IMPROVING THE REMOVAL OF PHENOLS IN THE BIOLOGICAL PORTION OF THE CONOCO OIL REFINERY WASTEWATER TREATMENT PLANT, BILLINGS, MT

by

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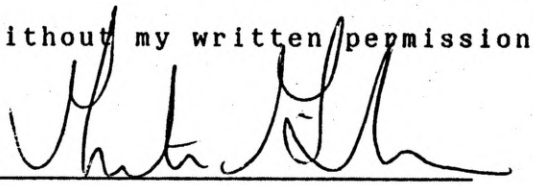
Signature 

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ABSTRACT

The biological removal of phenols in the wastewater treatment system of the Conoco Oil refinery in Billings, MT is not consistent. The purpose of this project was to examine low-capital-cost ways of improving the removal of phenols from the wastewaters generated by this refinery.

These wastewaters are of two types: API Separator effluent and sour-water stripper effluent. The API Separator effluent is of complex and varying composition. It contains low level phenols and may occasionally contain constituents that inhibit biological removal. The sour-water stripper effluent is of consistent composition and contains much higher phenol concentrations than the API Separator effluent. In the present treatment system, these two waste waters are combined for treatment.

Batch reactions were performed in the Environmental Engineering labs at Montana State University to determine the specific rate of substrate removal for these particular wastewaters and microorganisms. The specific rate of substrate removal for the combined wastewaters (API Separator effluent and sour-water stripper effluent) is 0.0006 mg phenol removed per hour per mg biomass. The specific rate of substrate removal for the sour-water stripper effluent alone is 0.0015 mg phenol removed per hour per mg biomass.

Using these specific removal rates, along with mass balance equations, various reactor configurations were analyzed. Based on this analysis, recommendations for possible improvements to the present Billings Conoco refinery wastewater treatment system are made.

INTRODUCTION

The purpose of this project is to examine low-capital-cost ways of improving the removal of phenols from the wastewaters generated by the Conoco oil refinery in Billings, MT. Presently, phenols are removed biologically in bioponds (aeration tanks) and in aerated holding ponds. Over the last five years, the refinery has had less than five violations of the phenol effluent standard (average of 0.3 ppm and a max of 0.5 ppm[1]). However, an emergency holding pond is quite often used to divert water that has been insufficiently treated in the bioponds before it contaminates the holding ponds. Also, the cost of aerating the holding ponds would be reduced if greater removal were accomplished in the bioponds. The following is a brief description of the biological portion of the present treatment system.

The Present Treatment System

The water flowing into the bioponds is of two types--roughly 230 gpm API Separator effluent and 65 gpm sour-water stripper effluent. The API Separator effluent contains low level phenol and 50-100 ppm suspended oil, and it is approximately 35 degrees C and pH 5. The sour-water

stripper effluent contains 50 - 75 ppm phenols and 20-60 ppm ammonia, and it is approximately 60 degrees C and pH 8.5[2].

There are two bioponds in series. The first (Biopond 1) has a volume of 76,000 gallons, and the second (Biopond 2) holds 119,000 gallons. Approximately 2/3 of the API Separator water flows into Biopond 1 and then into Biopond 2. 1/3 of the API Separator water flows directly into Biopond 2. All of the sour-water stripper effluent flows into Biopond 1. The residence time in Biopond 1 is roughly 5.5 hrs, and Biopond 2 residence time is slightly longer[1]. The bioponds have less than 100 mg/1 biomass in them, and they are approximately 60% efficient at BOD removal[2]. No form of biomass recycle is practiced at present.

After the wastewater leaves the bioponds, it flows into the first in a series of two aerated holding ponds. In these ponds, the remaining phenol concentration and BOD are reduced to the effluent standard. The holding ponds have volumes of 1 million and 1.7 million gallons respectively[1], and residence times of greater than two days.

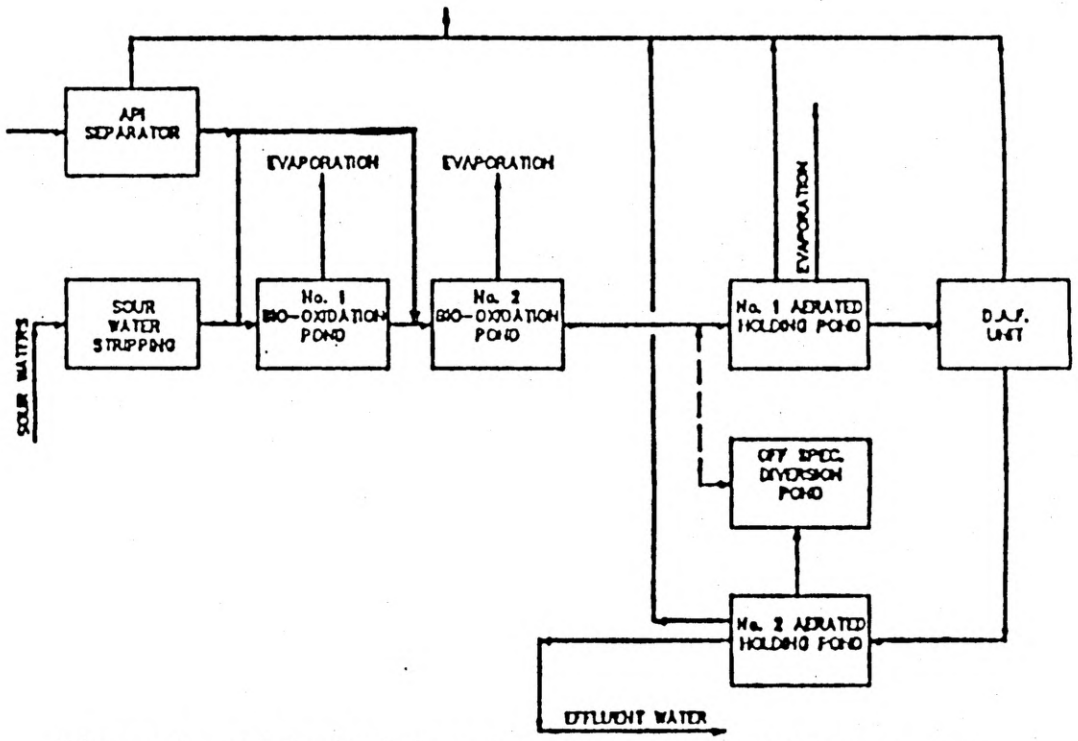

Figure 1. Biological Wastewater Treatment Portion of the Billings Conoco Oil Refinery

The sour-water stripper effluent is uniform in composition and delivers relatively constant organic and hydraulic loads to the biopond system[1]. This is not the case with the API Separator effluent. Due to the variety of processes contributing wastewater to the API Separator, its effluent (influent to the bioponds) is a variable waste stream which occasionally contains constituents that inhibit biological removal in the bioponds. These constituents are sometimes toxic to the microorganisms, but most often affect removal by altering system pH. When this occurs, the poorly treated biopond effluent must be diverted to an emergency holding pond before it contaminates the aerated holding ponds[1].

Ideally, biological treatment would be complete after the wastewater has passed through both of the bioponds. If this were the case, the holding ponds could be used for the purpose that their name suggests, with no need for aeration. If the capital cost of a system that could provide complete treatment in the bioponds were prohibitive, it would still be advantageous to provide more reliable removal of phenols in the bioponds and eliminate the need for diversion of water into the emergency holding ponds. The scope of this project will be narrowed to the examination of improvements to the treatment plant that will allow greater and more reliable removal of phenols without high capital cost or labor-intensive additions to the present system.

Phenols: Characteristics and Removal Techniques

Phenols are monohydroxy derivatives of benzene and therefore contain an aromatic ring. Phenol is produced in an oil refinery as a byproduct of catalyst cracking for gasoline. Because of its high aqueous solution solubility, it is found in refinery processing water effluent in quite high concentrations[3]. The concern about phenolics is primarily due to their toxicity to aquatic organisms and the high oxygen demand they impose on receiving streams. Also, even very low concentrations of phenolics cause a taste and odor problem when present in potable water supplies. This is particularly true when waters containing

phenolics are disinfected with chlorine, resulting in the formation of chlorophenolics[4]. The waste category termed "phenols" might also contain a variety of similar chemical compounds, such as poly-and chlorophenols[5]. Phenol is relatively easy to degrade: concentrations in the 150 to 250 mg/l range may be reduced by as much as 97% through biological methods[6].

Wastewaters, such as those treated at the Conoco refinery, containing phenol concentrations in the range of 5-500 mg/l (ppm) may be considered of intermediate strength. In the absence of high concentrations of toxic substances, biological treatment is widely employed for removal of intermediate level phenol concentrations[5], and the possibility of biological removal will be examined in this study. However, chemical and physical methods have also been successfully applied.

There are several types of chemical treatment for phenolic wastewaters, and these include treatment with chemical oxidizers such as chlorine, potassium permanganate, ozone, and hydrogen peroxide. In practice, the oxidizing agent cleaves the aromatic ring forming a straight-chain organic molecule[6]. However, this molecule continues to exert an organic loading, and for this reason, chemical treatment is not recommended in cases where organic reduction is required in addition to phenol removal[7]. Since the Conoco wastewater treatment plant must

meet BOD standards, chemical treatment will not be considered to be within the scope of this project.

Physical removal methods include extraction and activated carbon adsorption. Extraction is, by design, a method intended for the recovery of one material by the use of another. For this reason, it is only an attractive consideration when dealing with wastewaters containing high phenol concentrations (> 500 mg/1)[5]. Also, waters from extraction operations require additional "polishing" because the very low effluent standards cannot be met by this process[5]. Since the Conoco refinery wastewater does not contain high phenol concentrations and must meet low effluent standards, extraction is unlikely to be an effective means of removing phenol from this wastewater. Activated carbon adsorption can achieve phenol reductions to less than 1 mg/1[5], and it is an efficient and effective means of phenol removal. In general, capital and treatment costs are greater for carbon adsorption than for biological treatment[5]. However, activated carbon adsorption might be considered as a possible improvement to the Conoco wastewater treating system if the simpler and less expensive methods considered in this study prove to be ineffective.

BACKGROUND

Since the Conoco wastewater treatment system is already equipped with two aeration tanks, it is logical that treatment methods utilizing aerobic suspended growth processes be examined as possible improvements to the system. Activated sludge processes (aerobic suspended growth with recycle) have been able to reduce oil refinery wastewater phenol concentrations from 0.5-11 ppm to 0.1 ppm or less[8] and to reduce higher concentrations (40-80 ppm) down to less than or equal to 1 ppm[5]. However, these reductions were achieved with high biomass concentrations (over 1000 mg/l). The bioponds at the Conoco refinery contain only 20-65 mg/l volatile suspended solids[2].

The requirement of high biomass concentration for removing phenols within a limited reactor residence time can be explained by rate (kinetic) equations which are applicable to completely mixed and batch systems. Bacteria divide by binary fission, and consequently, the number of viable cells will increase in an exponential fashion under optimal conditions. Therefore, the reaction rate for bacterial growth can be expressed as a first order equation[9]:

$$r_x = uX$$

r_x = rate of production of biomass (mass/volume-time)
u = specific growth rate of biomass ($time^{-1}$)
X = concentration of biomass in reactor (mass/volume)

The rate at which substrate (phenol) is removed may also be expressed as a first order equation[9]:

$$r_s = -\frac{ux}{Y}$$

r_s = rate of substrate removal(mass/volume-time)
Y = growth yield (ratio of rate of cell growth to rate of substrate removal)

The specific rate of substrate removal (q) has been defined as[9]:

$$q = \frac{u}{Y}$$

Thus the rate at which substrate (phenol) is removed may be expressed as[9]:

$$r_s = - qX$$

q = specific rate of substrate removal (mg removed/mg cells-time)

From this equation, it is again obvious that the rate of phenol removal will be greater if the concentration of biomass in the reactor is higher.

The concentration of phenol in the influent to an aerobic suspended growth treatment system also affects the removal achieved by the biomass in the system. Using phenol concentrations of 180 mg/l and 360 mg/l in their test runs, Beltrame, Beltrame, and Carniti[10] showed that phenol degradation rate in a continuous stirred reactor is an inverse function of the phenol concentration in the feed. They attribute this to inhibition by secondary reaction products. Holladay, Hancher, Scott, and Chilcote[11] showed that washout factor (1/detention time)

was higher at lower phenol concentrations. Richardson and Temple[8] determined that the optimum phenol concentration for degradation by the organisms in the Billings Conoco wastewater treatment plant is 100-200 ppm. This is well above the concentration present in the wastewaters treated at the plant, and orders of magnitude above the diluted phenol concentrations in the present bioponds[2]. For this reason, phenol removal may possibly be improved by treating the sour-water stripper effluent alone (50-75 mg/l phenol) before mixing it with the API Separator effluent.

The present biopond system at the Conoco treatment plant can be considered a continuous stirred tank reactor (CSTR) if it is assumed that the vigorous aeration in the bioponds results in complete mixing. Using this assumption and applying the principle of conservation of mass to a CSTR system, the following differential equation represents the concentration of a particular constituent in the bioponds[12]:

$$V\frac{dC}{dt} = Q(C_i - C) + Vr$$

C = reactor concentration (mass/volume)
C_i = feed (influent) concentration (mass/volume)
Q = volumetric how rate (volume/time)
r = rate of production per unit volume (mass/time rt.)
V = volume of tank

C can represent biomass, substrate, oxygen, or any other constituent within the bioponds. When used to represent biomass, X is the symbol commonly used. S is commonly used to represent substrate.

If it is assumed that concentrations within the bioponds do not change with time, the system can be considered to be at steady state ($\frac{dC}{dt} = 0$), and the following mass balance equation can be used to represent the concentrations in the bioponds:

$$0 = \frac{dc}{dt} = \frac{Q}{V}(C_i - C) + \frac{V}{V} r \quad \text{------>}$$

$$D(C_i - C) = -r$$

D = Dilution rate = Q/V = 1/residence time
r = rate of production of biomass (mass/volume-time)

For substrate (S), this equation becomes:

$$D(S_i - S) = -r = qX$$

q = specific rate of substrate removal

Rearranging and substituting detention time ($\theta = D^{-1}$) for D results in the following relationship between substrate removal, biomass concentration, and detention time:

$$\frac{S_i - S}{X\theta} = q$$

Eckenfelder[18] arrived at a similar observational relationship between suspended solids and detention time in a completely mixed system for given influent and effluent BOD values:

$$\frac{S_o - S_e}{X_a t} = kS_e$$

S_o & S_e = BOD of influent and effluent respectively (substrate concentration, mass/volume)
X_a = average mixed liquor suspended solids (MLSS) (biomass concentration, mass/volume)
t = detention time
k = specific removal rate (volume/biomass-time)

In a subsequent investigation, Radhakrishnan and Ray[10] determined that the valve of q (= kS_e) for phenol is 0.0043 mg phenol/mg bacteria-hour. It is obvious from the inverse relationship between biomass concentrations (MLSS) and detention time that phenol removal can be improved without an increase in detention time by increasing the biomass concentration in the aeration tanks.

For biomass (X), the mass balance equation becomes:

$$D (X_i - X) = -r = -uX$$

u = specific growth rate constant ($time^{-1}$)

For the biopond system in question, the influent biomass concentration is 0 ($X_i = 0$), and the steady state mass balance equation for biomass becomes:

$$DX = uX$$

Dividing by biomass concentration (X) results in:

$$D = u$$

Therefore, it can be stated that dilution rate is equal to the rate of production of biomass in a CSTR at steady state. However, when dilution rate becomes greater than the highest possible growth rate of the biomass (u max), steady state conditions are no longer possible--D becomes greater than u max and biomass is washed out of the system before it has a chance to grow.

Richardson and Temple[3] have shown that the phenol degrading organisms within the Conoco biopond system have a doubling time of about 10 hours. Specific growth rate can

be related to doubling time by the following equation[12].

$$u = \frac{(\ln 2)}{g}$$

g = doubling time

For a doubling time of 10 hours this equation yields a specific growth rate of 0.07/hr. As stated previously the residence times in the Conoco bioponds are less than 7 hours, resulting in a dilution rate (D = 1/residence time) of greater than 0.14/hr. Since D > u in the bioponds, biomass is being washed out of the bioponds before it has a chance to grow. This explains that the low biomass concentration (20 - 65 mg/l VSS[a]) in the ponds is due to the short residence times. Theoretically, there should be no phenol degrading bacteria of the type studied by Richardson and Temple in the bioponds. However, some phenol degraders may be growing on the biopond walls or accumulated in the corners of the biopond where the system may not be completely mixed.

As previously stated and illustrated in the relationship established by Eckenfelder[13], phenol removal can be improved without an increase in detention time by increasing the biomass concentration in the aeration tanks. However it was just shown that a short residence time for a CSTR results in washout and a low biomass concentration. It follows that to achieve higher biomass concentrations, the bioponds must be modified to retain biomass--the steady state mass balance equation for biomass must be altered in

a way that allows biomass concentration (X) to be independent of dilution rate for a given specific growth rate. This can be done in several ways that fall into 3 categories: 1. biomass recycle 2. attached growth 3. completely changing the configuration of the reactor to operate it in a batch, rather than continuous flow, mode.

Biomass Recycle

An obvious way of allowing biomass concentration to be independent of dilution rate would be to collect biomass from the effluent and return it to the reactor. This process is termed recycle, and its incorporation would convert the present bioponds into activated sludge units. The conventional activated sludge unit consists of a reactor, a clarifier, and a solids-return line from the clarifier bottom to the reactor.

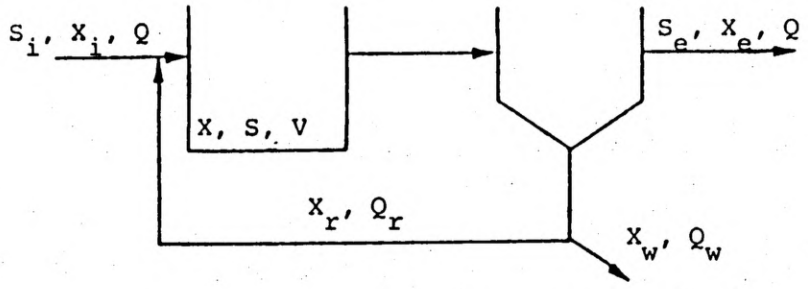

Figure 2. Conventional Activated Sludge Unit

The steady state mass balance equation for the biomass in the reactor (assuming no biomass in influent) is[15]:

$$0 = RX_r - (1 + R)X + r$$

$R = Q_r/Q$ = (recycle flowrate)/(volumetric flowrate of influent)
X_r = biomass concentration in recycle stream (mass/volume)
X = biomass concentration in reactor (mass/volume)
r = rate of production of biomass (mass/volume-time)

In the case of a CSTR without recycle, the residence time of the biomass in the system is the same as the residence time of the wastewater in the system ($\theta_c = V/Q$). However, the residence time of the biomass in a CSTR with recycle is longer because the biomass is returned to the system.

The steady-state residence time of biomass in a CSTR with recycle (the mean cell residence time in an activated sludge system) can be determined from the following equation[16]:

$$\theta_c = \frac{VX}{Q_w X_w}$$

θ_c = mean all residence time
V = volume of reactor
X = biomass concentration in reactor (mass/volume)
Q_w = wastage flowrate (volume/time)
X_w = biomass concentration in wastage stream

It can be seen from this equation that mean cell residence time in a CSTR with recycle is independent of the residence time of the wastewater in the reactor. Thus, it is possible to achieve a high θ_c, and therefore good treatment efficiency, without changing the wastewater

hydraulic residence time i.e. without changing the size of the aeration tanks or the flowrate of wastewater into them.

Incorporation of a conventional activated sludge unit into the Conoco wastewater treatment system would involve construction of a clarifier and the piping necessary for sludge recycle and wastage. However, part of the cost of construction may be avoided in two ways: 1. recycle sludge from the Dissolved Air Floatation (DAF) unit into the bioponds 2. convert a portion of Biopond 2 into a clarifier.

Attached Growth Systems

Attached Growth processes utilize a solid medium upon which a film of bacteria are allowed to grow and accumulate. The solid medium remains in the reactor, and therefore the majority of the biomass on the medium (biofilm) remains in the reactor. The mass balance for an attached growth process within a CSTR (assuming steady state and sterile influent) is[17].

$$DX = uX + u_f X_f$$

D - dilution rate ($time^{-1}$)
u, u_f - specific growth rate constants for suspended and attached biomass respectively ($time^{-1}$)
X, X_f - concentration of suspended and attached biomass respectively (mass/volume)

The $u_f X_f$ term is not seriously dependent on D, so wall growth functions as a second source of biomass which prevents washout[17].

Rotating Biological Contactors

One common type of attached growth process is a rotating-disc reactor or rotating biological contactor (RBC) on which closely spaced discs of polystyrene or polyvinyl chloride are mounted on a common horizontal shaft over a tank containing wastewater. The discs are partially submerged in wastewater and are rotated slowly allowing any point on a disc to be alternately submerged and exposed to the air. Biological growths become attached to the surfaces of the discs and eventually form a slime layer (biofilm). The rotation of the disc contacts the biofilm with wastewater and oxygen, maintaining aerobic conditions. The rotation also removes excess solids from the disc and provides sufficient turbulence to completely mix the wastewater in the tank. Consequently, the performance of an RBC can be modeled as a CSTR containing biofilm[12].

RBCs are generally more reliable than other fixed-film processes because of the large amount of biological mass present[18]. However, there are drawbacks to using this system as a modification of the existing bioponds at the Conoco plant in Billings. Rotating-disc systems must be protected by a roof since heavy rains may strip off biofilm growth, and in northern climates an enclosed heated building may be necessary to prevent freezing during the winter[18].

Porous Support Method (Captivated Sludge)

In the Captivated Sludge Process (CSP), microorganisms that are commonly found in activated sludge are entrapped inside reticulated foam supports (pads). These pads are not allowed to leave the treating system with the wastewater, so biomass remains and can accumulate to a concentration of 150 - 300 mg/pad[10]. With approximately 1100 pads per cubic foot, the concentration of biomass in the system can be as high as 14,000 mg/l.

In order to utilize the CSP, it is necessary to have 1. a method for aerating and mixing the reactor that will allow all of the pads to be exposed to the necessary substrate, oxygen, and nutrients 2. a method of keeping the pads in the reactor and 3. a method of cleaning the pads so that they do not become overfull to the point where substrate and nutrients cannot circulate through the pads. These factors, as well as the results of a pilot study, must be considered when determining the feasibility and costs of incorporating the CSP into the Conoco refinery wastewater treatment system.

Packed Bed Reactor

A third type of attached growth system cannot be modelled as a CSTR but still prevents washout by allowing biomass to accumulate on a solid medium within the reactor. This type of reactor is called a packed bed or a trickling filter, and Holladay et. al.[11] have shown that phenolic

waste can be successfully treated in this type of reactor. The trickling filter, a popular alternative to the activated sludge process, consists of a biofilm living on solid medium which loosely fills a vessel (void fraction of about 0.5[17]). Wastewater trickles over the medium in films sufficiently thin to continuously supply oxygen to the aerobic organisms in the biofilm--forced aeration is not needed because air is circulated through the trickling filter by air convection.

Although trickling filters have been used for a great many years, their operation is still not readily mathematically described--theoretical mathematical models have been suggested but they are generally impractical for design[20]. Holladay et.al.[11] determined that the minimum retention time in a packed bed reactor for which 99% conversion of phenols could be obtained was 0.30 hours for an influent concentration of 100 mg/l. They also note that an erroneous value for retention time will result if the initial void volume is used in this calculation, rather than the true void volume at a steady-state stage of biofilm growth. It is apparent, however, that the retention time required for a packed bed reactor system is much less than that required by a CSTR (approximately 14 hours).

A test of the feasibility of using a trickling filter to improve phenol removal must involve a pilot plant.

Using a trickling filter to improve phenol removal at the Conoco wastewater treating plant would involve the high capital cost of constructing the filter, the underdrain system, and the system for applying wastewater to the filter. Also, a housing is needed to protect the filter from heavy rains and freezing.

Sequencing Batch Reactor (SBR)

Another possible way to conserve biomass in the bioponds is to convert them to sequencing batch reactors (SBRs). The SBR treatment scheme is a batch operation composed of five steps: fill (the receiving of raw wastewater), react (completion of the desired reactions), settle (separate the organisms from the treated effluent), draw (discharge treated effluent), and idle (the time after discharge when sludge can be wasted if necessary)[21]. An SBR system may be composed of one or more tanks, with all of the five steps taking place in each tank. This system is simpler than the conventional activated sludge system because sludge recycle equipment is eliminated. If this treatment scheme is to be employed at the refinery under consideration, it would involve a retrofit of the two bioponds. Therefore, the feasibility of using a two tank SBR system to reduce BOD to the effluent standards should be examined.

Kim and Armstromg[22] compared the performance of CSTR and batch systems in the biological degradation of phenol.

Using saturation kinetics they determined that the phenol decomposition rate in a CSTR is:

$$r = \frac{kXS_e}{(K_s + S_e)}$$

and the phenol decomposition rate in a batch reactor is:

$$r = \frac{kXS}{(K_s + S)}$$

k - substrate utilization rate coefficient ($time^{-1}$)
X - biomass concentration in reactor (mass/volume)
S_e - substrate concentration in effluent (mass/volume)
S - substrate concentration in reactor (mass/volume)
K_s - half saturation constant (mass/volume)
(Michaelis - Menton Constant)

Since S is always greater than or equal to S_e, the phenol decomposition rate in the batch reactor will always be greater than or equal to the phenol decomposition rate in the CSTR. Therefore, conversion of the existing system to an SBR could serve the dual purposes of increasing biomass concentration and phenol decomposition rate in the tanks.

Since neither the tank volume nor the wastewater flowrate are design variables, the total cycle time for each tank is fixed. However, the % cycle time for each of the five steps must be determined. The steps critical to this determination are the react step and the settle step. The react step must be long enough to allow for the required phenol and BOD removal, and the settle step must be long enough to provide a low solids concentration in the effluent and a settled solids concentration in the bottom of the tank of about 8000 mg/l[23].

The time required for the react step can be estimated if the kinetics of removal in this particular system are known. The application of the principle of conservation of mass to a batch reactor system yields the following equation[12]:

$$dC/dt = -r$$

C = reactor concentration (mass/volume)
r = rate of production (mass/vol-time)
(a negative value denotes rate of removal)
t = time

In this particular wastewater treatment system, the concentration of concern is phenol. Therefore, a determination of the rate at which phenol is removed by the organisms in the system is a critical step in the examination of the feasibility of using an SBR to treat this wastewater. Pilot scale batch reactions, commencing with a high concentration of acclimated biomass (2000-5000 mg/1), could be used to measure the rate of phenol removal. Since rate of removal per unit volume should not change appreciably with the size of the system, these experimental values can be used to roughly approximate the time needed for the react step in the SBR cycle. A comparison of this time and the time constraint imposed by the tank size and wastewater flowrate is a first step in the examination of the feasibility of treating this wastewater in an SBR. Another critical step is a determination of the settling time necessary to achieve clear effluent during the draw stage.

Kim and Armstrong[22] also determined that the more concentrated the wastes become, the more efficient the batch systems are compared to the CSTR systems, as long as the initial substrate concentration is not toxic to the organisms. For this reason, it may be advantageous to treat the sour-water stripper effluent (50 - 70 ppm phenols[2]) separately for phenols instead of combining it with API separator water before treatment.

To test the feasibility of treating the Conoco wastewater in batch mode (as in an SBR) and to determine the specific rate of substrate removal (q) for use in substrate removal rate equations, batch reactions were performed in the Environmental Engineering labs at Montana State University. For several suspended solids concentrations, phenol concentration remaining in the batch reactor was measured for reaction times varying from 1 to 24 hours. This data was then used to compute the specific rate of substrate removal ($q = u/Y$) for these particular wastewaters and microorganisms.

MATERIALS AND METHODS

Equipment

Batch biological reactions were carried out using a Hach Chemical Co. 6 Bottle Manometric BOD Apparatus (Model 2173B). This apparatus consists of six magnetic stirrers, six 1-liter bottles (fitted with seal cups to hold lithium hydroxide crystals), and six closed-end mercury manometers.

For the purposes of this investigation the manometric apparatus was placed in an insulated housing. As a result of the heat generated by the apparatus, the temperature inside the housing remained constant at approximately 41°C.

Photometric measurements of phenol concentration were made using a standard model Bausch & Lomb Spectronic 20 Colorimeter/Spectrophotometer. Catalog No. 33-31-72. 1/2" test tubes were used as cells for holding the sample.

A Beckman Altex 30 pH Meter was used for pH measurements. No ATC (automatic temperature compensation) probe was used. Therefore 25°C was assumed by the instrument. This temperature was within 5°C of the sample temperatures.

Procedures

Supplies of API Separator effluent, sour-water stripper effluent, and mixed wastewaters were obtained from the refinery as needed. These supplies were siphoned from

the biopond inlet into 5 gallon Nalgene carboys and remained in these containers until used for purposes of this study. Organisms from the bioponds were also collected. These organisms were placed in an aerated 10-liter plexiglass reactor which was kept in a water bath at approximately 41°C. Mixed refinery wastewater was used as a substrate for the organisms, and it was supplied to the organisms in a batch mode: At regular intervals, aeration was discontinued, the biomass allowed to settle, and the supernatant drawn off. The reactor was then refilled with untreated wastewater, and aeration was resumed. Under these conditions, biomass was allowed to accumulate until amounts were sufficient for use in batch reactions with biomass concentrations similar to those in a SBR. A centrifuge was used to concentrate the biomass for use in these reactions.

A measured sample of wastewater and the concentrated biomass was placed in each bottle along with the magnetic stirring bar. A seal cup filled with lithium hydroxide was placed in the neck of each bottle. The bottles were then connected to the manometers, placed on the magnetic stirrers in the BOD apparatus housing, and allowed to react. The carbon dioxide produced by the oxidation of the organic matter was absorbed by the lithium hydroxide crystals, and therefore the pressure difference in the system was proportional only to the amount of oxygen

utilized. This pressure drop was recorded as indicated on the manometer scales as mg/l O_2 consumption.

One by one, at time intervals of approximately 1, 2, 3.5, 5, 8, and 24 hours, each bottle was removed, the contents centrifuged to remove biomass and then analyzed for phenol concentration. Oxygen consumption was also recorded (directly from the BOD apparatus manometers) at each time interval.

Phenol concentration was measured using the Direct Photometric Method from Section 510 C. of the 16th Edition of Standard Methods for the Examination of water and Wastewater[24], which is by far the most common method of assessing phenol concentration[25]. However, the preliminary distillation procedure for elimination of interferences was not used because standards prepared with wastewater containing no detectible phenol resulted in the same calibration curve as standards prepared with distilled water, indicating no interferences from wastewater components. Also, various dilutions of sour water stripper effluent resulted in identical calculated valves for phenol concentration in the undiluted effluent. The calibration curve constructed according to the Direct Photometric Method is presented in Appendix.

Biomass concentration in each 1-liter reactor was measured using the Total Suspended Solids method from Section 209 C. of Standard Methods, 16th ed.[24]. Whatman

934-AH 4.7 cm diameter glass microfibre filters were used. Due to the high concentration of biomass to be measured, 10 ml volumes of sample were filtered. The residue was dried at 103-105°C, but it was not ignited to differentiate between non-volatile and volatile suspended solids.

A similar procedure was followed using sour water stripper effluent in place of the mixed wastewaters. Before this second set of tests, sour water stripper effluent was used as a substrate for the biomass in the 10 liter reactor. This acclimation period lasted for eight days, after which the organisms ability to degrade the phenol in the sour water stripper effluent was determined.

Raw data for both sets of tests is presented in the Appendix.

RESULTS

The results of batch reactions performed with Conoco refinery wastewater (combined wastewaters and sour water stripper alone) are presented in the following tables and plots:

Table 1. Phenol Concentrations Remaining in the Combined Wastewater after Various Batch Reaction Times with Suspended Solids Concentrations of Approximately 2000 mg/l.

time (hours)	Phenol concentration (pp in)
0	3.8
1	1.6
2	1.0
3	0.6
5.5	0.5
8	0.4
24	0.4

Table 2. Phenol Concentrations Remaining in the Sour-Water Stripper Efflunet Alone after Various Batch Reaction Times with Suspended Solids Concentrations of 2000 - 3000 mg/l.

time (hours)	phenol concentration (ppm)
0	25.0
1	25.0
2	25.0
2	24.5
3	24.5
4	21.5
5	16.0
6	13.5
24	2.0

Table 3. Phenol Concentrations Remaining in the Sour-Water Stripper Effluent Alone after Various Batch Reaction Times with Suspended Solids Concentrations of 4000 - 5000 mg/l.

time (hours)	phenol concentration (ppm)
0	25.0
2	24.0
3	16.5
5	14.0
7	2.0
10	1.5
24	1.5

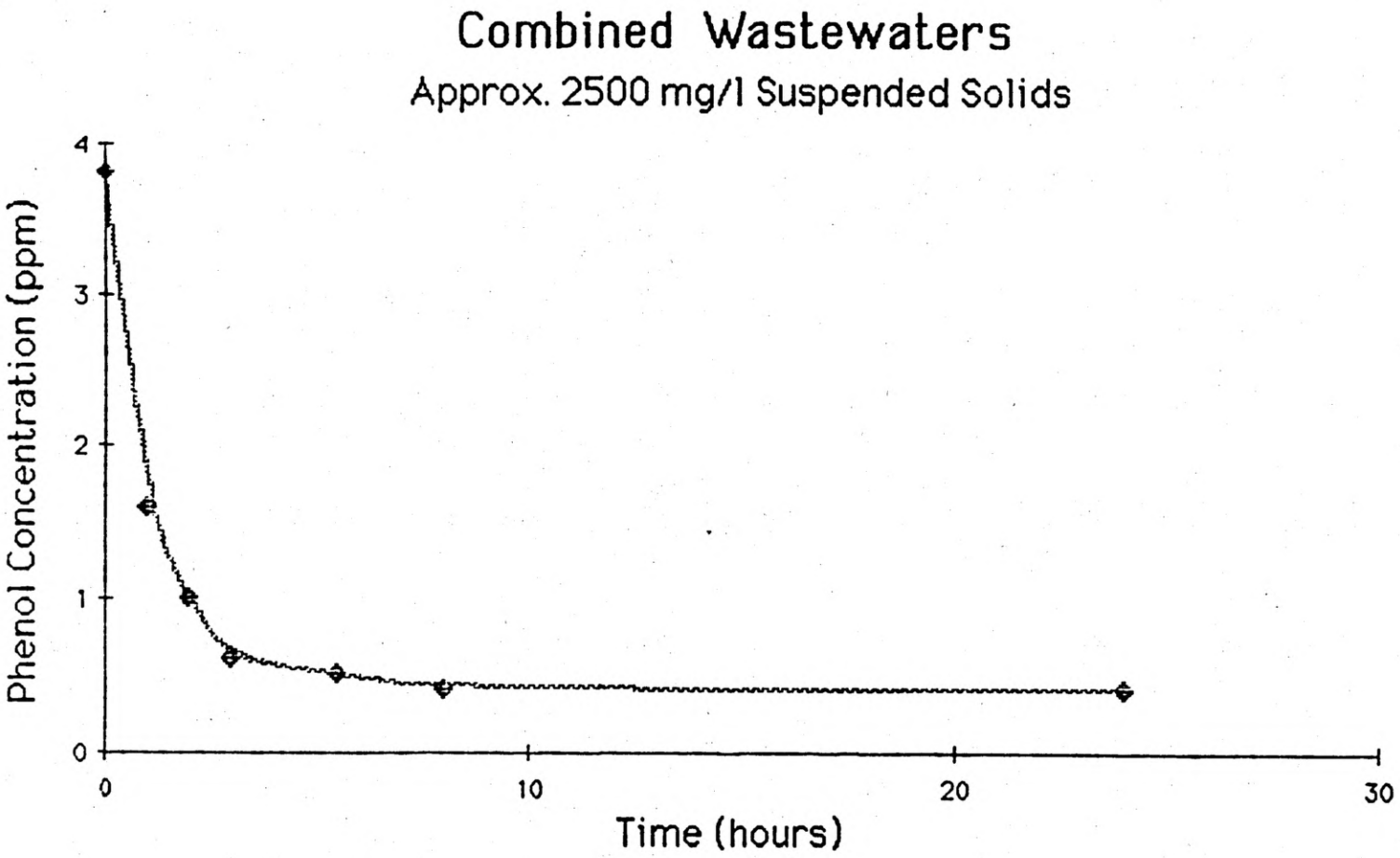

Figure 3. Phenol Concentration vs. Time for the Combined Wastewaters in a Batch Reaction with Approximately 2500 mg/l Suspended Solids.

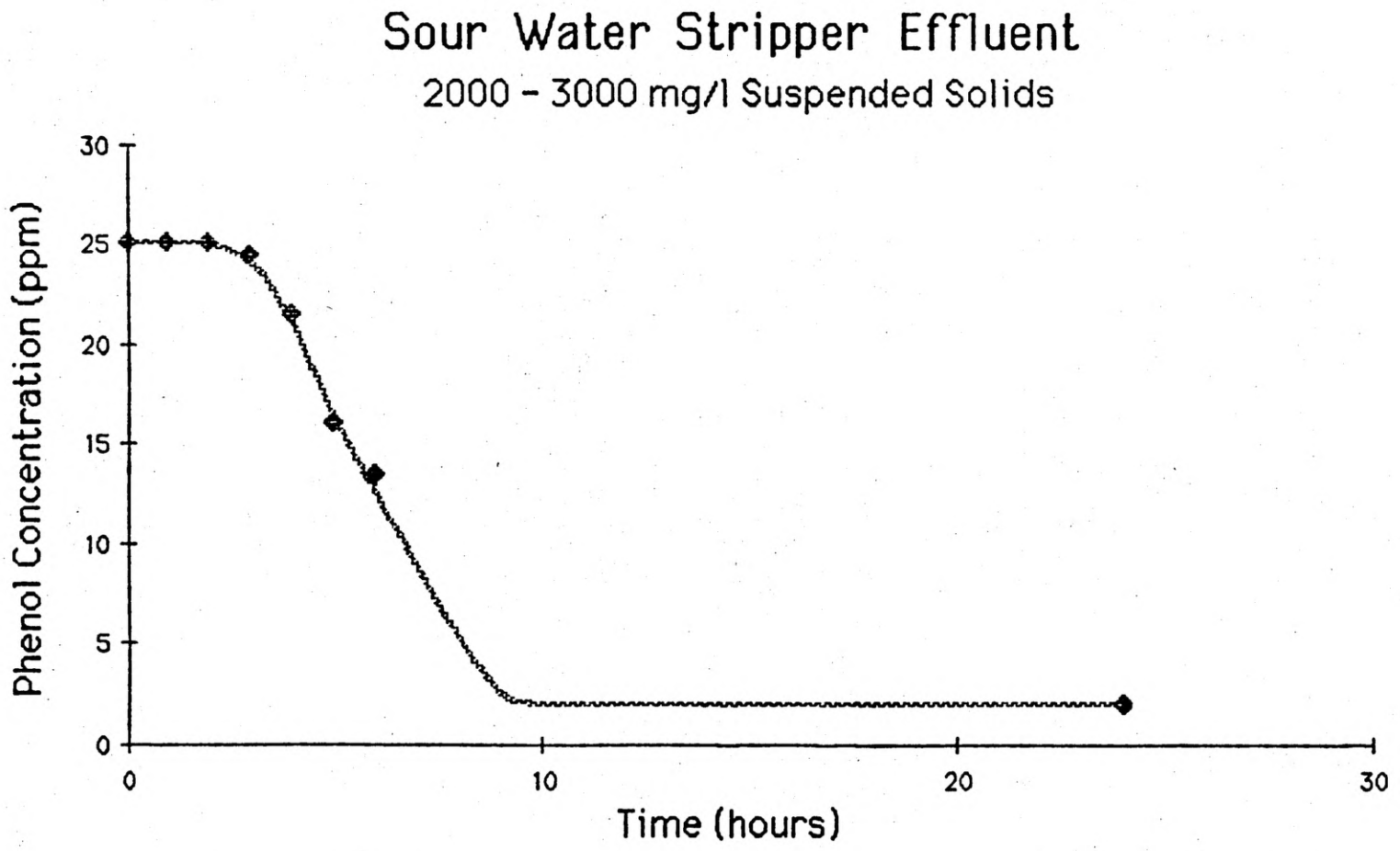

Figure 4. Phenol Concentration vs. Time for the Sour-Water Stripper Effluent in a Batch Reaction with 2000-3000 mg/l Suspended Solids.

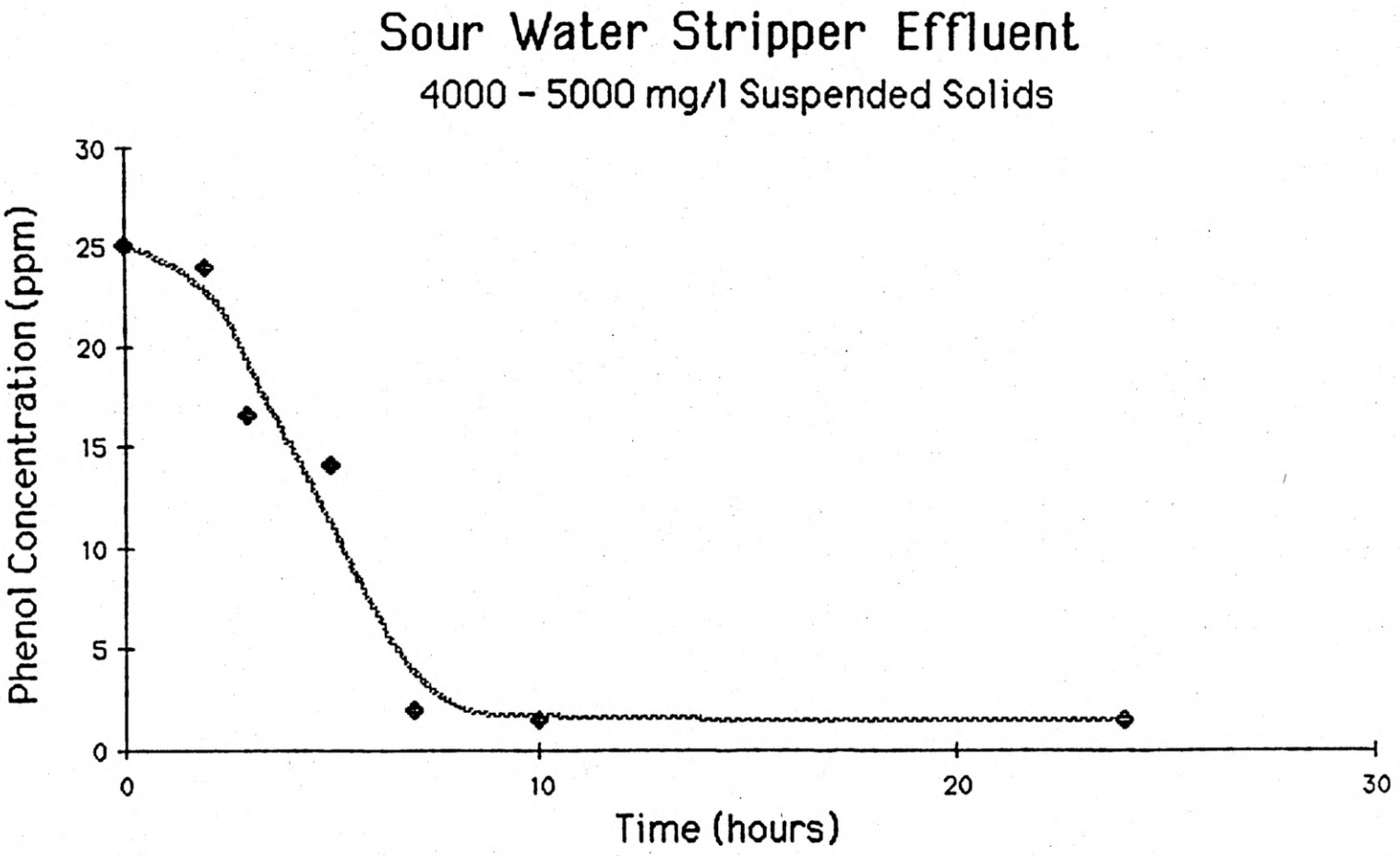

Figure 5. Phenol Concentration vs. Time for the Sour-Water Stripper Effluent in a Batch Reaction with 4000-5000 mg/l Suspended Solids.

Oxygen consumption values read from the BOD apparatus manometers do not relate well to phenol removal. Therefore this data will not be used in the analysis of the treatability of the wastewater.

DISCUSSION AND CONCLUSIONS

Using the slope of the log phase of the phenol concentration vs. time plots, the specific removal rate (q) is determined to be 0.0006 mg phenol removed per hour per mg biomass in the reactor for treatment of the combined wastewaters, and q is 0.0015 mg phenol removed per hour per mg biomass in the reactor for treatment of the sour-water stripper effluent alone. The 0.0015 mg/mg-hr value is quite a bit lower than the 0.0043 mg/mg-hr value determined by Radhakrishnan and Ray[14] for phenol alone. This could be attributed to their use of substrate phenol concentrations that are higher (400 - 800 mg/l) and therefore closer to the optimum for the microorganisms under consideration. There may also be constituents in the sour-water stripper effluent that partially inhibit the removal of phenol.

Using the rate equation for substrate (phenol) removal, the experimentally determined value of 0.0006 mg/mg-hr for combined wastewater specific removal rate, and the steady state mass balance equation for a CSTR, the biomass concentration necessary for complete removal of phenol in the bioponds within the present residence times (approximately 11 hours combined) can be calculated.

Steady state mass balance equation for a CSTR:

$$D(C_i - C) = -r = qX$$

D = dilution rate = 1/residence ($time^{-1}$)
C_i = concentration in influent (mass/volume)
C = concentration in reactor and effluent (mass/vol)
r = rate of production of biomass ($time^{-1}$)
q = specific rate of substrate removal ($time^{-1}$)
X = biomass concentration (mass/volume)

Rearranging to solve for X:

$$X = \frac{D(C_i - C)}{q}$$

Assuming a C_i value of 40 mg/l[2] and an effluent concentration (C) of 0,

$$X = \frac{(1/11 \text{ hrs})(40 \text{ mg/l})}{0.0003 \text{ mg/mg-hr}} = 6000 \text{ mg/l}$$

A biomass concentration of 6000 mg/l is within the design parameter range specified by Metcalf and Eddy[16] for a CSTR with recycle, and it is well under the 14,000 mg/l that could theoretically be achieved through the Captivated Sludge Process. Both of these processes should be considered as possible modifications to the Billings Conoco wastewater treatment plant.

For treatment of the sour-water stripper effluent alone (q = 0.0015 mg/mg-hr), the CSTR mass balance equation can again be rearranged to solve for dilution rate:

$$D = \frac{Xq}{(C_i - C)}$$

Assuming a C_i value of 75 mg/l and an effluent concentration (C) of 0, dilution rate (D) becomes a function of biomass concentration (X).

For X = 3000 mg/l:

$$D = \frac{(3000\ mg/l)(0.0015\ mg/mg\text{-}hr)}{(75\ mg/l)} = 0.06\ hour^{-1}$$

For X = 5000 mg/l, D = 0.1 $hour^{-1}$

Dividing sour-water stripper flowrate (65 gpm) by dilution rate (D) will give the volume (V) necessary to provide this dilution rate:

For X = 3000 mg/l (D = 0.06 $hour^{-1}$),

$$V = \frac{(64\ gal/min)(60\ min/hour)}{(0.06\ hour^{-1})} = 65{,}000\ gallons$$

For X = 5000 mg/l, V = 39,000 gallons.

With a biomass concentration of approximately 3000 mg/l, all phenols can be removed from the sour-water stripper effluent within a volume that is slightly less than the volume of Biopond 1 (76,000 gallons). At higher biomass concentrations, less volume is required. Once again, a CSTR with recycle or the Captivated Sludge Process can theoretically achieve these concentrations of biomass. Therefore, the possibility of using all, or a section of, Biopond 1 to treat sour-water stripper effluent alone should also be considered as a possible modification to the present treating system. This type of modification may result in a more stable system since phenol removing biomass would not be subject to the constituents in the API Separator effluent that are known to inhibit biological removal in the present biopond system. This type of modification may also have some effect on the treatment of

the API Separator effluent, so treatability studies on this effluent alone should be performed.

Using the batch reactor conservation of mass equation ($dC/dt = -r$) along with the specific removal rates (q) determined in this study, the time for the react step of a Sequencing Batch Reactor (SBR) can be determined:

$$dC/dt = -r = qX$$

Rearranging to solve for dt:

$$dt = dC/qX$$

Using dC = 40 mg/l (complete removal of phenols), q = 0.0006 mg/mg-hr for the combined wastewaters, and a typical SBR biomass concentration of 3500 mg/l,

$$dt = \frac{(40\ mg/l)}{(0.0006\ mg/mg\text{-}hr)(3500\ mg/l)} = 19\ hours$$

Assuming a typical react step time of 35% of the entire cycle time of an SBR[23], a 19 hour react time would correspond to a 54 hour SBR cycle. If the react and fill times were combined (60 % of total cycle), a 32 hour SBR cycle would be required. These values indicate that converting the present bioponds (residence times of approximately 6 hours) to SBR's is not be a feasible way to remove phenol from the mixed wastewaters.

Using dC = 75 mg/l (complete removal of phenols), q = 0.0015 mg/mg-hr for the sour-water stripper effluent alone, and a biomass concentration of 3500 mg/l,

$$dt = \frac{(75\ mg/l)}{(0.0015\ mg/mg\text{-}hr)(3500 mg/l)} = 14\ hours$$

Assuming that the react and fill steps of the SBR cycle are combined, the total reaction time would be approximately 60% of the entire cycle[23]. A 14 hour reaction time would correspond to a 24 hour total SBR cycle time. At the sour-water stripper effluent flowrate of 65 gpm, a 24 hour SBR would have to consist of at least two tanks with a combined volume of 93,600 gallons. This type of system could be provided at the Billings Conoco refinery treating plant by converting Biopond 2 into a two-tank SBR for treating the sour-water stripper effluent alone. However, this would leave only Biopond 1 for treating API Separator effluent, and it is doubtful that effluent BOD standards could be met in the residence time provided by Biopond 1 alone (5.5 hours).

Due to the large volumes required for this type of treatment system, converting the present bioponds into SBRs is not a feasible method of improving phenol removal from the wastewaters generated by the Billings Conoco refinery.

RECOMMENDATIONS

The results of this project lead to the following recommendations: 1. In depth study into the feasibility and costs of increasing the biomass concentration in the present biopond system by a) converting it to an activated sludge unit or b) the incorporation the Captivated Sludge Process. 2. Further study into the feasibility and costs of treating the sour-water stripper effluent alone for phenols before combining it with the API Separator effluent. 3. Incorporation of a pH control system capable of continually monitoring biopond pH.

Increasing Biomass Concentration in the Present Bioponds

Experimental batch reaction data, incorporated into a mass balance equation on the present bioponds, indicates that a biomass concentration of 6000 mg/l is required to completely remove phenols from the combined wastewater. Several methods of achieving this biomass concentration in the bioponds are discussed in this paper. Of these methods, two would involve relatively low capital costs: biomass recycle and the Captivated Sludge Process (CSP).

Biomass recycle may possibly be accomplished by returning dissolved air flotation (DAF) unit sludge to the bioponds. The feasibility of this procedure would depend on the composition of the DAF sludge. If the sludge is

mainly biological, without high amounts of hydrocarbons, it may be returned to the bioponds where it could contribute to biomass concentration. The capital costs involved in DAF unit sludge return would be the cost of piping and pumps to carry the sludge from the DAF unit to Biopond 1.

Another way to accomplish biomass recycle is to convert the present bioponds into a conventional activated sludge unit by utilizing a portion of Biopond 2 as a clarifier. This would involve constructing a baffle in Biopond 2 behind which there would be no aeration, or by constructing an insert to be placed within Biopond 2. In this portion of Biopond 2 (behind the baffle or within the insert), the biomass would be allowed to settle, as in a conventional clarifier. Then the treated supernatant would be removed over an effluent weir, and the biomass that has settled to the bottom would be piped out and returned with the influent to the biopond system or wasted. The capital costs involved in employing this type of system at Conoco would be the cost of the baffle or insert, effluent weir, and sludge return and wastage facilities (piping and pumps). The feasibility of this system would depend on the settling characteristics of the biomass present. However, it must be noted that continually returning settled biomass to the system would serve to select for biomass with good settling characteristics.

To test the feasibility of using the CSP to improve phenol removal in the bioponds, it must first be determined whether the organisms that remove phenols can grow on the pads. The effectiveness of these pads in water that contains oil must also be tested. Both of these determinations can be made using a CSP pilot plant with wastewater from the refinery. If pilot tests indicate that it would be possible to treat this water using the CSP, methods of cleaning the pads and keeping the pads within the bioponds must be considered when determining what modifications to the existing system are necessary.

Treatment of the Sour-Water Stripper Effluent Alone for Phenols

For the following reasons it may be advantageous to treat the sour-water stripper effluent separately for phenols instead of combining it with the API Separator effluent before treatment: 1. As discussed earlier, the sour-water stripper effluent is uniform in composition and (unlike the API separator effluent) does not intermittently contain constituents that can inhibit biological removal in the bioponds. 2. The higher phenol concentration in the sour-water stripper is closer to the optimum phenol concentration for the microorganisms in the Conoco system.

Experimental batch data indicates that, with a biomass concentration of 5000 mg/l, phenols can be completely removed from the sour-water stripper effluent in a 39,000

gallon tank operated as a CSTR. Therefore, it may be feasible to treat this effluent alone before combining it with the API Separator effluent. One possible way of doing this would be to baffle off half of Biopond 1 and allow only sour-water stripper effluent to flow into this portion of the biopond. Depending on the BOD of the sour-water stripper effluent after being treated alone in a portion of Biopond 1, this effluent could either be combined with the API Separator effluent for additional treatment or sent to the holding ponds.

In addition to the above recommendations for further study, it is also recommended that a pH control system, capable of continually monitoring biopond pH, be incorporated into the present treatment system. This would allow for adjustment of pH before biological removal has been severely inhibited by unfavorable pH conditions.

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REFERENCES CITED

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APPENDIX

RAW DATA

(Due to numerous experimental errors, Test 1 data has been disgarded.)

Table 4. Results of Test 2 - Combined Wastewaters

reaction time (hours)	O_2 consumption (mg/l)	% absorbance	phenol concentration (ppm)	pH final	suspended solids (mg/l)
1	5	56.5	1.6	6.9	2400
2	10	69.0	1.0	7.1	2400
3	15	79.0	0.6	7.2	2400
5.5	60	80.0	0.5	7.3	2600
8	115	83.0	0.4	7.4	2600
24	235	83.5	0.4	7.7	2400

Table 5. Results of Test 3 - Sour-Water Stripper Effluent Diluted (20 ml effluent/100 ml total)

reaction time (hours)	O_2 consumption (mg/l)	%absorbance of diluted sample	phenol concentration in undiluted sample (ppm)	pH final	suspended solids (mg/l)
1	0	16.5	25.0	7.9	2350
2	0	17.5	25.0	7.9	2650
3	5	31.0	16.5	7.8	5000
5.5	30	86.5	1.5	7.9	4500
10	85	86.5	1.5	7.9	4600
24	220	87	1.5	7.9	4900

Table 6. Results of Test 4 - Sour-Water Stripper Effluent Diluted (20 ml effluent/100 ml total)

reaction time (hours)	O_2 consumption (mg/l)	% absorbance of diluted sample	phenol concentration in undiluted sample (ppm)	pH final	suspended solids (mg/l)
2	0	14.0	25.0	7.6	2200
3	0	17.5	24.5	7.5	2300
4	0	22.0	21.5	7.5	2250
5	0	32.0	16	7.3	2300
6	10	37.5	13.5	6.9	2200
24	185	83.0	2.0	7.1	2400

Table 7. Results of Test 5 - Sour-Water Stripper Effluent Diluted (20 ml effluent/100 ml total)

reaction time (hours)	O_2 consumption (mg/l)	% absorbance of diluted sample	phenol concentration in undiluted sample (ppm)	pH final	suspended solids (mg/l)
2	0	16.5	24.0	7.9	4700
5	25	36.5	14.0	7.7	5000
7	90	86	2.0	7.7	4550

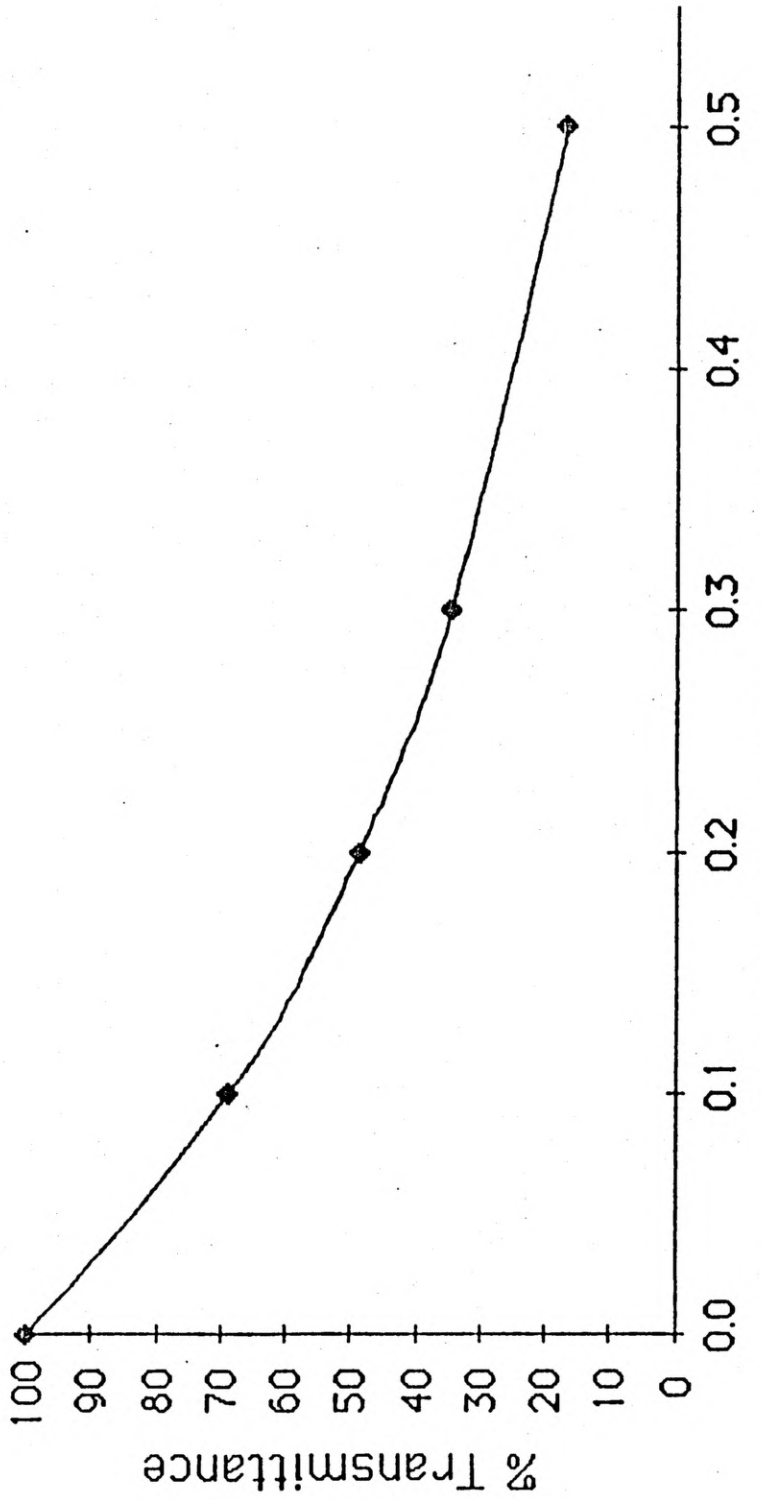

Figure 6. Calibration Curve for Direct Photometric Measurement of Phenol Concentration