739	0.2580	349.1	358.0
	2.1510	1.5330	1.3600	0.7910	0.1730	0.6180	357.0	

B.4 Batch Tests Data

The tables that follow (Table B.8 to Table B.19) present the main volume of data that was accumulated during the batch tests. Weights shown on the Tables are in grams, volumes are in cm^3.

The respective isotherms follow on Figures B.3 to B.11 .

Table B.8

F 400, Phenol Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Phenol Equil.	Vol. ml	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After
1	73.9779	73.9727	0.0052	39	1	38	66.5	87	50	0.68	132	6.8	6.8
2	74.0341	73.9838	0.0503	8	1	7	10	13	50	4.37	87	6.8	6.8
3	77.6070	77.1036	0.5034	3	1	1	0	0	50	5.02	10	6.8	6.8
4	75.6992	74.6287	1.0705	3	1	1	0	0	50	5.02	5	6.8	6.8
5	82.1565	79.7637	2.3928	3	1	1	0	0	50	5.02	2	6.8	6.8
6	78.4230	78.2230	0.2000	3	1	1	0	0	50	5.02	25	6.8	6.8
7	79.1252	79.1018	0.0234	22	1	21	36.5	48	50	2.65	113	6.8	6.8
8	73.5455	72.9803	0.5652	3	1	1	0	0	50	5.02	9	6.8	6.8
9 (Blank)	74.8292	73.1450	1.6848	2	1	0	0	0	50	—	--	6.8	7.0
10 (Blank)	77.3525	77.2346	0.1179	2	1	0	0	0	50	—	—	6.8	6.9
11 (Blank)	—	—	0	45	1	43	77	100	50	--	--	6.8	6.8

Table B.9

Al_2O_3, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	T.O.C. Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	77.6305	77.3760	0.16	12	2	15	24	50	0.30	1.9	6.7	6.8	+	-
2	75.4846	73.3428	1.35	10	1	8	12	50	0.90	0.7	6.7	7.2	+	-
3	89.7333	79.1010	6.69	13	3	7	11	50	0.95	0.2	6.7	8.6	+	-
4	46.5104	76.8251	12.38	14	2	6	9	50	1.10	0.1	6.7	2.2	+	-
5 (Blank)	57.2933	77.0746	6.30	13	9	3	4	50	—	—	6.7	9.6	-	-
6 (Blank)	—	—	—	21	1	19	30	50	—	—	6.7	6.7	-	+

Table B.10

F-400, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	73.1538	73.1462	0.0076	16	1	14	22	50	0.50	66	6.3	6.5	+	-
2	78.4347	78.4044	0.0303	10	1	8	12	50	1.00	33	6.3	6.7	-	-
3	73.2142	73.1387	0.0755	5	1	3	4	50	1.40	18.5	6.3	7.0	+	-
4	71.8660	71.7694	0.0966	5	1	3	4	50	1.40	15	6.3	7.1	+	-
5	74.1933	73.8977	0.2956	3	1	1	1	50	1.55	0.5	6.3	7.3	+	-
6	75.6345	75.1236	0.5109	4	2	1	1	50	1.55	3	6.3	7.3	+	-
7	71.5495	70.6369	0.9125	4	3	0	0	50	1.60	1.7	6.3	7.3	+	-
8	77.4057	76.2089	1.1958	4	3	0	0	50	1.60	1.4	6.3	7.3	-	-
9 (Blank)	83.2379	83.2323	0.0056	1	0	0	0	50	—	--	6.0	7.3	-	-
10 (Blank)	73.9609	73.8781	0.0828	1	0	0	0	50	--	—	6.2	7.2	-	-
11 (Blank)	72.5488	72.0316	0.5172	1	0	0	0	50	--	—	6.7	7.2	-	-
12 (Blank)	—	—	—	22	1	20	32	50	—	—	6.3	6.3	+	+

Table B.11
XAD-4, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	76.6196	74.5558	1.09	21	0.5	16	24	50	0.47	0.43	3.0	3.0	+	-
2	84.1046	83.2481	0.45	21	0.5	17	25	50	0.43	0.96	3.0	3.0	+	-
3	80.5220	74.2892	3.29	23	0.5	15	22.5	50	0.55	0.16	3.0	3.1	+	-
4	81.5702	74.0940	3.94	24	0.5	16	24	50	0.47	0.12	3.0	3.1	+	-
5	88.3965	85.0931	1.74	22	0.5	16	24	50	0.47	0.27	3.0	3.0	+	-
6	85.1051	75.2912	5.18	26	0.5	15	23	50	0.52	0.10	3.0	3.2	+	-
7	79.8699	74.8613	2.64	21	0.5	14	20.5	50	0.65	0.25	3.0	3.1	+	-
8	91.9521	78.8603	6.91	30	0.5	17	25	50	0.43	0.06	3.0	3.4	+	-
9	97.0327	81.4828	8.21	32	0.5	18	25.5	50	0.42	0.05	3.0	3.6	+	-
10 (Blank)	82.8072	78.4045	2.32	6	0.5	3	3	50	—	—	6.5	6.5	-	-
11 (Blank)	85.7919	81.3006	4.49	9	0.5	6	8	50	—	—	6.5	6.5	-	-
12 (Blank)	76.7676	76.2635	0.50	3	0.5	0	0	50	—	—	6.5	6.5	-	-
13 (Blank)	—	—	—	26	0.5	23	33.5	50	—	—	3.0	3.0	+	+

Table B.12

XAD-7, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Bef.	Aft.
1	88.6649	78.4653	10.18	32.5	0.5	6	9	50	1.22	0.12	2.9	5.4	+	-
2	78.4893	73.3439	5.14	25	0.5	10	14.9	50	0.95	0.18	2.9	4.3	+	+
3	79.5564	76.5010	3.05	22	0.5	16	23	50	0.52	0.17	2.9	3.5		-
4	82.9600	80.4932	2.47	21	0.5	12	17.5	50	0.80	0.32	2.9	3.4		-
5	79.0139	77.0727	1.94	20	0.5	13	18	50	0.77	0.40	2.9	3.3	+	-
6	78.9518	77.4352	1.52	20	0.5	14	19	50	0.72	0.48	2.9	3.1	-	+
7	78.3290	77.3674	0.96	19	0.5	14	19	50	0.72	0.76	2.9	3.0	+	
8	77.0774	76.6196	0.46	20	0.5	16	23	50	0.52	1.14	2.9	2.9	+	
9	75.8038	75.6253	0.18	21	0.5	18	26	50	0.37	2.08	2.9	2.9	+	
10 (Blank)	77.7032	76.8261	0.88	5	0.5	2	2	50	--	--	--	--	-	-
11 (Blank)	77.5356	77.3756	0.16	21	0.5	18	26	50	0.375	23.4	2.9	2.9		
12 (Blank)	--	--	--	26	0.5	23	33.5	--	--	--	2.9	2.9		

Table B.13

XAD-8, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g.	pH Before	pH After	Colour Bef.	Colour Aft.
1	74.0526	73.8832	0.20	24	0.5	21	30	50	0.15	0.75	2.9	2.9	-	-
2	82.5922	82.0942	0.50	23	0.5	20	29	50	0.20	0.40	2.9	3.0	-	-
3	77.8898	76.7930	1.10	23	0.5	20	29	50	0.20	0.18	2.9	3.1	-	-
4	82.5219	79.7597	2.76	23	0.5	20	29	50	0.20	0.07	2.9	3.2	-	-
5	84.1710	82.6206	1.55	23	0.5	20	29	50	0.20	0.13	2.9	3.1	-	-
6	24.2536	82.0502	2.20	23	0.5	20	29	50	0.20	0.09	2.9	3.2	-	-
7	85.1600	80.9922	4.17	23	0.5	20	29	50	0.20	0.05	2.9	3.5	-	-
8	84.9641	71.9795	12.98	24	0.5	20	30	50	0.15	0.01	2.9	5.5	-	-
9 (Blank)	74.8257	73.1382	1.69	3	1	0	0	50	--	--	6.6	6.5	-	-
10 (Blank)	80.3830	80.2546	0.13	4	1.2	0	0	50	--	--	6.6	6.6	-	-
11 (Blank)	--	--	--	26	0.5	23	33	50	--	--	2.9	2.9	+	+

Table B.14

IRA-458, Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	73.5150	73.2742	0.24	21	0.5	18	26	25	0.19	0.79	3.1	3.5	-	-
2	74.6562	74.0066	0.65	17	0.5	14	20	25	0.34	0.52	3.1	4.1		-
3	74.9376	73.9867	0.95	14.5	0.5	11.5	16	25	0.44	0.116	3.1	4.8	-	-
4 (Blank)	77.6626	76.3279	1.33	2.5	0.5	0	.0	25	—	—	6.7	5.5	-	-
5	73.6046	71.8691	1.73	13.5	0.5	10.5	15	25	0.46	0.27	3.1	6.1	-	-
6	74.9077	72.1725	2.73	14	0.5	11	15.5	25	0.45	0.16	3.1	6.5	-	-
7	76.8119	73.0494	3.73	14	0.5	11	15.5	25	0.45	0.12	3.1	6.5	-	-
8	89.6515	83.2980	6.35	15	0.5	12	17	25	0.41	0.06	3.1	6.4	-	-
9 (Blank)	—	—	—	26	0.5	23	33.5	25	—	—	3.1	3.1		

Table B.15

Al_2O_3 Residual Organics Adsorption Isotherm Data

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	100.9426	74.0076	17.72	32	10	4	5	50	1.42	0.08	2.9	9.6	+	+
2	95.7526	72.1912	15.50	30	9	5	7	50	1.32	0.08	2.8	9.5	+	+
3	91.4047	78.1933	8.69	22	5.5	6	8	50	1.27	0.15	2.9	9.2	+	+
4	81.9113	73.7939	5.27	18	4	6	8	50	1.27	0.24	2.9	9.0	+	+
5	81.6336	74.5675	4.65	17	3	7	10	50	1.17	0.25	2.9	8.9	+	+
6	83.6774	78.0704	3.69	16	2.5	7	10	50	1.17	0.31	2.9	8.8	+	+
7	78.3640	73.2014	3.39	16	4.5	6	8	50	1.27	0.37	2.9	8.5	+	+
8	72.5176	69.0369	2.29	13	2.5	6	8	50	1.27	0.55	2.9	8.2	+	+
9	75.9863	73.9844	1.32	13	2.5	7	10	50	1.17	0.89	2.9	7.4	+	+
10	79.7230	78.7635	0.63	16	2.5	11	16	50	0.87	1.38	2.9	6.7	+	+
11 (Blank)	76.3886	72.2550	2.69	20	13	3	4	50	—	—	7	9.2	-	-
12 (Blank)	—	—	—	26	0	23	33.5	50	—	—	2.9	2.9	+	+

Fig.B.3 Residual Organics Adsorption Isotherm for XAD-4 at pH=3.

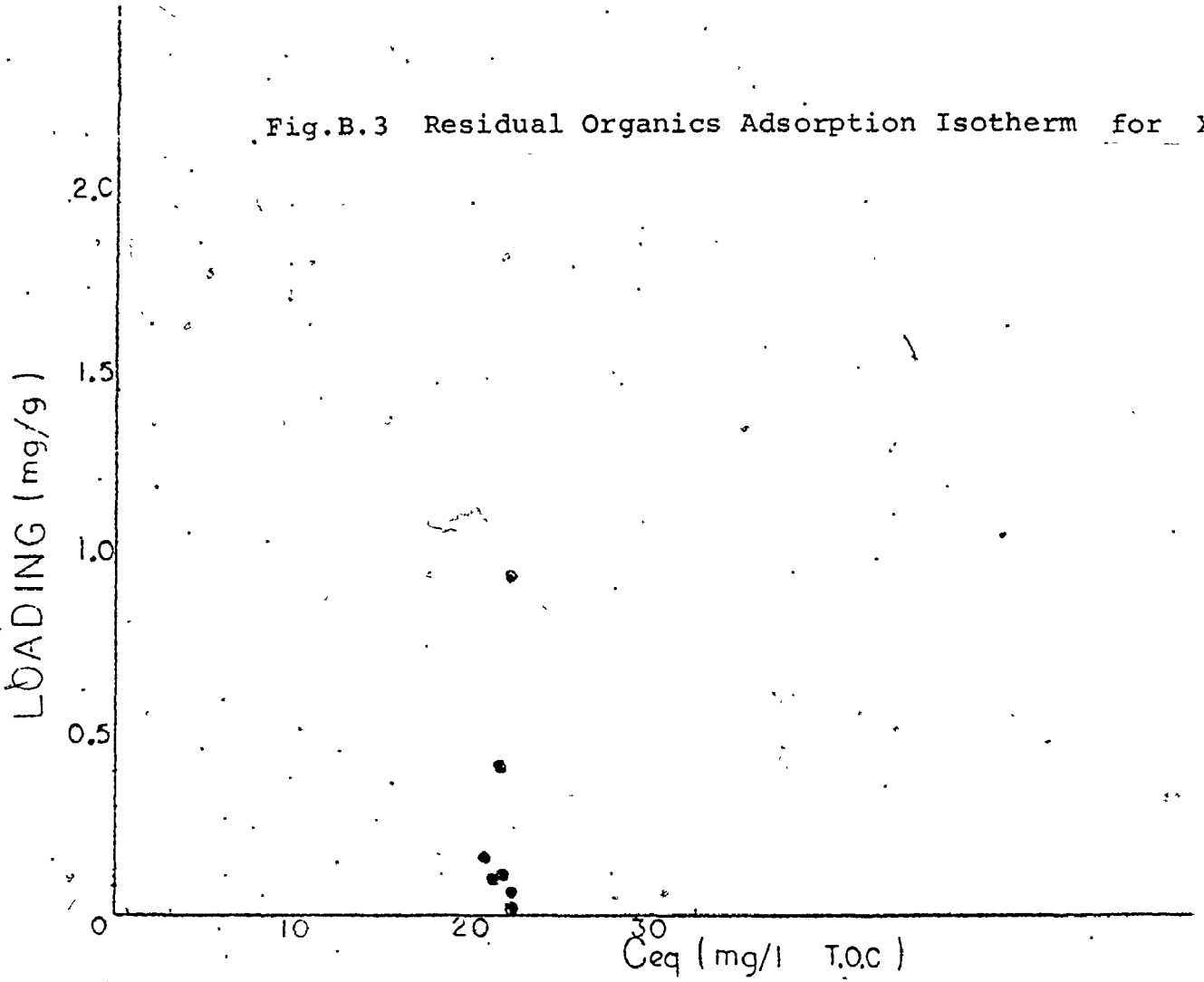


Fig.B.4 Residual Organics Adsorption Isotherm for XAD-7 at pH=3.

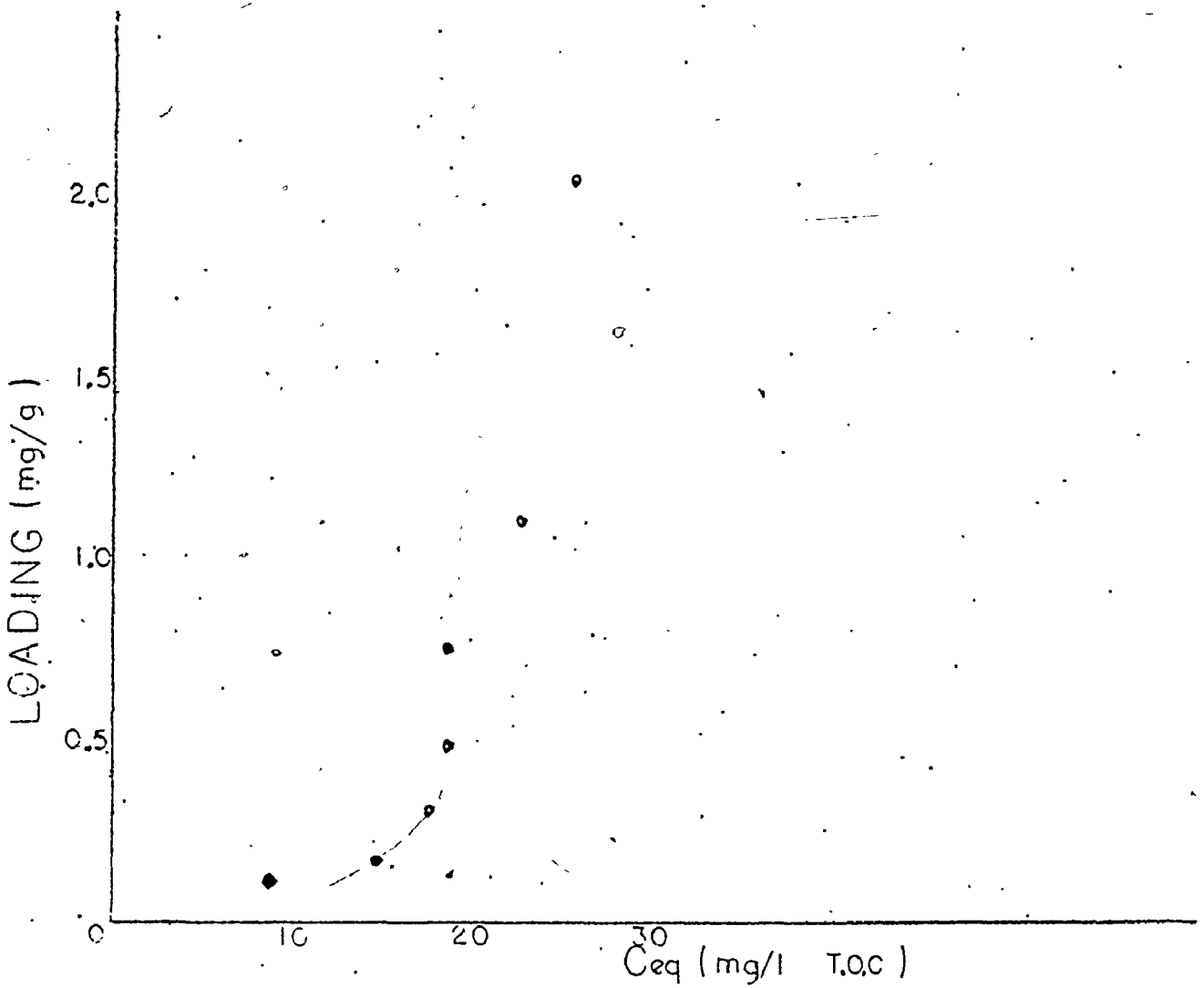


Fig.B.5 Residual Organics Adsorption Isotherm for XAD-8 at pH=3 .

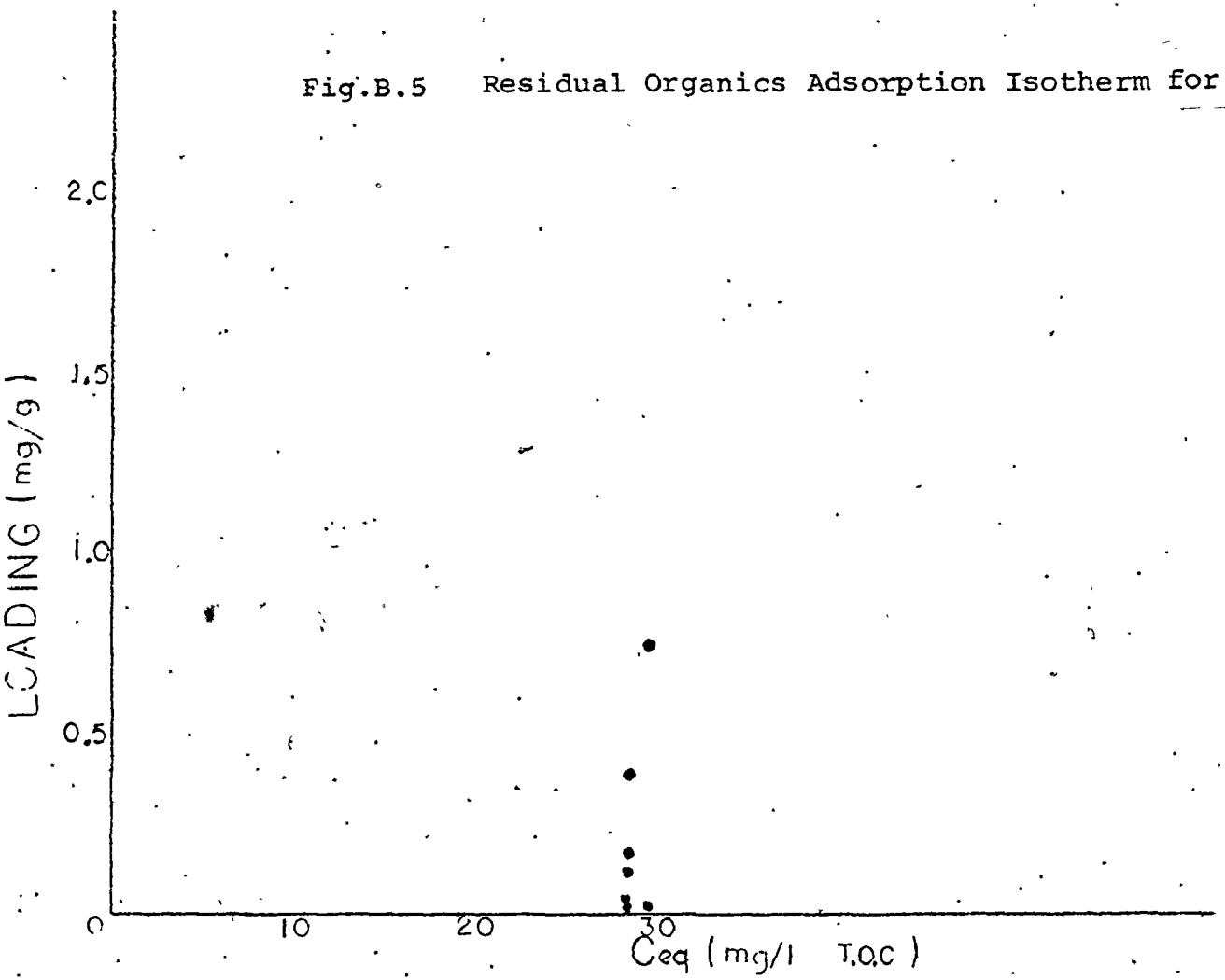


Fig.B.6 Residual Organics Adsorption Isotherm for IRA 458 at pH=3.

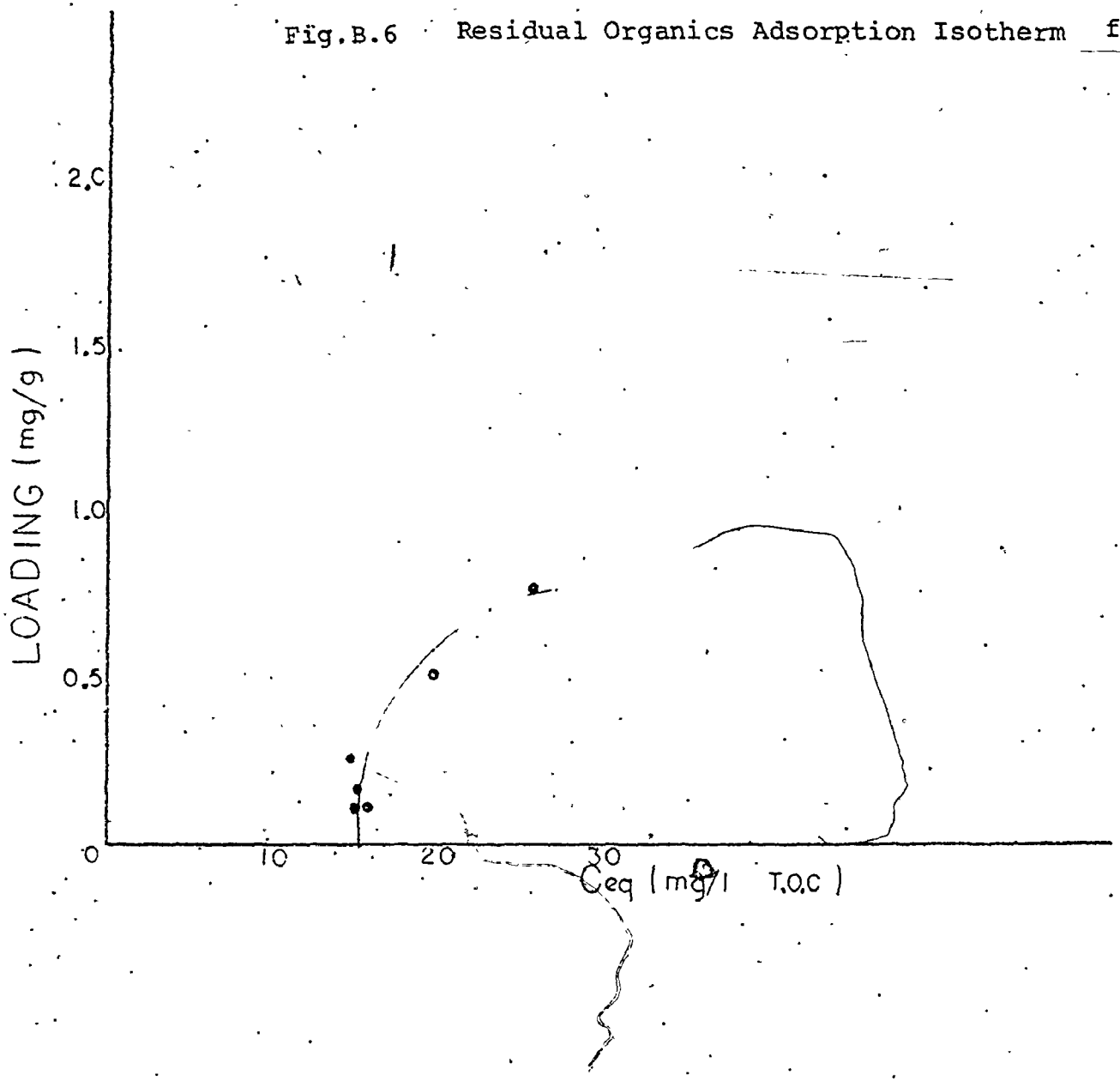


Fig.B.7 Residual Organics Adsorption Isotherm for Al_2O_3 at pH=3 .

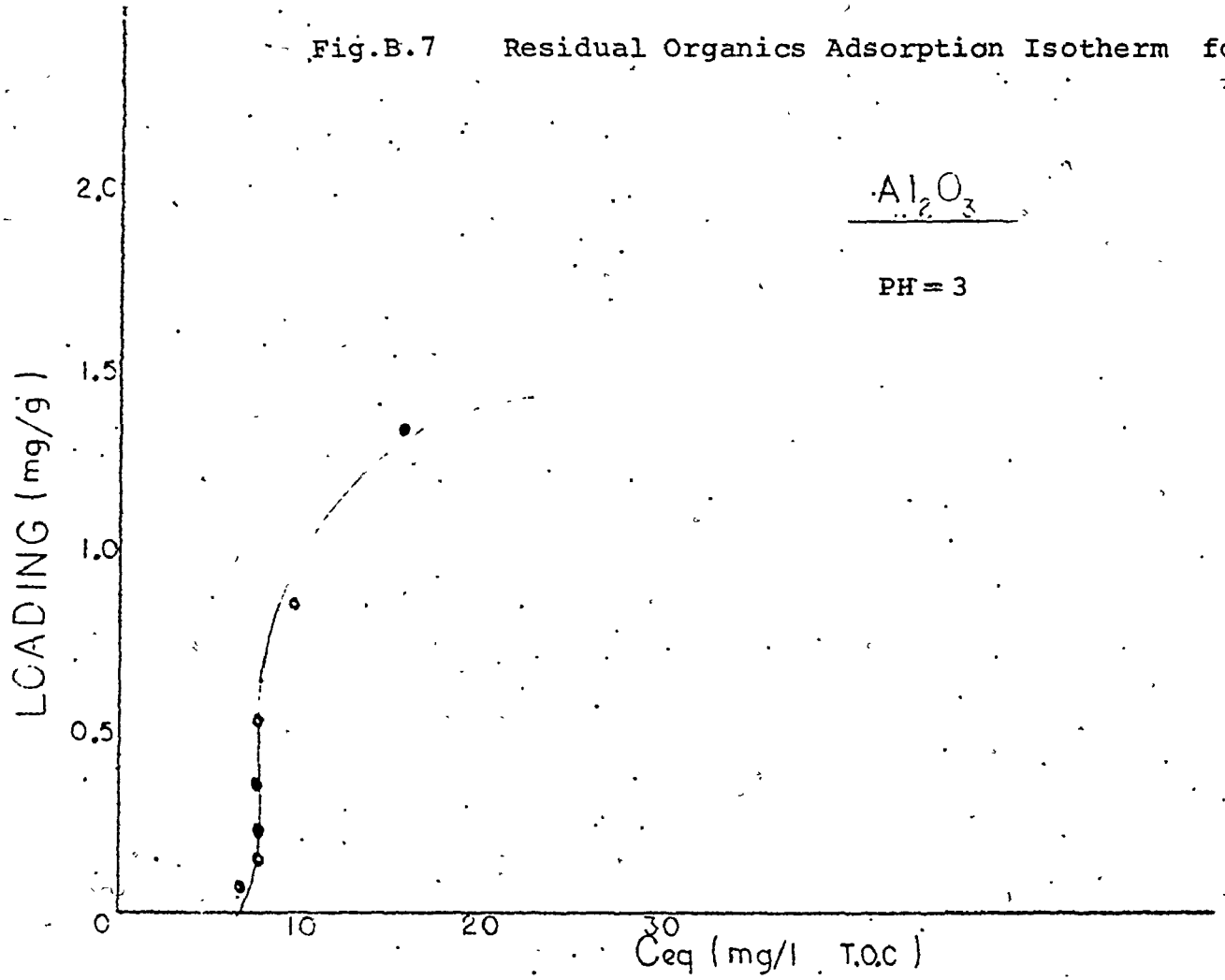


Fig. B.7

Table B.16

XAD-7, Residual Organics Adsorption Isotherm Data (pH 6.7)

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	76.8634	76.7614	0.10	19	2	15	23	50	0.35	3.5	6.7	6.7	+	+
2	73.2855	72.2514	1.03	20	2	15	23	50	0.35	0.34	6.7	6.8	+	
3	82.5652	77.3660	5.20	16	3	10	15	50	0.75	0.14	6.7	6.9	+	
4	87.5267	79.7645	7.76	14	3	8	12	50	0.90	0.12	6.7	7.0	+	+
5 (Blank)	74.0211	73.8830	0.14	3.5	0.5	2	3	50	—	—	6.7	7.0	-	-
6 (Blank)	84.6901	82.0487	2.64	10.5	4	6	9	50	—	—	6.7	7.3	-	-
7 (Blank)	—	—	—	21	1	19	30	50	—	—	6.7	6.7	+	+

Table B.17

IRA-458, Residual Organics Adsorption Isotherm Data (pH 6.7)

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	82.7175	82.6149	0.10	22	2	19	30	50	0	0	6.7	7	+	+
2	72.9990	71.9738	1.02	20	2	19	30	50	0	0	6.7	7.3	+	+
3	83.1912	76.5027	6.69	19	2	18	29	50	0.05	0.007	6.7	7.5	+	+
4	83.6644	80.4862	3.18	18	2	17	28	50	0.10	0.03	6.7	7.5	+	+
5 (Blank)	76.5569	74.3267	2.23	2	0	1	1	50	—	—	6.7	5	-	-
6 (Blank)	77.9931	77.4350	0.56	1	0	0	0	50	—	—	6.7	4.7	-	-
7 (Blank)	—	—	—	21	1	19	30	50	—	—	6.7	6.7	+	+

Table B.18

WRL-200A, Residual Organics Adsorption Isotherm Data (6.7)

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	T.O.C. Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	pH Before	pH After	Colour Bef.	Colour Aft.
1	81.5877	81.4970	0.02	22	4	18	28	50	0.15	7.5	6.7	6.7	+	+
2	89.2844	85.0405	0.05	22	1	18	28	50	0.15	5	6.7	6.8	+	+
3	84.8470	83.1536	0.37	25	3	17	27	50	0.20	0.6	6.7	7.3	+	+
4	76.1141	72.9893	0.68	28	5	16	25	50	0.30	0.5	6.7	7.6		+
5	79.6547	74.4580	1.14	30	6	14	22	50	0.45	0.4	6.7	7.8	+	+
6	86.8795	78.8405	1.76	35	9	12	19	50	0.60	0.3	6.7	8.0	+	+
7 (Blank)	78.1216	77.9136	0.05	4	1	2	3	50	—	—	6.7	7.6	-	-
8 (Blank)	77.5686	75.8740	0.37	7	2	4	6	50	—	—	6.7	8.6	-	-
9 lank)	85.950k	80.9145	1.10	17	6	10	15	50	—	—	6.7	9	-	-
10 (Blank)	82.3267	76.6394	1.24	16	6	9	14	50	—	—	6.7	9	-	-
11 (Blank)	—	—	—	22	1	20	31	50	—	—	6.7	6.7		

Table B.19

Special A, Residual Organics Adsorption Isotherm Data (6.7)

No. of Sample	Weight of Flask and Adsorbant	Weight of Empty Flask	Mass of Adsorbant	TC Peak	IC Peak	TOC Peak	Equil. (mg/l) T.O.C. Concentration	Vol.	Adsorbed Mass of Organics	Loading mg/g	Before	After	Colour Bef.	Colour Aft.
1	72.4712	78.4661	0.0051	23	1	21	31	50	0	0	6.5	6.7	+	+
2	78.0788	78.0685	0.0103	22	1	20	31	50	0	0	6.5	6.8	+	+
3	73.8511	73.7918	0.0593	19	3	15	23	50	0.40	6.7	6.5	7.4	+	+
4	78.8619	78.7619	0.1000	16	3	12	19	50	0.60	6.0	6.5	7.6	+	+
5	77.1946	77.1142	0.0804	18	3	14	22	50	0.45	5.6	6.5	7.5	+	+
6	73.3893	73.1868	0.2025	15	4	10	15	50	0.75	3.7	6.5	7.8	+	+
7	72.7884	72.1889	0.5995	14	7	6	9	50	1.10	1.8	6.5	8.1	+	+
8	75.6090	74.5663	1.0427	16	8	5	8	50	1.15	1.1	6.5	8.2	+	+
9	79.7526	78.6566	1.6660	17	10	6	9	50	1.10	0.7	6.5	8.3	+	+
10	77.4446	77.4322	0.0124	3	1	1	1	50	1.5	0.9	6.5	7.9	-	+
11 (Blank)	81.0505	80.9877	0.0628	3	2	0	0	50	—	—	6.7	8.7	-	+
12 (Blank)	74.8320	74.7239	0.1081	3	2	0	0	50	—	—	6.2	8.9	-	+
13 (Blank)	77.5026	76.5014	1.0012	9	8	0	0	50	—	—	6.2	8.8	-	+
14 (Blank)	—	—	—	22	1	20	31	50	—	—	6.5	6.5	+	+

Fig.B.8 Residual Organics Adsorption Isotherm for XAD-7 at pH=6.7

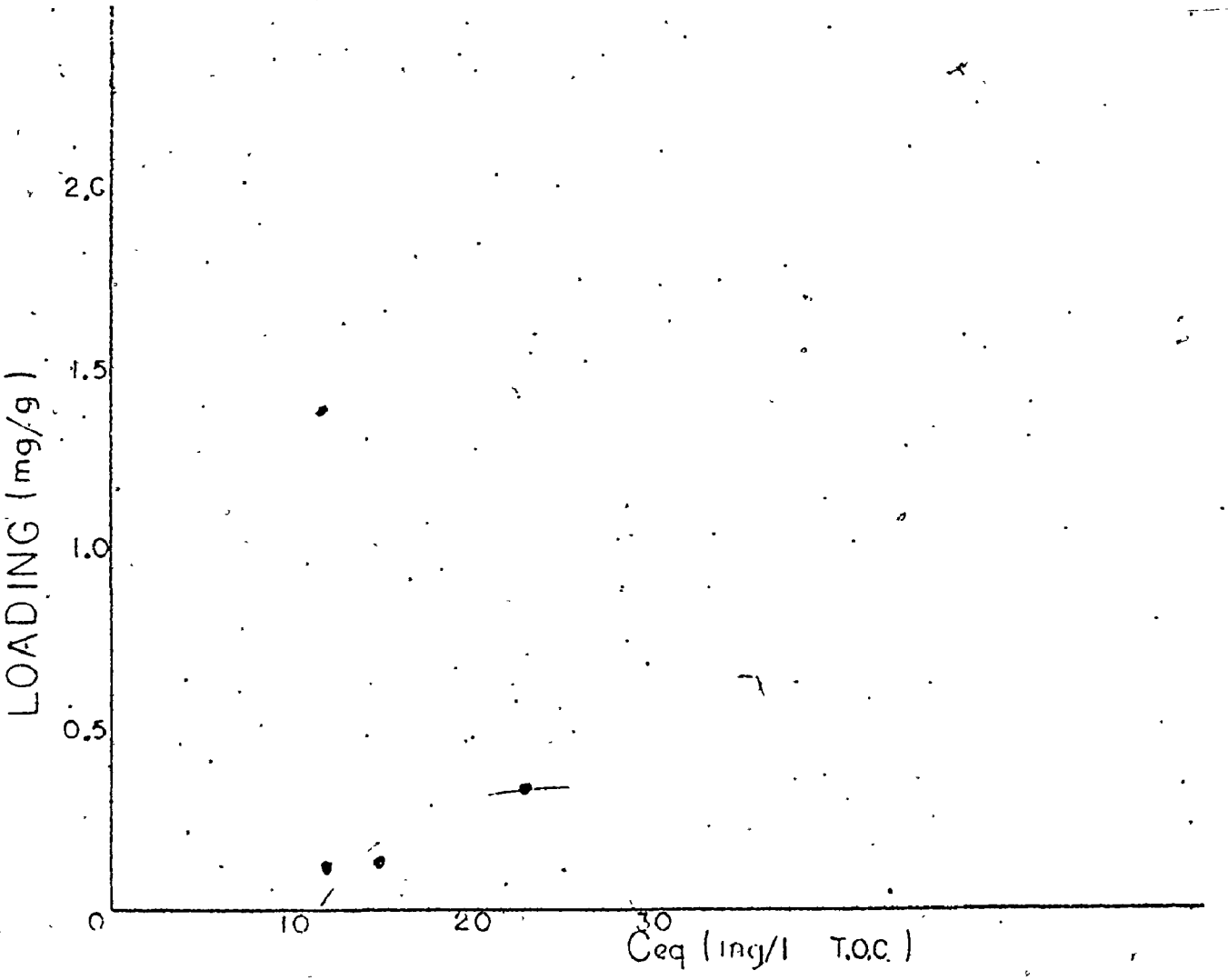


Fig.B.9 Residual Organics Adsorption Isotherm for IRA 458 at pH=6.7.

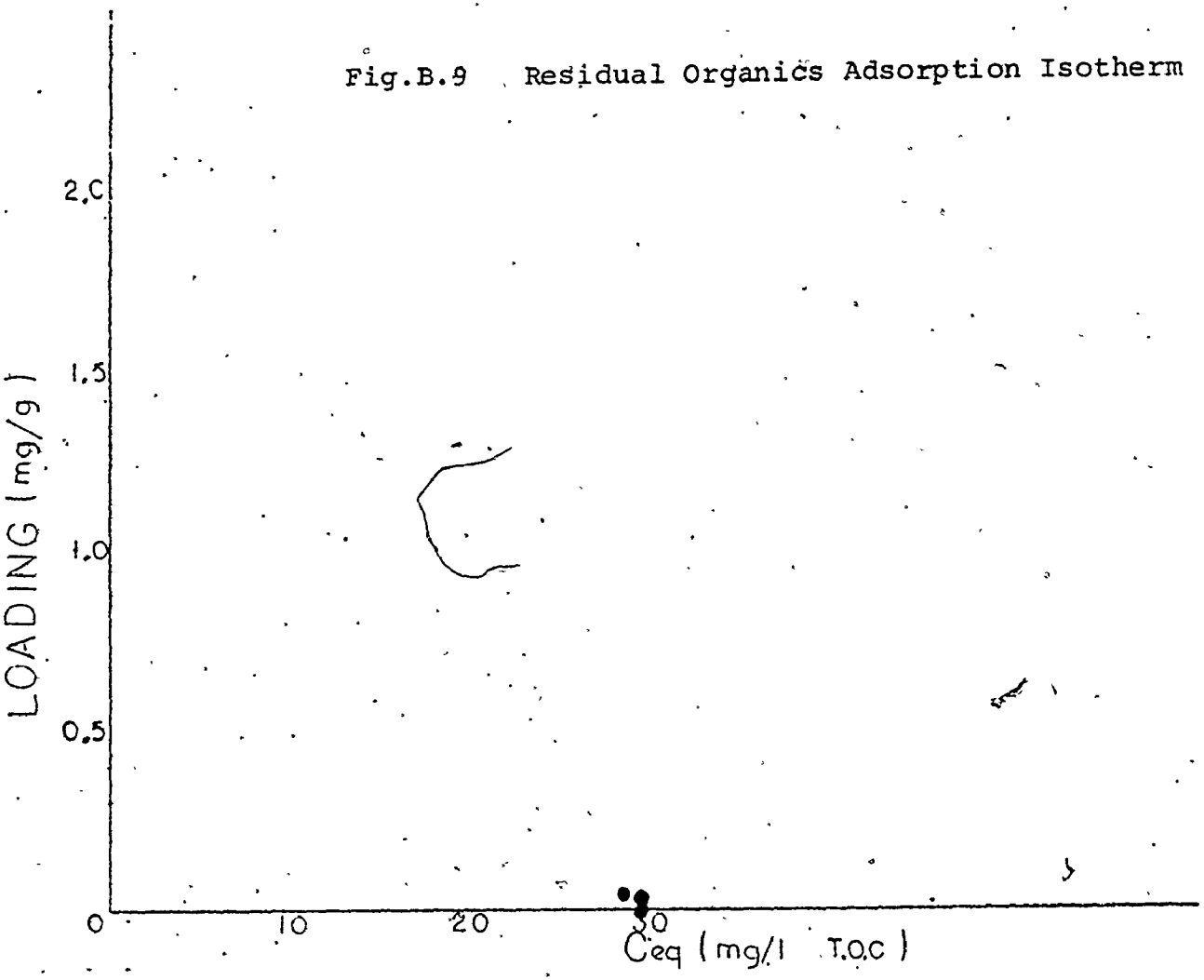
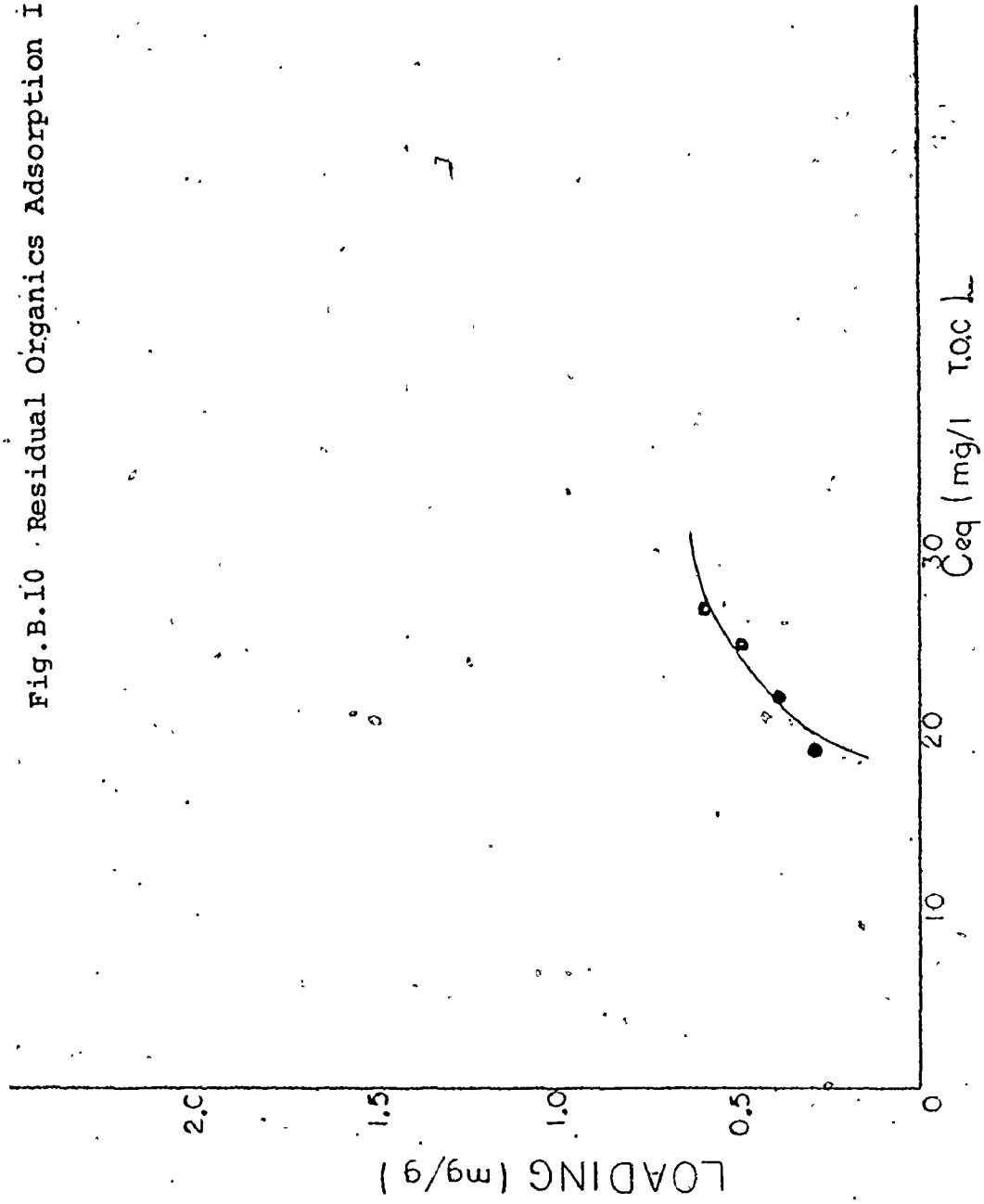


Fig.B.10 Residual Organics Adsorption Isotherm for WRL 200A at pH=6.7.



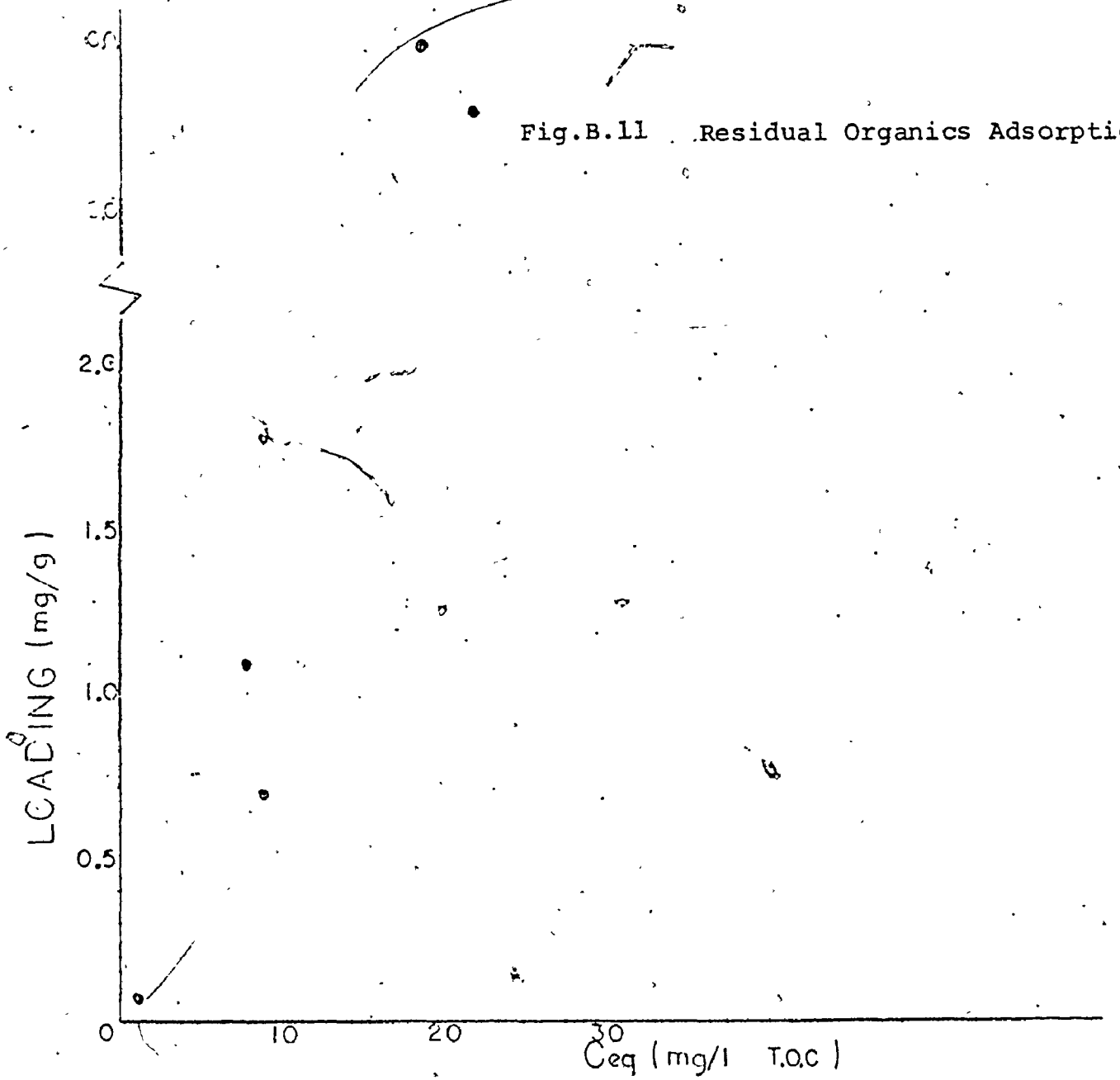


Fig.B.11 Residual Organics Adsorption Isotherm for Special A at pH=6

APPENDIX C

Analytical Determinations -- Comments

A number of different parameters were used in the process of data accumulation and automatic or semi-automatic procedures were involved in the effort of their measurement. The application of these methods resulted in a number of difficulties, that sometimes required considerable time and effort to be eliminated.

1. T.O.C. Measurements

These measurements were done by the use of the Beckman carbon analyser (B.12). Calibration of the instruments is necessary so that the peak readings can be converted to concentration of organic carbon in mg l^{-1}. Therefore a number of reference standards have to be prepared. The standards were prepared by dilution to desired levels of a 1000 mg/l Phenol solution. The dilution of the concentrated Phenol solution was executed in 100ml volumetric flasks, so that the concentration of the reference standards was known exactly.

The peak readings of the instrument resulting from the Total Carbon channel, are plotted on the X axis and the relative Total Organic Carbon concentration in

mg/l is plotted on the Y axis. The calibration curve is very sensitive to the accuracy the reference standards are prepared with.

High purity liquified Phenol was used to prepare the initial concentrated solution. Because of the volatile nature of the liquified Phenol, the transfer of the liquified Phenol from the 100ml beaker where it was weighed to the 2 l volumetric flask had to be done very quickly. The rate of evaporation of the liquified Phenol could be followed by the slow change of the fourth digit ($mg.10^{-1}$) of the weight the Mettler balance was giving, whenever the sample was staying for a while on the balance's weighing tray. About $\frac{3}{4}$ of the total water necessary for the make up of the concentrated solution was at first used to dissolve completely the Phenol, and then more water was added up to the 2 l line of the volumetric flask. This way the reduction in the volume of the solution due to the solvation of the Phenolic molecules by the water molecules did not affect the concentration of the solution.

A second calibration curve is necessary for the inorganic carbon channel. A known exact weight of dry Na_2CO_3 was diluted to form one liter of concentrated (100 ppm) solution. Using 100 ml volumetric flasks, lower concentrated inorganic carbon reference standards were prepared. The reading of each standard by the

Total Carbon and the Inorganic Carbon channels were recorded and they were plotted to form the second calibration curve. On the X axis we have the peak reading of the Inorganic Carbon, and on the Y-axis the peak reading of the Total Carbon channel. This way, the Inorganic Carbon channel reading can be converted to equivalent Total Carbon units and, the peak reading of the T.O. carbon of a sample can be calculated by subtraction. Using then the first curve we convert the Total Organic Carbon peak reading to Total Organic Carbon concentration (mg/l).

Precision and accuracy of the T.O.C. determination depend on the linearity and accuracy of the calibration curves, as well as on some other parameters. The sample volume has been found to affect the output of the instrument significantly. During the time of the present work, 20 μl volume of sample was injected in the carbon analyser channels, each time a determination was executed. A difference of 2 or 3 units could result from a minor change in the 20 μl volume. Therefore, it was found to be very significant, for the precision of the analysis, to inject each time exactly the same volume of sample. The Total Carbon channel was found to be much more sensitive to sample volume variations than the Inorganic Carbon channel.

Another parameter that influenced the output of the analyser drastically was the way the sample was injected in the channel. If the sample was injected with two different speeds, the peak reading of the sample that was injected with the lower speed was always 50-70% of the peak reading of the sample that was injected faster.

A third parameter that was found to affect the results of the carbon analyser was the time the injection syringe was left at the injection position, although the sample had already been injected in. The time must be at least 5 seconds, to allow the carrier oxygen gas to carry along the products of combustion of the sample, without any interuption of the flow. A 10 second time was used in all T.O.C. determinations.

The complete warm up and stabilization of the infrared detection unit and the recorder were found to be necessary for the accuracy and repeatability of the readings. The T.C. and I.C. tubes were ON permanently so their steady state functioning was ensured.

The gain used was always the same, since it was found that the behavior of the instrument changes when the gain is changed. In other words, a complete recalibration is necessary each time the gain changes.

The instrument has to be left on for about 30 minutes to reach steady state as can be seen by the stability of the base line, before any sample is injected in any of the channels. A shorter period of time is necessary also to be allowed for the stabilization of the base line when we switch from the Total Carbon channel to the Inorganic Carbon channel or vice versa.

It is very important to allow the recorder to return to its base line between sample injections, in order to assure repeatability of peak readings. The injection of the standards must be performed periodically to make sure that the calibration curves are still valid for the determinations under way. It must be noted here that the Na_2CO_3 standards have to be prepared fresh each time because they quickly change their concentration due to the presence of CO_2 in the air, and the $CO_2 - CO_3^{2-} - HCO_3^-$ equilibrium.

A reading is accepted only when it is repeated twice.

It is very important to clean the injection syringe between every injection, especially when the expected concentration of T.O.C. are low, because a minor interference can result to a high relative error. It can be seen from the information stated above that the precision as well as the accuracy of determinations through the carbon analyser

are subjected to a large number of parameters, but if properly executed, the results are precise. The accuracy of the determinations can also be assured to a great extent, as the results of the present work showed. An accuracy of ±1 mg/l T.O.C. can be considered as applicable to the results, mainly due to the fact that a graphic representation of the calibration curve is necessary, and the peak readings are converted to concentrations graphically as well. (Hals , 1974)

2. Phenol Measurements

The direct colorimetric determination of Phenol that was applied, is simple in execution and reliable. A calibration of the spectrophotometer is necessary. The process of the preparation of the standards was the same as for the carbon analyser. Again the accuracy of the concentration of the standards is necessary to assure a linear calibration curve.

The method itself has an accuracy of ±1 mg/l (Standard Methods 1971) , but this accuracy can be greatly reduced if the reading of the spectrophotometer is more than 0.2 absorbance units. Readings below that level are more reliable due to greater validity of Beer's law in dilute solutions

The sensitivity of the method was also reduced significantly at concentrations resulting to readings below 0.01.

The instrument had to be warmed up for at least 30 minutes before any reading could be taken, as the drifting of the zero setting within the first half-hour of operation proved.

Multiple analysis of the same samples revealed that the precision of the results lies between ±1 mg/l and ±2 mg/l , depending on the arithmetic value of the reading and its relative position on the adsorbance scale. It is quite possible that a digital spectrophotometer would result in a much higher precision and accuracy.

APPENDIX D

Additional Information on Continuous Runs

D.1 Additional Information on Pilot Plant Structure and Operation

They are made of plexiglass, 4 inch inside diameter tubes. Each column consists of three parts. The lower part is the flow distribution system. It is 6 inches long, 4 inch I.D. plexiglass tube, equipped with a draining valve at the bottom. The flow of the waste comes in this part, from the side, about 2 inches above the bottom through a ½ inch nominal diameter stainless steel pipe. This pipe goes along the diameter of the cross section of the 4 inch tube. The end of the pipe is plugged, and 5 holes of 1/8 inch diameter are drilled along its length pointing downwards (Fig. D.1). The flow of the waste goes in the flow distribution part through these 5 holes and is therefore distributed along the diameter of the cross section of the 4 inch tube. The flow is directed towards the bottom where it reflects and spreads over the cross section of the 4 inch tube. Ceramic saddles used as tower packing material fill the flow distribution part, resulting in an even better distribution of the waste flow.

The second part that lies on top of the flow distribution system is the main (fluidized bed) reactor. It is 8'10" long with 4 inch I.D. It consists of two

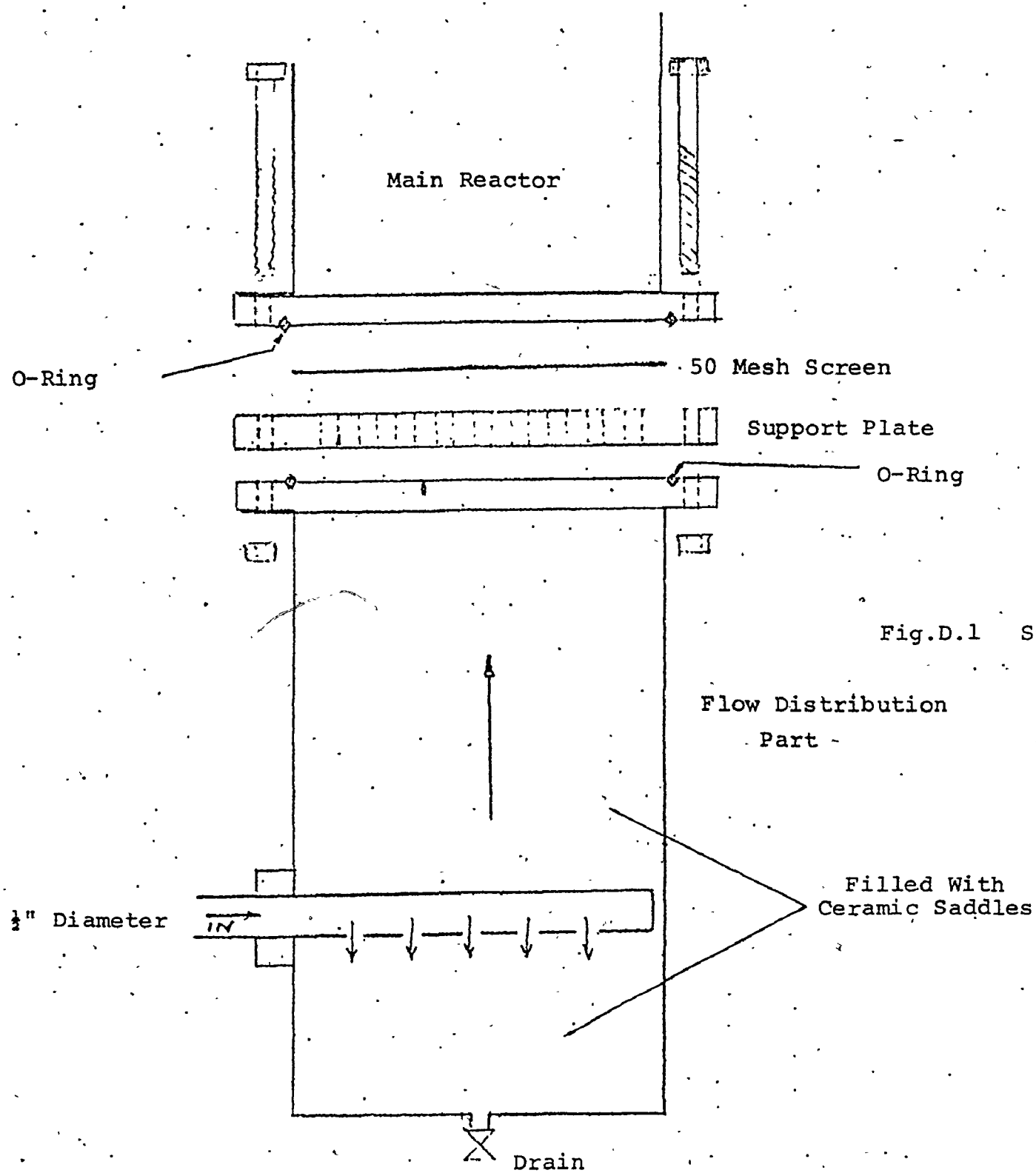


Fig.D.1 Structural Details of Flow Distribution System

parts that are connected with flanges and O-rings. Between the flow distribution system and the main reactor there is a plexiglass bed support plate that bears a system of holes, in order to allow the flow to move free and uniformely up into the main reactor. The holes are uniformely distributed over the surface of the bed support plate. Their diameter is approximately 5 mm.

A 50 mesh stainless screen exists between the support plate and the bed particles and does not allow the small bed particles to go through the support plate holes, in the flow distribution system.

The third part is the top of the reactor. It is made of a 4 inch diameter plexiglass rod that has been machined inside, in the form of a cone, that decreases gradually the diameter from 4 inches to ½ inch flow cross section diameter. In addition, this part does not allow the retention of gas in the reactor and therefore the formation of gas pockets that disturb the flow doesn't occur. (Picture 3 in Appendix D.3)

After each reactor, a filtering system exists that retains the particles of the bed that may be washed out. The filters are made of 50 mesh stainless steel screen, and their existence prevents the plugging by washed out bed particles, of the inlet of the second reactor and of the back pressure regulator that exists after the second reactor.

The filtering systems are made of P.V.C. The outer shell is cylindrical in shape, 12 inches tall and 8 inches in diameter. Inside the shell there is the filter itself, which is cylindrical, a length of 8 inches and a diameter of 4 inches. The flow comes in the outer shell through the side tangentially (Fig. D.2) and after passing through the filter, goes out through the center of the top part of the filtering system. The filtering systems are equiped with a ½ inch drain valve and since the top can be removed, then the filter can be taken out to be cleaned whenever excessive growth results in a pressure build-up. A fine tube of 1/64 inch outside diameter installed as Fig. D.2 shows, bleeds the gas - whenever used - that accumulates at the top part of the shell into the flow of the waste, past the filtering system. Whenever gas bubbles were present in the flow the gas was accumulating inside the outer shell of the filters, at the top part of it, and beyond a certain volume accumulated, a slug of gas was released to the flow, that was going through the second reactor in the form of a big gas cup upsetting the bed and washing out a part of it. The above mentioned fine tube was always releasing the existing gas in fine bubbles into the flow that did not obstruct the normal operation of the bed.

The supply of O_2 at desired flow rates and in

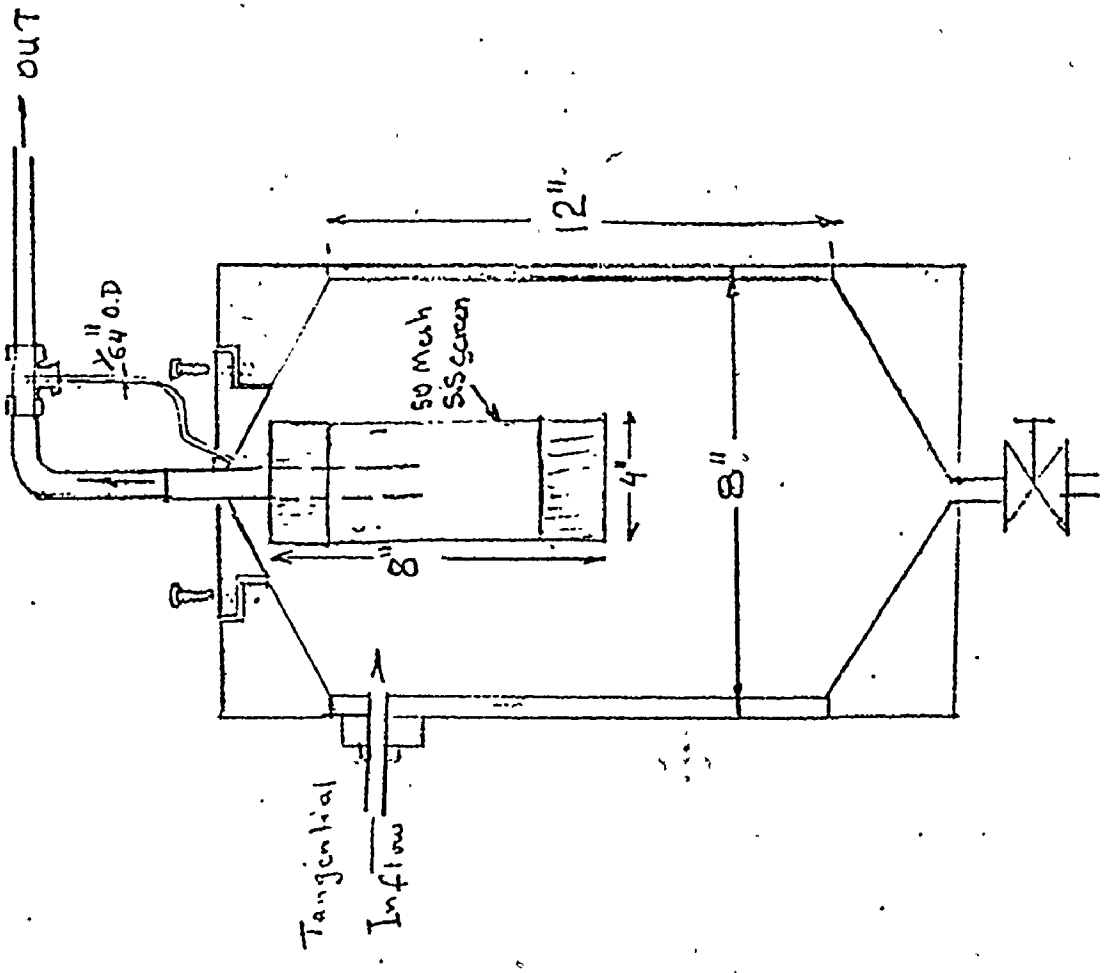


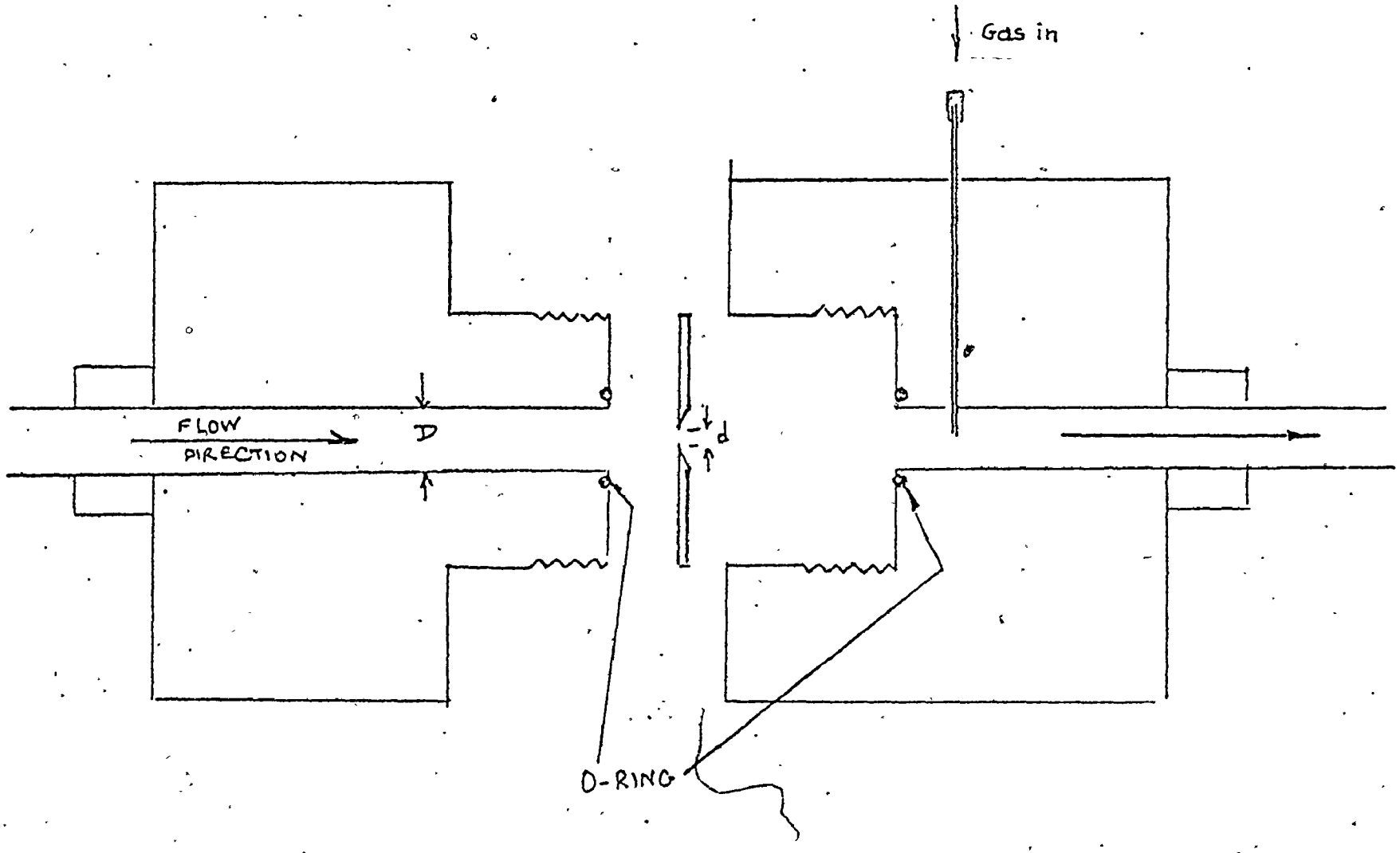
Fig.D.2 Structural Details of Separator

the form of small bubbles to the waste flow was possible by the use of an orifice (Fig. D.3). The orifice results to a maximum contraction of flow cross section and therefore a maximum increase in the flow velocity about 1 pipe diameter downstream from the orifice. At that point a fine needle is releasing O_2 at the desired flow rate. The oxygen gas is sheared off the needle by the high velocity flow in the form of small bubbles that are uniformely distributed in the waste flow.

The dilution water that was used for the making up of the waste stream, was withdrawn from Hamilton's municipal water supply system. The temperature of this water, which is taken from Lake Ontario is, around the winter season, about $6^{o}C$ and was adjusted in temperature to $24^{o}C$, by mixing it with high temperature ($55^{o}C$) water supplied by the University facilities. The free residual chlorine as well as some of the organics of the dilution waterwere removed by an activated carbon packed bed. The bed was 6 feet tall and 6 inches in diameter, it was packed with Filtrasorb 400, - 12 +14 mesh particle size activated carbon, and was operating down flow by gravity.

Dechlorinated water was then directed to a 30 gallon overflow tank for the control of the Dissolved Oxygen concentration. Whenever a D.O. concentration higher than the equilibrium value was necessary, pure gaseous

Fig.D.3 Structural Details of Gaseous Oxygen Injection System



Oxygen was dispersed finely in the tank resulting in an increase of the D.O. concentration.

Dissolved Oxygen concentration lower than the equilibrium ones were achieved by the use of Na_2CO_3 solution that reacts with the Dissolved Oxygen to form sulfate.

Kinetic tests of the D.O. reduction rate by addition of sulfite made clear that for the specific system that was being operated, the detention time of the 30 gallon tank was not enough because the reaction rate was slow, and Co^{2+} was necessary to be present as a catalyst for the reaction (Benedek, Bennet & Ho, 1974)

$$SO_3^{2-} + \tfrac{1}{2} O_2 \xrightarrow{Co^{2+}} SO_4$$

A variable speed mixer provided the necessary mixing conditions, and the D.O. level was continuously monitored by a D.O. probe connected to a D.O. meter.

Due to its toxicity, the Na_2SO_3 solution was supplied at the exact stoichiometric quantities for the desired D.O. reduction, so that no excess sulfite would be left in the flow to go in the reactors and affect the biological growth.

The dilution water with the adjusted D.O. concentration was then taken by the Flotec-pump to be mixed with the concentrated Phenol solution, and to make up the desired strength waste that was subsequently driven in the reactors.

For the piping, where liquid was flowing, ½ inch high density polyethylene tubing was used, along with nylon fittings. For the gas flow, and the concentrated Phenol solution, ¼ inch high density polyethylene tubing with nylon fittings were used also.

All the samples before any analysis (except D.O. determinations) were filtered through 0.45 μ membrane filter. Each filter was washed before use with 250 ml of distilled deionized water, and the first 20 ml of the filtrate were discarded. This way no change in the T.O.C. concentration of the filtrate resulted due to either adsorption or desorption of oganics by the filter. All samples were filtered immediately after they were withdrawn so that the biological activity would not change their characteristics. In cases where it was necessary to store the sample for a short period, they were kept in darkness at 4 ^{o}C inside a thermostatically controlled refrigerator.

D.2 Additional Data on Continuous Runs

The main volume of the accumulated data during the continuous runs is presented in Tables D2.1 to D2.7.

Run 1:

Due to the frequent feed interruptions no Phenol mass balance was done for Run 1.

Run 2:

The table that follows summarizes the Phenol mass balance for Run 2. The average of the beginning and end concentrations are used for each time period.

TABLE D.2.0

Phenol Balance Run # 2

Time Hrs	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 17	153.0	18.7	
17 - 41.5	194.8	222.2	130
41.5 - 51.5	79.5	75.7	
51.5 - 65	107.3	78.8	171
65 - 126	522.0	471.2	
126 - 132.5	48.7	46.8	57.6
132.5 - 138	36.1	31.4	
138 - 156	148.0	124.2	29.0
156 - 161	42.0	36.4	6.5
	1331.4	1105.4	113.2

Thus; 112.5 g is equal to the mass of unaccounted and therefore accumulated Phenol on the carbon.

Given that the total A.C. existing in the reactor was 1246 g and that the lower 27 cm of the 38 cm of the bed did not develop growth (Appendix D.3) then:

$$(27/38) \times 1246 = 885 \text{ g}$$

of activated carbon of the bed having developed no biological growth on them, remained in equilibrium with the influent concentration of Phenol (56 mg/g as per Table 4.1.2).

The adsorbed Phenol on this part of the bed is according to Fig. 4.2

$$885\text{g} \times 115 \frac{\text{mg}}{\text{g}} \times 10^{-3} \frac{\text{g}}{\text{mg}} = 102 \text{ g}$$

The remaining 10.5 g were adsorbed on the rest part of the bed (361 g) that had developed biological growth. The resulting average loading on this part is therefore:

$$10500 \text{ mg Phenol} / 361 \text{ g A.C.} = 29 \text{ mg/g.}$$

Table D 2.1

Run # 1, Reactor # 1, Data

Time (Hrs)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In (mg/l)	T.O.C. Out (mg/l)	S^{-2} mV In	S^{-2} mV Out	pH In	pH Out	Temp. °C	ΔD.O. mg/l	ΔO.C.P. / ΔT.O.C.
4.5	11.2	4.5	71	28	60.6	54.4	21.5	55	18	-268	-268	8.5	8.5	24	6.7	5.5
12.7	11.5	3.4	56	35	32	42.9	29.0	42	30	-268	-268	8.5	8.5	24	8.1	1.5
40.5	12.4	2.7	0	15	--	0	11.5	0	12	-268	-268	8.1	8.1	24	9.8	-
66.5	12.0	1.2	43	31	28	32.9	23.7	32	22	-268	-268	8.2	7.8	24	10.8	0.9
76.0	11.0	1.6	60	40	32.5	46	30.1	46	29	-268	-268	7.8	7.8	24	10	1.7
89	11.5	1.6	48	43	11	36.8	32.8	32	33	-268	-268	7.7	7.7	24	9.9	0.4
102	11.6	3.0	0	11	—	0	8.4	0	8	-268	-268	7.2	7.8	24	8.6	-
116	11.6	1.7	57	43	24	43.6	32.9	42	32	-268	-268	7.9	7.9	24	9.9	1.0
126	11.6	1.6	63	52	18	48.2	39.8	44	39	-268	-268	7.6	7.6	24	10.0	0.5
							Reactor # 1									
45	4.5	1.6	28	0	100	21.5	0	18	0	-268	-268	8.5	8.5	24	2.9	
27	3.4	1.0	35	0	100	29.4	0	30	0	-268	-268	8.5	8.5	24	2.4	
40.5	2.7	1.1	15	0	100	11.5	0	12	0	-268	-268	8.1	8.1	24	9.6	
66.5	1.2	0.9	31	15	97	23.7	1.1	22	1	-268	-268	7.8	7.7	24	0.3	
76	1.6	1.1	40	2	95	30.6	1.5	29	2	-268	-268	7.8	7.7	24	0.5	
89	1.6	0.9	43	8	81	32.8	6.0	29	31	-268	-268	7.7	7.7	24	0.2	
102	3.0	2.6	11	12	82	8.4	13.0	8	9	-268	-268	7.8	7.8	24	0.4	
116	1.7	1.6	43	19	51	32.9	14.5	29	35	-268	-268	7.9	8.0	24	0.1	
126	1.6	1.4	52	24	62	39.8	18.4	37	40	-268	-268	7.6	7.7	24	0.2	

Q = 2.5 lt/min.
4727g of F-400 in Reactor # 1 and 2500g in Reactor # 2

Table D 2.2

Run # 2, Data

Time (Hrs)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In (mg/l)	T.O.C. Out (mg/l)	S^{-2} In mV	S^{-2} Out mV	pH In	pH Out	Temp. °C	Δ D.O. mg/l	Δ O.C.P. / T.O.C.
15	13.4	0.1	50	0	100	38	0	38	0	-268	-268	7.7	7.7	24	4.3	8.8
17	13.1	6.0	50	21	58	38	16	37	16	-268	-268	7.7	7.7	24	7.1	3.1
17.5	9.5	4.6	52	43	17	40	32	38	31	-268	-268	7.6	7.5	24	4.9	1.6
21.5	10.0	2.4	57	53	7	43	40	44	40	-268	-268	7.6	7.5	24	7.6	0.5
51.5	9.8	1.6	50	49	2	38	37	38	36	-268	-268	7.7	7.6	24	8.2	0.12
53	10.3	1.8	53	51	3	40	39	40	39	-268	-268	7.6	7.6	24	8.5	0.2
65	10.1	1.0	56	51	9	43	39	43	37	-268	-268	7.6	7.6	24	9.1	0.4
72	10.0	0.7	56	51	9	43	39	43	38	-268	-268	7.6	7.6	24	9.3	0.4
77	10.0	0.7	56	51	9	43	39	44	39	-268	-268	7.5	7.5	24	9.3	0.4
89	9.8	0.3	56	52	9	43	40	45	41	-268	-268	7.4	7.4	24	9.5	0.3
97	9.8	0.3	58	54	7	44	41	44	39	-268	-268	7.4	7.4	24	9.5	0.4
135	9.9	0.3	58	52	10	44	40	45	39	-268	-268	7.4	7.4	24	9.6	0.5
126	9.9	0.4	58	52	10	44	40	45	41	-268	-268	7.4	7.4	24	9.5	0.5
132.5	14.4	0.9	52	45	13	40	34	41	36	-268	-268	7.5	7.4	24	13.5	0.4
138	14.4	0.5	56	48	14	43	36	43	35	-268	-268	7.4	7.3	24	13.9	0.5
150	14.4	0.5	55	45	18	42	34	42	34	-268	-268	7.5	7.4	24	13.9	0.6
156	15.0	0.5	54	46	15	41	35	41	36	-268	-268	7.4	7.4	24	14.5	0.4
161	15.0	0.5	58	51	12	44	39	44	40	-268	-268	7.4	7.4	24	14.5	0.4

Q = 2.5 lt/min.

124g of F-400 Used

Table D 2.3

Run # 3, Data

Time (Hrs.)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In mg/l	T.O.C. Out mg/l	S^{-2} mV In	S^{-2} mV Out	pH In	pH Out	Temp. °C	ΔD.O. mg/l	Co^{2+} In (mg/l)	Co^{2+} Out (mg/l)
5	17.8	13.8	50	0	100	38	0	38	0	-268	-268	6.8	6.8	24	4.0	0	0
17	17.8	2.1	50	40	20	38	30	39	29	-268	-268	6.8	6.8	24	15.6	0	0
27	18.4	7.5	42	32	24	32	24	32	24	-268	-268	6.8	6.8	24	10.9	0	0
41.5	18.4	2.5	40	39	2.5	31	30	31	29	-268	-268	6.9	7.0	24	15.9	0	0
45.5	18.3	2.4	41	39	5	31	30	31	30	-268	-268	7.0	7.0	24	15.9	0	0
46.5	17.8	1.7	41	35	14	31	27	32	28	-268	-268	7.0	7.0	24	16.1	0	0
51.5	17.6	1.7	44	39	11	34	30	35	30	-268	-268	7.0	7.1	24	15.9	0	0
55	9.0	0.5	44	39	11	34	30	34	32	-268	-268	7.0	7.0	24	8.5	0	0
66	8.6	0.2	45	40	12	34	30	35	30	-268	-268	7.0	7.0	24	8.4	0	0
68	4.5	0.2	45	40	15	35	30	35	29	-268	-268	7.0	6.9	24	4.5	0	0
70.5	4.5	0.2	46	46	0	35	35	35	35	-268	-268	7.0	7.0	24	4.3	0.25	0.21
76	4.6	0.2	51	50	2	39	39	40	38	-268	-268	7.0	7.1	24	4.3	0.25	0.22
87	4.4	0.1	47	46	2	35	35	34	36	-268	-268	7.0	7.0	24	4.3	0.32	0.29
98.5	4.5	0.2	52	51	2	39	39	39	40	-268	-268	7.0	7.0	24	4.3	0.26	0.25
112.5	4.5	0.2	65	63	1.5	48	48	48	47	-268	-268	7.2	7.2	24	4.3	0.25	0.24
123	4.6	0.3	64	63	0	50	48	50	49	-268	-268	7.2	7.2	24	4.3	0.23	0.22
140	3.0	0.3	66	65	1.5	50	50	50	51	-268	-268	7.3	7.3	24	2.7	9.29	0.22

Q = 2 lt/min.

835g of F-400 used

Table D 2.4

Run # 4, Data

Time (Hrs.)	D.O. In (mg/l)	D.O. Out	Phenol In	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In	O.C.P. Out (mg/l)	T.O.C. In	T.O.C. Out (mg/l)	pH In	pH Out	ΔD.O. mg/l	Temp. °C	O.C.P. / ΔD.D.O.
5	16.0	14.0	15	1	93	11.5	-	12	-	7.4	7.4	2.0	24	-
10	16.0	13.2	15	7	53	11.5	5	12	5	7.4	7.4	2.8	24	2.3
20.5	16.0	6.8	17	13	23	13	10	12	9	7.4	7.4	9.2	24	0.3
25.5	16.0	6.2	16	14	12	12	11	12	11	7.4	7.4	9.8	24	0.1
29	18.5	6.6	15	7	53	11.5	5	12	6	7.4	7.4	11.9	24	0.5
35	19.0	8.2	15	6	60	11.5	4.5	12	5	7.4	7.4	10.8	24	0.6
45	18.6	7.2	16	7	56	12	5	12	5	7.4	7.4	11.4	24	0.6
55	18.5	6.5	15	5	67	11.5	4	12	4	7.4	7.4	12.0	24	0.5
61	16.0	4.5	15	8	47	11.5	6	12	6	7.3	7.3	11.5	24	0.5
70	10.2	1.1	14	9	36	11	7	11	7	7.4	7.3	9.1	24	0.4
74	24.5	5.3	15	4	73	11.5	3	12	3	7.4	7.4	19.2	24	0.4
83	27.0	3.3	17	3	82	13	2	12	2	7.3	7.3	23.7	24	0.5
94	10.6	0	16	10	60	12	8	11	9	7.4	7.4	10.6	24	0.4
99	27.0	4.1	16	3	81	12	2	12	2	7.4	7.5	22.9	24	0.4
105	19.5	1.0	15	3	80	11.5	2	11	2	7.4	7.4	18.5	24	0.5
122	22.0	2.5	14	0	100	11	0	11	0	7.4	7.4	19.5	24	0.5
125	27.8	2.3	15	0	100	12	0	12	0	7.4	7.4	25.5	24	0.5
132	29.8	2.5	14	0	100	11	0	12	0	7.4	7.4	27.3	24	0.4
137	29.0	2.0	16	0	100	12	0	12	0	7.4	7.4	27.0	24	0.4

Q = 2 lt/min.

800 g of F-400 Used

Table D 2.5

Run # 5, Data

Time (Hrs)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In (mg/l)	T.O.C. Out (mg/l)	pH In	pH Out	Temp. °C	ΔD.O. mg/l	ΔO.C.P. / ΔD.O.
5	16.5	16.5	18	1	94	12	1	12	1	7.1	7.1	24	0	--
15.5	19.5	16.0	28	11.5	94	21	9	21	10	7.3	7.2	24	3.5	3.4
20	19.0	2.0	18	11.5	94	12	9	13	9	7.3	7.3	24	17	0.2
26	26.3	3.0	18	12	94	12	9	12	9	7.3	7.3	24	23.8	0.1
35	26.0	3.2	18	3	84	14.5	2	15	4	7.4	7.3	24	22.8	0.5
46	26.0	2.6	18	2	89	14	15	14	2	7.4	7.4	24	23.4	0.1
52	26.0	2.6	18	2	89	14	15	13	2	7.4	7.4	24	23.4	0.1
63	26.0	0.6	18	5	72	14	4	15	4	7.4	7.3	24	25.4	0.4
71	36.0	3.0	17	0	100.	13	0	15	1	7.2	7.2	24	33	0.4
77	38.2	13.0	18	0	100	14	0	15	0	7.2	7.2	24	36.9	0.4
87	40.2	0.3	30	4.5	85	23	3	24	3	7.2	7.2	24	39.9	0.5
93	38.0	1.5	18	0	100	14	0	14	1	7.2	7.2	24	36.5	0.4

Q = 2 lt/min.

800 g of F-400 Used

Table D 2.6

Run # 6, Data

Time (Hrs)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In (mg/l)	T.O.C. Out (mg/l)	pH In	pH Out	ΔD.O. mg/l	Temper. °C	O.C.P. / D.O
12	14.2	9.2	35	5	86	27	4	27	4	7.5	7.5	5.0	24	4.6
18	44.0	13.5	35	9	74	27	7	28	7	7.5	7.4	30.5	24	0.6
24.5	48.6	3.4	35	7	80	27	5	27	5	7.5	7.5	45.2	24	0.5
36	30.1	9.6	35	22	37	27	17	27	16	7.5	7.5	20.5	24	0.5
42	44.0	13.2	38	21	45	29	16	29	16	7.5	7.5	30.8	24	0.4
48	44.0	10.1	46	24	48	35	18	34	18	7.5	7.4	33.9	24	0.5
59	42.2	2.2	52	22	58	40	17	40	17	7.5	7.4	40.0	24	0.6
64	42.0	3.2	35	18	49	27	14	27	15	7.5	7.5	38.8	24	0,3
70	42.0	1.4	37	17	54	28	13	28	13	7.5	7.5	40.6	24	0.4
75	42.0	0.8	35	15	57	27	11	28	12	7.5	7.4	41.2	24	0.4
85	42.2	0.3	39	16	59	30	12	30	12	7.5	7.5	41.9	24	0.4
89	42.0	0.4	35	11	69	27	8	28	9	7.5	7.5	41.6	24	0.4

Q = 2 lt/min.

802 g of F-400 Used

Table D 2.7

Run # 7, Data

Time (Hrs)	D.O. In (mg/l)	D.O. Out (mg/l)	Phenol In (mg/l)	Phenol Out (mg/l)	Removed % Phenol	O.C.P. In (mg/l)	O.C.P. Out (mg/l)	T.O.C. In (mg/l)	T.O.C. Out (mg/l)	pH In	pH Out	ΔD.O. mg/l	Temp. °C	ΔO.C.P. / ΔD.O.
12	35.8	16	34	8	77	26	6	25	6	7.5	7.4	19.8	24	1.0
18.5	28.2	27	37	9	76	28	7	28	8	7.5	7.5	35.5	24	0.6
22	36.4	4	33	11	67	25	8	24	9	7.5	7.5	32.4	24	0.5
35.5	36.4	24	34	19	44	26	15	26	16	7.5	7.5	32.0	24	0.3
39.5	38.8	25	35	15	57	27	11	27	11	7.5	7.4	36.3	24	0.4
44	36.1	1.6	32	16	50	25	12	25	13	7.5	7.5	34.5	24	0.4
49	43.2	1.2	31	18	42	24	14	25	14	7.5	7.5	42	24	0.2
63	39.3	0.2	34	15	54	26	11	26	12	7.5	7.5	39.1	24	0.4
67	45.0	0.4	40	11	72	30	8	30	9	7.5	7.5	44.6	24	0.5
69	44.8	0.2	33	12	64	25	9	25	10	7.5	7.5	44.6	24	0.4

Q = 2 lt/min.

800 g of F-400 Used

Run 3:

A Phenol mass balance across the reactor for Run 3 in Table D.2.8 follows:

TABLE D.2.8

Phenol Balance Run # 3

Time hrs.	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 5		0	1.4
5 - 17	102	28.8	13.4
17 - 27	55.2	43.2	7.8
27 - 46.5	96	86.6	
46.5 - 68	113.5	103.2	42.1
68 - 70.5	13.3	12.9	
70.5 - 98.5	166.3	109.0	
98.5 - 140	323.7	318.7	22.2
TOTAL	870.5	702.4	86.9

Balance:
81.2 g (accumulated Phenol).

The lower 11 cm of the fluidized bed did not develop biological growth and therefore remained in equilibrium with the influents Phenol concentration of 50 mg/l.

The adsorbed Phenol, on this part of the bed is therefore equal to:

$$(11/26.5) X\ 835 - 115 = 41000 \text{ mg}$$

(835 g = total mass of A.C. in the reactor)

The remaining 40.2 g of Phenol were adsorbed on the part of the bed that had developed biological growth. The resulting loading on this second part of the bed is equal to:

$$40.200 / [(26.5-11 / 26.5)\ 835] = 82 \text{ mg/g}$$

Run 4:

The supplied Oxygen during this run was more than the stoichiometrically necessary as can be seen by the fact that D.O. existed in the effluent. Therefore no Oxygen limitation existed throughout the run.

The removal behaved as in the previous runs. After the initial adsorption phase, bio-oxidation took over and the removal reached 100% by the end of the run (bed wash out).

This time the Phenol isotherm of the spent carbon was determined (Appendix D.4). The activated carbon

particles of the bed exhibited an adsorption isotherm similar to the one of the virgin carbon, with lower loadings, indicating that almost all Phenol was biodegraded rather than being adsorbed.

A Phenol mass balance across the reactor for Run # 4 is summarized in Table D.2.9.

TABLE D.2.9

Phenol Balance Run # 4

Time hrs.	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 10		4	1
10 - 25.5		22	12
25.5 - 70		38	37
70 - 137		16	110
TOTAL	263	80	160

The accumulated (adsorbed) Phenol is according to Table D.2.9 : 23 g. Given that 11 cm of the 25.5 cm of the bed did not develop growth, they remained in equilibrium with the influent Phenol concentration of 15 mg/l. Therefore, the respective mass of Phenol adsorbed on this part of the bed is (Fig. 4.1.2).

$$(11/25.5) \times 800\ g - 85\ \frac{mg}{g} \times 10^{-3}\ \frac{g}{mg} = 29\ g$$

Therefore the part of the bed that developed growth is Phenol free, by the end of the run.

9 gr. of wet spent carbon was placed in a respirometer. The equivalent dry mass was evaluated in the same way as for the WRL 2000A samples (Appendix B), as being 3.08 g. There was a 0.02 mV deflection of the recorder, indicating some Oxygen consumption. Since the current was 0.2 A the total time of Oxygen production is:

$$0.02 \times 64.48 = 1.29 \text{ min.} \quad \text{or}$$

$$0.2 \times 12.9 \times 4.97 = 1.28 \text{ mg oxygen}$$

which can be attributed to endogenous respiration of the bacteria attached on the spent activated carbon sample used.

Run 5:

No Oxygen limitation was experienced during this run. Consequently, a very fast expansion (growth) rate of the bed was experienced and washed out which started only 95 hours of operation.

The determination of the Phenol adsorption isotherm of the bed's carbon, at the end of the run, (Appendix C) indicates loadings close to the ones of the virgin carbon but lower, as the residual organics adsorption limits the Phenol adsorption capacity of the carbon.

A 0.05 mV deflection of the recorder of the respirometer indicates a minor Oxygen consumption which is the endogenous respiration of the bacteria of the seed. It also shows that there were no biodegradable molecules adsorbed on the carbon particles of the active part of the bed, because otherwise they would have exerted positive Oxygen demand.

Table D.2.10

Phenol Mass Balance Run # 5

Time hrs.	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 26	56	33	12
26 - 63	80	19	64
63 - 93	72	0	75
TOTAL	218	52	151

The Phenol mass balance across the reactor (Table D.2.10) indicates that the amount accumulated in the reactor is 15 g.

Given that 8 cm of the 25.5 of the activated carbon bed did not develop growth and remained in equilibrium with the influent 18 mg/l Phenol concentration:

$$(8 / 25.5) \times 800 \text{ g} = 251 \text{ g} \qquad \text{(using Fig. 4.1.2)}$$

$$251 \text{ g} \times 85 \frac{\text{mg}}{\text{g}} \times 10^{-3} \frac{\text{g}}{\text{mg}} = 21.3 \text{ g Phenol}$$

21.3 g Phenol were adsorbed on this part of the bed. Therefore, the rest of the particles that had developed biological growth, were Phenol free. The fact that there is a difference among the total accumulated Phenol given by Table D.2.10 and the 21.3 g calculated above has to be viewed in the context of the average values used for the mass balances. The same comment applies to all the Phenol mass balances caculated for the continuous runs.

Run 6:

Oxygen limitation was experienced during Run 6. That is why the removal of the Phenol did not reach 100%, although pseudo steady state was reached in the reactor, as we can see from the effluents DO and Phenol concentrations (Fig. D2.6.A)

The adsorption isotherm of the spent carbon that had formed the active fluidized bed showed (Appendix D.4) reduced Phenol loadings. This fact can be interpreted as the effect of residual organics and Phenol that existed

on the activated carbon particles, by the end of the run.

Total loadings are used for the plotting of the isotherms. Total loading is the sum of the loading resulting from Phenol uptake during the isotherm determination, plus the loading resulting from the previously (during the run) adsorbed Phenol, as determined through the mass balances.

Table D.3.11 below summarizes a Phenol mass balance across the reactor, and indicates a total accumulation of 62 g of Phenol.

Table D.2.11

Phenol Mass Balance Run # 6

Time hrs.	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 12	50	3	4
12 - 24.5	53	6	16
24.5 - 36	48	26	27
36 - 42	27	15	11
42 - 48	30	16	14
48 - 59	65	31	29
59 - 64	26	12	14
64 - 85	93	43	62
85 - 89	18	7	12
TOTAL	410	159	189

As 4.5 cm at the bottom of the bed did not develop any growth and they are therefore in equilibrium with the influent Phenol concentration. In other words:

$$(4.5 / 25.5) \times 800 = 144 \text{ g}$$

of A.C. are in equilibrium with 35 mg/l Phenol and they have adsorbed (Fig. 4.1.2).

$$144 \times 106 = 15.000 \text{ mg}$$

The remaining 47 g are adsorbed on the carbon particles that developed growth and they result to an average loading of:

$$47.000 / (800 - 144) = 72 \text{ mg/g.}$$

The total deflection of the recorder during the respirometer study was 2.1 mV which is equivalent to a total time of oxygen production:

$$2.1 \times 65.45 \frac{\text{min}}{\text{mV}} = 138.9 \text{ min}$$

Given that the current was 0.205 A the produced Oxygen was

$$0.205 \times 138.9 \times 4.97 = 1334 \text{mg Oxygen}$$

The equivalent mass of Phenol is (assuming total oxidation and Oxygen demand equal to the Biological Oxygen Demand)

$$\frac{141.6 \text{mg}}{1.7 \text{ mg/mg}} = 83.3 \text{ mg Phenol}$$

Since the dry mass of carbon in the respirometer was 1.3 g the resulting loading is:

$$83.3 \text{ mg Phenol} / 1.3 \text{ g carbon} = 64 \text{ mg/g}$$

Therefore the total accumulated Phenol in the active part of the bed is:

$$64 \frac{mg}{g} \times (800 - 144)_g = 42 \text{ g}$$

Run 7:

Table D.2.12 below summarizes the Phenol mass balance for the seventh run. The total accumulation of Phenol according to the mass balance is 41 g.

Since 4 cm of the bed did not develop growth remained in equilibrium with the 34 mg/l influent Phenol concentration, thus having adsorbed

$$(4 / 25.5) \times 800 \times 106 \times 10^{-3} = 13.3 \text{ g}$$

The remaining 27.7 g were adsorbed on the active part of the bed resulting to an average loading of:

$$27.7 \, 10^3 / (800 - 144) = 42 \text{ mg/g}$$

The total deflection of the recorder during the respirometer study was 1.77 mV and the current 0.21A. The produced Oxygen therefore was:

$$(1.77 \times 65.45) \times 0.2 \times 4.97 = 115.4 \text{ mg Oxygen}$$

Given that 2.0 g of spent (dry) carbon were used, the equivalent loading is:

$$115.4 / 1.7 \sim 67.9 \text{ mg Phenol}$$

$$67.9 / 2.0 - 34 \text{ mg/g}$$

Therefore the accumulated Phenol in the active part of the bed was:

$$34 \times (800 - 144) \times 10^{-3} = 22.3 \text{ g}$$

which corresponds well with the value the mass balance evaluated.

The existence of adsorbed Phenol on the spent activated carbon, resulted to total loadings lower than the loading exhibited by virgin Filtrasorb 400 as shown on Figure 4.1.2.It is the same phenomenon as the one experienced during the isotherm determination of the spent carbon of Run 6 (Fig. D.4.3).

Table D.2.12

Phenol Mass Balance Run # 7

Time hrs.	Phenol In (g)	Phenol Out (g)	Biodegraded Phenol (g)
0 - 18.5	80	10	15
18.5 - 22	15	4	9
22 - 35.5	54	25	31
35.5 - 44	46	17	20
44 - 63	74	38	55
63 - 67	18	6	12
67 - 69	9	3	10
TOTAL	296	103	152

Table D2.13

Cumulative Applied Versus Cumulative Removed TOC Data

Run	Time Period	Time (hrs)	Applied TOC (g)	Cumulative Applied TOC	Removed TOC (g)	Cumulative Removed TOC
	0-27.5	27.5	156.7	156.7	24.9	94.9
	27.5-51.5	24	133.2	289.9	15	112.9
	51.5-72	21.5	129.1	419.5	12.3	125.2
2	72-89	17	112.2	531.7	12.7	137.9
	89-113.5	24.5	165.4	697.1	18.4	156.3
	113.5-126	12.5	84.4	781.5	9.4	165.7
	126-161	35	220.5	100.2	31.5	197.2
	0-17	17	79.5	79.5	51.0	51
	17-51.5	34.5	136.6	216.1	37.3	88.3
	51.5-66	14.5	60.9	277	6.9	95.2
3	66-70.5	21.5	18.9	295.9	2.2	97.4
	70.5-98.5	28	117.6	413.5	0	97.4
	98.5-140	41.5	244.0	657.5	10.0	107.4
	0-10	10	14.4	14.4	11.4	11.4
	10-25.5	15.5	22.3	36.7	3.7	15.1
	25.5-55	29.5	42.5	79.2	24.8	39.9
4	55-70	15	21.6	100.8	9.0	48.9
	70-83	13	18.7	119.5	14.1	63.0
	83-105	22	29.0	148.5	18.5	81.5
	105-137	32	46.1	194.6	46.1	127.6

Table D2.13

Run	Time Period	Time (hrs)	T.O.C. In (g)	T.O.C. In (g)	T.O.C. (g)	T.O.C. (g)
	0-5	7.2	7.2	7.2	7.2	7.2
	5-15.5	21.4	28.6	28.6	13.9	21.1
5	15.5-26	18.9	47.5	47.5	7.6	28.7
	26-63	57.7	105.2	105.2	40.0	68.7
	63-77	23.5	128.7	128.7	20.2	88.9
	77-93	34.6	163.3	163.3	32.6	121.5
	0-12	12	38.9	38.9	36.0	36
	12-24.5	12.5	42.0	80.9	34.5	70.5
6	24.5-42	17.5	58.8	139.7	33.6	104.1
	42-64	22	87.1	226.8	44.9	149.0
	64-75	11	37.0	263.8	19.8	168.8
	75-89	14	48.7	312.5	30.1	198.9
	0-12	12	36	36.0	31.7	31.7
	12-22	10	31.2	67.2	21.6	53.3
	22-35.5	13.5	40.5	107.7	22.7	76.0
7	35.5-44.5	9	28.1	135.8	14.0	90.0
	44.5-49	4.5	13.5	149.3	5.9	95.9
	49-63	14	42.0	191.3	20.2	116.1
	63-69	6	19.4	210.7	11.5	127.6

Fig.D.2.1A Phenol, D.O. Behavior With Time . Run 1

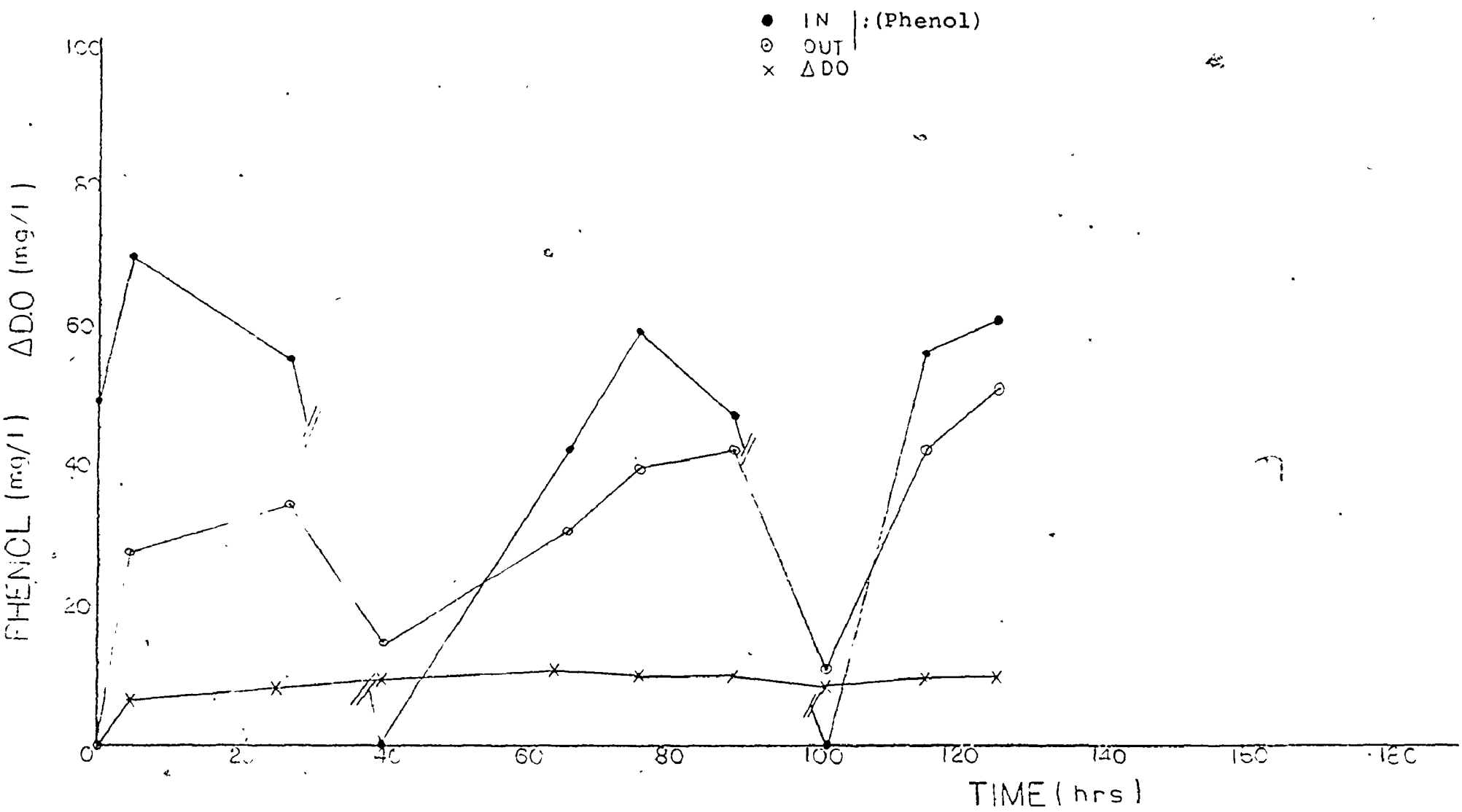


Fig.D.2.1B Effluent T.O.C. and O.C.P. Variation with Time . Run 1

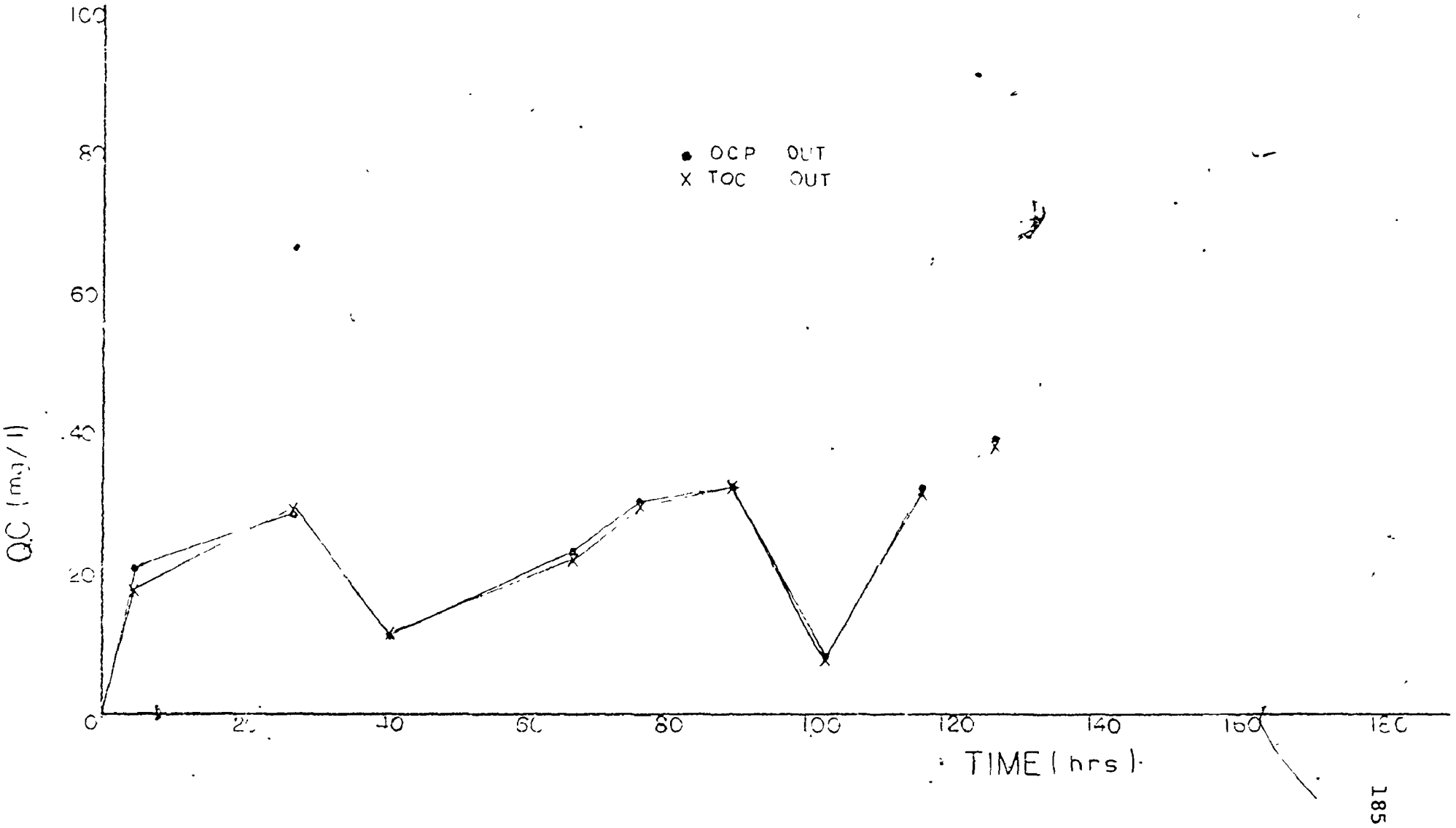


Fig.D.2.2A Phenol, D.O. Behavior With Time . Run 2

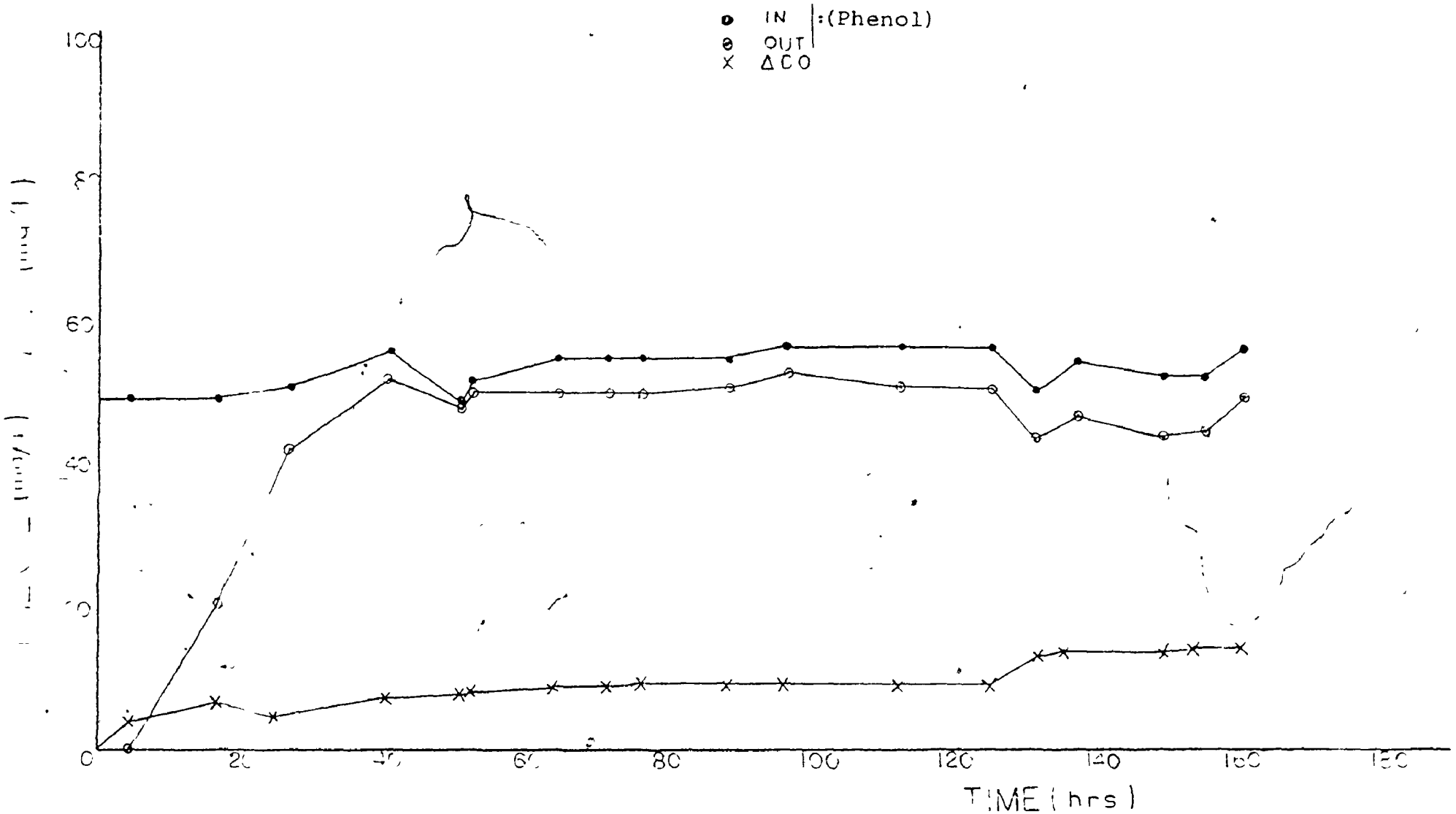


Fig.D.2.2B Effluent T.O.C. and O.C.P. Variation With Time. Run 2

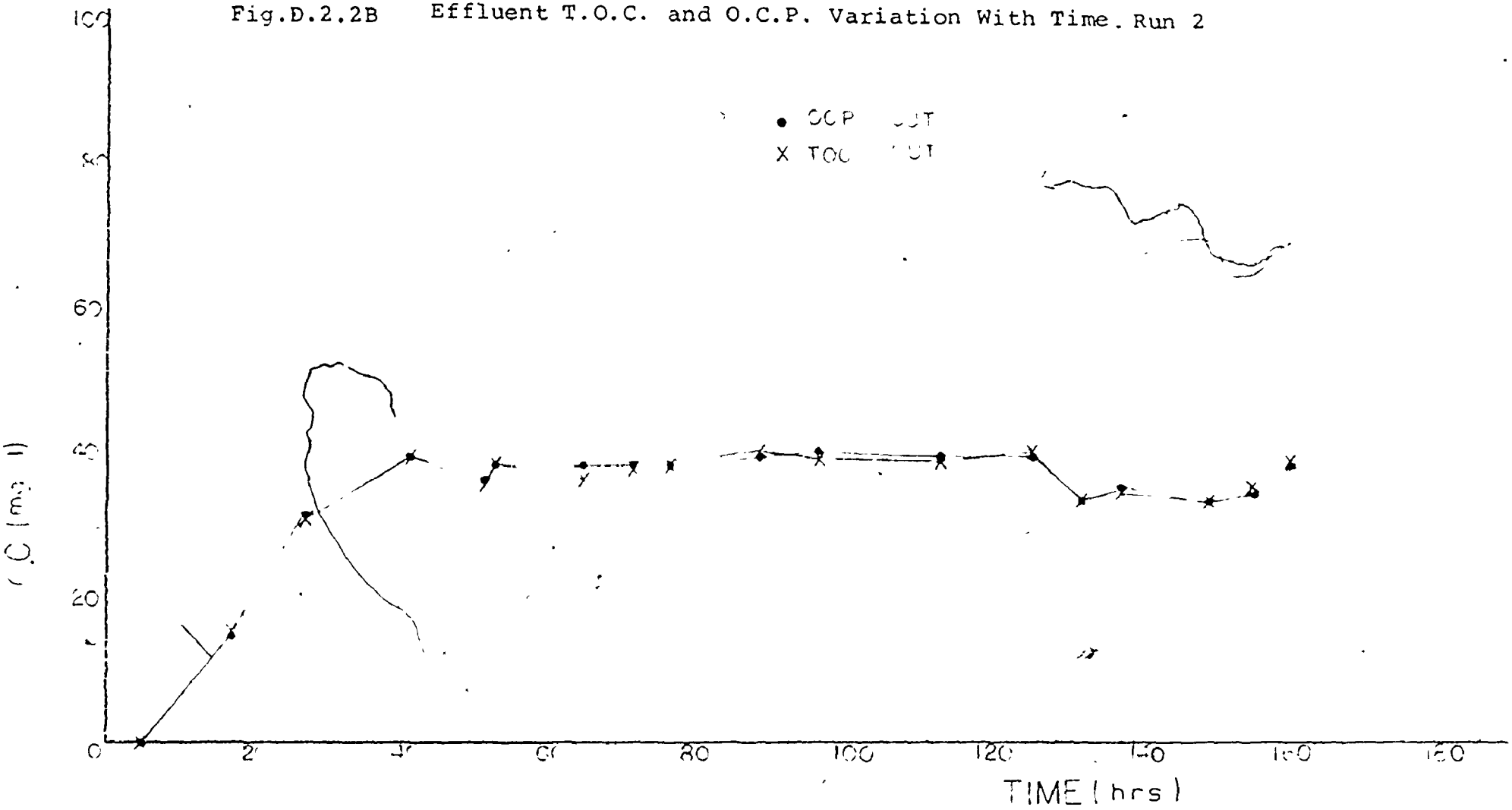


Fig.D.2.3. Phenol, ~~D.O.~~ Behavior With Time . Run 3

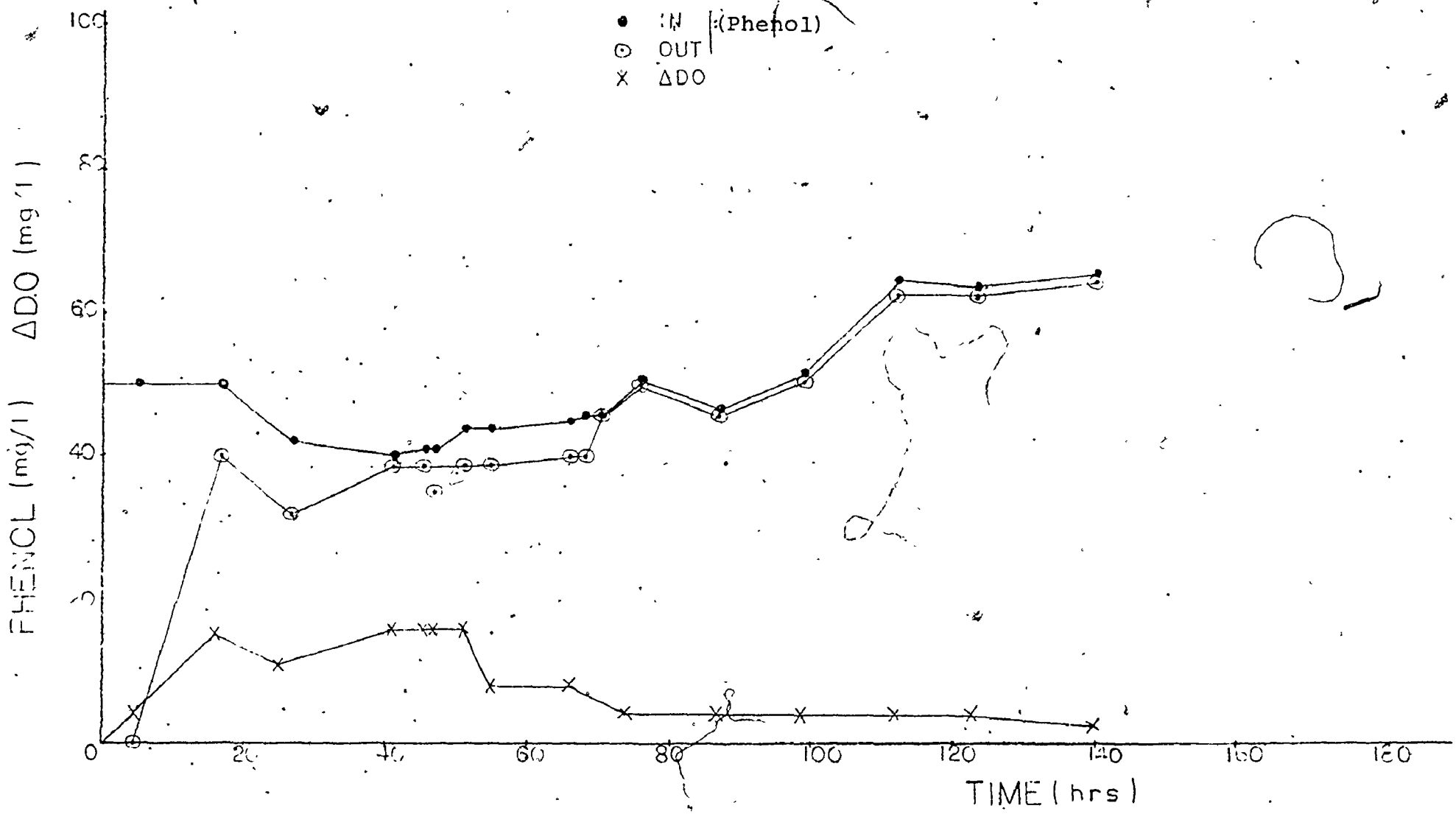
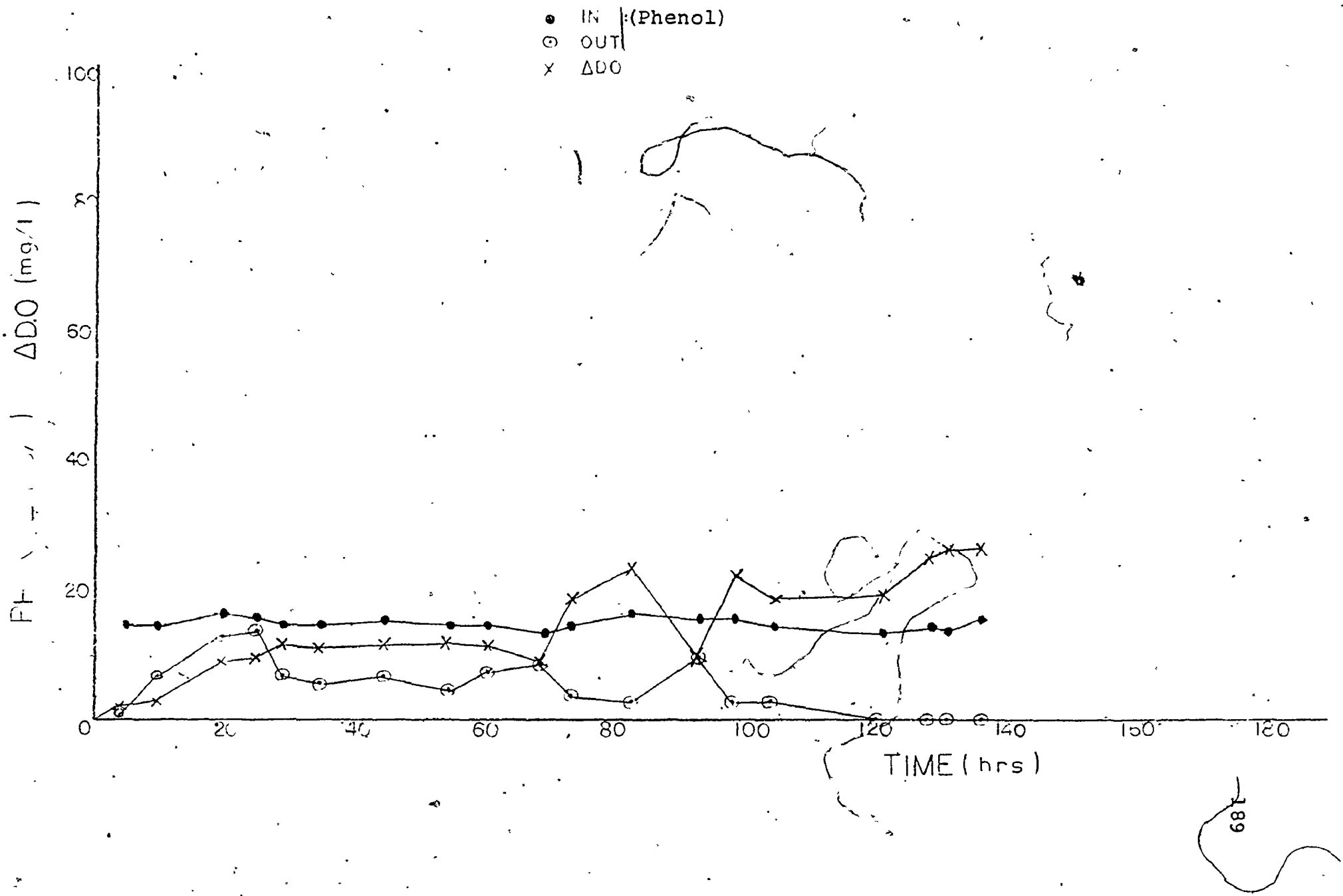


Fig.D.2.4A. Phenol, D.O. Behavior With Time . Run 4



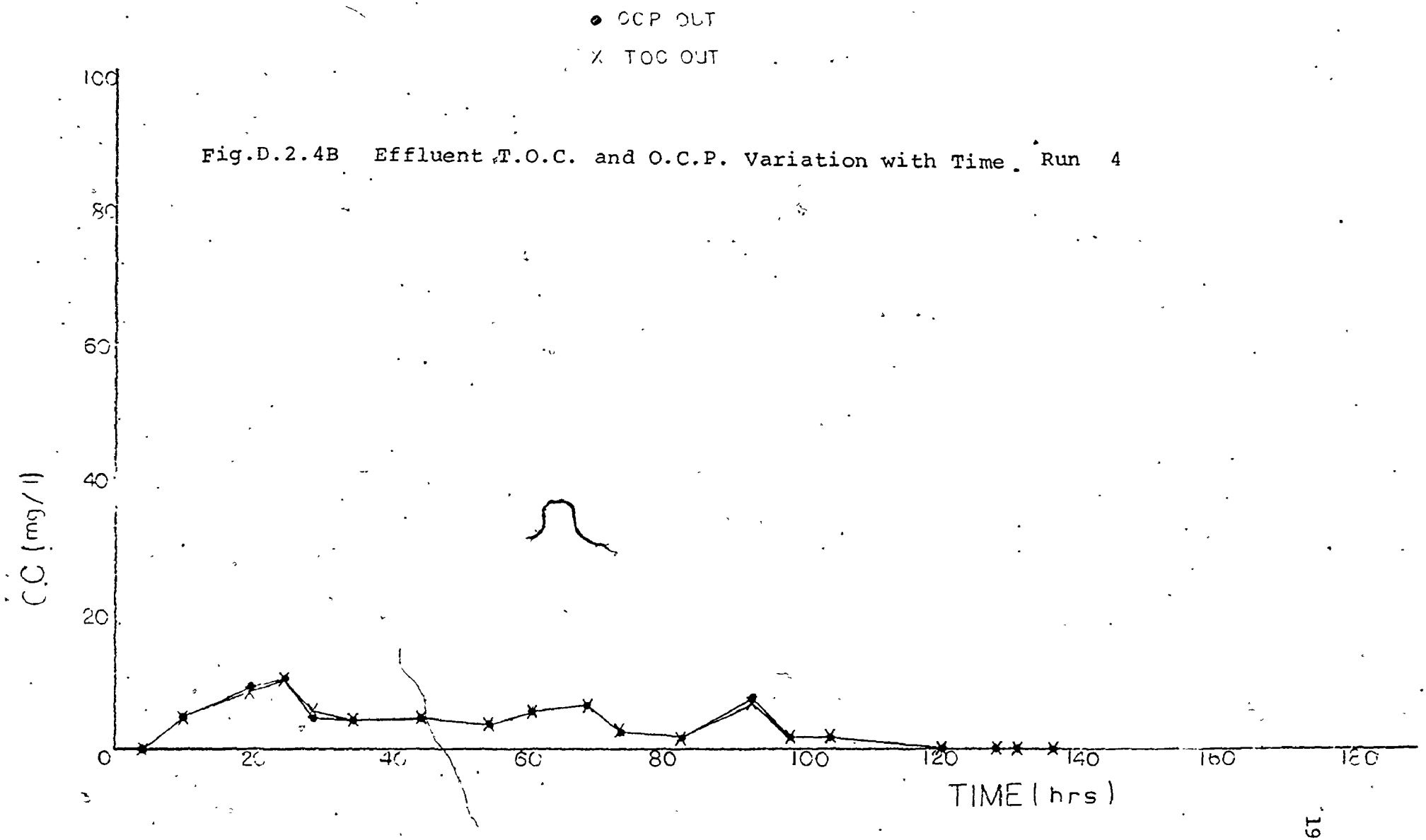


Fig.D.2.4B Effluent T.O.C. and O.C.P. Variation with Time. Run 4

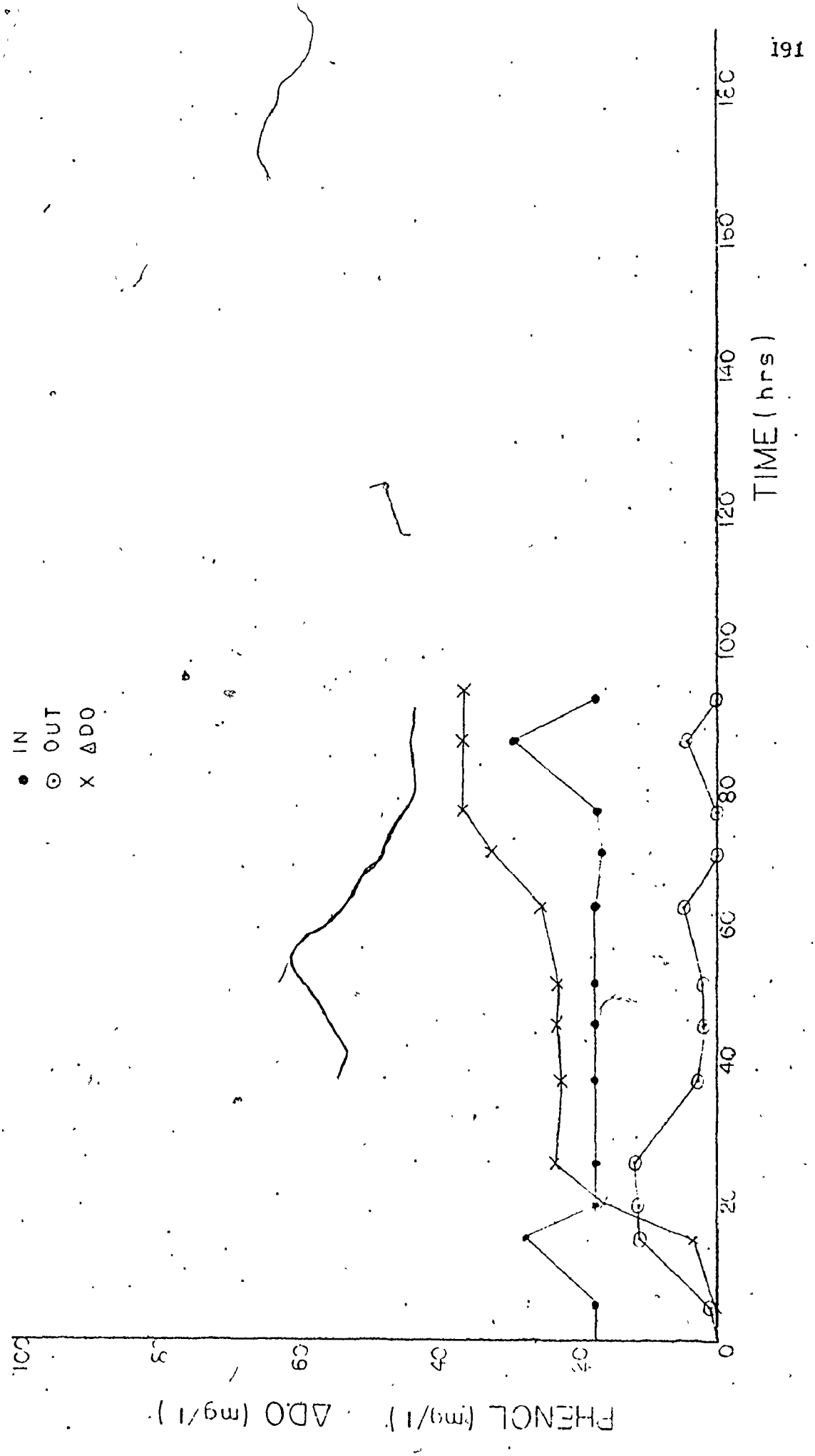


Fig.D.2.5 Effluent T.O.C. and O.C.P. Variation with Time . Run 5

Fig.D.2.6A Phenol, D.O. Behavior With Time . Run 6

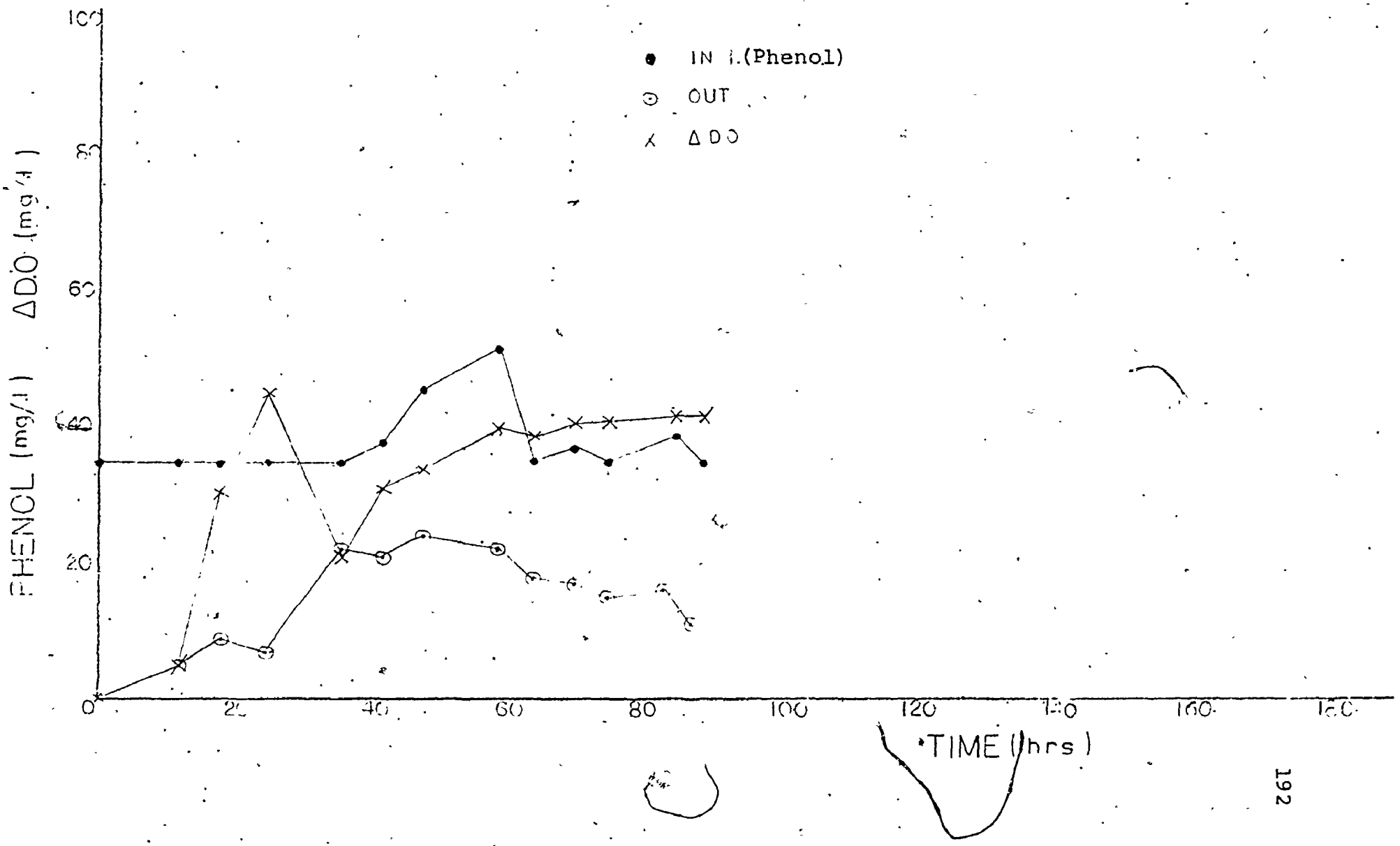


Fig.D.2.6B . Effluent T.O.C. and O.C.P. Variation With Time . Run 6

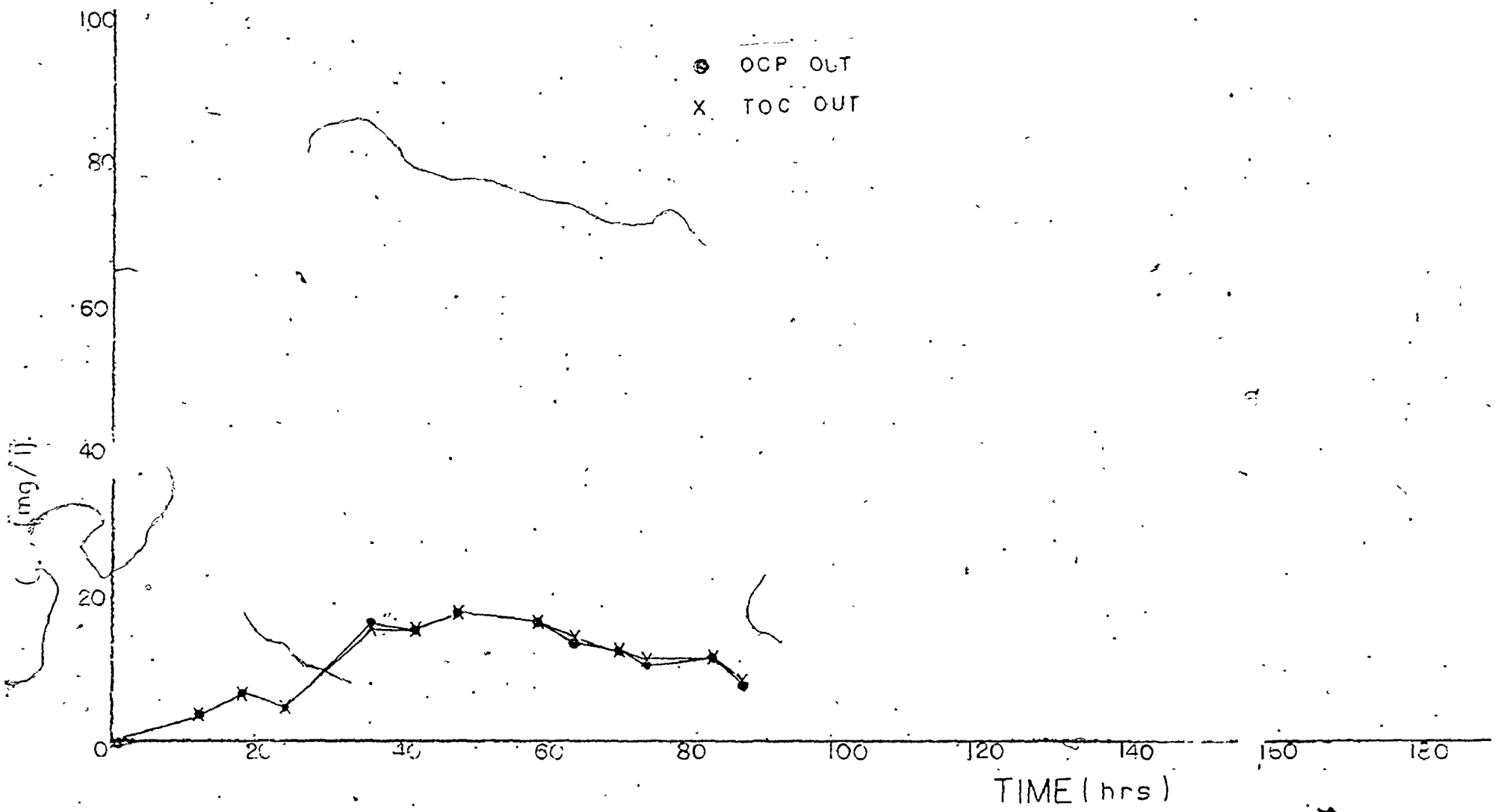


Fig. D.2.7A Phenol, D.O. Behavior With Time . Run 7

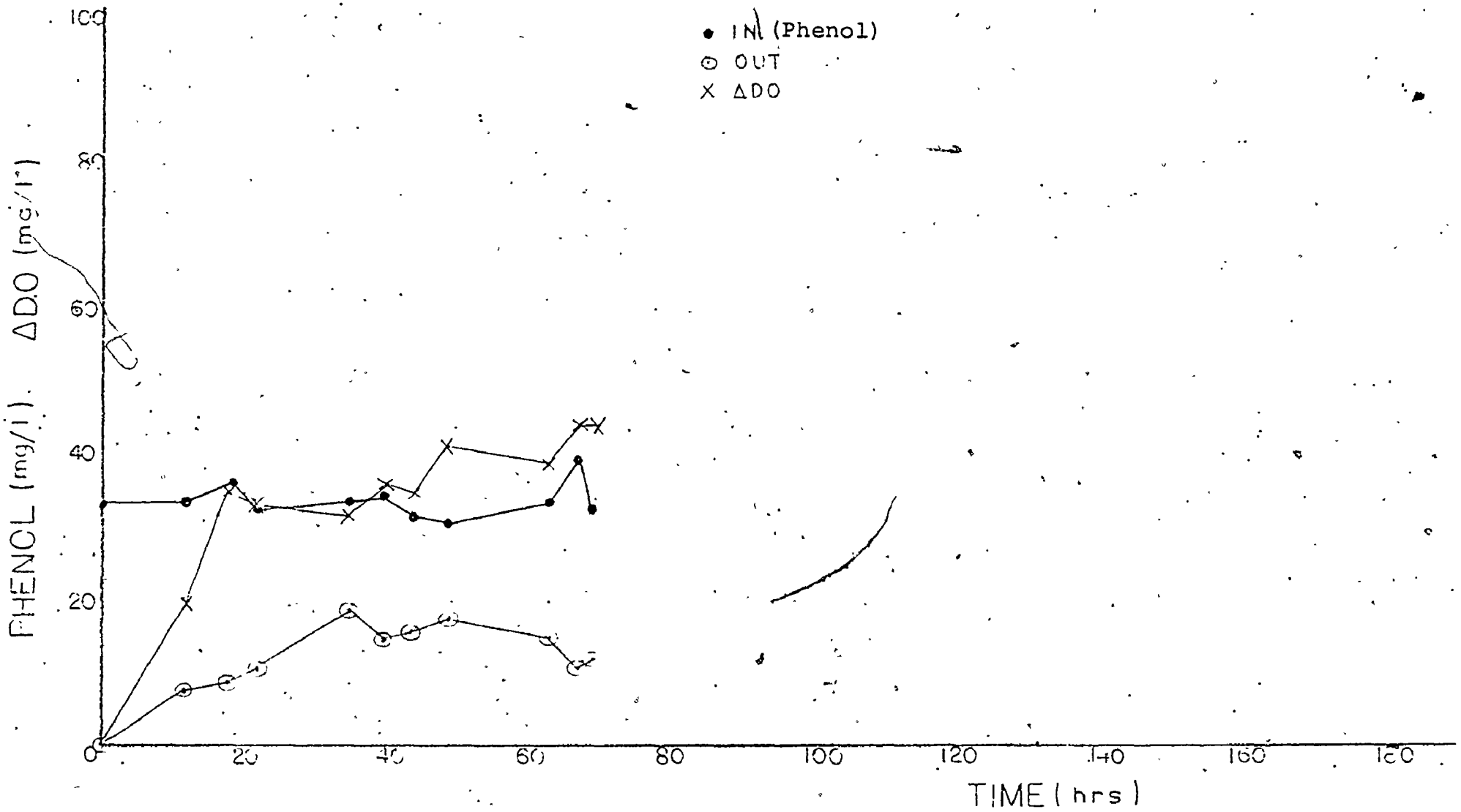


Fig.D.2.7B Effluent T.O.C. and O.C.P. Variation with Time Run 7

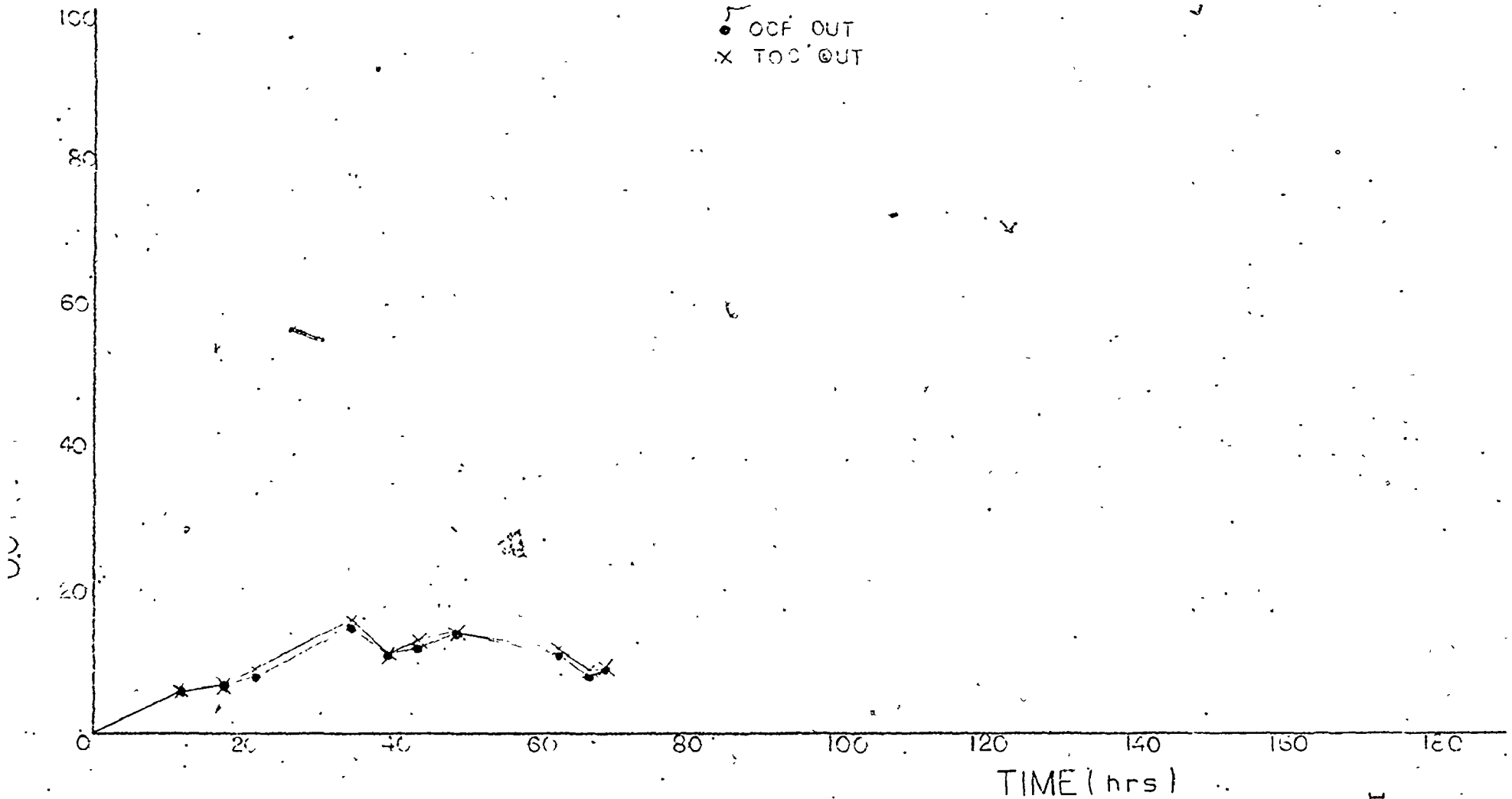


Fig.D.2.8 Phenol Removal . Run 1

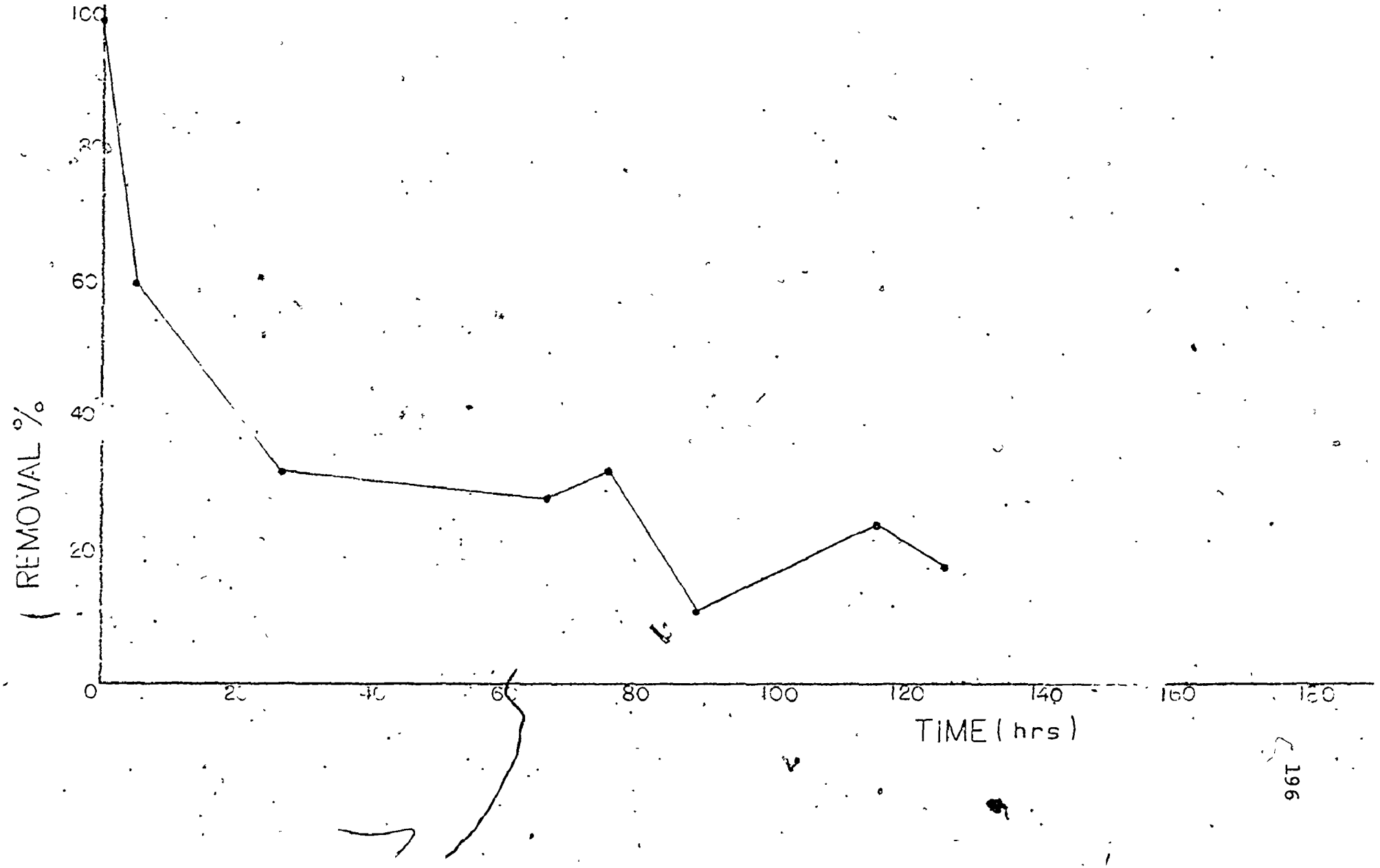


Fig.D.2.9 Phenol Removal and K Ratio Variation With Time . Run 2

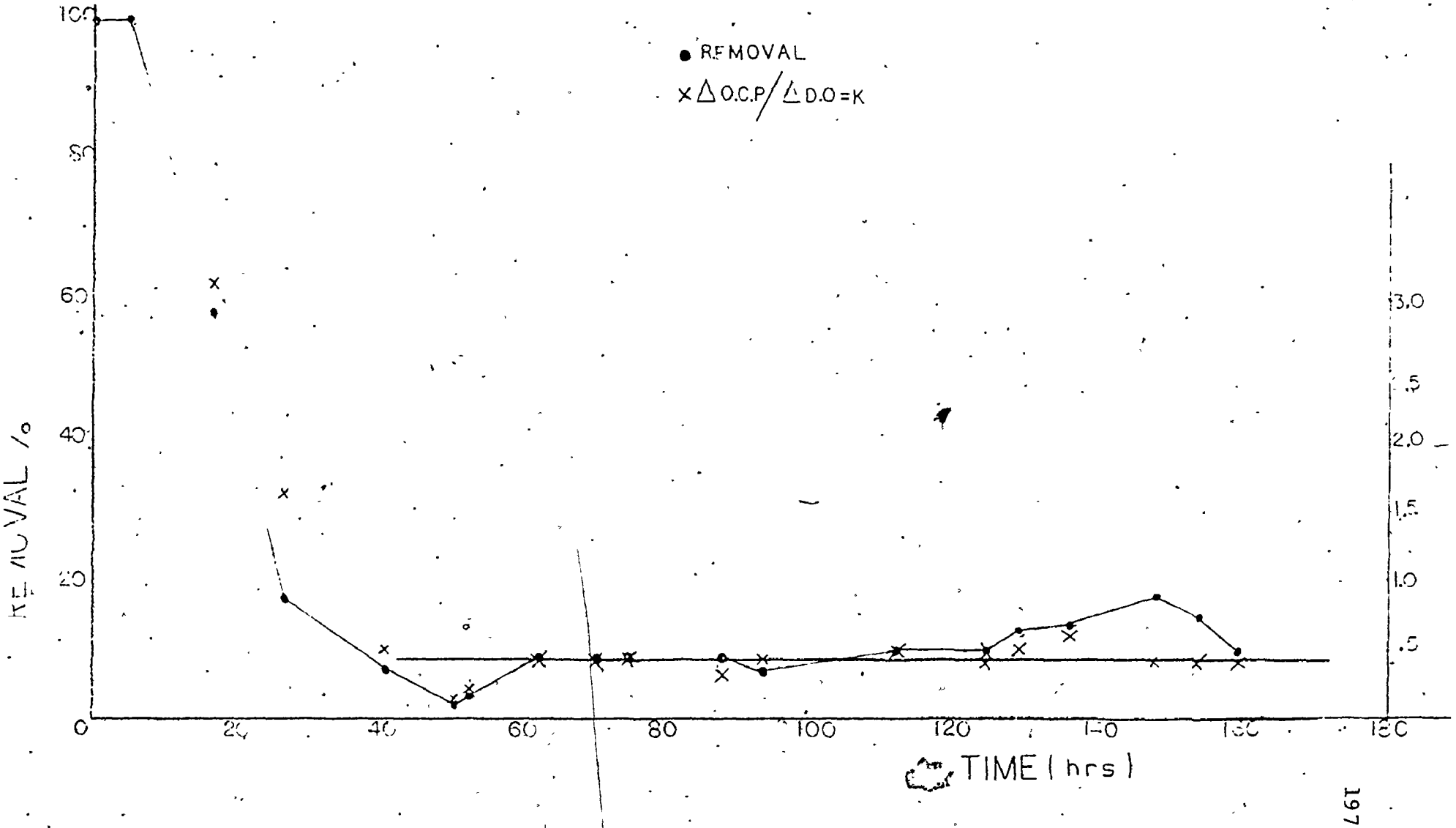


Fig.D.2.10 Phenol Removal and K Ratio Variation With Time . Run 3

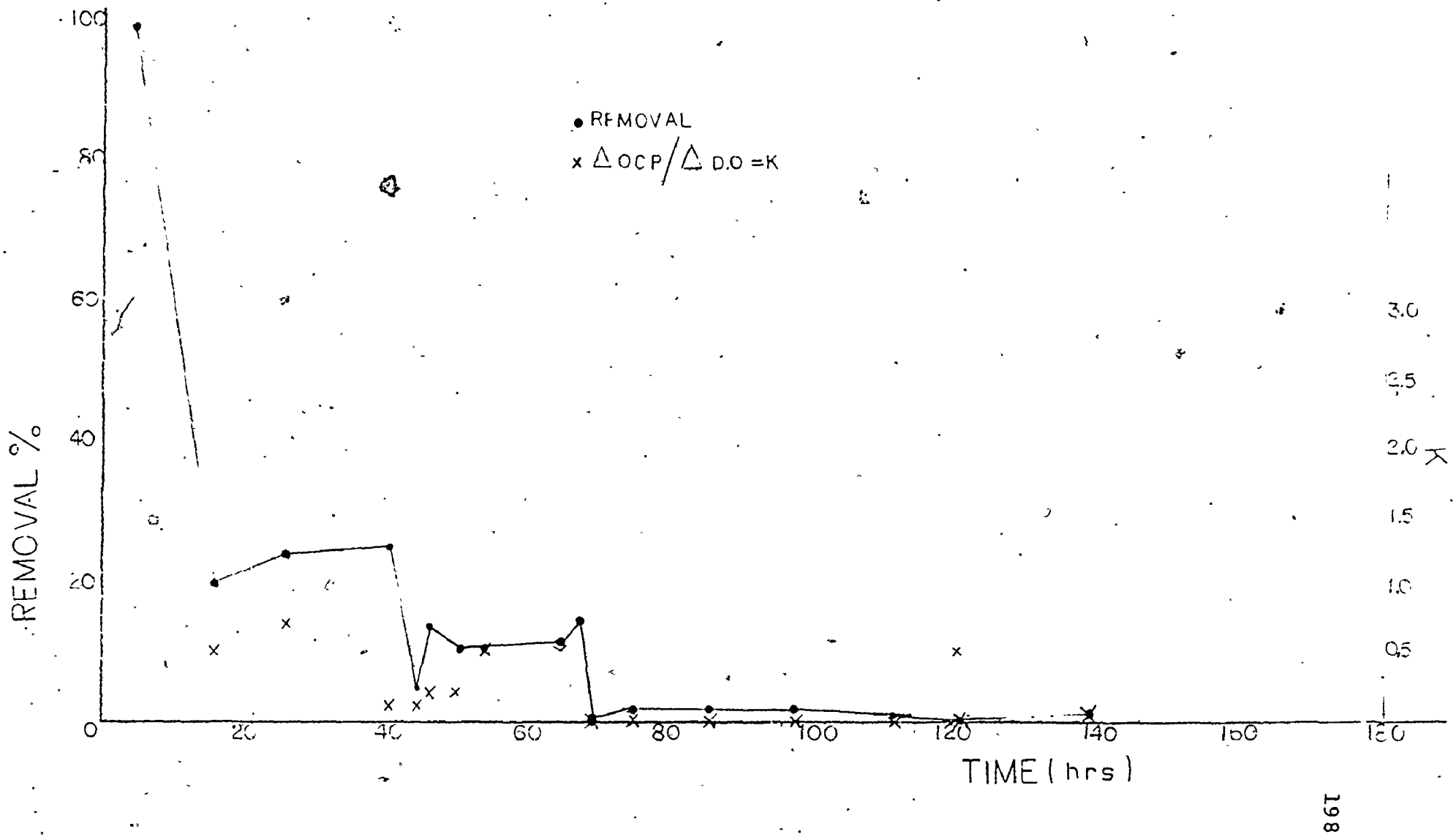


Fig.D.2.11 Phenol Removal and K Ratio Variation With Time . Run 4

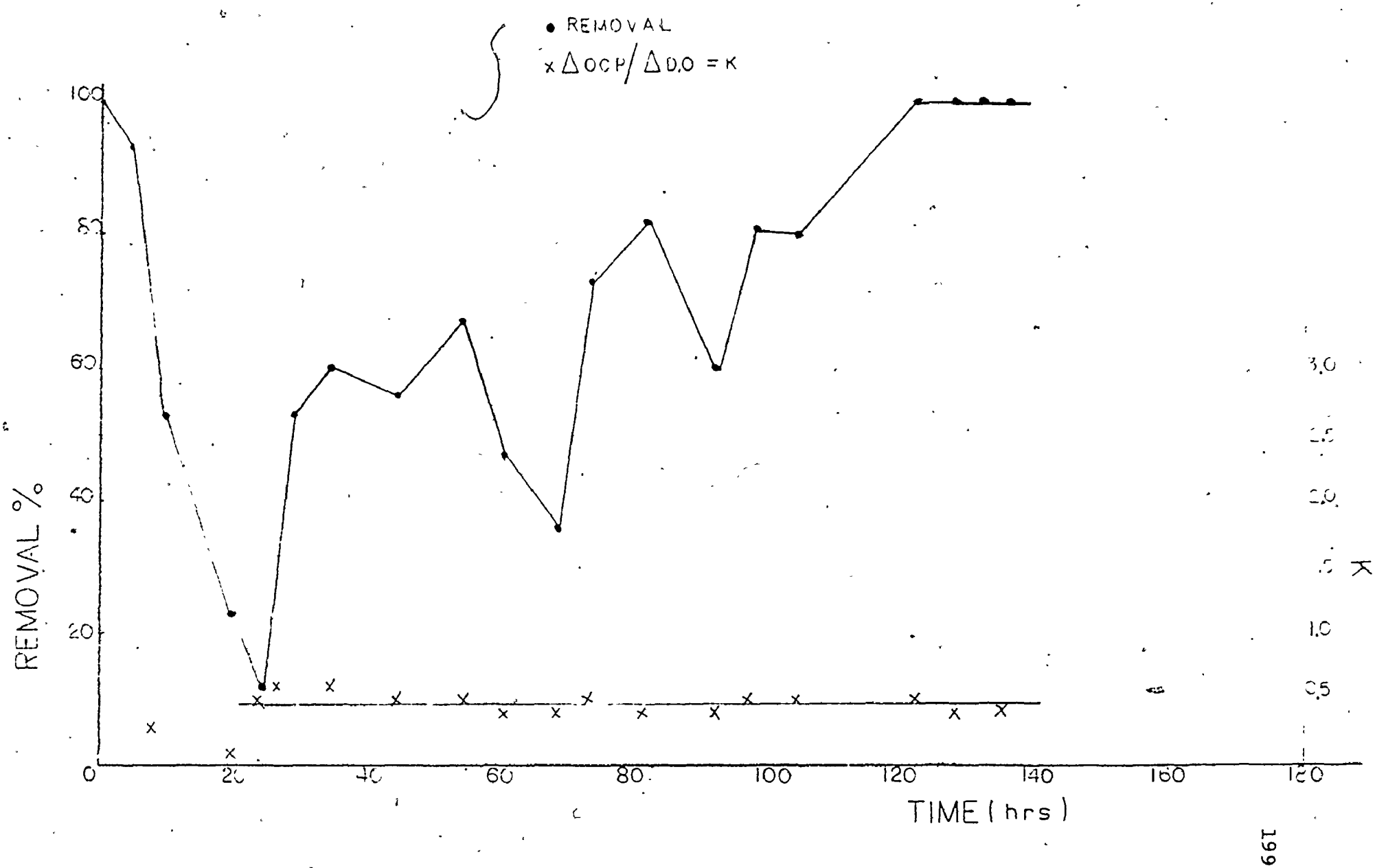


Fig.D.2.12 Phenol Removal and K Ratio Variation With Time . Run 5

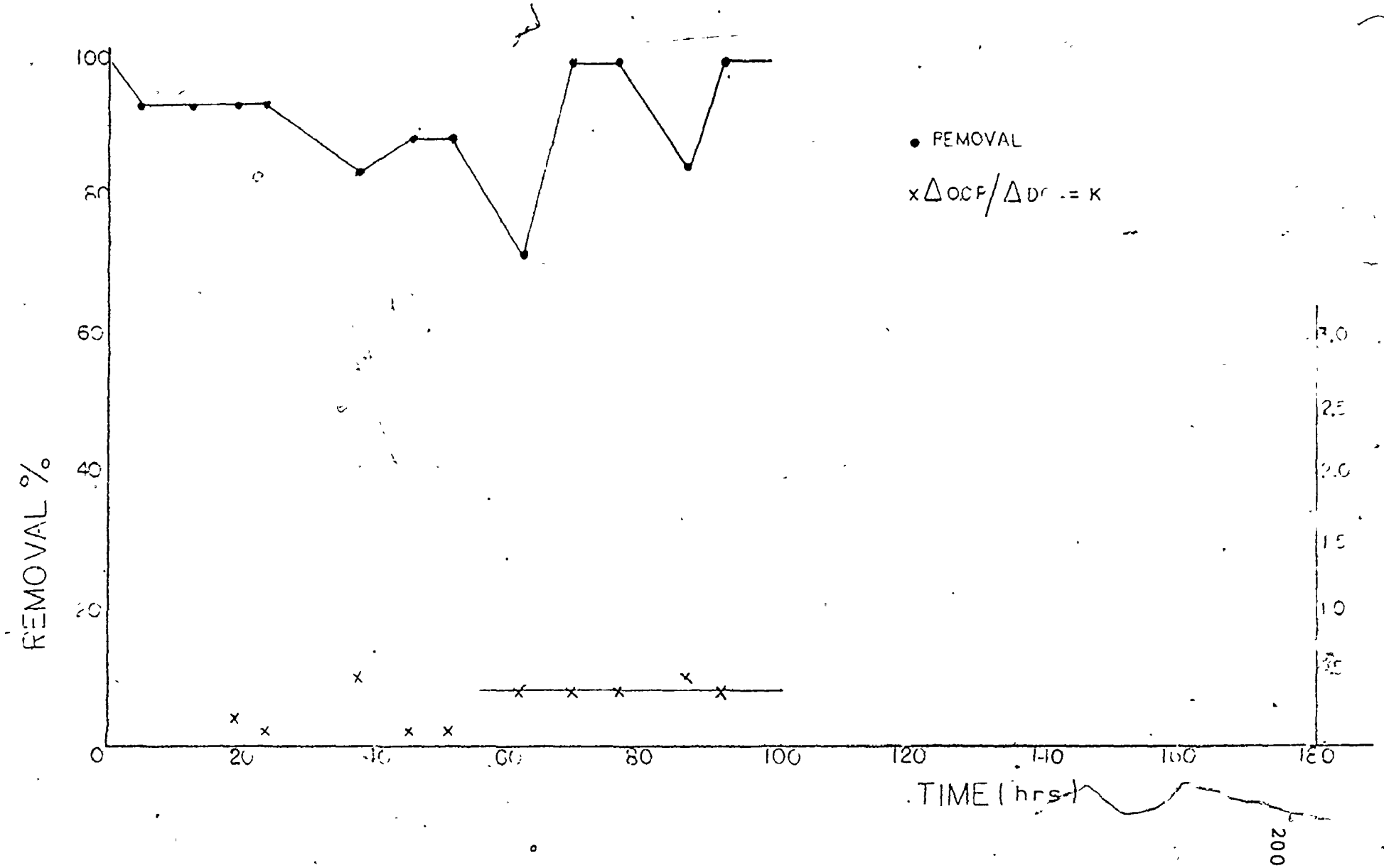


Fig.D.2.13 Phenol Removal and K Ratio Variation With Time Run 6

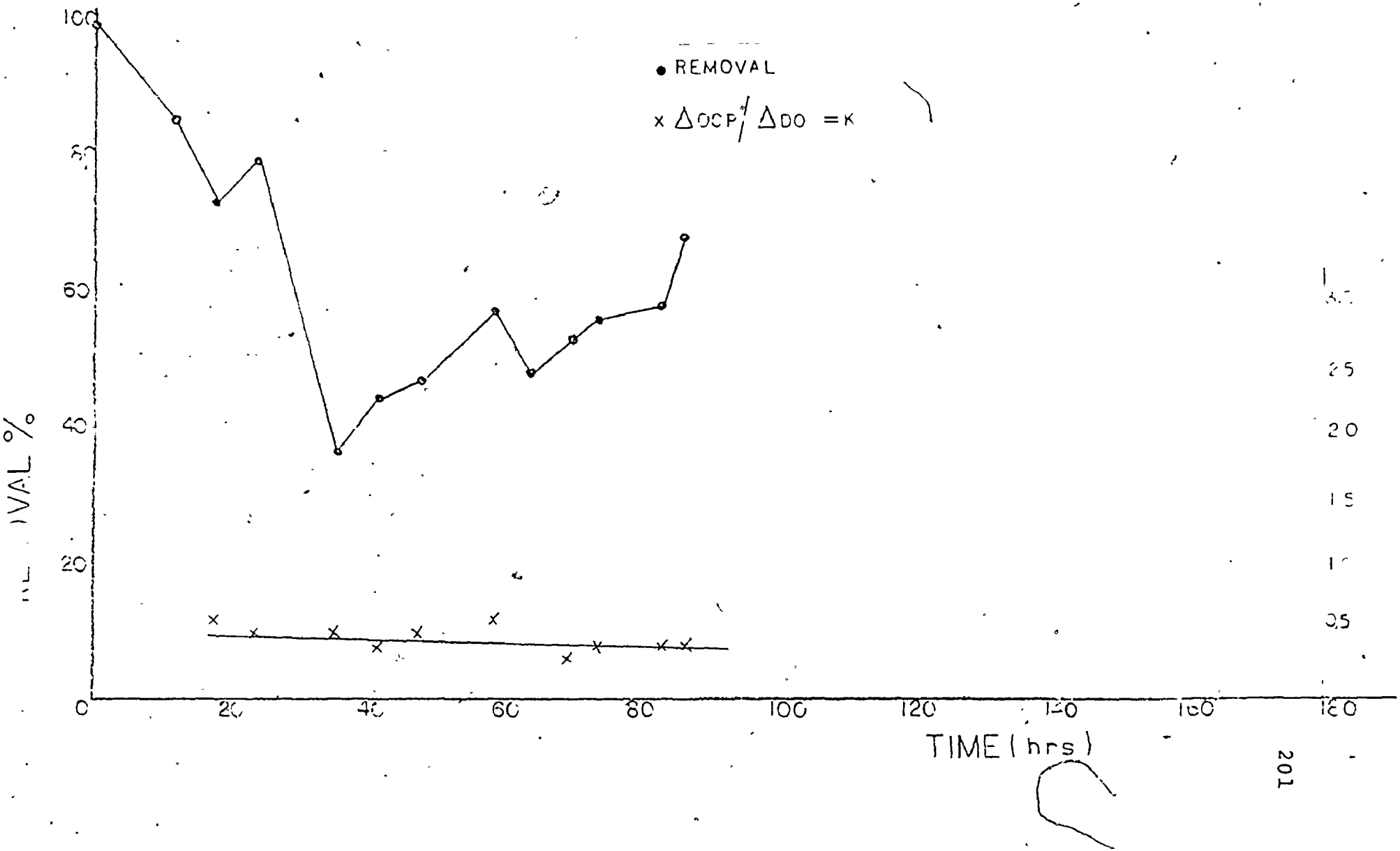


Fig.D.2.14 Phenol Removal and K Ratio Variation With Time Run 7

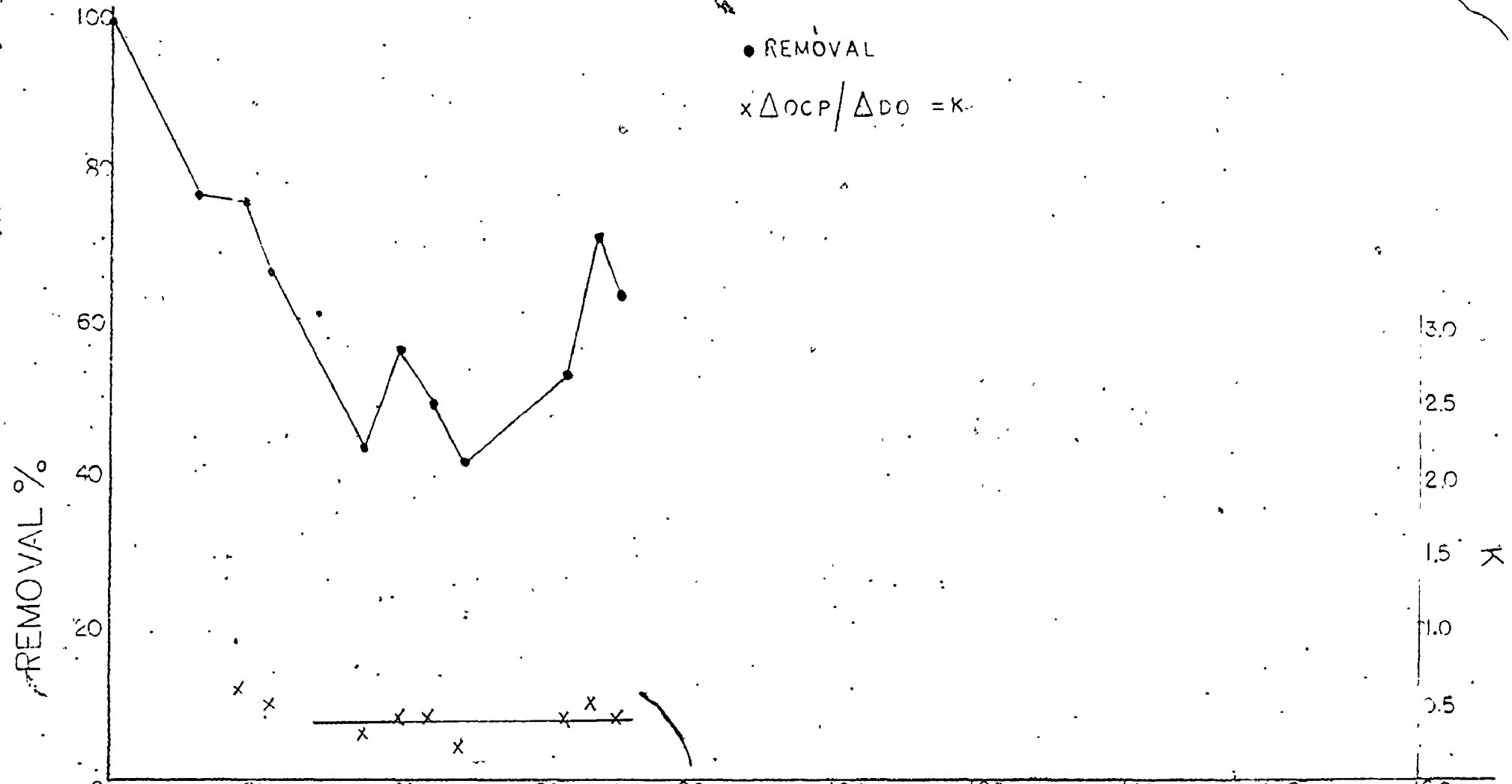


Fig.D.2.15 Cumulative Plots of Removed Versus Applied T.O.C. Run 2

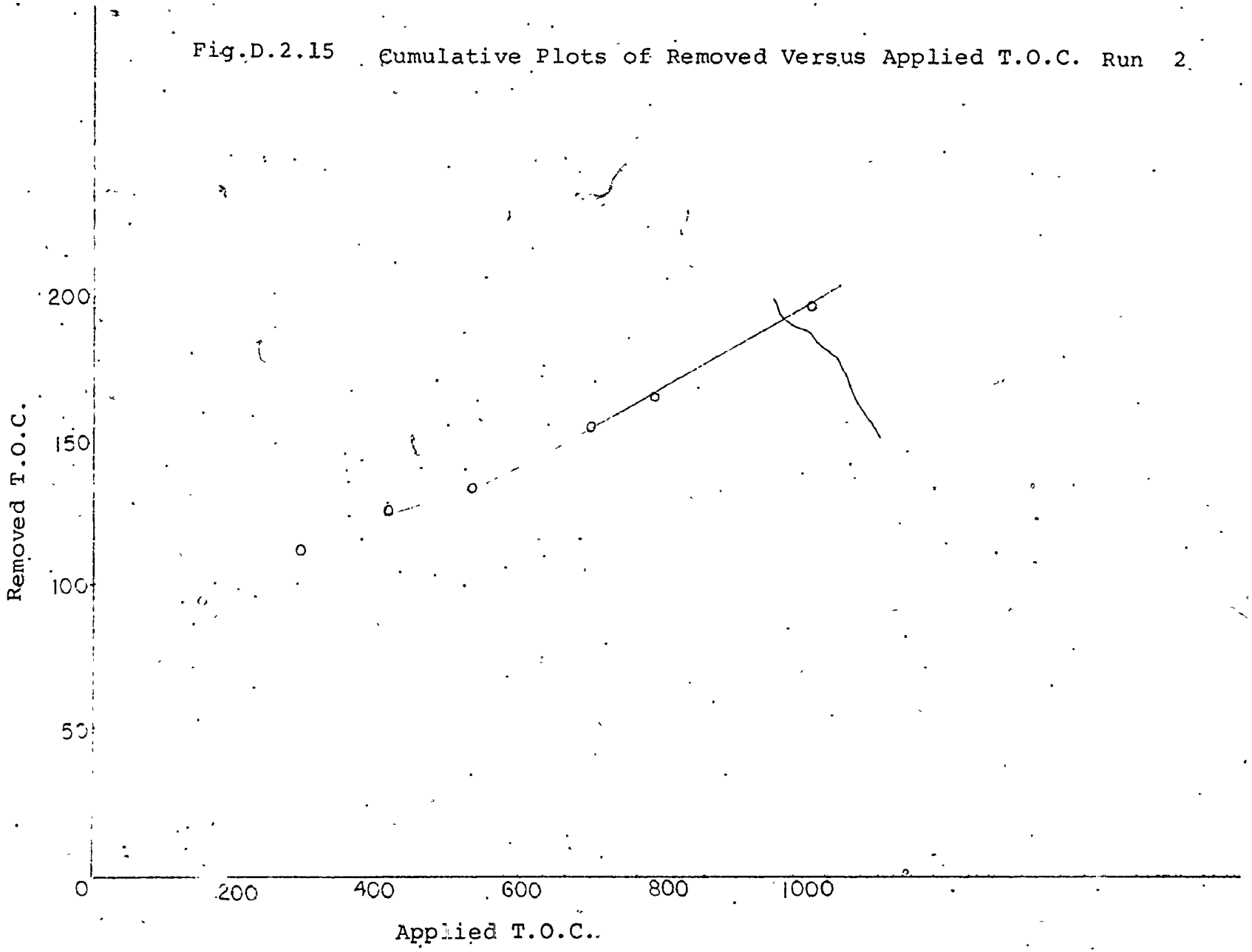


Fig.D.2.16 Cumulative Plots of Removed Versus Applied T.O.C. Run 4

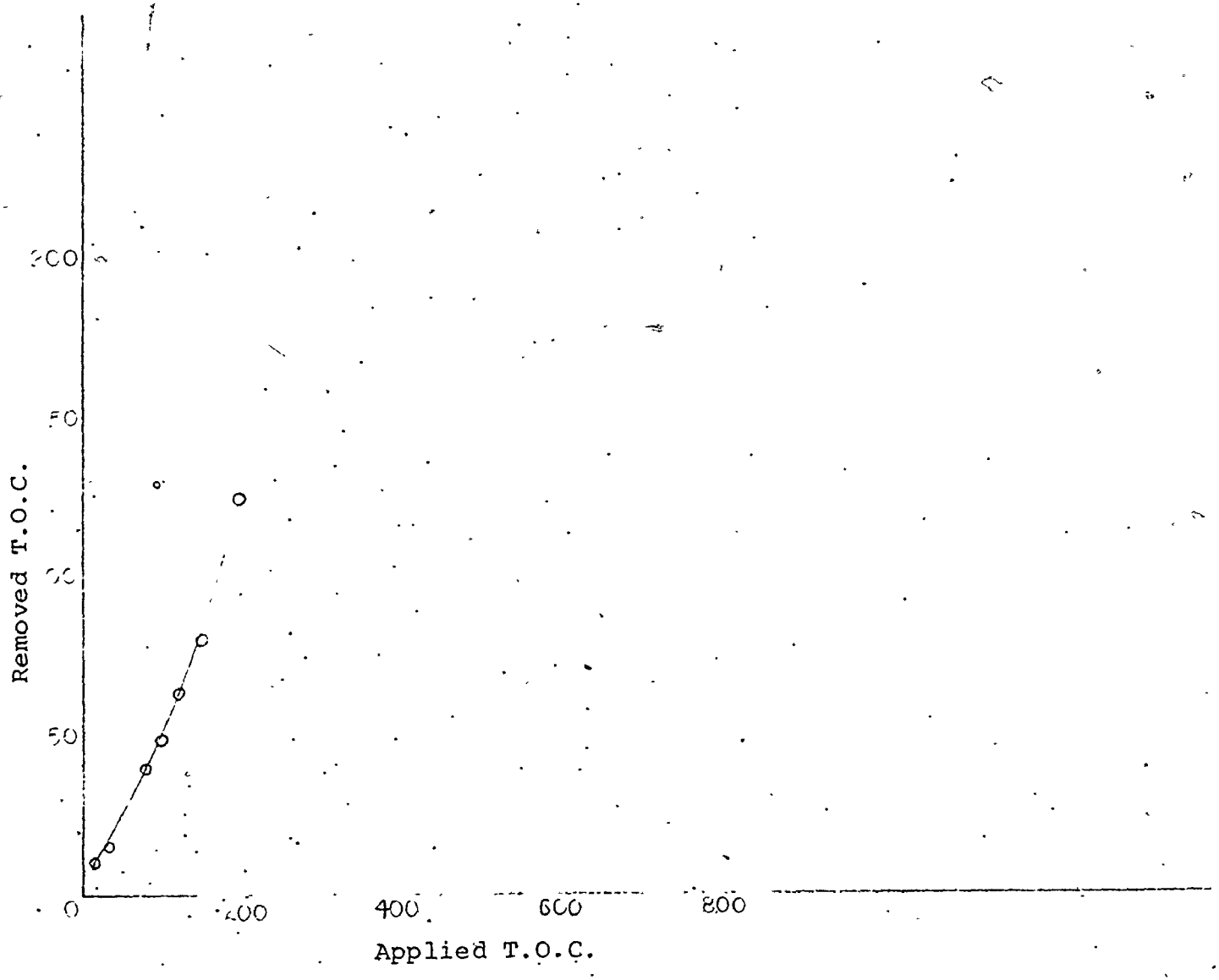


Fig.D.2.17 Cumulative Plots of Removed Versus Applied T.O.C. Run 6

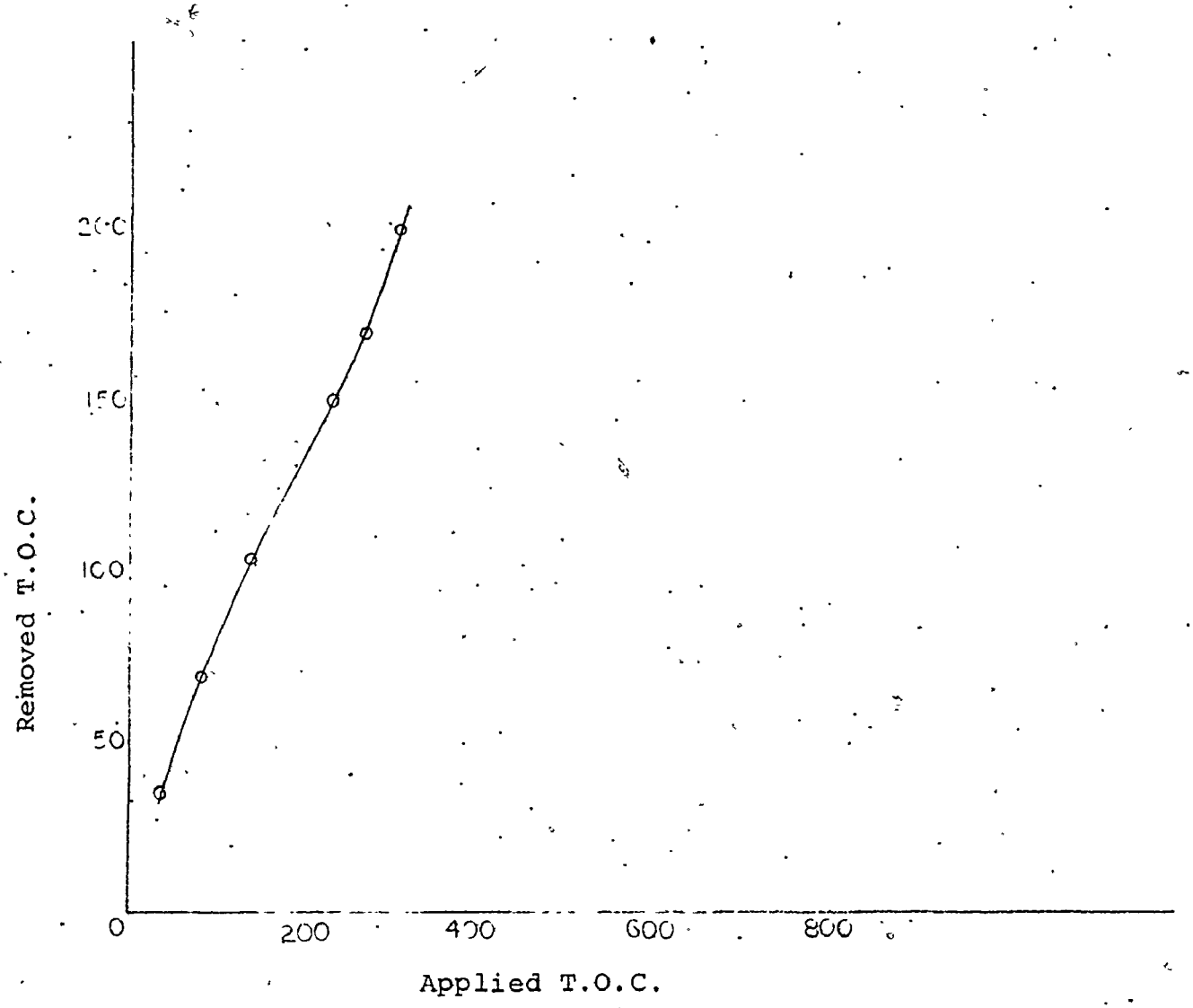
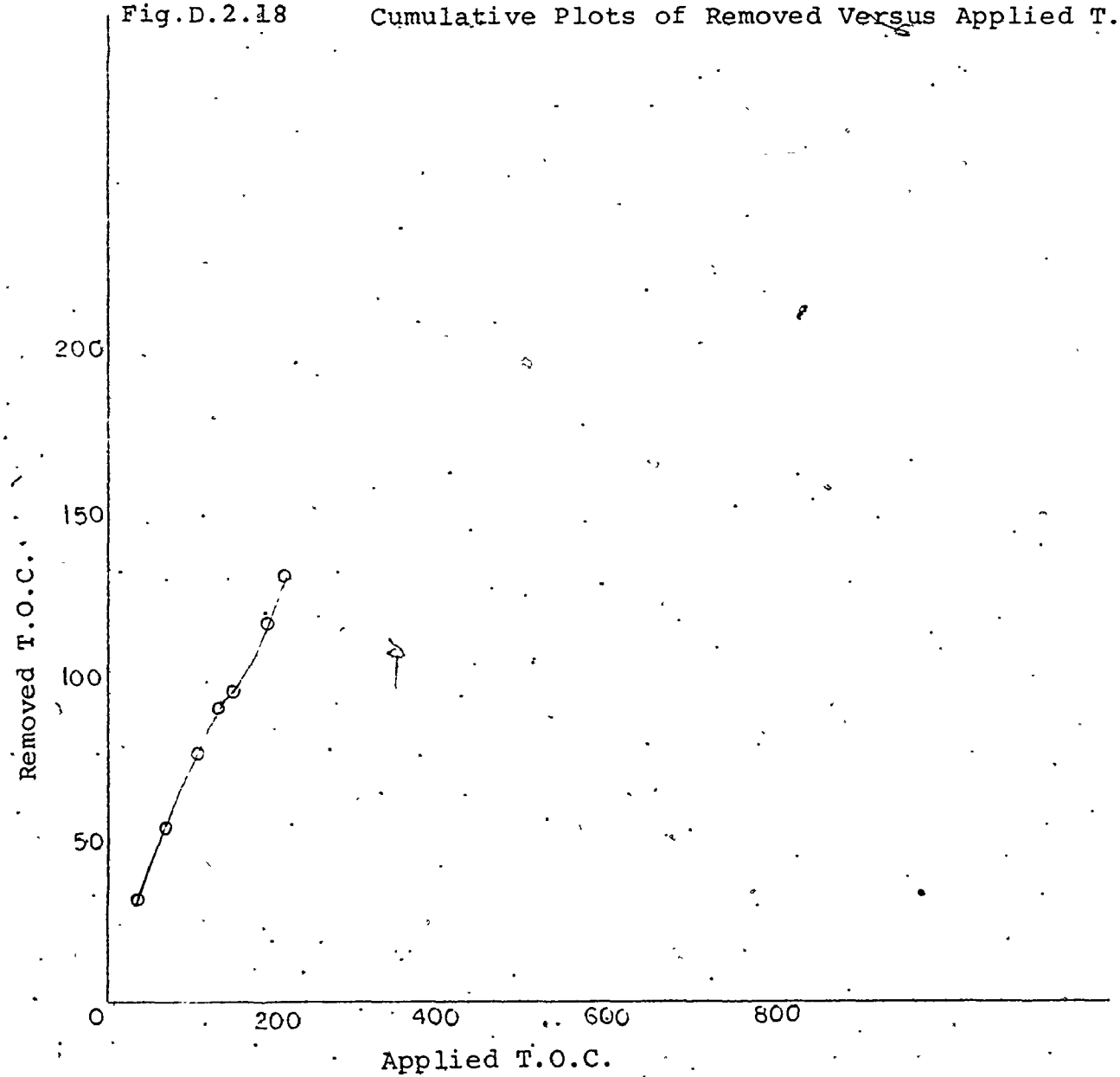


Fig.D.2.18 Cumulative Plots of Removed Versus Applied T.O.C. Run 7



D.3 Additional Information on Average Particle Size and Biological Growth

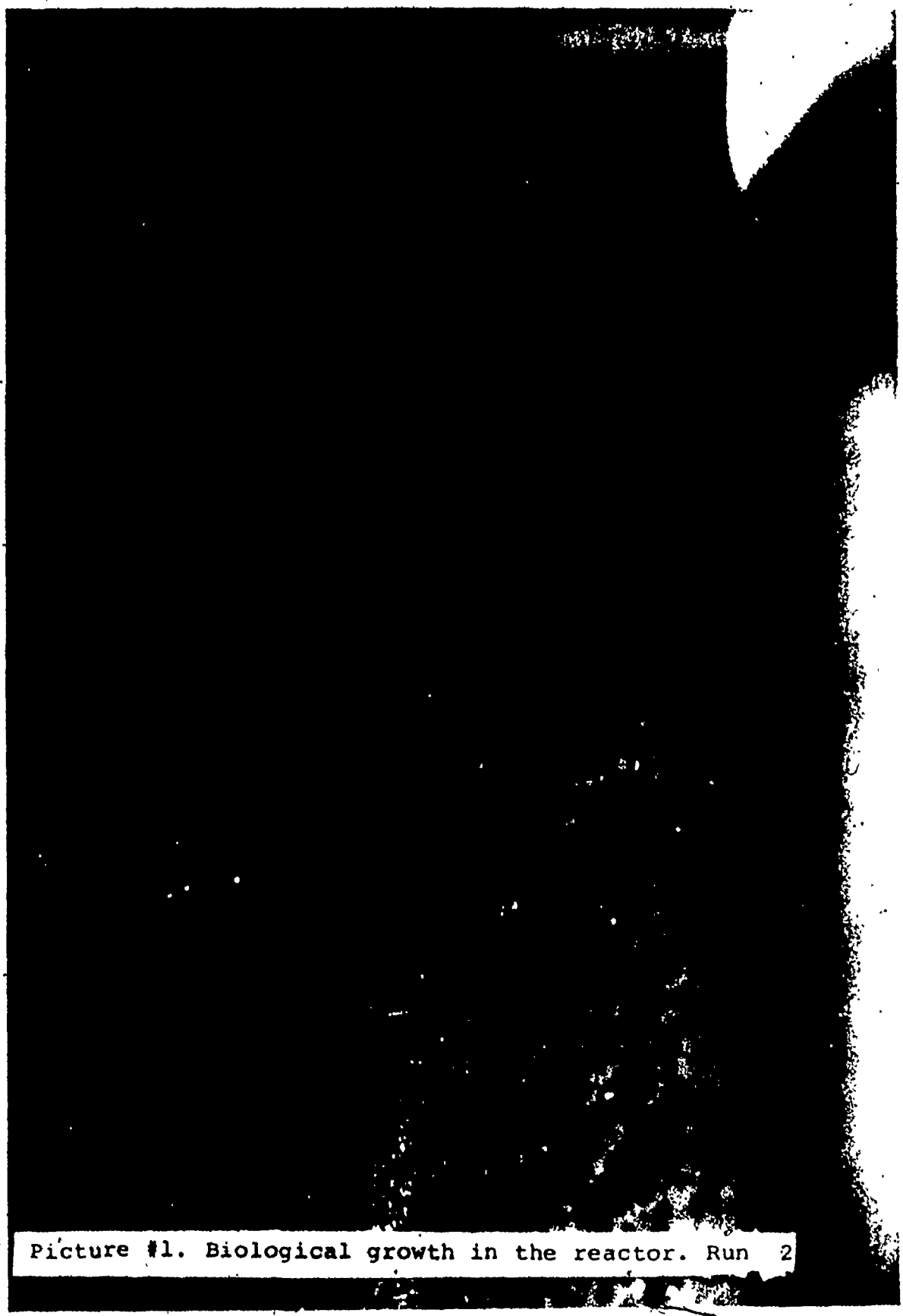
A number of pictures taken during the course of the continuous runs, show clearly the carbon particles. Due to the fact that the aerobic growth has a very light beige colour, and is transparent, the carbon particles as well as the biological film that has developed around them can be seen clearly and distinctly. There is a picture (# 1) showing the middle part of the bed where the well-developed prolific growth is obvious, and three more showing the top (# 2, # 3) of the bed and the bottom of the bed (# 4). The presence of a clear distinct interface at the top of the bed shows that the selected narrow particle size that formed the fluidized bed resulted to a uniform behavior that lasted through all the continous runs. In picture # 2, the structure of the top part of the column that was described in paragraph B.2.2 can also be seen.

Picture # 4 shows a phenomenon that was observed during the course of all the continuous runs. It shows the interface that developed between two parts of the bed, the upper one that developed prolific biological growth and the lower part that never did develop due to the effect of the

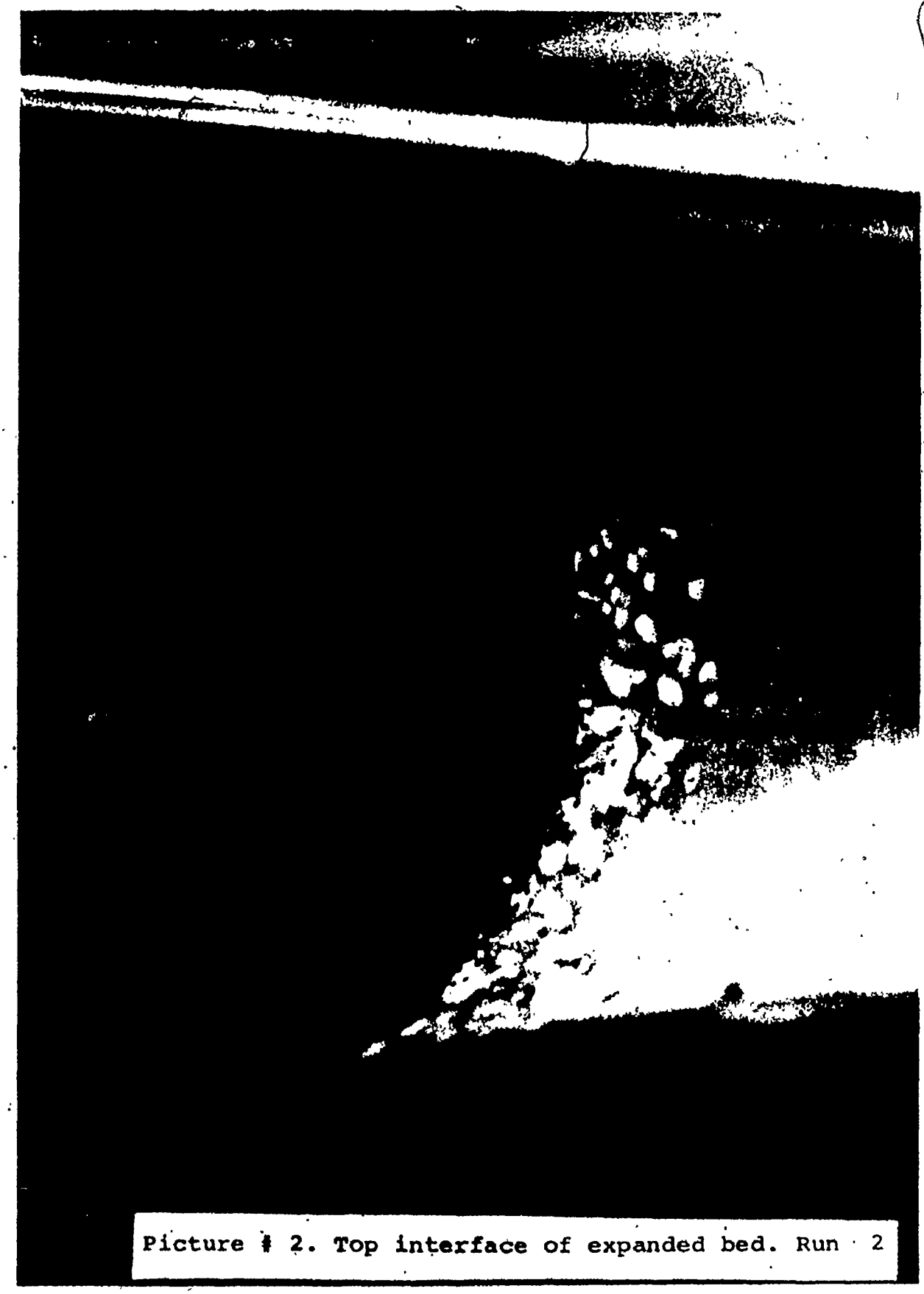
high velocity hydraulic jets of waste coming in through the bed support plate. The flow pattern was different in the two regions. The part that had no growth was under the state of intensive imbueing while plug flow conditions dominated the biologically active part of the fluidized bed. The resulting attrition among the bed particles in the back mixing zones, prevents the development of growth on the particles as well as on the reactor walls while in the plug flow zone, above, the growth is active and abundant.

Due to the fact that illumination of the reactor from behind was impossible and due to the cylindrical surface of the reactor and the resulting optical effect, a large number of pictures were taken, and the ones presented here are the most clear and representative.

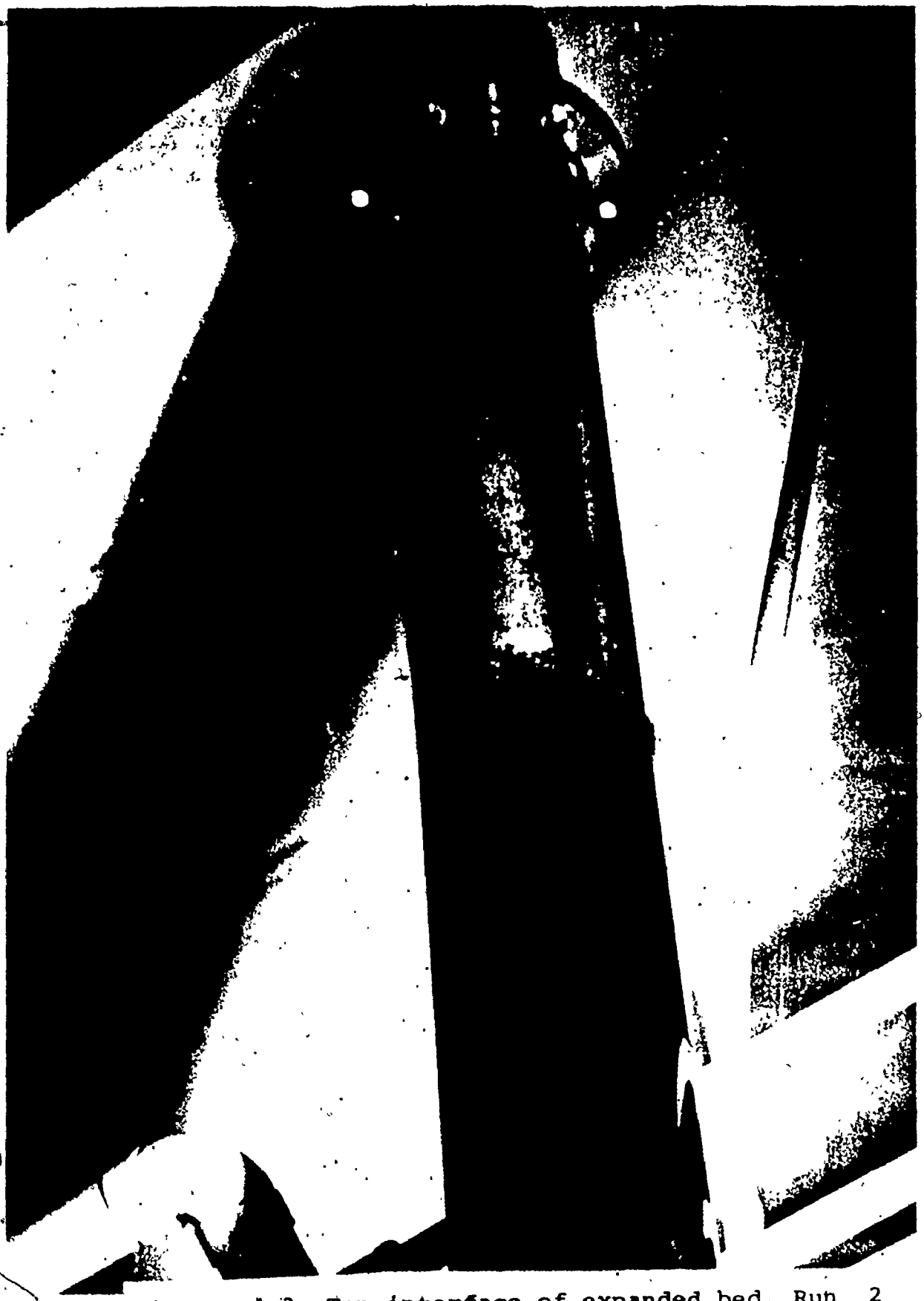
Safranin was decided to be used to stain the biological growth around the carbon particles so that pictures of the biological films could be taken. As can be seen from the pictures that follow there is satisfactory agreement between the average particle diameter we can read on pictures and the values the equations (2.7) predict. All the pictures have been taken at the end of each run. Table 4.5 summarizes the above comparisons.



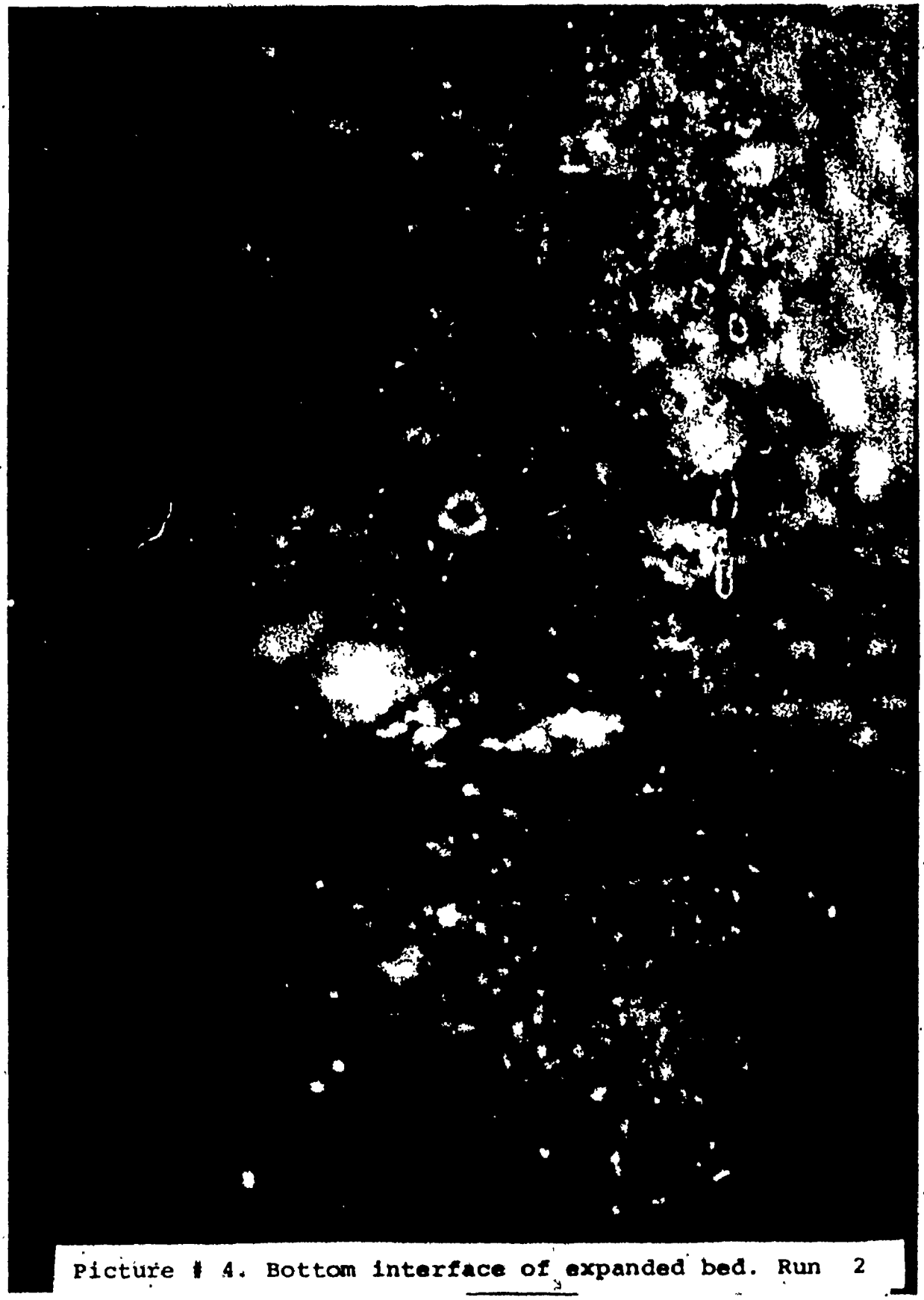
Picture #1. Biological growth in the reactor. Run 2



Picture # 2. Top interface of expanded bed. Run 2



Picture # 3. Top interface of expanded bed. Run 2

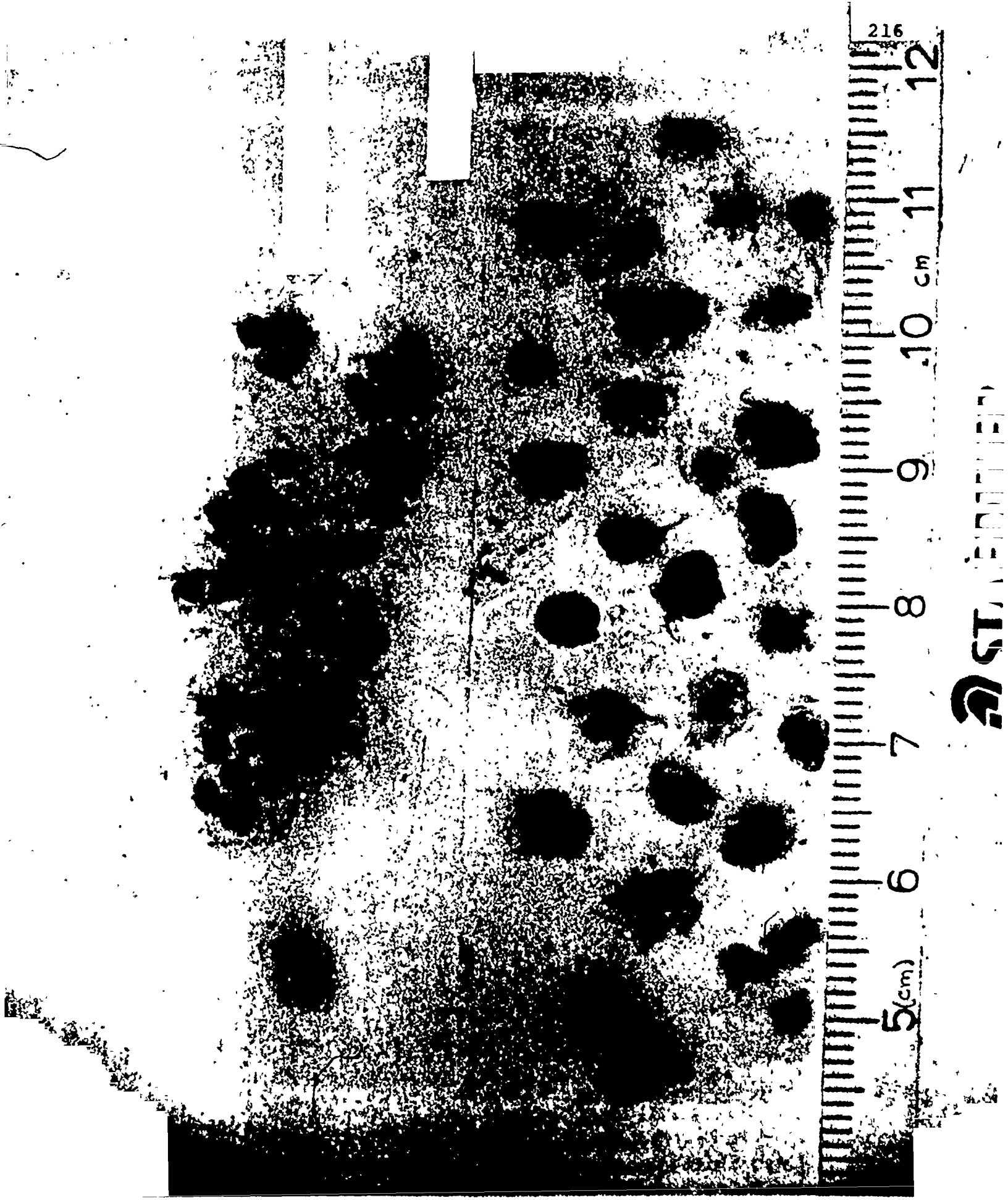


Picture # 4. Bottom interface of expanded bed. Run 2

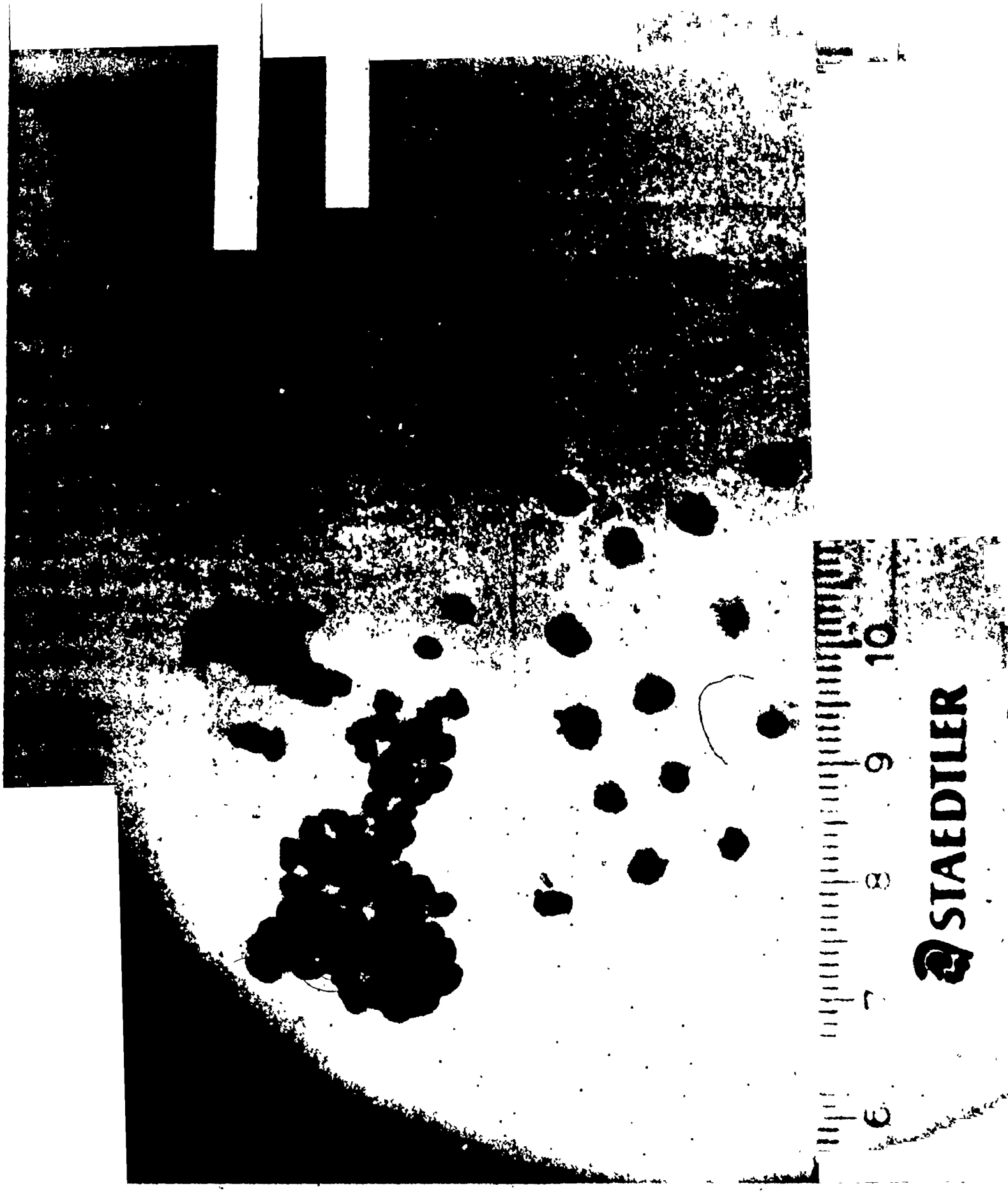
Picture # 5. Particles showing biological growth.End of Run 2

Picture # 6. Biological growth in the reactor. Run 4

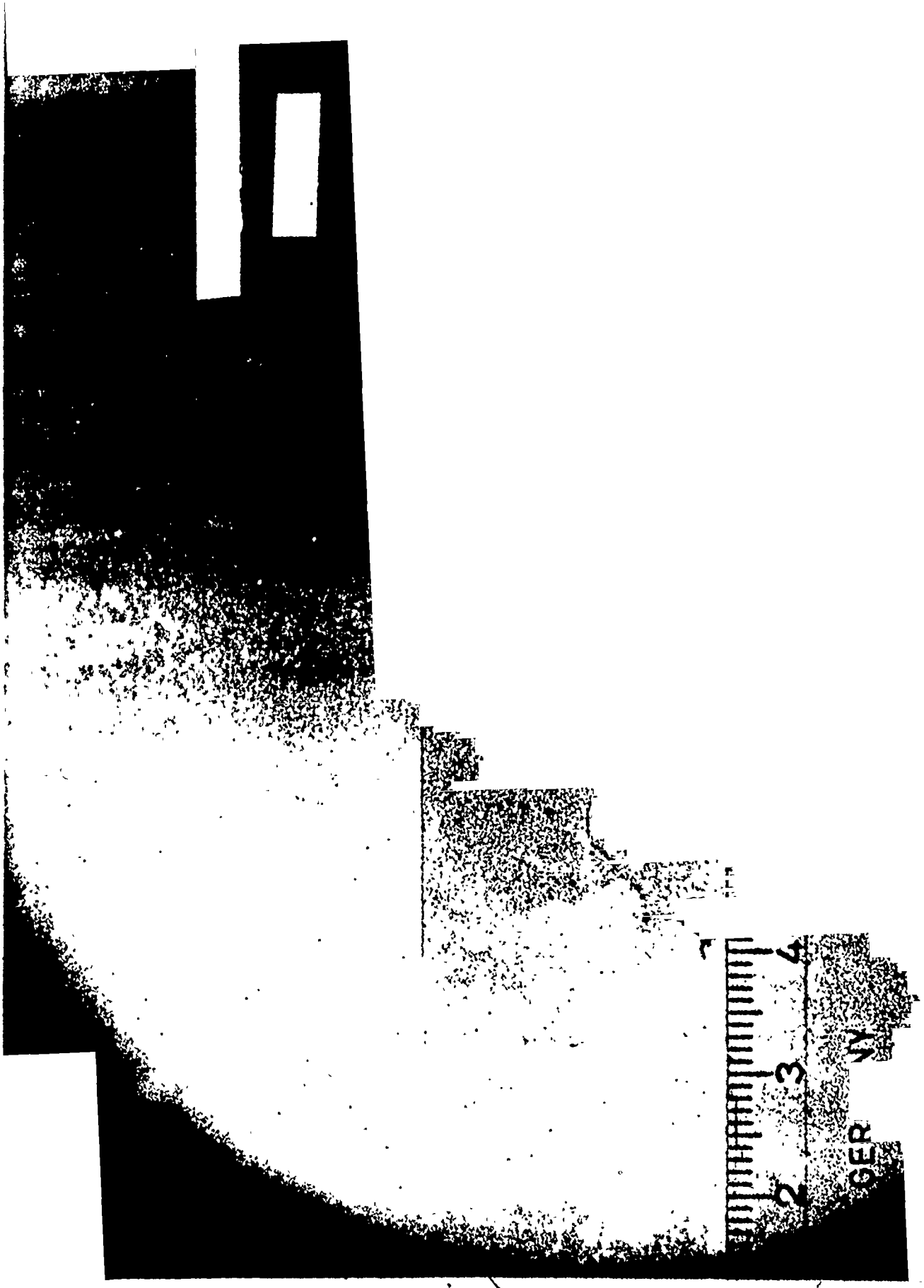
Picture # 7. Particles showing biological growth.End of Run 4



Picture # 8. Particles showing biological growth.End of Run 5



Picture # 9. Particles showing biological growth.End of Run 6



Picture # 10. Particles showing biological growth. End of Run 7

Table D.3.1

Run # 1, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height with Growth (cm)	Dp' (cm)	MA (cm^3)
50.5	57	0.205	1445
60.5	78.5	0.228	2424
64	86	0.235	2762
68	91.5	0.241	3008
69	93	0.242	3075
71.5	98	0.246	3298
74	100	0.248	3387
75	108	0.252	3631
76	105.5	0.254	3741
82	134	0.273	4883
83	138	0.276	5057
85	147	0.281	5447
86.5	153	0.285	5707
87	155	0.286	5793
88	158	0.288	5923
93	169	0.294	6396
94.5	186	0.304	7123
104.5	198	0.310	7634
106.5	216	0.318	8396
107.5	216.5	0.319	8417
111	218	0.319	8481
114	226	0.323	8818

Total Mass of Carbon in Reactor : 2077 g

Table D.3.2

Run # 2, Reactor # 1

Calculated Particle Size and Biomass Volume

Bed Height with Growth (cm)	Time hrs.	$\bar{D}p$ (cm)	MA (cm^3)
10.5	4.5	0.194	256
11	17	0.197	279
12	29	0.203	325
14.5	42	0.215	440
16	43.5	0.222	509
17	47	0.226	554
21	52	0.242	734
22	53.5	0.245	778
47.5	66	0.313	1884
51.5	68	0.321	2053
56	70	0.329	2243
65	73	0.345	2618
67	73.5	0.348	2701
73.5	75.5	0.358	2970
74.5	78	0.360	3093
76.5	78.5	0.363	4651
115	89.5	0.412	4890
121	91.5	0.419	5444
135	97.5	0.433	5719
142	102	0.440	5818
144.5	103.5	0.443	6404
159.5	115	0.456	6190
154	118.5	0.451	6033
150	119	0.447	4929
122	120	0.420	4929
122	121	0.423	5048
121	121.5	0.446	5955
148	127	0.493	8159
205	138	0.513	9224
230.5	144	0.540	10803

Total Mass of Carbon in Reactor : 1246 g.

Table D.3.3

Run # 3, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height with Growth (cm)	$\overline{Dp}'$ (cm)	MA (cm^3)
5.5	10.3	0.199	279
17.5	14	0.220	455
27.5	23.5	0.259	899
42	66.5	0.359	2808
47	87	0.391	3686
48	95	0.402	4024
51.5	97.5	0.405	4130
53.0	127	0.440	5361
56.5	151	0.465	6319
67	190.5	0.499	7931
67.5	196	0.504	8172
69	192	0.501	8011
70	190	0.499	7931
71.5	189	0.498	7890
77.5	182	0.493	7608
89.5	183	0.493	7649
94	189	0.498	7890
95.5	190.5	0.500	7951
99.5	198	0.506	8252
113.5	204.5	0.511	8513
115.5	210	0.515	8733
119.5	211	0.516	8792
122.5	215.5	0.519	8932
136.5	216.5	0.520	8992

Total Mass of Carbon in Reactor : 835 g

Table D.3.4

Run # 4, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height with Growth (cm)	Dp (cm)	MA (cm^3)
5	13.8	0.215	447
10	14.0	0.218	447
20.5	14.8	0.219	456
25.5	16.0	0.223	494
29	16.5	0.229	551
35	18.0	0.231	575
55	19.5	0.237	646
61	22.0	0.244	716
70	25.0	0.253	833
74	30.5	0.263	972
83	45.0	0.280	1225
94	68.0	0.317	1879
96	72.0	0.361	2892
99	78.0	0.368	3066
101	85.0	0.377	3325
105	106.5	0.387	3626
118	114.0	0.416	4541
122	136.5	0.425	4857
123	139.5	0.449	5707
129	172.0	0.452	5922
132	242.5	0.483	7260
137	265.5	0.537	10106

Total Mass of Carbon in Reactor : 800 g

Table D.3.5

Run # 5, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height with Growth (cm)	Dp (cm)	MA (cm^3)
6	13.5	0.215	432
16	13.6	0.217	437
20.5	14.7	0.223	490
27	14.8	0.223	495
39	19.5	0.244	717
47	29.5	0.278	1179
50.5	35.5	0.294	1452
53	42.0	0.310	1745
64	87.0	0.390	3712
72	133.0	0.446	5652
79	180.0	0.490	7587
88	229.0	0.528	9566
93.5	273.0	0.558	11310

Total Mass of Carbon in Reactor : 800 g

Table D.3.6.

Run # 6, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height With Growth (cm)	Dp (cm)	MA (cm^3)
5	13.5	0.214	432
60	47.5	0.260	1840
61	49.5	0.263	1933
63.5	53.5	0.270	2118
65.5	60.0	0.280	2417
68	68.0	0.291	2783
71	81.0	0.308	3372
76	104.5	0.334	4423
86	147.5	0.372	6310
87	233.5	0.429	9986
90	267.5	0.448	11413
91	276.5	0.453	11789

Total Mass of Carbon in Reactor : 800 g

Table D.3.7

Run # 7, Reactor # 1

Calculated Particle Size and Biomass Volume

Time hrs.	Bed Height with Growth (cm)	$\overline{Dp}$ (cm)	MA (cm^3)
12	13.5	0.200	373
18	15.0	0.208	446
22	16.2	0.213	504
35.5	44.4	0.292	1815
39	62.5	0.326	2628
44	98.0	0.375	4183
48.5	125.0	0.405	5341
62.5	191.5	0.400	8207
66	243.0	0.404	8571
67	258.5	0.428	10397

Total Mass of Carbon in Reactor 800 g

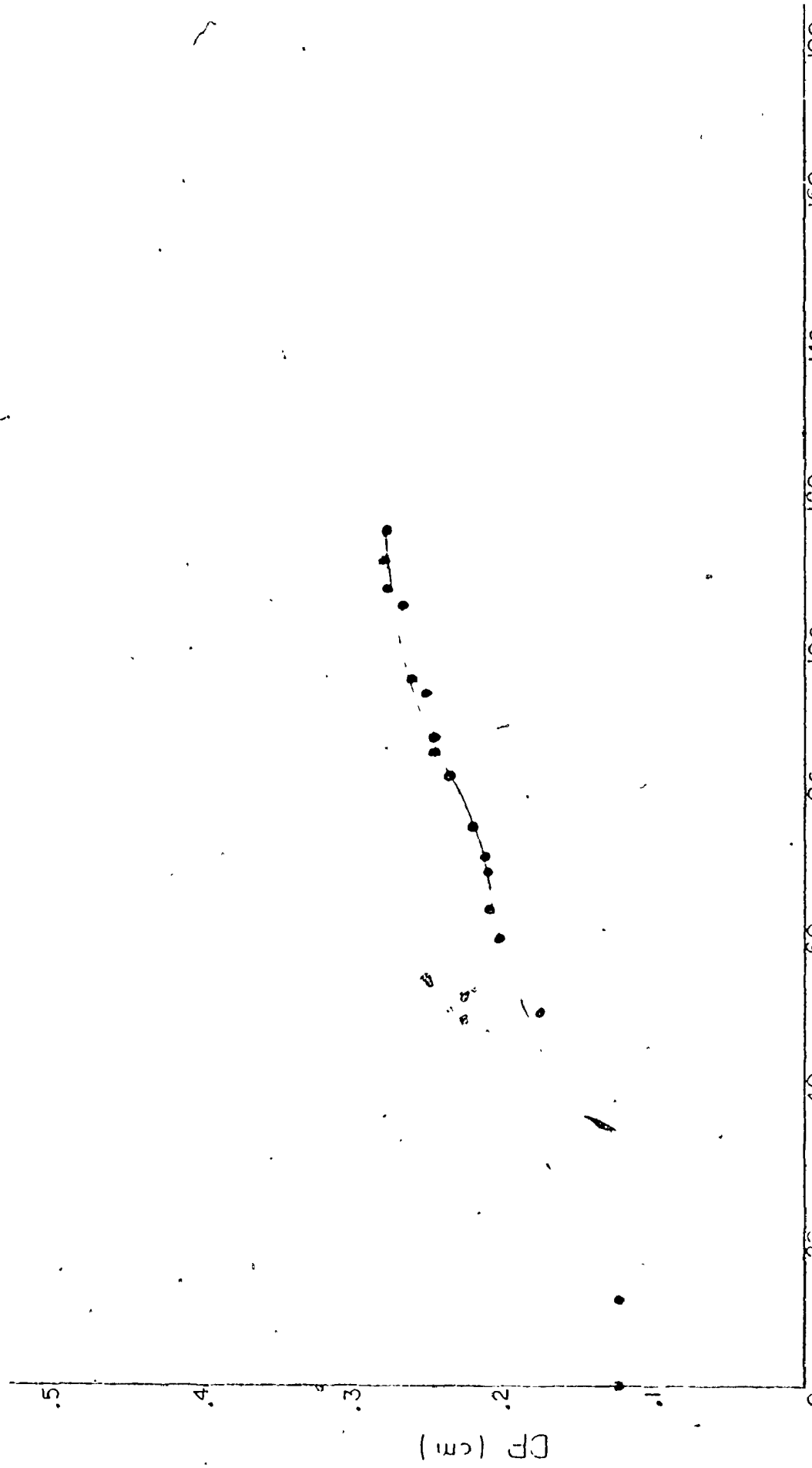


Fig.D.3.1 $\bar{D_p}$ Progression with Time. Run 1

Fig.D.3.2 $\bar{D}p$ Progression with Time . Run 2

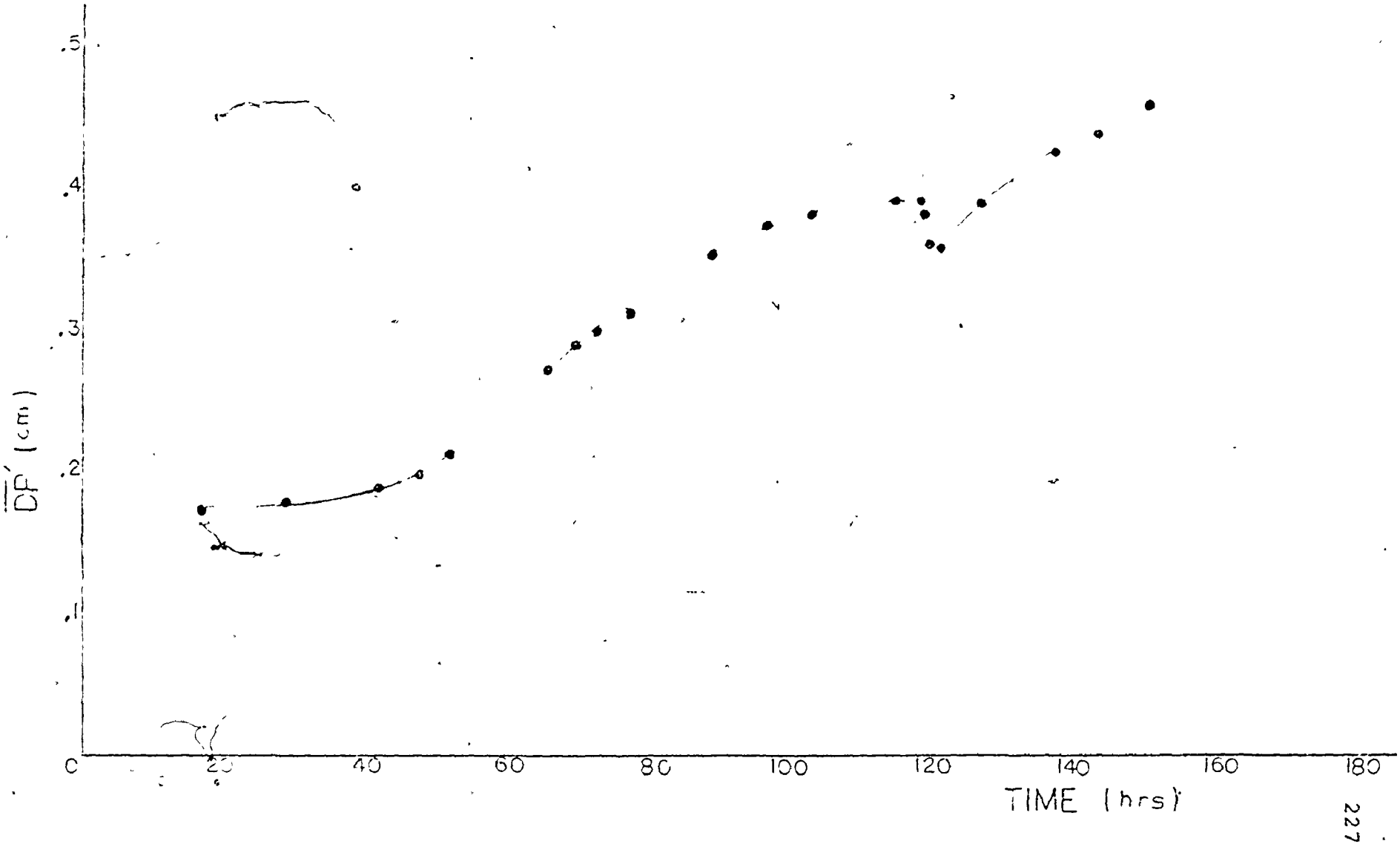


Fig.D.3.3 $\overline{Dp}'$ Progression with Time . Run 3

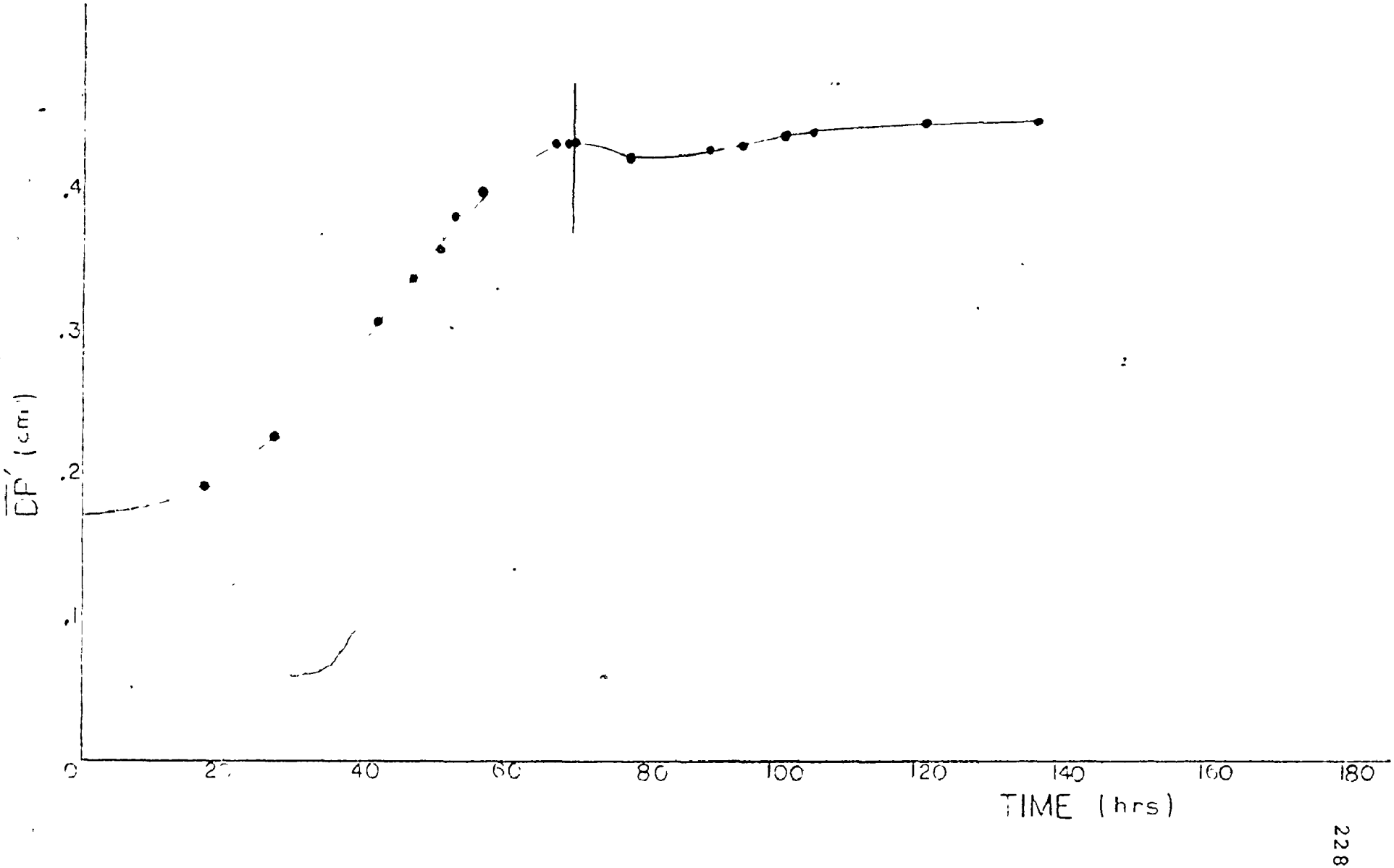


Fig.D.3.4 $\bar{D}_p'$ Progression with Time . Run 4

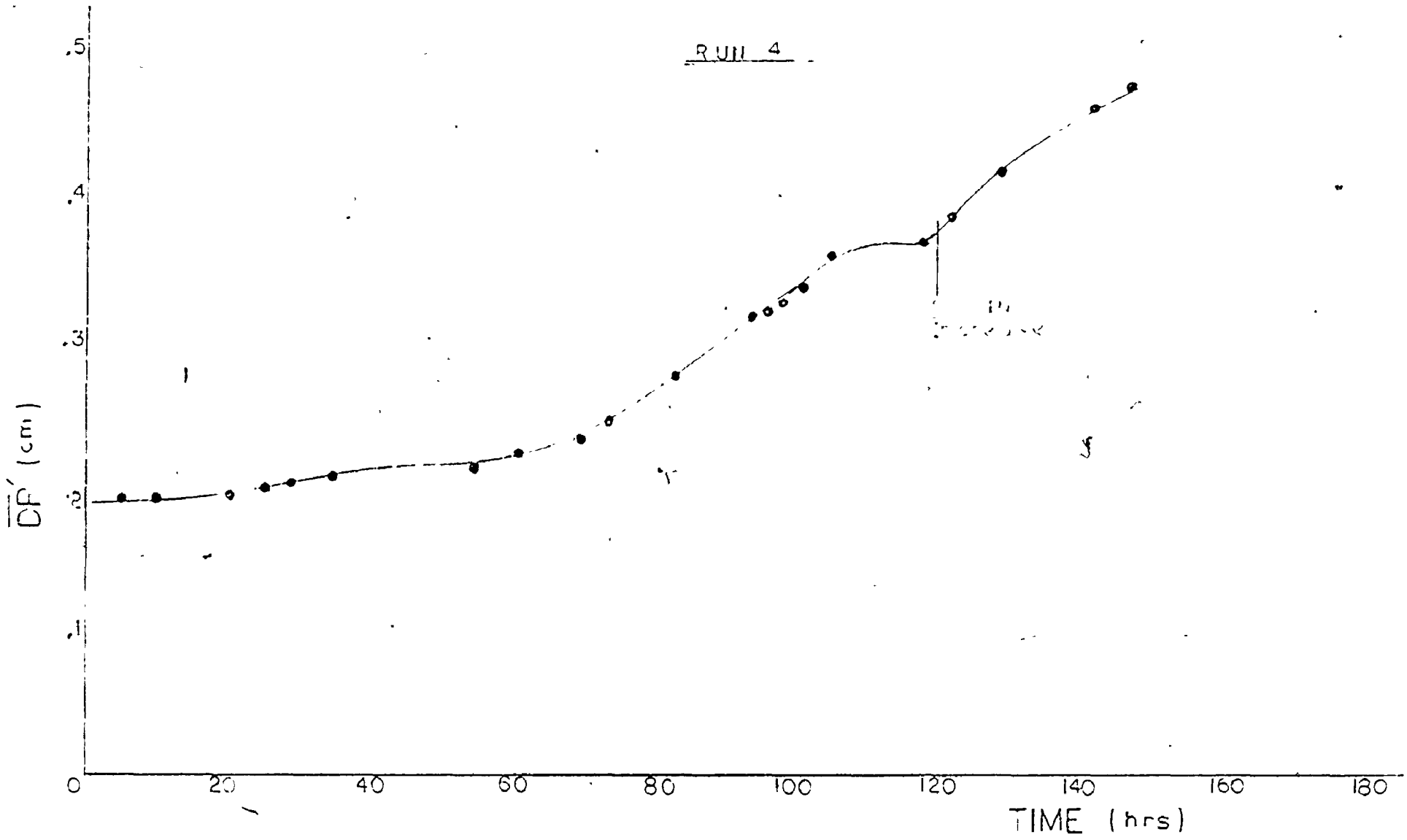
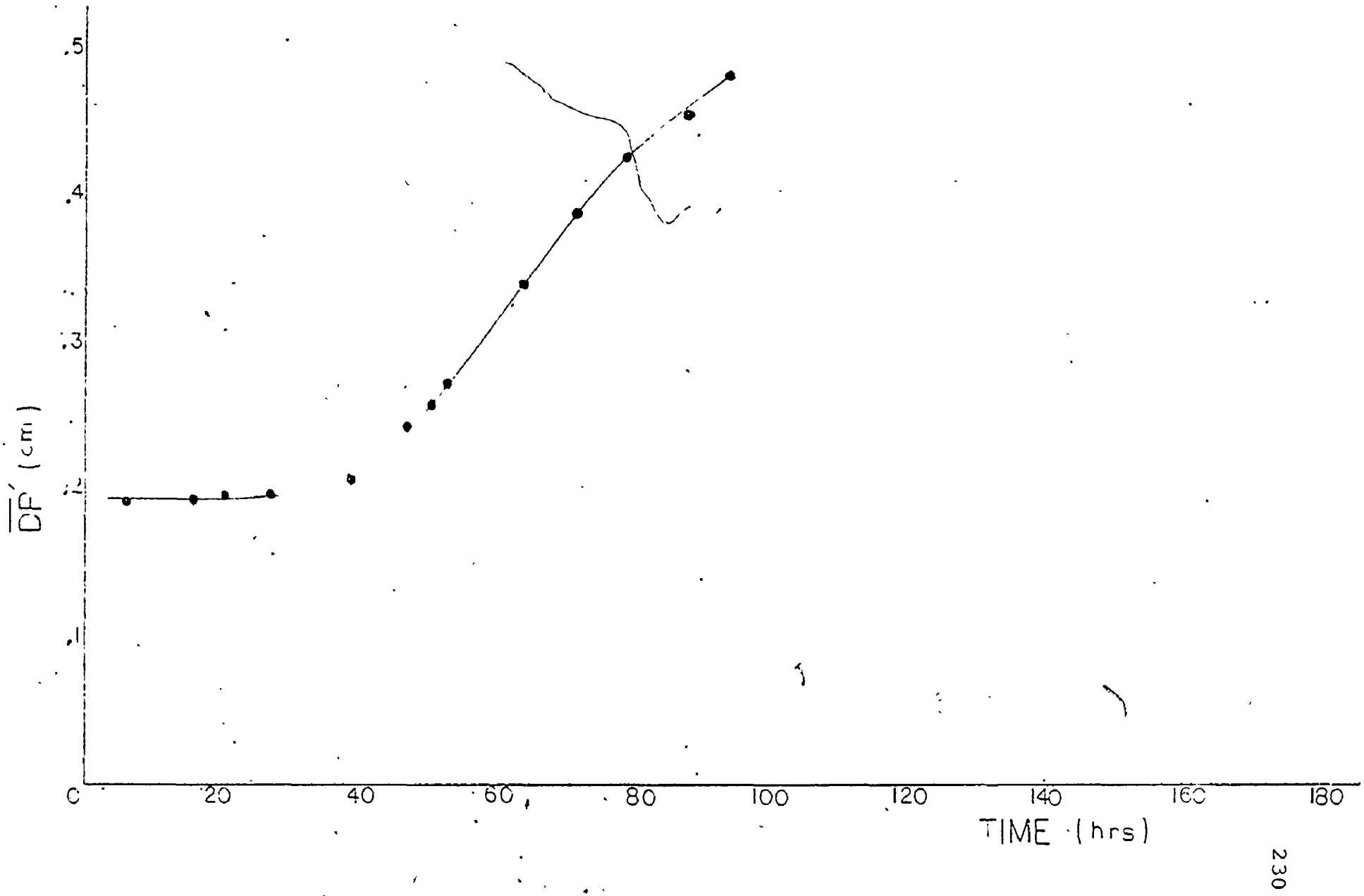


Fig.D.3.5 $\overline{Dp}$ Progression with Time , Run 5



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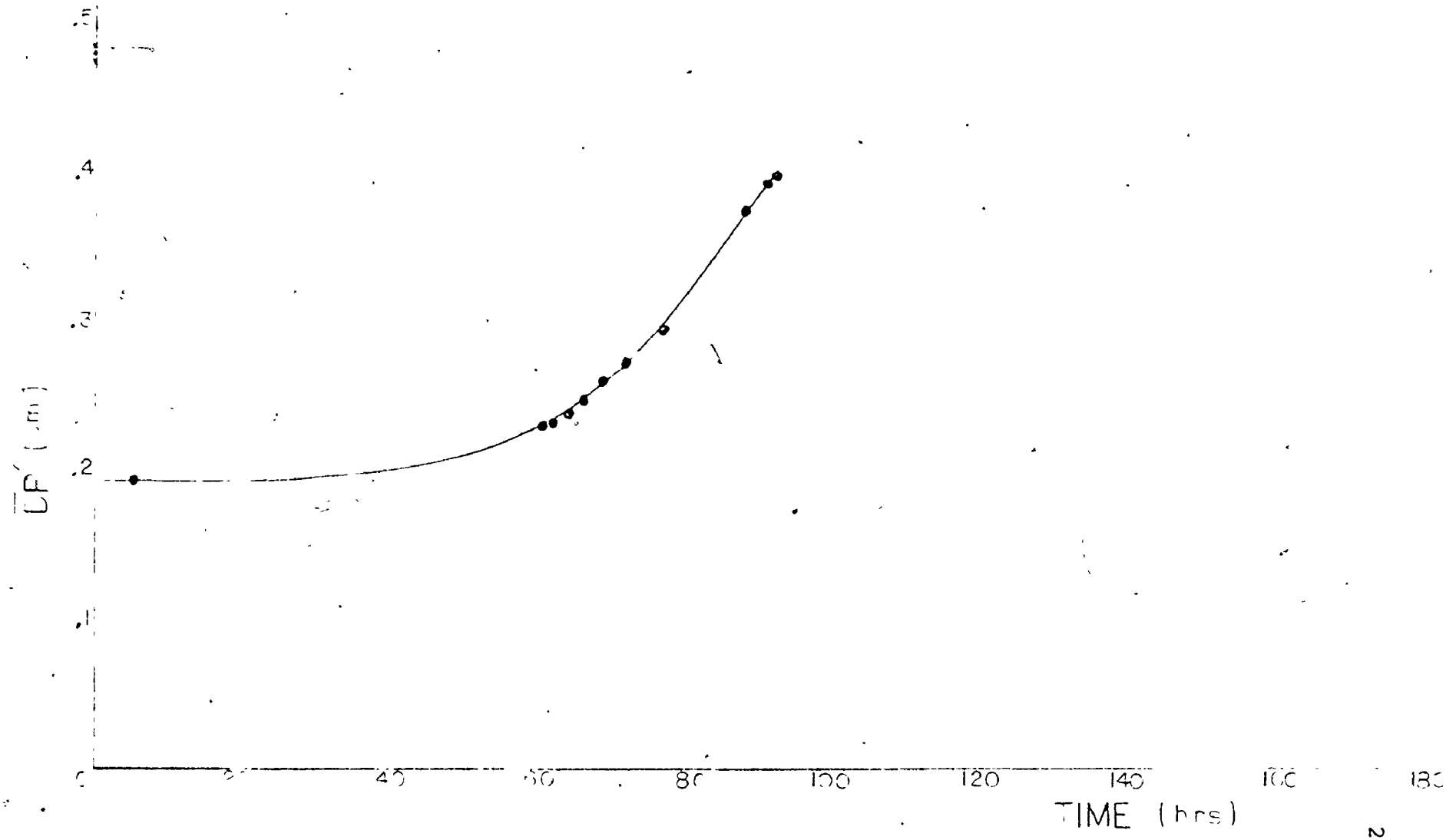


Fig.D.3.7 $\overline{Dp}'$ Progression with Time . Run 7

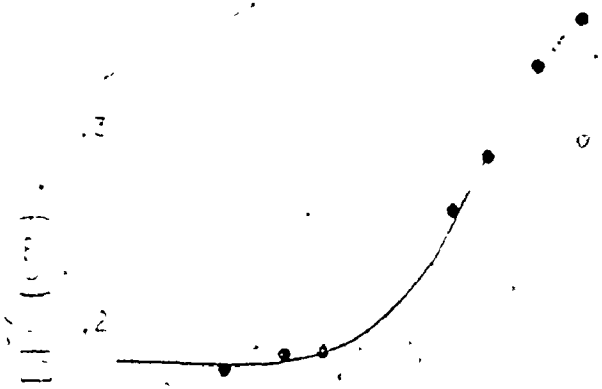


Table D.3.8

Volume Yield Evaluation Data

Run #	Time Period Used	Time Hrs.	TOC in mg/l	TOC out mg/l	Flow l/hr	ΔTOC mg/l	ΔTOC g	ΔTOC per g of Bed Carbon	Cumulative ΔTOC per g of Bed Carbon	ΔMA cm^3	ΔMA per g of Bed Carbon	Cumulative ΔMA per g Bed Carbon
	0 - 17.5	17.5	38	16	150	22	58	16.0 10^2	16.0 10^2	304	0.8	0.8
	17.5 - 51.5	34	40	38	150	2	10	2.8 10^2	18.8 10^2	1493	4.1	4.9
	51.5 - 77	25.5	42	38	150	4	15	4.1 10^2	22.9 10^2	1040	2.8	7.7
2	77 - 97	20	44	40	150	4	12	3.3 10^2	26.2 10^2	830	2.2	9.9
	97 - 126	29	45	40	150	5	22	6.1 10^2	32.3 10^2	255	0.6	10.5
	126 - 138	12	43	35	150	8	14	3.9 10^2	36.2 10^2	1442	4.0	14.5
	138 - 150	12	43	35	150	8	14	3.9 10^2	40.1 10^2	469	1.3	15.8
	0 - 17	17	39	14	120	25	51	10.4 10^2	10.4 10^2	198	0.4	0.4
	17 - 45.5	28.5	32	28	120	4	14	2.9 10^2	13.3 10^2	2740	5.5	5.9
	45.5 - 55	9.5	33	30	120	3	3	0.6 10^2	13.9 10^2	2673	5.4	11.3
3	55 - 68	13	35	30	120	5	8	1.6 10^2	15.5 10^2	2170	4.4	15.7
	68 - 76	8	36	34	120	3	3	0.6 10^2	16.1 10^2	-346	-0.7	15.0
	76 - 98.5	22.5	38	38	120	0	0	0	16.1 10^2	396	0.8	15.8
	98.5 - 112.5	14	44	44	120	0	0	0	16.1 10^2	346	0.7	16.5
	112.5 - 140	27.5	49	49	120	0	0	0	16.1 10^2	198	0.4	16.9
	0 - 20.5	20.5	12	5	120	7	17	3.7 10^2	3.7 10^2	--	-	-
	20.5 - 29	8.5	12	9	120	3	3	0.6 10^2	4.3 10^2	96	0.2	0.2
4	29 - 55	26	12	5	120	7	22	4.8 10^2	9.1 10^2	95	0.2	0.4
	55 - 70	15	12	6	120	6	11	2.4 10^2	11.5 10^2	189	0.4	0.8
	70 - 105	35	12	3	120	9	38	8.3 10^2	19.8 10^2	3708	6.6	7.4
	105 - 13	27	12	0	120	12	39	8.7 10^2	28.5 10^2	5564	9.7	17.1

Table D.3.8

Volume Yield Evaluation Data

Run #	Time Period Used	Time Hrs.	TOC in mg/l	TOC out mg/l	Flow l/hr	ΔTOC mg/l	ΔTOC g	ΔTOC per g of Bed Carbon	Cumulative ΔTOC per g of Bed Carbon	MA cm^3	MA per g of Bed Carbon	Cumulative ΔMA per g Bed Carbon
	0 - 15.5	15.5	11	4	120	7	13	2.4 10^2	2.4 10^2	5	-	-
	15.5 - 26	10.5	15	9	120	6	8	1.5 10^2	3.9 10^2	57	0.1	0.1
5	26 - 63	37	15	4	120	11	49	8.9 10^2	12.8 10^2	3035	5.5	5.6
	63 - 77	14	15	2	120	13	22	4.0 10^2	16.8 10^2	3500	6.4	12.0
	77 - 99.5	16.5	18	1	120	17	33.6	6.1 10^2	22.9 10^2	4284	7.8	19.8
	0 - 12	12	27	2	120	25	36	5.5 10^2	5.5 10^2	174	0.2	0.2
	12 - 24.5	12.5	27	5	120	22	33	5.0 10^2	10.5 10^2	311	0.4	0.6
6	24.5 - 42	17.5	28	13	120	15	32	4.8 10^2	15.3 10^2	436	0.6	1.2
	42 - 59	17	34	17	120	17	35	5.3 10^2	20.6 10^2	500	0.7	1.9
	59 - 75	16	31	14	120	17	33	5.0 10^2	25.6 10^2	2360	3.5	5.4
	75 - 89	14	29	12	120	17	29	4.4 10^2	30.0 10^2	5805	10.1	15.5
	0 - 12	12	25	3	120	22	32	4.8 10^2	4.8 10^2	70	0.1	0.1
	12 - 22	10	26	8	120	18	22	3.3 10^2	8.1 10^2	131	0.2	0.3
7	22 - 44	22	26	12	120	14	37	5.6 10^2	13.7 10^2	3679	5.7	6.0
	44 - 63	19	25	13	120	12	27	4.1 10^2	17.8 10^2	4521	6.9	12.9
	63 - 67	4	27	10	120	17	8	1.2 10^2	19.0 10^2	2480	3.8	16.7

Fig.D.3.8 Volume Yield Evaluation Curve . Run 2

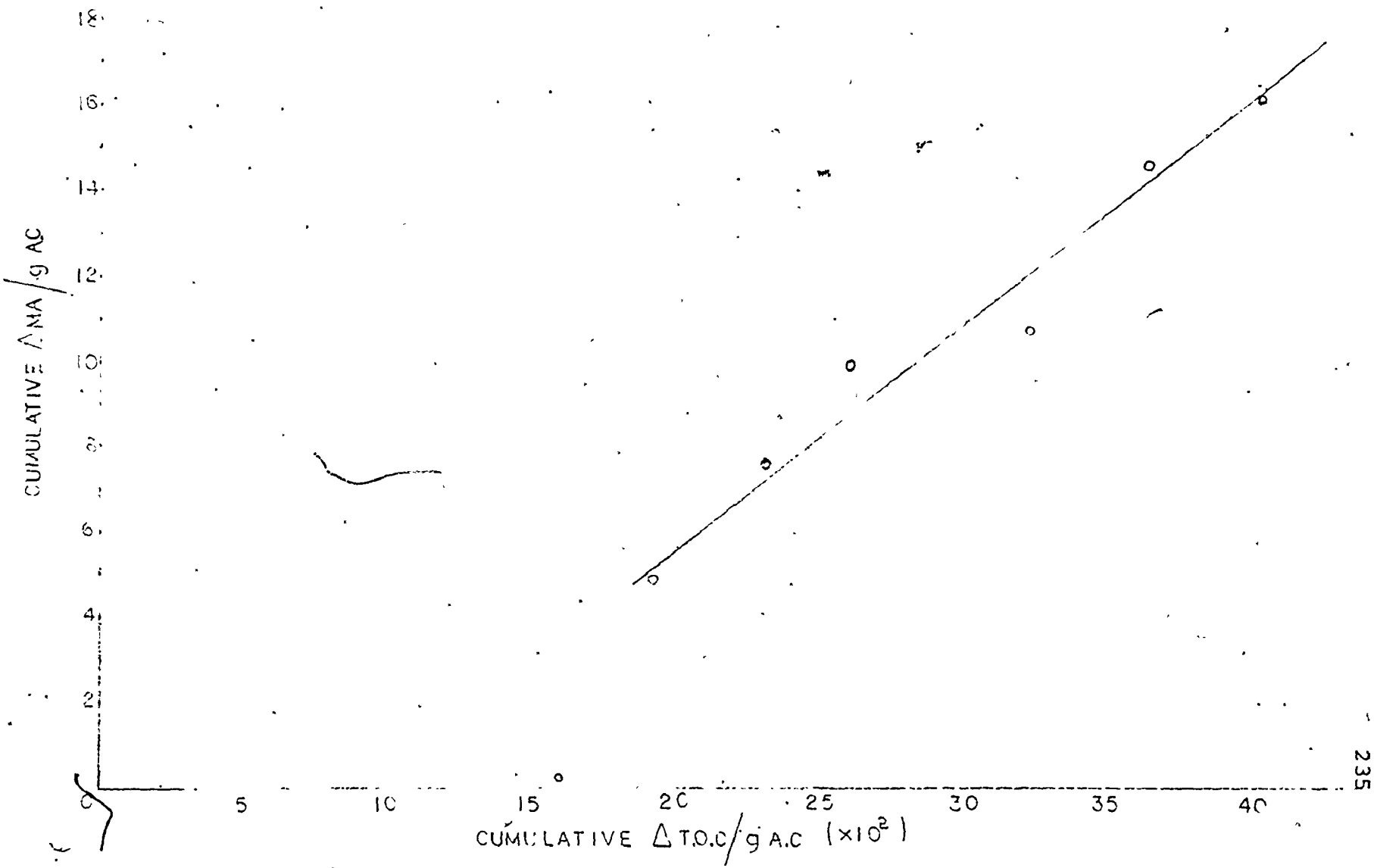


Fig.D.3.9 Volume Yield Evaluation Curve Run 3

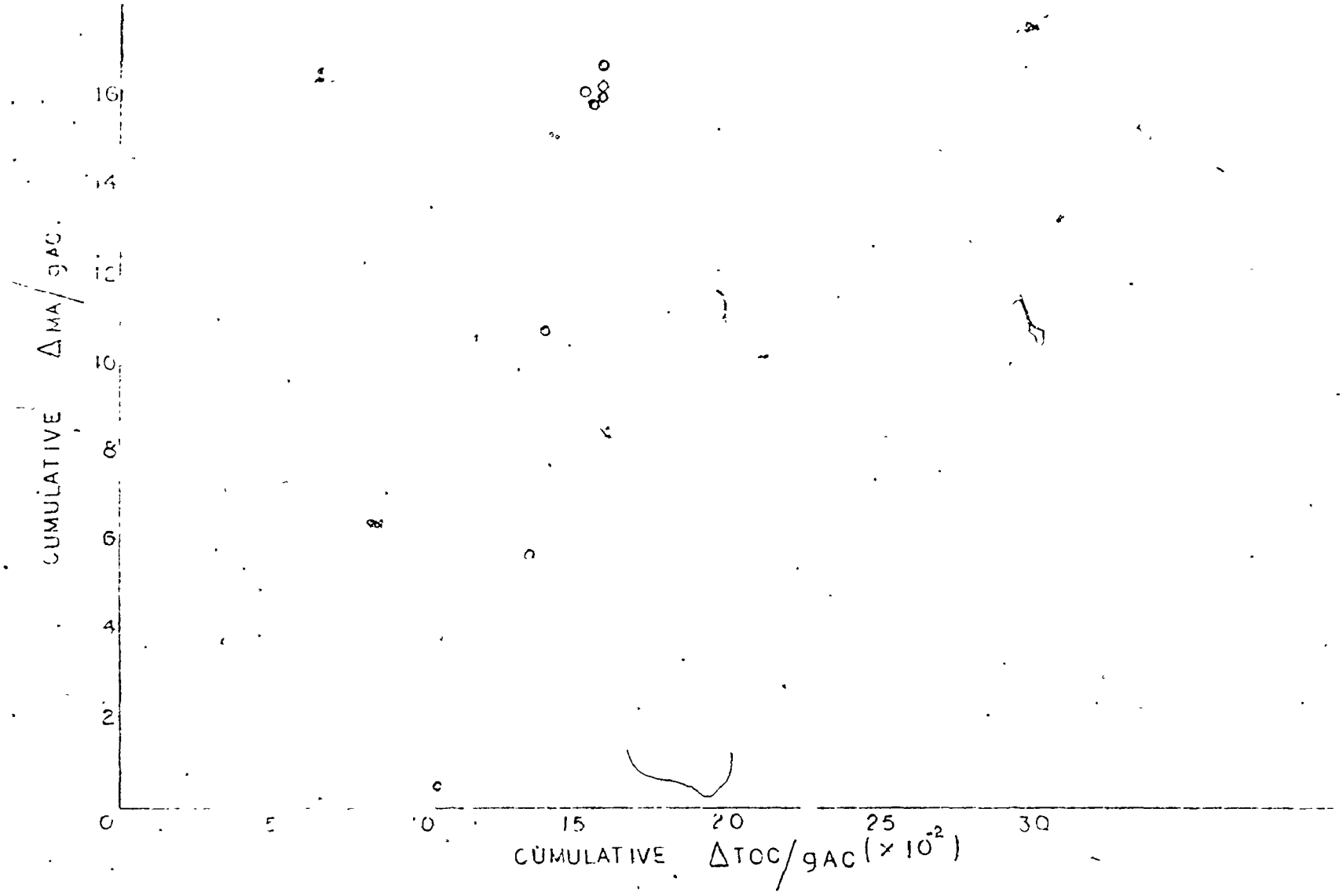


Fig.D.3.10 Volume Yield Evaluation Curve . Run 4

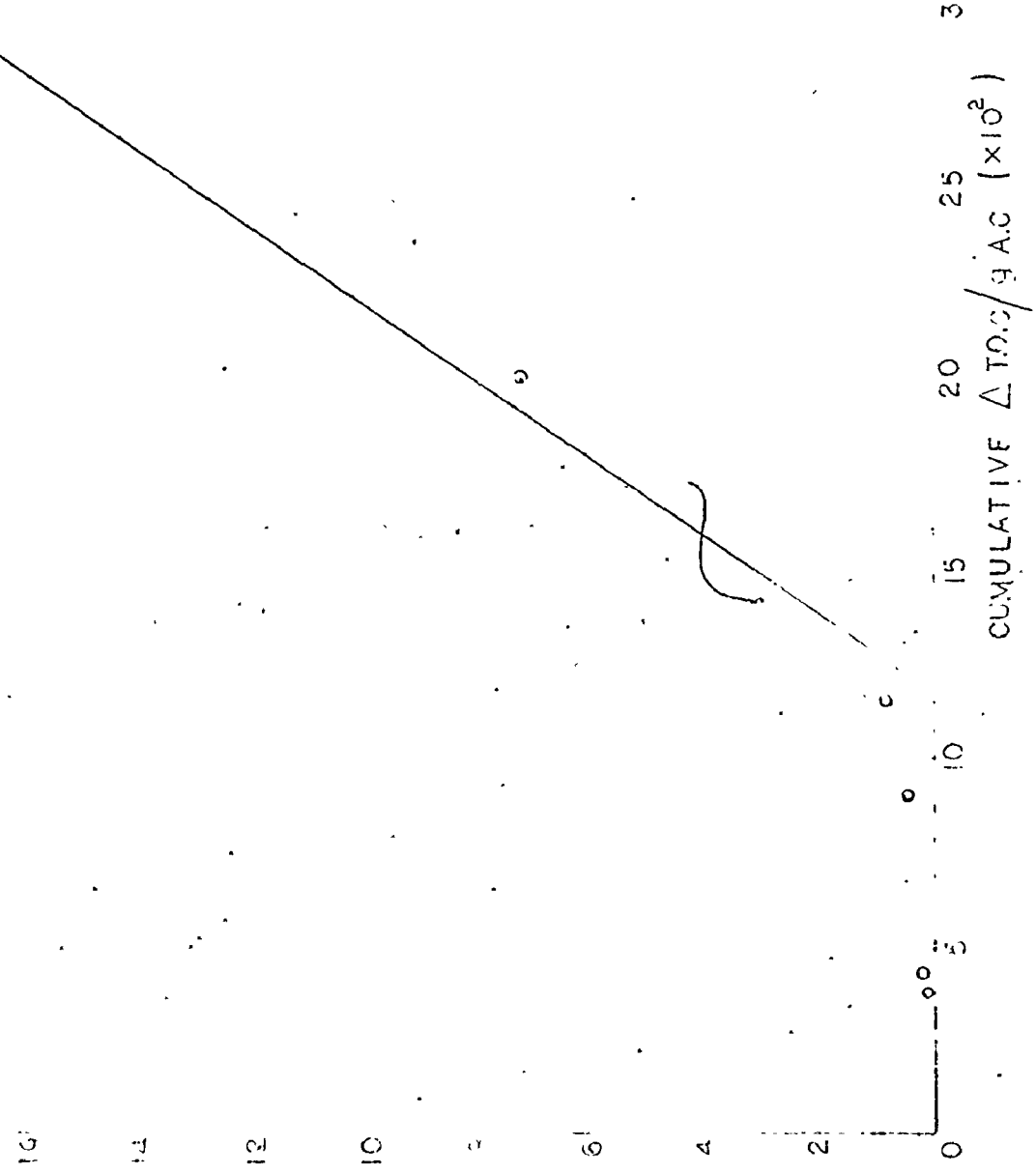


Fig.D.3.11 Volume Yield Evaluation Curve Run 5

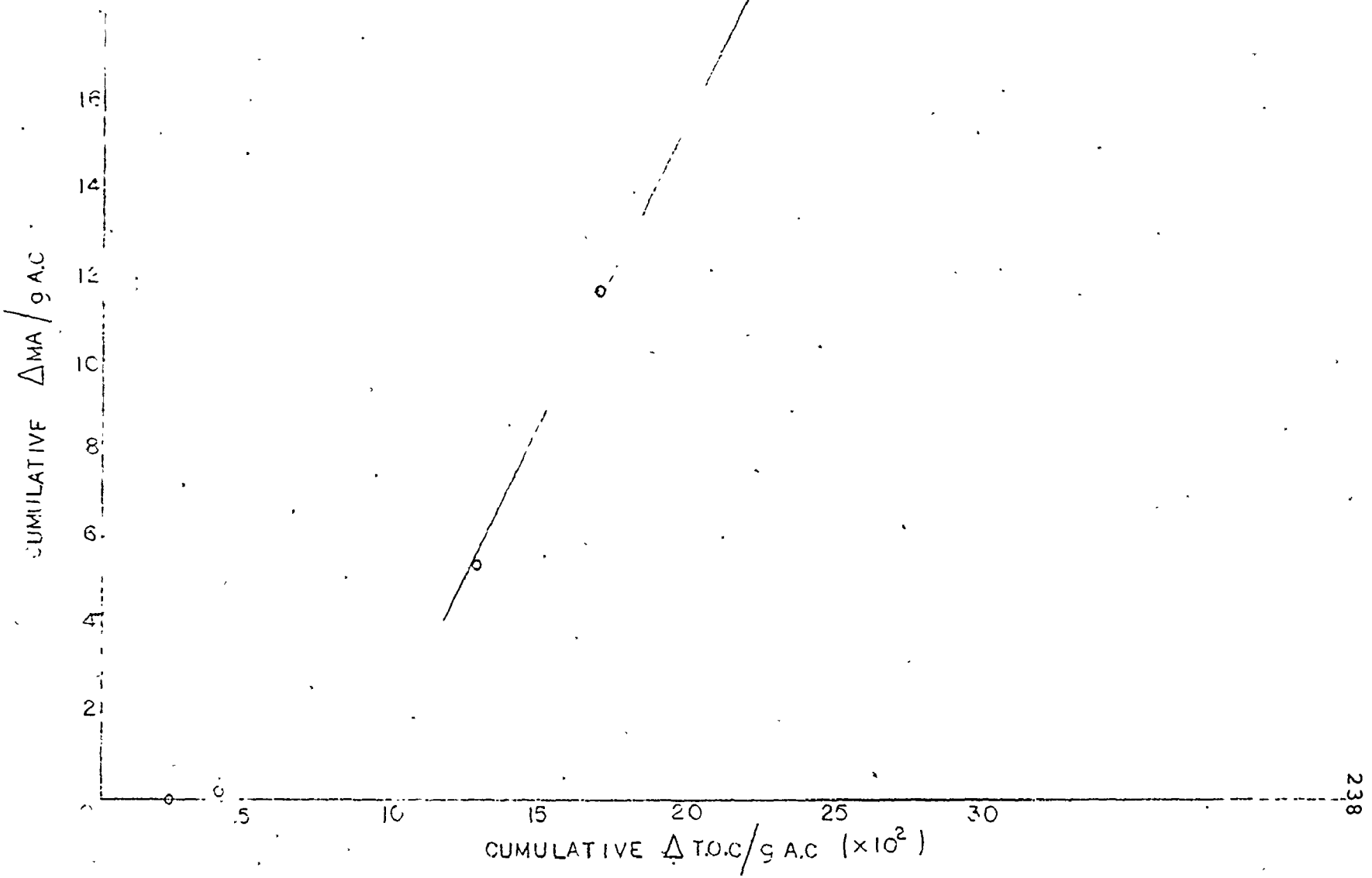


Fig.D.3.12 Volume Yield Evaluation Curve , Run 6

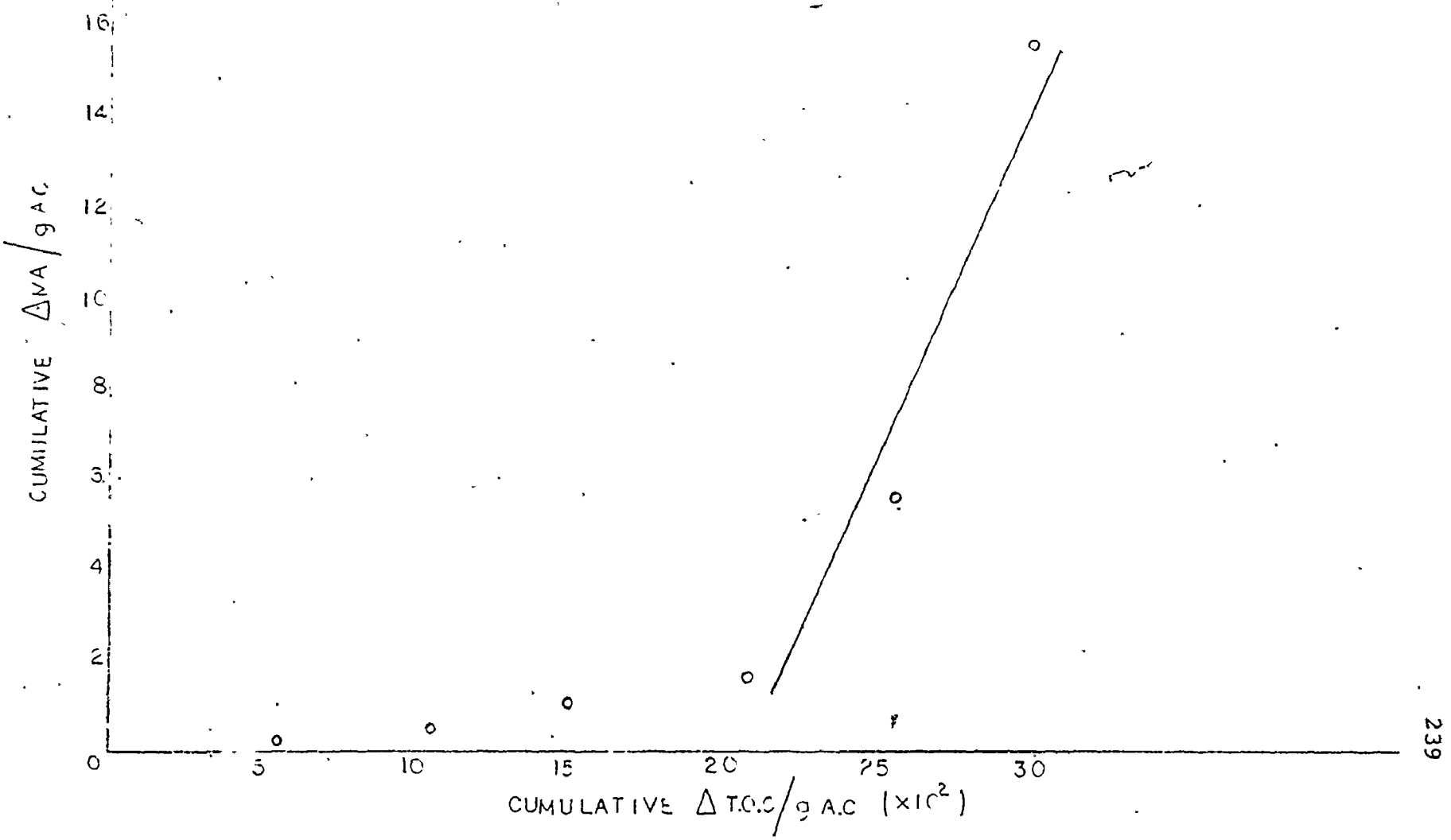


Fig.D.3.13 Volume Yield Evaluation Curve Run 7

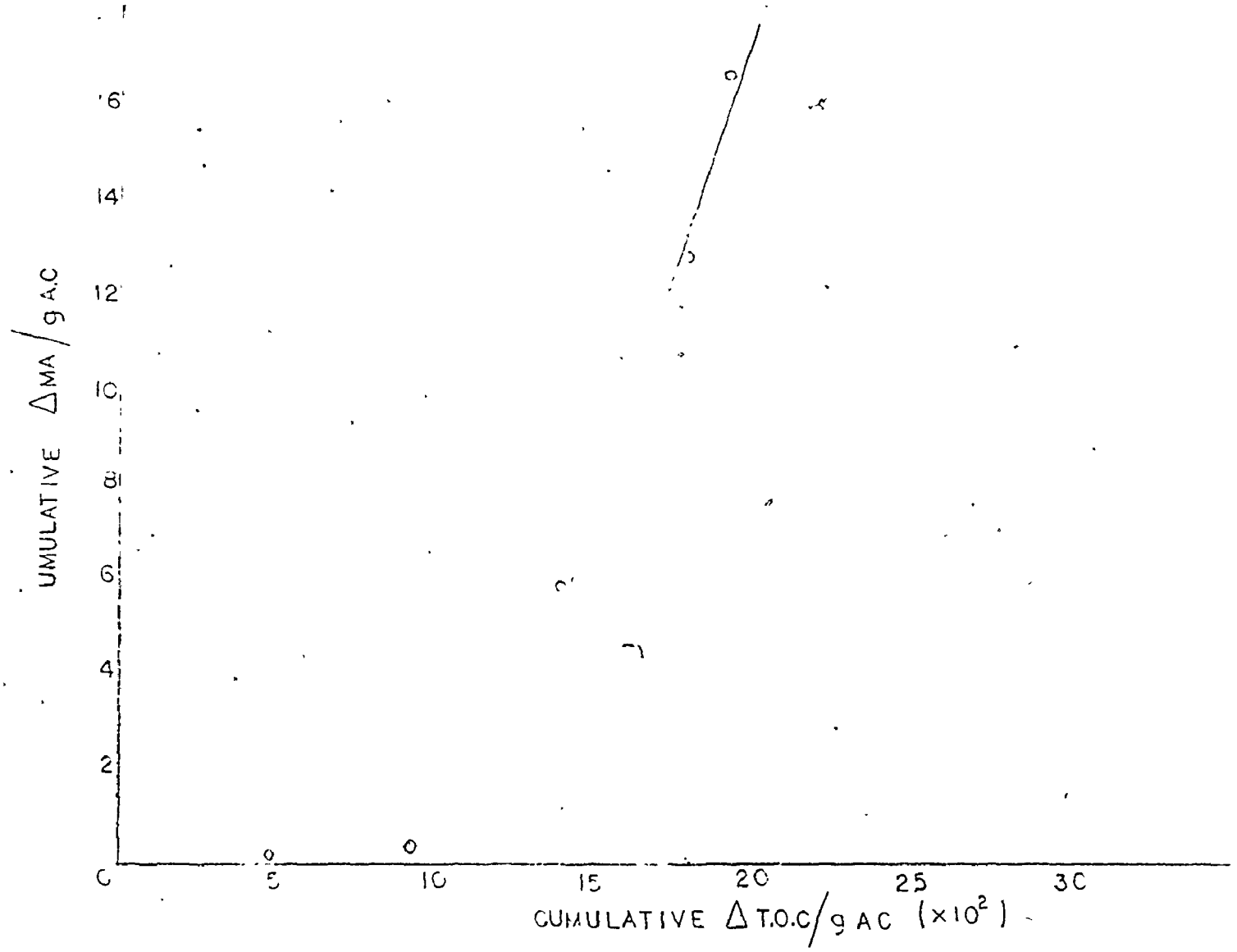


Table D.4.1

Spent Carbon, Phenol Adsorption Isotherm, Run 4

Flask No.	Flask+A.C. (g)	Flask (g)	Volume ml	Ceq Phenol mg/l	Phenol Adsorbed mg	Dry AC (g)	Loading mg/g
1	77.4157	77.3982	60	58	0.84	0.0068	123.5
2	78.0084	77.9509	60	40	1.92	0.0223	86.1
3	75.3111	75.9509	60	12	3.6	0.0607	59.3
4	74.2156	75.1542	60	2	4.2	0.1106	38.0
5	75.8623	73.9298	60	0	4.32	0.1763	24.5
6	79.8440	78.2628	60	0	4.32	0.6117	7.1
7	Blank Phenol	--	60	72	--	--	--
AC Blank	72.0710	71.8084	60	0	--	0.1024	--

Water-Content of Carbon for Isotherm Determination

	Sample I	Sample II
Wet Weight of Carbon (g)	0.1964	0.5171
Dry Weight of Carbon (g)	0.0760	0.2001
H_2O Content % of Wet Carbon	61.3	61.3

Table D.4.2

Spent Carbon, Phenol Adsorption Isotherm, Run 5

Flask No.	Flask (g)	Flask AC (g)	Dry AC (g)	Adsorbance (1:00)	Ceq Phenol mg/l	ΔC mg/l	Volume ml	Adsorbed Phenol mg	Loading mg/g
1	74.6720	74.6909	0.0074	0.110	63	16	55	0.88	119.
2	78.1032	78.1558	0.0208	0.072	44	35	55	1.95	92.5
3	78.9664	79.1078	0.0558	0.022	7	72	55	3.96	70.9
4	71.8917	72.1582	0.1053	0.010	0	79	55	4.35	41.
5	72.1795	73.1774	0.3912	0.010	0	79	55	4.35	4.3
6	72.1377	73.5532	1.4155	0.010	0	79	55	---	3.
7	Phenol Blank	--	--	0.118	79	--	55	--	--
AC Blank	77.3688	77.5303	0.0482	0.010	0	--	55	--	--

Water Content of Carbon for Isotherm Determination

	Sample I	Sample II
Wet Weight of Carbon (g)	0.2838	0.7542
Dry Weight of Carbon (g)	0.1121	0.2982
H_2O Content % of Wet Carbon	60.5	60.5

Table D.4.3

Spent Carbon, Phenol Adsorption Isotherm , Run 6

Flask No.	Flask + AC (g)	Flask (g)	Dry AC (g)	Ceq Phenol mg/l	ΔC mg/l	Volume ml	Adsorbed Phenol mg	Loading mg/g	Total Loading
1	74.3775	74.3566	0.0079	65	5	60	0.3	38	110
2	81.6012	81.5216	0.0302	45	25	60	1.5	49	121
3	80.5517	79.7866	0.2907	5	65	60	3.9	13	85
4	79.0893	78.7940	0.1133	25	45	60	2.7	24	96
5	83.3757	83.1877	0.0714	30	40	60	2.4	34	106
AC Blank	75.8984	75.6634	0.0890	0	--	--	--	--	
Phenol Blank	--	--	--	70	--	--	--	--	

Water Content of Carbon for Isotherm Determination

	Sample I	Sample II
Wet Weight of Carbon (g)	0.8862	0.6860
Dry Weight of Carbon (g)	0.3335	0.2599
H_2O Content % of Wet Carbon	62	62

Table D.4.4

Spent Carbon, Phenol Adsorption Isotherm , Run 7

Flask No.	Flask + AC (g)	Flask (g)	Dry AC (g)	Ceq Phenol mg/l	ΔC mg/l	Adsorbed Phenol mg	Volume ml	Loading mg/g	Total Loading
1	76.7879	76.7678	0.0074	66	9	0.54	60	73	115
2	76.8853	76.8449	0.0150	62	13	0.78	60	52	94
3	73.5780	73.4323	0.0539	44	31	1.86	60	34	76
4	77.9602	77.5848	0.1389	18	57	3.42	60	24	66
5	78.4506	77.3633	0.4023	6	67	4.14	60	10	52
Phenol Blank	--	--	--	75	--	--	60	--	--
Carbon Blank	69.5716	69.2882	0.2834	3	--	--	60	--	--

Water Content of Carbon for Isotherm Determination

	Sample I	Sample II
Wet Weight of Carbon (g)	0.4938	0.9232
Dry Weight of Carbon (g)	0.1811	0.3416
H_2O Content % of Wet Carbon	63	63

Total loading is the loading that results because of adsorption during the isotherm determination plus the loading of Phenol existing of the carbon by the end of the run, as determined in Appendix D2 through Phenol mass balances.

Fig.D.4.1 Spent A.C Phenol Adsorption Isotherm . Run 4

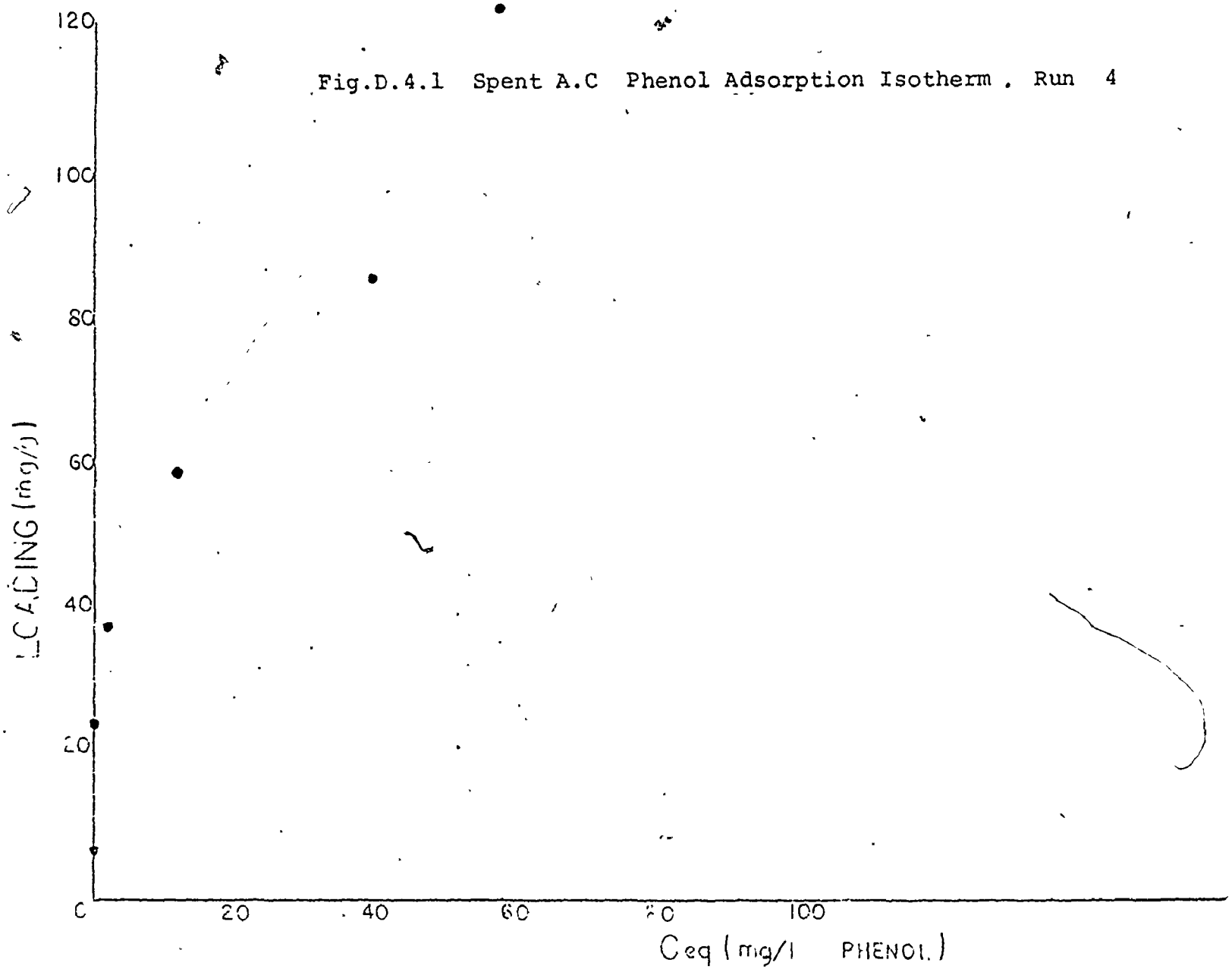


Fig.D.4.2 Spent A.C. Phenol Adsorption Isotherm Run 5

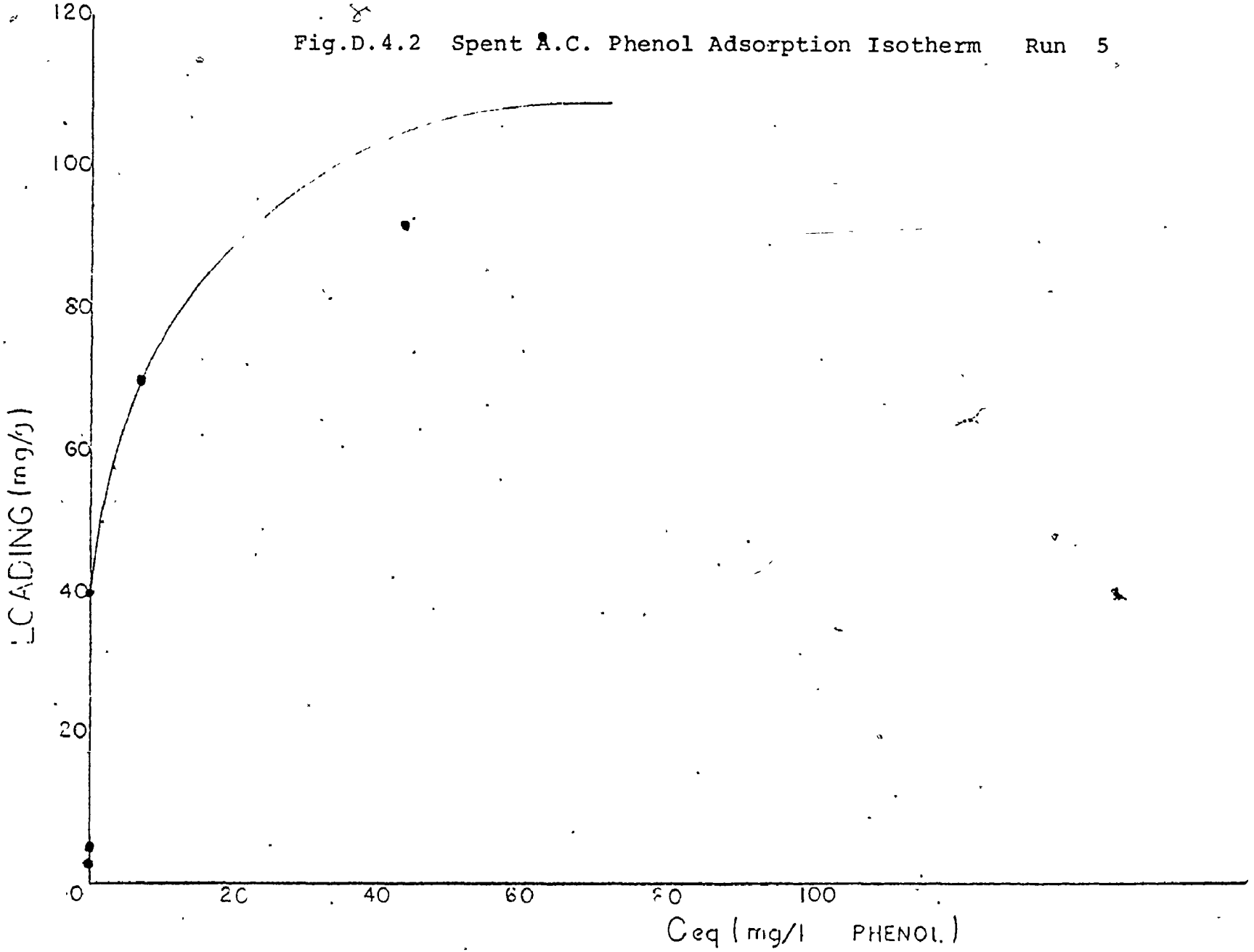


Fig.D.4.3 Spent A.C Phenol Adsorption Isotherm Run 6

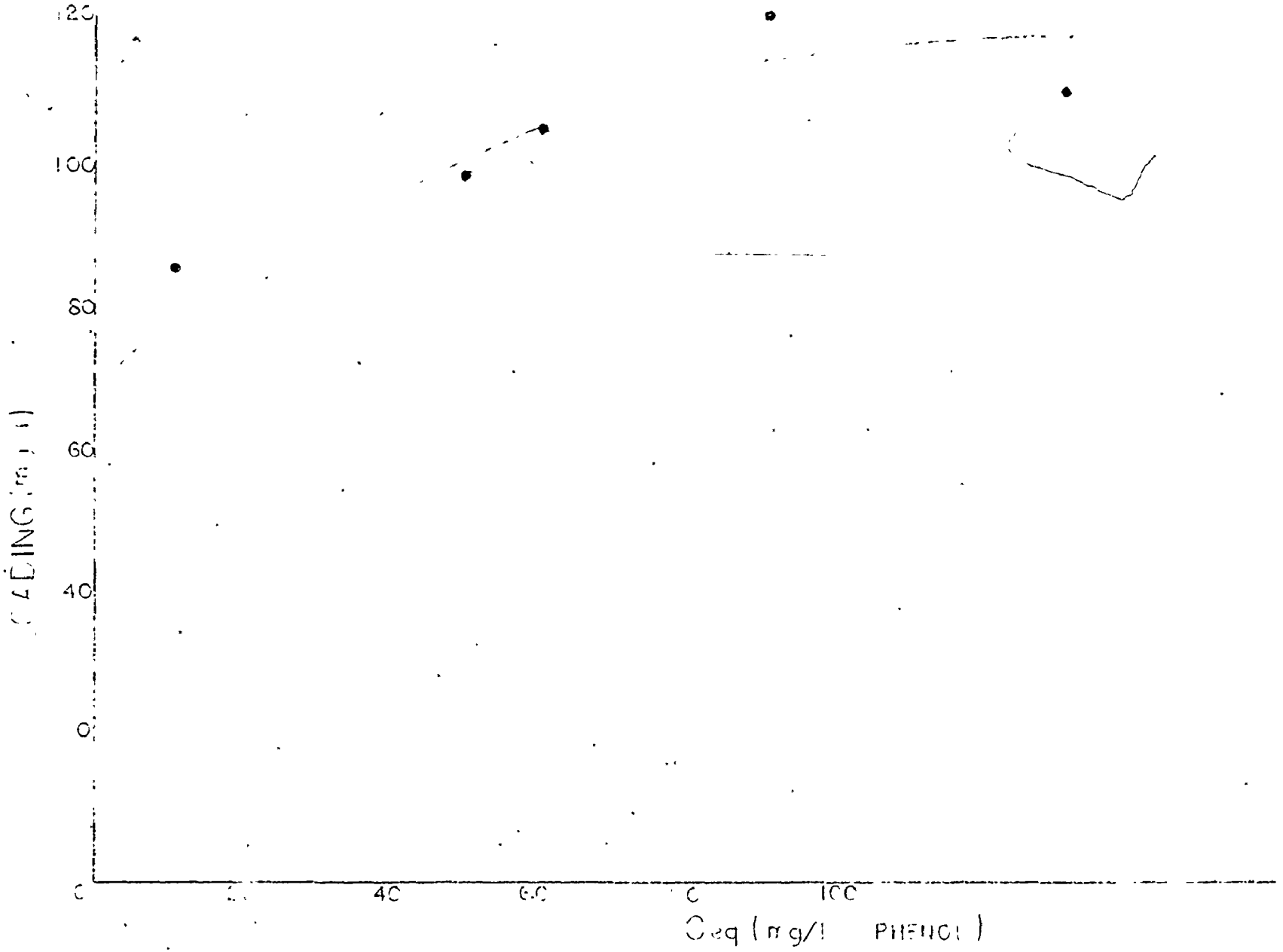
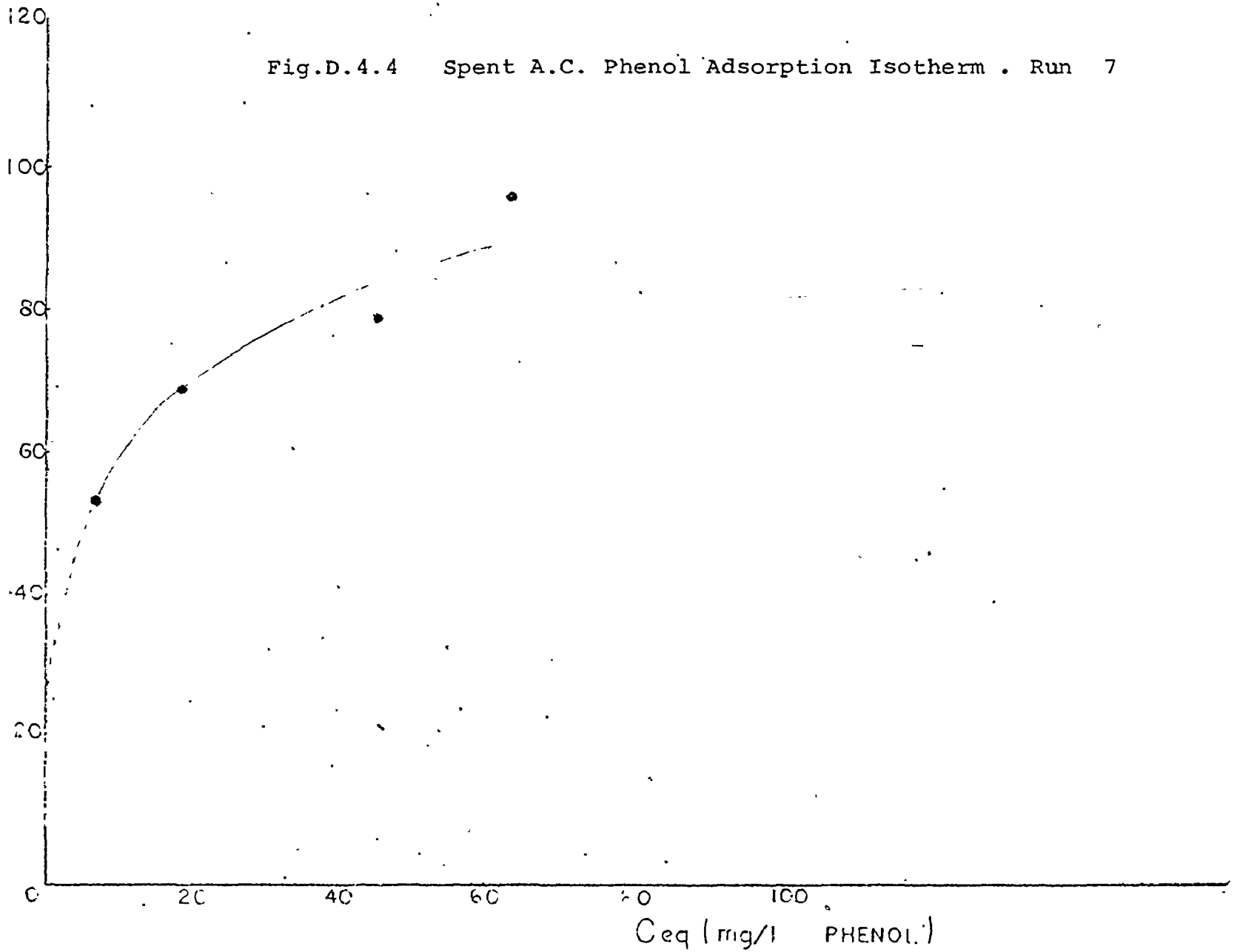


Fig.D.4.4 Spent A.C. Phenol Adsorption Isotherm . Run 7



APPENDIX E

Abbreviations

A^o	Angstrom
	Equal to 10^{-8} centimeters or 10^{-10} meters
A.C	Activated Carbon
^oC	Degrees Celsius or Centigrade
cm	Centimeter. Equal to 10^{-2} m.
cc	Cubic Centimeter, cm^3
D.O.	Dissolved Oxygen
g	Gram, It is a mass unit and can also be
	written as g (SI)
hr(s)	Hour(s)
F^o	Degrees Fahrenheit
IC	Inorganic Carbon
kg	Kilogram, equal to 1000 g.
l	Liter, equal to $10^3 cm^3$
μ	Micron, equal to 10^{-6}m.
m	Meter, Unit of length (S.I)
mg	Milligram, equal to 10^{-3}g.
μl	Microliter, equal to 10^{-6} l.
ml	Milliliter, equal to 10^{-3} l.
mm	Millimeter, equal to 10^{-3}m.
meq	Unit of mass equal 10^{-3} gram equivalent
	which is the apparent weight of an
	electrolyte multiplied by the ionic charge

p.s.i.	Pounds per square inch. Unit of pressure (British Units System)
Peak	The reading of the peak the Carbon Analyser recorder gives for a certain sample. It is expressed in arbitrary units of the recorders chart.
q	Loading of an adsorbant. It is the mass of adsorbate adsorbed per unit mass of adsorbant. It is expressed in terms of mg of adsorbate per gram of adsorbant.
T.C.	Total Carbon content of a sample, organic and inorganic.
T.O.C.	Total Organic Carbon of a sample (elemental)
#	Number
%	Percent
ID	Inside Diameter of tube-pipe
OD	Outside Diameter of type or pipe
Ceq.	Equilibrium Concentration after adsorption
Co	Initial concentration
O.C.P.	Organic Carbon content of Phenol concentration.
R	Continuous Run

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