POWDERED ACTIVATED CARBON IN BIOLOGICAL REACTORS

by

Gregory Thomas Farrell

and

Earnest F. Gloyna

CRWR 176

Center for Research in Water Resources
Bureau of Engineering Research

THE UNIVERSITY OF TEXAS AT AUSTIN

August 1980

SUMMARY

The addition of powdered activated carbon (PAC) to the acitivated sludge process (ASP) is presently being studied as a means of improving the removal of residual organics from industrial wastewaters. The effectiveness of the PAC-ASP system must be evaluated for each wastewater.

The wastewater evaluated in these studies contained aldehydes and other fairly bioresistant organic materials. Bench-scale, aeration-tanks, both batch and continuous feed, were used to evaluate the treatability of these wastewaters.

The addition of PAC improved the performance of the activated sludge process. This improvement varied with the strength of the organics in the wastestream.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	iii
SUMMARY	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
INTRODUCTION	1
Objective	2
Scope	2
LITERATURE EVALUATION	3
PAC Plus Activated Sludge	3
Economics of PAC and Activated Sludge	5
Benefits of Adding PAC to the Activated Sludge System	5
Pretreatment Requirements	7
Carbon Handling	9
Wasting vs. Regeneration of PAC	9
Adsorption Mechanics and Kinetics	10
Kinetics of the Activated Sludge System	15
Kinetics of the PAC and Activated Sludge Treatment System	21
DESCRIPTION OF EQUIPMENT AND PROCEDURES	29
Reactor Types	29
Aeration Technique	29
Feeding of Reactors	29
Temperature	32
Nutrients	32
Waste	32
Seeding the Reactors	32

TABLE OF CONTENTS
(Continued)

Page

Sludge Ages 34
PAC Type 34
Parameters Tested 34

RESULTS AND DISCUSSION 37

Optimum Detention Time Experiment 37
Optimum PAC Dose Experiment 37
Experiment to Test the Effects of Adding PAC to the Activated Sludge Process 43

CONCLUSIONS AND RECOMMENDATONS 57

Conclusions 57
Recommendations 57

BIBLIOGRAPHY 58

LIST OF TABLES

Table Number	Description	Page
1	Treatment Costs for PAC Plus Activated Sludge	6
2	Removals For Different Wastes Treated by Activated Sludge and PAC Plus ASP	8
3	Average Raw Waste Characteristics	33
4	Optimum Detention Time Test Results For Waste "A"	39
5	Optimum Detention Time Test Results For "B"	40
6	Optimum Carbon Dose Experiment Results for Waste "A"	44
7	Optimum Carbon Dose Experiment Results for Waste "B"	45
8	Waste "A" Experimental Results For Activated Sludge With No PAC Added	50
9	Waste "A" Experimental Results For Activated Sludge and 200 mg/L PAC	51
10	Waste "A" Experimental Results For Activated Sludge and 400 mg/L PAC	52
11	Waste "B" Experimental Results For Activated Sludge With No PAC Added	53
12	Waste "B" Experimental Results For Activated Sludge and 200 mg/L PAC	54

LIST OF FIGURES

Figure Number	Description	Page
1	Linear Forms of Adsorption Isotherm Equations	14
2	Completely Mixed, Continuous Flow Activated Sludge System	16
3	Determination of k and K Coefficients	19
4	Determination of k_d and Y Coefficients	20
5	PAC and Activated Sludge Process	23
6	Reactors Used for Experiments	30
7	Water Trap Used to Filter Compressed Air	31
8	Typical Millipore Filter Apparatus Set-Up	36
9	Experiment Flow Chart	38
10	Change in COD Concentration in Waste "A" With Respect to Detention Time	41
11	Charge in COD Concentration in Waste "B" With Respect to Detention Time	42
12	Effect of Mixed-Liquor Carbon Concentration on Effluent Soluble COD For Waste "A"	46
13	Effect of Mixed-Liquor Carbon Concentration on Effluent COD Removal for Waste "B"	47
14	Effect of Mixed-Liquor Carbon Concentration on Effluent Soluble TOC for Waste "B"	48

LIST OF FIGURES
(Continued)

Figure Number	Description	Page
15	Performance of Activated Sludge Process and Activated Sludge Process Plus Powdered Activated Carbon When Used to Treat Waste "A"	55
16	Performance of Activated Sludge Process and Activated Sludge Process Plus Powdered Activated Carbon When Used to Treat Waste "B"	56

INTRODUCTION

In recent years the world has experienced an increasing demand for manufactured goods. Keeping with this demand, industrial growth has occurred both in the cities and in the rural areas. As more industrial and municipal wastewaters accumulated, it became apparent that additional environmental control measures had to be taken.

In 1972, Congress took additional steps towards regulating the quality of wastewaters that were released to the environment with the Water Pollution Control Act (PL 92-500).(1) In 1977, this act was ammended as the Clean Water Act (PL 95-217). In this measure, it was stated that industries had until 1984 to develop and implement the best available technology economically achievable (BATEA) in treating their wastewaters. This legislative action also gave the Environmental Protection Agency (EPA) the authority to set effluent standards, and to enforce these limitations. (1,2) Congress stated its intent by enforcing this law: "To restore and maintain the chemical, physical and biological integrity of the Nation's Water".(2)

For many of the industrial plants whose wastes consisted of concentrated pollutants, the most feasible method of achieving BATEA standards was considered to be secondary biological treatment, followed by granular activated carbon (GAC) absorption.(1) While providing high degrees of pollutant removal, this process often requires large capital and operational costs. In an attempt to minimize treatment costs, different methods of achieving BATEA standards have been researched.

One treatment scheme providing considerable potential involves the addition of powdered activated carbon (PAC) directly into the activated sludge basin. In theory, this process would provide the positive purification aspects of treatment with activated carbon in addition to activated sludge treatment, without adding any sizeable capital or operating costs. It is this process which is evaluated herein.

OBJECTIVE

The objective of this research was to evaluate the process of adding PAC to the acitivated sludge basin as a means of treating a particular industrial waste.

SCOPE

In evaluating the powdered activated carbon (PAC) plus activated sludge process (ASP), a literature search and analysis was performed, along with several laboratory experiments.

Treatability studies involved one industrial waste. Comparisions were made using the activated sludge process and the combination of PAC plus ASP. All experiments were conducted at controlled temperature ($25 \pm 2^{\circ}C$) and nutrient conditions. Both batch and continuous feed were utilized.

The chemical oxygen demand (COD) served as the primary means of evaluating treatment. This analysis was performed as described in Standard Methods for the Examination of Water and Wastewater.(3) In addition, total organic carbon (TOC) analyses were performed as outlined in Methods for Chemical Analysis of Water and Wastes.(4)

LITERATURE EVALUATION

Industrial wastewater treatment is often a complicated process involving many variables. Some industrial waste streams vary greatly with respect to flow rate and chemical make up. This variability in wastestreams often requires that treatment techniques other than typical secondary biological methods be utilized to achieve required effluent limitations.

Activated carbon, which removes pollutants from the wastestream through adsorption, rather than biological utilization, has proven useful in the treatment of some wastes that are considered to be bioresistant or toxic. Hundreds of different types of activated carbon have been developed to aid in the treatment of industrial wastes.(5) Until recently, however, activated carbon was used primarily in the granular form which resulted in high capital and operating costs for those industries treating with the carbon.(6,7) These high costs may have prevented activated carbon from being utilized to its fullest potential. The use of activated carbon in wastewater treatment may increase in the future, however, if early studies on the use of PAC prove to be accurate indicators of its economic feasibility.

PAC Plus Activated Sludge

Laboratory research, as well as actual treatment plant case histories, have shown that use of activated carbon improves process performance. These imporvements include increased amounts of pollutants removed from the wastestreams, as welll as improved process stability.(1,8,9,10) However, the high costs often associated with the use of granular carbon columns may have limited the utilization of this process in wastewater treatment.(21) The use of PAC, on the other hand, has proven to be a less costly alternative. In some cases the addition of PAC to the activated sludge system has decreased treatment costs.(7,11,12)

The PAC is added directly to the activated sludge system, in either dry or slurry form. It passes through the aerator along with the wastestream, until it flows into the final clarifier. The settled carbon, along with the materials it has adsorbed, is either reprocessed or wasted.

The basic aerobic oxidation process which occurs during the activated sludge process involves the uptake of organics by microorganisms, utilizing oxygen and nutrients (phosphorous and nintrogen). These organics are then removed from the liquid (by settling), providing a suitably treated wastewater.

There are several mechanisms, as described by Adams,(11) to explain how PAC improves the activated sludge process:

a. Carbon acts as an adsorbent to concentrate the pollutants, oxygen and bacteria. Since the reaction depends on the concentration of the reactants, adsorption serves to drive the reaction further towards completion.(11)

b. The effective retention time is increased. Without the adsorption action of PAC the residence time is limited to a few hours. With PAC the refractory compound may be recycled and kept in the sludge mass for a much longer total time. Using the PAC concept, less readily degraded materials are kept in contact with adapted bacterial species longer, allowing time for the bacteria to more completely degrade the more complex waste material.(11)

c. The settled carbon is continuously regenerated by biological action. Diological organics degrade and digest the adsorbed pollutants, thereby renewing the adsorptive surface.(11)

d. Carbon improves solids settling in secodary clarifiers. For example, carbon will increase the weight of the sludge and improve sedimentation. When the organic loading is light resulting in dispersed biological suspensions, carbon acts as a seed for flocculation and thereby active biological solids are recovered through sedimentation.

e. Rapid adsorption of toxic compounds by carbon protects a biological system from periodic upsets.(11)

Economics of PAC Plus Activated Sludge

When a treatment system is upgraded through the addition of carbon it is often assumed that costs of treatment will increase. However, chemicals required to keep ordinary activated sludge plants -- in compliance with regulations in certain cases have served to lower the relative total cost of PAC and ASP treatment.(7,11,12) One way that the addition of PAC saves on costs is due to the carbons ability to reduce or eliminate aerator foaming problems.(7,11,12) In many cases, this foaming must be controlled through the use of commercial defoaming chemicals. Since the PAC eliminates the foam, it eliminates the need for the defoamers. Another cost saving characteristic of the PAC is its ability to serve as a seed for flocculation.(7,11,12) This can reduce or eliminate the need for coagulants. The combined PAC and activated sludges are heavier and denser than ordinary biological sludges. The sludges containing PAC dewater more readily and reduce solids handling costs.(7,8,11,12) Finally, an activated sludge treatment facility can be upgraded by the addition of PAC with little capital expenditure -- no new basins need to be built, no additional land is required, and no additional power is needed. The carbon is simply added to the existing system in dry or slurry form.

When all costs of chemicals, land, manpower, construction and power are considered, the addition of PAC may be a cost effective method of attaining a high quality effluent from an industrial wastewater treatment system. Table 1 presents the costs of treating several different types of industrial wastes with the PAC plus ASP.

Benefits of Adding PAC to the Activated Sludge System

A summary of the benefits which are attained by adding PAC to the activated sludge system, as reported by DeJohn and Adams,(7,12) and Adams,(11) and not including those benefits discussed in the section above on the economics of PAC are:

Table 1
Treatment For PAC + ASP

Type of Waste	Treatment Costs (¢/1,000 gal)	Reference
Petroleum Refinery	1.7 - 8.1	1, 13
Dye and Finishing Plant	2.3 - 5.3	11

a. Improved organic pollutant removals (BOD, TOC and COD);
b. More uniform operation and effluent quality, particularly during periods of widely varying organic and hydraulic loads;
c. Adsorption of organics, such as detergents, oils and dyes that are refractory to the biological system;
d. Protection of the biological system from toxic waste components;
e. More effective removal of phosphorous and nitrogen;
f. Greater treatment flexibility than other methods since carbon dosages can be varied to match waste strengths and flow rates.

The important factors that will determine how efficient the PAC plus ASP system works are: (a) the type of waste being treated, (b) the amount of waste, (c) the carbon type, and (d) the PAC dosage. Research has shown that this process can be applied to many different industrial wastes successfully. A summary of results of using PAC to increase the efficiency of the activated sludge sytem is given in Table 2.

Pretreatment Requirements

Depending on the individual cases and the particular waste, pretreatment practices will vary from plant to plant. There are, however, certain general pretreatment requirements which should be performed in order to permit proper conditions for the most efficient treatment of the wastewater.

Primary treatment should be utilized to remove as much solid material as possible previous to the wastestream entering the aeration tank. These solids can overload the aerators if they are left in the system, while typing up some of the carbon that otherwise would be available to remove organics.

Equalization of flow may be needed to minimize fluctuations in flow and waste concentration.

Table 2
Removals For Different Wastes Treated By Activated Sludge and PAC Plus Activated Sludge

Type of Waste and Treatment Process	Experiment Scale	Carbon Dose (mg/L)	BOD Reduction (Percent)	COD Reduction (Percent)	NH_3-N Removal (Percent)	Phosphorus Removal (Percent)	Reference
Oil Refinery							
ASP	Pilot Plant	0	--	68.2	----	--	1
PAC + ASP	Pilot Plant	4,000	--	86.0	----	--	1
ASP	Pilot Plant	0	--	68.3	98.1	--	6
PAC + ASP	Pilot Plant	3,200	--	87.6	99.2	--	6
Dyeing and Finishing							
ASP	Full Scale	0	72.0	----	----	--	11
PAC + ASP	Full Scale	900	89.0	----	----	--	11
Acidic Dye and Fine Chemicals Manufacture							
ASP	Full Scale	0	--	27.0	----	43	13
PAC + ASP	Full Scale	85	--	57.0	----	85	13
Poultry Processing							
ASP	Full Scale	0	97.0	----	----	--	13
PAC + ASP	Full Scale	1,000-2,000	99.0	----	----	--	13
Municipal Plus 10 Percent Knitting Mill							
ASP	Full Scale	0	90.0	74.0	----	--	13
PAC + ASP	Full Scale	400	96.0	76.0	----	--	13
Night Soil							
ASP	Pilot Plant	0	96.4	69.5	----	--	14
PAC + ASP	Pilot Plant	9,960	99.4	96.2	----	--	14

If the wastestream contains oils or greases, it should be pre-treated with oil removal or separator devices before it enters the aeration basin.(6) A build-up of oily substances can reduce the overall oxygen transfer efficiency and inhibit both the nitrifying and organic carbon utilizing organisms.

Carbon Handling

One of the positive aspects of treating waste by adding PAC to the activated sludge system is the minimal amount of operation and maintenance required for the PAC addition. The exact manner or location at which the PAC is added to the activated sludge system is not critical. The carbon can be added at any easily accessible point, whether this be into the aeration basin directly, into the sludge return line, influent channels, or even through the secondary clarifier.(12) The carbon can be added as a batch in either a dry or slurry form at any convenient time perhaps during the daily maintenance schedule.

Handling the PAC can be messy, therefore, it is preferable that the operator not come in direct contact with the carbon. One type of useful carbon feed bag is described by Adams.(11)

Wasting vs. Regeneration of PAC

When research was begun on the addition of PAC to the activated sludge system, it was with the basic assumpton that the carbon would be wasted along with the excess biological sludge. Although this practice of wasting may appear to be wasteful, it was found to be economical, especially as the sludge age increased. The carbon that remains in the recycled sludge is biologically regenerated to a certain degree, allowing it to "sorb" additional materials. In order to replace the carbon that is wasted with the sludge, virgin PAC is added to the system.

With larger applications, the amount of virgin carbon needed as makeup can become sizable and regeneration of carbon becomes cost efficient. One method suggested for recycling PAC is the wet-air oxidation process. This method had been tested successfully and full-scale units are in operation.(14,15,16) In this process the PAC containing sludges is concentrated in a gravity thickener. The thickened sludge mixture is then pumped to the regeneration process where oxygen is added, and the combined oxygen-slurry mixture is passed through heat exchangers. Thus, the carbon is regenerated and the biological matter is destroyed.(14) This process is autothermal, so the only heat required is that from a steam generator used for start-up.

The quality of the regenerated carbon obtained using the wet oxidation process is relatively high, according to Meidl, et al.(14) A full-scale PAC-ASP plus wet oxidation regeneration system is presently in operation in Kimitsu, Japan. This plant has been studied, and the results show that, compared to virgin carbon, the regenerated carbon exhibits acceptable adsorbitive qualities. While the adsorbtive efficiency was slightly lower for the regenerated carbon, the regeneration proved to be adequate for the effluent quality that was desired. However, if it was determined that the regenerated carbon should have a higher adsorbtion efficiency, an increase in the temperature during the wet oxidation process would improve the carbon's adsortive qualities.

The total carbon losses due to the wet oxidation have been found to be less than 5 percent.(14) Virgin carbon is added to the system to make up for the lost carbon.

The treatment of industrial wastestreams through the addition of PAC to the activated sludge system has proven to be a cost-effective method. Whether the carbon should be regenerated or wasted depends on the amount of waste to be treated, the type of waste, and the effluent quality desired. These factors must be studied closely for each application of the PAC plus ASP so that the most economical design can be utilized.

Adsorption Mechanics and Kinetics

The phenomenon of adsorption occurs in an aqueous system when a solute (absorbate) moves out of solution and is accumulated in the absorbent.

In general, high surface area and pore structure are the prime considerations in adsorption of organics from water.(17)

In a system where the absorbent is a solid, and the absorbate is a material in solution (such as with the PAC process), adsorption of the solute onto the solid occurs as the result of one of two properties of the system. These properties include the lyophobic (solvent-resisting) character of the solute, and the degree of affinity of the solute for the solid. Adsorption, and the degree to which a solute is adsorbed, results from the combined action of these two forces.

The first of these properties involves the extent of the chemical compatibility between a solvent system and the solute that it is dissolved in. The more hydrophylic (solute-liking) a solute is, the less attracted it will be towards moving out of solution. On the other hand, a hydrophobic (water-disliking) material will be adsorbed more readily.(5)

The second property is the result of a specific affinity of the solute for the solid. Due to different affinities, there are three separate ways in which particles are adsorbed onto the solid. These adsorption types are physical, chemical, and electrostatic force attraction.

The physical adsorption process occurs as folows:

a. Molecules in the interior of any solid are subjected to equal forces in all directions, while molecules at the surface are subjected to unbalanced forces.

b. The resulting inward forces can only be satisfied if other molecules, usually gaseous or liquid, become attached to the surface.

c. These attractive forces are the same as those responsible for surface tension and condensation in liquids and are known as Van der Waal's forces. This physical adsorption is relatively weak in nature, thus molecules which are adsorbed in this manner can be easily removed from the surface of the absorbent.(18)

Chemical adsorption occurs when a chemically bound molecular layer of the absorbate on the surface is formed through residual valence forces of the surface molecules. The resulting bond is much greater in strength than the bond formed during physical adsorption, and it is much more difficult to separate.(19)

The third type of adsorption, electrostatic adsorption, describes the influence of electrical attractive forces responsible for adsorbing solutes on activated carbon. Also, electrical attraction between negatively charged carbon particles and postively charged adsorbate molecules or ions reduces barriers to diffusion, and thus increases the adsorption efficiency.(19)

The mechanisms by which adsorption occurs when a liquid containing dissolved components comes in contact with activated carbon can be described in the following manner. First the adsorbate is transported to the exterior surface of the adsorbent. Next, most of the adsorbate, save a small amount which is adsorbed at the exterior surface of the adsorbent, is diffused into the carbon pores. Here the solute is adsorbed onto the interior surfaces of the adsorbent.(19)

In the adsorption process, the adsorbate will be removed from a solution until an equilibrium occurs between the adsorbate in the adsorbent and the solute in the solvent. At this point, there is a defined distribution of solute between the liquid and solid phases. This distribution can be represented by an adsorption isotherm, where the amount of solute adsorbed per until weight of solid absorbent (q_e) is expressed as a function of the concentration of solute remaining in solution at equilibrium (C) at a fixed temperature. These isotherms give a functional expression for the variation of adsorption with concentration of adsorbate in solution at constant temperature.(5)

<u>The Langmuir Equation</u>: One type of adsorption isotherm developed is the Langmuir isotherm. This method assumes that maximum adsorption of the adsorbate occurs on the adsorbent surface, with a constant energy of adsorption, with no movement of the absorbate in the plane of the surface.

This Langmuir isotherm is represented by Equation 1.

$$q_e = \frac{Q^o \, bC}{(1 + bC)} \qquad (1)$$

where q_e is the number of moles of solute adsorbed per unit weight at concentration C, Q^o is the number of moles of solute adsorption, and C is the measured concentration in solution at equilibrium.

A linear form of Equation 1, as illustrated in Figure 1(a), is Equation 2,

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{(bQ^o)} \frac{(1)}{C} \qquad (2)$$

The Langmuir equation can be used to describe equilibrium conditions for adsorption, as well as to provide the parameters Q^o and b which are useful in the comparison of different systems.(5)

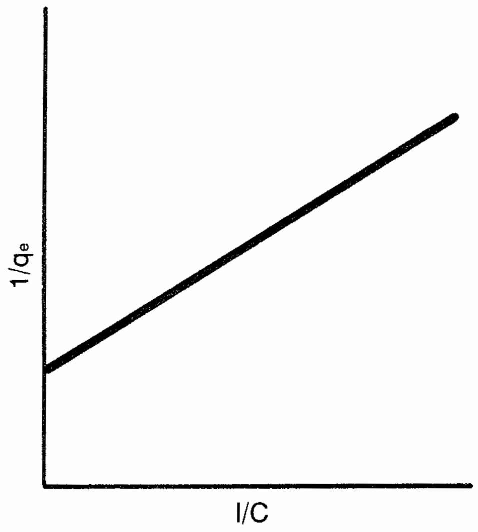
<u>The Freundlich Equation</u>: Another adoption of the Langmuir Equation which describes isothermal adsorption is the Freudlich Equation. In this approach allowance is made for heterogeneous surface energies where b (Langumuir's energy term) varies with surface coverage due to variation in heat of adsorption. The Freundlich Equation is represented by Equation 3,

$$q_e = K_F \, C^{1/n} \qquad (3)$$

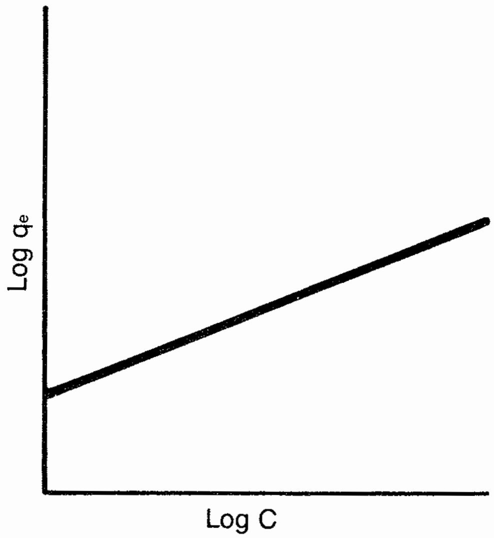
where K_F and n are constants which must be evaluated for each solute and temperature.

Equation 3 is usually expressed in a logarithmic form, Equation 4,

$$\log q_e = \log K_F + \frac{1}{n} \log C \qquad (4)$$



A. Langmuir



B. Freundlich

FIGURE 1 LINEAR FORMS OF ADSORPTION ISOTHERM EQUATIONS

Using this form, adsorption data can be plotted, yielding a straight line, Figure 1(b).

The Freundlich Equation can be adjusted to represent the adsorption of pollutants onto PAC, Equation 5,

$$q_e = (C_o - C)/D_o \qquad (5)$$

where C_o is the initial concentration of the pollutant, and D_o is the carbon dosage.(5) Substituting Equation 5 into Equation 4 yields

$$\log \frac{C_o - C}{D_o} = \log K_F + \frac{1}{n} \log C \qquad (6)$$

Kinetics of the Activated Sludge Sytem

The activated sludge process (ASP) is illustrated in Figure 2. In order to model the activated sludge process, it is assumed that all organic removal that occurs during the process will occur only in the aeration basin, and that none will occur in the settling tank. Since this first assumption is being made, it must also be assumed that the total biological mass in the system includes only the biological mass in the aeration tank.

For this system, the biological detention, or sludge age ($_c$) is shown in Equation 7,

$${}_{c} = \frac{XV}{Q_w X_w + (Q - Q_w) X_e} \qquad (7)$$

where

Q_w = flow rate of waste solids which is removed from the system (volume per time),

X = concentration of biomass (sludge) in the aeration tank (mass per volume),

X_w = concentration of bacteria in the underflow from the settling tank (mass per volume),

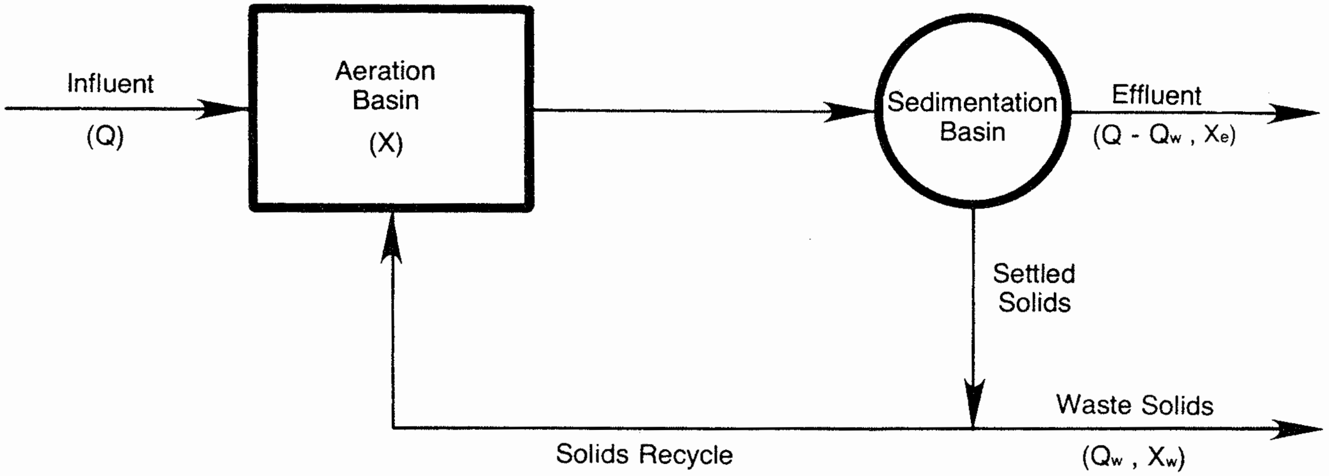


FIGURE 2 COMPLETE-MIXED, CONTINUOUS-FLOW ACTIVATED SLUDGE PROCESS

V = volume of the aeration basin,

Q = flow rate of the wastestream (volume per time), and

X_e = biomass (sludge concentration of the settling tank effluent (mass per volume).(20,21)

Since the amount of biological solids leaving the system through the overflow of the clarifier ($Q_x C_c$) is small when compared to the amount removed by solids wasting (Q_w x X_w), Equation 7 can be rewritten as Equation 8,

$$ {}_c = \frac{V}{Q_r} \qquad (8)$$

Thus, it can be seen that the sludge age can be varied independent of the reactor hydraulic detention time. Because of this, long sludge ages (${}_c$) can be used to attain high organic removal efficiencies, while the sytem is operating to minimize reactor volume.(20,21) This relationship between the sludge age, the maximum yield coefficient, the substrate utilization and endogenous decay rate is expressed in Equation 9.

$$\frac{1}{{}_c} = YU - k_d \qquad (9)$$

where:

Y = maximum yield coefficient measured during a period of log growth, it is the ratio of the mass of cells formed to the mass of substrate utilized,

K_d = endogenous decay coefficient (time^{-1}), and

U = the specific substrate utilization rate.

$$U = \frac{S_o - S}{X} \qquad (10)$$

$$U = \frac{KS}{K_s + S} \qquad (11)$$

S_o = the concentration of substrate introduced into the aeration basin,

S = the concentration of the substrate upon leaving the activated sludge system, and

= the hydraulic detention time of the aeration tank,

K_s = the half velocity constant, the substrate concentration at one-half the maximum growth rate, and

k = the maximum rate of substrate utilization per unit mass of microorganisms.(20)

If Equation 10 and 11 are equated, the result is Equation 12.

$$\frac{kS}{K_s + S} = \frac{S_o - S}{X} \tag{12}$$

Taking the inverse of expression Equation 12 results in Equation 13.

$$\frac{X_o}{S_o - S} = \frac{K_s}{k}\frac{1}{S} + \frac{1}{k} \tag{13}$$

Equation 13 can be used to determine the k and K_s coefficients for a given wastestream. These coefficients can be determined by performing laboratory experiments. The waste is fed into several bench-scale, continuousflow reactors which contain acclimated microorganisms. The test variables are X, $_c$, and $_h$. The influent and effluent BOD, COD, or TOC concentrations must be measured. Also, the volatile soilds in the aeration basin must be measured.

Using these data in conjunction with Equation 13, it is possible to calculate values for k and K_s. The data are plotted as shown in Figure 3. The numerical value of the y-intercept is equal to 1/k, while the slope of the line is equal to K_s/k. From these, the values of k and K_s can be determined. Using the data from the experiment described above the values of Y and k_d can be determined as shown in Figure 4. The value of Y is equal to the slope of the graph, while k_d is found by multiplying the Y-intercept by -1.(20)

By substituting the values of k_d, k, K_s, and Y determined above into Equation 11 and Equation 12, an activated sludge system can be designed.

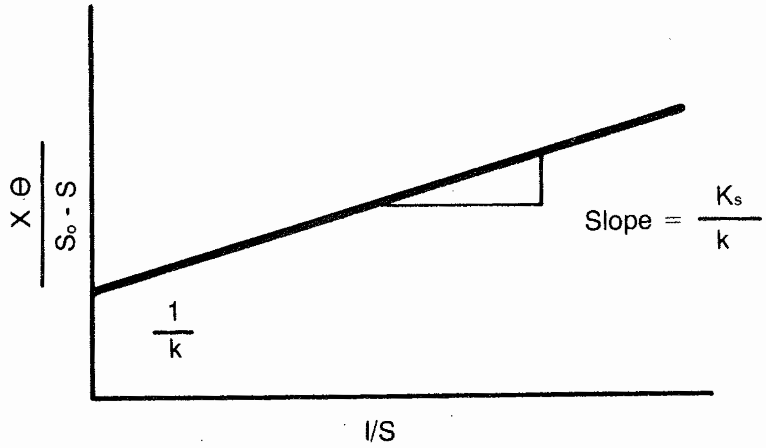


FIGURE 3 DETERMINATION OF k and K_s COEFFICIENTS

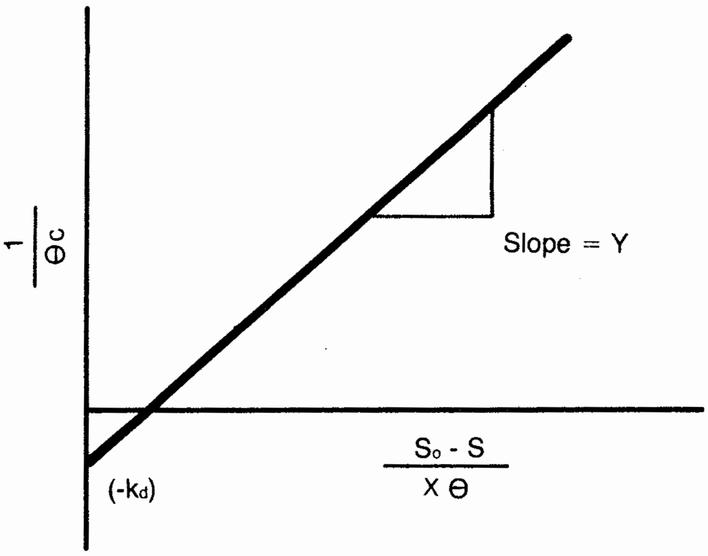


FIGURE 4 DETERMINATION OF k_d AND Y COEFFICIENTS

Kinetics of the Powdered Activated Carbon Plus Activated Sludge Treatment System

There is usually a combination of different compounds in given wastestream. The removal of these various materials from the wastestream may involve different mechanisms. Basically, a pollutant may be classified into one of the following catagories: biodegradable, non-biodegradable, or slowly biodegradable. In terms of carbon adsorption, this same pollutant may be either adsorbable or non-adsorbable. By combining the biological degradation and adsorption characteristics, a waste could contain components in each of the following areas: biodegradable and adsorbable, biodegradable and non-adsorbable, non-biodegradable and adsorbable, non-biodegradable and non-adsorbable, and slowly contact degradeable adsorbable. Non-adsorbable and slowly contact degradeable characteristics together are considered impossible, since adsorbtion is the method of contact.(22,23)

When the activated sludge system is used by itself, only the biodegradable constituents are removed. However, when PAC is added to the activated sludge system, the non-biodegradable adsorbable, as well as the slowly biodegradable adsorbable constituents can be removed from the wastestream. Since this added removal capacity of the PAC plus activated sludge is not considered in the activated sludge kinetics, new mathematical models are required. One such interpretation of this process has been developed by Flynn,(22) and is presented below.

When the PAC plus ASP is used, the major methods of removing constituents from the wastestream are biodegradation and adsorption. Since adsorption and degradation rely primarily on sludge age, temperature, and carbon dosage these are also the variables in any model describing the PAC and ASP. Separate equations have been developed to describe the kinetics of each of the following groups of compounds: normally biodegradable components (including both adsorbable and non-adsorbable); adsorbable, non-biodegradable components and slowly degradable, adsorbable materials.

Normal Biodegradable Components: For the biodegradation case, it was assumed that those materials which would normally be degraded in the absence of PAC will degrade at the same rate whether or not they are adsorbed. Experiments have shown that this is a valid assumption.(24)

The kinetics of the removal of constitutents from a wastestream by biodegradation can be described using Monod kinetics.(21) Effluent biodegradable sludge concentrations can be related to sludge age by Equation 14,

$$S = \frac{K_s \, (1 + k_d \; _c)}{_c \, (Yk - k_d) - 1} \qquad (14)$$

where all the symbols are the same as the ones used in the section on activated sludge kinetics.

For the PAC plus ASP, which is shown schematically in Figure 5, sludge age is defined exactly as it was for the ASP alone. It is shown here in Equation 15.

$$_c = \frac{VX}{(Q - Q_w) \, X_e + Q_w \, X_w} \qquad (15)$$

Adsorbable, Non-Biodegradable Components: To model the removal of adsorbable, non-biodegradable materials from the wastestream, a material balance at steady state must be made as shown in Equation 16.

$$\begin{aligned} &Q \, S_{and_o} - (Q - Q_w) \, S_{and_1} - Q_w \, S_{and_1} - \\ &Q_w S_{and_c} C_{cw} - (Q - Q_w) \, S_{and_c} C_{ce} = 0 \end{aligned} \qquad (16)$$

where

C_{cw} = activated carbon concentration in waste sludge (mg C/L),

C_{ce} = activated carbon concentration in clarifier effluent (mg C/L),

S_{and_o} = concentration of absorbable, non-biodegradable materials in feed (mg TOC or COD/L),

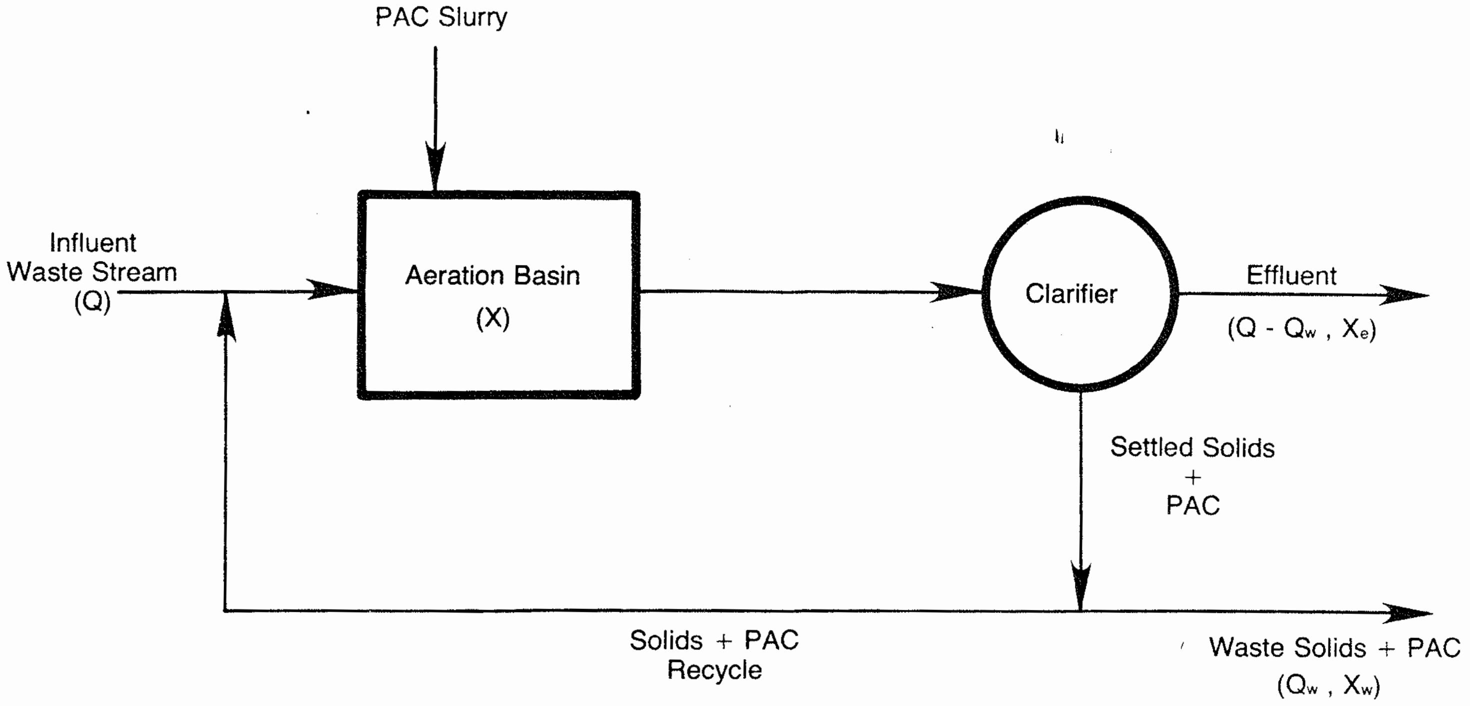


FIGURE 5 PAC + ACTIVATED SLUDGE PROCESS

S_{and} = concentration of absorbable, non-biodegradable materials in influent (mg COD or TOC/L),

S_{and_1} = concentraton of absorbable, non-biodegradable materials in the effluent (mg COD or TOC/L),

S_{and_c} = the concentration of absorbable non-biodegradable materials in the carbon (mg COD or TOC/L).

The loading of adsorbable, non-biodegradable materials on carbon (mg COD or TOC/mg carbon) can be found in Equation 17,

$$L_{AN} = \frac{S_{and_c} Q_w + S_{and_c} (Q - Q_w)}{C_{cw}(Q_w) + C_{cw} (Q-Q_w)} \qquad (17)$$

where

L_{AN} = loading of adsorbable, non-biodegradable materials on carbon (mg COD or TOC/mg C)

However, since the material can only be removed by adsorption, it is necessary to use Equation 18,

$$S_{and_c} = S_{and_o} - S_{and} \qquad (18)$$

By substituting Equation 18 into Equation 17, Equation 19 is derived.

$$L_{AN} = \frac{Q\,(S_{and_o} - S_{and})}{Q_w C_{cw} + (Q - Q_w)\, C_{ce}} \qquad (19)$$

However, under steady state conditions, the rate of carbon wastage is equal to the rate at which carbon is fed as shown in Equation 20,

$$L_{AN} = \frac{(S_{and_o} - S_{and})}{C_o} \qquad (20)$$

where C_o equals feed carbon concentration (mg carbon/L). Using a Langmuir adsorption model$^{(5,25,27)}$ at steady state the rate of desorption equals the rate of adsorption, Equation 21,

$$k_c S_{and_c} = k_a S_{and} (S_m - L_{AN}) \quad (21)$$

where: k_c = desorption rate constant (mg C/day),

k_a = adsorption rate constant (mg carbon - L/mg COD - day), and

S_m = maximum possible carbon loading (mg COD or TOC/mg C)

A rearrangement provides Equation 22,

$$S_{and_c} = \frac{k_a S_m S_{and}}{k_c + k_a S_{and}} \quad (22)$$

which can be combined with Equation 20 and linearized to form Equation 23,

$$S_{and_c} = \frac{k_a S_m S_{and}}{k_c + k_a S_{and}} \quad (22)$$

which can be combined with Equation 20 and linearized to form Equation 23,

$$\frac{1}{K_a} \left(\frac{1}{S_{and}}\right) + \frac{K_c}{K_a} = \frac{C_o}{S_{and_o} - S_{and}} \quad (23)$$

where:

K_a = adsorption coefficient (l/mg C), and

K_c = desorption coefficient (mg COD or TOC/l)$^{-1}$

Slowly Contact Degradable Constitutents: A materials balance at steady state conditions for the slowly contact degradable constituents of the wastestream yields Equation 24,

$$0 = QS_{Ad_o} - (Q - Q_w) S_{ad_1} -$$

$$Q_w S_{ad_1} - (Q - Q_w) L_{Ad_1} C_{ce} - Q_w L_{Ad_1} C_{cw} -$$

$$Vk X_1 L_{Ad_1} C_c = 0 \tag{24}$$

where:

S_{ad_o} and S_{Ad_1} = concentration of slowly contact degradable material in the feed and effluent, respectively (mg COD or TOC/L),

L_{Ad_1} = loading of slowly degradable material on the carbon (mg COD or TOC/mg carbon),

C_c = activated carbon concentraton in the aerator (mg/L), and

k = second order bacterial reaction rate for degration of slowly contact degradable materials on carbon (L/mg MLSS-d).

Since the rate of carbon loss is equal to the rate of carbon addition at steady state, and assuming a Langmuir type adsorption, Equation 25 can be obtained.

$$\frac{S_{Ad_o} - S_{AD_1}}{C_o} = L_{Ad_1} = (1 + 0_c kX) \frac{K_a' S_{ad_1}}{1 + K_c' S_{ad_1}} \tag{25}$$

where K_a' equals absorption for adsorbable slowly contact degradable materials (L/mg C), and K_c' equals desorption coefficient for adsorbable slowly contact degradable material (L/mg COD or TOC).

Rearranging Equation 25, Equation 26 can be obtained.

$$(1 + 0_c kX) \frac{1}{L_{Ad_1}} = \frac{1}{K_a'} \left(\frac{1}{S_{ad_1}} \right) + \frac{K_c}{K_a'} \tag{26}$$

To solve Equation 26, a k value can be assumed. Then one can determine the sum of the errors squared for the resulting linear regression or $(1 + O_c kX) \frac{1}{L_{ad_1}}$ against $1/S_{ad_1}$. The k value is iterated until this sum of the errors is minimized. The evaluation then determines all three constants. It should be noted that the bacterial mass available for slow contact degradation is assumed to be the same as the total bacterial mass in the aeration basin. If only a fraction of the bacteria is available for slow contact degradation, the ka rate will change.

A method of determining the values of the constants used in the above models for a particular wastestream has been suggested by Flynn.(22) To accomplish this, the following experiments are performed using bench-scale reactors:

1. Several ASP units are run in parallel at different sludge ages, keeping all other conditions constant.
2. Several ASP units are run in parallel varying only in carbon dosage (including one reactor with no carbon).
3. Several ASP units are run in parallel with various carbon dosages, each over a range of temperatures and sludge ages.

Each day the influent and effluent organic loadings (TOC or COD) values for each reactor are measured, as well as their mixed liquor, volatile suspended solids concentration (X). These data are used to determine the various constant values in the following manner.

1. Data gathered from the tests run on the ASP reactors at various sludge ages are used to determine Y, k_d and K_s values, as well as the value of residual substrate concentration.
2. The data gathered from the tests run on the ASP reactors which had varying amounts of PAC added to them is compared with data gathered from the tests run on the ASP units run at various sludge ages. Assuming that the differences in the amount of organic removal which occurs is due to adsorption, an apparent carbon loading value can be determined.
3. To determine the non-adsorbable, non-biodegradable portion of the waste, the effluent from the ASP reactor which had the PAC added is contacted with an amount of PAC -- say 2,000 mg/L -- for a period of two hours. Whatever portion of

the waste remains after this test is considered to be non-adsorbable, non-biodegradable.

4. To determine the effluent adsorbable, non-biodegradable concentration of the waste, the non-adsorbable, non-biodegradable value is substracted from the effluent value from the PAC and ASP reactors.
5. Organic reference loading lines are constructed by plotting the mg TOC or COD/mg carbon concentration versus the inverse of S_{and_1}.
6. Compare the apparent carbon loadings with the reference carbon loading and attribute the difference to be the slowly-contact degradable portion of the waste.
7. Using the data collected from ASP reactors that were run in parallel with various carbon doses over a range of temperatures and sludge ages, the differences in the values calculated in step (6) above can be regressed.

Using the methods described above, the model of the PAC plus ASP has been tested over a range of sludge ages, temperatures, and carbon dosages. The resulting data have been successfully fitted to the models.(22)

DESCRIPTION OF EQUIPMENT AND PROCEDURES

In addition to the literature analysis presented earlier, the evaluation of the PAC plus ASP process in this study included laboratory exercises performed on a specific industrial waste. The purpose of these experiments was to test the effects of treating the waste by the activated sludge process both with and without powdered activated carbon present. Since these experiments were run keeping everything constant, comparisons could be made between the system containing PAC and the system without PAC. In doing this, the ASP plus PAC system could be evaluated for its ability to increase treatment efficiency.

Reactor Types

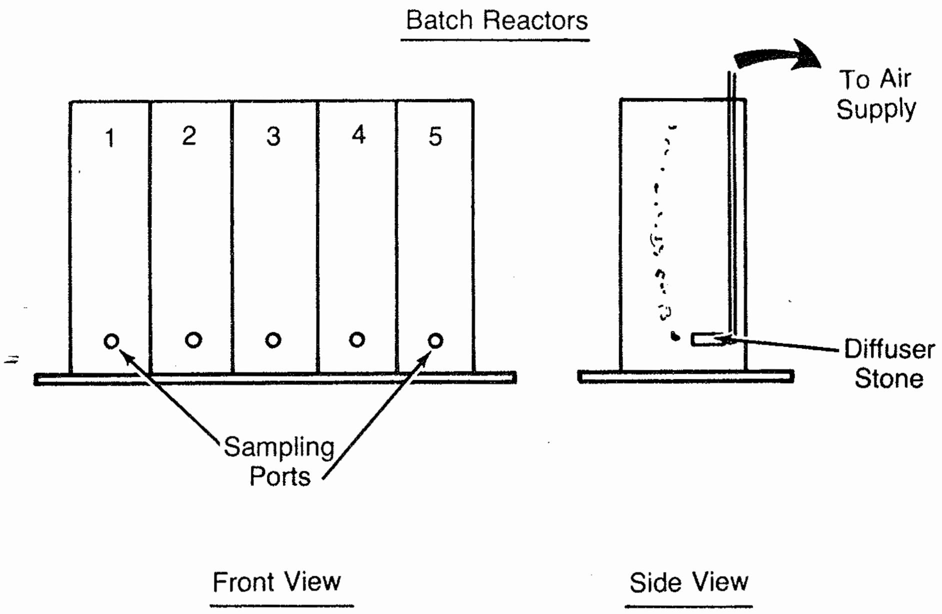
Laboratory-scale aeration basins provided the environment necessary for the controlled experimentation in these studies. Five basins, which are illustrated in Figure 6, were 1.5-liter, batch-type reactors, and two were 10-liter, continuous-flow, well-mixed reactors. All of the reactors were made of plexiglass.

Aeration Technique

Compressed air forced through diffuser stones provided aeration. The air was cleaned using a water trap as shown in Figure 7.

Feeding of Reactors

Feeding of waste to the continuous reactors was accomplished using Cole-Palmer capillary action pumps. The pump's capillary tubing was changed daily to provide accurate feed rates. The remainder of the tubing which led from the feed bucket to the capillary tubing and from the pump head to the reactor was cleaned twice a week to prevent any biological organisms from growing in them.



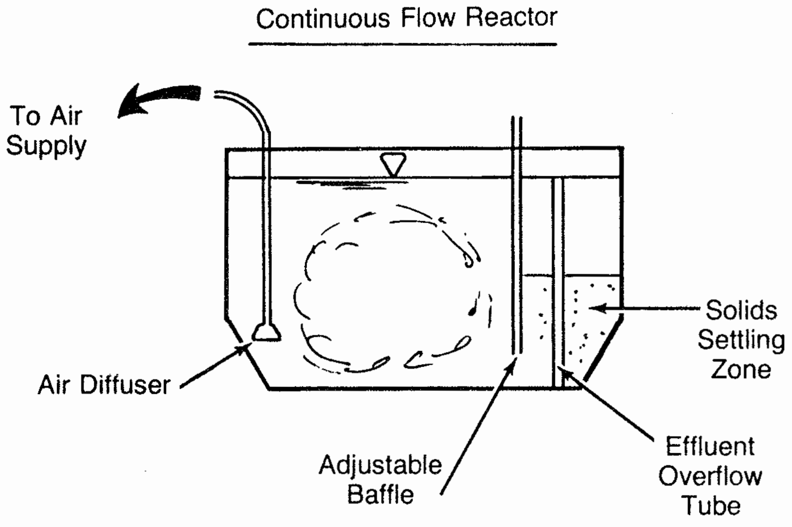


FIGURE 6 REACTORS USED FOR EXPERIMENTS

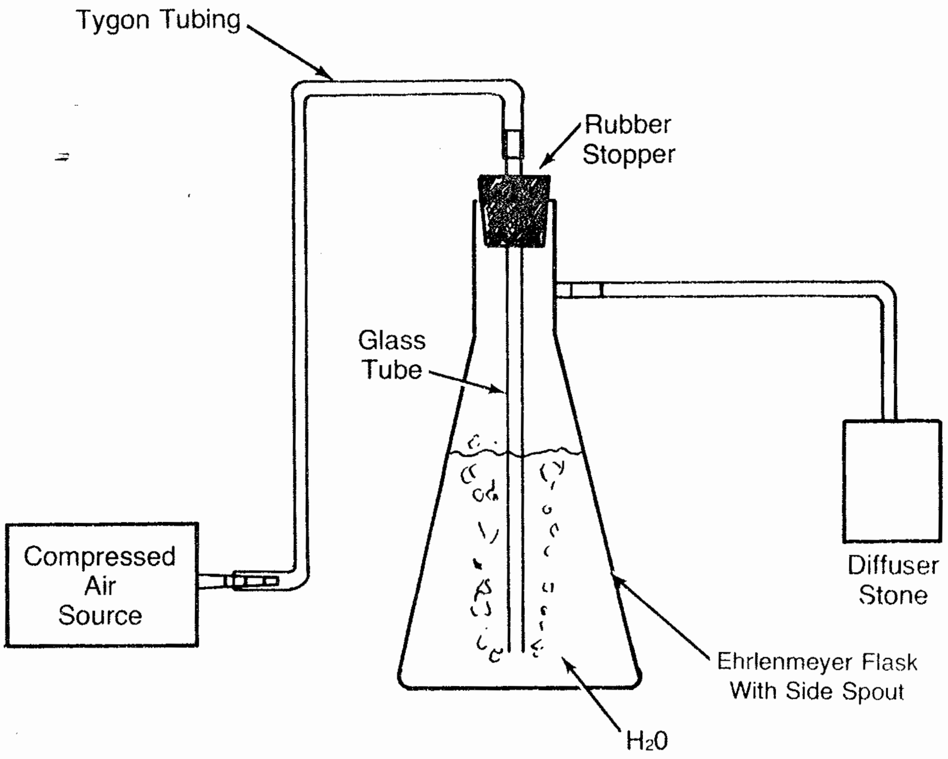


FIGURE 7 WATER TRAP USED TO FILTER COMPRESSED AIR

Feeding of the batch reactors was done once a day for detention times of 24 hours. At the end of each daily cycle the air supply was turned off and the solids were allowed to settle. After 30 minutes of settling the supernatant was removed and the displaced volume replaced with fresh waste. Aeration was resumed for another cycle.

Temperature

The air temperature surrounding the reactors was kept at $25^{\circ} \pm 2^{\circ}C$.

Nutrients

Nutrients were added each day. Nitrogen as ammonium sulfate was added at a rate of 10 mg per liter of reactor volume. Similarily phosphorous as potassium dihydrogen phosphate was added at 1 mg per liter of reactor volume.

Waste

The industrial waste used in the study was derived from an aldehyde-producing process. The experiments were performed on both undiluted samples, and samples that had been diluted to 3.5 percent of their initial volume with distilled water. Herein, the undiluted sample will be called sample "A", and the diluted sample will be called sample "B". The characteristics of these waste samples are given in Table 3.

To impede biological degradation of the bulk waste sample reactors, it was maintained at $4 \pm 1^{\circ}C$. Before the waste was removed the storage drum, the contents were completely mixed.

Seeding the Reactors

To accomplish acclimation of the biomass, mixed liquor from a municipal treatment plant (ASP) was placed into two, ten-liter reactors and aerated. The feed to these reactors was 99 percent (by volume) distilled water and one percent raw waste. After three days, influent waste concentration was increased to two percent raw waste. The feed in the first

Table 3
Average Raw Waste Characteristics

Waste	COD (mg/L)	TOC (mg/L)	BOD_5 (mg/L)	pH
A	27,300	8,750	16,400	6.4
B	945	310	590	6.9

reactor was kept at a 2 percent raw waste concentration constantly, while the waste concentration in the second reactor was doubled every four days until it was receiving only raw waste (100 percent). After the batch reactor tests were completed, it was decided to strengthen the waste concentration in reactor number one to 3.5 percent raw waste. This was done because the original waste concentration was not high enough to support an active biomass with good settling characteristics.

Sludge Ages

The sludge ages for both of the reactors was set at twenty days. To assure that this was the case, once a day the effluent of the reactors was plugged, and the baffle was removed to allow complete mixing of the materials within the reactor. Once complete mixing had occurred, 500 milliliters of the mixed liquor was removed and allowed to settle. Once settled, the supernatant was returned to the reactor, while the solid portion was discarded. The baffle would be replaced, and the effluent was opened once again.

PAC Type

The PAC used in these studies ws developed by the ICI Chemical Company of Wilmington, Delaware (DARCO). It was specifically developed for use in wastewater purification.

Parameters Tested

Chemical Oxygen Demand (COD) provided the primary analysis. This was run as outlined in Standard Methods.(3) During one of the batch experiments, the Total Organic Carbon (TOC) analysis was run in addition to the COD analysis. This test was run as explained in Environmental Protection Agency's Manual, Methods for Chemical Analysis of Water and Wastes.(4)

In addition to the above analyses, both total mixed liquor suspended solids (MLSS) and mixed liquor volatile solids (MLVSS), were measured three times each week. These analyses were run as described below.

A known volume of the mixed liquor from a reactor was filtered, using a millipore filter apparatus (as shown in Figure 8). The filter paper was preweighted and the dry weight recorded. Reeve Angel's, Whatman 42 (five porosity) paper, 5.5 centimeter diameter, removes 98 percent of the 2μm particles. After the sample was filtered, the filter paper was placed into a preweighted weighing pen and heated at 104°C for two hours. The pan and filter paper were cooled in a dissicator and recorded. Finally, the pan and contents were placed in an oven at 550°C for twenty minutes, after which they were cooled and weighed once again. Thus the MLSS and MLVSS were calculated.

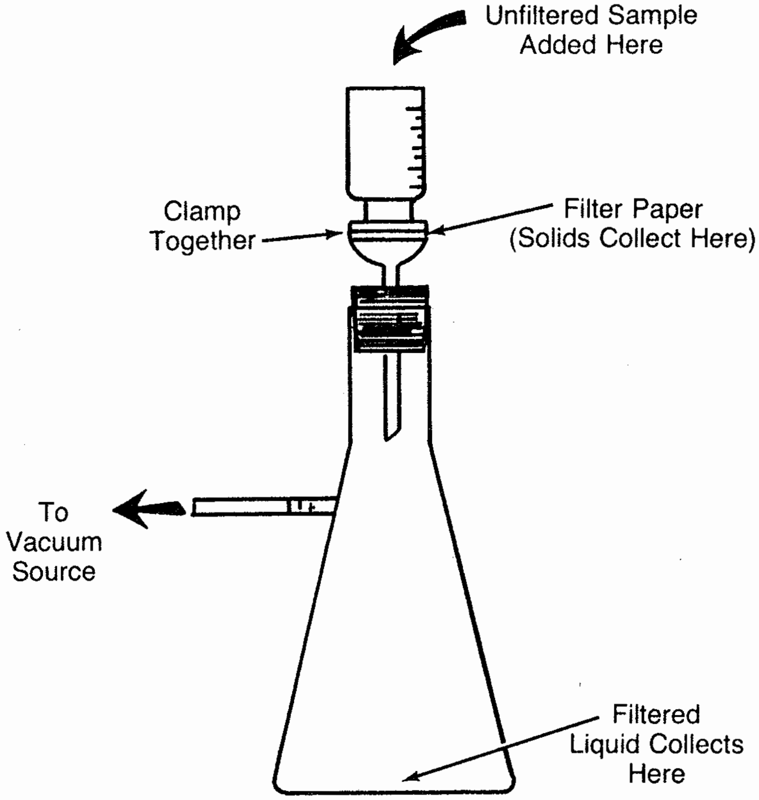


FIGURE 8 TYPICAL MILLIPORE FILTER APPARATUS SETUP

RESULTS AND DISCUSSION

Experiments were conducted to study the effects of treating an organic waste by adding PAC to an activated sludge plant. The logic flow chart for these experiments is shown in Figure 9.

Optimum Detention Time Experiment

An experiment was designed to determine the optimum detention time at which the respective wastes should be treated. This experiment was conducted by mixing the mixed liquor from the continuous rectors with "raw" wastewater (either "A" or "B") to form a certain MLVSS concentration (2,400 mg/L for waste "A" and 840 mg/L for waste "B"). Batch reactors were then filled with this mixture and aerated. The COD of the influent waste was measured at predetermined intervals, samples were withdrawn and the soluble COD measured.

These data are shown in Tables 4 and 5, and Figures 10 and 11. For waste "A", a hydraulic detention time of five days was chosen. Although increased COD reduction could have been obtained with longer detention times, the laboratory set up was not developed for larger tests. Five days of aeration for waste "A" provided a 32 percent COD reduction.

In the case of waste "B", the laboratory results showed that a twenty-four hour detention time provided a 67 percent COD reduction. Therefore, a hydraulic detention period of one day was chosen for experiments in the case of waste "B".

Optimum PAC Dose Experiment

To determine the optimum concentration of PAC which would be used to treat the two wastes, another experiment was designed using the batch reactors. As in the earlier experiments, each reactor was filled with a mixture of wastewater and activated sludge and aerated. In the experiment, PAC was added to four of the reactors in concentrations of 200, 300, 400, and

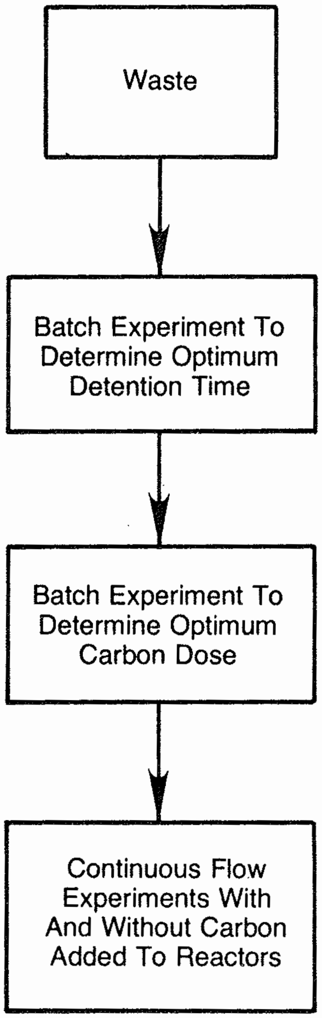


FIGURE 9 EXPERIMENT FLOW CHART

Table 4
Optimum Detention Time Test Results For Waste "A" *

Time (Days)	Effluent COD (mg/L)
0	28,600
3	25,670
5	19,500
8	20,000
10	15,860
12	16,650
13	16,050
14	16,150

*Initial MLVSS = 2,400 mg/L

Table 5
Optimum Detention Time Test Results For Waste "B"*

Time (hrs)	Effluent COD (mg/L)
0	315
2	238
6	185
10	150
24	104

*Initial MLVSS= 840 mg/L

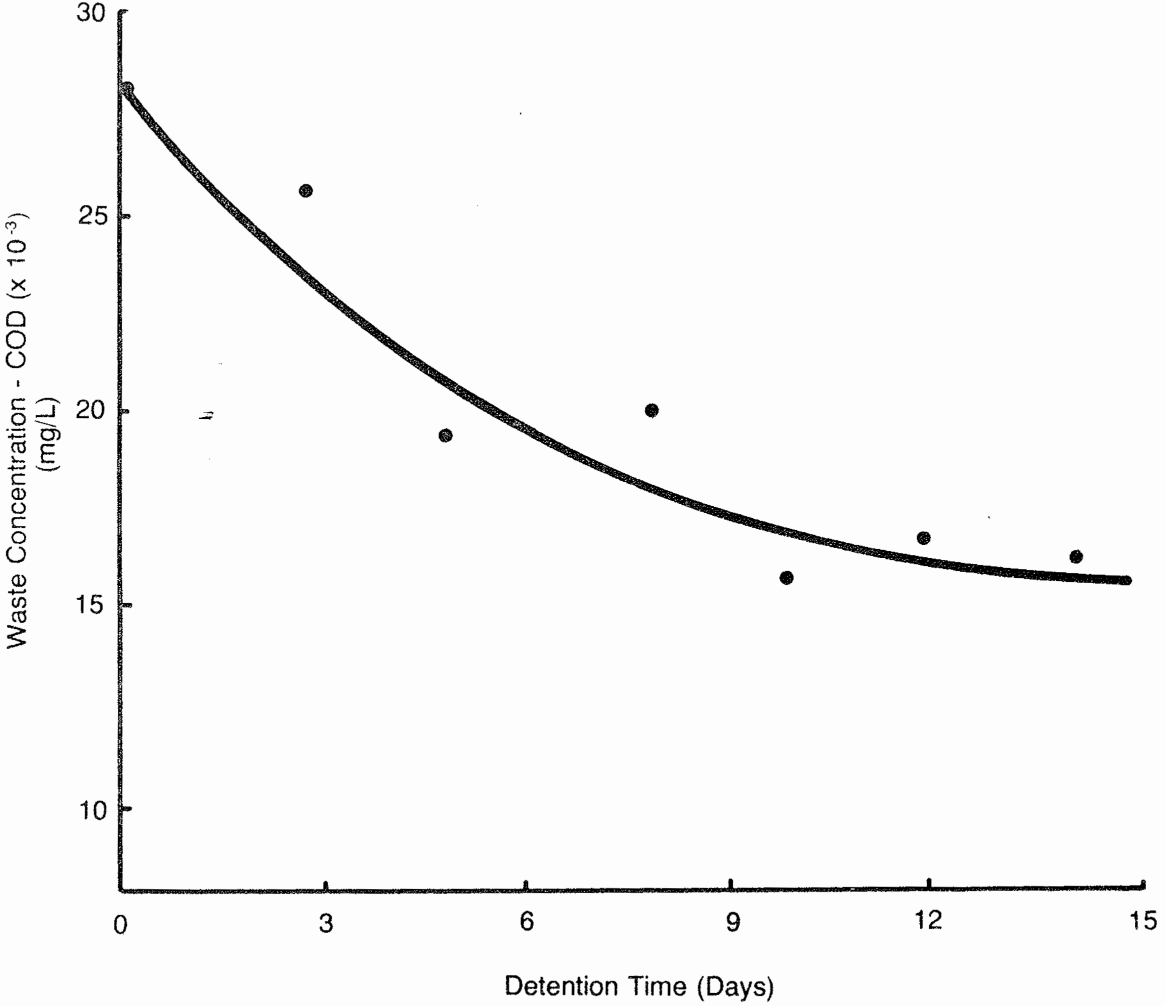


FIGURE 10 CHANGE IN COD CONCENTRATION IN WASTE "A" WITH RESPECT TO DETENTION TIME

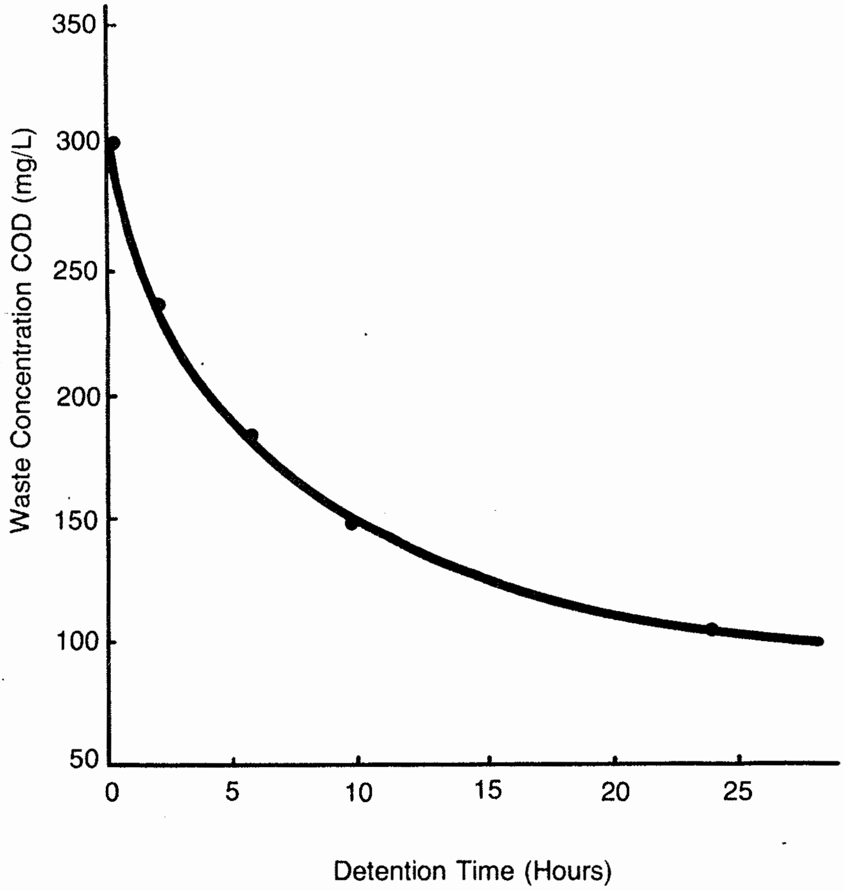


FIGURE 11 CHANGE IN COD CONCENTRATION IN WASTE "B" WITH RESPECT TO DETENTION TIME

500 mg/L for waste "A", and 100, 200, 300, and 400 mg/L for waste "B". After 24 hours the soluble COD was determined by the reactor contents. In the case of waste "B" TOC measurements were also made at the same time. The objective of the TOC measurement was to determine if the influent/effluent relationships for COD and TOC were similar. The results from these tests are shown in Tables 6 and 7 and Figures 12, 13, and 14.

Inspection of the data derived from the experiment performed on waste "B" (see Figures 13 and 14) reveals that the removal percentage of COD and TOC is similar at each of the PAC concentrations tested. This apparent correlation between COD and TOC data indicates that an estimate of the TOC removal occurring can be made when measuring COD removal. Both of these parameters are indicators of the amount of pollutants present in the wastewater.

As a result of this experiment, PAC concentrations of 200 and 400 mg/L were chosen for treating waste "A", and a PAC concentration of 200 mg/L was picked to treat waste "B".

Experiment to Test the Effects of Adding PAC to the Activated Sludge Process

An experiment designed to compare the results of treating a wastewater using both the ASP and the ASP plus PAC was run. In this test, continuous flow reactors were run in parallel, two for each wastewater tested. In one of these reactors, the waste was treated by contact with activated sludge only, while in the other reactor, the waste was treated by activated sludge plus activated carbon. The hydraulic detention for the reactor, as well as the carbon dose used in one reactor each for waste "A" and waste "B" were detected by the results of the tests run earlier.

The hydraulic detention was five days and one day, respectively for wastes "A" and "B". Waste "A" was tested at PAC concentrations of 200 and 400 mg/L, while waste "B" was tested at a PAC concentration of 200 mg/L. The sludge age for all reactors was 20 days.

Table 6
Optimum Carbon Dose Experiment Results For Waste "A" *

Reactor No.	Carbon Dose (mg/L)	Influent COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	200	28,000	23,100	18
2	300	28,000	22,550	19
3	400	28,000	22,500	20
4	500	28,000	22,100	21

*Initial MLVSS = 3,200 mg/L
Θ_h = 24 hours

Table 7
Optimum Carbon Dose Experiment Results For Waste "B" *

Reactor No.	Carbon Dose (mg/L)	COD at Time = 0 (mg/L)	COD at Time = 24 hrs (mg/L)	COD Removal (Percent)	TOC at Time = 0 (mg/L)	TOC at Time = 24 hrs (mg/L)	TOC Removal (Percent)
1	0	270	99	63	95	35	63
2	100	270	93	66	95	35	63
3	200	270	79	71	95	29	70
4	300	270	69	75	95	26	73
5	400	270	68	75	95	25	74

*Initial MLVSS = 780 mg/L
Θh = 24 hours

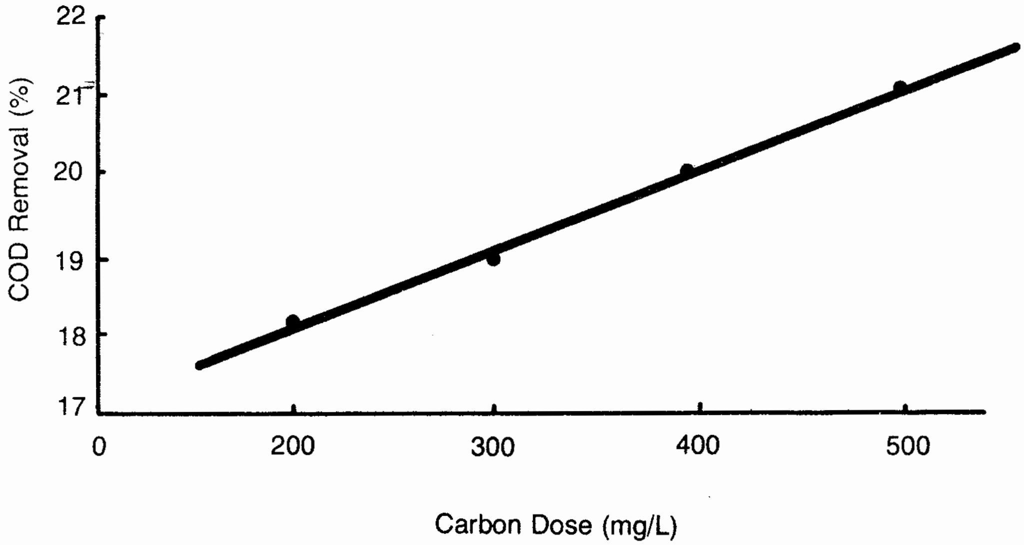


FIGURE 12 EFFECT OF MIXED-LIQUOR CARBON CONCENTRATION ON EFFLUENT SOLUBLE COD FOR WASTE "A"

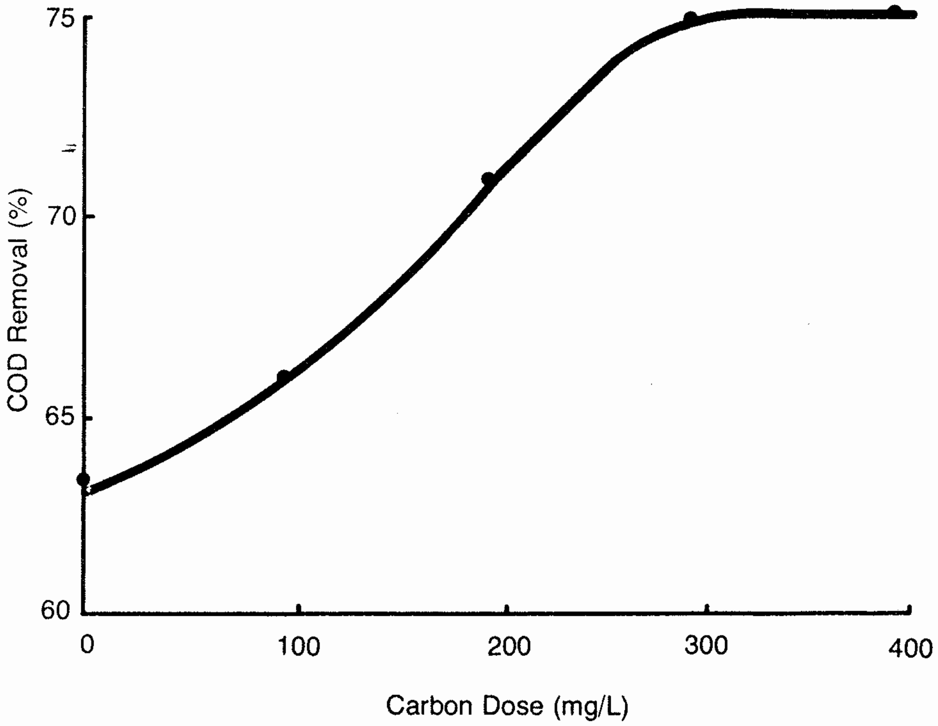


FIGURE 13 EFFECT OF MIXED-LIQUOR CARBON CONCENTRATION ON EFFLUENT COD REMOVAL FOR WASTE "B"

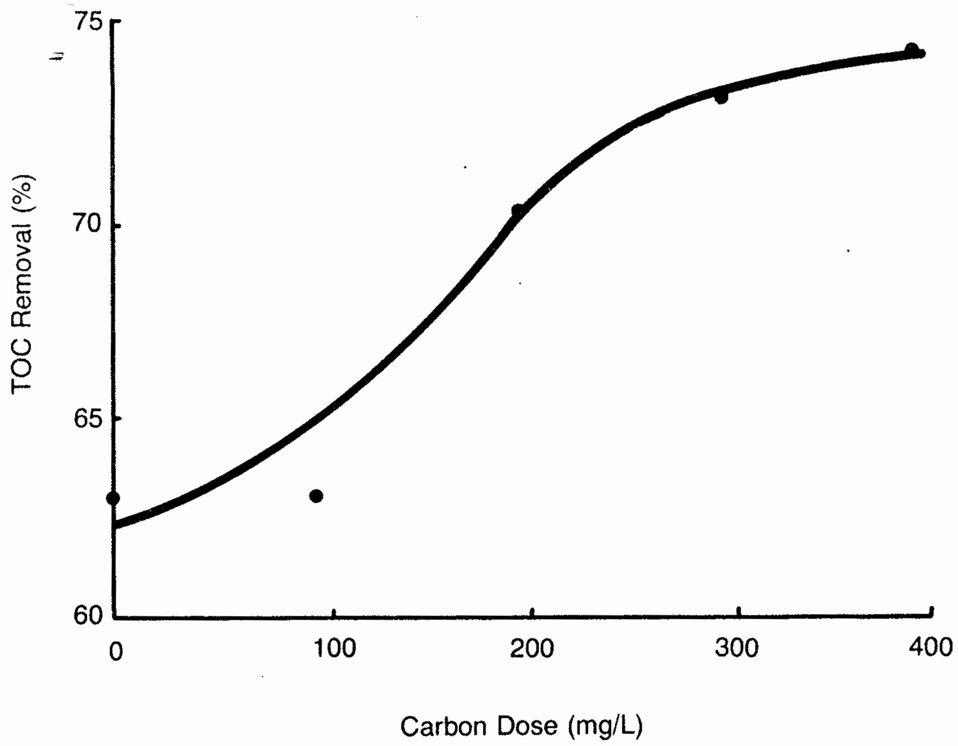


FIGURE 14 EFFECT OF MIXED LIQUOR CARBON CONCENTRATION ON EFFLUENT SOLUBLE TOC FOR WASTE "B"

Each day, the soluble COD of the influent and effluent for each reactor was measured. These data are shown in Tables 8 through 12 and Figures 15 through 16.

The experiment yielded the following results:

1. Waste "A"
    a. The addition of 200 mg/L of PAC to the activated sludge process improved COD removal, on the average, by 4 percent.
    b. The addition of 400 mg/L of PAC to the activated sludge process improved the removal of COD, on the average, by 6 percent.
2. Waste "B" -- The addition of 200 mg/L of PAC to the activated sludge process improved the removal of COD by 30 percent.
3. The standard deviation of the COD reduction (percent COD removal) was lower for the cases involving PAC additions as compared to cases where no PAC was added. This indicates less variability in process performance.

While the results of the experiment show that the addition of PAC to the ASP will improve treatment of both waste "A" and waste "B", they also indicate that this improvement varies greatly depending on the strength of the waste. While PAC and ASP treatment was able to remove almost 81 percent of the soluble COD present in waste "B", it was only able to remove about 16 percent of the soluble COD from waste "A". This finding suggests that wastestreams above certain organic concentrations may not be effectively treated by the PAC and plus method.

Table 8
Waste "A" Experiment Results For Activated Sludge With No PAC Added*

Time (days)	Feed COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	26,500	23,900	10
2	26,500	24,000	9
4	26,050	23,100	11
5	25,950	22,750	12
7	25,900	23,150	11
8	25,950	23,500	9
9	25,850	23,250	10
11	25,800	22,900	11
12	25,900	22,950	11

Mean = 10%
Standard Deviation = 1.01

*$\text{MLVSS}_{\text{AVG}}$ = 2,400 mg/L
Θ_h = 5 days

Table 9
Waste "A" Experiment Results
For Activated Sludge + 200 mg/L PAC*

Time (days)	Feed COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	25,950	22,200	15
3	25,880	22,260	14
4	25,850	22,050	15
6	25,900	22,350	14

$\overline{X}$ = 14.5%
Standard Deviation = 0.58

*MLVSS = 3,000 mg/L
Θ_h = 5 days

Table 10
Waste "A" Experiment Results
For Activated Sludge + 400 mg/L PAC*

Time (days)	Feed COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	26,800	22,650	16
2	25,950	21,900	16
3	26,200	21,850	17
5	26,050	21,700	17
6	25,900	21,650	16

X = 16.4%
Standard Deviation = 0.55

*MLVSS = 3,400 mg/L
Θ_h = 5 days

Table 11
Waste "B" Experiment Results
For Activated Sludge With No PAC Added*

Time (days)	Feed COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	950	432	55
3	942	433	54
6	973	557	43
12	960	430	55
13	992	551	45
14	974	502	49
15	963	449	54
16	935	438	53
17	930	492	47

$\overline{X}$ = 50.6%
Standard Deviation = 4.6

*$MLVSS_{AVG}$ = 1,650 mg/L
Θ_h = 24 hours

Table 12
Waste "B" Experiment Results
For Activated Sludge + 200 mg/L PAC*

Time (days)	Feed COD (mg/L)	Effluent COD (mg/L)	COD Removal (Percent)
1	970	186	81
2	932	190	80
4	922	182	80
6	942	166	82
9	950	194	80
10	934	178	81
11	940	180	81
12	954	172	82
13	947	183	81
14	942	185	80
15	944	166	82

$\overline{X}$ = 80.9%
Standard Deviation = 0.83

*$MLVSS_{AVG}$ = 1,700 mg/L
Θ_h = 24 hours

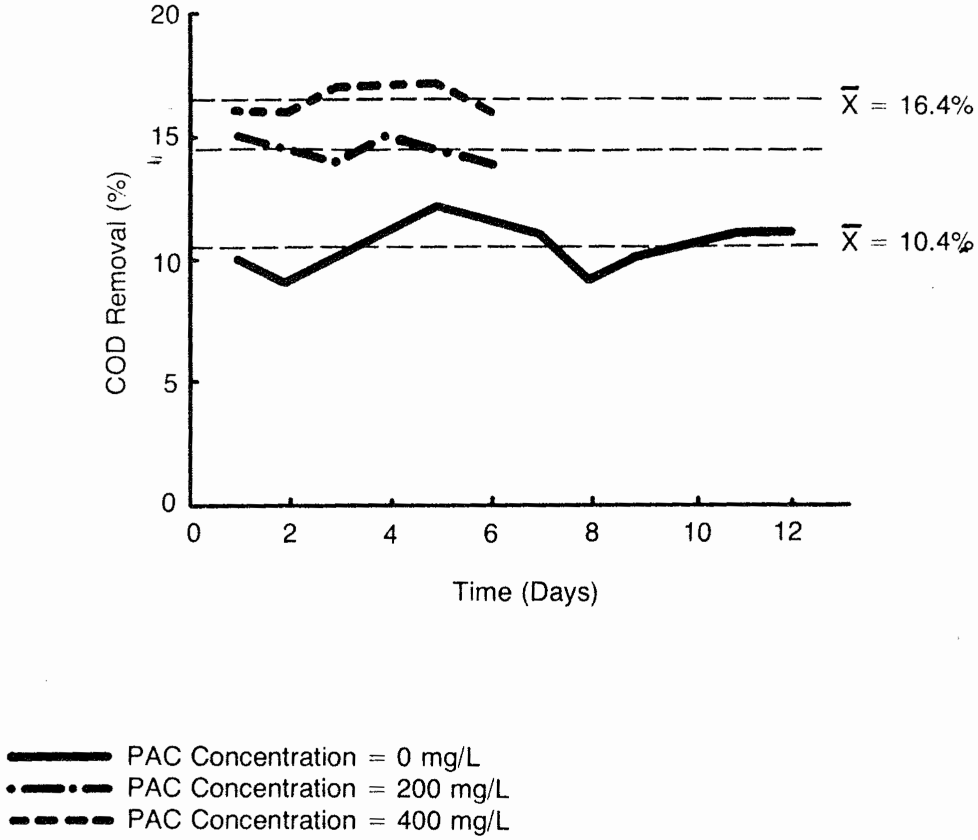


FIGURE 15 PERFORMANCE OF ACTIVATED SLUDGE PROCESS AND ACTIVATED SLUDGE PROCESS + POWDERED ACTIVATED CARBON WHEN USED TO TREAT WASTE "A"

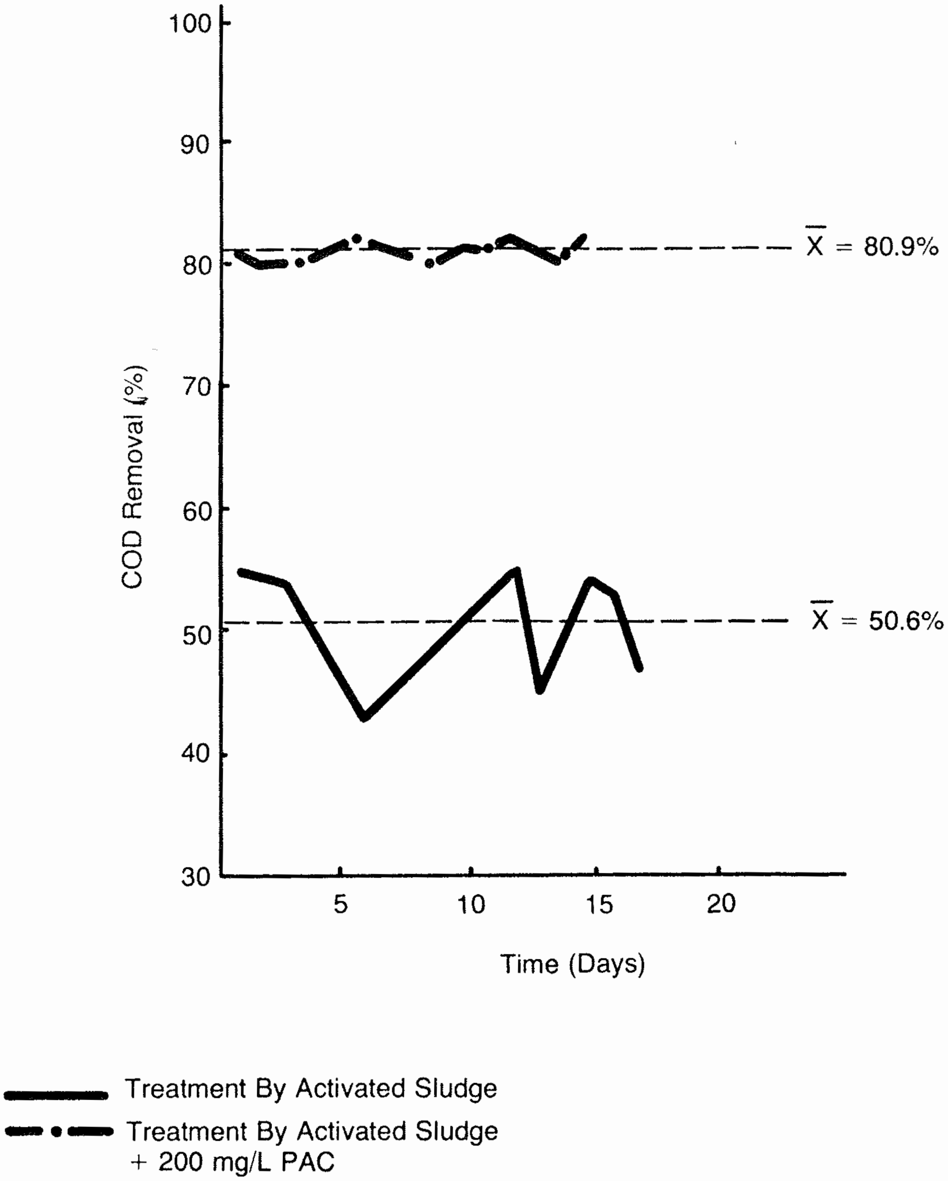


FIGURE 16 **PERFORMANCE OF ASP AND ASP + PAC WHEN USED TO TREAT WASTE "B"**

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are offered:

CONCLUSIONS

1. The treatment of an aldehyde wastestream with influent chemical oxygen demand (COD) equal to 270 mg/L by the addition of powdered activated carbon (PAC) to the aeration basin of an active activated sludge process (ASP) results in increased organic removal. When 200 mg/L of PAC was added, the COD removal was increased by 30 percent over that of the ASP with no PAC added.

2. The treatment of a concentrated wastestream (COD equal to 27,000 mg/L) by the additiion of 200 mg/L of PAC to the ASP only incresed the COD removal by 4 percent over the use of the ASP alone. Similarly, when 4090 mg/L of PAC was added, the COD removal was increased by 6 percent over that of ASP with no PAC added. The concentrated wastewater was not amenable to either PAC and ASP or ASP treatment. The overall efficiency of COD removal in a ASP plus PAC was only 16 percent.

3. The standard deviations of the COD removals were lower for cases when the wastes were treated by the combination of PAC and ASP as compared to those cases when the wastes were treated by the ASP alone. This may indicate that the addition of PAC reduces the variability in treatment performances.

RECOMMENDATIONS

To evaluate the limitations of the PAC and ASP process, the following parameters should be varied:

a. sludge age of the reactors,
b. PAC types, and
c. influent waste dilution.

BIBLIOGRAPHY

1. Grieves, C.G.; Crame, L.W.; Vernados, D.G.; Ying, W., "Powdered Carbon Enhancement Versus Granular Carbon Adsorption for Oil Refinery BATEA Wastewater Treatment." 51st Annual Conference, Water Pollution Control Federation, pg. 1-24, Anaheim, California (October 1978).

2. Anon.; "The Clean Water Act Showing Changes Made By the 1977 Amendments", 95th Congress 1st Session Serial No. 95-12, pg. 1-10, U.S. Government Printing Office, Washington D.C. (December 1977).

3. Anon.; Standard Methods for the Examination of Water and Wastewater, 14th Ed., Amer. Public Works Association, pg. 550-554 (1976).

4. Anon.; Environmental Protection Agency; Methods for Chemical Analysis of Water and Wastes, U.S. EPA, pg. 236-38, Washington D.C. (1974).

5. Weber, W. J., Jr.; Physiochemical Processes for Water Quality Control, pg. 199-211, John Wiley and Sons, New York (1972).

6. Grieves, C.G.; Stenstrom, M.K.; Walk, J.D.; and Grutsch, J.F.; "Powdered Carbon Improves Activated Sludge Treatment", Hydrocarbon Processing 56:125-30 (October, 1977).

7. DeJohn, P.B. and Adams, A.D; "Treatment of Oil Refinery Wastewaters With Granular and Powdered Activated Carbon", Proceedings, 30th Annual Purdue Industrial Waste Conference, pg. 216-31, Lafayette, Indiana (May 1975).

8. Parcell, L.J., "Enhancement of Refinery Activated Sludge Treatment" 51st Annual Conference, Water Pollution Control Federation, pg. 1-35, Anaheim, California (October 1978).

9. Ferguson, J.F.; Keay, G.F.; Merrill, M.S.; Benedict, A.H.; "Powdered Activated Carbon Biological Treatment: Low Detention Time Process", Proceedings, 31st Annual Purdue Industrial Waste Conference, pg. 468-78, Lafayette, Indiana (May 1976).

10. Flynn, B.P.; Barry, L.T.; "Finding A Home For The Carbon: Aerator (Powdered) or Column (Granular)", Proceedings, 31st

Annual Purdue Industrial Waste Conference, pg. 649-9-. Lafayette, Indiana (May 1976).

11. Adams, A.D.; "Carbon Adsorption Aids Activated Sludge Treatment at Dyeing and Finishing Plants", American Dyestuff Reporter 65:32-8 (April 1976).

12. DeJohn, P.B., and Adams, A.D.; "Activated Carbon Improves Wastewater Treatment", Hydrocarbon Processing 54:104-7 (October 1975).

13. Cheremisinoff, P.N.; Ellerbusch, F.; Carbon Adsorption Handbook. Ann Arbor Science, Ann Arbor, Michigan (1978).

14. Meidl, J.A.; Berndt, C.L.; Nomoto, K.; "Experience With Full-Scale Wet Oxidation of Spent Carbon From the 'PACT' Process", 51st Annual Conference, Water Pollution Control Federation, pg. 1-17, Anaheim, California (October 1978).

15. Anon.; "Putting Powdered Carbon in Wastewater Treatment", Environmental Science and Technology 11:854-5 (September 1977).

16. Culp, G.L.; Shuckrow, A.J.; "Appraisal of PAC Processes for Municipal Wastewater Treatment". Environmental Protection Agency Technology Series, EPA-600/2-77-156. Contract No. 68-03-2211 (September 1977).

17. Environmental Protection Agency; "Process Design Manual for Carbon Adsorption", EPA 625/1-71-002a (October 1973).

18. Anon.; "Basic Concepts of Adsorption on Activated Carbon", Brochure from Filtrasorb Department, pg. 1-11, Water Management Division, Calgon Corporation, Pittsburgh, Pennsylvania (No Date).

19. Wang, L.K.; Leonard, R.P., Wang, M. and Goupil, D.W.; "Adsorption of Dissolved Organics From Industrial Effluents on the Activated Carbon", Journal of Applied Chemistry and Biotechnology, 25:491-502 (July 1975).

20. Metcalf and Eddy, Wastewater Engineering: Treatment-Disposal, Reuse, Second Edition, pg. 424-434. McGraw-Hill Company, New York (1979).

21. Lawrence, A.W. and McCarty, P.L.; "Unified Basis for Biological Treatment Design and Operation." Journal of the American Society of Civil Engineers, Sanitary Engineering Division 96: No. SA3, 757-778 (June 1970).

22. Flynn, B.P.; "A Model for the Powdered Activated Carbon-Activated Sludge Treatment System", Proceedings. 30th Annual Purdue Industrial Waste Conference, pg. 233-254, Lafayette, Indiana (May 1975).

23. Flynn, B.P.; Robertaccio, F.L.; Barry, L.T.; "Truth or Consequences: Biological Fouling and Other Considerations in the Powdered Activated Carbon-Activated Sludge System", Proceedings, 31st Annual Purdue Industrial Waste Conference, pg. 855-62, Lafayette, Indiana (May 1976).

24. Flynn B.P.; "The Determination of Bacterial Kinetics in a Powdered Activated Carbon Reactor", Proceedings, 29th Annual Purdue Industrial Waste Conference, pg. 302-18, Lafayette, Indiana (May 1974).

25. Sawyer, C.N. and McCarty, P.L.; Chemistry for Sanitary Engineers, Second Edition, pg. 206-209, McGraw-Hill, New York (1967).

26. DeWalle, F.B.; Chain, E.S.K; Small, O.M.; "Organic Matter Removal by Powdered Activated Carbon Added to Activated Sludge", Water Pollution Control Federation Journal, 49:439-46 (April 1977).

27. Lent, D.S.; "Treatment of Power Laundry Wastewater Utilizing Powdered Activated Carbon and Cationic Polyelectrolyte", Proceedings, 30th Annual Purdue Industrial Waste Conference, pg. 751-759 (May 1975).

28. Berndt, C.L. and Polkowski, L.B.; "PAC Upgrades Wastewater Treatment", Water and Wastes Engineering, 15:49-50 (May 1978).

29. DeWall, F.B. and Chain E.S.K., Biological Regeneration of Powdered Activated Carbon Added to Activated Sludge Units, Water Research, 11:439-48 (May 1977).

30. Hutton, D.G.; "Removal of Priority Pollutants By the DuPont PACT Process", Proceedings, 7th Annual Industrial Pollution Conference, pg. 369-377, Philadelphia, Pennsylvania (June 1979).

31. Flynn, B.P.; Bettler, C.R.; Weaver, K.R.; Miles, J.E.; "Process and Economic Improvements For A 40 MGD 'PACT' Wastewater Plant", 51st Annual Conference, Water Pollution Control Federation, pg. 1-36, Anaheim, California (October 1978).