REMOVAL OF PHENOLS FROM A REFINERY WASTE STREAM UTILIZING POROUS BIOMASS SUPPORTS IN AN AERATED REACTOR

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Ray Center

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5/20/88
Date

Howard J. Curry
Chairperson, Graduate Committee

Approved for the Major Department

20 May '88
Date

Howard E. Curry
Head, Major Department

Approved for the College of Graduate Studies

10 June '88
Date

M. P. Malone
Graduate Dean

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ABSTRACT

Phenol is one of the many contaminants produced during the oil refining process. The Conoco Oil Refinery in Billings, Montana, has an existing wastewater treatment system for the removal of contaminants prior to discharge to a drainage ditch. The current wastewater treatment system provides for phenol removal, however, the refinery wishes to increase the efficiency of the process. Previous studies have determined that an increase in biomass within the plant could increase the efficiency of the phenol removal.

One means of increasing the biomass is to add porous biomass supports to the aeration tank. The purpose of this investigation was to determine whether phenol degrading organisms will colonize the supports, and if so, attempt to determine the minimum detention time in a reactor for 99% phenol removal, and the corresponding biomass concentration in the supports.

The investigation showed that a microbial population to degrade phenol in the refinery wastewater can be grown within porous biomass supports. A 98% reduction in the phenol concentration in the wastewater was achieved with a reactor detention time of less than four hours. A maximum degradation rate of 0.29 g/l-d was observed during the investigation.

INTRODUCTION

Oil refinery waste streams contain many contaminants which would be objectionable if released to receiving waters. Phenol, an aromatic benzene ring hydrocarbon, is one such contaminant.

The Conoco Oil Refinery in Billings, Montana, has an existing wastewater treatment system for removal of contaminants prior to discharge to a drainage ditch. The current wastewater treatment system provides for phenol removal, however, an increase in the efficiency of the process is desired.

The refinery waste streams are currently treated in a series of two bioponds, followed by two aerated holding ponds and an emergency diversion pond. The wastewater flows from the bioponds to the aerated holding ponds, or the emergency diversion pond, depending on the level of treatment achieved in the bioponds. A more complete description of the existing treatment system has previously been presented by Gilman (1987).

Gilman made three recommendations for improving the efficiency of phenol removal within the existing refinery wastewater treatment plant. One recommendation was to investigate the feasibility of increasing the biomass concentration in the present biopond system by utilizing biomass recycle or the incorporation of porous biomass supports within one of the bioponds.

This investigation was performed to determine whether phenol degrading organisms would colonize porous biomass supports, and if so,

to attempt to determine the minimum detention time in a reactor for 99% phenol removal, and the corresponding biomass concentration in the supports.

BACKGROUND

Porous biomass support systems (PBSS) have been in the developmental stages for a number of years and are considered one of the emerging innovative and alternative wastewater treatment technologies by the U.S. Environmental Protection Agency (Givens, et al., 1987). The objective has been to produce a biomass support that will allow the growth of a microbial population on the surface and within the support, thereby providing a significant increase in biomass concentration within a reactor. Of particular interest is the potential to retain biological solids in low biomass growth situations.

Early work by Atkinson, et al. (1979), used glass ballotini, stainless steel mesh, and single strands of wire to make numerous types of supports. These supports included spherical solid glass ballotini, rectangular and spherical cages of wire mesh, and spherical particles manufactured from a single strand of wire, knitted, and then crushed into a sphere. The work by Atkinson, et al., led to the following observations. 1) The important physical characteristics of the supports were determined to be high porosity, a very open structure, and lattice material of small cross section. 2) Protozoa were identified within the supports when using mixed cultures grown on sewage, indicating that an ecological balance could be maintained similar to activated sludge. 3) They concluded that supports of almost any size and shape could be colonized by virtually any organism and used in a biological reactor.

Since the early studies by Atkinson, et al., the basic technology has been developed along two different lines by Simon-Hartley Ltd. in England, and Linde AG in West Germany. Both of these companies manufacture rectangular biomass supports from open celled polyurethane foam. The size of the supports produced by each company, and the open cells within each support are somewhat different, but the main differences are in cleaning of the supports and the use of secondary clarifiers in the treatment scheme. Simon-Hartley Ltd., has concentrated on cleaning the supports outside of the reactor to waste excess biomass and avoid the use of secondary clarification. Their process has become known as the CAPTOR process. Linde AG, does not artificially clean the supports and has developed their process for secondary treatment along the lines of conventional activated sludge using a combination of suspended and attached biomass with final clarifier and sludge recirculation for suspended biomass control. This process is known as the Linpor process. In both processes, as the supports move through the wastewater, the wastewater also moves through the supports. This movement brings nutrients, oxygen, and particulate matter into contact with the biological growth that is either attached to the support or entrapped within the pores.

Studies have shown that the biomass accumulated within the supports is a mixture of fixed film and suspended growth organisms (Tharp, & Frymier). These studies also indicated that operation of a reactor without solids removal causes the center portion of the supports to become biologically inactive and causes excess solids to be continually

lost from the supports and discharged with the flow of wastewater from the aeration tank.

Other investigators using foam biomass supports in municipal and industrial waste treatment found that as the biomass aged within the supports it became mineralized and tended towards a granular consistency (Walker and Austin, 1981). Eventually the biomass appeared to release breakdown products causing a degree of souring, and began to become detached from the supports. These investigators found that to maintain an effective population within the supports it was necessary to control the age of the biomass by deliberate cleaning. They also found it useful to maintain a proportion of empty or partially empty supports in the reactor. The biomass trapped by the empty supports acted as a seed for new growth and, because the trapped biomass was removed from suspension, it was no longer free to pass out of the reactor as effluent suspended solids.

The biomass supports used in the experimental work described herein were provided by Simon-Hartley. The following descriptive information about the use of these supports was taken from their literature (Austin and Walker, 1986, & Tharp and Frymier).

The biomass supports produced by Simon-Hartley are pieces of a special reticulated polyurethane foam, approximately 25mm x 25mm x 12.5mm in size. The foam has the cellular windows removed by a thermal treatment process resulting in a skeletal structure with 97% voids that, it is claimed, has almost no resistance to flow through it. The opening size within the supports is nominally 11.8 pores per centimeter. The polyurethane is non-toxic, resistant to chemical and biochemical attack,

and has been specially formulated to resist abrasion. According to Simon-Hartley, the pore size of the foam has been selected to optimize biological growth and entrapment functions. Larger pores give better communication but less protection and therefore growth is easily washed out. Smaller pores give better protection but the outer zones of the support soon clog the access to the inner cells. Also, the overall size of the support has been selected to minimize diffusion limitations while maintaining a geometry that is convenient to produce and handle.

Literature from Simon-Hartley Ltd. states that approximately 40,000 of the foam supports are added to each cubic meter of aeration tank volume. In the CAPTOR systems that have been operated, between 150 and 350 milligrams per support of dry solids have been measured. These concentrations are equivalent to 6,000 to 14,000 milligrams per liter of activated sludge suspended growth. Other investigators have also obtained biomass concentrations within this range (Givens & Sack, 1987).

They recommend a minimum air flow of 18 cubic meters per hour per square meter of basin floor area, to provide mixing of the supports. The air must be supplied in such a way that the supports are completely mixed. The supports are restricted to the aeration tank by a screen across the aeration tank outlet, thus keeping the biomass within the aeration tank. The removal of excess growth from the system is accomplished by removing the biomass directly from the supports. In this way, sludge settlement and the resulting sludge recycle to the aeration tank is not required. The cleaned supports are then returned to the aeration tank for recolonization.

MATERIALS AND METHODS

A microbial population was acclimated to a phenol bearing waste stream in a laboratory reactor operating in batch mode. There were no porous biomass supports in the reactor during the acclimatization period. Once a flocculent growth of biomass was achieved, the biomass supports were added to the reactor. The reactor with biomass supports was operated in a continuous flow mode for the remainder of the experiment.

Laboratory Setup

The equipment layout for this experiment is shown in Figure 1. A clear plexiglass vessel, 9.783 liters in volume, was used as the reactor in the experiment. The reactor was immersed in a water bath to maintain a temperature of 35° to 40°C within the reactor liquid. Two plexiglass baffles were placed in the reactor to create three compartments in series (Figure 2). The influent waste stream entered at the bottom of the first compartment. A Sigmamotor T6S finger pump fitted with Tygon tubing was used to feed the influent to the reactor during continuous flow operation. The influent was pumped from 5 gallon carboys which were covered to minimize evaporation and reduce airborne contamination. Initially one carboy was used as the influent reservoir. When the feed rate increased to the point that one carboy would not last through the night, a second carboy was installed in parallel with the first, and influent was drawn equally from each carboy.

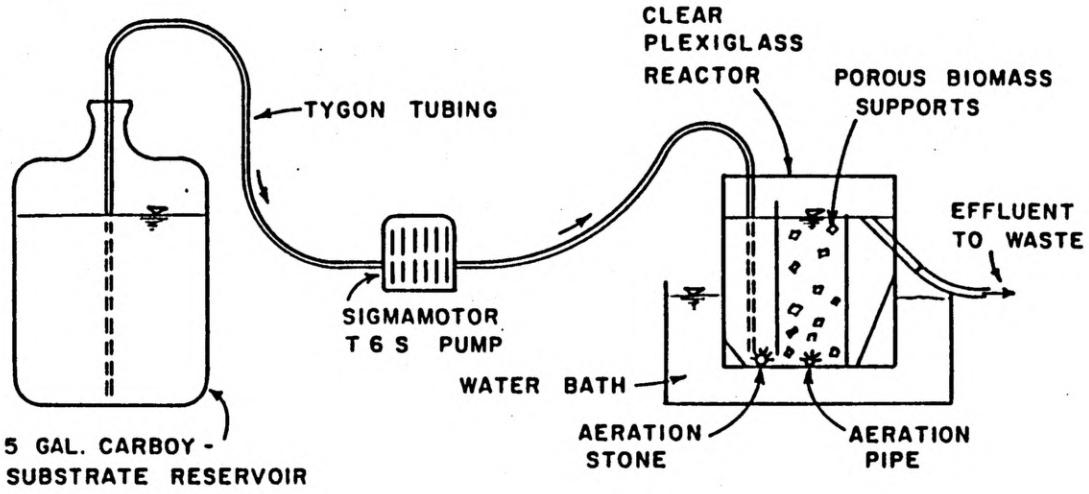


Figure 1. Schematic of Reactor System

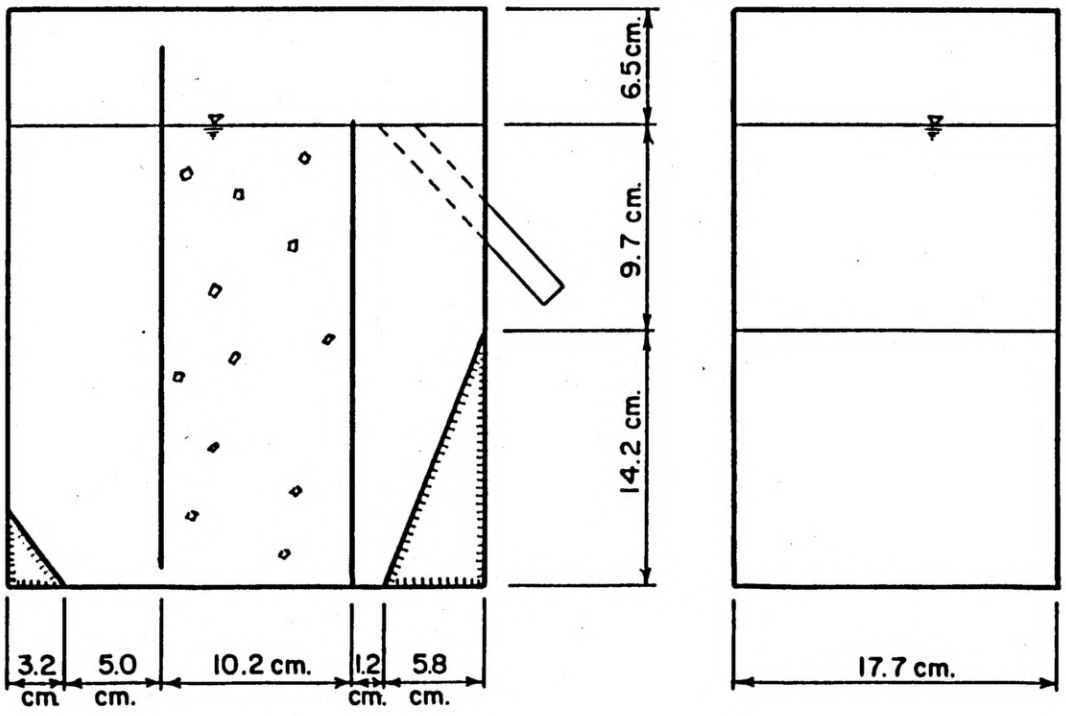


Figure 2. Interior Dimensions of Reactor

The liquid in the reactor flowed under the first baffle, which was raised approximately 0.5 centimeters above the bottom of the reactor, and into the middle compartment containing the porous biomass supports (sponges). One hundred ninety five sponges were added to the middle compartment of the reactor at random (45.3 sponges per liter). A galvanized wire screen was placed over the top of the sponges, just below the water line, to keep the sponges submerged. The random installation of the sponges resulted in a sponge matrix similar to a soil matrix. The sponges formed a structure similar to the solid particles in a soil and the liquid filled voids between the sponges functioned like the pore spaces of a saturated soil. A second plexiglass baffle separated the sponges from the third compartment. During continuous flow operation of the reactor, the reactor liquid flowed out of the third compartment to waste.

An aeration stone placed next to the influent line in the bottom of the first compartment aerated and mixed the liquid in the compartment. A 1.27 centimeter diameter PVC pipe with five holes drilled along the top of the pipe was installed along the bottom of the middle compartment to provide aeration to the sponges. The aeration pipe created large diameter bubbles which helped circulate the liquid within the compartment. The air flow to the aeration stone in the first compartment and the aeration pipe in the second compartment was regulated by the use of an air flow meter in the air lines. During continuous flow operation, the flow of air to the first compartment was 1.25 liters per minute and the air flow to the second compartment was

1.75 liters per minute. There was no aeration or mixing of the third compartment.

Originally the baffles on either side of the sponges had galvanized wire centers so that the flow could move horizontally through the sponge compartment. Part way through the experiment the baffles were changed in an attempt to have the flow move vertically up through the sponges. The baffle between the second and third compartments was intended to be sealed along the sides and the bottom so that the flow would be over the top of the baffle. The investigator did not want to permanently change the existing reactor, so an attempt was made to temporarily seal the bottom and sides of the second baffle against the reactor walls. Flow between the walls of the reactor and the second baffle was able to be reduced, but flow still occurred between the baffle and the bottom of the reactor. There was certainly some short circuiting along the bottom of the second compartment, however, it is believed that the aeration of the second compartment was helpful in reducing the short circuiting. Ultimately the majority of the flow from the second to the third compartment was under the second baffle.

Test Procedures

The reactor effluent was tested for phenol concentration, pH, and temperature on a daily basis. The phenol concentration and pH of the influent was tested on a daily basis and each time that a new carboy of influent was put on line. Phenol concentration was measured using the Direct Photometric Method described in Section 510C of Standard Methods of the Examination of Water and Wastewater (16th Edition). Dual dilutions were made of all samples to provide a check on the calculated

concentrations, and to obtain two concentration data points that were averaged to arrive at the concentration to be used in later analysis. The calibration curve, constructed as directed in Section 510B.4a of Standard Methods, is presented in the Appendix.

A Beckman Altex 30 pH meter was used for pH measurements. The automatic temperature compensation probe was not used during the pH measurements, therefore, 25°C was assumed by the instrument. The temperature of the samples was within 5°C of this temperature.

A standard thermometer, reading in degrees Centigrade, was used to determine the temperature of the reactor liquid. The temperature was measured at the middle of the third compartment.

Experimental Procedure

The reactor was initially filled with liquid obtained from Biopond #2 at the Conoco Oil Refinery. This liquid was used to provide a microbial seed that was already somewhat acclimated to a phenolic waste. Sour water stripper bottoms, taken directly from the refinery plumbing, was used as the phenol containing substrate in the experiment. During the period of operation of the experiment, the phenol concentration of the sour water stripper bottoms varied from 45 to 54 milligrams per liter (mg/l). The temperature of the water coming from the refinery was approximately 45°C. The water had typically cooled to 25°C (but was never more than 35°C) before being added to the reactor.

The reactor was operated in batch mode until a flocculent growth of microorganisms was obtained. During batch operation, 1000 milliliters of substrate were added to the reactor each day. Prior to addition of the substrate, aeration of the reactor was stopped and the accumulated

biomass was allowed to settle. Supernatant was then decanted to allow addition of the substrate without overflowing the reactor. After sufficient microbial growth had occurred, the sponges were added to the middle compartment of the reactor. The reactor was operated in the batch mode for an additional day to allow some of the biomass to attach to the sponges prior to operation on a continuous flow basis.

Upon commencement of continuous flow operation, the influent flow of substrate was set at approximately 9 milliliters per minute (ml/min.). During the first four days of operation, the influent feed varied from 8.7 to 9.5 ml/min. Over this period, the effluent phenol concentration slowly increased until the reactor was only providing 11.5% removal. Also during this period the amount of biomass observed in the reactor liquid was significantly reduced. Therefore, after four days of continuous flow operation, the reactor was returned to the batch mode of operation.

During the second operation in batch mode approximately one liter per day of substrate was added to the reactor. Over a period of eight days the phenol concentration of the reactor liquid was reduced to 75.5% of the substrate phenol concentration. At this time it was decided to add phosphorus to the reactor in an attempt to stimulate the growth of biomass. One hundred fifty milliliters of distilled water containing 0.3 grams of dissolved dibasic sodium phosphate (Na_2HPO_4) were added to the reactor. The following day the same amount of phosphorus was added. On the third day after beginning the addition of phosphorus to the reactor, the phenol concentration of the reactor liquid was only 4% of that of the substrate phenol concentration. Because of the significant

reduction in the phenol concentration of the reactor liquid, the reactor was returned to operation in the continuous flow mode. The addition of 0.65 grams of Na_2HPO_4 to each 5 gallon carboy of substrate was made immediately prior to putting the carboy on-line to the reactor.

At the beginning of the second period of continuous flow operation the substrate feed rate was set at 6.8 ml/min. The phenol concentration of the reactor effluent was checked over the next three days and was found to be only 2.8% of the substrate phenol concentration. Because of the continuing phenol reduction in the reactor effluent, the substrate feed rate was increased for the next 24 hour period. The percent phenol reduction through the reactor increased to 97.7% over the period, so the substrate feed rate was increased again. The percent removal through the reactor continued to be high throughout the experiment. The substrate feed rate was increased on a daily basis, up to a rate of 44 ml/min. when the experiment ended. The final substrate feed rate corresponds to a detention time of 3.7 hours within the entire reactor, and a detention time of 1.6 hours within the middle compartment containing the sponges.

It was intended to continue the experiment until the effluent phenol concentration began to rise. The objective was to determine the maximum feed rate that could be sustained while achieving maximum phenol reduction. This goal could not be achieved because of the increasing time and travel costs of obtaining substrate from the Conoco Oil Refinery. It had also been planned to determine the biomass concentration within individual sponges during the experiment. The investigator had intended to correlate the increase in the biomass

within the sponges to the decrease in the effluent phenol concentration. This was not possible because the phenol concentration in the reactor effluent dropped too fast, and because any disturbance of the sponges knocked the flocculent biomass out of the sponges and into the surrounding liquid. Thus, any data obtained would have been inaccurate. An estimate of the biomass within the sponges was made after the experiment was concluded. The liquid was carefully drained from the reactor and the sponges were removed one at a time. The mass of biomass contained in two sponges from each of five different levels was measured. The total biomass within the sponges was estimated by multiplying the average mass of the ten sponges by the total of 195 sponges within the reactor.

RESULTS

The data obtained from this experiment indicate that a phenol degrading biological culture can be grown on and within a porous biomass support. The average biomass concentration within the middle compartment containing the sponges was approximately 1,000 mg/l at the end of the experiment. The weight of biomass per sponge varied from an average of 14.2mg near the top of the liquid to 31.1mg near the bottom of the reactor, just above the aeration pipe. A plot of biomass per sponge versus depth is shown in Figure 3. The literature provided by Simon-Hartley Ltd indicates that systems using the CAPTOR sponges have been operated with between 150 and 350 mg/support of dry solids. Their literature indicates that this is equivalent to 6,000 to 14,000 mg/l of activated sludge suspended growth.

The sponges did not appear to be full of biomass at the end of the experiment. A visual inspection of the sponges indicated that biomass was growing on all of the sponges within the reactor, and that significant additional biomass could be retained within each sponge. It is not possible to predict, from the limited data developed during this experiment, the maximum amount of biomass that can be sustained within a reactor utilizing the CAPTOR biomass supports to treat a phenol contaminated refinery waste stream. However, it is reasonable to state that a significant increase in the biomass could be achieved.

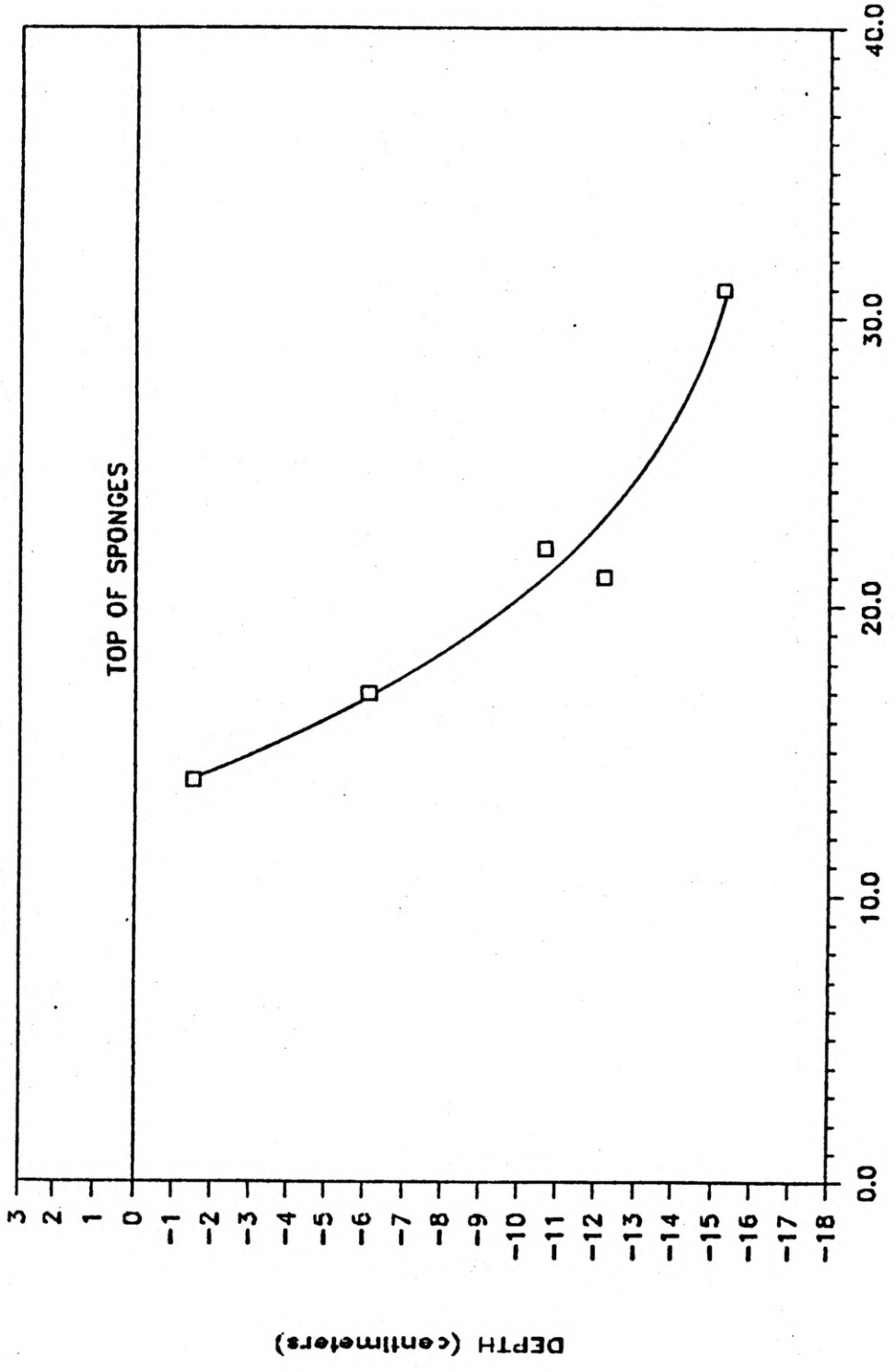


Figure 3. Biomass vs. Depth - Milligrams of Biomass per Sponge vs. Depth from Top of Reactor Liquid.

Phenol removal through the reactor was poor in the initial stages of the experiment. The phenol concentration of the effluent during the first three days of continuous flow operation actually increased. During this time phosphorus was not added to the reactor or the substrate. Once phosphorus was added to the substrate, the removal of phenol through the reactor imporved to and stabilized at 98% efficiency. A plot of the phenol concentration of the substrate and the effluent versus time is shown in Figure 4.

It is quite possible that 99% phenol removal could have been achieved if the substrate feed rate had been held constant instead of being increased on a daily basis. Unfortunately it was impossible to continue the experiment for a longer period of time and to higher flow rates due to a lack of time and funds to make the increasing number of trips to the Conoco Oil Refinery to obtain additional substrate.

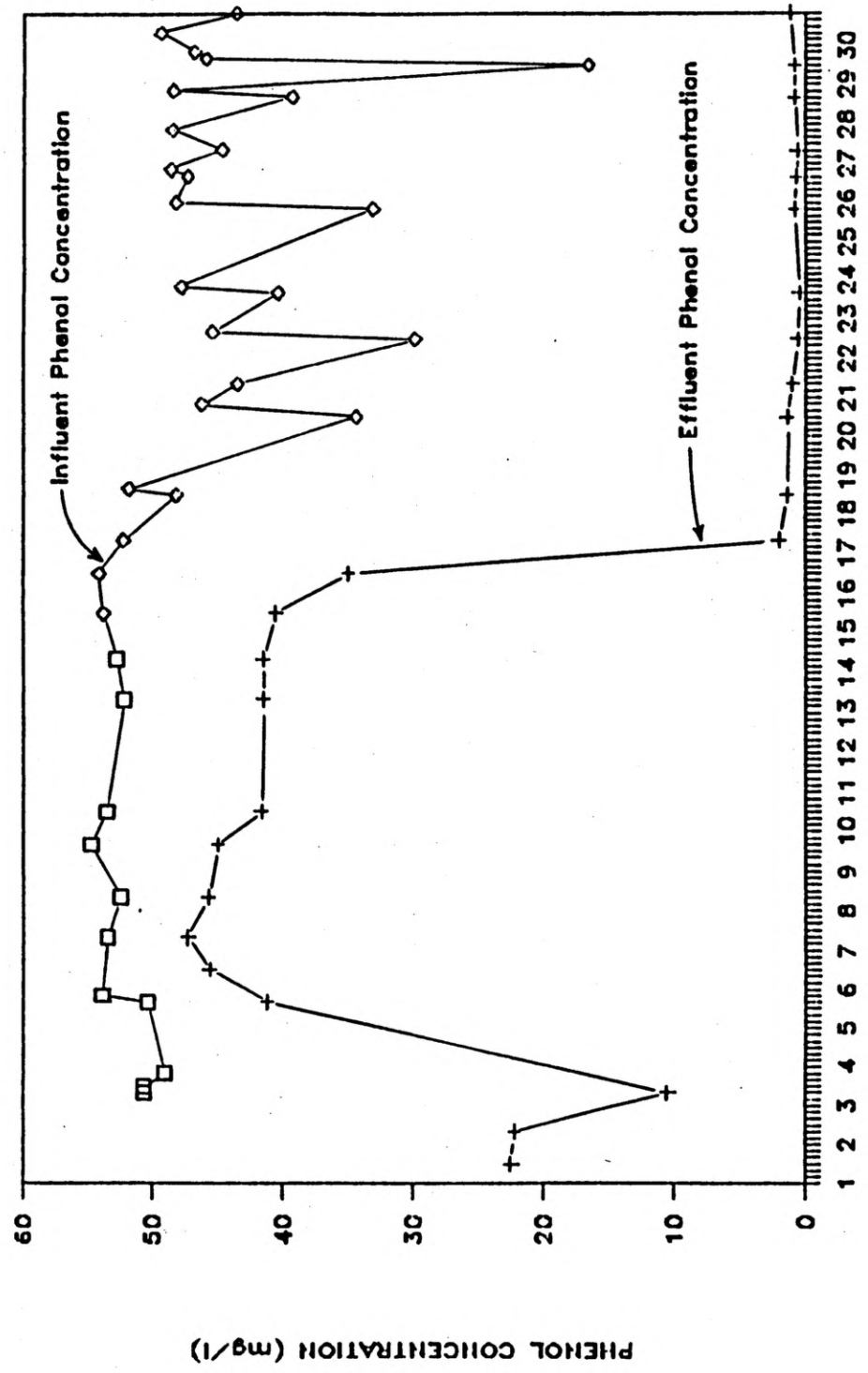


Figure 4. Phenol Concentration vs. Time - Influent & Effluent Phenol Concentration vs. Time.

DISCUSSION AND RECOMMENDATIONS

Cell Growth and Substrate Utilization

The overall rate of biomass generation within a continuous-flow stirred tank reactor without recycle is the sum of biomass growth and biomass decay and can be represented by Equation 1

$$R_g = \mu X - k_d X = (\mu - k_d)X \qquad (1)$$

R_g = net rate of biomass growth ($ML^{-3}T^{-1}$)
μ = specific growth rate (T^{-1})
k_d = endogenous decay coefficient (T^{-1})
X = biomass concentration within the reactor (ML^{-3})

The term (μX) represents the rate of biomass growth during the log-growth phase. The term ($-k_d X$) represents the rate of endogenous decay of biomass in the reactor.

Experimentally it has been found that the specific growth rate (μ) can be defined as

$$\mu = \frac{\mu_{max} S}{K_s + S} \qquad (2)$$

μ_{max} = maximum specific growth rate (T^{-1})
K_s = half-velocity constant, substrate concentration at one-half the maximum growth rate (ML^{-3})
S = substrate concentration within the reactor (ML^{-3})

The rate of substrate utilization is related to the rate of biomass growth by

$$R_{su} = -\frac{\mu X}{Y} \qquad (3)$$

R_{su} = substrate utilization rate ($ML^{-3}T^{-1}$)
Y = maximum yield coefficient, measured during any finite period of logarithmic growth, and defined as the ratio of the mass of cells formed to the mass of substrate consumed, (MM^{-1})

Substituting $\mu X = -R_{su}Y$ from Equation 3 into Equation 1 yields

$$R_g = -YR_{su} - k_dX \tag{4}$$

A mass balance for the mass of microorganisms in a continuous-flow stirred tank reactor (see Figure 5) can be written as follows

$$V \frac{dX}{dt} = QX_o - QX_e + VR_g \tag{5}$$

V = volume of the reactor (L^3)
Q = volumetric flowrate into and out of the reactor (L^3T^{-1})
X_o = biomass concentration in influent (ML^{-3})
X_e = biomass concentration in the effluent (ML^{-3})

Under steady state conditions, $dX/dt = 0$. Additionally, for the wastewater under consideration, it can be assumed that $X_o = 0$. These assumptions, can be substituted into Equation 5 to give the following equation

$$\frac{Q}{V} = \frac{R_q}{X_e} = \frac{1}{\theta} \tag{6}$$

where θ = the hydraulic detention time (V/Q). From Equations 4 and 6

$$\frac{1}{\theta} = \frac{-YR_{su} - k_dX}{X_e} \tag{7}$$

rearranging

$$\frac{X_e}{X} \cdot \frac{1}{\theta} = -Y\left(\frac{R_{su}}{X}\right) - k_d \tag{8}$$

A mass balance for substrate corresponding to the mass balance for microorganisms given in Equation 5, can be written as follows

$$V \frac{dS}{dt} = QS_o - QS + VR_{su} \tag{9}$$

S_o = influent concentration of growth-limiting substrate (ML^{-3})
S = concentration of growth-limiting substrate within the reactor (ML^{-3})

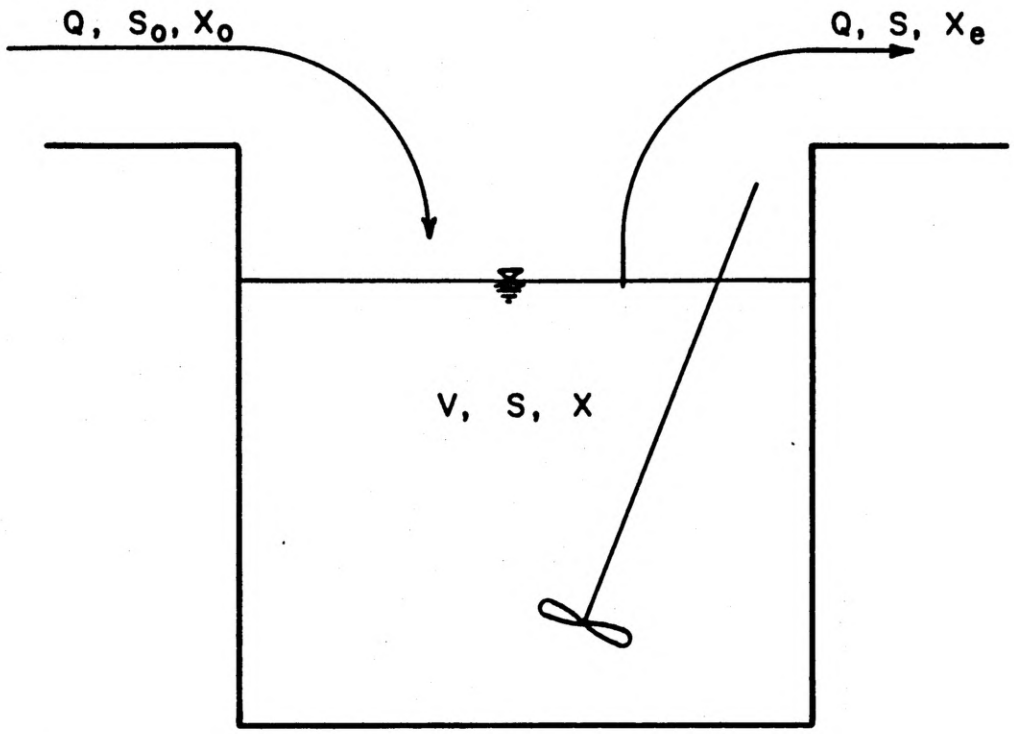


Figure 5. Schematic of a Continuous-Flow Stirred Tank Reactor

At steady state, dS/dt = 0, the resulting equation is

$$0 = \frac{Q}{V}(S_o - S) + R_{su} \tag{10}$$

Rearranging and substituting $1/\theta$ for Q/V yields

$$R_{su} = -\frac{(S_o - S)}{\theta} \tag{11}$$

Equations 2 and 3 can be combined and substituted for R_{su} in Equation 11 to give

$$\frac{\mu_{max} XS}{Y(K_s + S)} = -\frac{(S_o - S)}{\theta} \tag{12}$$

or

$$\frac{k\,S}{K_s + S} = -\frac{(S_o - S)}{\theta X} \tag{13}$$

where $k = \mu_{max}/Y$.

Taking the inverse of Equation 13 yields

$$\frac{K_s}{k}\left(\frac{1}{S}\right) + \frac{1}{k} = \frac{\theta X}{S_o - S} \tag{14}$$

The kinetic coefficients Y, k_d, K_s, and k can be determined by the procedure outlined in Metcalf and Eddy (1979). Equations 8 and 14 above are in linear form, therefore, the values of Y and k_d in Equation 8 may be determined by plotting $[(X_e/X)(1/\theta)]$ versus (R_{su}/X) and the values of K_s and k in Equation 14 can be determined by plotting the term $[\theta X/(S_o - S)]$ versus (1/S). The slope of the straight line drawn through the data points plotted from Equation 8 is equal to Y, and the y-axis intercept is equal to k_d. The slope of the straight line drawn through the data points of Equation 14 is equal to the quantity (K_s/k), and the y-axis intercept is equal to the quantity (1/k). The values for K_s and k can be solved by substitution. Measuring the mass of biomass within

the supports was not feasible in this experiment, therefore, calculation of the kinetic coefficients for the experiment is not possible.

Experimental Results

The reactor in this experiment was initially conceived to be a continuously mixed flow reactor with porous biomass supports circulating within the reactor. Numerous attempts at circulating the supports with air proved fruitless because air bubbles within the supports prevented them from submerging and moving with the currents in the water created by the aeration. For this reason the configuration of the reactor was changed so that the supports remained stationary and the reactor liquid flowed around and through the supports. Thus, the reactor in the experiment was configured similar to a packed bed rather than a continuous mixed flow reactor.

Other investigators have noted difficulties with circulation of the supports. Boyle and Wallace (1986) mention instances of poor mixing conditions and periods where large rafts of supports floated on the surface of aeration tanks. They state that design requirements to ensure proper support mixing and distribution need to be better defined. At the end of this experiment it was observed that the supports did not contain air bubbles and that they did not tend to float. A potential solution to floating of the supports might be to add them to the aeration tank in small numbers over a period of days or weeks. Biomass could attach and grow within the sponges, slowly expelling the air and allowing the sponges to circulate. This method of operation seems feasible in situations where the biomass grows slowly, and therefore only a small number of supports are being cleaned daily. If large

numbers of supports were cleaned each day, the large rafts of supports mentioned above could again build up.

The daily increases in the substrate feed rate did not result in an increase in the effluent phenol concentration. Possible reasons for this observation are 1) the phenol concentration of the substrate was not high enough to cause a significant shock to the reactor biomass, 2) the increases in the feed rate were not high enough to produce a significant increase in the mass of phenol seen by the biomass, 3) the configuration of the reactor as a packed-bed reactor, which recovers quickly from shock loading and step hydraulic shocks (Holladay, 1978), overcame the increased phenol loading placed on it and prevented a spike in the effluent phenol concentration. Additional experimental work is necessary to determine what variations in substrate concentration or substrate feed rate will cause the effluent phenol concentration to increase.

Five times over the last ten days of the experiment the substrate phenol concentration in the carboy reservoirs declined significantly. The cause of these reductions is not known. The reduction in the substrate phenol concentration was 19% on one occasion, 31% to 33% on three occasions, and 66% on one occasion. The last mentioned phenol reduction of 66% occurred at the same time as the first upset in the reactor. A new carboy had been put on line and the substrate feed rate increased at 8:00pm one evening. At 11:00am the next morning, the reactor was observed to be approximately 2 liters low on water and the substrate feed line was full of air from the reactor back to the pump. It is possible that liquid from the reactor was pumped back into the

carboy reservoir, with the resulting biological activity reducing the phenol concentration within the reservoir. However, the other four occasions of reduced substrate phenol concentration occurred prior to this time during normal operation of the reactor. Possible explanations for the phenol reduction include 1) volatilization, 2) chemical reactions within the substrate, or 3) microbial action caused by contamination of the reservoir.

The possibility of volatilization does not seem reasonable because, if this were the cause, it should have occurred from the beginning of the experiment. During the first 2½ weeks of the experiment there was no significant reduction in the substrate phenol concentration with time. Also, during the first continuous flow operation of the reactor, the phenol reduction through the reactor was only 11% compared to the much higher reductions overnight within the carboy reservoirs.

It is also unlikely that a purely chemical reaction was occurring within the reservoirs. If this were the case then the phenol reduction should have begun while the substrate was stored in the Nalgene carboys waiting for use in the experiment. Testing of the substrate within each carboy prior to use showed no signs of significant phenol reduction, thus it does not seem that a chemical reaction is the cause of the observed reductions.

It is interesting to note that the reductions in substrate phenol concentration were not observed until after phosphorus had begun to be added to the substrate in the reservoirs. Any microbial contamination of the reservoirs could have been enhanced by the addition of phosphorus producing enough growth to cause the reduction. The time between the

last normal substrate phenol concentration and the reduced observation varied from 18 to 48 hours. The time between occurrences varied from 64 to 77 hours. Changes to the substrate and the feed rate within the preceding 24 hours also varied between occurrences. One time a new carboy of substrate was put on line, one time the feed rate was increased, and one time both the substrate and the feed rate were changed. It is not possible to definitely identify the cause of the reduction in substrate phenol concentration, however, it is believed that microbial degradation was involved. Means of preventing a recurrence of the problem include adding the phosphorus to the reactor separately instead of adding it to the substrate, and to carefully clean the reservoirs between additions of new substrate.

Holladay, et al. (1978), investigated the biodegradation of phenolic waste liquors in stirred-tank, packed-bed, and fluidized-bed reactors. They investigated operational parameters such as substrate flow rate, pH, substrate concentration, and air flow rate to determine the most efficient type of reactor for degrading phenolic-type substrates derived from coal processes. The phenol concentration in the substrate in their investigation was considerably higher than that used in the current investigation. The detention times in their stirred tank reactor were also significantly higher than those in this investigation. Their substrate feed concentration varied from 416 mg/l to 2387 mg/l and the detention time varied from 11.7 hours to 79.5 hours in the stirred-tank reactor. In their packed-bed reactor, the substrate feed concentration varied from 100 mg/l to 775 mg/l and the detention time varied from 0.10 hours to 10.63 hours. The mass rate of flow of

substrate into the reactors varied from 0.5 mg/min. to 6.5 mg/min. in the stirred-tank reactor and 0.2 mg/min.to 14.3 mg/min. in the packed-bed reactor. In comparison, the feed concentration and detention time in the current investigation varied from 40.4 mg/l to 47.8 mg/l and 3.7 hours to 17.9 hours respectively, and the mass rate of flow of the influent substrate varied from 0.4 mg/min. to 1.9 mg/min. (Table 1).

Table 1. Phenol Degradation Rate and Fractional Conversion.

Date	Flow Rate ml/min	Avg Inf Conc. mg/l	Eff. Conc. mg/l	Frac. Conv.	Degrad. Rate g/l-d	Detent. Time hr.	Inf. Phenol mg/min.
3-15	9.1	44.85	1.0	0.98	0.06	17.9	0.41
3-16	13.0	36.70	0.6	0.98	0.07	12.5	0.48
3-17	11.5	42.90	0.5	0.99	0.07	14.2	0.49
3-19	10.3	40.40	0.8	0.98	0.06	15.8	0.42
3-20	18.7	47.75	0.7	0.98	0.13	8.7	0.89
3-21	24.4	46.65	0.6	0.99	0.17	6.7	1.14
3-22	30.8	43.90	0.8	0.98	0.20	5.3	1.35
3-23	36.5	40.45	0.8	0.98	0.21	4.5	1.48
3-24	43.5	46.40	1.2	0.97	0.29	3.7	1.90

The maximum phenol degradation rate, with 99% phenol conversion, measured by Holladay, et al., was 2.67 g/l-d for the stirred-tank reactor and 4.7 g/l-d for the packed-bed reactor. However, the influent mass flow rate of phenol for these two degradation rates was 7.0 mg/min. and 9.3 mg/min. respectively. In contrast, during the current investigation the maximum phenol degradation rate, with 98% phenol reduction, was 0.29 g/l-d at an influent mass flow rate of phenol of 1.9 mg/min. (Figure 6). Interpolation of the data presented by Holladay, et al., for 99% phenol removal at a mass flow rate of 1.9 g/l-d, gives degradation rates for the stirred-tank and packed-bed reactors

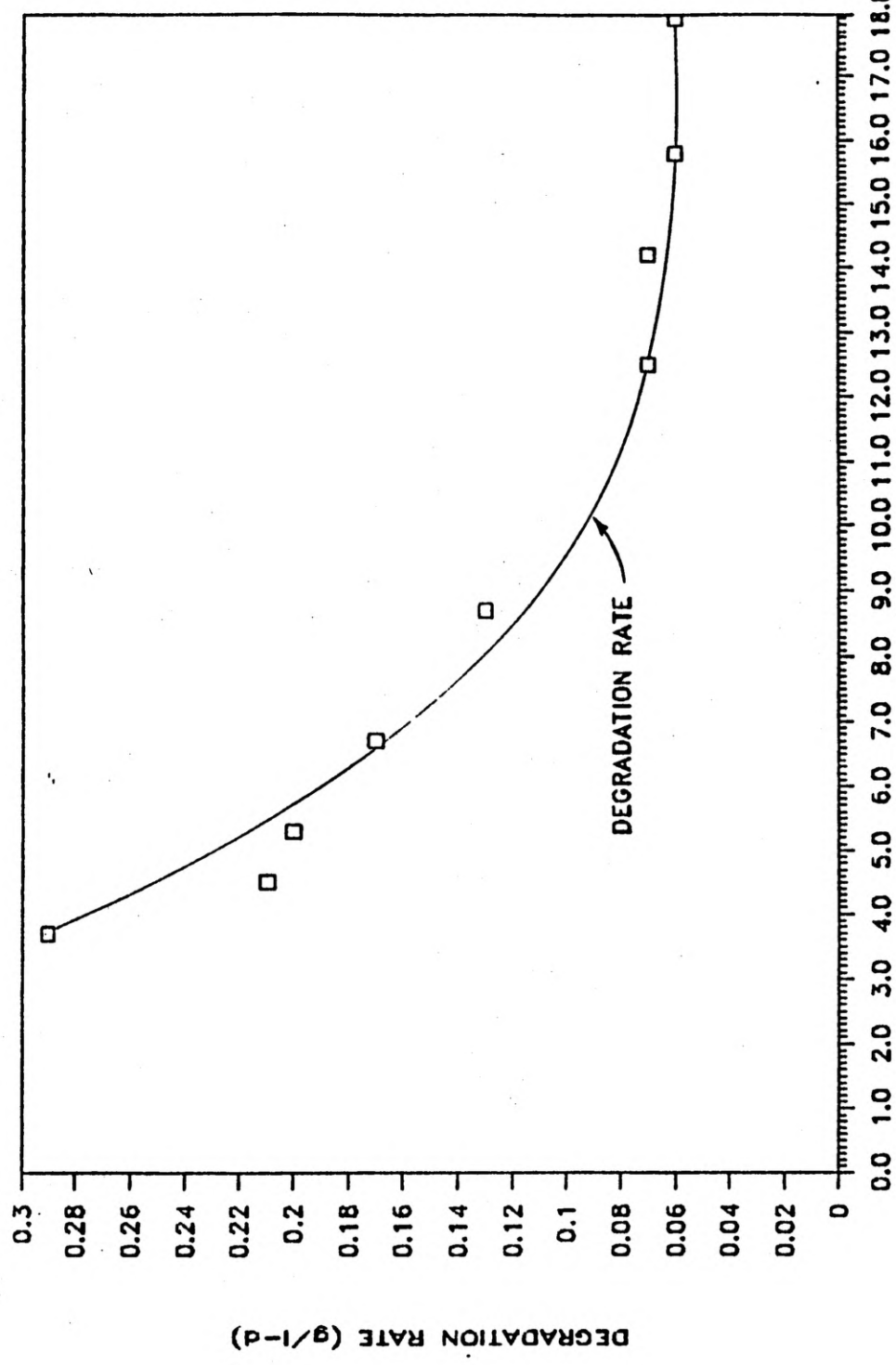


Figure 6. Degradation Rate vs. Detention Time - Rate of Phenol Degradation vs. Detention Time.

of approximately 0.8 g/l-dand 3.2 g/l-d respectively. These values are 2.7 and 11.0 times greater than the highest degradation rate determined in this investigation.

In the work by Holladay, et al, the degradation rate peaked at a relatively short detention time. A peak in the degradation rate is not apparent in Figure 6, thus, it may be possible to decrease the detention time still more and obtain even higher phenol degradation rates. Exactly what the maximum degradation rate might be cannot be determined without further laboratory work. It is also possible that the higher degradation rates observed by Holladay, et al. were due to their use of substrates with higher phenol concentrations and therefore closer to the optimum for the microorganisms present. There may also be constituents in the sour water stripper bottoms used in this study that partially inhibit the removal of phenol.

Gilman (1987) states that Biopond #1 at the Conoco Refinery has a detention time of 5.5 hours and a biomass concentration of less than 100 mg/l. Within the limited time frame of this investigation a biomass concentration of 1000 mg/l was established within the middle compartment of the reactor, and a minimum detention time of 3.7 hours was achieved while maintaining a consistent phenol reduction of 98%. The 3.7 hour detention time is a 32% reduction from the detention time of the existing biopond. Because the phenol degradation rate showed no signs of peaking at the end of this experiment, it is possible that a longer laboratory run could produce a higher biomass concentration and a lower detention time while maintaining the same phenol reduction.

Recommendations

It is recommended that a pilot plant with a configuration similar to that shown in Figure 7 be operated at the Conoco Refinery so that the kinetic coefficients for the phenol degradation process can be determined. Substrate should be obtained from the refinery waste stream on a daily basis so the pilot plant receives, as nearly as possible, the same waste as the actual treatment system. Parameters to be monitored during the operation of the pilot plant include 1) temperature, 2) pH, 3) influent flow rate, 4) influent substrate concentration, 5) biomass concentration within the supports, 6) effluent substrate concentration, and 7) effluent biomass concentration. The results of the pilot plant operation will allow calculation of the kinetic coefficients and the maximum phenol degradation rate per gram of biomass within the reactor (grams of phenol degraded per gram of biomass per day). The degradation rate and the kinetic coefficients will provide the basis for design or modification of the treatment process for the sour water stripper bottoms.

Once the optimum hydraulic detention time of the pilot plant is defined, it should be operated at this detention time for at least 30 days to determine the stability of the operation. The parameters listed above should be monitored during this period to provide data for analysis should the pilot plant experience an upset. If the plant does experience an upset, the cause should be determined and a new runs made until stability is achieved.

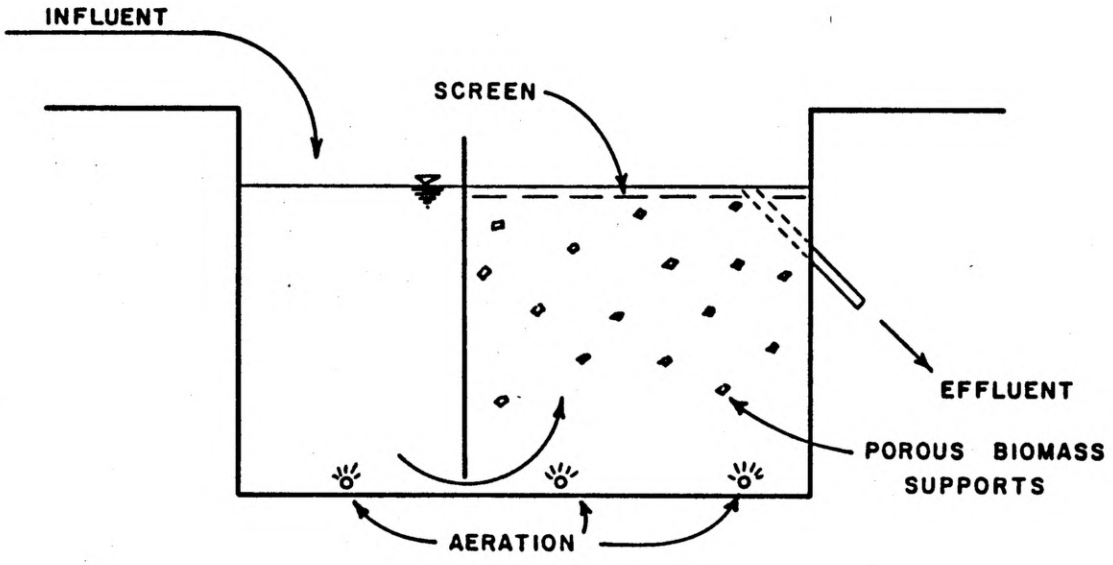


Figure 7. Schematic of Pilot Plant

CONCLUSIONS

This investigation has shown that a microbial population to degrade the phenol in the sour water stripper bottoms of the Conoco Oil Refinery can be grown within porous biomass supports supplied by Simon-Hartley Ltd.. It has also been shown that 98% reduction in the phenol concentration can be achieved with a reactor detention time of less than four hours utilizing the porous biomass supports.

Additional experimental data, ideally developed from laboratory experiments conducted at the Conoco Refinery where substrate is readily available, will be needed to determine the optimum biomass concentration per support, the maximum degradation rate, and the minimum detention time within a reactor for optimum phenol removal.

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APPENDIX

Table 2. Laboratory Data.

Date	Time	Influent SWS Feed Rate (ml/min.)	Influent Phenol Conc. (mg/l)	Effluent Phenol Conc. (mg/l)	Influent SWS pH	Effluent Reactor pH	Reactor Temp. °C	Remarks
2-24	11:50am	Batch	. . .	22.5	. . .	. . .	35	Air Flow: 2.5 l/min. Inf. & 2.75 l/min. Pads
2-25	9:30am	"	. . .	22.2	. . .	7.9	35	
2-26	8:30am	"	50.7	10.6	8.0	7.9	35	
"	11:15am	8.7	50.7	. . .	. . .	. . .	. . .	Begin continuous feed of substrate
"	6:00pm	8.7	49.1	. . .	8.9	. . .	. . .	Feed rate up to 12.9, reset to 8.7
2-27	9:20pm	9.0	. . .	. . .	8.4	. . .	32	
2-28	2:45pm	9.7	50.4	41.2	. . .	. . .	35	Air Flow: 2.5 l/min. Inf. & 2.75 l/min. Pads
"	7:00pm	7.0	53.4	. . .	8+	. . .	. . .	
2-29	11:45am	0/8.7	. . .	45.6	. . .	8.1	34	Air in feed line - No flow. Reset to 8.7
3-1	8:45am	9.5	53.4	47.3	. . .	8.1	. . .	
"	11:55am	. . .	. . .	. . .	. . .	. . .	. . .	Turn off substrate feed. Return to Batch Mode
3-2	9:15am	Batch	52.4	45.7	8.4	8.1	35	
3-3	5:45pm	"	54.6	45.0	8.9	8.2	38	Added 1 l. distilled water to reactor @ 2:30pm
3-4	11:30am	"	53.5	41.7	8.8	8.0	37	Air Reset: 1.0 l/min. Inf. & 1.75 l/min. Pads
3-5	5:45pm	"	. . .	. . .	8.6	7.9	36	

Table 2. Laboratory Data (continued).

Date	Time	Influent SWS Feed Rate (ml/min.)	Influent Phenol Conc. (mg/l)	Effluent Phenol Conc. (mg/l)	Influent SWS pH	Effluent Reactor pH	Reactor Temp. °C	Remarks
3-6	1:00pm	"	. . .	. . .	8.6	8.0	39	
3-7	8:40am	"	52.2	41.6	8.6	8.0	38	
3-8	8:45am	"	52.8	41.6	8.4	8.0	38	
3-9	11:00am	"	53.7	40.6	8.3	7.6	40	
"	3:45pm	"	. . .	. . .	. . .	. . .	. . .	Added 0.3g Na_2HPO_4 in 100ml D.W. to reactor
3-10	11:20am	"	54.0	35.0	8.3	8.0	37	Added 0.3g Na_2HPO_4 in 150ml D.W. to reactor
3-11	9:30am	"	52.2	2.0	8.2	8.1	38	
"	4:45pm	5.7	. . .	. . .	. . .	. . .	. . .	Begin continuous feed of substrate. Added 0.65g Na_2HPO_4 in 400ml D.W. to carboy.
3-12	1:00pm	6.8	48.2	1.4	7.9	8.0	36	Air Reset: 1.5 l/min. Inf. & 1.75 l/min. Pads
"	2:00pm	6.8	51.8	. . .	. . .	. . .	. . .	New carboy on line
3-14	11:30am	0/9.0	34.4	1.4	7.6	8.1	38	Feed line floated in reservoir
"	6:00pm	9.0	46.2	. . .	. . .	. . .	. . .	Changed reactor configuration from flow-thru to under & over. Put new carboy on line. Air Reset: 1.25 l/min. Inf. & 1.75 l/min. Pads
3-15	9:00am	9.2	43.5	1.0	8.7	7.7	37	
"	11:45am	13.0	. . .	. . .	. . .	. . .	. . .	Increase substrate feed rate

Table 2. Laboratory Data (continued).

Date	Time	Influent SWS Feed Rate (ml/min.)	Influent Phenol Conc. (mg/l)	Effluent Phenol Conc. (mg/l)	Influent SWS pH	Effluent Reactor pH	Reactor Temp. °C	Remarks
3-16	2:15pm	13.0	29.9	0.6	7.4	7.4	35	
"	4:00pm	13.0	45.4	. . .	8.8	. . .	. . .	New carboy on line
3-17	2:30pm	10.0	40.4	0.5	8.6	7.3	35	
"	8:45pm	10.0	47.8	. . .	. . .	. . .	. . .	New carboy on line
3-19	9:15pm	10.8	33.1	0.8	7.8	7.6	39	
"	11:00pm	19.0	48.2	. . .	9.0	. . .	. . .	Increase feed rate & new carboy on line
3-20	2:45pm	18.4	47.3	0.7	8.9	7.4	36	
"	7:00pm	24.2	48.6	. . .	9.0	. . .	. . .	Increase feed rate & new carboy on line
3-21	8:35pm	24.6	44.7	0.6	8.8	7.4	37	
"	9:20pm	30.0	48.5	. . .	8.9	. . .	. . .	Increase feed rate & new carboy on line
3-22	3:30pm	31.6	39.3	0.8	8.5	7.1	36	
"	8:00pm	36.0	48.4	. . .	9.0	. . .	. . .	Increase feed rate & new carboy on line
3-23	11:00am	0/37.0	. . .	. . .	. . .	. . .	. . .	Liquid volume in reactor 2.5 l low & feed line below pump full of air. Reset feed to 37.
"	4:00pm	37.0	16.6	0.8	8.7/7.2	7.4/7.4	35	Samples taken of substrate & effluent, covered w/parafilm for analysis on 3-24. Dual values are for when sampled/when tested.

Table 2. Laboratory Data (continued).

Date	Time	Influent SWS Feed Rate (ml/min.)	Influent Phenol Conc. (mg/l)	Effluent Phenol Conc. (mg/l)	Influent SWS pH	Effluent Reactor pH	Reactor Temp. °C	Remarks
3-23	4:00pm	43.0	45.9	. . .	9.0	. . .	. . .	Increase feed rate & new carboy on line
"	9:00pm	44.0	46.8	. . .	8.9	. . .	. . .	Add 11 l substrate to existing carboys
3-24	8:10am	43.5	47.7	. . .	8.8	. . .	36	Add 16.5 l substrate to existing carboys
"	10:10pm	48.8	43.6	1.2	8.8	7.1	37	Increase feed rate & new carboys on line
3-25	9:00am	. . .	. . .	. . .	. . .	. . .	. . .	Reactor liquid level down 8 l. Experiment terminated.

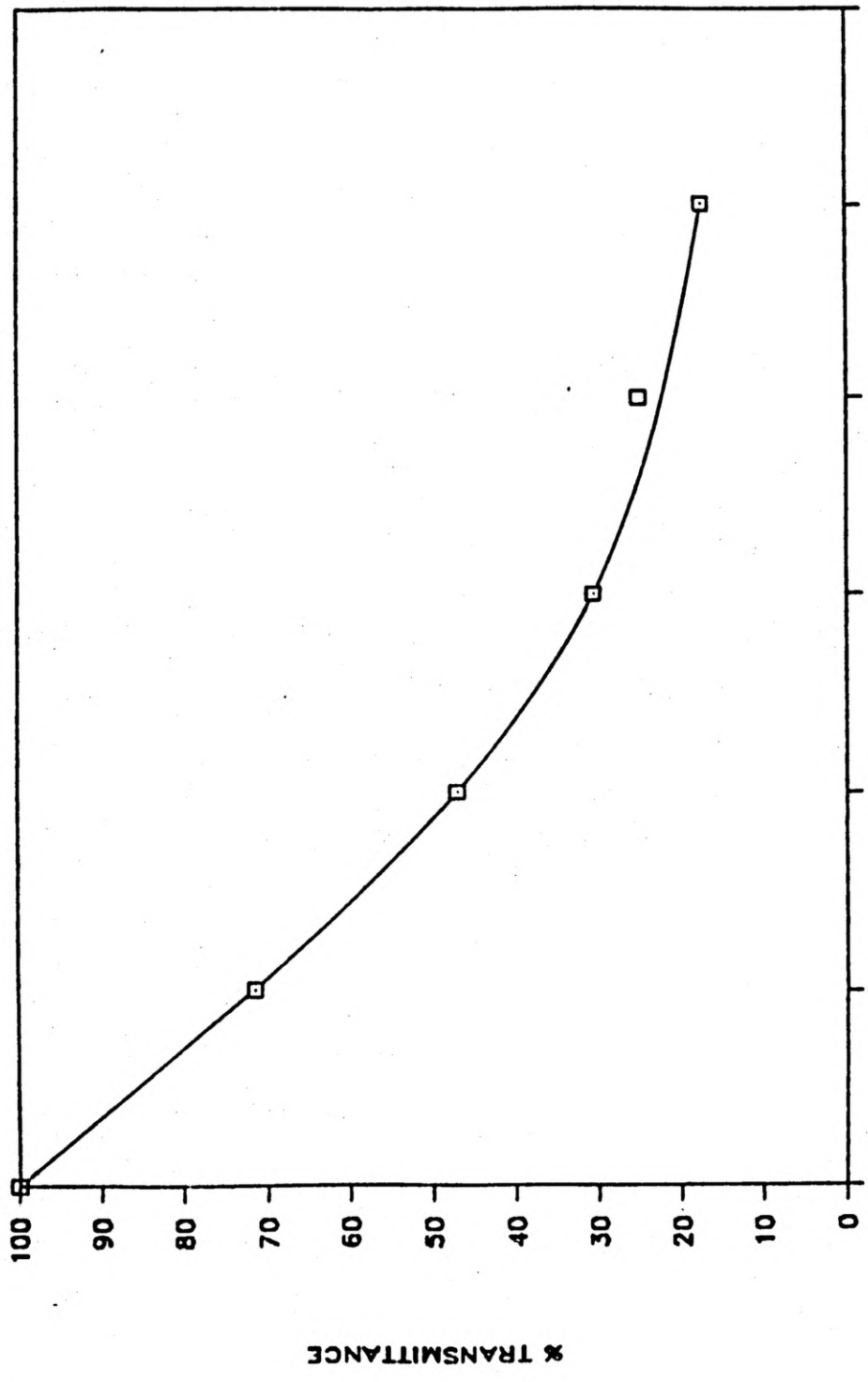


Figure 8. Standard Phenol Calibration Curve - for Direct Photometric Measurement of Phenol Concentration.