

BIOLOGICAL REGENERATION OF ACTIVATED CARBON

by

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I. INTRODUCTION

Then God said, "Let the waters team with shoals of living creatures . . ." and so it was (1). Years later, thousands of newly synthesized organic compounds, some of them toxic, are annually released into the aquatic environment. Many of those creatures, that served and still serve as man's richest diet, are now endangered. The problem is known as water pollution. It may become, if not solved, one of man's most dangerous enemies.

Since the turn of the century, industry has been the major source of water pollution. Phenol is one of the more toxic pollutants. Concentrations of this chemical may result in fish kills, in contamination of the flesh of fish that decreases their value as a source of food and in impairment of water supplies (2). It is lethal to many constituents of the flora and fauna of the aquatic world.

Until recently, it was hard for man to believe that an ecosystem that is unhealthy would not be healthful for humans (3). Phenol not only affects the fish, it also affects the fisherman. According to all reports on toxic materials, phenol is a dangerous, deadly poison for man. Oral uptake of 1.5 grams is lethal (4). Death has resulted from its absorption through a skin area of 64 in². Human symptoms related to phenol toxicity are available

in all books on hazardous chemicals (4,5). Do the above facts imply that phenol has to be banned from the market?

The answer is NO. Phenol is used in the manufacture of various resins, disinfectants, plastics, and pharmaceuticals, products that are essential to today's society. Man doesn't have to stop manufacturing a chemical that is helping in his survival. However, it is the duty of man to find a solution to treat efficiently the industrial wastewater that is contaminated with such chemical.

Treatment of industrial wastewater started growing in the early 1960's. The United States, Germany, and England initiated the use of granular activated carbon to remove organic contaminants from wastewaters (6). This chemical process is known as adsorption and actually is widely used throughout industry.

Activated carbon columns have long been used to treat phenolic wastes and other toxic organic compounds encountered in wastewaters. However, once these columns are exhausted, the activated carbon must be regenerated or replaced. The regeneration techniques used in the industry are often cumbersome and costly. The most commonly used one is the off-site thermal regeneration (7). Problems such as transportation and attrition (10-15% by weight of the carbon is lost during the burn out) are associated with this process. The biological regeneration

technique of activated carbon, however, is an in situ process expected to overcome the above mentioned problems. The theory behind this new technology is still vague.

For this reason, and for economic reasons, biological processes are still rare. Until 1970, little is reported on applications of appropriate methods to the biological degradation of toxic chemical and/or biochemical wastes (3). Now, for economic reasons, treatment of wastewater using microorganisms is flourishing. Some of these microbes are phenol degraders. As one TV commercial would put it, "Let the bug do the cleaning."

One biological treatment of wastewater that is receiving wide attention in industry uses the fluidized bed technology. The basic concept of this process consists of passing wastewater through a fluidized bed of granular or powdered particles. Appropriate biological microorganisms are added to the bed to degrade specific contaminants. The purpose of the particles is to provide an enormous surface area for microbial growth (9). On a laboratory scale, sand, coal, and activated carbon are used as support media (10).

This thesis will be concerned with:

- 1) The extent to which an activated carbon fluidized bed, treating phenol, could be bioregenerated.
- 2) The evaluation of the performance of treating phenolic artificial wastewater in:

- a) the presence of activated carbon
- b) the absence of activated carbon.

II. LITERATURE REVIEW

A. Activated Carbon-Phenol System

Activated carbon, as well as the activated carbon-phenol system, are widely investigated in the literature. In the early 1970's, Bartell and Miller (11) were interested in the chemistry of adsorption by activated carbon and examined the adsorption of electrolytes by activated carbon. Later, Boehm (12), Garten and Weiss (13), Snoeyink and Weber (14), Mattson and colleagues (15) discussed the structural and surface characteristics of activated carbon. The complexities of the structure and the surface of this material are responsible for the diversity of sorptive reaction mechanisms for organic compounds of interest in water and wastewater treatments. This section will be mainly concerned with:

1. The chemistry of active carbon and phenol.
2. The theory of adsorption and the adsorption isotherms.
3. The factors affecting phenol adsorption on active carbon.
4. The regeneration of spent activated carbon.

1. The Chemistry of Active Carbon and Phenol

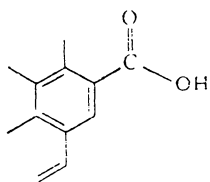
a. Structure and Surface Properties of Active Carbon

The sorptive behavior of activated carbon depends on its structure and surface properties. Active carbon is composed of microcrystallites. Each microcrystallite consists of a stack of graphitic planes. Within a plane, sigma (σ) bonds join each carbon atom to the three adjacent ones. In addition, the fourth electron of the atom participates in a Pi (π) bond. It is likely that part of the carbon within a microcrystallite is highly disordered, thus deviating from the ideal graphite structure. Highly reactive free valences (free radical-sites) are located at the edges of the graphitic planes. It is probably these free radical carbon atoms, in conjunction with van der Waals forces which serve to bind the microcrystallite into a rigid unit (16).

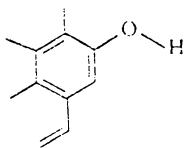
Active carbon is a porous material. It possesses a high surface-area per unit weight (up to 1000 m^2 of surface-area/g). Its porosity results from the burn out of the non-carbon impurities, located between the microcrystallites during the activation process. This is achieved by exposing the raw materials such as coal and coke to oxidizing gases (O_2 , CO_2 , H_2O) at temperatures above 200°C . The result is an extensive heterogeneous surface. Zarifyanz and colleagues (17), Blyholden and Eyring (18), and many others

(19, 20) investigated the reaction of carbon with oxygen at different temperatures and under various atmospheres.

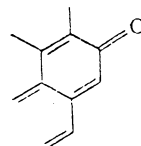
As a result of the oxidation process, a diversity of functional groups form on the edges of the microcrystallites. This diversity in functional groups is due to the high reactivity of the free valences and the variety of substances used in the preparation of such carbons. Not all of these groups have been characterized. The few that have been identified (21) are proving very important in the waste water treatment application. The groups most often suggested are carboxyl groups (I), phenolic hydroxyl groups (II) and quinone-type carbonyl groups (III). Slightly less often there are suggestions of ether, peroxide, and ester groups, in the forms of normal (IV) and fluorescein-like lactones (V) (cyclic esters) carboxylic acid anhydrides (VI) and the cyclic peroxide (VII).



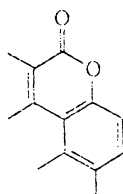
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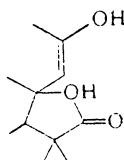
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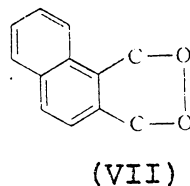
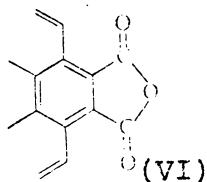
(III)



(IV)



(V)



Certainly, the presence of oxygen-containing functional groups on the surface of carbon markedly affects the adsorption of certain compounds. Beebe and co-workers (22) and Wright (23) studied the adsorption of a variety of organic materials on two different carbons, Graphon^{*} and Spheron^{**} (24). They observed significant differences in the nature and degree of adsorption of those materials on the two carbons. They suggested that these differences in adsorption characteristics are due mainly to differences in the amount of chemisorbed oxygen on the carbons during the oxidation process.

Mattson, Mark and Weber (25) studied the surface reaction of phenol and activated carbon using infrared internal reflectance. They found that carbonyl type functional groups on the carbon surface interact with the sorbed phenol.

^{*} Graphon: Trademark by Graphite Metallizing Corp., for a group of graphite and resin materials that exhibit extremely high chemical inertness.

^{**} Spheron: Trademark, by Cabot Corp., for pelleted channel carbon blacks for rubber.

Coughlin and colleagues (26, 27) investigated the importance of the nature of the oxygen-containing functional groups on phenol adsorption by carbon in aqueous systems. They found that a carbon that has been extensively oxidized adsorbs less than one that has not. The surface of an active carbon was extensively oxidized with ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in order to increase the quantity of acidic oxygen on the surface. The capacity of the carbon for adsorption of phenol was reduced by a factor of eight on a weight basis and by a factor of four on a surface area basis. However, the original capacity was partially restored by treatment of the surface with a reducing agent or vacuum outgassing at elevated temperature.

Bartell and Miller (28), Garten and Weiss (29), and Snoeyink and Weber (30) found that oxygen functional groups play a significant role in the sorption of strong acids.

Activated carbon has negatively charged sites on its surface. Phenols are fairly acidic and, therefore, they have an affinity to the negatively charged surface of the activated carbon. The affinity of phenols to the activated carbon and its uptake by this later is termed adsorption.

2. The Theory of Adsorption and the Adsorption Isotherm

a. Adsorption Theory

The adsorption process consists of two steps: the first

step is the migration of molecules from the solution to the solid surface. The second step is the attachment (adherence) of these molecules to the solid surface by chemical and physical bonds. The molecules are called adsorbate and the solid is called adsorbent. The adsorbate and the adsorbent interact in different ways. If the interaction is very strong and irreversible then chemical adsorption or chemisorption is said to have occurred. (This is the process that occurs when oxygen-containing groups are adsorbed on the surface of the carbon during the oxidation process.) On the other hand, if the interaction is weak as is characteristic of bonds formed by van der Waals forces, then physical adsorption is said to have occurred (23). This latter adsorption is reversible and it is the one that occurs most frequently when removing phenols from wastewaters by activated carbon.

In practice, for economic reasons, activated carbon is the most effective adsorbent used in wastewater treatment for the removal of non-polar materials such as phenol. Activated carbon is an inexpensive material and can adsorb many non-polar materials that are found in wastewaters. Activated carbon differs from silicon gel in that it doesn't attract polar materials such as water. According to Mulligan and Fox (10), the primary driving forces for adsorption are a combination of the hydrophobic (water disliking)

nature of the solutes (adsorbate) in the wastewater and the affinity of the solute for the solid (adsorption). The second driving force is due to a combination of electrostatic attraction, physical adsorption, and chemisorption. Electrostatic forces occur when sorbate molecules carry a net charge and are attracted to surface sites of opposite charge. Most adsorption phenomena are combinations of the above three types. One can directly relate solute solubility in water to its hydrophobic behavior. Dissolved organics with low solubility are most readily adsorbed. Since solubility decreases with increasing molecular weight within a given class of chemicals, high-molecular weight organic molecules of homologous type adsorb preferentially. For example, adsorption increases in the order: formic, acetic, propionic, and butyric acids. As mentioned earlier, adsorption of non-polar molecules is favored over polar molecules. Thus, non-polar, high molecular weight contaminants such as benzene are easily removed from wastewater; low molecular weight polar organics such as methanol are poorly removed from wastewater by adsorption. The fact that benzene adsorbs better than phenol implies that the hydroxyl group of the phenol molecule is not the determining factor in the adsorption of phenol on activated carbon.

The hydroxyl group, however, affects the electrophilic nature of the ring. Drago (32) showed that phenol forms

strong donor-acceptor complexes with oxygen containing groups and that these aromatic compounds adsorb on active carbon by a donor-acceptor complex mechanism involving carbonyl oxygens of the carbon surface acting as the electron donor and the aromatic ring of the solute surface acting as the acceptor. This implies that the aromatic ring is the determining factor in the adsorption of aromatics. In the case of phenol, the hydroxyl group decreases the electrophilic nature of the ring, making it less adsorptive than benzene. The rule relating adsorption to molecular weight or molecular size doesn't apply infinitely. It has a lower and an upper limit. It only applies to organic molecules of three or more carbon atoms. The molecule may become so large that pore diffusion to the vast internal surface area of activated carbon is inhibited.

Due to adsorption, there is an accumulation of materials at the liquid-solid interface that is used in wastewater treatment. Dissolved materials tend to either accumulate at an interface or to disperse away from it depending on their relative strength of attraction for themselves or for the solvent (as mentioned earlier, non-polar molecules are hydrophobic and therefore tend to migrate toward the interface). Two significant results of this accumulation are considered. The first one is the lowering of the surface

tension of the solvent (33). It can be shown from thermodynamic considerations that if surface tension decreases upon addition of solute, the solute will tend to migrate toward a solid surface where it can be adsorbed. Heat is released; adsorption is an exothermic process. The second result is the concentration of the dissolved material in close proximity to the sorbent surface. This latter result is important because the rate of adsorption is proportional to the concentration of the sorbate. This proportionality of rate of adsorption to concentration of sorbate is the subject of the next subsection.

b. Adsorption Isotherms

Adsorption processes are described by the equilibrium isotherms they follow. These isotherms are simply relationships between the quantity of adsorbate that can be adsorbed by a given weight of activated carbon and the concentration of sorbate remaining in solution at equilibrium at a constant temperature (isothermal). Experimental determination of an isotherm is usually accomplished by contacting weighed amounts of carbon with a given volume of liquid of known initial sorbate concentration. The system is allowed to come to equilibrium at a selected temperature and the final liquid-phase sorbate concentration is measured. Let X be the weight of organic adsorbed, and M be the weight of

carbon used in the adsorption of the organic compound. If X/M represents the quantity adsorbed per unit weight of carbon and C_e the equilibrium concentration, then an isotherm for a pure sorbate such as phenol will take the form of the curve in Figure 1.

Most equilibria data follow one of three commonly used models: The Brunauer, Emmett, Teller (BET) isotherm; the Langmuir isotherm; or the Freundlich isotherm. Both BET and Langmuir isotherms are based on theoretical developments while the Freundlich isotherm is an empirical relationship. The BET isotherm is based on the concept of multiple-layer adsorption, i.e., multiple layers of materials being adsorbed on the surface, while the Langmuir model assumes that only a single (mono) layer can be adsorbed. In practice, the Freundlich isotherm is the form of choice for activated carbon.

The equation describing the Freundlich isotherm has been derived from empirical considerations and has the form:

$$\frac{X}{M} = KC_e^{1/n}$$

where X/M = amount adsorbed per unit weight of activated carbon

C_e = equilibrium concentration of adsorbate in solution after adsorption

K, n = empirical constants.

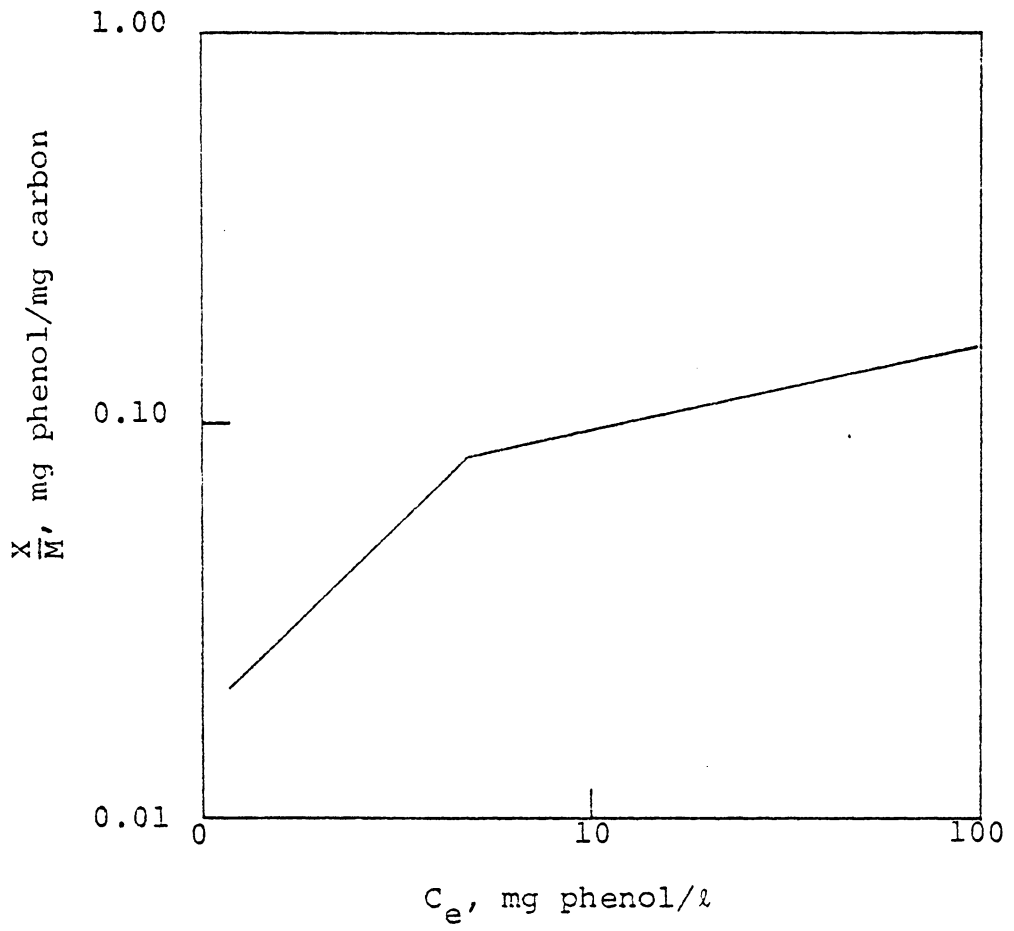


Figure 1. Isotherm for phenol.
(T. J. Mulligan, and R. D. Fox, Chem.
Eng./Deskbook Issue/p. 49, October 18,
1976).

To facilitate determination of model validity and the values of the coefficients K and n , the Freundlich isotherm is plotted on log-log paper. A straight line whose slope is $1/n$ and whose intercept is K , is expected from the plot. Typical Freundlich isotherm constants are reported in reference 6. For phenol, K is found to be equal to 24 mg/g while $1/n$ has a value of 0.271.

Theoretical carbon demand can be obtained by using the following equation (6).

$$Y = C_o / (X/M_{C_o})$$

where Y = weight of carbon required per unit volume of contaminated liquid

C_o = Influent concentration (ppm)

X/M_{C_o} = maximum amount of contaminant adsorbed per unit weight of carbon when the carbon is in equilibrium with the untreated contaminant concentration.

Figure 1 shows that the adsorption isotherm for phenol on carbon usually shows two clear plateaus. Each plateau fits a Freundlich type equation with different constants. This indicates that two different processes are taking place, one at low concentrations and one at high concentrations of solute (26, 34). To explain these observations, Giles and co-workers (35) suggested that the second step

(second plateau) of the isotherm involved an uncovering of part of the surface (an increase in available surface), followed by readsorption of the phenol molecules in a different orientation. They also suggested that this re-orientation involved a change from a flat (with respect to the aromatic ring of the phenol) configuration to an end-on configuration where the hydroxyl group is directed away from the carbon surface.

Physical adsorption is primarily responsible for removal of organic contaminants and the process itself is reversible; therefore, one would expect that all the molecules that have been adsorbed under a set of conditions can be recovered under the same set of conditions through a desorption process. Snoeyink and co-workers (16) studied the degree of reversibility of the sorption reaction for phenol on active carbon. Their procedure consists of contacting a known weight of already loaded activated carbon (the activated carbon was brought to equilibrium with a 5×10^{-3} mole per liter solution of phenol in distilled water) with distilled water. The carbon is then allowed to re-equilibrate with the new solution. After equilibrium is achieved, the solution concentration, C_e is measured. Similar to what has been done during the adsorption process, the values of X/M have been determined and plotted versus C_e . Their results indicate a definite

hysteresis effect in the desorption of the phenol. Snoeyink and colleagues (16) suggest that an irreversible chemical reaction that results in the breakdown of phenol occurs after the phenol is sorbed from solution by the active carbon. This supports the hypothesis that the adsorption process is a combination of three forces: electrostatic, physical adsorption, and chemisorption.

3. Factors Affecting Phenol Adsorption on Active Carbon

In the previous subsection the adsorption theory and the adsorption isotherm were discussed. Let us now look at the major factors that affect adsorption. Factors such as temperature, pH, size of molecules, salts and acids play an important role in the adsorption of phenol or other organics on activated carbon.

a. Effects of Temperature

Equilibrium studies of phenol sorption on activated carbon were performed at different temperatures by Snoeyink and co-workers (16). Their results show that adsorption decreases with increasing temperature. This is consistent with the fact that adsorption is an exothermic reaction.

b. Effects of pH

Isotherms for sorption of phenol at pH values of 2.0, 5.6, 7.5, and 10.6 are given by Snoeyink and co-workers (16).

Adsorption increases as the pH increases. Once the pH approaches the pKa value of phenol, i.e., 9.89, a drop in adsorption is observed. The reason is that the principle adsorbing species above this pH is most likely anionic. Ions adsorb less than the neutral species.

c. Effects of Size

The effect of the size of sorbate on adsorption has been discussed earlier. For organic molecules of the same chemical class, adsorption on activated carbon increases with increasing molecular size. This rule is adversely affected when the diameter of the organic molecule approaches the diameter of the micropores.

d. Effects of Inorganic Salts on Acid Adsorption

Steenberg (36) found that the nature of the inorganic salt present in the adsorption system could significantly affect the extent of acid uptake. He studied the effect of different salts (KSCN, KI, KBr, NaCl, KCl, Na₂SO₄) on acid adsorption. He noted that the order of the anion effect on the adsorption capacity of protons on active carbon was $\text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-}$. Snoeyink and Weber (37) studied the HCl - NaCl system. They found an increase in acid adsorption on activated carbon upon increase in the salt concentration. The same effect was exhibited when they worked on the P-nitro phenol-NaCl and phenol-NaCl

systems. Their result is important when dealing with a basic solution of phenol that has a pH equal to the pKa value ($pK_a = 9.89$). Phenol is mostly in the ionic form at that pH, resulting in poor adsorption. The high salt concentration may counteract this effect of adsorption at high pH by increasing the degree of ion pairing of the cation with the phenol anion. No significant differences in adsorption capacity of carbon were noted when they repeated the same work at pH 2.0 (16).

e. Competitive Adsorption of Organics with Acids

Experiments done by Steenberg (36) and others (38, 39) show that adsorbed acid is easily desorbed on addition of organic materials such as phenol, arylalcohol, toluene, picric acid, and methylene blue. These types of materials have the capability to desorb anions. Upon addition of the organic material, the anion is competitively desorbed.

4. The Regeneration of Spent Activated Carbon

Once exhausted, activated carbon can be regenerated in several fashions. Regeneration techniques are chosen on an economical basis. Some of the current practices in activated carbon regeneration are classified into two major classes, the destructive and the nondestructive regeneration. For the destructive regeneration, about 10-15% by weight of the activated carbon is lost due to attrition.

a. Destructive Regeneration of Activated Carbon

i. Thermal regeneration techniques for granular activated carbon

Thermal regeneration is accomplished by passing the exhausted carbon through a furnace. Drying, using preheated air, takes place in the first step followed by pyrolysis and oxidation in an oxygen-starved atmosphere. The purpose of controlling the oxygen is to minimize the oxidation of the carbon itself. Finally, the sorbate (the contaminant) is oxidized; either becoming part of the activated carbon or being driven off as oxidized gaseous end products (10). Monstre furnaces are often used for this purpose. These are multiple-hearth furnaces. They consist of a cylindrical refractory-lined steel shell containing several hearths and a central rotating shaft to which rabble arms are attached (7). This technique is economical only for big treatment plants. It is not used for small treatment plants.

ii. Thermal regeneration technique for powdered activated carbon

Two techniques are developed for this carbon. These techniques also work for the granular carbon.

α. Shirco's electric furnace. Heat for regeneration, in this case, is provided by infrared radiation from quartz or silicone carbide heating elements (38). The Shirco furnace is attractive for small industrial wastewater treatment plants.

β. Wet oxidation. In this process, a slurry of carbon is mixed with air pressurized to about 800 psi. The resulting stream then passes through heat exchangers and a heated reaction vessel, where oxidation takes place at about 450 to 500°F. Wet oxidation has many advantages on other thermal regeneration techniques. It costs less. The slurry is regenerated without dewatering (7). The carbon loss is less than 7% by weight (recall that 10-15% by weight of the carbon is lost in most thermal regeneration techniques). Also, the oxidation step is self-supporting, i.e., no fuel is needed. The wet oxidation process is also known as the Zimmerman process (2).

iii. Fluid-Bed Work

The carbon is regenerated by blowing a hot gas through it. The carbon is fluidized by the gas stream creating an expanded bed. The advantages of this technique over the multi-hearth furnace technique are: (1) no internal moving parts, so the cost on maintenance is low; (2) the heat transfer between the gas and the carbon particles is excellent due to the high area of contact (this results in low fuel outlays); and (3) the equipment is less bulky--it costs less and occupies less space. All fluidized-bed units in use today have been, so far, designed to regenerate granular activated carbon. The powdered-carbon particles can easily be entrained by the hot gas used for reactivation. To

increase the contact time between the particles and the gas. Nichols Engineering are using a fluidized bed of sand and carbon particles. This will allow the sand to blow out first, giving spent carbon more time to reactivate.

b. Nondestructive Regeneration Techniques

There are three general types of nondestructive regeneration in use nowadays: pH change, solvent, and steam.

i. Regeneration by use of pH change.

This procedure is commonly used in the recovery of phenols and cresol from wastewater streams. The organic chemical is primarily ionized, then adsorbed as a free acid or base. It is then recovered from the adsorbent as the ionized salt by using an alkaline or acidic regeneration stream. The pH change technique can be used only for organic chemicals whose adsorption on activated carbon is affected by change in pH. As mentioned earlier, the adsorption of phenol on activated carbon is affected by pH change.

ii. Solvent regeneration.

Activated carbon can be regenerated by using a solvent phase to desorb the organic chemicals. The only requirement is that the organics to be removed be soluble in the solvent.

iii. Steam regeneration.

Steam regeneration of activated carbon is also a possible technique. In this case, the increased temperature

changes the equilibrium conditions and the sorbate moves into the gas liquid phase from the solid phase (31). We have already mentioned that adsorption decreases with increasing temperatures.

iv. Biological regeneration.

Biological regeneration consists of on-site reactivation of the exhausted active carbon using microorganisms. Rodman and Shunney (40) treated textile dye waste using activated carbon. The carbon was initially contacted for 2-1/2 hours with dye (contamination process), then regenerated by feeding, for 6 hours, the carbon bed with a bacterial culture (regeneration process). This cycle was repeated on and on; however, the authors did not mention anything about the role of the bacteria remaining in the bed once the regeneration process was over. The pilot plant used for this work consisted of a bed of activated carbon as supporting medium, and an aerobic culture reservoir used to feed the bed during the regeneration process. The wastewater was fed to the bed in a downflow mode during the contamination cycle. Hence, the column was operated in a packed bed mode. During the regeneration cycle, the bacteria were fed to the bed in an upflow mode. The adsorbent bed was then fluidized.

In the first contamination process, the rate of COD removal went down from approximately 100% to 30%, then

went up to 40%. After 6 hours of bioregeneration, the rate of COD removal went up to 70%, then dropped to 40% at the end of the contamination process. When the bioregeneration cycle was increased to 12 hours instead of 6 hours, an increase in removal efficiency was observed.

c. Options in Handling Exhausted Activated Carbon

According to Rizzo and Shepherd (6), there are four options in handling exhausted carbon. The first one is to throw away the carbon once exhausted and use virgin carbon for each batch. It can be economical on a small scale. The second option is offsite reactivation. In this case the exhausted carbon is transported to another plant where reactivation occurs. The company opting on offsite regeneration doesn't have to deal with all the burden associated with the operation of an onsite reactivation furnace. The third option is the onsite reactivation where the technique used has to be close to the treatment plant. No transportation fees are required for that option. Maintenance may be the only problem. The fourth option is to arrange for a service company that does the whole job at an offsite location. All those options are chosen on an economical basis.

B. Microbiology and the Treatment of
Phenol from Wastewaters

Factors such as temperature and pH affect both physical and biological processes for removal of wastewater

contaminants. Factors such as dissolved oxygen (only in the case of aerobes), substrate concentration, microbial ecology, and metabolic products are important variables in biological processes. In view of the importance of biological treatment the following review is restricted to:

1. The fundamentals of wastewater microbiology.
2. Effects of substrate concentration, temperature, pH, and contaminants on the growth of the microorganisms.
3. Microorganisms important in the treatment of wastewaters with special emphasis on the phenol metabolizing microbes.
4. Biochemistry of phenol metabolism.

1. The Fundamentals of Wastewater Microbiology

a. Bacteria

Bacteria are industrially important because they can be used to accumulate both intermediate and end products (41). They are also important in wastewater treatment because they can often metabolize organic materials and some undesirable minerals (31, 2). Bacteria that utilize organic materials as a source of energy and carbon are called heterotrophs. Those species that oxidize reduced inorganic compounds (such as NH_3) for energy and can use CO_2 as their carbon source are known as autotrophs. Both types are of interest to the wastewater engineer in the sense that the

majority of toxic compounds encountered in waters are either organic or inorganic.

b. Viruses

Viruses are important in wastewater treatment in the sense that the sanitary engineer has to keep them under control. This is usually done by chlorination and proper disposal of the plant effluent (2, 31, 41).

c. Fungi

In wastewater engineering some species of yeast are heterotrophs and are involved in removal of organic compounds from wastewater streams. Although most fungi are strict aerobes, yeasts are capable of both aerobic and anaerobic growth (2, 31, 41).

d. Protozoa

Protozoa function in removing bacteria and particulate organic matter from wastewaters (2, 31, 41).

e. Growth Media for Microorganisms

The basic microbial growth requirements are a source of energy, a source of carbon, a source of nitrogen and, finally, a source of minerals. As mentioned earlier, heterotrophs utilize organic materials as a source of energy and carbon while autotrophs oxidize reduced inorganic compounds (such as SO_4) for energy and use CO_2 as their carbon source.

The formulation of a favorable medium for a certain microorganism is not a simple problem. Aiba and colleagues (41) tabulated the range of concentrations of some inorganic constituents found in bacteria, fungi, and yeast. From their table, one can conclude that phosphorous, potassium, sulphur, and magnesium are major components in microorganisms. An understanding of the composition of the cell also helps in the formulation of a medium.

Porges and colleagues (42) developed a commonly used formulation for the cell. The formula is $C_5H_7O_2N$. Pauling and co-workers (43) took phosphorous into account and derived the following formula $C_{42}H_{100}N_{11}O_{13}P$. These elements have to be found in any growth medium and in the right amount. Shortage of any could affect growth. Water is the major component of cells. In a bacterial cell, for example, 80% of its weight is water while 20% is dry material, of which 90% is organic and 10% is inorganic. The density (31) of wet bacteria is nearly always close to 1.1 g/cm^3 .

Different media for growth of microorganisms exist in the literature. Ralston and Vela (44) suggest the following medium to detect phenol-degrading bacteria: NaHCO_3 (0.125 g/l), KH_2PO_4 (0.1 g/l), NH_4Cl (0.07 g/l), Na_2SiO_3 (0.02 g/l), $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$ (0.01 g/l), $\text{MnCl}_2 \cdot 4 \text{ H}_2\text{O}$ (0.007 g/l), $\text{ZnSO}_4 \cdot 7 \text{ H}_2\text{O}$ (0.0015 g/l), Bacto Vitamin-Free Casamino Acids (0.01 g/l). The pH value is adjusted to

8.0 with 1 N NaOH. Drew and Pal (45) proposed another medium to grow phenol degrading bacteria or yeast. Their medium has been used in our experimental work. It consists of

Na_2HPO_4 (0.2 g/l), NH_4Cl (0.12 g/l), $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (0.001 g/l), $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.006 g/l), $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.01 g/l), $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.006 g/l), tap water (200 ml), Casamino Acids (0.01 g/l), Yeast Extract (0.06 g/l), the final pH is adjusted with 1 N HCl to 7.0. Sands and colleagues (46) formulated a medium capable of detecting fluorescent pseudomonads, a class of phenol biodegraders. The medium contains mineral salts, pectin, proteose-peptose, the antibiotics novobiscin, penicillin, and cycloheximide.

f. Metabolism of Microorganisms

In general metabolism is divided into two parts: catabolism, the breakdown of organic materials; and anabolism, the synthesis of molecules needed by the cell. For example, carbohydrate molecules are metabolized in the following ways (31, 41):

i. Aerobic carbohydrate metabolism

The molecule is first converted to Acetyl Coenzyme A through the glycolytic pathway. The energy released through the oxidation reactions is stored as the reduced coenzyme of nicotinamide adenine dinucleotide ($\text{NADH} + \text{H}^+$). The acetyl

Co A is then degraded to carbon dioxide through the tri-carboxylic acid cycle on the Krebs cycle (TCA cycle). The energy released during the process is stored as the reduced coenzyme $\text{NADH} + \text{H}^+$, the reduced prothetic group flavin adenine dinucleotide (FADH_2) and the phosphate ester bonds of butanosine triphosphate (GTP) which can be directly converted to adenosine triphosphate* (ATP). Finally $\text{NADH} + \text{H}^+$ and FADH_2 are oxidized through the electron transport system which involves oxygen as a terminal exogenous electron acceptor. The energy available as the result of the reactions of the TCA cycle and the electron transport chain is 215 kcal/mole of acetylene Co A. Part of this released energy is trapped by the cell in the form of ATP, the rest is lost as heat.

ii. Anaerobic carbohydrate metabolism

In this case, the carbohydrate molecule is converted to acids and alcohols excreted into the environment. Stokes and others (47, 48) determined the range of anaerobic fermentation products produced by a bacteria such as Escherichia coli. They found that ethanol, acetic acid, lactic acid, carbon dioxide and hydrogen gas are major end products of the fermentation of glucose by E. coli.

* ATP: Adenosine triphosphate is a high energy phosphate bond.

Many facultative bacteria, under anaerobic conditions, have the ability to utilize nitrate (NO_3^-) or sulfate ($\text{SO}_4^{=}$) as an electron acceptor instead of oxygen. The end products are nitrite (NO_2^-) or hydrogen sulfide (H_2S) instead of H_2O .

2. Factors Affecting the Growth of Microorganisms

Factors such as substrate concentration, temperature, pH, and contaminants influence the growth of microorganisms.

a. Substrate Concentration

The Michaelis-Menten (41) model for enzyme kinetics relates the reaction rate to the substrate concentration. The equation is

$$v = \frac{V_{\max} S}{K_m + S}$$

where: v = reaction rate or the change in product concentration with time

S = substrate concentration

$V_{\max}$ = maximum reaction rate

K_m = Michaelis' constant

Monod (41) proposed an empirical equation, based on the Michaelis-Menten type of relationship, that relates specific

growth rate to the concentration of the growth-limiting substrate. This equation is:

$$\mu = \frac{\mu_{\max} S}{K_s + S}$$

where: μ = specific growth rate

$\mu_{\max}$ = maximum specific growth rate

K_s = saturation constant, corresponds to a value of $\mu = \frac{\mu_{\max}}{2}$

S = concentration of growth limiting substrate

Powell (49) and others (50) have proposed an extension of the Monod model that includes consideration of maintenance-energy requirements, transport limitations, and multiple-product formation. The equation has the form

$$\mu = \frac{\mu_{\max} S}{K_s + S} - k_d$$

where: k_d = microorganism decay coefficient.

Other models that describe microbial growth are described by Hultman (51), Andrews and colleagues (52), Gaudy and co-workers (53), and Deindoerfer (54).

b. Temperature

Temperature plays an important role in the growth of microorganisms. The rate of bacterial growth roughly doubles with every 10°C rise in temperature until some limiting temperature is reached (2). In wastewater treatment

studies, the equation used to describe growth in relation to temperature is:

$$R_g = R_g(20) \psi^{T-20}$$

where: R_g = rate of growth at 20°C

ψ = constant = 1.0-1.15

Microorganisms can be classified according to the temperature range in which they function best. Some microbes may be thermophilic, such as lactobacilli, cellulose digesters, and methane producers. They can grow at temperatures as high as 70°C (2). Other organisms grow best at very low temperatures (-2 to 30°C) and, as such, are known as psychrophilic. Prasad and Jones (55) found that some psychrophilic bacteria were able to degrade nitrogen-containing organics at both 2°C and 20°C. They concluded that psychrophilic bacteria may be effective in waste treatment at lower temperatures. Mesophiles are microorganisms that grow best in the range of 25°C to 35°C. The thermophilic organisms have the advantage that contaminants usually grow better at lower temperatures, and thus the growth of competing cultures is likely to be retarded at higher temperatures. In situations like this, the biodegrader can effectively degrade a toxic compound with few competing species.

c. pH

The pH of a medium is very important in the growth of microorganisms. Some organisms can tolerate extremes of pH. Yeast and lactobacilli can grow easily at pH 4.5; many fungi are able to tolerate highly acidic media (pH = 2.0). As with the thermophilic organisms, microorganisms that tolerate low pH offer the advantage that growth of contaminants is not likely to occur. As such, they are important in waste treatment in the sense that the biodegrader that can survive a pH of 2.0 could effectively degrade a toxic compound with few other microorganisms competing for the available substrates. Although pH optimum for microbial growth is usually narrowly defined, Hall (56) states that the ammonia-oxidizing bacteria grow independently of pH in the range of 7 to 9.

d. Mixed Cultures

Mixed microbial organisms have the advantage of adapting themselves to changing conditions. A change in any variable that affects growth of microorganisms would possibly change the growth rate of species making up the culture, increasing some and decreasing others. The strength of the mixed culture is that metabolism of the waste materials continues and may overcome any change in environmental conditions (31).

3. Microorganisms Important in the Treatment of Wastewaters with Special Emphasis on the Phenol Metabolizing Microbes

a. Microbial Degradation of Chemicals

Wastewaters are rich in microorganisms and thousands of different species have been isolated. Some of the microbes are able to degrade chemical compounds that are hazardous to the aquatic environment. Stern and Gasner (57) found that ozonated lignin was partially biodegraded by strains of the yeast Candida utilis. The efficiency of lignin biodegradation was influenced by the degree of ionization. Spencer and colleagues (58) isolated yeasts that were capable of degrading up to 39% of the pulp waste resin acids in amended kraft mill effluent. Bellamy (59) found that thermophilic actinomycetes were able to decompose cellulose waste into single cell protein. Levina and colleagues (60) were able to grow Candida strains on organic acids found in waste streams. Kalisz (61) observed that the nitrogen removed from a wastewater stream was proportional to the dry weight of algae. He also found that phosphorus removal exceeded the level expected in relation to algal dry weight. Methanogenic bacteria were also found to be part of the wastewater population (62). Ammonia-oxidizing bacteria are common in activated sludge. Hall (56) stated that their maximum growth rate became independent of pH in the range of 7 to 9 but did vary according to wastewater

composition. Mohan and Li (63) were able to reduce nitrate (NO_3^-) and nitrite (NO_2^-) to molecular nitrogen (N_2). Willets (64) observed that bacillus strains could be induced to degrade alkylbenzene sulfonate (ABS). He demonstrated that the metabolism of ABS isomers was eased if the alkyl side chain of the molecule was degraded before destruction of the aromatic nucleus. Jones and colleagues (65) demonstrated that ultraviolet irradiated polyethylene and polypropylene but not polystyrene could be degraded by wastewater microorganisms. Giulet and co-workers (66) proved that polystyrene-vinyl ketone copolymers could be biodegraded with microbial populations in activated sludge.

b. Phenol Metabolizing Microbes

In the previous section, we looked at some microorganisms that are able to biodegrade few of the chemicals found in wastewater streams. In this section, we will review some of the phenol metabolizing microbes that are useful in the biological treatment of phenolic wastewaters. Fluorescent pseudomonas (67) (Pseudomonas aeruginosa, Pseudomonas putida and Pseudomonas fluorescens) are the most extensively studied phenol degrading bacteria. They are also able to biodegrade other organics such as benzoate. Radhaksishnan and Ray (68) reported that Bacillus cereus (another phenol biodegrader) could consume more phenol per unit weight of cell mass under conditions of nitrogen deficiency than nitrogen sufficiency.

Phenobac (69), a product of Polybac Corporation, is a freeze-dried, biochemical complex which is readily dispersible in wastewater. It contains adapted mutant bacteria and a wide spectrum of biochemical accelerators. This combination of ingredients rapidly degrades phenol and various hydrocarbons and chemical intermediates not readily broken down by naturally existing microbiological populations.

Drew and Pal (45) isolated RS17 (a yeast) and CP6A (a bacteria) from a sewage treatment stream. Both microorganisms were able to degrade phenols.

4. Biochemistry of Phenol Metabolism

The biochemistry of aromatic compound metabolism has been widely investigated in the literature. Dagley and co-workers (70) have shown that microorganisms can decompose phenol and substituted phenols through the meta-cleavage pathway shown in Figure 2 (67). Catechol, an intermediate, occurs not only in the metabolism of phenol but also in the metabolism of many other aromatic compounds. Benzoate, for example, is cleaved via that same intermediate through another pathway known as the ortho cleavage pathway, shown in Figure 3 (67). Davies and Evans (71) suggested that the cleavage of catechol by two different pathways is determined by the aromatic catechol precursor with which the organism is grown. That is to say that the meta cleavage

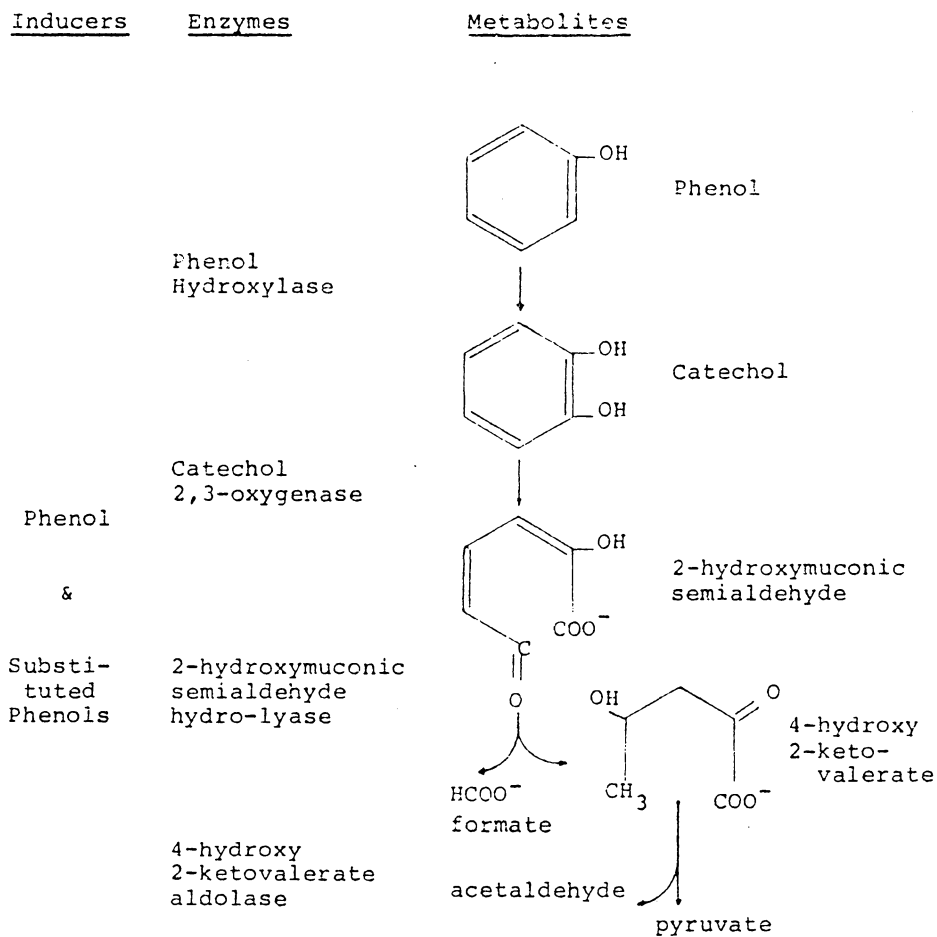


Figure 2. The meta cleavage pathway for oxidation of phenol.
(C. F. Feist, and G. D. Hegemen, J. Bacteriol.,
100, 859, 1969.)

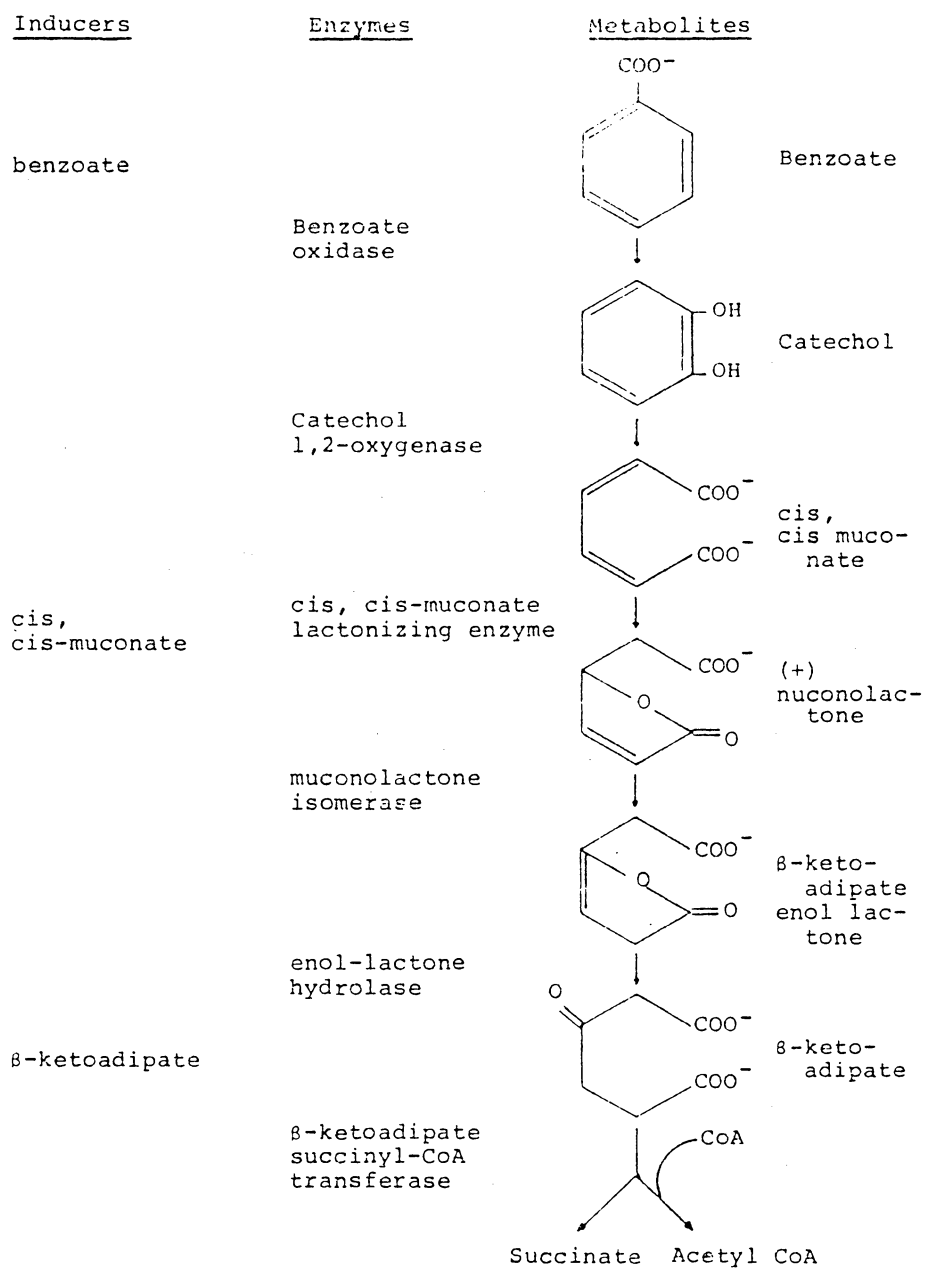


Figure 3. The ortho cleavage pathway for oxidation of benzoate. (C. F. Feist, and G. D. Hegemen, J. Bacteriol., 100, 869, 1969.)

pathway is induced after growth of the microorganism with phenol, and the ortho cleavage pathway is induced after its growth with benzoate. Feist and Hegemen (67) observed that various alkyl derivatives of catechol, derived from substituted phenolic compounds, are catabolized through the meta pathway. Catechol is only one of a number of intermediates metabolizable via the meta pathway. The ortho pathway, however, seems to be quite specific for catechol. Kemp and Hegeman (72) and Ornston and Stanier (73) observed that catechol 1,2-oxygenase is induced by cis, cis-muconate and not benzoate. The formation of cis, cis-muconate was also the inducer of most enzymes of the ortho cleavage pathway. In the meta cleavage pathway, the enzymes were induced by the primary substrate.

Most of the products of phenol metabolism are acidic in nature. Products such as formate, pyruvate, and 4-hydroxy 2-ketovalerate have been reported to be metabolized by phenol biodegraders such as Pseudomonas putida (44). A lowering in the pH of the medium in which the microorganisms were grown was detected.

C. Processes Used in the Biological Treatment of Wastewaters

Among the processes used in the biological treatment of phenols and other toxic organics from wastewaters are:

1. The activated sludge system (suspended growth system).
2. The fixed growth system including trickling filter and rotating biological contactor systems.
3. The fluidized bed technology.

In the following section, I will review these systems and the innovations brought to them since their invention.

1. Activated Sludge System

In 1914, Ardern and Lockett (2) developed a process known as activated sludge. The process consists of growing a mass of microorganisms capable of aerobically decomposing waste materials found in wastewater streams. Schroeder (31) describes the process as consisting of an aeration tank in which aerobic microbes are mixed with wastewater. The cells are then physically separated in a sedimentation tank. The settled culture (sludge) is finally recycled to the main reactor tank. Ford and Tischler (74) refer to this process as a suspended-growth system and rate it as one of the most "popular high rate systems" used in the industry to treat toxic organics from wastewaters.

The activated-sludge process has been modified over the last six decades. Initially, it was designed as a nominal plug flow system. The organic load was later found not to be evened. Concentration gradients existed along the reactor

affecting the biological activity of the microorganisms (75). During the early 1950's, Busch and McKinney (76) worked on the completely mixed activated sludge process where the "incoming wastes are completely mixed throughout the entire aeration tank." According to Ford and colleagues (74), this process is highly flexible. It allows adjustments in waste load variations and provides a measure of organic-load equalization. When compared to the conventional activated sludge system (nominal plug flow system), the completely mixed process was found to be more efficient. Gould (77), in 1959, worked on an inexpensive way to improve the efficiency of the pre-1950's wastewater treatment plants. Those plants used activated sludge processes designed as nominal plug flow systems. Gould's idea was to split the influent waste stream and introduce it at different points along the aerated reactor. The results were satisfactory. He was able to approach the behavior of a continuous stirred tank reactor (CSTR).

In the late 1960's, more attention was given to the pure-oxygen activated sludge systems where oxygen, rather than air, was introduced into the aerated tank. The Union Carbide Unox process is currently the most commonly used pure-oxygen system. The process consists of a series of concurrent gas-liquid contacting stages in a sealed aeration tank. In each section, homogeneity is achieved by

mechanical mixing. As such, the entire system approaches complete mixing (78). The major advantage of the pure-oxygen activated sludge system over the conventionally air-aerated process is that the sludge settling rate is high. Humenick and Ball (79) attribute this larger and more advantageous settling to lower shearing rates between the cells and the fluid. Other advantages are given by Mulligan and Fox (28). Lower land requirements, the ability to supply oxygen at high rates, increased self-neutralization of highly alkaline wastes further contribute to the success of the process.

One other version of the activated sludge process is the contact stabilization system. The microorganisms are briefly contacted with the wastewater, "then separated and finally reaerated to degrade sorbed organics" (74). This modified activated sludge process has proved to be very efficient in the removal of suspended and colloidal organics from industrial wastes. Schroeder (31) in his book on water and wastewater treatment discusses another modification of the activated sludge process known as the extended aeration process. According to the author, the process consists of minimizing the cell washing rate from the system (i.e., increase the mean residence time of the cells in the bioreactor).

One final suspended growth process worth mentioning is the aerated lagoon. According to Schroeder (31), the

term "lagoon" is used to cover a wide variety of systems, the simplest of which is nothing more than a holding basin with air supplied to the bacteria. It is similar to the activated sludge process with no recycle stream (31). Ford and Tischler (74) remark that the aerated lagoon system can approach or equal the organic removal capability of an activated sludge process under suitable environmental factors in the plant location.

Many investigators worked on the development of models for design and operation of activated sludge. Ramanathan and Gaudy (80) derived a model in which the recycle cell concentration was chosen as the system design constant. The validity of this model was later investigated by Gaudy and Srinivasaraghaves (53). They found that it was suitable for the heterogeneous populations of the activated sludge process. They also observed that the classical model, derived by Herbert (81) for pure cultures, was not valid for an activated sludge system when the recycle cell concentration factor (the ratio of sludge concentration in the recycle to sludge concentration in the reactor) was selected as the system constant. McKinney (82) derived models for complete mixing in activated sludge systems. He tested the validity of his models by collecting data from three different plants where activated sludge processes were used to treat water. One of those plants uses the Unox process version of activated sludge.

In the mid 1970's, studies on the addition of activated carbon to an activated sludge system were made. Muller (83) found that the performance of an activated sludge process can be improved when powdered activated carbon is added to aeration tanks of suspended growth systems. Perrotti and Redman (84) have shown that addition of activated carbon to an activated sludge unit treating a glucose-phenol mixture improved organic matter removal performance. They performed their work on a laboratory scale activated sludge unit and partially attributed the high performance of the system to the ability of carbon to remove the phenol from the system, "thus reducing the inhibitory effect of high phenol concentrations on bacterial growth." Adams (85) reported a 25% increase in COD removal and 20% in BOD removal when powdered activated carbon was added to a full scale activated sludge plant treating a petrochemical waste. Ferguson (86) indicated that addition of powdered activated carbon to activated-sludge systems provides exceptional resistance to shock loading by trichlorophenol, presumably due to "the larger reservoir of carbon carried in the mixed liquor suspended sludge (MLSS)" (11). Giusti (87) describes a process known as the Aimpro Wet-Air Oxidation-Biophysical treatment process. It has been successful in treating cyanide, acrylonitrile and pesticide wastes. The first step consists of breaking down the large and cyclic

molecules by wet-air oxidation (this process has been described earlier). The smaller molecules obtained are now more amenable to the biological treatment system that follows. Activated carbon is added to the biological treatment part to adsorb those substances that have passed wet-air oxidation. In other words, the activated carbon serves as a "toxic sink" for those large molecules inert to wet-air oxidation. The final step of the process consists of reactivating the carbon and returning it to the aeration tank. Carbon makeup is added continuously.

2. Fixed Growth Systems

The two most important fixed-film biological processes are the trickling filter and the rotating biological contactors.

a. The Trickling Filter

The trickling filter (74, 10, 31, 2) entered into operation in 1893 in England. The current process utilizes a packed bed of rocks or some synthetic medium like plastic on which cell growth occurs. Wastewater is sprayed over the bed and allowed to contact the biological slime. Oxygen and organic matter diffuse into the slime film where consumption of organic components occurs. End products counterdiffuse back out of the film and appear in the

underdrain system. The effluent stream contains some spent cells along with the treated water.

Schroeder (31) observed that the organic uptake was expected to increase as the thickness of the biological film increases up to a certain value. Atkinson (88) found that the optimum biological film thickness for maximum organic uptake was in the range of 70 to 100 μm . Schroeder (31), Metcalf and Eddy (2) reported that the effect of the hydraulic shear on the slime became greater as the thickness of the biological film increased and thus a maximum thickness was associated with a given flow rate. They also observed that the increase in the biological layer prevented the organic material or oxygen from reaching the microorganisms near the supporting medium surface. As a result of having no external organic source available and no oxygen, the microorganisms near this interface entered into an endogeneous phase of growth and turned to anaerobic metabolism.

Due to the anaerobic conditions under which the slime close to the medium is subjected, gas (H_2S and possibly CH_4) and organic acids would be expected to be produced and could cause pieces of slime to slough off by pushing the slime away from the medium or by decreasing the local pH and killing the lower layer of cells. A more probable situation is starvation (endogeneous phase) of the lower levels

of cells as the slime becomes thicker. In this phase, the microorganisms lose their ability to cling to the supporting medium surface. The liquid then washes the slime off the medium and a new slime layer will start to grow. This phenomenon of losing the slime layer is called sloughing and is primarily a function of the organic and hydraulic loading of the filter.

Atkinson and co-workers (89, 90) developed a model that would describe the interaction between the biological film layer and the organic material being degraded. They assumed that the concentration of the organic material was independent of time. The model they obtained is:

$$D \frac{\partial^2 C}{\partial y^2} - R = 0$$

where D is the constant of diffusion and R is the reaction rate in the slime layer. R can be represented by a Monod type equation.

b. The Rotating Biological Contactor (RBC)

According to Mulligan and Fox (10), the rotating disk process operates as a fixed-film biological reactor. Large diameter plastic disks support the biological slime. The disks are mounted on a shaft and rotated slowly. The bottom one-fourth to one-third of the rotating disks is immersed in a basin containing the wastewater. Rotation brings the

biological film into contact with the wastewater for removal of organic matter. Rotation also provides a means of aeration by exposing the cells and the film of entrained wastewater to the air. During the process there is some air entrainment into the basin.

Ford and Tischler (74) state that the continuous shearing of the fixed biomass as the disks pass through the water prevents accumulation of inactive material. In that sense, the thickness of the biological film is being controlled. This on and off exposure of the slime makes the overall oxygen transfer throughout the biomass more efficient. The oxygen transfer rate coefficients are higher than those obtained on trickling filters (31).

Schroeder (31) remarks that conceptually RBC units are similar to trickling filters and that removal rate expressions for this process should be similar to those developed for trickling filters. Some of the advantages over suspended growth systems are lower energy requirements, low maintenance and stable operation.

3. Fluidized Beds

According to Squires (91) "fluidized bed" is a unit operation where a fluid is brought into contact with a granular solid. The fluid can be either liquid, gas, or a mixture of a gas and liquid. Kunii and Levenspiel (25) define fluidization as "the operation by which fine solids

are transformed into a fluid-like state through contact with a gas or liquid." The key advantage in using the fluidized bed technique in bioreactors is the enormous surface area provided by the particles, allowing greater specific reaction rates. Jeris and colleagues (9) report a surface area of sand of $3300 \text{ m}^2/\text{m}^3$ of reactor volume. Another advantage is the ease with which one can periodically remove some of the particles and add fresh ones. This partial replenishment of the fluidized bed helps in maintaining its high reactivity. The fluidized bed technique is an extremely high-rate process which combines the best features of activated sludge and trickling filtration (9).

In the literature, two types of fluidized beds have been investigated: the tapered fluidized bed and the constant cross-sectional fluidized bed. Scott and Hancher (92) described the tapered bed as an "inverted truncated cone." Both types had been used as bioreactors. Some of the features that differentiate a tapered bed from the more conventional one are: i) the gradual increase of the cross-section of the column allows the bed to accommodate a wide range of flow rates without loss of bed material. This is due to the fact that the velocity of the fluid decreases with increasing reactor height; ii) it was also found that at fluidization, the pressure drop across the bed decreases with increasing fluid velocity (92). In the case of the

constant cross-sectional column, the pressure drop maintains a constant value as the velocity increases. All of the models used for the conventional fluidized bed can be applied to an infinitesimal height of the tapered bed. Carbon beds and biological fluidized beds have been used in treating wastewater.

a. Carbon Beds

Carbon bed adsorption systems consist of columns loaded with granular activated carbon. Flow can either be down (fixed-bed operation) or up (expanded-bed operation). One has to inspect the breakthrough curve to choose between a single fixed bed and a countercurrent configuration. The breakthrough curve is that part of the curve between the appearance of traces of impurity in the effluent stream and the point where the column effluent concentration is the same as the influent. The breakpoint occurs when the concentration in the effluent stream exceeds the treatment objective. According to Rizzo and Shepherd (6), it is advisable to use fixed bed, nonstaged systems when the slope of the breakthrough curve is very steep. In other words, when short contact time columns are needed, fixed-bed, nonstaged systems are favored. Countercurrent systems are used when the slope of the breakthrough curve is gradual or the contact time needed is long. Fifteen minutes of contact between the water treated and the carbon is

considered short while sixty minutes is considered long. A loading rate of 2.5 gal/min/ft² of bed cross-section is considered typical of carbon adsorbers (10).

Various configurations of fluidized beds have been considered on an industrial scale for economical treatment of waste streams. The parallel configuration consists of a number of columns placed in parallel with each receiving the same feed. The effluents from each column are combined to form a composite product. Startup of units is staggered to ensure that each is at a different level of carbon exhaustion. When a column reaches equilibrium with the effluent stream, as evidenced by breakthrough of sorbate, the carbon in the column is replaced by virgin or regenerated carbon.

The lead column in a configuration where the beds are arranged in series, can be easily removed from operation as soon as its carbon is exhausted. The next column will become the lead column and the new one brought to replace the exhausted column will be placed at the end of the line. The effluent from the last column of a properly designed system will still be of high quality at the time the lead column becomes saturated (6, 10).

The pulsed-bed column (10) is similar in concept to columns in series. One single column is employed instead of multiple columns. The system is designed so that bottom

removal of spent carbon and top addition of fresh carbon is easy to achieve. Removal of small amounts of carbon in periodic pulses lead to a "high degree of saturation of the carbon with a minimum carbon inventory."

Two parameters must be specified for design of activated carbon adsorption systems. There are the equilibrium capacity of the carbon (isotherm) and the rate of adsorption of the sorbate. Allen and colleagues (93) fitted data obtained from a liquid-phase adsorption system to an empirical equation. They were able to use that equation to study a wide range of plant design and operation variables. Rizzo and Shepherd (6) have studied the economies of carbon-bed systems.

b. Biological Fluidized Beds

In this system, the wastewater passes upward through the column partially filled with particles. The result is an expanded bed. Like the trickling filter, biological mass grows on the medium surface. Attached cells help in the consumption of the waste as it passes. This system has been tested on a laboratory scale. Sand, coal, and activated carbon have been used as support media (10).

Jeris and colleagues (9) used sand as a medium in a constant cross-section fluidized bed. They successfully demonstrated that fluidized bed technology can be used for removal of carbonaceous BOD (biochemical oxygen demand) and

nitrogenous compounds from wastewater. Their work was performed with a moderate size pilot facility of 150 to 300 m³/d (40000 to 80000 gpd). With such a facility, they obtained 93% BOD removal in 16 min, 99% NH₃-N removal in 11 min, and 99% NO₃-N removal in less than 6.5 min. They also concluded that fluidized bed technology requires less than 5 percent of the reactor space required for conventional treatment and therefore this technique should be significantly less expensive than conventional treatment technology based on the savings in space and rapid time for treatment.

Ecolotrol, Inc. (94) used constant cross-sectional columns, filled with fine-grained media coated with bacteria to study the treatment of wastewaters by fluidized bed technology. The company reported 90% BOD, 99% NH₃-N and 99% NO₃-N removals for a reaction time of less than one hour. They also reported that the land area required when using this technology is reduced from conventional requirements by approximately 80 percent.

At Oak Ridge National Laboratory, Holladay and colleagues (95) studied the biodegradation of phenolic waste liquors in a continuous stirred-tank bioreactor (CSTBR), a three-phase (air, liquor, and coal particles coated with bacteria) packed bed bioreactor (PBBR), and a three-phase fluidized bed bioreactor (FBBR). The FBBR consisted of a

tapered column with coal particles used as supporting medium. The best performance was achieved by the FBBR. With this system they obtained the highest degradation rates and lowest retention times of the other bioreactors. Under a volumetric flow rate of 1330 ml/hr and a retention time of 2.17 hours, 99% conversion of 750 mg/l phenol feed was observed. The PBBR and the FBBR proved to be resistant to system perturbations. According to the same authors, the chief disadvantage of the FBBR was its inability to effectively convert any compound requiring long retention times. The CSTBR has proved to be more competitive for compounds requiring long retention times.

Rodman and Shunney (40) treated textile dye waste using activated carbon. When the carbon was exhausted, the bed was then inoculated with bacteria. The result was a partial regeneration of the carbon. The reactivated bed was ready to further remove dye from a wastewater stream. However, the authors did not mention anything about the role of the bacteria left in the bed once the regeneration process was over. The pilot plant used for their work consisted of a bed of activated carbon as medium and an aerobic biological culture reservoir used to feed the bed during the regeneration process.

Eckenfelder and colleagues (96) compared the performance of sterile, aerobic and anaerobic columns. They

found that for a biologically resistant waste, the breakthrough curves for the sterile and the aerobic columns were similar. For a less resistant waste, the performance of the aerobic column was superior. Anaerobic columns were found to be inferior to either the sterile or the aerobic columns. "This was attributed to rapid coverage of the carbon surface with anaerobic film." Friedman and colleagues (97) later confirmed that an aerobic column was more efficient in TOC (Total Organic Carbon) removal than a similar column operated anaerobically. In their work, 78% of TOC was removed in the aerobic column while the anaerobic one was able to achieve a 66% of TOC removal. Anaerobic columns are used for pretreatment of high strength industrial wastes including high-temperature wastes.

III. EXPERIMENTATION

A. Experimental Equipment

The equipment used in carrying out the fluidized bed experimental work is shown in Figure 4. Letters in parentheses in the following text refer to Figure 4.

1. The Tapered Column

The tapered column for the fluidized bed bioreactor was a donation from Oak Ridge National Laboratory (Dr. S. E. Shumate, III, ORNL, Oak Ridge, Tennessee). The column was constructed from Pyrex glass using a carbon mandrel. Its diameter increased from 2.5 cm at the bottom to 7.6 cm at the top. It was 107 cm long and had an angle of taper of 1.37° .

2. The Air-Liquid Contactor

The contactor consisted of an air sparger and a 5 cm diameter stainless steel cylindrical case tapered at both ends (refer to Fig. 4). The air sparger was made of a rubber pipet bulb (2 ml) pierced with holes. Air was supplied from the line air source, passed through glass fiber filters, then blown through the sparger into the central part of the case where it contacted the recycled liquid

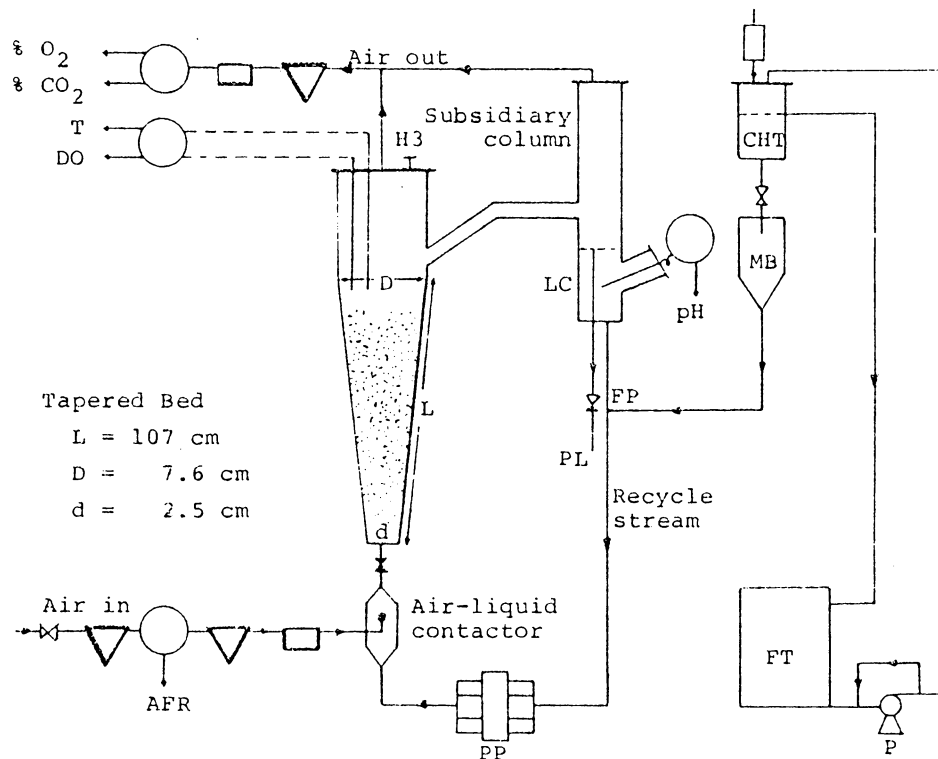
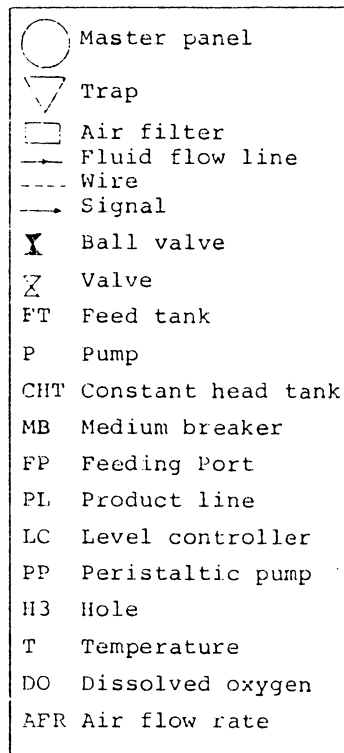


Figure 4. Schematic diagram of the equipment.

stream. A peristaltic pump with variable speed was used to recycle the liquid.

3. The Subsidiary Column

The subsidiary column consisted of a 5 cm diameter Pyrex glass tube with a side-arm made of the same material. A pH probe was introduced into the sidearm. The liquid level in this column was controlled by a 3/8" standtube (LC). The standtube was an extension of the product line introduced into the column (refer to Fig. 4).

4. The Recycle Loop

The recycle loop was that portion of the system that included the tapered-bioreactor-bed, the subsidiary column and all of the connections in between. Mixing in the tapered-bioreactor-bed was achieved by aeration and by continuous recycle of the fluid being treated.

5. The Feed Line

This line consisted of two feed tanks, and a medium breaker. The main feed tank had a volume of 200 liters. The artificial wastewater was prepared in that tank and then passed up to a second constant head tank of 1 liter volume. The bed was then fed by gravity. The medium

breaker was designed to keep the microorganism from back-contaminating the feed tanks.

6. Other Features

A thermocouple and a dissolved oxygen probe were introduced into the bed through the top head plate covering the tapered column. A third hole (H3) in the same plate was used to introduce the activated carbon particles into the bed. H3 was also used to add antifoam and base to control the pH of the medium. Air outlets from the tapered column and the subsidiary column were continuously sampled for CO₂ and O₂ analysis. All probes and sensors were connected to a master panel where values of the different variables were read. Further, the panel was interfaced to a PDP 11/40, where the values were logged as a function of time.

B. Materials

1. Organism

The bacterium used in this study was isolated in our laboratories. It was known as CP6A, a phenol biodegrader. It had been obtained from a wastewater stream in a Roanoke sewage treatment plant. Stock cultures were maintained on basal agar medium slants and stored at 4°C.

2. Chemicals

Liquefied phenol was purchased from Fischer Scientific Company, Fair Lawn, New Jersey. Dow-Corning antifoam A compound was obtained from Dow-Corning Corporation, Midland, Michigan. Yeast extract and casamino acid were purchased from Difco Laboratories, Detroit, Michigan and nutrient broth was obtained from Division Becton Dickinson and Company, Cockeysville, Maryland. Activated carbon (Nuchar WV-G, 12x40 mesh) was donated by Westvaco Chemical Division, Carbon Department, Covington, Virginia.

C. Methods

1. Mixing Characteristics of the Recycle Loop

The mixing state of the system under a recycle flow rate of 2.7 l/min and an air flow rate of 5.7 l/min was determined in two pulse response experiments.

a. Response to a Pulse Input at H3

The loop was filled with 5.8 liters of distilled water. The recycle pump and the air line were turned on. Liquefied phenol was used as a tracer. A few drops of that chemical were introduced into the bed from port H3. Samples were intermittently withdrawn through the product

line,* then analyzed with a Varian Techtron model 635 UV-VIS Spectrophotometer. Their optical densities were measured at 270 nm.

b. Response to a Pulse Input at FP (the feed port)

The tracer was injected into the bed through port FP. The procedure followed was similar to that presented in part a (Methods, subsection 1).

2. Residence Time Distribution (RTD)

The RTD curve was determined to further characterize the loop-reactor. The loop was filled with 5.8 liters distilled water. The main feed tank was filled with 10 gallons of distilled water. Liquefied phenol was added to the tank. The continuous process was started by turning on the recycle pumps, the air flow, the feed pump, the feed and the product lines. The feed flow rate was adjusted to 1.36 l/hr. Samples were taken from the effluent stream and analyzed in the same way as in a and b of the previous section.

3. Growth Curve for CP6A on Nutrient Broth

Eight grams of nutrient broth for 1 liter of water were autoclaved for 20 minutes at 135°C. Phenol was then

*The level controller, LC (refer to Fig. 4) was taken out of the system during this study.

added to bring its concentration in the medium to 100 mg/l. The purpose of adding phenol was to acclimate the micro-organism to the biodegradation of phenol. Incubation was carried out in 250 ml Erlenmeyer flasks in a Psychrotherm Incubator Shaker (New Brunswick Scientific Company) at 28°C and 250 rpm. Klett reading of the medium turbidity was taken intermittently using a Klett-Summerson Photoelectric Colorimeter (Klett Mfg. Co.). The time needed for the cell growth rate to reach the logarithmic (log) phase was then determined.

4. Activated Carbon

Activated carbon particles from a 12 x 40 mesh stock were sieved through a 20 mesh sieve and collected on a 30 mesh sieve. The resulting 20 x 30 mesh size particles were washed three times in distilled water to remove carbon fines. They were then dried at 125°C and finally steam autoclaved for 30 minutes at 135°C. The purpose of sterilizing the carbon before its use was to minimize the presence of contaminants in the bioreactor.

5. Medium

The medium used during the biodegradation study was that of Drew and Pal (45). The composition was as follows: Na_2HPO_4 (0.2 g/l), NH_4Cl (0.12 g/l), $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

(0.001 g/l), FeSO_4 (0.0033 g/l), $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.01 g/l), $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (0.003 g/l), tap water (200 m/l), Casamino acid (0.01 g/l), yeast extract (0.06 g/l). The final pH was 7.3.

6. Inoculum

CP6A was grown aseptically on a solution of nutrient broth (8 g/l) containing 100 ppm of phenol for 12 hours, the time needed for the cell growth rate to reach the log phase as determined in subsection 3 of "Methods" section. The cells were collected by centrifugation of the turbid solution and decantation of the supernatant. Sterile water was then used to resuspend the cells and, as such, the cells were ready to be injected into the bed.

7. Phenol Biodegradation by CP6A in the Absence of the Active Carbon

The purpose of this first run was to test the equipment built for this work. The loops were filled with 5.8 l of sterile medium (Methods, subsection 5). The initial phenol concentration of the medium was 23 mg/l. The inoculum (Methods, subsection 6) was then injected into the loop through port H3. The air flow rate and the recycle flow rate were respectively set at 2.7 l/min and 5.7 l/min. The temperature range under which this experiment was performed

was 27-31°C. Samples were intermittently withdrawn through the product line and assayed for phenol concentration in the medium. During this experiment, the instrument panel was interfaced to a PDP 11/40 where values of variables such as temperature, pH, air flow rate, dissolved oxygen, % CO₂ in the gas phase and % O₂ in the gas phase were logged as a function of time and then displayed as a computer output.

8. Bioregeneration of Activated Carbon Study

The procedure used in this study consisted of four phases. Some steps in the procedure were executed aseptically to minimize contaminant survival in the medium and to insure the CP6A culture a good environment for its growth.

a. Phase I: Loading of Activated Carbon Batchwise

The loop was filled with 5.8% of sterile medium (Methods, subsection 5) containing phenol. The initial concentration of phenol in the medium during each of the four runs performed in this work is shown in Table I. The high starting phenol concentration would help in minimizing the presence of contaminants in the medium (phenol is toxic to most microorganisms). Fifty-five grams of 20 x 30 mesh activated carbon (Methods, subsection 4) were added

Table I
Starting Phenol Concentration for Each of
The Four Runs

Run No.	Initial phenol concentration, mg/l
1	22
2	1334
3	965
4	1230

to the phenolic medium in the column during runs 2, 3, and 4. The recycle flow rate and the air flow rate were respectively set at 2.7 l/min and 5.7 l/min. The temperature range under which the three runs were performed was 27-31°C. Under these conditions, the activated carbon bed expanded from an initial volume of 74 cm³ to a final one of 680 cm³. Samples were intermittently withdrawn from the bed through the product line. When the concentration of phenol in the medium approached the equilibrium concentration C_e predicted by the Freundlich isotherm (Appendix C), the adsorbent was then considered exhausted. The activated carbon was loaded and Phase I was over.

b. Phase II: Growth Phase, Biodegradation of Phenol Batchwise

The inoculum (Methods, subsection 6), was injected into the bed. Samples were intermittently withdrawn from the bed through the product line. Due to technical problems, the data on CO₂ evolution was impossible to obtain in Runs 2 and 4 (Run 3 failed). In Run 2, the pH change with time was determined. However, in Run 4, the pH was held in the range 6.9 to 7.1. Phase II was considered over when the concentration of phenol in the medium reached approximately 5 ppm.

c. Phase III: Continuous Process

Now that a biomass buildup was achieved (Phase II) little concern about contaminants was given. The main feed tank was filled with 50 liters of nonsterile medium (Methods, subsection 5) containing 20 mg/l of phenol. The feed and the product lines were turned on. The feed flow rate was adjusted to 1.16 l/hr. The residence time was calculated to be approximately $5.8/1.16 \approx 5$ hours. The first sample to be analyzed was taken 5 hours after the start of the continuous process, so that any phenol degradation detected in the effluent stream would be mostly attributed to bacterial action and not to dilution. Due to technical problems, the continuous process failed in Runs 2 and 3.

d. Phase IV: Desorption Study

Samples of activated carbon were withdrawn from the bed at the end of the experiment. Each of these samples was transferred to a 250 ml Erlenmeyer flask filled with 50 ml of phenol-distilled water solution. The concentration of phenol in the solution was equal to the equilibrium C_e reached during Phase I for that particular run. The flasks were then shaken at 28°C and 250 rpm in a Psychrotherm Incubator Shaker (New Brunswick Scientific Company). The concentration of phenol in the solution was determined after three hours incubation. The solution was then

decanted. The flasks with the activated carbon samples were dried in a 100°C oven for 2 hours. The dry sample was then weighed.

9. Preparation of the Sample Prior to GC Analysis

Samples of 3 ml each were collected in test tubes, then transferred to 5 ml plastic syringes. The sample was then filtered through a 0.22 μ m millipore filter (Millipore Corporation) to prevent any powdered activated carbon or any microorganism from entering the gas chromatograph. The technique also prevented the microorganism from reacting with the phenol in the sample. The cell-free, carbon-free sample was then placed in an ice bath to minimize any enzymatic reaction. Prior to its injection into the gas chromatograph, the sample was taken from the ice bath and warmed in a room temperature bath.

10. Gas Chromatography

Phenol was assayed by flame ionization gas chromatography. A Perkin Elmer model 3920 gas chromatograph was used. The carrier gas was helium at 20 psig pressure at the tank's regulator and a flow rate of 2.0 (32 ml/min) as registered in the chromatograph's rotameter. The flame ionization detector, the column and the injection port temperature were respectively set at 185°C, 144°C, and 200°C.

IV. RESULTS AND DISCUSSION

This section is mainly concerned with presentation and discussion of the results of the experimental procedures outlined in the previous section. Performance of the air-liquid contactor of the experimental equipment (Fig. 4) will also be reported.

A. Performance of the Air-Liquid Contactor

The air-liquid contactor generated air bubbles of 1/16" to 1/4" diameter under a recycle flow rate of 2.7 ℓ /min and an air flow rate of 5.7 ℓ /min (STP). No slugging was seen, i.e., no air bubbles of diameter greater than half the column diameter were observed. The value of the volumetric coefficient, $k_L a$, under the above conditions was not determined in the study. Such data would have helped in the evaluation of the aeration system.

B. Mixing Study

Mixing studies were undertaken to determine the fluid dynamic characteristics of the fluidized bed reactor. The study involved addition of a tracer (phenol) and determination of mixing parameters as described in Section III (Methods, subsection 1).

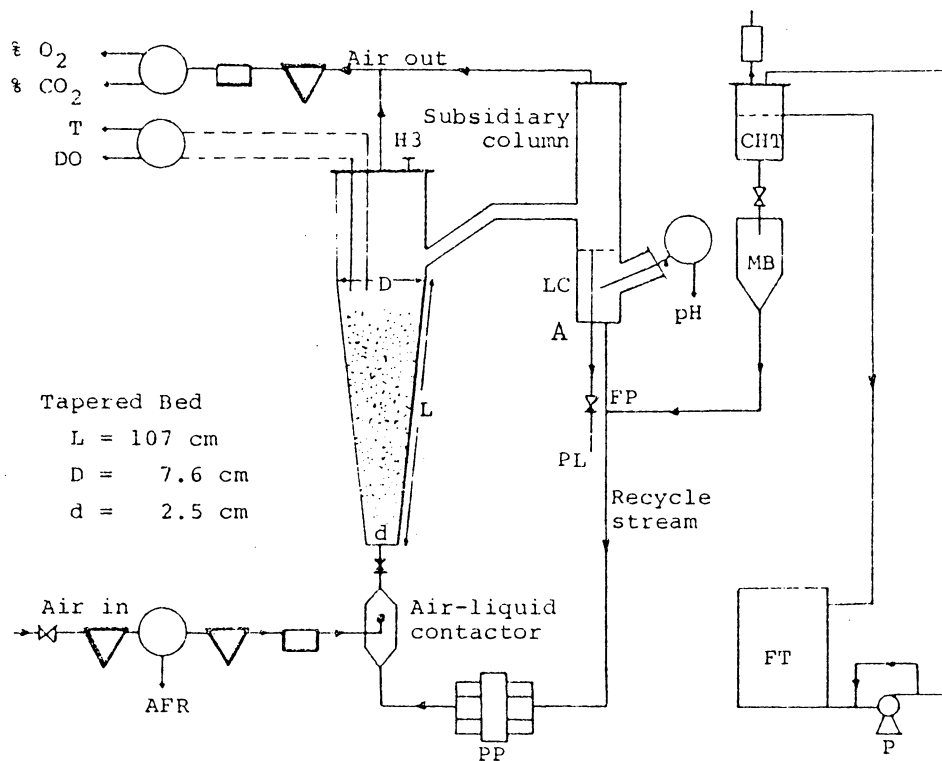
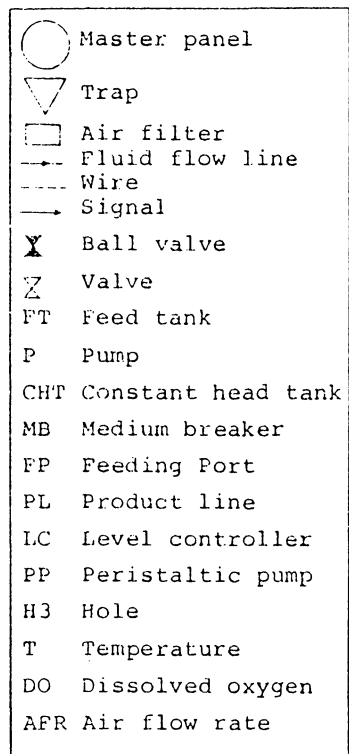


Figure 4. Schematic diagram of the equipment.

The time needed for the tracer to homogeneously disperse throughout the reactor loop was 255 seconds. This result is obtained from the two response curves shown in Figure 5 (point C). Curve 1 (Δ) is the response curve to a pulse input at port H3 (top headplate of the tapered column) while curve 2 ($\circ$) is the response curve to a pulse input at FP (feeding port to the loop, refer to Fig. 4). The steep slope (segment ab) of curve 1 suggests that plug flow is occurring between port H3 and port A (sampling port at the product line, refer to Fig. 4).^{*} This type of flow means that practically no mixing occurs in that portion of the reactor loop. The smooth slope of curve 2, however, suggests a well mixed region between FP and H3. The tracer study, so far performed, leads to the conclusion that the reactor loop behaves as a hybrid of stirred tank reactor and plug flow reactor when operating under a recycle flow rate of 2.7 l/min and an air flow rate of 5.7 l/min.

C. Residence Time Distribution (RTD) Study

This study was undertaken to determine the residence time distribution (RTD) of the elements of fluid in the

^{*} The level controller (LC) was taken out of the system during the study.

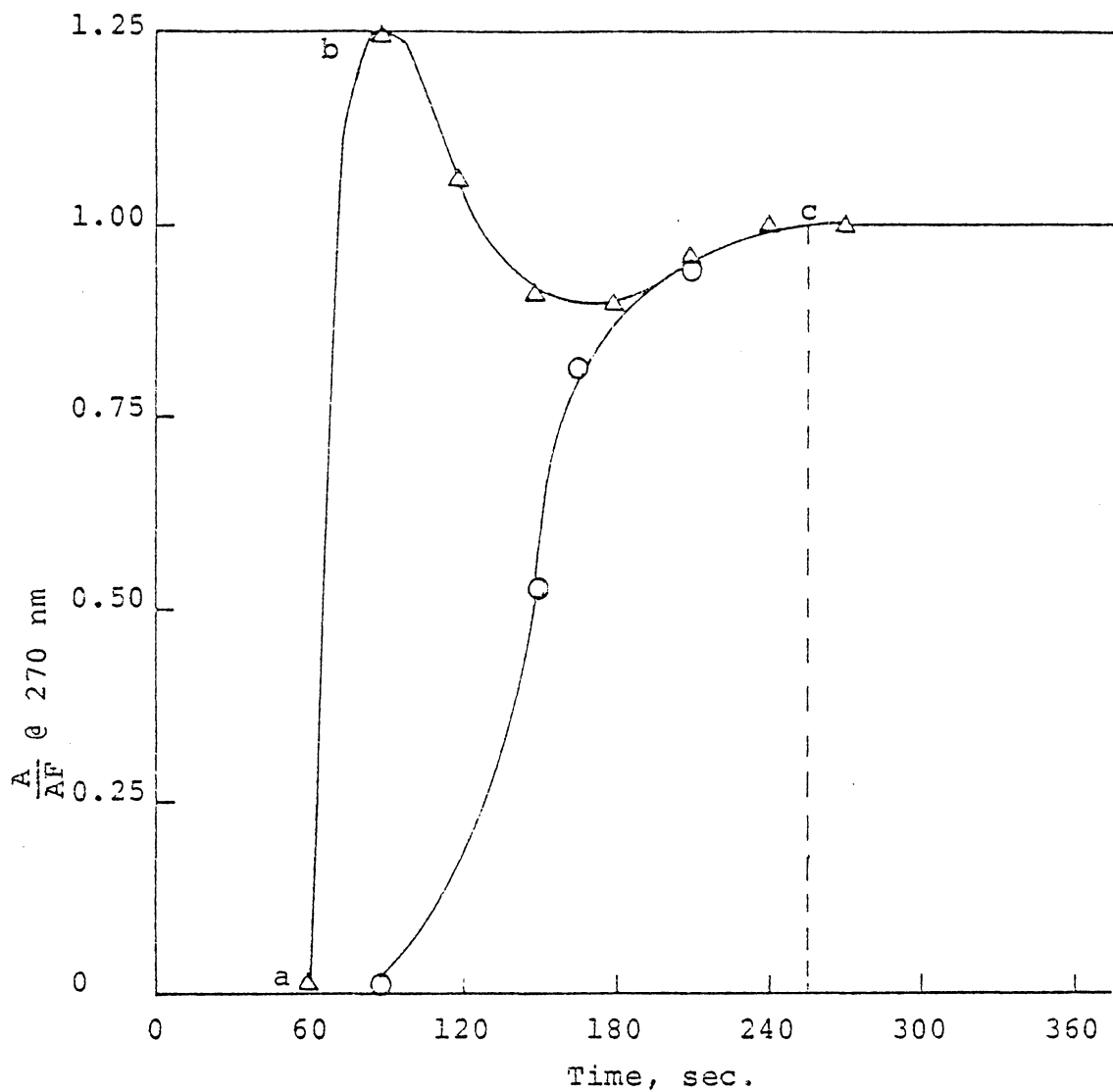


Figure 5. Response curves for "loop reactor" when used in the batch mode: ($\circ$) to a pulse input at the feed entrance (FP), (Δ) to a pulse input at port H3.

reactor. RTD curves provide all the information necessary to calculate a correct conversion for first order kinetics. Since no successful continuous process was achieved during this work, it was impossible to make use of these results for conversion study. However, the data obtained are helpful in further characterizing the fluidized bed when operating at a recycle flow rate of 2.7 l/min, an air flow rate of 5.7 l/min and a feed flow rate of 1.36 l/hr. The tracer used was phenol.

Figure 6 is a plot of $J(t)$ (the fraction of the total molecules that have the residence time range t) versus t . From this plot, t_m , the mean residence time was calculated to be equal to 4.26 hours (t_m is represented by the shaded area of Fig. 6). The value of t_m obtained from the ratio v/Q (the reaction volume over the volumetric feed flow rate) was also 4.26 hours.

Figure 7 shows a plot of $J(t)$ vs t/t_m . The response data obtained here, were interpreted by use of the dispersion model,

$$\left(\frac{A}{A_F}\right)_{\text{step}} = \left(\frac{C}{C_F}\right)_{\text{step}} = 1/2 \left[1 - \operatorname{erf}\left(1/2 \sqrt{\frac{UL}{D_L}} \left(1 - \frac{t/t_m}{\sqrt{t/t_m}}\right)\right) \right]$$

where A/A_F = absorbance in the product stream at time t
over the absorbance in the feed stream.

D_L = effective diffusivity

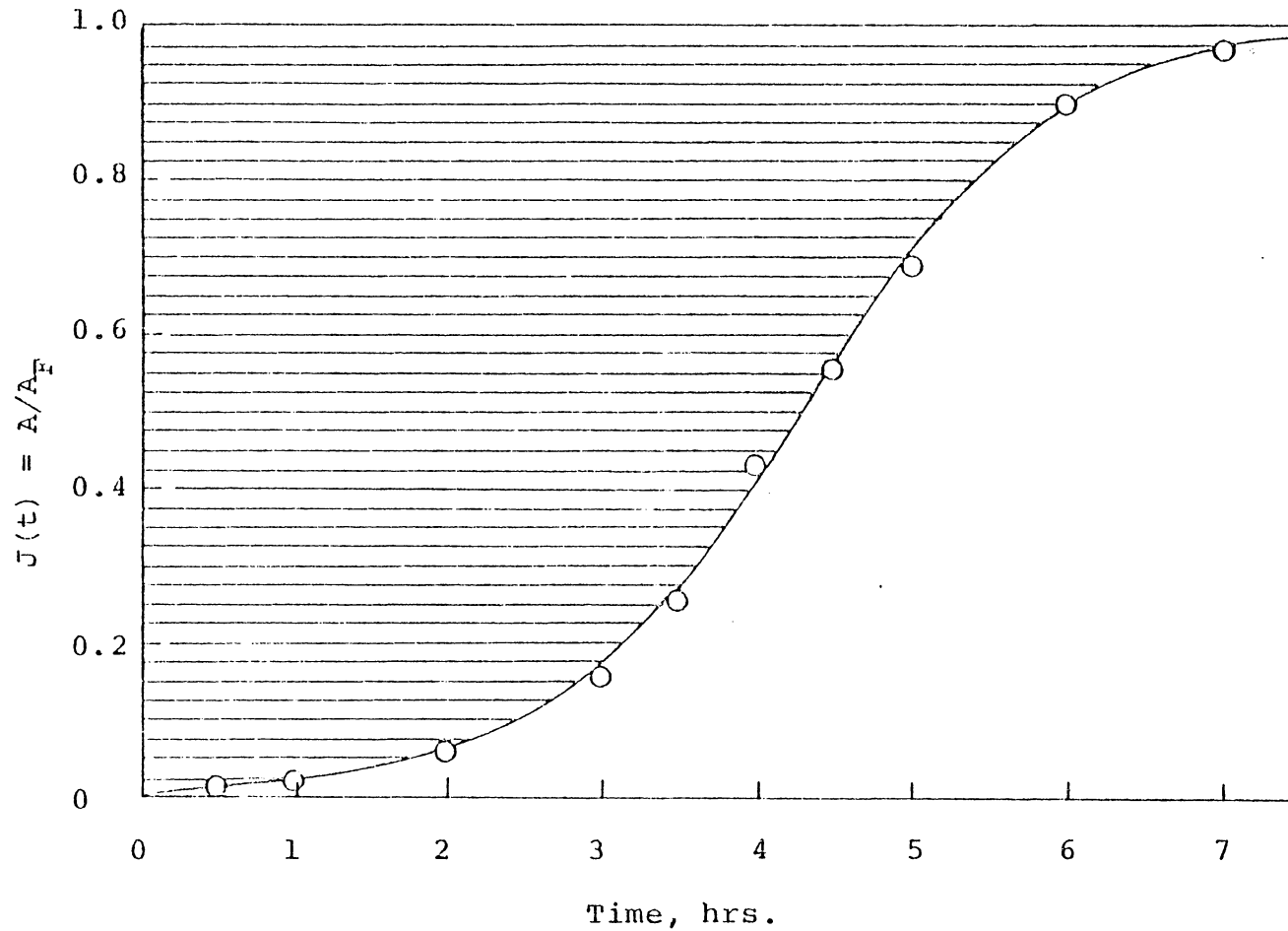


Figure 6. Response of the bioreactor effluent to a step input in the feed stream (continuous flow mode). The shaded area represents the mean residence time t_m (8).

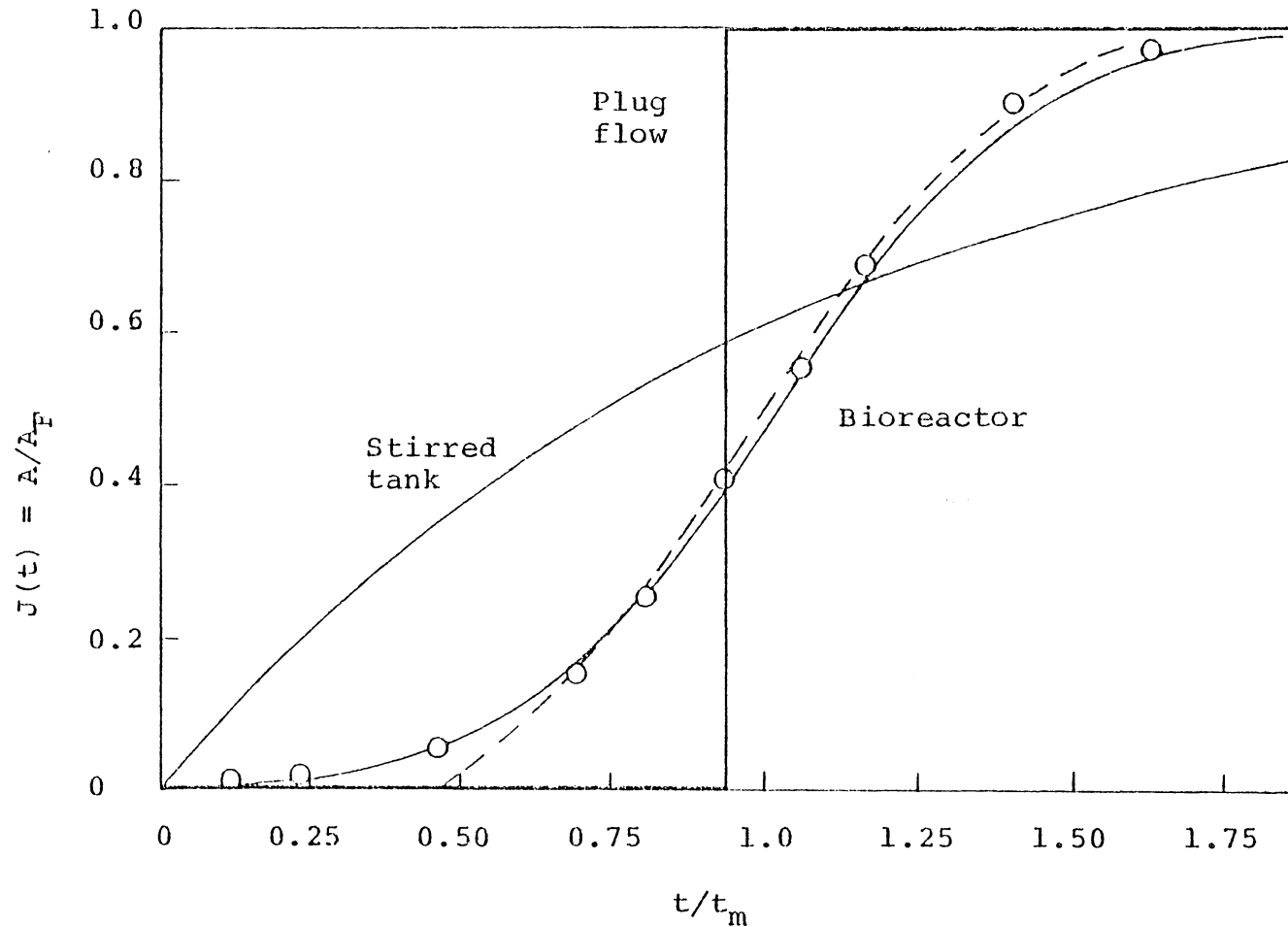


Figure 7. Fit of the dispersion model to RTD data. For a stirred tank $D/uL = \infty$, for a plug flow $D/uL = 0$, for the bioreactor $D/uL = .04$. The dashed line is the best fit of the dispersion model to the data.

U = axial velocity

L = effective length of reactor

t = time

$$t_m = \text{mean residence time} = v/Q = \frac{\int_0^1 \theta dJ(\theta)}{\int_0^1 dJ(\theta)}$$

$\frac{UL}{D_L}$ = inverse of the Peclet number

The value of the Peclet number $\frac{D_L}{UL}$ was found to be 0.04. Levenspiel's (100) correlation for a turbulent fluid flowing in a pipe shows that a value of 0.2 - 0.3 is what one would expect for the Peclet number, $\frac{D}{Ud}$ (d is diameter of the pipe or the reactor in Levenspiel's correlation). If we assume that the ratio of the reactor diameter to its length, d/L , is 1/50, then for the turbulent flow in a pipe, the range that one would expect for the Peclet number D/UL is 0.004 to 0.006. The value of 0.04 obtained during the study implies that under the operating conditions, the mixing state in the reactor loop was approximately 10 times more than in a turbulent regime plug flow reactor of similar dimensions. This value also confirms the hybrid behavior reported during the mixing study of the reactor loop when operating under the same conditions.

D. Growth Curve for CP6A on Nutrient Broth Containing 100 mg/l of phenol

This experiment was undertaken to determine the time needed for CP6A to reach the log phase in a nutrient broth

medium containing 100 mg/l of phenol. Once the log phase was reached, the inoculum was prepared as described in Section III (Methods, subsection 6), to be later transferred to the fluidized bed for the purpose of phenol biodegradation. The growth curve is shown in Figure 8.

At the incubation temperature of 28°C and an initial pH of 7.2, the doubling time (t_2) was found to be 1.67 hours, the maximum specific growth rate ($\mu_{\max}$) was, therefore, estimated to be 0.4 hr^{-1} . The log phase started after 10 hours of incubation and lasted for about 3 hours. The inoculum was transferred from the shaker flask to the bed 12 hours after the start of incubation.

E. Phenol Biodegradation by CP6A in the Absence of Active Carbon--A Fermentation Process

This experiment was undertaken to test the equipment built and sketched in Figure 4. The medium breaker in the feed line was not installed during this first run. Its absence from the system led to the failure of the continuous process due to back contamination. The starting phenol concentration in the main feed tank was 10 mg/l. Ten hours later, the concentration of phenol in the same tank was undetectable by GC analysis (less than 1 mg/l). The heat and the smell observed when the head plate covering the feed tank was removed, suggested that bacteria were growing

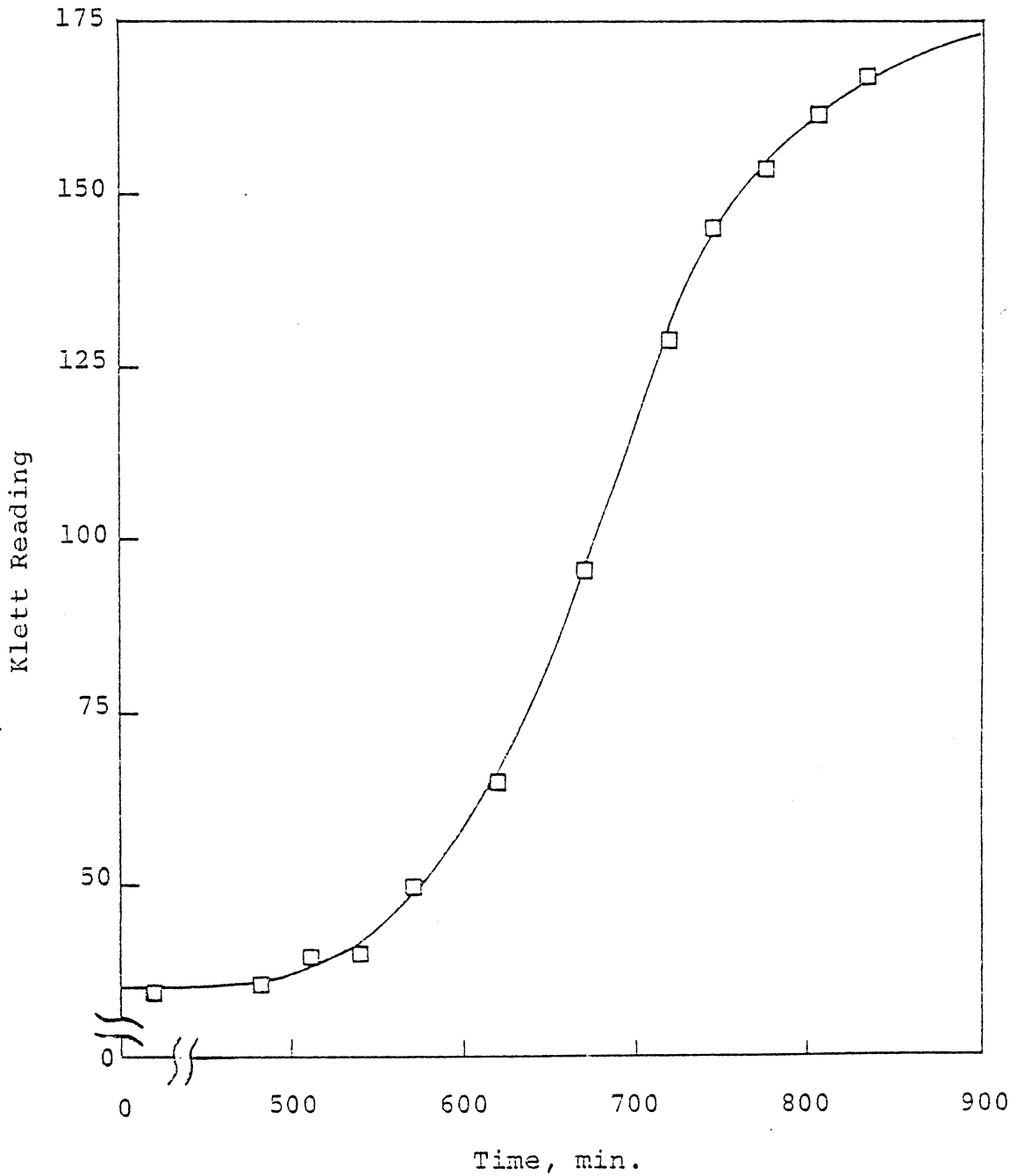


Figure 8. Growth of CP6A on a nutrient broth solution containing 100 mg/l of phenol.

on the nutrients available in that vessel. At the small feed flow rate (1.46 l/hr in a 1/2" tube) it was possible for the microorganism to travel upstream from the loop reactor to the constant head tank, and from there to the main feed tank. The addition of the medium breaker eliminated this problem. The partial success of the continuous process of Run 4 (Results and Discussion, subsection 5) was attributed to this change in the design of the feed line.

The batch process was running smoothly as shown by the results printed on the computer output (Appendix A). The plots of the six variables (air flow rate, % O₂ evolved, % CO₂ evolved, dissolved oxygen, pH, temperature) monitored during this fermentation were presented in Appendix B. The average volumetric air flow rate was 5.7 l/min at STP (Fig. A1). The % O₂ evolved during the first five hours was stabilized at 21% (Fig. A2). The sporadic behavior shown during the late hours was attributed to a wiring problem in the control panel. The pH drop (Fig. A3) observed two hours after the start of the batch process was expected. Ralston and Vela (44) found that most of the products of phenol metabolism were acidic in nature. Products such as formate, pyruvate and 4-hydroxy-2-ketovalerate had been reported to be metabolized by phenol biodegraders such as Pseudomonas putida (67). Drew and Pal (45) reported a lowering in pH when RS17 (a

yeast) was grown on a phenolic medium.

The data on dissolved oxygen (Fig. A4) show rapid drops in the oxygen content of the medium. This was the result of turning off the air flow for periods of one minute. The drop (an average of 20% per minute) was related to the rate of oxygen uptake by the bacteria. The higher the rate (the change in the dissolved oxygen content with time) the greater the cell mass concentration in the medium and/or net metabolic activity. Although the cell mass concentration for this drop in dissolved oxygen was not measured, the turbidity of the medium observed indicated that a healthy aerobic culture was behind the relatively high oxygen uptake. (The initial concentration of phenol in the medium was only 23 mg/l; based on this, one would not expect a very high cell mass concentration.)

The percent in CO_2 evolved during the run (Fig. A5) raised from 0.05% to 0.13% and then dropped to 0.12% at the end (the ambient level of CO_2 was 0.03%). The increase was an indication of bacterial activity. The decrease was attributed to the fact that the culture was entering the stationary growth phase. Because the cell mass concentration was not determined, it was impossible to perform a complete mass balance on the system using the CO_2 data.

The variation in temperature, attributed to the environment and to the bacterial activity, during the eight-hour period (Fig. A6) could be represented by a

sinusoidal function. The average temperature was 30°C. From the plot, it was impossible to determine the temperature change due to bacterial growth only (a biological oxidation reaction is always accompanied with heat evolution; in a sense, it is an exothermic reaction). The temperature rise related to bacterial activity could be determined only if the temperature rises in the environment during the period of the experiment were known.

The results on the phenol biodegradation by CP6A during the first run (batchwise) were simultaneously shown with the variations in % CO₂ evolved (Fig. 9) and with the variations in pH (Fig. 10). The data as presented reveal that during the first two hours, the rate of phenol disappearance (Table II), as well as the rate of pH change and the rate of % CO₂ evolved, were low. This observation was attributed to a small bacterial activity. The cells did not begin metabolizing nutrients immediately on contact but needed time to adjust to the new environment. This lag in bacterial activity is still not understood. Schroeder (31) mentions that the initial slow bacterial activity is probably due to the fact that a number of enzyme systems needed for biodegradation of the chemicals making the new medium must first be synthesized.

The plots on both Figures 9 and 10 also suggest that the maximum rates in CO₂ evolution, pH change, and phenol

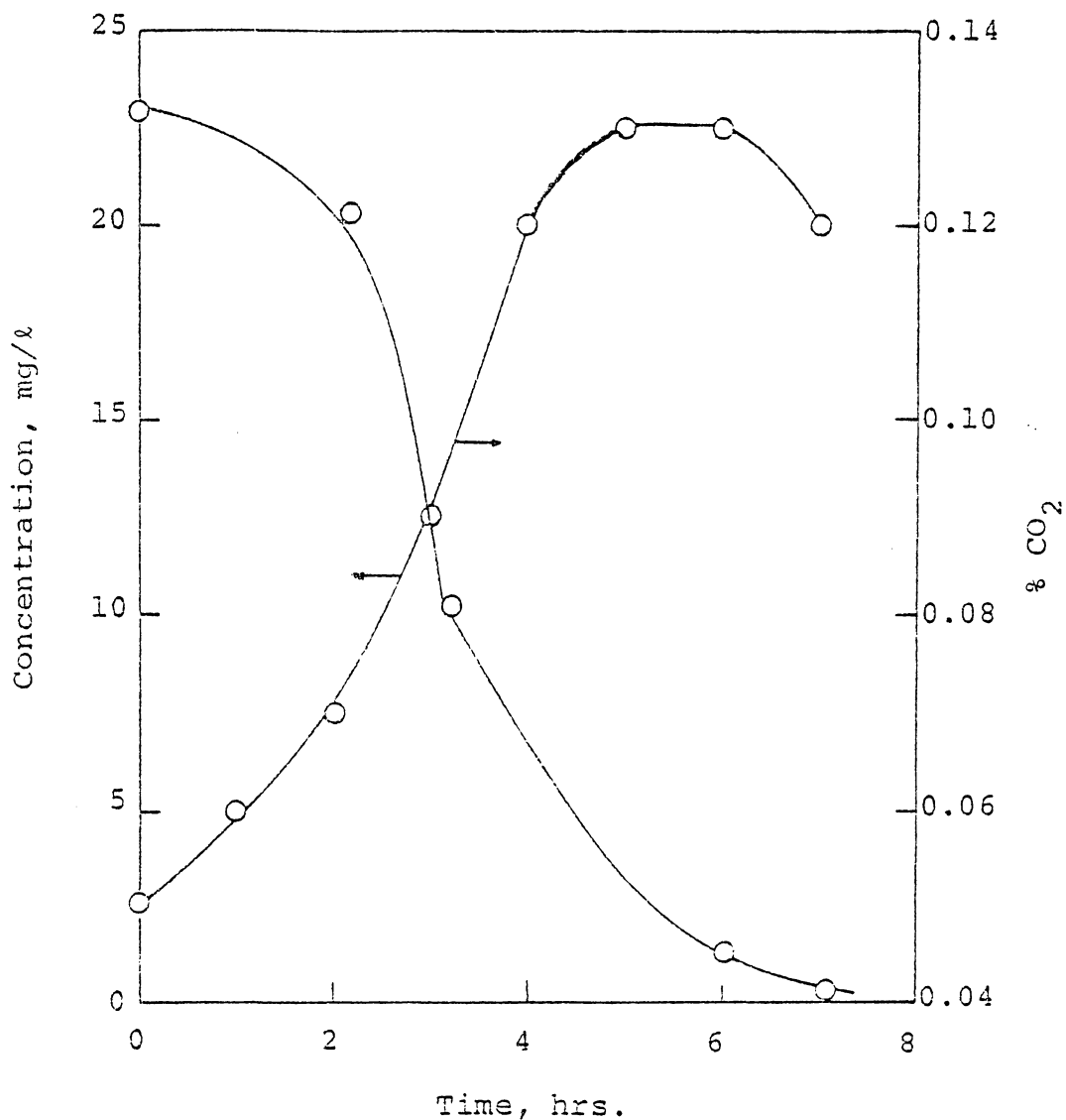


Figure 9. Variation with time of both the phenol concentration and the percentage of CO₂ evolved during Run 1 (phenol biodegradation in the absence of active carbon).

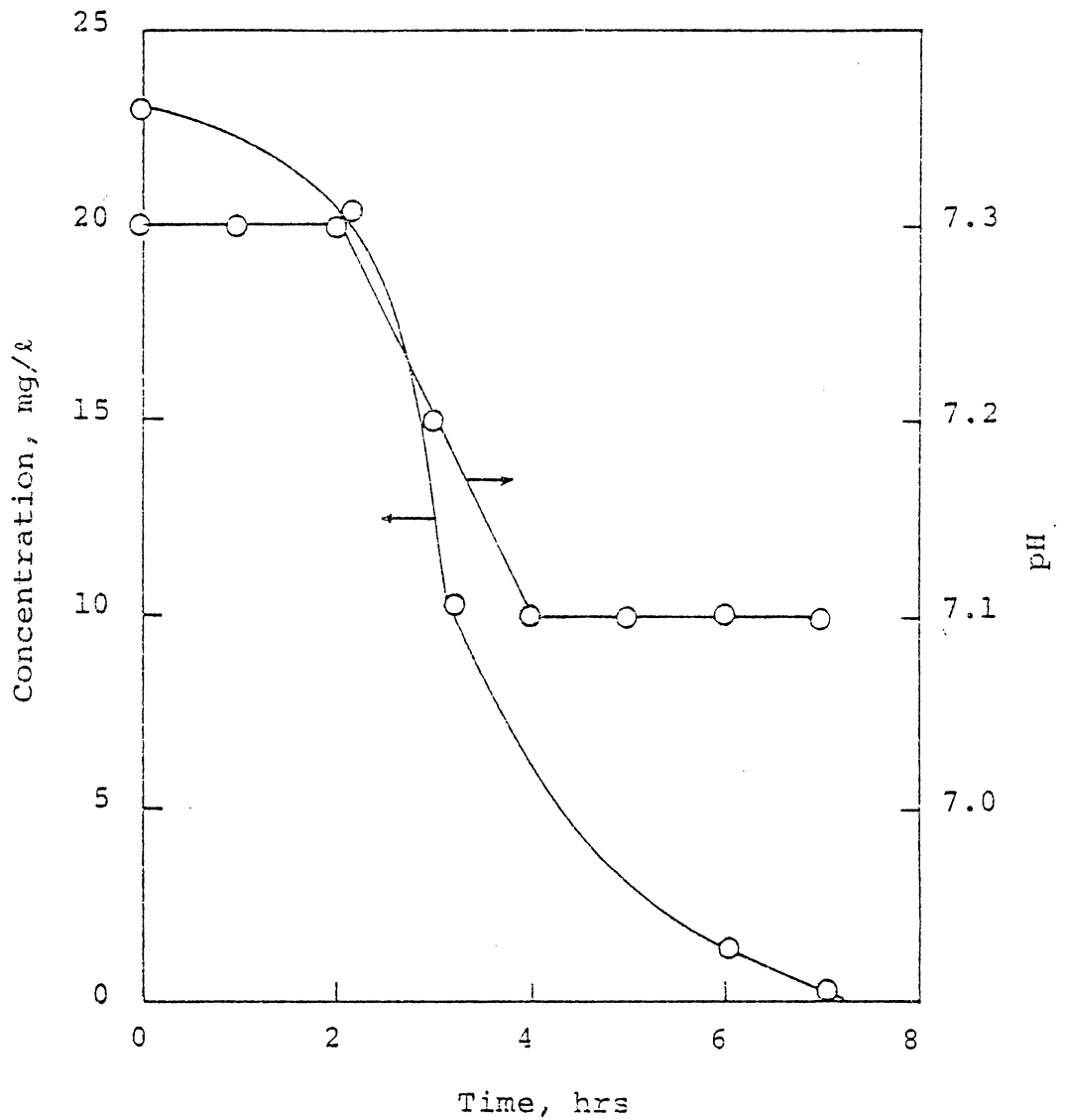


Figure 10. Variation with time of both the phenol concentration and the pH during Run 1 (phenol biodegradation in the absence of active carbon).

Table II
Rate of Phenol Biodegradation (Batchwise)
in the Absence of Active Carbon for:

Run 1

Rate, $\Delta C/\Delta t$ mg/l/hr	$\bar{C} = (C_1 + C_2)/2$ mg/l
1	21.5
12	15.0
3.5	6.0
< 1	< 1.0

Note: These rates were obtained using the data plotted on Figure 9.

degradation occurred at about 2.7 hours after inoculation of the medium. This led to the conclusion that the bacteria was undergoing a logarithmic growth in its population. The rate of phenol biodegradation at that particular time was 12 ± 2 mg/l/hr at a concentration of 15 mg/l (Table II).

During the last hour (hour 6 to hour 7 in Fig. 9), the % CO₂ evolved went down from 0.13 to 0.12, suggesting a decrease in the rate of culture metabolism. The concentration of phenol in the medium was dropping to less than 1 mg/l (Table B4, Appendix B) (The GC used can detect concentrations down to 1 mg/l). This implied that the phenol in the medium was a limiting nutrient. Its complete metabolism would stop growth. However, nothing could be inferred on the limiting role of the other nutrients in the medium.

F. Bioregeneration of Activated Carbon Study

Bioregeneration of activated carbon studies were performed to determine the extent to which an activated carbon bed could possibly be regenerated. These studies involved the four phases described in Section III, subsection 7.

1. Phase I: Loading of the Activated Carbon Bed in the Batch Mode

The adsorption kinetics for runs 2, 3, 4 of phenol on 20 x 30 mesh activated carbon were shown in Figure 11.

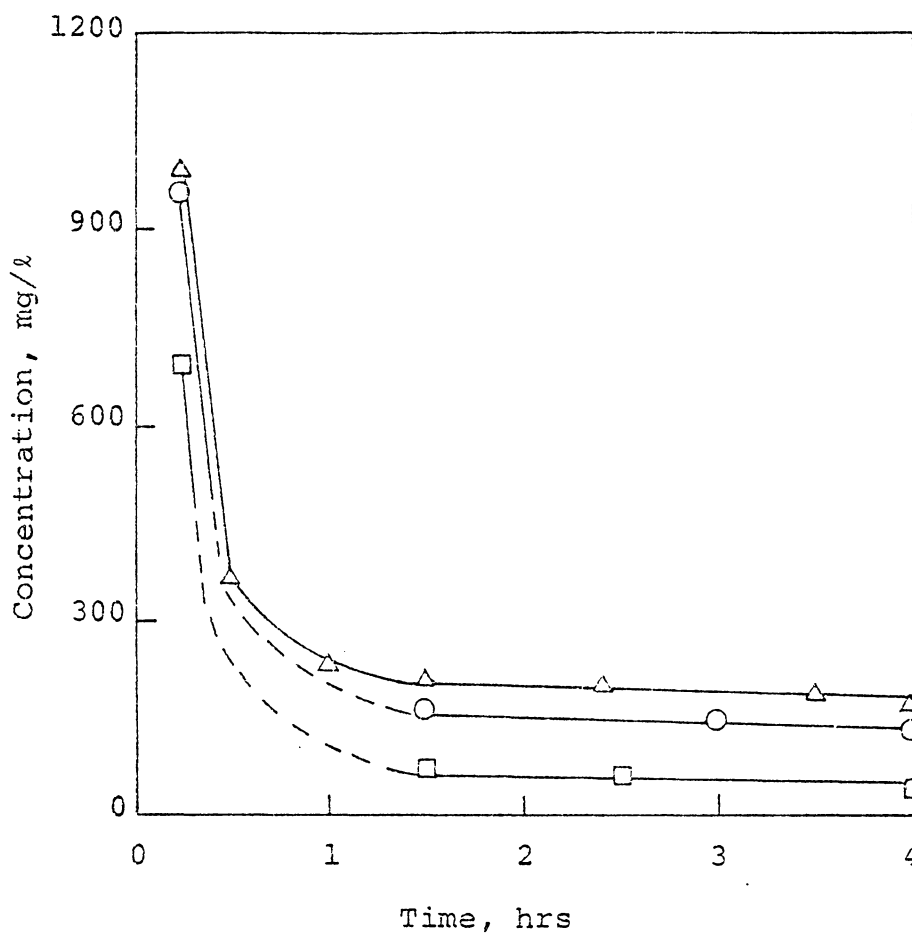


Figure 11. Adsorption of phenol on 20 x 30 mesh activated carbon (Phase I) for:
(Δ) Run 2, ($\square$) Run 3, ($\circ$) Run 4.

The average rate of phenol adsorption after four hours, for all three runs, was 0.6 mg/l/hr as reported in Table III. This rate was small enough to assume that the adsorption process for this carbon size was over, that the carbon was almost at equilibrium with the medium. This assumption was based on the results reported by Fichte (Appendix C). He studied the adsorption kinetics of phenol on 20 x 30 mesh activated carbon at 28°C. Interpretation of his data (Appendix C) showed that the capacity of the carbon reached 95% of the equilibrium capacity in four hours. An increase of only 3% in adsorption by the carbon was observed during the next fourteen hours.

2. Phase II: The Biodegradation of Phenol Batchwise

The results on the biodegradation of phenol in the batch process for runs 2 and 4 are plotted in Figure 12. The data as shown reveal that during the first hour, for both runs, the rate of phenol disappearance was low (also refer to Table IV). This was attributed to a low bacterial activity. As mentioned earlier (Results and Discussion section, subsection 4), a number of enzyme systems had to be synthesized before the bacteria would start its phenol metabolism.

During the subsequent hours, the rate of phenol biodegradation was at its maximum (an average value of

Table III

Average Rate of Phenol Adsorption on 20 x 30 Mesh Activated
Carbon During Phase I, for Runs 2, 3, 4

Rate, $\Delta C/\Delta t$ mg/l/hr	Time (hrs)
3000	0.1
3000	0.16
3000	0.2
10	2.0
8	3.0
0.4 - 0.8	4.0

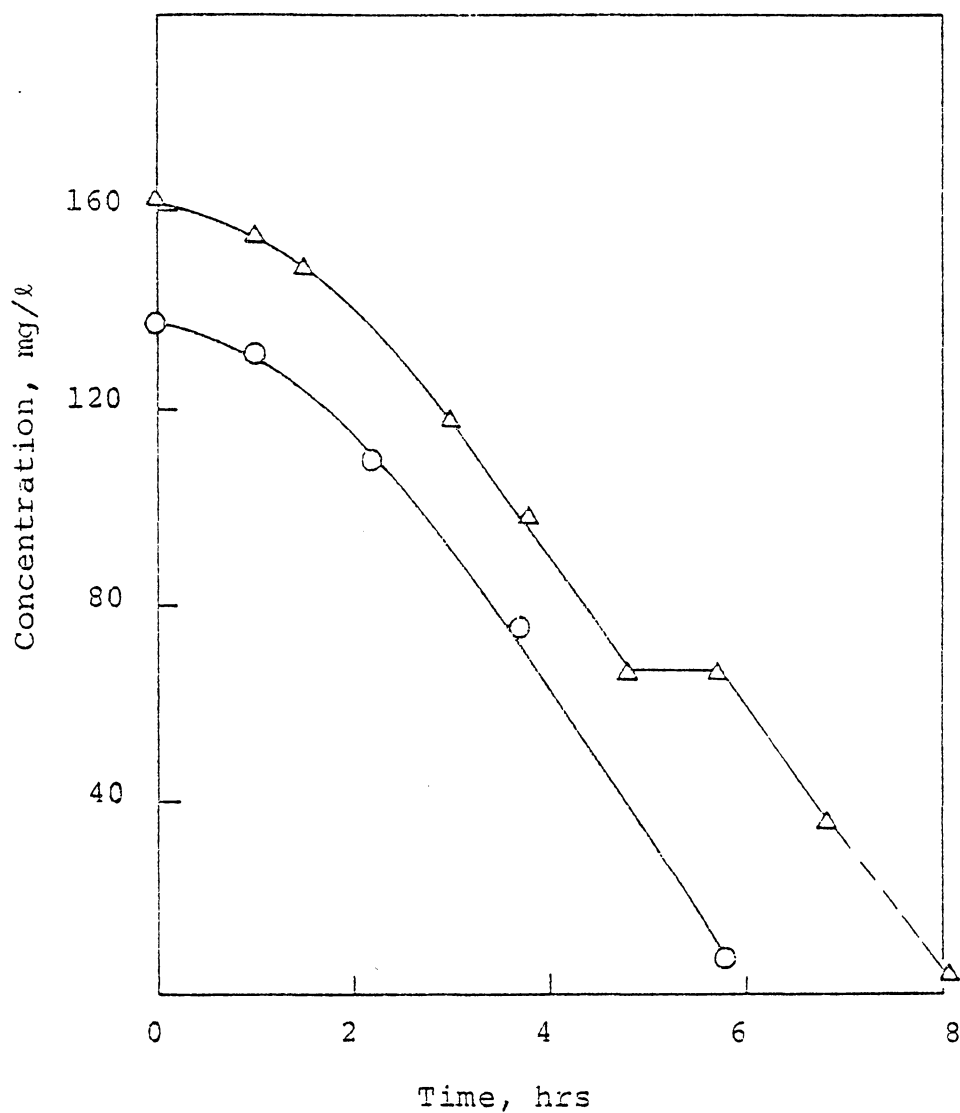


Figure 12. Phenol biodegradation batchwise in the presence of active carbon (Phase II) for: (Δ) Run 2, ($\circ$) Run 4.

Table IV

Rate of Phenol Biodegradation (Batchwise) in
the Presence of Active Carbon for:

Run 2

Rate, $\Delta C/\Delta t$ mg/l/hr	$\bar{C} = (C_1 + C_2)/2$ mg/l
8	158
10	152
21.3	133
25	108
26	51
24	20

Run 4

Rate, $\Delta C/\Delta t$ mg/l/hr	$\bar{C} = (C_1 + C_2)/2$ mg/l
6.5	136
16	124
26	95
30	< 40

Note: These rates were obtained using the data
plotted on Figure 13.

26 mg/ℓ/hr at $\bar{C} < 108$ mg/ℓ for Run 2 and $\bar{C} < 95$ for Run 4) as shown in Table IV. At a medium concentration of 15 mg of phenol per liter, this average value (26 mg/ℓ/hr) would represent an increase of 110% over the rate of phenol removal in the absence of activated carbon (12 ± 2 mg/ℓ/hr). Adams (85) reported 25% increase in COD removal and 20% increase in BOD removal when powdered activated carbon was added to an activated sludge system. Perrotti and Rodman (84) attributed this improvement in the system performance to the ability of carbon to remove phenol. The inhibitory effect of high phenol concentration on bacterial growth was, as such, reduced. Ferguson (86), however, found that the activated carbon added to the activated sludge system provided exceptional resistance to shock-loading by trichlorophenol. An important factor is keeping the culture exposed to a "homogeneous" medium. The concentration of trichlorophenol in the medium would not change drastically. A rapid increase in the concentration might inhibit the activity of the culture.

The above arguments might be acceptable for a continuous process where a variation in the influent stream organic concentration was probable. In the case of the batch process performed during this study, these explanations might be of trivial importance. The starting concentrations of phenol in the medium (after loading the carbon) were not

high enough to be significantly inhibitory (139 mg/l for Run 4, 162 mg/l for Run 2). This assumption was based on studies made in our laboratories (45). The bacteria (CP6 A) was able to grow on a concentration of phenol as high as 800 mg/l. This led us to the conclusion that some explanation, other than the ones proposed by Ferguson, Perrotti and Rodman, should be formulated. The adsorption-desorption (later in this section, we will show that activated carbon loaded with phenol desorbs when in contact with a bacterial culture) reaction might be the key factor. The performance of the system in the presence of an inert material (coal and sand) as supporting medium would firmly confirm this point. A higher performance in the presence of an inert material would be attributed to the ability of the bacteria to attach to the particle. It was reported that bacteria could grow on sand (9) and coal (95). In our laboratories, we never observed growth of bacteria on activated carbon particles. A lower performance in the presence of an inert material would be mainly due to the adsorption-desorption reaction of the activated carbon.

The increase in performance (110%) due to the addition of activated carbon, obtained during this study, was superior to the ones (20% for BOD, 25% for COD) reported by Adams (85). The fluidized bed technique adopted during this work might have partly contributed to this difference.

Jeris and colleagues (9) described this technique as an extremely high rate process, a combination of the best features of activated sludge (the process adopted by Adams) and trickling filtration. This suggested that fluidization technology would give a higher performance than either process (activated carbon or trickling filtration). The second contribution might be attributed to the medium itself. The phenolic solution prepared was absolutely void of particulates. The presence of those particles, as in the case of Adams' sewage, would probably block some of the pores of the active carbon, resulting in a lower surface area available for adsorption (99). In other words, the adsorptive capacity of the carbon would decrease, an ipso facto reduction in the system's efficiency. A batch process (this work) would be considered more efficient than continuous process (Adams' work). Other possibilities the author was not aware of could be factors in this discrepancy in performance (i.e., 110% vs. 25%).

In Run 2 (Fig. 13), between hour 5 and hour 6, the rate of biodegradation dropped to approximately zero. A glance at the pH profile suggested that a pH of about 5 or below might have inhibited the activity of CP6A (the bacteria used in this study). A low pH was also known to decrease the rate of adsorption of phenol on activated carbon (16). In the case where the rate of phenol

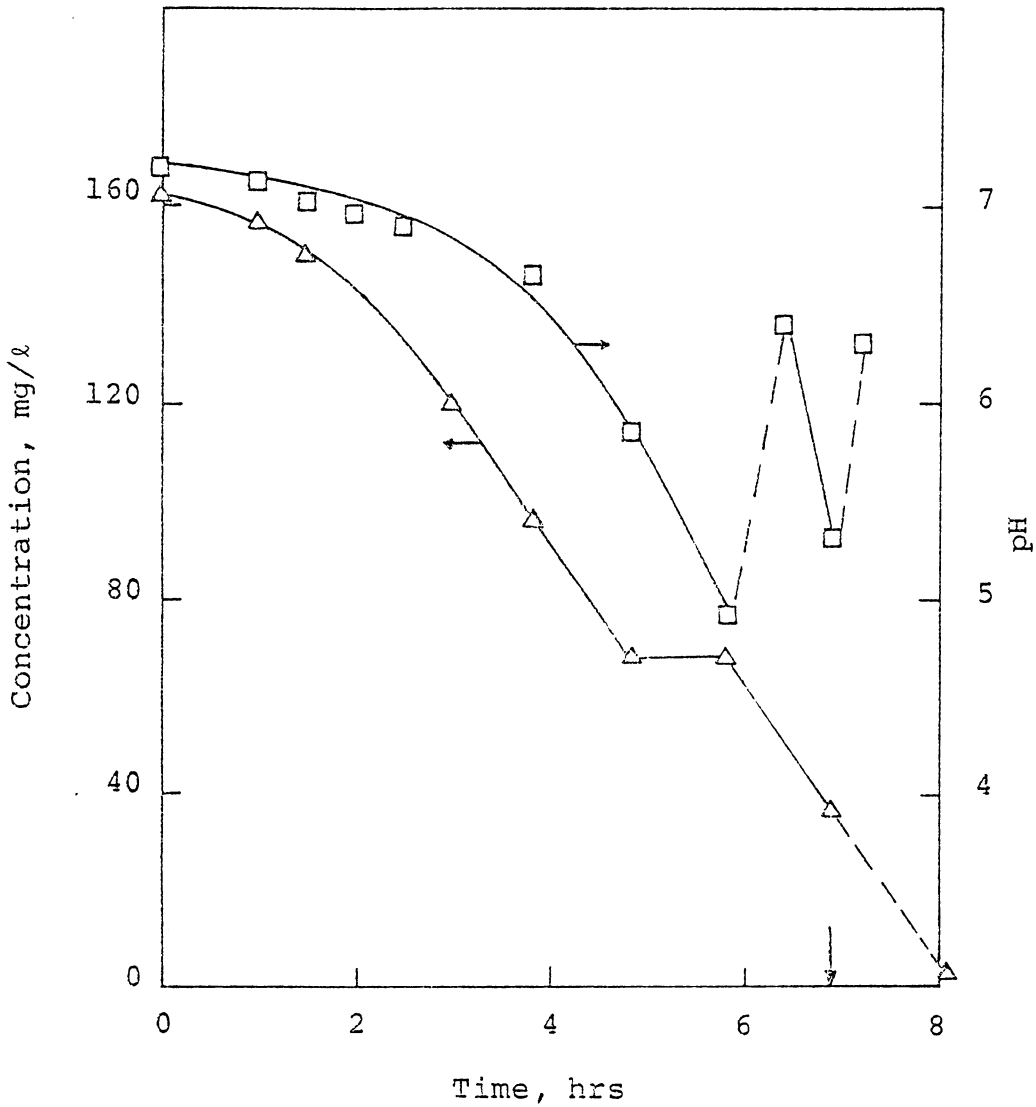


Figure 13. Variation with time of both the phenol concentration (Δ) and the pH ($\square$) during Phase II (phenol biodegradation, batch-wise, in the presence of active carbon) for Run 2. (-----) Addition of base (1 N KOH).

disappearance was governed by adsorption and biological degradation, a pH decrease would be expected to negatively affect the overall reaction. In Run 4 (Fig. 12), the pH was kept in the range of 7.0. No such discontinuity in bacterial activity was observed. This implied that a pH control would be necessary to keep the system working. Because of the complexity of the problem, it would be hard to draw a firm conclusion on the role of pH on the adsorption-biodegradation reaction. No optimization work was performed on pH and other variables (temperature, dissolved oxygen, etc.) for the system CP6A-activated carbon-phenol in a tapered fluidized bed.

3. Phase III: The Continuous Process

The continuous process failed in Run 2 due to a technical failure in the pumping system. In Run 4, however, the feed line was turned on for 12 hours. The feed flow rate was set to 1.16 l/hr. The concentration of phenol in the influent stream was 20 mg/l. The data obtained during this phase are plotted in Figure 14. During the eight hours following the batch process (hour 6 to hour 14), no data points were collected. The phenol degradation then detected, in the effluent stream, could be assumed to be due to bacterial action and not to dilution (at the end of the batch process, for Run 4, the concentration of phenol

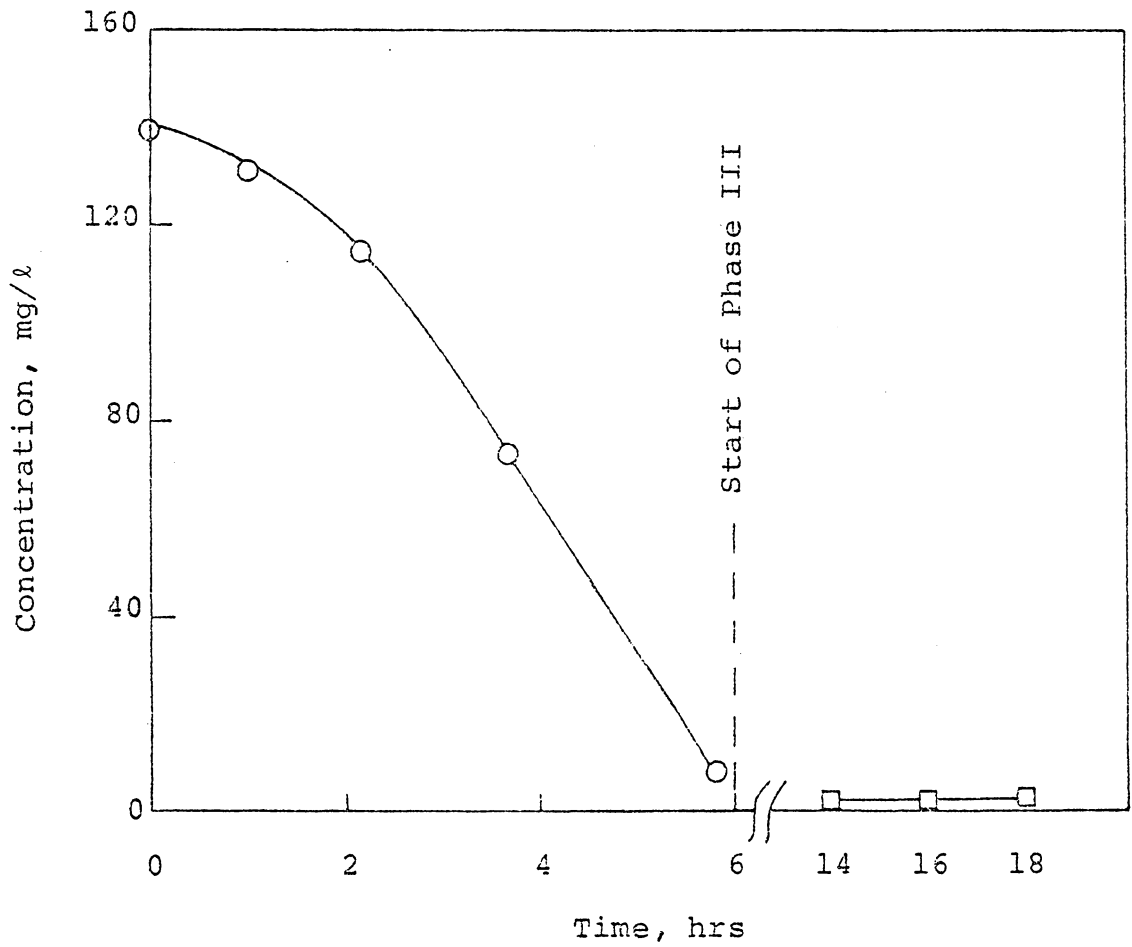


Figure 14. Variation of phenol concentration during (○) Phase II (phenol biodegradation batchwise in the presence of active carbon), and (□) Phase III (phenol biodegradation in the continuous mode and in the presence of active carbon), for Run 4.

in the medium was 8 mg/l, compared to 20 mg/l in the feed stream. The mean residence time for a feed flow rate of 1.16 l/hr would be 5 hours. Phenol degradation detected in the effluent stream eight hours after the start of the continuous process would then be attributed to bacterial degradation and not to dilution.)

The conversion of phenol over the four-hour period (hour 14 to hour 18) was greater than 95%. (See Appendix C for a sample calculation.) Because the rubber tubing in the peristaltic pump wore down during operation and became unreliable after 24 hours continuous use, a complete breakthrough curve was impossible to achieve. During this continuous portion of Run 4, the medium breaker installed on the feed line proved to be useful. The microorganism was not able to travel upstream from the loop reactor to the constant head tank as observed during Run 1 (Results and Discussions section, Subsection 4).

4. Phase IV: Extent of Bioregeneration

The bioregeneration study was performed during Runs 2, and 4. The results are presented in Table V. During Run 2, 26% of the carbon capacity available for adsorption was regenerated (Appendix C shows a sample calculation). This was achieved 8 hours after the incubation of the bed (at the end of the batch process of Phase II). However, the

Table V

Percent of the Total Activated Carbon (20 x 30 Mesh)
Capacity that has been Bioregenerated
During Runs 2, 4

Run	Time (hrs)	% of the total capacity bioregenerated
2	8	26
4	18	67

extent to which the active carbon bed was bioregenerated during Run 4 was 67%. The time of bacterial exposure to the bed was 18 hours (at the end of the continuous process). The phenol feed flow rate and the mean residence time were respectively equal to 23.2 mg/l and 5 hours.

The procedure followed during this study consisted of transferring a sample of wet activated carbon from the bed to a 250 ml Erlenmeyer flask filled with 50 ml of phenol-distilled water solution (Methods, Subsection 8, part d). This suggested that some traces of bacteria might have been entrained with the activated carbon sample. The chances that the bacteria degraded some of the phenol in the flask, where the bioregeneration study was undertaken, were slim. The distilled water (deionized water is void of inorganics and organics) used as a medium would hinder the activity of the microorganism for at least three hours (the time the study was performed). This would rule out any bacterial action during this last phase. The ruling out of this biological reaction would validate the above results.

In the literature, biological regeneration of activated carbon had rarely been investigated. Rodman and Shunney (40) reported some data on the bioregeneration of an activated carbon bed in a pilot plant treating textile dye waste. Analysis of their results showed that 50% of the bed was bioregenerated during the first cycle (each

cycle consisted of loading the carbon with dye for 2-1/2 hours continuous flow, then regenerating it by feeding the carbon bed with a bacterial culture for 6 hours; later, the regeneration time was extended to 12 hours). During the loading process, kinetics on the percentage of COD removal went through a minimum (the curve depicted a drop from 80% removal of COD to 30%, then went up to 40%). Work on adsorption kinetics of phenol on activated carbon (Fichte, Appendix C) showed that the percentage of phenol removal with time was described by a decaying exponential function. Neretnicks (98) found similar results when he studied the adsorption kinetics of different chemicals on active carbon.

The parabolic type behavior reported by Rodman and Shunney might be attributed to bacterial action. The lack of a medium breaker on the line connecting the culture reservoir and the active carbon bed could be responsible for a bacterial leak from the growth tank to the bed during the early hours. This bacterial action during the loading of the carbon would explain the observed increase in percentage removal of COD. This explanation would then invalidate the conclusions on bioregeneration reported by the authors.

Because of the complexity of the problem, it would be hard to define the factors that govern the time-% capacity

bioregeneration relationship (Table V shows an increasing relationship). The only firm conclusion that one could deduce from this study was that activated carbon could be bioregenerated in situ.

V. CONCLUSION

As a result of this study on biological regeneration of activated carbon, the following conclusions were made:

1. The addition of activated carbon to the system of phenol and bacteria increased its ability to remove phenol.
2. On-site biological regeneration of activated carbon was successful.

VI. RECOMMENDATIONS

The following are recommendations for use as a guide for further study:

1. Aeration. Characterization of the sparger should be done. The volumetric coefficient, $k_L a$, should be determined for different air flow rates, different recycle flow rates. In the case of continuous processes the feed flow rate should be considered. This study should be performed in the presence of activated carbon.
2. Residence time distribution (RTD). Characterization of the reactor should be performed. RTD curves at different air flow rates, recycle flow rates and feed flow rates should be determined.
3. Performance of system when an inert material is used as supporting medium. A fermentation run, in the presence of an inert material such as sand or coal, should be undertaken. The comparison of this system with the activated carbon system would help in specifying the role of activated carbon in treating wastewaters.
4. Determination of cell concentration in the presence of activated carbon or in the presence of an inert material. Cell concentration in the medium is impossible to determine using the available techniques (Klett reading, etc.). The cells are not homogeneously spread in the whole loop reactor.

They usually gather in the bed region. A criterion to determine cell concentration in the medium would be the % CO₂ evolved from the system. A calibration curve relating the % CO₂ evolved to cell concentration could be determined in the absence of supporting media.

5. Material balance. Once recommendation 4 is done, a carbon balance on the system would be easier to perform and is recommended.

6. System modeling. Modeling of the system is also recommended.

BIBLIOGRAPHY

1. The Complete Bible, Genesis 1:20, translated by J. M. Powis Smith, the University of Chicago Press, 1970.
2. Metcalf and Eddy, Inc., Wastewater Engineering, McGraw-Hill, Inc., New York, 1972.
3. A. G. Hansen, Proceedings of the Third Symposium on Hazardous Chemicals Handling and Disposal. Purdue University, Lafayette, Indiana, 1972.
4. N. I. Sax, Dangerous Properties of Industrial Materials, 4th edition. Van Nostrand Reinhold Co., New York, 1975.
5. The International Technical Information Institute. Toxic and Hazardous. Distributed by Maruzen Co., Tokyo, Japan, 1975.
6. J. L. Rizzo and A. R. Shepherd, Chem. Eng., 84, No. 1, 95, 1977.
7. R. Ramirez, Chem. Eng., 84, No. 19, 95, 1977.
8. J. M. Smith, Chemical Engineering Kinetics, Mc-Graw Hill, Inc., New York, 1970.
9. J. S. Jeris, R. W. Owens, and R. Hickey. J. WPCF, 49, 816, 1977.
10. T. J. Mulligan and R. D. Fox. Chem. Eng./Deskbook issue 1, 83, 49, 1976.
11. F. E. Bartell and E. J. Miller. J. Amer. Chem. Soc., 44, 1866, 1922.
12. H. P. Boehm. Advances in Catalysis, 16, 179, Academic Press, New York, 1966.
13. V. A. Garten and D. E. Weiss, Australian J. Chem., 10, 309, 1957.

14. V. L. Snoeyink, and W. J. Weber, Environ. Sci. Technol., 1, 228, 1967.
15. J. S. Mattson, H. B. Mark, and W. J. Weber. Anal. Chem., 41, 355, 1969.
16. V. L. Snoeyink, W. J. Weber, and H. B. Mark, Environ. Sci. Technol., 3, 918, 1969.
17. Y. A. Zurifyanz, V. F. Kiselev, N. N. Lezhnev, and O. V. Nikitina. Carbon, 5, 127, 1967.
18. G. Blyholder and H. Eyring. J. Phys. Chem., 62, 263, 1968.
19. E. A. Gulbransen and K. F. Andrew. Ind. Eng. Chem., 44, 1034, 1952.
20. G. Blyholder and H. Eyring. J. Phys. Chem., 63, 1004, 1959.
21. J. S. Mattson and H. B. Mark. Activated Carbon. Marcel Dekker, Inc., New York, 1971.
22. R. A. Beebe, J. Biscoe, W. R. Smith, and C. B. Wendell. J. Amer. Chem. Soc., 69, 95, 1947.
23. E. H. Wright. J. Colloid Interface Sci., 24, 180, 1967.
24. The Condensed Chemical Dictionary, 9th Ed. Van Nostrand Reinhold Co., New York, 1977.
25. J. S. Mattson, H. B. Mark, W. J. Weber. Anal. Chem. 41, 355, 1969.
26. R. W. Coughlin and F. S. Ezra. Environ. Sci. Technol. 2, 291, 1968.
27. R. W. Coughlin, F. S. Ezra, and R. N. Tan. J. Colloid Interface Sci., 28, 386, 1968.
28. F. E. Bartell and E. J. Miller. J. Phys. Chem., 28, 992, 1924.
29. V. A. Garten and D. E. Weiss. Aus. J. Chem., 10, 309, 1957.

30. V. L. Snoeyink and W. J. Weber. Environ. Sci. Technol., 79, 112, 1968.
31. E. D. Schroeder, Water and Wastewater Treatment. McGraw-Hill, Inc., New York, 1977.
32. R. S. Drago, R. J. Niedzielski, and R. L. Middough. J. Amer. Chem. Soc., 86, 1594, 1964.
33. S. H. Maron and C. F. Prutton. Principles of Physical Chemistry, 4th ed. Macmillan Co., New York, 1968.
34. W. J. Weber and J. C. Morris. J. Sanit. Eng. Div. 90, 79, 1964.
35. C. H. Giles, T. H. MacEwan, S. N. Nakhwa, and D. Smith. J. Chem. Soc., 1960, 3973.
36. B. Steenberg. Adsorption and Exchange of Ions on Activated Charcoal. Almquist and Wiksells, Uppsala, Sweden, 1944.
37. V. L. Snoeyink and W. J. Weber. Advan. Chem. Ser., 79, 112, 1968.
38. E. J. Miller. J. Phys. Chem., 31, 1197, 1927.
39. V. A. Garten and D. E. Weiss. Aust. J. Chem., 10, 309, 1957.
40. C. A. Rodman and E. L. Shunney. E.P.A. Water Poll. Control Res. Series, 12090 DWM 01/71, 1971.
41. S. Aiba, A. E. Humphrey, and N. F. Millis. Biochemical Engineering. Academic Press, Inc., New York, 1973.
42. N. Porges, L. Harewicz, and S. R. Hoover. Biological Oxidation of Dairywaste, VII, Proc. 10th Ind. Waste Conf., 1969.
43. L. Pauling, and R. B. Corey. Proc. Int. Wool Textile Res. Conf., 1975.
44. J. R. Ralston and G. R. Vela. J. Appl. Bact., 37, 347, 197.
45. S. W. Drew and H. S. Pal. Unpublished semi-annual progress report to the American Iron and Steel Institute, project no. 77-354, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 1976.

46. D. C. Sands. *Phytopath.*, 62, 998, 1972.
47. J. L. Stokes. *Bacteriology*, 57, 147, 1949.
48. A. C. Blackword, A. C. Neish, and G. A. Ledingham. *Bacteriology*, 72, 497, 1956.
49. G. O. Powell. *Lab. Pract.*, 14, 1145, 1965.
50. S. S. Lee, A. P. Jackman, and E. D. Schroeder. *Water Res.*, 9, 491, 1975.
51. B. Hultman. *J. WPCF*, 47, 843, 1975.
52. G. F. Andrews and C. Tien. Reprinted from AICHE Symposium Series, 71, 164, 1977.
53. A. F. Gaudy, Jr. and R. Srinivasaraghaven. *Biotechnol. Bioeng.*, 16, 723, 1974.
54. F. H. Deindorfer. Continuous Culture, Vol. 6, Ellis Horwood Ltd., London, 1976.
55. D. Prasad and P. H. Jones. *J. WPCF*, 46, 1686, 1974.
56. I. R. Hall. *Water Poll. Control (G.B.)*, 73, 1686, 1974.
57. A. M. Stern and L. L. Gasner. *Biotechnol. Bioeng.*, 16, 78, 1974.
58. J. F. T. Spencer. *Can. J. Microbiol.*, 20, 1288, 1974.
59. W. D. Bellamy. *Biotechnol. Bioeng.*, 16, 869, 1974.
60. Z. V. Levina. *Appl. Biochem. and Microbiol.*, 7, 105, 1973.
61. L. Kalisz. *Biol. Abs.*, 58, 34298, 1974.
62. R. F. Unz. *J. WPCF*, 47, 1559, 1975.
63. R. R. Mohan and N. N. Li. *Biotechnol. Bioeng.*, 16, 513, 1971.
64. A. J. Willets. *Antonie van Leeuwenhoek*, 40, 561, 1974.
65. P. H. Jones. *Environ. Sci. Technol.*, 8, 919, 1974.

66. J. E. Guillet. Environ. Sci. Technol., 8, 923, 1974.
67. C. F. Feist and G. D. Hegemen. J. Bacteriol., 100, 869, 1969.
68. I. Radhakeishnan and A. K. S. Ray. J. WPCF, 46, 2393, 1974.
69. Phenobac, Technical Data Sheet, 1176A. Polybac Corp., 505 Park Ave., New York, 10022.
70. S. Dagley, W. C. Evans, and D. W. Ribbons. Nature, 188, 560, 1960.
71. I. J. Davies and W. C. Evans. Biochem. J., 91, 251, 1964.
72. M. B. Kemp and G. D. Hegemen. J. Bacteriol., 96, 1488, 1968.
73. L. N. Arnston and R. Y. Stanier. J. Biol. Chem., 241, 3800, 1966.
74. D. L. Ford and L. F. Tischler. Chem. Eng., p. 131 (August 1977).
75. K. L. Murphy and P. L. Timpany. J. Sanit. Eng. Div., ASCE, 93, 1, 1967.
76. R. E. McKinney. J. Sanit. Eng. Div., ASCE, 89, 71, 1963.
77. R. H. Gould. Sewage Ind. Wastes, 23, 815, 1959.
78. J. G. Albertsson. Water Pollution Control Research Series, 17050 DNW 05/70, 1970.
79. J. M. Humenick and J. E. Ball. Water Pollut. Control Fed., 46, 735, 1974.
80. M. Ramanathan and A. F. Gaudy. Biotechnol. Bioeng., 11, 207, 1969.
81. D. Herbert. Soc. Chem. Ind. (London), Monog. No. 12, 21, 1956.
82. R. E. McKinney. Biotechnol. Bioeng., 16, 703, 1974.
83. J. A. Miller. Paper presented at the 21st Summer Institute on Biologic Waste Treatment. Manhattan College, New York (May 1976).

84. A. E. Perrotti and C. A. Redman. Paper presented at 75th National Meeting, A.I.Ch.E., 1973.
85. A. D. Adams. Water and Wastes Eng., 11, 88, 1974.
86. J. F. Ferguson. Paper presented at the 31st Purdue Industrial Waste Conference, Purdue University, Lafayette, Indiana (May 1976).
87. D. M. Giusti, R. A. Conway, and C. T. Lawson. JWPCF, 46, 947, 1974.
88. B. Atkinson. Biochemical Reactor Engineering. Pioneer Press, London. 1974.
89. B. Atkinson and S. Y. How. Trans. Inst. Chem. Eng., Part I, 1974.
90. B. Atkinson, I. J. Daview, and S. Y. How. Trans. Inst. Chem. Eng., Part II, 1974.
91. A. M. Squires. In Alternative Energy Sources. Academic Press, New York, 1976.
92. C. D. Scott and O. W. Hancher. Biotechnol. Bioeng., 18, 1393, 1976.
93. J. B. Allen, R. S. Joyce, and R. H. Kasch. J. WPCF, 39, 217, 1967.
94. Ecolotrol, Inc. Paper presented at New York American Society of Civil Engineers Conference, April 23, 1976.
95. D. W. Holladay, O. W. Hancher, D. D. Chilicote, and C. D. Scott. 69th Annual Meeting, A.I.Ch.E., Chicago (1976).
96. W. W. Eckenfelder, T. Williams, and G. Schlossnagle. In Applications of New Concepts of Physical-Chemical Wastewater Treatment. Pergamon Press, New York, 1972.
97. L. D. Friedman, W. J. Weber, R. Bloom, and C. B. Hopkins. E.P.A. Water Poll. Control Res. Series, 17020 GDN 07/71, 1971.
98. I. Neretnicks. Chem. Eng. Soc., 31, 1029, 1976.

99. O. Levenspiel. Chemical Reaction Engineering. John Wiley and Sons, Inc., New York, 1972.
100. G. F. Andrews, and C. Tien. A.I.Ch.E. Symposium Series, 71, 164, 1974.

APPENDIX A

The Computer Output for Run 1

The variables involved during this first run are:

<u>Variable Number</u>	<u>Figure Number</u>	<u>Variable Name</u>
1	A1	Air flow rate
2	A2	% O ₂ evolved
3	A3	pH
4	A4	Dissolved oxygen
5	A5	% CO ₂ evolved
6	A6	Temperature

PRINT FOR VARIABLE NUMBER

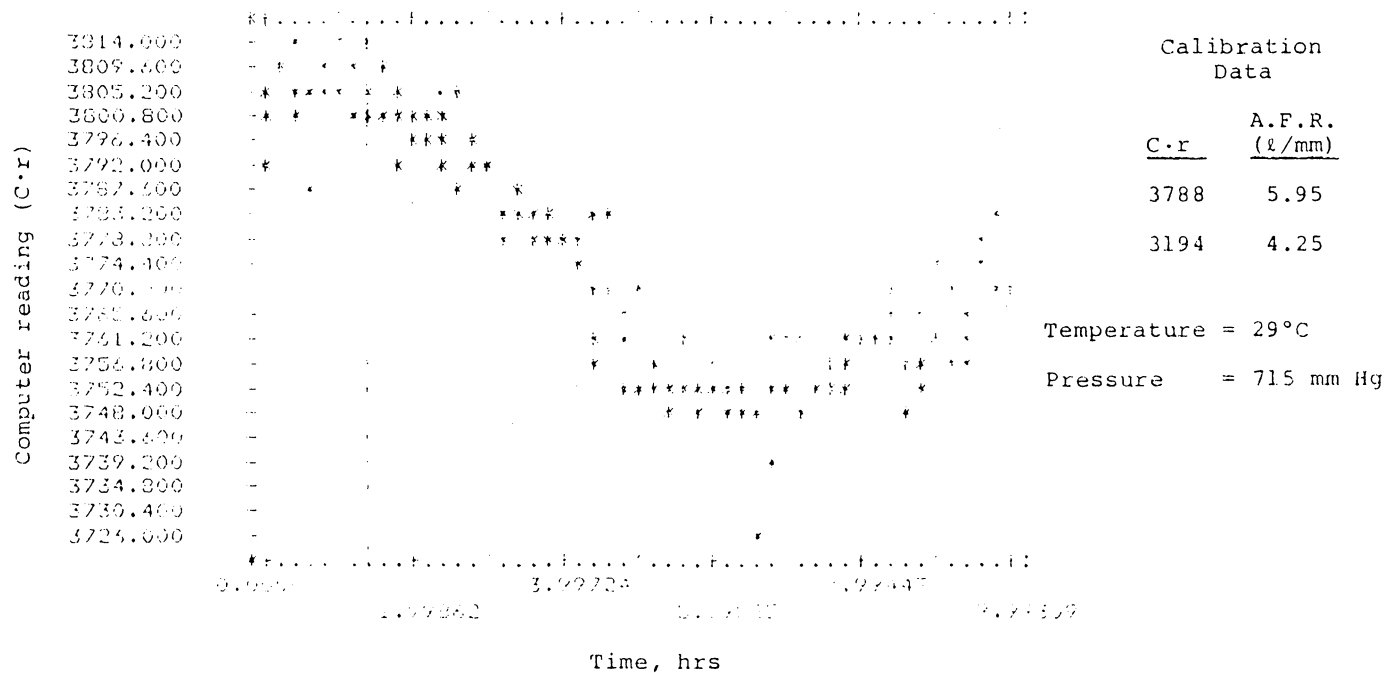


Figure A1. Air flow rate (A.F.R.) as a function of time during Run 1 (dashed line indicates the start of the experiment).

PLOT FOR VARIABLE NUMBER 2

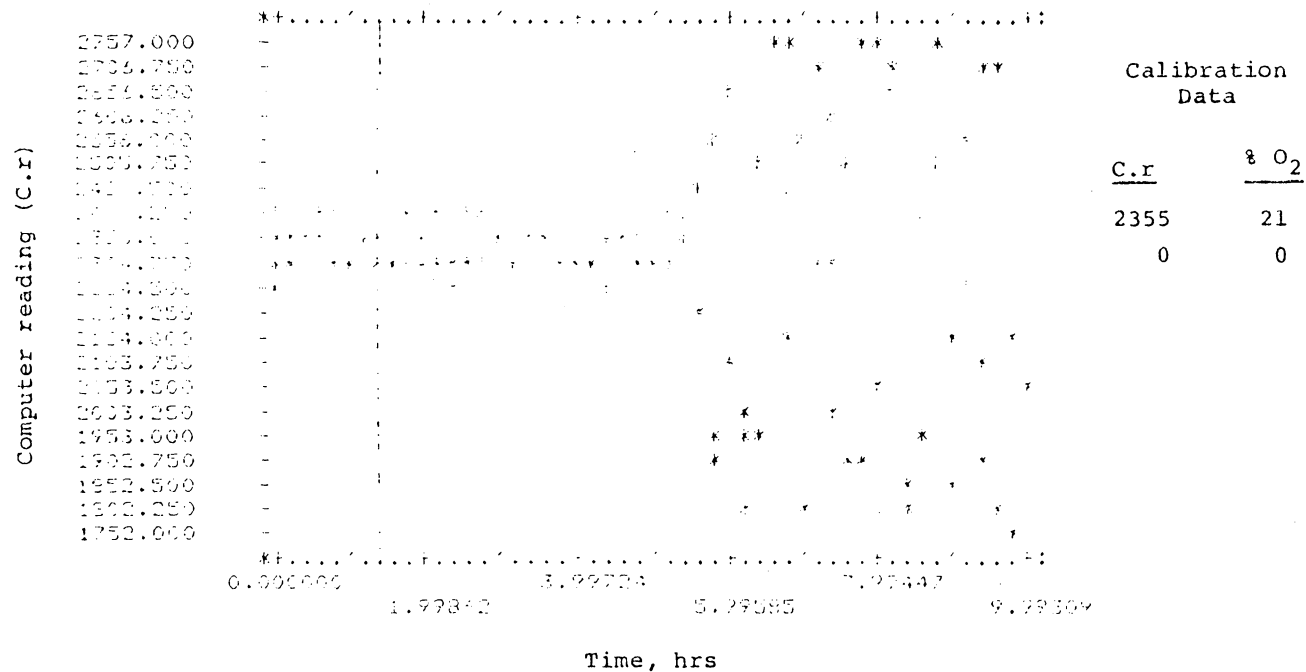


Figure A2. Percent of oxygen evolved as a function of time during Run 1 (dashed line indicates the start of the experiment).

PH OF THE MEDIUM RUN 1

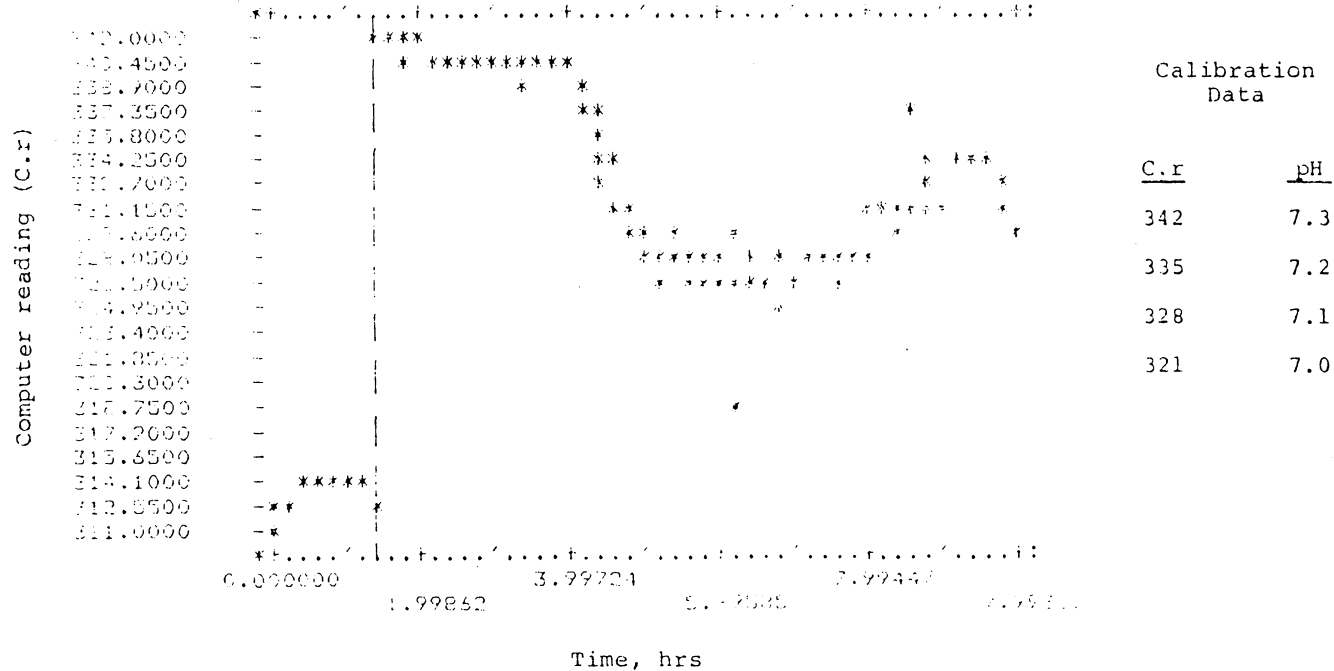


Figure A3. pH of the medium as a function of time during Run 1 (dashed line indicates the start of the experiment).

PLOT FOR VARIABLE NUMBER 4

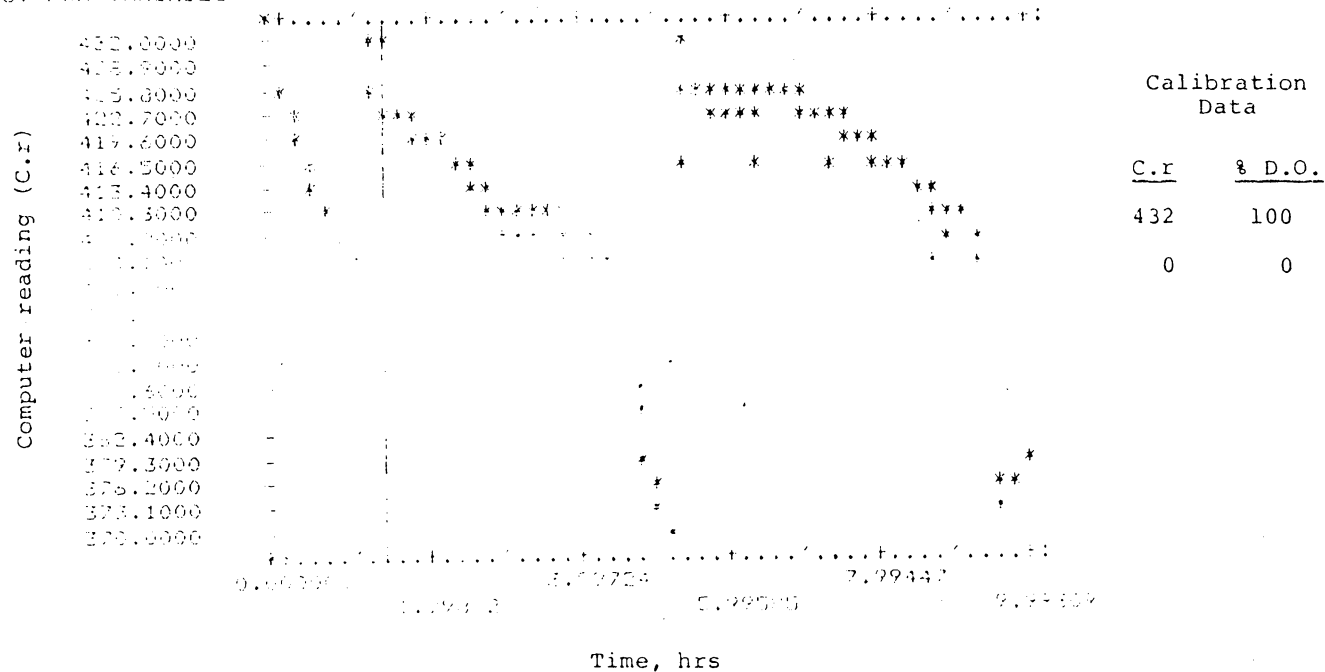


Figure A4. Dissolved oxygen (D.O.) in the medium as a function of time during Run 1 (dashed line indicates the start of the experiment).

Plot for Variable Number 5

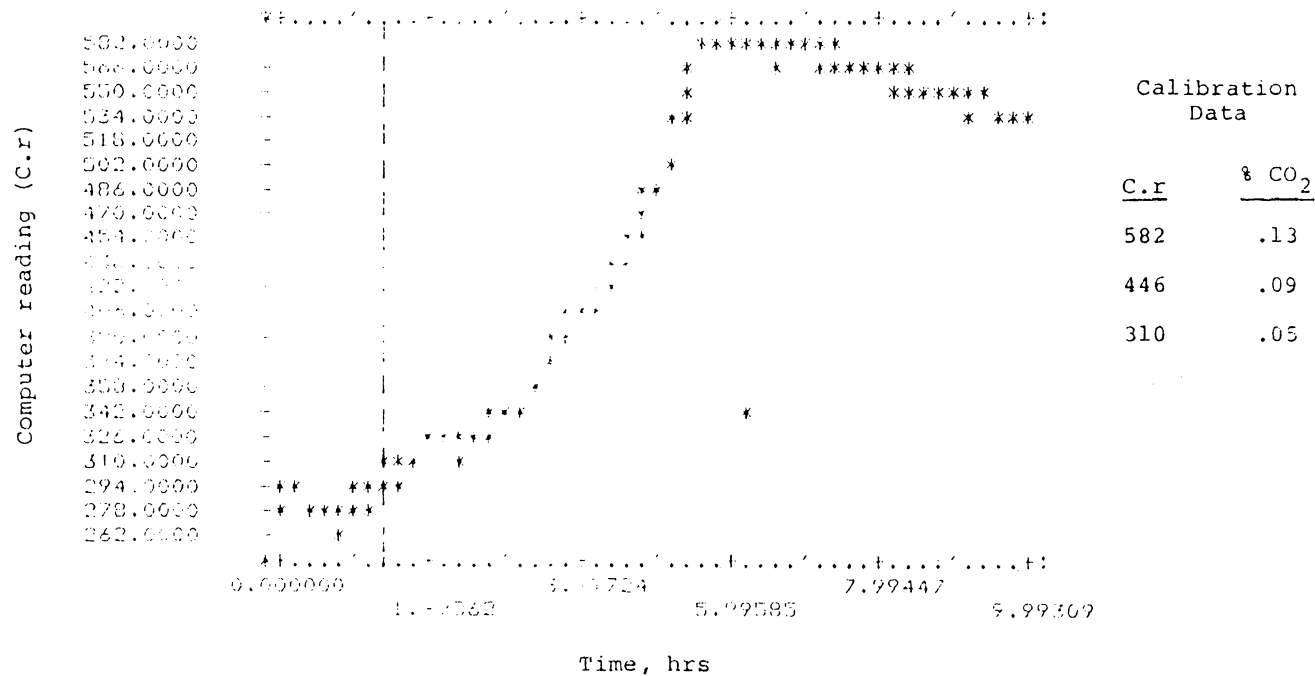


Figure A5. Percent of carbon dioxide evolved as a function of time during Run 1 (dashed line indicates the start of the experiment).

PLOT FOR VARIABLE NUMBER 4

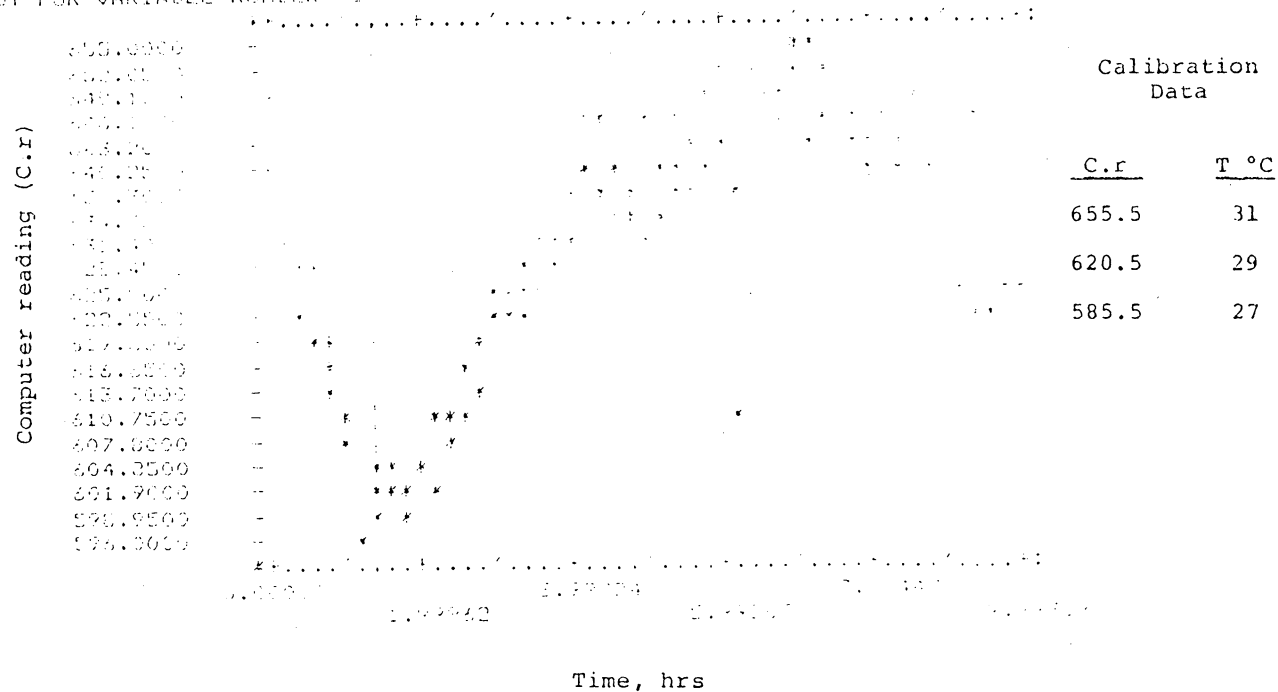


Figure A6. Variation of temperature with time during Run 1 (dashed line indicates the start of the experiment).

APPENDIX B

Data Tables

Table B1
Mixing Studies

Recycle flow rate = 2.7 l/min

Reactor volume = 5.8 l

Air flow rate = 5.7 l/min

Tracer = phenol

A = Absorbance at 270 nm

A_F = Equilibrium absorbance at 270 nm

Time (sec.)	Response data to a pulse input at:			
	Port H3		Port FP	
	A	A/A_F	A	A/A_F
30	0	0	0	0
45	0	0	0	0
60	0.01	0.015	0	0
90	0.83	1.25	0.01	0.016
120	0.70	1.06	--	--
150	0.60	0.91	0.32	0.52
165	--	--	0.50	0.82
180	0.59	0.90	--	--
210	0.64	0.97	0.58	0.94
240	0.66	1	--	--
270	0.66	1	--	--
$A_F = 0.66$		$A_F = 0.58$		

Table B2

Response Data to a Step Input in the Feed

Residence Time Distribution Study

Recycle flow rate = 2.7 l/min Reactor volume = 5.8 l
 Air flow rate = 5.7 l/min Tracer = Phenol
 Feed flow rate = 1.36 l/hr

Time (Min.)	A	$J(t) = A/A_F$	t_m
0	0	0	0
30	0.01	0.011	0.12
60	0.017	0.02	0.23
120	0.05	0.06	0.47
180	0.14	0.16	0.70
210	0.23	0.26	0.82
240	0.36	0.41	0.94
270	0.49	0.56	1.06
300	0.60	0.69	1.17
360	0.78	0.90	1.41
420	0.84	0.97	1.64

The mean residence time, $t_m = 4.26$ hours

Table B3
Growth of CP6A on Nutrient Broth
Containing 100 mg/% of Phenol

Time (min.)	Klett Reading	Time (min.)	Klett Reading
0	--	540	40
45	36	570	49
110	34	620	65
200	35	670	95
270	34	720	128
350	34	745	144
420	34	775	153
480	36	805	162
510	39	835	167

Table B4

Phenol Biodegradation by CP6A in the Absence
of Active Carbon (Run 1)

Recycle flow rate = 2.7 ℓ /min

Air flow rate = 5.7 ℓ /min

Reactor volume = 5.8 ℓ

Time (hr.)	Phenol concentration + .95 confidence interval, mg/ ℓ
0	23 $\pm$ 2.0
2.13	20.4 $\pm$ 2.0
3.16	10.3 $\pm$ 1.5
6.00	1.4 $\pm$ 1.5
7.08	<1 $\pm$ --

Table B5

pH, % CO₂ Evolved versus Time During the Phenol
Biodegradation by CP6A in the Absence of
Active Carbon

Time (Hr.)	pH	% CO ₂
0	7.30	0.05
1	7.30	0.06
2	7.30	0.07
3	7.20	0.09
4	7.10	0.12
5	7.10	0.13
6	7.10	0.13
7	7.10	0.12
-Ambient level for CO ₂ is .03%		

Note: The data was collected from the computer
output obtained during Run 1.

Table B6

Bioregeneration of Activated Carbon Studies.

Adsorption of Phenol on 20x30 Mesh Activated

Carbon for Runs 2, 3, 4 (Phase I)

Recycle flow rate = 2.7 l/min

Reactor volume = 5.8 l

Air flow rate = 5.7 l/min

Weight of the Acti-
vated Carbon Bed
= 55 g

Time (Hr.)	Phenol concentration, mg/l		
	Run 2	Run 3	Run 4
0	1334	965	1230
0.25	990	695	960
0.50	370	--	--
1.00	251	--	--
1.50	234	70	165
2.50	--	--	--
3.00	202	--	--
3.50	183	60	150
4.00	162	57	137

Table B7

Bioregeneration of Activated Carbon Studies. Phenol
Biodegradation in the Presence of Active Carbon for
Run 2 (Phase II). The pH Variation During
This Run is Also Tabulated

Recycle flow rate = 2.7 ℓ /min Reactor volume = 5.8 ℓ
Air flow rate = 5.7 ℓ /min Weight of the Activated
Carbon Bed = 55 g

Time (Hr.)	Phenol Concentration + .95 confidence interval, mg/ ℓ	pH
0	162	7.22
1	154	7.11
1.5	149	7.00
2.0	--	6.96
2.50	--	6.87
3.0	117	--
3.83	98	6.64
4.83	66	5.84
5.75	66	4.89
6.33	1N KOH was added	6.36
6.83	37 $\pm$ 2.0	5.30
7.20	1N KOH was added	6.27
----- Pump broke down -----		
8.16	4.0 $\pm$ 1.5	5.20

Table B8

Bioregeneration of Activated Carbon Studies. Phenol
 Biodegradation in the Presence of Active Carbon for
 Run 4 (Phase II). The pH was Kept in the Range
 6.8 - 7.1 by Adding 1N KOH

Recycle flow rate = 2.7 l/min Reactor volume = 5.8l
 Air flow rate = 5.7 l/min Weight of the Activated
 Carbon Bed = 55 g

Time (Hr.)	Phenol concentration + .95 confidence interval, mg/l
0	139.2
1.08	132.0
2.16	115.0
3.67	76
5.83	9.4 $\pm$ 1.5

Table B9

Bioregeneration of Activated Carbon Studies.

Phenol Biodegradation in the Continuous

Process of Run 4 (Phase III)

Recycle flow rate = 2.7 ℓ /min Reactor volume = 5.8 ℓ
Air flow rate = 5.7 ℓ /min Weight of the activated
Feed flow rate = 1.16 ℓ /hr carbon bed = 55 g

Time (Hr.)	Phenol concentration, mg/ ℓ	
	Influent stream	Effluent stream
0	20	<1
2	20	<1
4	20	<1

Table B10
 Bioregeneration of Activated Carbon Studies.
 Desorption Studies (Phase IV)
 for Runs 2, 4

Sample number	Weight of the activated carbon sample, g	Initial concentration of phenol in solution, mg/l	Final concentra- tion of phenol in the solution + .95 confidence interval, mg/l
----- Run 2 -----			
1	1.838	250	51 $\pm$ 2.0
2	1.609	250	54 $\pm$ 2.0
----- Run 4 -----			
1	.358	140	3.7 $\pm$ 1.5
2	.687	140	2.7 $\pm$ 1.5

APPENDIX C

Sample Calculations and Dr. Fichte's Data on Phenol
Adsorption on 20 x 30 mesh Activated Carbon

Sample Calculations

This section contains examples of calculations made in the course of this investigation.

Calculation of the percent of the total activated carbon (20 x 30 mesh) capacity that has been bioregenerated during Runs 2, 4.

A certain amount (m, in grams) of activated carbon was transferred from the bed to a 50 ml solution of phenol and distilled water (the concentration of phenol in the solution varied from one run to the other). The procedure followed to calculate the extent to which the activated carbon was bioregenerated consisted of 6 steps.

Step 1. The amount (X_s) of phenol adsorbed from the 50 ml solution, by the sample of activated carbon that has been transferred (m) was:

$$X_s = (0.05 \text{ l}) (C_i - C_F)$$

where X_s = amount of phenol adsorbed from the solution by m, mg.

C_i = initial concentration of phenol in the solution, mg/l.

C_F = final concentration of phenol in the solution, mg/l.

Step 2.

The total phenol content (X_t) of the activated carbon sample (m) was then:

$$X_t = X_s + X_o$$

where X_t = total phenol content of the sample m, mg.

X_o = phenol content of the sample when transferred from the bed, i.e., before the contact of the sample with the 50 ml solution of phenol and distilled water.

The value of X_t was obtained by using the Freundlich isotherm relation reported by Dr. Fichte (Appendix D).

$$\frac{X_t}{m} = KC_F^{1/n} \quad \text{or} \quad X_t = mKC_F^{1/n}$$

where m = mass of the activated carbon sample transferred from the bed to the 50 ml solution of phenol and distilled water, g.

K and n = constants.

Step 3

The initial phenol content of the sample (X_o) when transferred from the bed was therefore:

$$X_o = X_t - X_s = (mKC_F^{1/n}) - (0.05)(C_i - C_F)$$

Step 4

The initial phenol content of one gram of activated carbon sample that has been transferred from the bed was:

$$\frac{X_o}{m} = KC_F^{1/n} - \left(\frac{0.05}{m}\right)(C_i - C_F)$$

Step 5

The phenol content of one gram of activated carbon inside the bed, at the end of the loading process, just before the inoculation of the bed (Phase I of the bio-regeneration study) was:

$$\frac{X}{M} = \frac{V(C_s - C_e)}{M}$$

where $\frac{X}{M}$ = phenol content of one gram of activated carbon, mg/g

V = Volume of the medium, l

M = Mass of the activated carbon bed

C_s = Starting phenol concentration of the medium, mg/l

C_e = Final phenol concentration of the medium, mg/l

Step 6

The percent of the activated carbon capacity that has been bioregenerated was:

$$\left[\{ (X_o/m) - (X/M) \} / (X/M) \right] \times 100$$

During Run 4, the following data were collected during the bioregeneration study (table, Appendix A).

$$m = .358 \text{ g}$$

$$M = 55 \text{ g}$$

$$C_i = 140 \text{ mg/l}$$

$$V = 5.8 \text{ l}$$

$$C_F = 3.7 \text{ mg/l}$$

$$C_S = 1230 \text{ mg/l}$$

$$K = 41.34$$

$$C_e = 139 \text{ mg/l}$$

$$n = 4.26$$

$$\frac{X_O}{m} = 41.34 (3.7)^{.234} - \left(\frac{0.05}{.358}\right) (140 - 3.7) = 37.00 \text{ mg/g}$$

$$\frac{X}{M} = \frac{5.8(1230 - 139)}{55} = 115 \text{ mg/g}$$

$$\begin{array}{l} \% \text{ of the activated carbon capacity} \\ \text{that has been bioregenerated} \end{array} = 67\%$$

Calculation of the percent of phenol biodegraded during the Continuous Process of Run 4

$$\text{The percent of phenol biodegraded} = \left(\frac{C_{\text{eff}} - C_{\text{inf}}}{C_{\text{eff}}} \right) \times 100$$

where C_{eff} = concentration of phenol in the effluent stream, mg/l

C_{inf} = concentration of phenol in the influent stream, mg/l

during Run 4 (table , Appendix), $C_{\text{eff}} = 20 \text{ mg/l}$

$$C_{\text{inf}} < 1 \text{ mg/l}$$

and the percent of phenol biodegraded $> \left(\frac{20 - 1}{20} \right) \times 100 = 95\%$

MEMO TO: Dr. S. Drew
Mr. S. Atieh

FROM: P. Fichte, Dept. of Chem. Eng., VPI & SU

DATE: August 15, 1977

SUBJECT: Analysis of Isothermal Kinetic and Equilibrium
Data for Adsorption of Phenol on 20 x 30 Mesh
Activated Carbon at 28.0°C.

A. Adsorption Kinetics

A 1.07084 gm sample of activated carbon ("Nuchar" 20 x 30 mesh) was placed in a 250 ml Erlenmeyer Flask and allowed to come to thermal equilibrium at 28°C. 100 ml of 1000 ppm phenol solution, also at 28°C, was added to the flask, which was then placed in a rotary shaker set to operate at 200 rpm. A timer (Precision Scientific) was actuated immediately after the phenol solution had been added to the flask.

1-ml samples of the solution being shaken were removed with filtering, using a syringe-filter (SXGS 013 OS 0.22 μ m, Swinnex-13 by Millipore, Inc.) combination, every 5 minutes for one hour, every 10 minutes during the next hour, every 20 minutes during the following 80 minutes, and at increasingly longer intervals during the subsequent days. A final sample was removed after approximately 86 hours. 19 samples were taken in all.

The samples were analyzed with a Perkin-Elmer Gas Chromatograph (Model 3920) employing Flame Ionization Detector. Residual phenol concentrations were determined by comparing mean peak heights with a calibration curve. The amount of phenol removed by the activated carbon for each sample (mg phenol per gram of activated carbon) was calculated, and the values obtained $[\frac{X}{M}]$, where X = mass phenol removed, in mg, and M = mass of activated carbon = 1.07084 gm] plotted against various functions of time in minutes.

A reasonably good straight line fit was obtained up to the time that the adsorbed phenol had reached 90% of its calculated equilibrium value (after 50 minutes)

when the mass of adsorbed phenol per gm of activated carbon plotted against the square root of the time (see attached Table C1).

The shape of the $\frac{X}{M}$ vs. $\sqrt{t}$ curve is similar to that of diffusion into a hollow sphere or hollow cylinder with the surface maintained at a constant concentration (Crank, pp. 82, 83, 98, 99).¹ Such a linear square foot relationship indicates a diffusion-controlled reaction (Crank, op. cit., and p. 37).

Present GC-phenol calibration indicate that the concentration of residual phenol are known to $\pm 10\%$ (although the individual sample mean precision is $\bar{y}$ and large within a standard deviation of $\pm 5\%$).

B. Adsorption Isotherm

15 samples of activated carbon, ranging in mass from 3.07678 gm to 0.42206 g were placed in separate 250 ml Erlenmeyer Flasks and equilibrated to 28°C. To each flask was added 100 ml of 1000 ppm phenol solution at 28°C. The flasks were shaken at 200 rpm in a rotary shaker for 7 days at 28°C. Eight of these systems, spanning the range of sample weight, were analyzed for residual phenol concentration in the supernatant, using the Perkin-Elmer Gas Chromatograph with FID attachment.

The $\frac{X}{M}$ for each of the samples was calculated and plotted in both the Langmuir and Freundlich Isotherm modes. Excellent linearity was obtained with the Freundlich plot up to and including a residual phenol concentration of 150 ppm (the lowest concentration was 2.5 ppm). After that the plot became horizontal, as if to indicate a saturation phenomenon. The equation for the linear section was of the form:

$$\frac{X}{M} = K C_F^{1/n} \quad \frac{X}{M} = K C^{1/n} \quad \text{where } K = 41.23 \quad \left(\frac{1}{n} = \frac{1}{4}\right).$$

$$\text{and } n = 4.26$$

(Isotherm II)

Results from a prior preliminary set of adsorption equilibrium experiment (also at 28°C) fell within the scatter of the present results, and also exhibited a saturation phenomenon (Isotherm I).

¹The Mathematics of Diffusion, Clarendon Press, 2nd ed., 1975.

Table C1

Conversion of Kinetic Data to $\frac{X}{M}$ vs $t(\text{min})$

$t(\text{min})$	$\frac{X}{M}(\frac{\text{mg}}{\text{g}})$
5	29.88
10	53.70
19	68.36
30	76.58
40	79.66
50	81.11
60	83.49
70	83.80
80	84.67
90	85.26
100	85.63
110	86.19
120	86.37
230	86.47
340	87.22
1140	89.18
2945	89.56
4110	90.68
5180	90.77

APPENDIX D

Discussion of the Technique Used to Assay Phenol

Introduction

The peak height technique was adopted to assay phenol solutions during this study. This technique requires that:

1. The calibration curve be fully obtained for each GC (gas chromatograph) run.
2. The chromatogram shapes be all similar.

The error generated by neglecting the first requirement will be discussed in this appendix. For this purpose, the following was undertaken:

1. A calibration curve was obtained using the peak height technique. This curve was then compared to two previous calibration curves determined in a similar way.
2. A calibration curve was obtained using the internal standard technique (ethylene glycol was used as internal standard, 150 μ l of 11080 mg/l of ethylene glycol was added to 7 ml of each of the phenol solutions to be analyzed).
3. Two unknown solutions were determined using each of the calibration curves obtained from each technique (peak height technique and internal standard technique).

The gas chromatograph used during this study was a Perkin Elmer GC (model 3920). The specifications of the column were as follows:

Column material	:	SS
Length	:	5'
Support	:	Chromosorb W
Mesh range	:	60-80
Liquid phase	:	10% FFAP
Weight percent	:	10

During the assay of phenol solutions (peak height technique), the flame ionization detector, the column, and the injection port temperatures were respectively set at $185^{\circ}\text{C} \pm 2^{\circ}\text{C}$, 144°C , and $200^{\circ}\text{C} \pm 2^{\circ}\text{C}$. During the assay of phenol-ethylene glycol solutions (internal standard technique), the flame ionization detector, the column, and the injection port temperatures were respectively set at $185^{\circ}\text{C} \pm 2^{\circ}\text{C}$, 160°C and $200^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The carrier gas was helium, at a 20 psig pressure at the tank's regulator, and at a flow rate of 2.0 (32 ml/min) as registered in the chromatograph's rotameter.

Results and Discussions

1. Peak height technique

Table D1 shows the results of three calibration curves obtained at three different GC runs. Set No. 1 and 2 were performed last year (1977), set No. 3 was performed in June, 1978. Figure D1 compares the results obtained during set No. 3 to the results of set No. 1. The solid line represents the relation between those two sets. The dashed line

Table D1
Results for Three Calibration Curves
Performed at Different Times

Phenol concentration mg/l	Peak height		
	Set No. 1	Set No. 2	Set No. 3
1	10.3	12.4	10
5	48.7	--	46
10	83	83.8	89
20	223	177	193

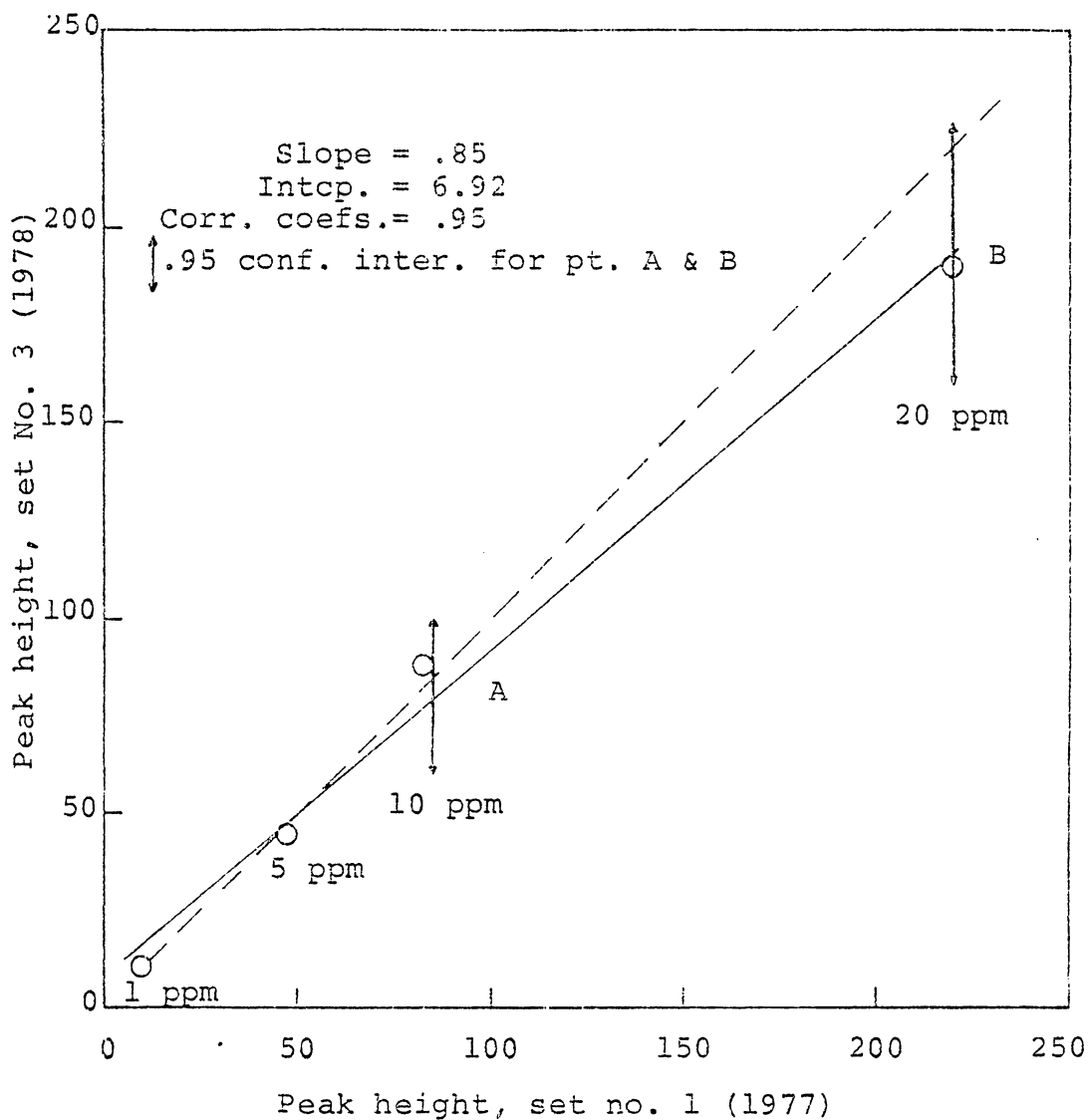


Figure D1. Plot of GC calibration data for phenol solutions obtained using the peak height technique; set No. 3 vs set No. 1. The dashed line represents the one-to-one relation one will expect if the GC response is reproducible for any run.

represents the relation one will expect if the GC response is reproducible for each of its runs. Comparison of those two lines gives us an idea about the error generated when the first requirement mentioned previously is neglected (Table D2). This table also compares set No. 2 to set No. 3. Figure D2 is a plot of set No. 2 versus set No. 3. Table D2 shows an error of 20% when assaying a phenol concentration of 1 mg/l at two different times. It also shows a 13% error when assaying a phenol concentration of 20 mg/l. The inconsistency in the error at different concentrations is clear (20% at 1 mg/l, 7% at 15 mg/l, etc.). This suggests that the first requirement (calibration curve for each GC run) be applied for each GC run.

Table D3 displays the mean peak height for set No. 1 and No. 2 versus the peak height for set No. 3 at different concentrations. The error generated comparing those two sets is less than the one shown in Table D2. This suggests that neglecting the first requirement will generate less error if the standard curve is a combination of two sets of calibration curves taken at different GC runs. Figure D3 confirms this suggestion (the slopes of the solid line and the dashed line are respectively .96 and 1.0. The slopes in Figures D1 and D2 are respectively .85, 1.11 for the solid lines and 1.0 for the dashed lines.

Table D2

Comparison of the Peak Heights Obtained for Set No. 3 (h_3)
to the Peak Heights Obtained for Sets 1 and 2 (h_1 and h_2)

Phenol concentration mg/l	$[h_3 - h_1 /h_2] \times 100$	$[h_3 - h_2 /h_2] \times 100$
1	3%	20%
5	5.8%	--
10	7%	7%
20	13%	9%

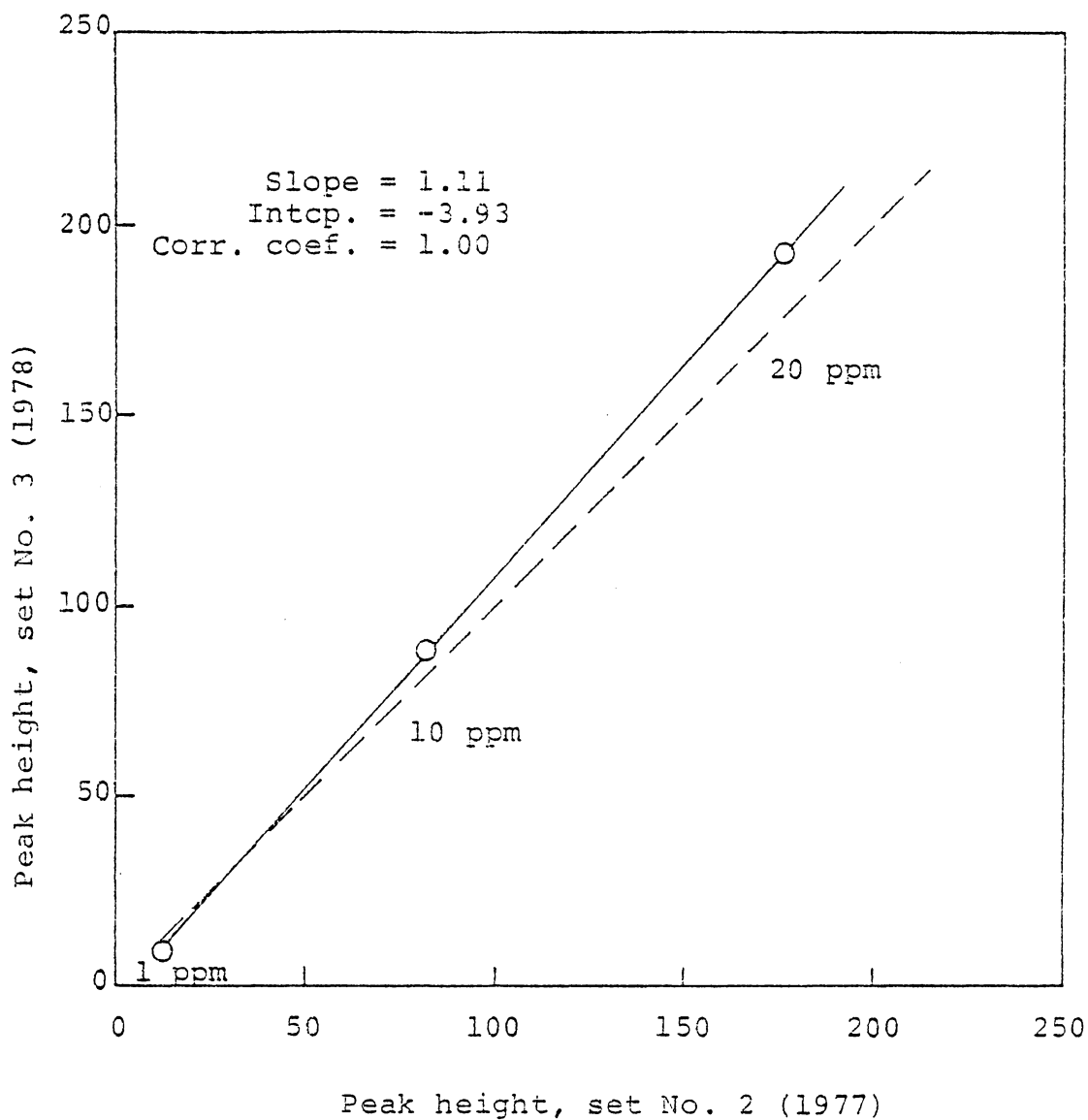


Figure D2. Plot of GC calibration data for phenol solutions obtained using the peak height technique; set No. 3 vs set No. 2. The dashed line represents the one-to-one relation one will expect if the GC response is reproducible for any run.

Table D3

Comparison of the Peak Heights Obtained for Set No. 3
 (h_3) to the Average Peak Heights of Sets 1 and 2.

Phenol concentration mg/l	$100 \times [h_3 - (\frac{h_1 + h_2}{2}) / (\frac{h_1 + h_2}{2})]$
1	14%
5	6%
10	6.7%
20	3.6%

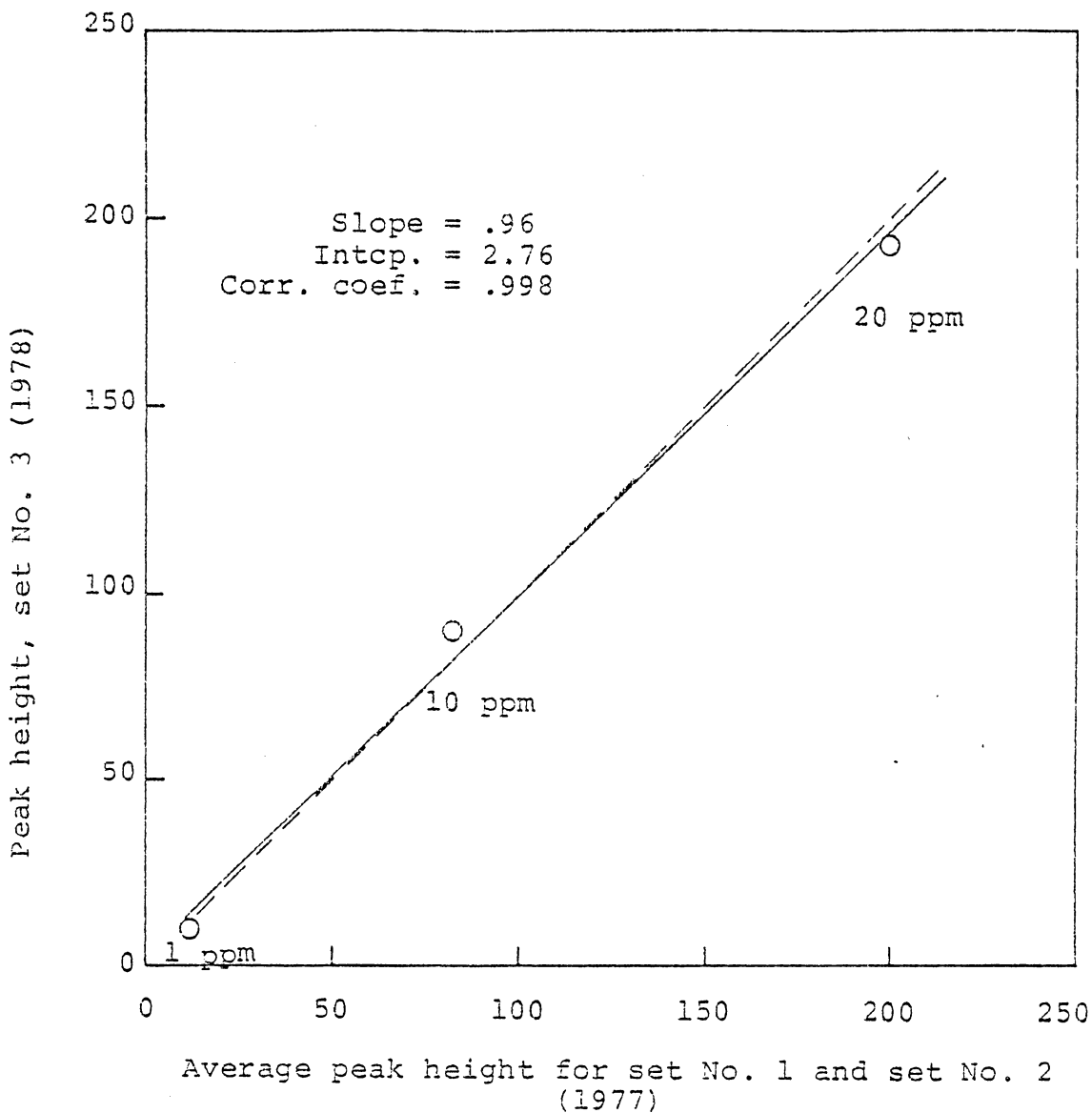


Figure D3. Plot of GC calibration data for phenol solutions obtained using the peak height technique; set No. 3 vs the average peak height for set No. 1 and set No. 2. The dashed line represents the one-to-one relation one will expect if the GC response is reproducible for any run.

The error generated by neglecting the first requirement is expected to be even less if the standard curve combines three sets of calibration data. Figure D4 shows the standard curve one will obtain when the three sets of data (Table D1) are considered as one set. The conclusions drawn during the biological regeneration of activated carbon study are at phenol concentrations of 50 mg/l and less. One will expect that the standard curve of Figure D4 can be used to determine the experimental data (phenol concentrations) obtained in this thesis, with an error of less than 10%. Table D4 displays the mean height, the standard deviation, and the relative error of the three sets of data.

2. unknown determination

The calibration data as well as the unknown data for the peak height technique and the internal standard technique are tabulated in Tables D5 and D6. Figure D5 is a plot of the peak height versus the concentration of phenol. The solid line is generated using the circular points (○). The solid points (●) represent the two unknowns. Figures D6 and D7 are, respectively, a plot of the relative peak height h_P/h_{EG} versus phenol concentration and the relative weight of peak areas W_P/W_{EG} versus phenol concentration. The solid points represent the unknowns. Table D7 tells us how accurately one can determine the actual concentrations

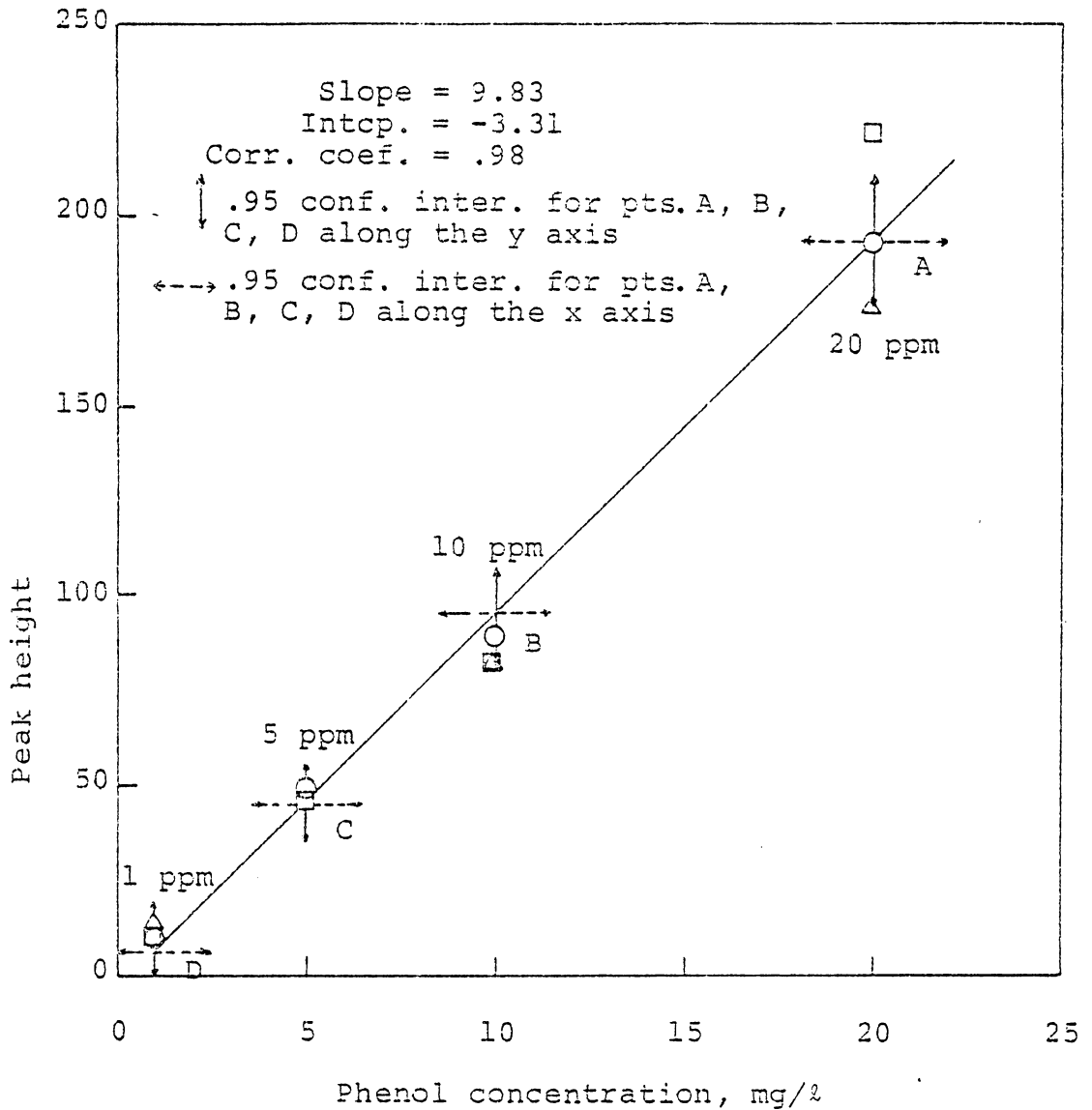


Figure D4. Plot of peak heights set No. 1 ($\square$), set No. 2 (Δ), and set No. 3 ($\circ$), versus phenol concentrations. Here the three sets of calibration data are considered as one set.

Table D4

Mean Height ($\bar{h}$), Standard Deviation (σ), and
Relative Error (σ_r) of Sets 1, 2, and 3

Phenol concentration mg/l	$\bar{h}$	σ	σ_r
1	10.9	1.3	11%
5	47.4	1.90	4%
10	85.3	3.25	4%
20	197.7	23.4	10%

Table D5

Calibration Data Using the Peak Height Technique

Phenol concentration mg/l	Peak height*	Peak height**
1	10	9.7
5	46	44.8
10	89	88
15	138	135
20	193	188
25	238	232
Unknown A	118	115
Unknown B	59	57.2

* The volume of the sample generating those peaks is 2.0 μ l.

** The volume of the sample generating those peaks is 1.95 μ l.

Table D6

Calibration Data Using the Internal Standard Technique.

The Internal Standard Chosen was Ethylene Glycol.

Phenol concentration mg/l	Relative peak heights, h_{ϕ}/h_{EG}	Relative weight of peaks. W_{ϕ}/W_{EG}
5	.152	.139
10	.42	.34
15	.71	.49
20	.96	.70
Unknown A	.60	.42
Unknown B	.197	.179

h_{ϕ}/h_{EG} = height of the peak generated by the phenol in the sample over the height of the peak generated by ethylene glycol.

W_{ϕ}/W_{EG} = weight of the area under the peak generated by the phenol in the sample over the weight of the area under the peak generated by ethylene glycol.

Table D7

Determination of the Unknown Concentrations by use of
the Peak Height Technique and the Internal
Standard Technique

Technique	<u>Unknown (mg/l)</u>		<u>% off from the actual value*</u>	
	A	B	A	B
Peak height	12.5	6.30	0	0.8
Relative height	13.2	5.81	5.6	7.0
Relative weight	12.6	6.00	0.8	4.0

* The actual value for: A is 12.5 mg/l.

B is 6.25 mg/l.

Note: Graduated cylinders were used in the preparation of the unknown solutions. A 5% error might have been generated.

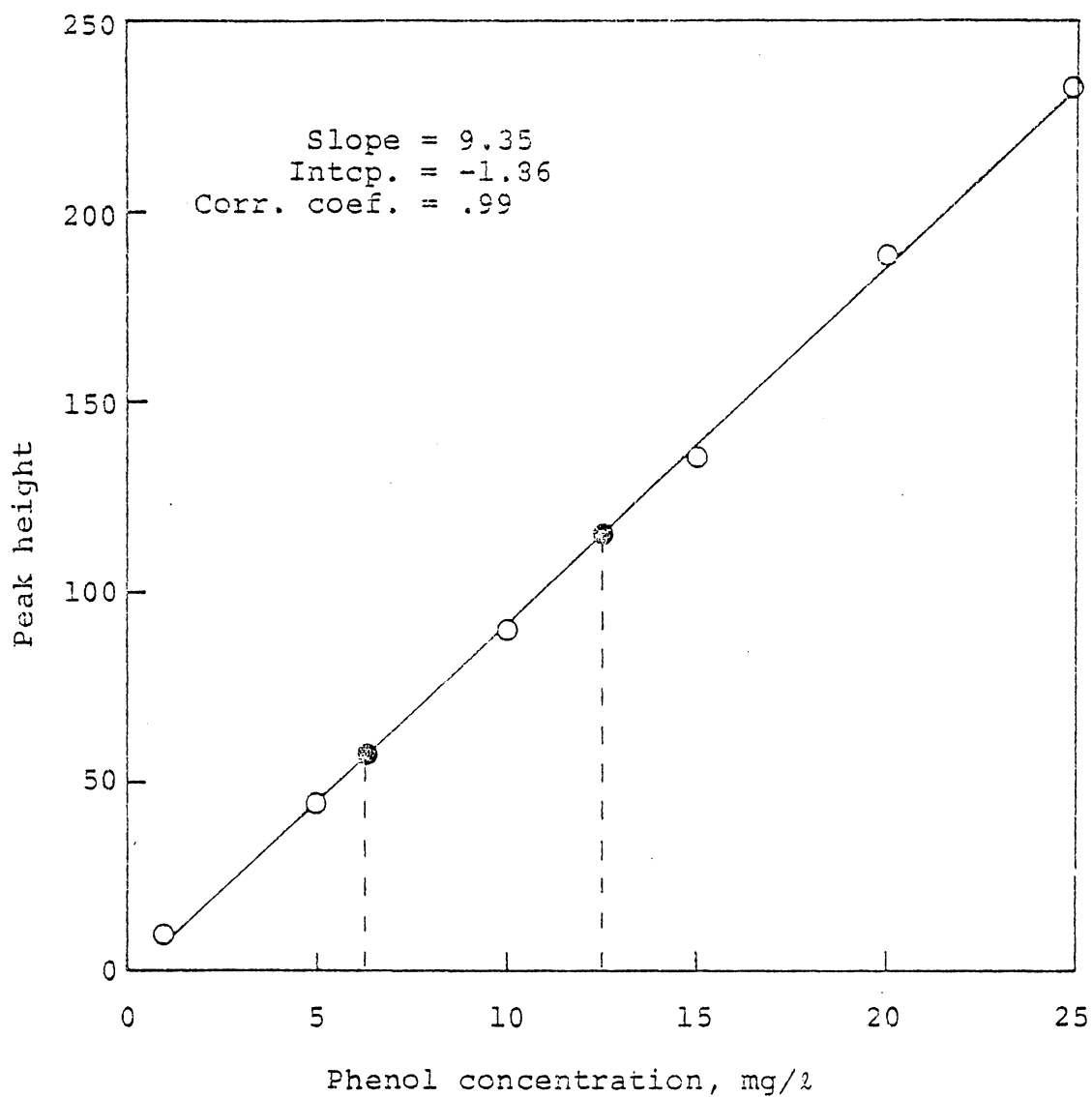


Figure D5. Peak height versus phenol concentration. The solid points represent the two unknowns as determined experimentally. The dashed lines indicate the actual values of the unknowns.

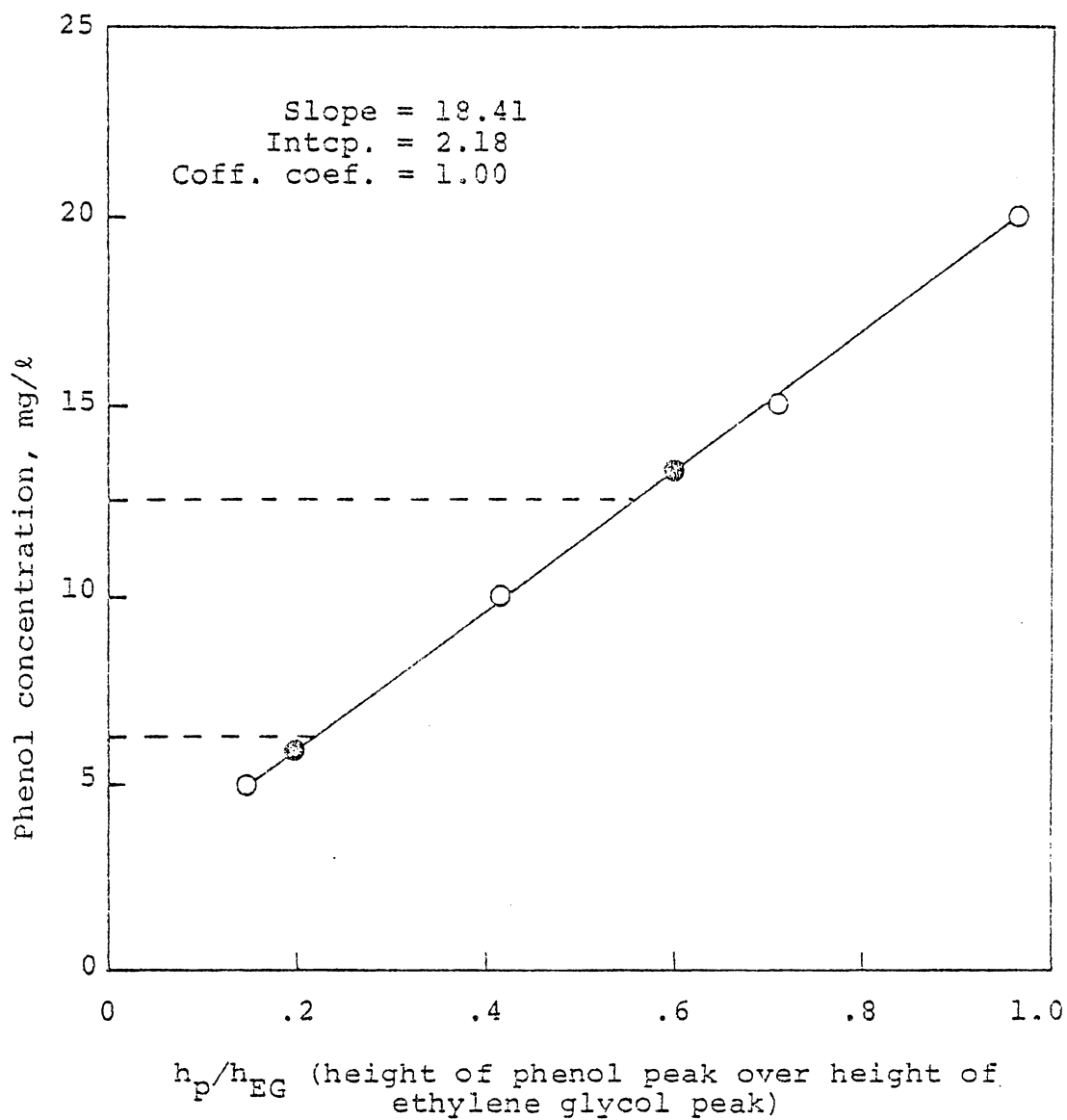


Figure D6. Phenol concentration versus relative peak height. The solid points represent the two unknowns as determined experimentally. The dashed lines indicate the actual values of the unknowns.

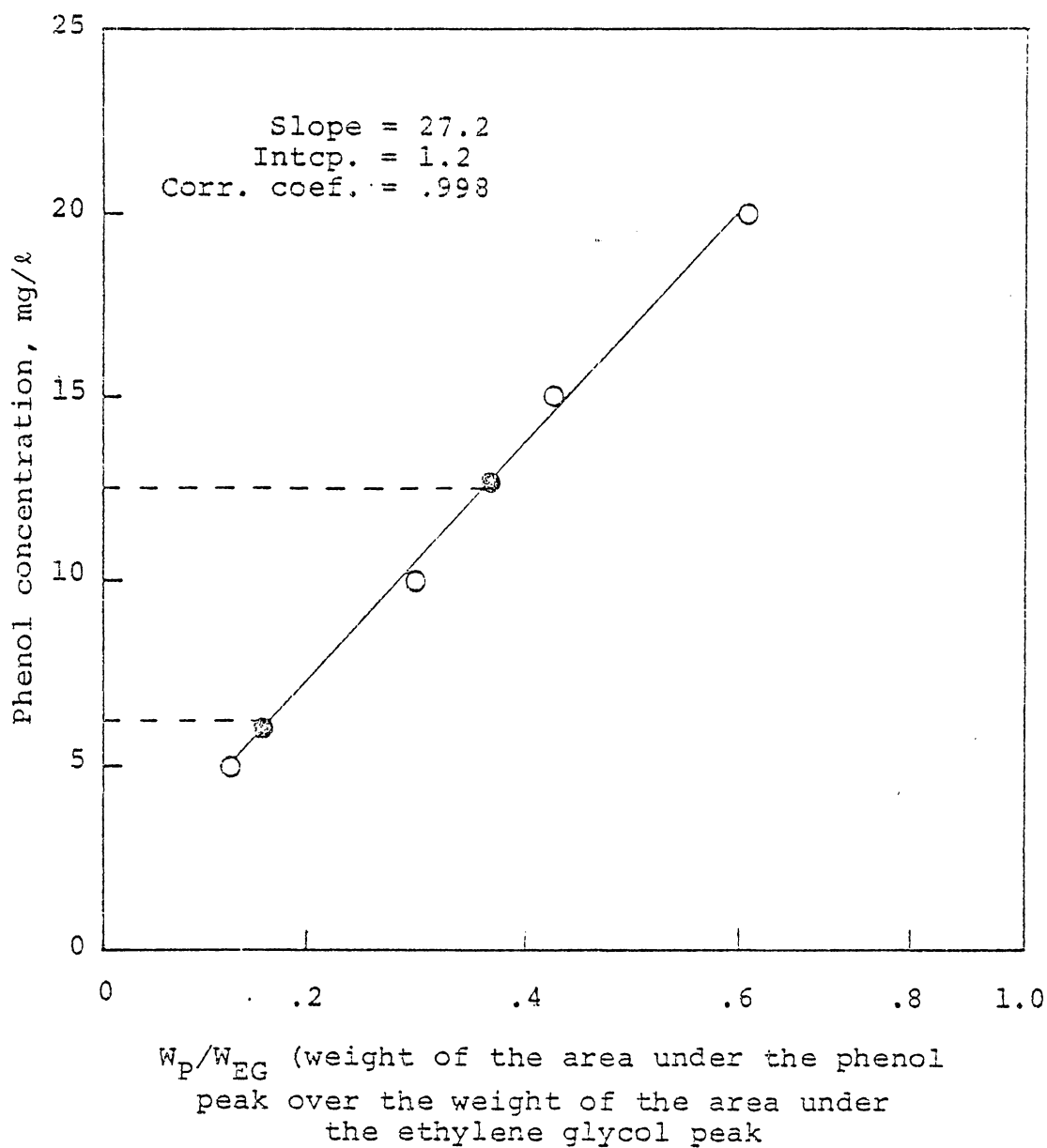


Figure D7. Phenol concentration versus relative peak weight of area. The solid points represent the two unknowns as determined experimentally. The dashed lines indicate the actual values of the unknowns.

of the unknowns, by use of the different techniques. It can be seen that the peak height technique is quite accurate. The internal standard technique gives better results when using the relative weight of peaks instead of the relative height. The difference in accuracy between the peak height technique and the relative weight technique may not be significant because of the technique used in preparing the unknowns (graduated cylinders were used in the preparation of the unknown solutions and an error of 5% might have been easily generated).

3. Internal standard technique versus peak height technique

A plot of h_P/h_{EG} , W_P/W_{EG} versus peak height (set No. 3) is shown in Figure D8. The internal standard technique has the following advantages.

- a. Only one standard curve is needed. This curve does not have to be repeated for each GC run.
- b. The volume of the samples injected doesn't have to be the same.

Those two advantages make the internal standard technique superior to the height technique.

5. Final note

Butanol, hexanol, heptanol, glycol were tried as internal standards to assay phenol solutions. They proved to be

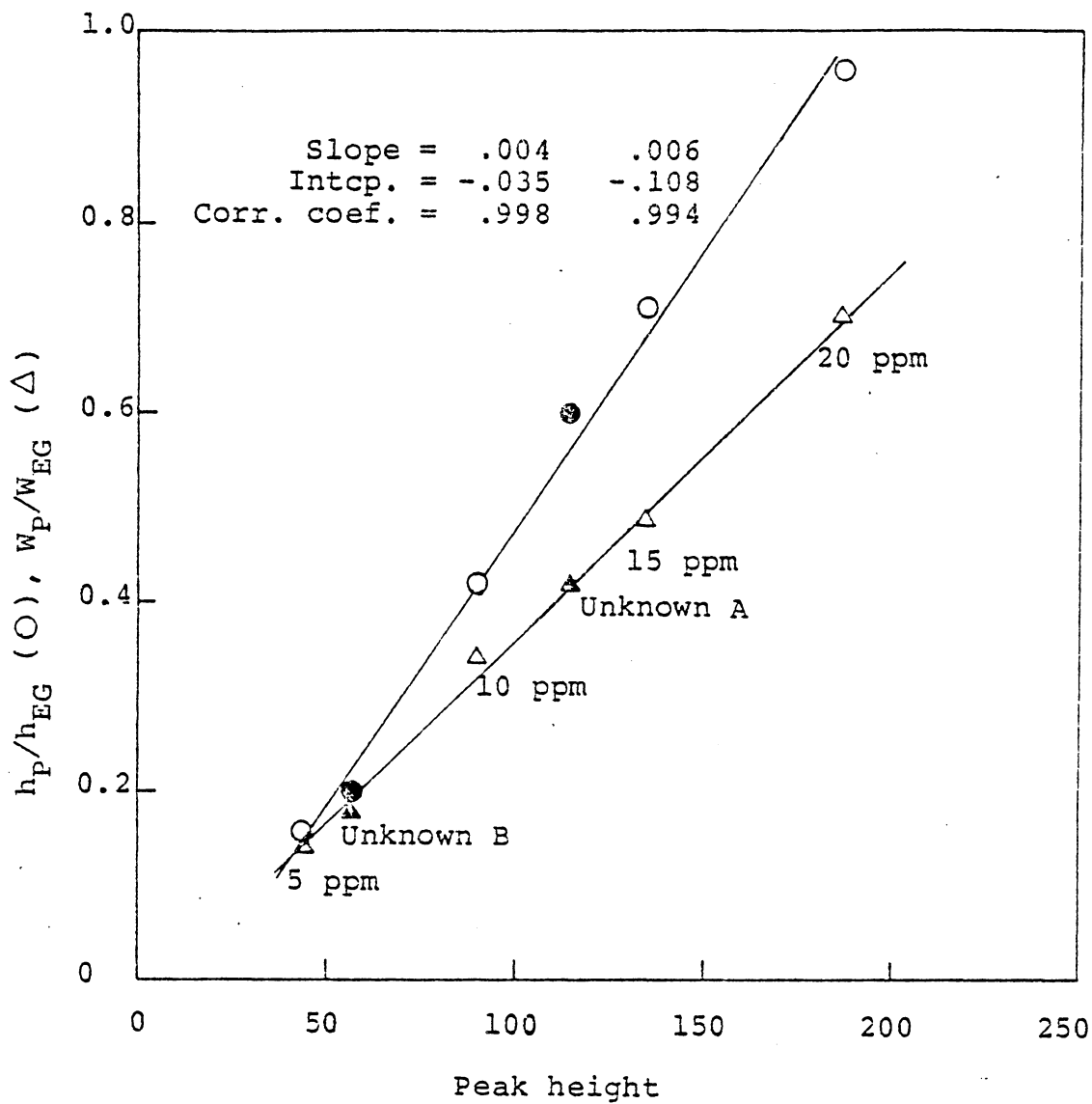


Figure D8. Relative peak height, h_p/h_{EG} (O), and relative weight of peak area, W_p/W_{EG} (Δ) versus peak height.

unacceptable because of their high vapor pressures.

p-nitrophenol failed to be a good internal standard because of its pKa. The pK_a value of its dissociation constant is 7.2 which is very close to the pH of the phenol solution we are dealing with. One expects the p-nitrophenol to dissociate, something to be prevented, when dealing with internal standards.

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BIOLOGICAL REGENERATION OF ACTIVATED CARBON

by

Sabah A. Atieh

(ABSTRACT)

A bioreactor using a tapered fluidized bed was built, characterized and tested. The test consisted of biologically removing phenol from an artificial wastewater in the absence of activated carbon. The data collected during this fermentation were logged on a PDP 11/40 minicomputer. Variables such as oxygen and carbon dioxide percent by volume evolved, the dissolved oxygen concentration, temperature, pH and volumetric air flow rate were monitored. The rate of phenol disappearance was also determined.

This system was then used to study the biological regeneration of activated carbon. The bioregeneration study showed that up to 67% of the activated carbon adsorptive capacity could be recovered. It also proved that the rate of phenol biodegradation was higher in the presence of activated carbon than in its absence.