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Fixed-Film, Fluidized-Bed Bioreactors for Biooxidation of Coal Conversion Wastewaters: Progress Report for the Period October 1, 1984–September 30, 1985

T. L. Donaldson
G. W. Strandberg
R. M. Worden

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Chemical Technology Division

FIXED-FILM, FLUIDIZED-BED BIOREACTORS FOR BIOOXIDATION OF COAL CONVERSION WASTEWATERS: PROGRESS REPORT FOR THE PERIOD OCTOBER 1, 1984—SEPTEMBER 30, 1985

T. L. Donaldson
G. W. Strandberg
R. M. Worden

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FIXED-FILM, FLUIDIZED-BED BIOREACTORS FOR BIOOXIDATION OF COAL CONVERSION WASTEWATERS: PROGRESS REPORT FOR THE PERIOD OCTOBER 1, 1984–SEPTEMBER 30, 1985

T. L. Donaldson, G. W. Strandberg, and R. M. Worden

ABSTRACT

The technical feasibility of biooxidation treatment of 50% strength actual wastewater was successfully demonstrated using a fluidized-bed bioreactor. The wastewater was stripped to remove ammonia and sulfides prior to biotreatment. Additional experimental and modeling work confirmed the need to supply substantial oxygen to maintain high reaction rates. The reaction kinetics were shown to depend on the physical characteristics of the biofilms. Dynamic modeling and experimental studies have shown that classical reaction and diffusion concepts used in catalysis are adequate to describe the dynamic behavior of bench-scale bioreactors when the pH is constant. Oscillations in the reaction rate and phenol concentration were seen when the pH was not controlled. A status summary of the fluidized-bed bioreactor process for biooxidation of organics in coal gasification wastewaters is presented.

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1. INTRODUCTION

Wastewaters generated in coal gasification processes contain significant quantities of monohydric and substituted phenols (cresols, etc.), tars and oils, ammonia and sulfides, cyanides and thiocyanides, and a wide variety of other organic chemicals in lesser quantities. The chemical oxygen demand (COD) can be ~50,000 mg/L. There is considerable variation in the detailed composition of the wastewaters from different gasification technologies and types of coal. Treatment requirements and the technologies to be used in commercial-scale plants will depend on the particular coal, the conversion technology, and site-specific factors

related to the fate of the wastewater (e.g., reuse, discharge).[1] It is frequently postulated that integrated treatment trains will be required, consisting of clarification, tar and oil separation, ammonia and sulfide stripping, pH adjustment, solvent extraction and recovery of phenols, biotreatment of dissolved organics, and polishing.[1,2] Optimal design of the overall treatment train will require optimal sequencing and interfacing of the various unit operations.

A number of investigators have shown that the majority of the dissolved organics are amenable to destruction by biooxidation.[3-6] For several years, the use of fluidized-bed bioreactors for biooxidation of coal gasification wastewaters has been under development at Oak Ridge National Laboratory (ORNL). Wastewater treatment technology utilizing fluidized-bed bioreactors for biodenitrification has been successfully developed at ORNL,[7] with the present work on biotreatment of coal gasification wastewaters being a logical extension of this program.

Fluidized-bed bioreactors offer several advantages relative to conventional suspended-growth processes such as activated sludge. Relatively high concentrations of cells can be retained in the bioreactor as immobilized films on the support particles, which leads to high reaction rates at low hydraulic retention times. This is somewhat analogous to long solids retention times in conventional suspended-growth systems. The columnar configurations of fluidized-bed bioreactors promote optimal hydraulic behavior. In addition, these bioreactors typically exhibit improved resistance to environmental stress and improved process stability relative to suspended-growth processes. These features are directly related to the immobilized films of microorganisms. The "washout"

phenomenon that plagues suspended-growth systems does not occur because the microorganisms are immobilized. Biofilms tend to be more resistant to variations in substrate concentrations, toxic chemicals, heavy metals, etc. It is believed that the outer surfaces of the films absorb the insult, thus protecting the inner regions of the films, which can then quickly reestablish normal bioactivity once the stress condition has passed. Several experimental studies have supported these hypotheses.[8,9] Recognition of these potential advantages and recent process development work have led to increased utilization of fluidized-bed bioreactors for a variety of wastewater treatment applications. Previous work at ORNL[10] has established the technical feasibility for use of fluidized-bed bioreactors and has suggested that the costs may be significantly less than for activated sludge treatment.

This report covers work performed in FY 1985, which included treatability of actual coal gasification wastewaters, dependence of reaction rate on dissolved oxygen, significant characteristics of the biofilms, and dynamic modeling of kinetic phenomena that govern bioreactor performance. A final section is devoted to a summary of the technical and economic factors that affect the current status of the fluidized-bed bioreactor process for treatment of coal gasification wastewaters.

2. TREATABILITY STUDIES

2.1 FLUIDIZED-BED BIOREACTOR

Earlier reports have described the laboratory-scale, fluidized-bed bioreactor used for treatability studies with actual wastewaters.[10-12]

As seen in the schematic representation in Fig. 1, the bioreactor has an ~5-cm ID and 150-cm height. The mixed-culture microbial films are attached to the anthracite coal particles. A flow rate of 0.4 to 1.0 L/min is sufficient to fluidize the bed of bioparticles without undue carryover of solids. An earlier report describes startup and operation procedures.[12]

2.2 WASTEWATER CHARACTERISTICS

Wastewater from the fixed-bed gasifier at the Morgantown Energy Technology Center (METC) was shipped to ORNL in 210-L drums by common carrier. The particular wastewater treated in these studies was obtained from the recirculating decanter during air-blown gasification of a Blacksville (bituminous) coal, Test Run No. 102, and stored at 4°C with no further treatment. Prior to biotreatment, the wastewater was passed through a cartridge filter to remove oil and was stripped to remove ammonia and sulfides. A description of the stripper, constructed at ORNL, has been reported earlier.[10]

Characteristics of the wastewater have been described previously[10] and are included in Table 1 for convenience. After stripping with nitrogen, the concentration of ammonia was reduced to <2000 mg/L, and the concentration of sulfides was reduced to <1 mg/L. These levels are satisfactory for biotreatment with no apparent inhibitory effects. Supplementary mineral salts and micronutrients were added to the wastewater prior to its introduction to the bioreactor.

2.3 ANALYTICAL TECHNIQUES

Samples of influent and effluent wastewater were routinely analyzed for phenols using the 4-aminoantipyrene (4-AAP) colorimetric assay method.[13]

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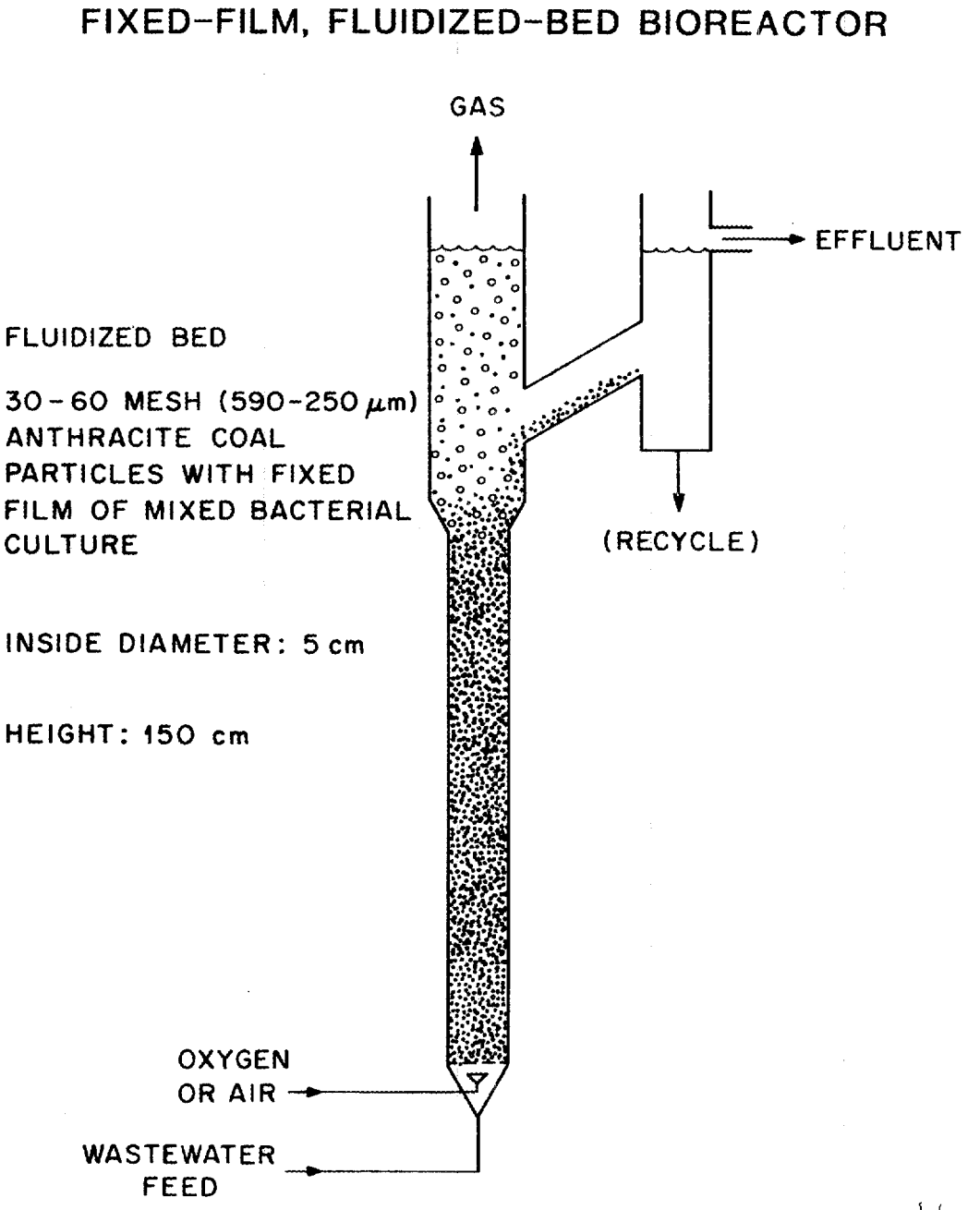

Fig. 1. A fixed-film, fluidized-bed bioreactor.

Table 1. Composition of METC recirculating decanter wastewater[a]

Parameter	Concentration (mg/L)
COD	50,000
TOC	6,500
Ammonia	15,000
Sulfides	200-400
Phenolics	6,000 (4-AAP) 8,000 (HPLC)

[a]Taken from G. W. Strandberg, R. M. Worden, J. D. Hewitt, and T. L. Donaldson, Fixed-Film, Fluidized-Bed Bioreactors for Biooxidation of Coal Conversion Wastewaters: Progress Report for the Period October 1, 1983-September 30, 1984, ORNL/TM-9395, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., March 1985.

Under certain conditions, this method approximates the total concentration of the major wastewater phenolics. Phenol, o-cresol, and m,p-cresol have been identified by high-pressure liquid chromatography (HPLC).[14] However, during operation with high-strength feed and high recycle, substantial 4-AAP-reacting components accumulated which did not appear to be phenols. Therefore, the major phenolics were also quantitated by gas chromatography. A 2-mm-ID, 1.8-m-long glass column packed with 250 to 175 μm (60-80 mesh) Tenax GC (Alltech Assoc., Deerfield, Ill.), operated isothermally at 190°C, was used to separate the phenols.

Ammonia and sulfide concentrations were estimated using CHEMets water analysis test kits (CHEMetrics, Inc., Warrenton, Va.). The chemical oxygen demand was determined using the Hach procedure.[15] Total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to Standard Methods for the Examination of Water and Wastewater.[16]

2.4 TREATMENT OF HIGH-STRENGTH WASTEWATER

The principal objective was to demonstrate that relatively high-strength wastewater could be treated directly with minimal dilution to simulate the front-end portion of a large-scale process. It has already been established that the fluidized-bed bioreactor works well with dilute wastewaters and can produce effluent water with <1 mg/L of phenols.[10-12]

The bioreactor was operated with substantial recycle of effluent water in order to maintain the fluidized condition in the bed. This procedure allows great conservation of actual wastewater for laboratory experiments; to operate on a once-through basis with high-strength wastewater would require an inordinate quantity of wastewater feed. Stripped wastewater, supplemented with mineral salts,[12] and process water diluent were blended in-line and fed to the bioreactor. Actual feed rates of blended waters were typically 10 to 50 mL/min, compared with the ~740 mL/min used to fluidize the bed.

To acclimate the culture, initially only <5% wastewater (after blending) was used, gradually increasing the concentration over a period of several weeks. Once a concentration of 50% wastewater was reached, with equal flow rates of wastewater and process water diluent, the flow rates of both were increased in order to decrease the recycle ratio and increase the concentrations of organics in the bioreactor.

The bioreactor was successfully operated for ~1 week with the phenolics concentration in the 500 to 900 mg/L range and 50% strength actual wastewater. Although no problems were encountered under these conditions, the operation time was limited by our supply of wastewater. The results of this run are presented in Table 2.

Table 2. Performance of bioreactor at high phenolics concentration[a]

Date	Feed strength (%)	Phenolics[b] (mg/L)	Phenolics degradation rate[c] [mg/(L bed•min)]	Phenolics removal (%)	COD (mg/L)	COD degradation rate[c] [mg/(L bed•min)]	COD removal (%)	Organic carbon (mg/L)	Organic carbon degradation rate[c] [mg/(L bed•min)]	Organic carbon removal (%)
11/30	53	498	11	78	3792	27	54	1000	9	57
12/1	ND[d]	370	ND[d]	ND[d]	4519	ND[d]	ND[d]	1040	ND[d]	ND[d]
12/3	46	838	8	58	5713	10	21	1360	5	31
12/4	51	955	8	57	5646	14	29	1420	6	35
12/5	49	729	8	66	5192	15	32	1330	6	36
12/6 am	47	808	7	60	5257	12	29	1290	5	36
pm	47	748	7	63	5133	12	30	1300	5	35

[a] Bed volume, 1.23 L; feed flow rate, 0.007 to 0.008 L/min; liquid recycle, 0.74 L/min; temperature, 27 to 28°C; O_2 flow rate, ~100 cm^3/min.

[b] Analyzed by gas chromatography.

[c] Degradation rates obtained from overall material balance on bioreactor system; the change in concentration across the bed is small relative to the concentration and cannot be directly determined accurately.

[d] ND = not determined.

The degradation rates of the phenolics were similar to those obtained previously at much lower (<100 mg/L) concentrations of phenolics using dilute wastewater and lower feed rates. However, the COD degradation rates and total COD removal were substantially less than what was observed at the lower phenolics concentrations. The reason for this phenomenon has not been determined.

Using a smaller, bench-scale bioreactor, shown schematically in Fig. 2, the treatability of actual wastewaters was also studied briefly in conjunction with work to determine the kinetic dependence of reaction rate on the concentration of dissolved oxygen. The small, fluidized-bed bioreactor (~100 mL) was connected in series with a well-stirred reservoir (~300 mL) in which the oxygen was sparged into the liquid. In this manner, the concentration of dissolved oxygen could be controlled by adjusting the gas flow rate and/or the gas composition. Wastewater was circulated through the bioreactor and returned to the reservoir at a flow rate sufficient to fluidize the bed, ~150 to 200 mL/min. Blended wastewater feed was supplied to this recycle system at a slow rate, 1 to 10 mL/min, and effluent was removed at an equal rate. In principle, the consumption of oxygen in this small fluidized bed was small, so that the concentration changed very little across the bed, and reaction conditions were reasonably uniform at the dissolved oxygen concentration maintained in the reservoir. In practice, however, it was found that under some conditions, there was substantial consumption of oxygen in the bed. It was also seen that degradation of phenols occurred in areas such as the reservoir and connecting tubing due to the action by microorganisms in suspension and extraneous films. Corrections were made for these phenomena, as discussed in the following section.

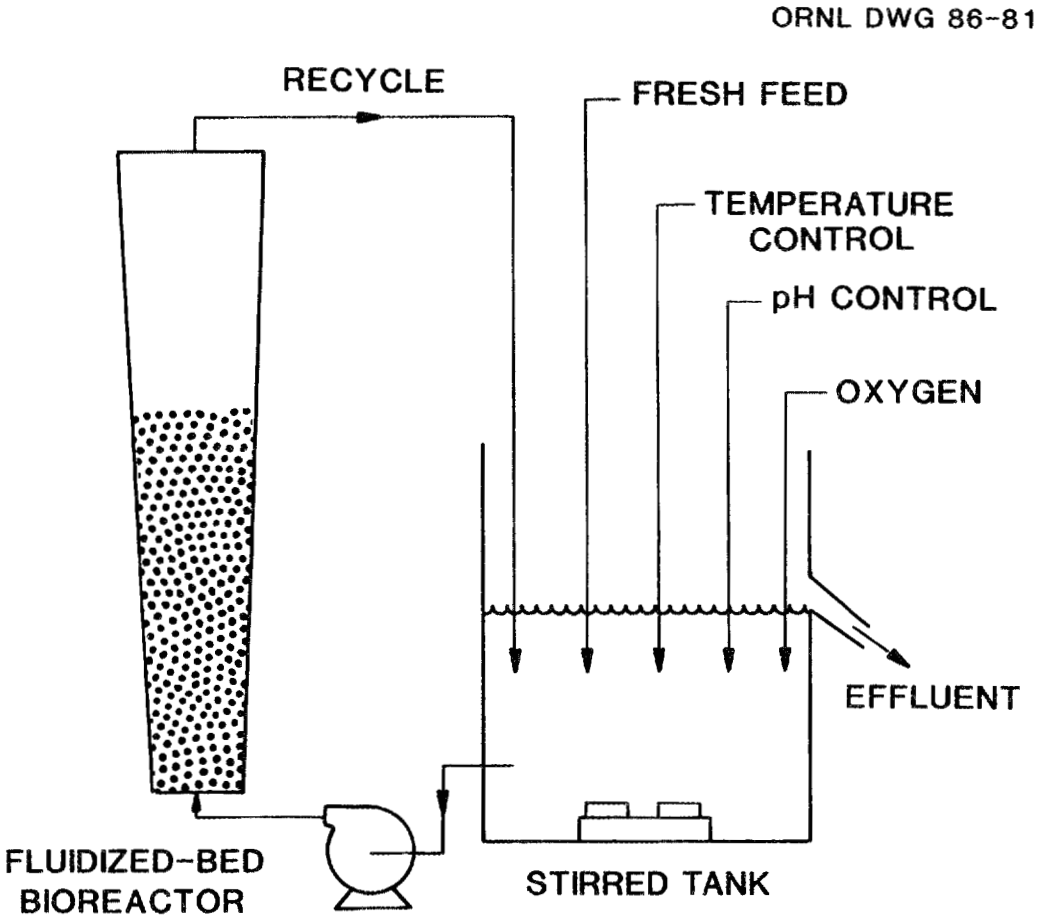

Fig. 2. A bench-scale bioreactor system with fluidized bed and mixed reservoir.

Experiments were conducted with 2, 5, and 13% strength wastewater. Several days of adaptation were required for the microbial culture each time the wastewater strength was increased. In each case, a steady state was established at a particular concentration of dissolved oxygen, and the performance of the bioreactor system was calculated from the inlet and outlet concentrations of phenols and the flow rate. The oxygen concentration was then changed, a new steady state was obtained after ~2 h, and the procedure was repeated. The contribution of the microorganisms in suspension to the reaction rate was evaluated periodically by bypassing the fluidized bed, discontinuing the fresh feed for a few minutes, and monitoring the decrease in phenolics with time in a batch mode.

It was found that the contribution of the microorganisms in suspension was typically half of the total reaction rate. When this correction was made, the degradation rate in the fluidized bed was typically 20 mg/(L bed•min) at the higher oxygen concentrations. (The effect of oxygen concentration is discussed later.) These degradation rates are a factor of 2 greater than the rates usually observed in the laboratory-scale bioreactor in which the oxygen is sparged into the bottom of the column. The improved performance is no doubt largely due to the ability to maintain higher oxygen concentrations in the smaller bioreactor and suggests potential for better performance of larger bioreactors at higher oxygen concentrations.

These results, showing that the degradation rate for phenols is greater in small bioreactors with good oxygen transfer than in larger bioreactors, have also been observed previously with synthetic wastewaters. In several cases, the degradation rates have been as high as

100 mg/(L bed•min) under controlled conditions and (apparently) favorable biofilm conditions (discussed later).

3. REACTION KINETICS: DEPENDENCE ON DISSOLVED OXYGEN

Considerable evidence has accumulated to suggest that the performance of the fluidized-bed bioreactor is strongly dependent on the concentration of dissolved oxygen in the fluidized bed. This is quite reasonable, since the solubility of oxygen is relatively low compared with the concentration of organics, and, thus, the driving force for diffusion of oxygen from the bulk liquid phase to the biofilm surface and through the biofilm is also relatively low. The dependence of the overall reaction kinetics on dissolved oxygen will be a combination of mass transfer from the bulk liquid to the biofilm and the intrinsic reaction kinetics. Experimental and modeling studies have been conducted to address these phenomena.

3.1 EXPERIMENTAL STUDIES

Both synthetic and actual wastewaters have been used in small, bench-scale, fluidized-bed bioreactors similar to the previously described system (see Fig. 2) to determine the dependence of the phenol degradation rate on the concentration of dissolved oxygen.

A synthetic wastewater containing 100 mg/L of monohydric phenol was used to determine the reaction rate over a range of oxygen concentrations from 15 to 84% of saturation (~7 to 34 mg/L). With this synthetic wastewater, the degradation rate was a function of the dissolved oxygen concentration, as seen in Table 3. These data were obtained in a period of ~1 d with one bed of bioparticles. Changes in the bioparticle properties over this period are believed to be minimal, and the changes in

Table 3. Effect of oxygen concentration on phenol degradation rate (~7% biomass; 30°C)

Oxygen saturation (%)	Degradation rate [mg/(L bed•min)]
84	28
64	26
48	24
25	19
15	15

degradation rate are believed to be directly related to the oxygen concentration. The change in oxygen concentration across the bed was ~5 mg/L in these experiments. Effects of suspended microorganisms and extraneous films were negligible because of extra precautions (see Sect. 5.1). Experiments conducted at other times with other bioparticles gave different numerical results but exhibited the same trend with respect to oxygen concentration. In addition, several different biofilm conditions were investigated and will be discussed later.

Experiments were also performed with actual wastewater from the METC in this small, bench-scale bioreactor as described in Sect. 2.4. Wastewater at 2, 5, and 13% strength was used over a range of oxygen concentrations. The dependence of the overall reaction rate (fluidized bed plus suspended microorganisms and extraneous films) on the oxygen concentration is shown in Fig. 3. Above 10 mg/L of dissolved oxygen, the degradation rate is effectively independent of oxygen concentration, whereas below 10 mg/L, the rate is a strong function of oxygen concentration.

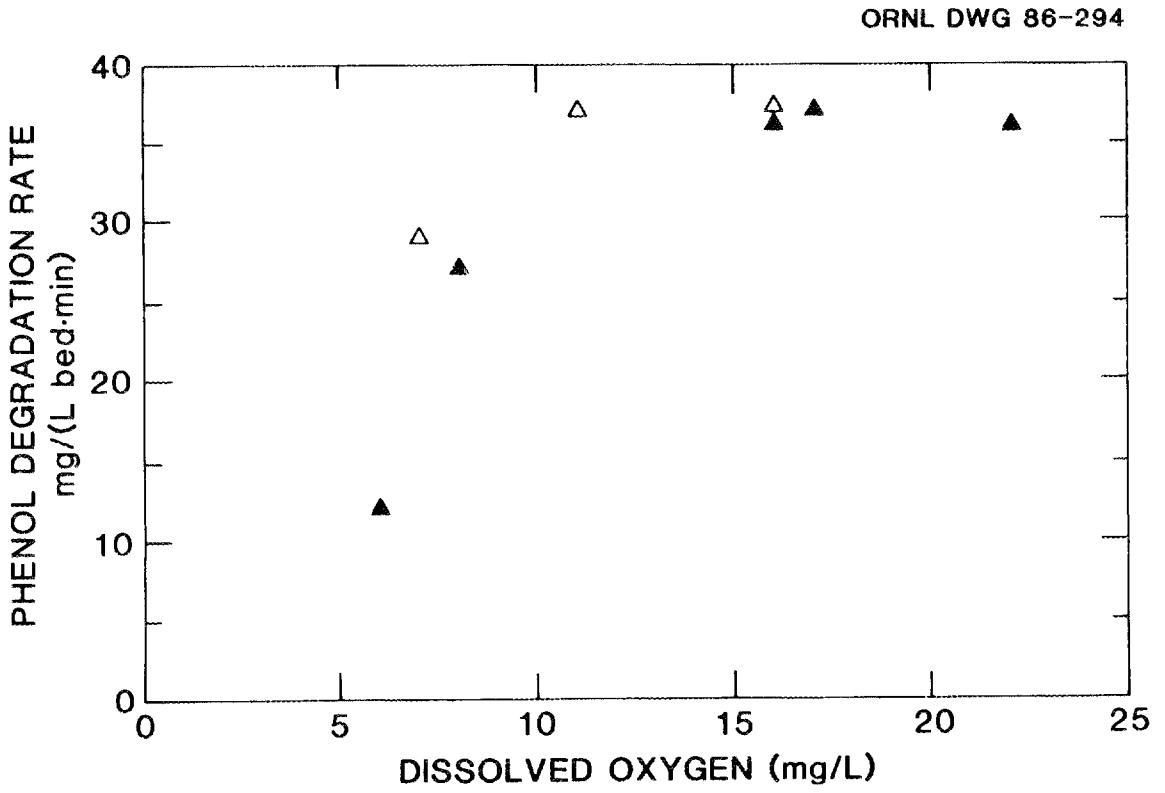

Fig. 3. Dependence of global degradation rate on concentration of dissolved oxygen for 2% strength actual wastewater in two experiments with a bench-scale bioreactor (see Fig. 2).

The oxygen concentration shown on the abscissa is the value measured in the well-stirred reservoir and, thus, the value at the inlet to the fluidized bed. The concentration of oxygen in the effluent from the bed was substantially lower and approached zero, in some cases. This condition makes it difficult to evaluate the local instantaneous oxygen concentration that must be maintained to avoid a decrease in the reaction rate. This value is surely less than the 10 mg/L seen in Fig. 3 but greater than zero. Further work remains to be done with smaller bed volumes to reduce the oxygen consumption and maintain more uniform conditions in the bed.

It was noted earlier that the degradation rate in the fluidized bed is approximately half of the overall observed degradation rate, with the other half of the degradation due to suspended microorganisms and other films. Thus, for the data shown in Fig. 3, the maximum degradation rate in the bed is ~20 mg/(L bed•min). This rate is greater than the rates generally obtained in the larger bioreactor, suggesting potential for improved performance with better availability of oxygen.

3.2 MODELING STUDIES

The dissolved oxygen in the liquid phase must diffuse to the biofilm surface (and into the biofilm) in order to participate in the biooxidation of the organics. The organics must do likewise; however, since the solubility of oxygen limits the concentration to values significantly less than the concentration of organics, it is reasonable to hypothesize that the rate-limiting step is diffusion of oxygen. Mass transfer coefficients for diffusion of solutes from the bulk phase to the surface of spherical particles may be estimated from the following correlation:[17]

$$Sh = 2.0 + 0.31\ (Sc)^{0.33}\ (Gr)^{0.33}\ . \qquad (1)$$

In this equation, Sh is the Sherwood number (which contains the mass transfer coefficient, k_L), Sc is the Schmidt number, and Gr is the Grashof number. Terminal settling velocities were measured experimentally as a function of bioparticle size; the terminal settling velocity is a reasonable approximation to the relative velocity of the particle and liquid in the fluidized bed. Diffusivities were estimated using the Wilke-Chang correlation.[17] For conditions typical of those in the fluidized bed, the computed mass transfer coefficients (k_L) are shown in Table 4.

Table 4. Calculated interphase mass transfer coefficients[a]

Condition	Solute	$k_L(min^{-1})$
Thick biofilms, 0.2-cm particle diam, ~15% biomass (dry wt)	Phenol	2.8
	Oxygen	5.0
Thin biofilms, 0.07-cm particle diam, <1% biomass (dry wt)	Phenol	22
	Oxygen	38

[a] 30°C; k_L based on volume of settled bed of particles.

Apparent reaction rates can now be estimated for the limiting condition of rapid intrinsic reaction such that the concentrations of phenol and oxygen at the biofilm are maintained at zero. Thus, mass transfer is the sole rate-limiting step. The results are shown in Table 5 for the assumption that oxygen is the rate-limiting species due to its much smaller concentration driving force (40 mg/L vs 100 mg/L). Two different

Table 5. Maximum phenol degradation rates[a]

Oxygen saturation (%)	Phenol degradation rate [mg/(L bed•min)]	
	Thick biofilms[b]	Thin biofilms[b]
100	153	1170
50	77	585
25	38	292
10	15	117

[a] Assuming interphase transfer of oxygen (liquid-to-biofilm) to be the sole resistance.
[b] See Table 4.

biofilm conditions are considered and will be discussed more completely later. It can be seen that for thick films (see Table 4), the predicted rates are comparable to experimental observations (e.g., Table 3). For thin films, the predicted rates exceed experimental observations considerably; very likely, other phenomena are rate-limiting under these conditions, such as the intrinsic reaction kinetics. However, these modeling results do support the hypothesis that mass transfer of oxygen (and perhaps phenol) from the bulk liquid phase to the biofilm is a significant rate-limiting step.

4. CHARACTERIZATION OF BIOFILMS

The microorganisms immobilized in the form of biofilms on the surface of the anthracite coal particles (30-60 mesh) are catalysts for the biooxidation of dissolved organics. Unlike inorganic catalysts, these biocatalysts are dynamic; they are continually growing, decaying, and undergoing other changes. More than one species of microorganism is

present, and a variety of interspecies relationships act to maintain the overall integrity of the biofilms. Earlier studies[11] have shown that the microbial species are similar to those found in suspended growth systems (activated sludge) used to treat similar wastewaters.

In light of these characteristics, it is not surprising that the observed activity of the biocatalyst particles varies with time in response to complex conditions and interactions that are poorly understood and often unrecognized. Much more research is needed in this general area to take maximal advantage of the capabilities of biofilms. We have made several observations that have improved our understanding of the activity of biofilms in fluidized-bed bioreactors.

4.1 BIOFILM THICKNESS

Experiments were performed with a synthetic wastewater containing 100 mg/L of monohydric phenol, using the bench-scale bioreactor described earlier (Fig. 2). The biocatalyst particles were obtained from a somewhat larger fluidized-bed bioreactor maintained on synthetic wastewater for the express purpose of providing an active bed of biocatalyst particles for such use. Degradation activity was measured in the small, well-controlled bioreactor as a function of the quantity of biofilm on the coal particles. In a general sense, the extent of biofilm loading on the coal could be controlled by the operating conditions in the source bioreactor. The biofilm loading was determined by measuring the dry weight of a sample of bed material both before and after removing the biomass with NaOH. This procedure allowed determination of the mass density of the biofilm as well as the quantity of biofilm per coal particle.

Table 6 illustrates the activity of the fluidized bed as a function of the biofilm loading. Thin films produce a more active bed than do thick films. This can be explained by a relatively straightforward effectiveness factor argument, analogous to the activity of porous inorganic catalyst particles. The biofilm can be considered to be "porous" in the sense that reactants can penetrate into the interior and undergo reaction. As the biofilms become thicker, diffusion limits the contribution of the inner regions of the films, while the overall particle dimensions increase. The active biofilm increases approximately with the square of the particle radius (i.e., increased surface area), whereas the bed volume increases with the cube of the radius. As seen in Table 6, the overall result is a decrease in the volumetric reaction rate.

Table 6. Effect of biomass concentration on maximum phenol degradation rate (~85% oxygen saturation; 30°C)

Biomass concentration (% dry wt)	Degradation rate [mg/(L bed•min)]
15	25
7	35
1	100

This behavior has been described previously in modeling work.[10] The biofilm thickness for maximum bed activity was estimated to be 5 to 10×10^{-4} cm. The 1% biofilm condition in Table 6 translates to a film thickness of $20\text{-}40 \times 10^{-4}$ cm, which is in the same range as predicted.

Note that the bed activity with 1% biomass was as high as 100 mg/(L bed•min). This result serves to illustrate that improved

performance may well be possible if effective means can be found to control and maintain the biofilms in the desired form. However, it should be remembered that the results in Table 6 were obtained with dilute synthetic wastewater.

4.2 DENSITY OF BIOFILMS

An interesting observation was made during attempts to correlate the activity of the bioparticles with the biofilm loading. The dry weight of the biofilms was found to correlate well with the degradation rate in the bed. As shown in Fig. 4, a direct relationship exists between the concentration of biomass in the film and the amount of activity. This observation supports the intuitive concept that the biofilm is heterogeneous, with active and inactive portions. The inactive portions may include the extracellular polysaccharides that hold the biofilm together. The intercept in Fig. 4, showing no activity for a concentration of <0.007 g/cm^3, is also consistent with this interpretation.

These results suggest an opportunity to improve the performance of the biocatalyst particles by maintaining dense films. At the present time, the methodology for accomplishing this has not been established. The film density does appear to depend on the local environmental conditions — that is, the operating conditions in the bioreactor. Changes in film density appeared to correlate with changes in feed batches as well as an apparent time trajectory that could not be identified with anything in particular. More study is needed to learn how to take advantage of these phenomena.

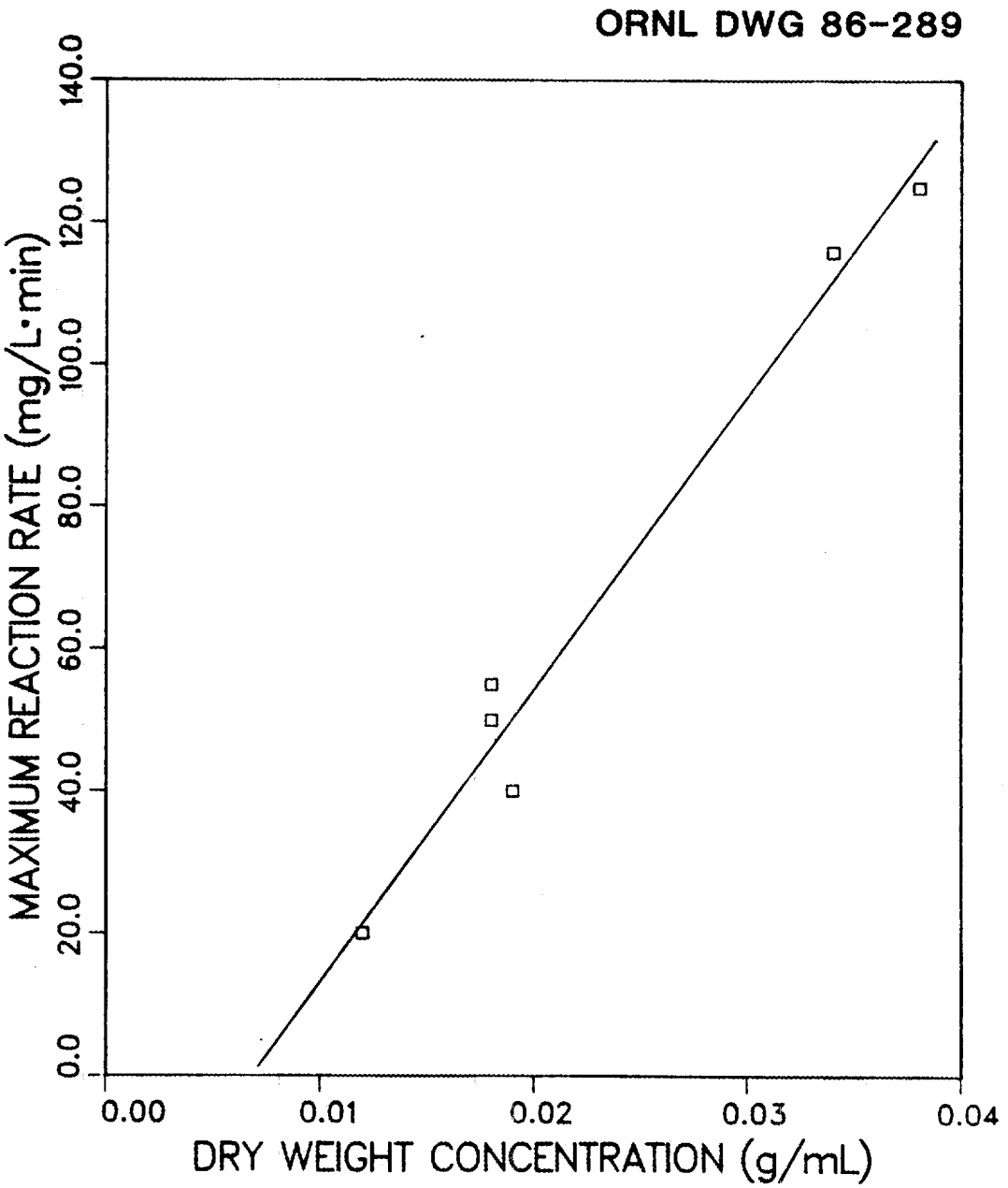

Fig. 4. Degradation rate (synthetic wastewater) as a function of dry weight concentration of biomass in the biofilm.

5. DYNAMIC BEHAVIOR OF BIOFILMS

It is important to consider how biofilms behave under transient, unsteady-state conditions. In a large, commercial-scale bioreactor, operating conditions are rarely truly constant for a significant period of time; rather, conditions oscillate around some average state. The behavior of the biofilms and the reaction kinetics under these constantly changing conditions are important to process control strategies to maintain a stable process.

5.1 EXPERIMENTAL STUDIES

Several dynamic experiments were performed with synthetic wastewater, using the small fluidized bed and mixed reservoir illustrated in Fig. 2. An initial steady state was established, a pulse of phenol was added, and the phenol concentration was monitored continuously thereafter by uv absorbance in a flow-through cell.

For these experiments, a uv sterilizer was placed in line between the reservoir and the fluidized bed. The purpose of the sterilizer was to prevent growth of microorganisms in the bulk liquid phase and subsequent phenol degradation. It was shown experimentally that the sterilizer was highly effective in preventing growth of free cells.

To obtain the reaction rate, a phenol material balance equation was used:

$$V_T \frac{dC}{dt} = Q(C_{in} - C_{out}) - RV_{FB} \quad . \qquad (2)$$

accumulation flow in flow out degradation

In this equation, Q is the liquid flow rate, C is the phenol concentration, t is time, R is the phenol degradation rate, V_T is the total liquid volume in the system, and V_{FB} is the volume of the fluidized bed.

The rate of change of phenol concentration was determined from the experimental data, and the flow terms were known experimentally. Thus, the instantaneous reaction rate could be calculated.

Typical responses recorded in these experiments are shown in Figs. 5 and 6. Figure 5, illustrating results obtained without pH control, shows oscillations in the return to steady state following the pulse of phenol. The pH was initially 5.5 and decreased 1.2 units with the increase in reaction rate in response to increased substrate, presumably due to production of acidic products, including CO_2. In contrast, when pH was controlled at 7.0, no oscillations were seen, as shown in Fig. 6. These results suggest that pH control may be a useful strategy for bioreactor control. However, the oscillatory behavior in the absence of pH control has not been fully characterized. Experiments to date show a damped return to a stable steady state.

Figure 7 shows results of a dynamic experiment at higher concentrations of phenol. In this case, the pulse of phenol appeared to inhibit the reaction rate. However, the reaction rate does recover to the initial value. Modeling studies, discussed in Sect. 5.2, have shown that this behavior can be produced with a simple substrate inhibition model for the reaction kinetics. However, it has not been proven that substrate inhibition is the correct or sole cause of this behavior.

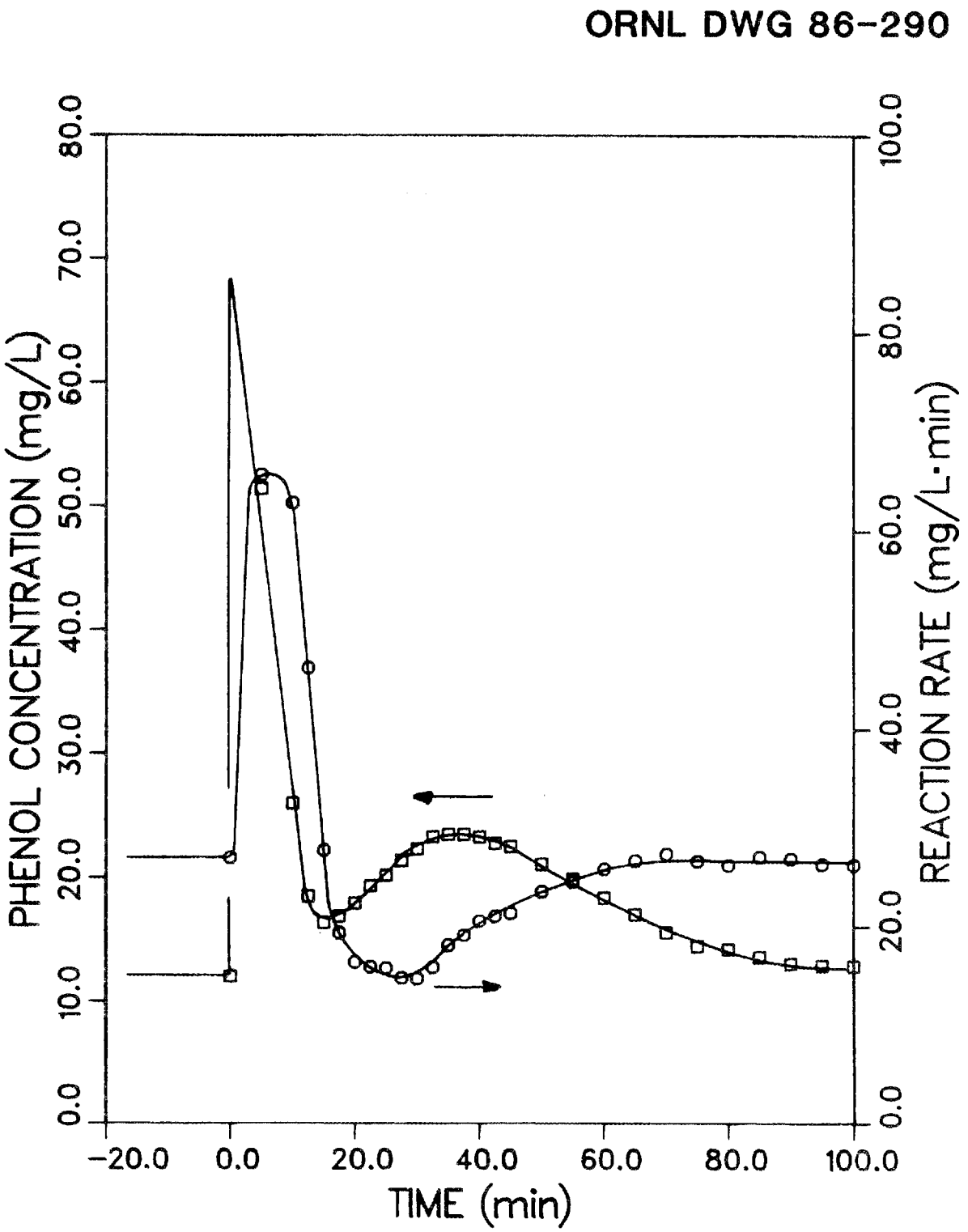

Fig. 5. Dynamic response of a bench-scale bioreactor (Fig. 2) to a pulse of phenol using synthetic wastewater without pH control.

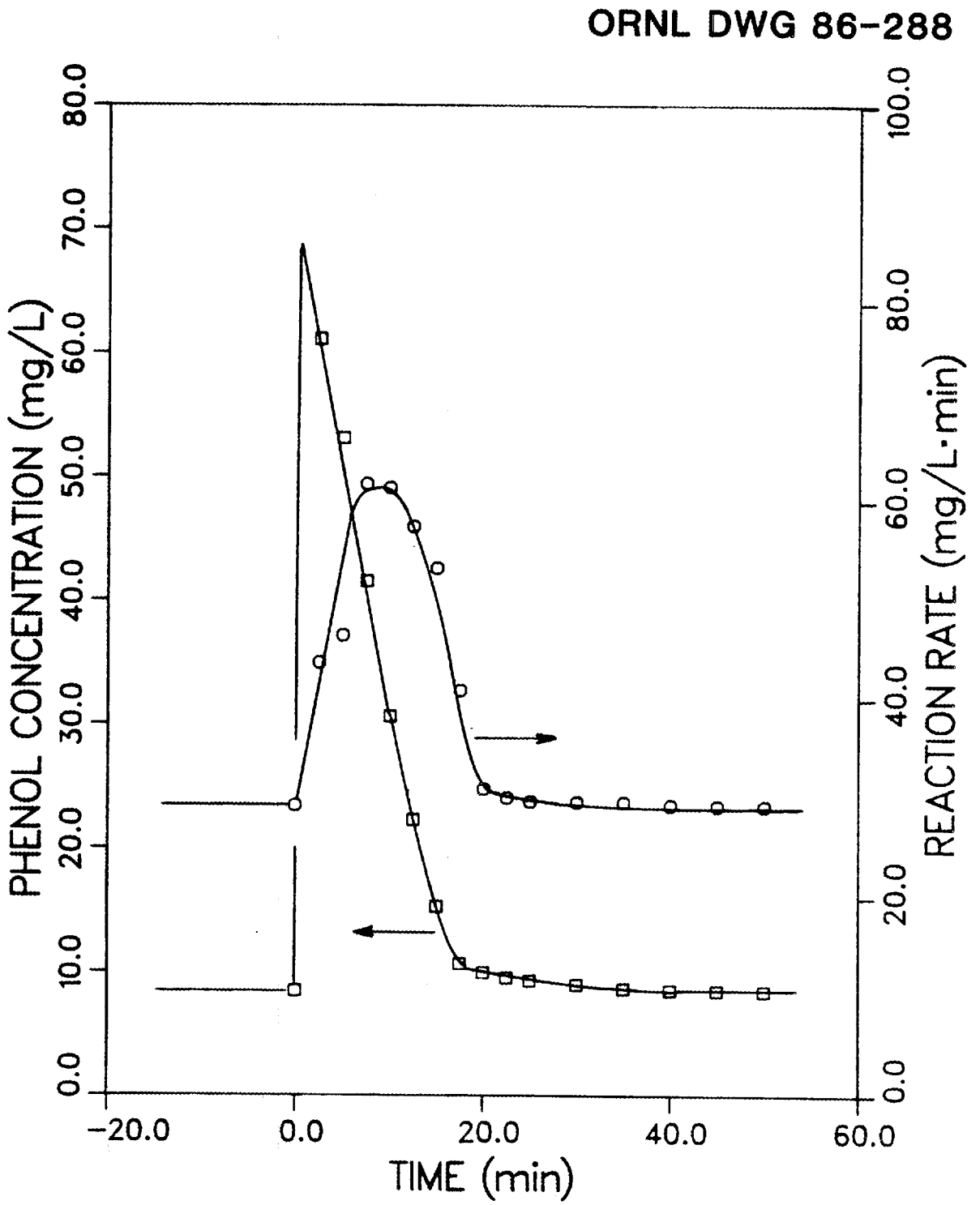

Fig. 6. Dynamic response of a bench-scale bioreactor (Fig. 2) to a pulse of phenol using synthetic wastewater with the pH controlled at 7.0.

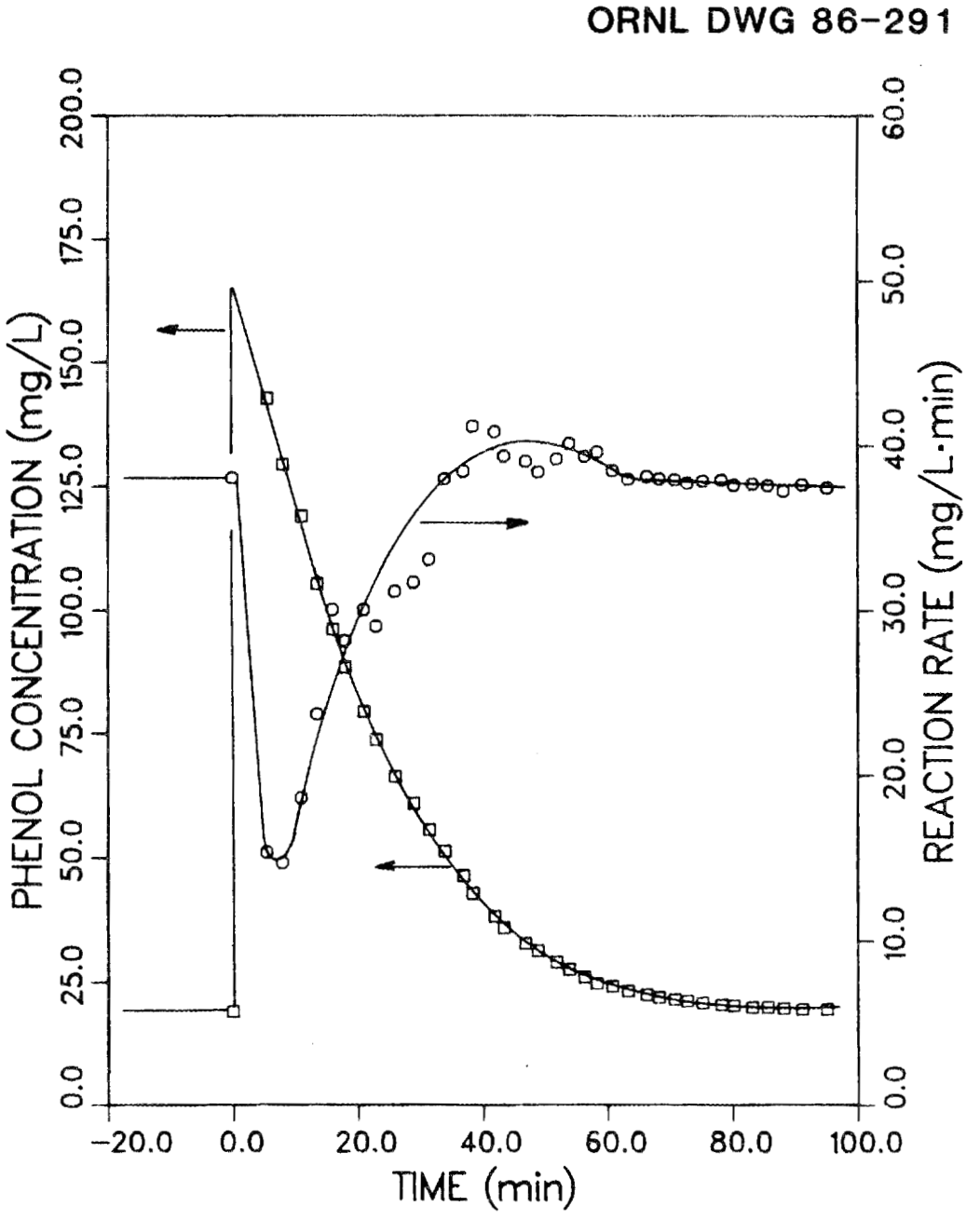

Fig. 7. Dynamic response of a bench-scale bioreactor (Fig. 2) to a pulse of phenol using synthetic wastewater with the pH controlled at 7.0.

5.2 MODELING STUDIES

Steady state models for biofilm kinetics and bioreactor behavior have been presented previously.[10] These models have been extended to include unsteady state conditions for better understanding of biofilm phenomena and for development of process control strategies.

The integrated model consists of a bioparticle model and a reactor model. The bioparticle model postulates that a spherical, inert pellet is coated with a uniform, homogeneous, biological film. Substrates (phenol and oxygen) diffuse into the film from the bulk liquid and react at a rate, R, which is described by the following double-Monod relationship:

$$R_{phenol} = \beta K_{max}\left(\frac{C_{O_2}}{K_{O_2} + C_{O_2}}\right)\left(\frac{C_p}{K_p + C_p + C_p^2/K_I}\right), \tag{3}$$

$$R_{O_2} = \gamma R_{phenol}, \tag{4}$$

where C_{O_2} and C_p are the concentrations of oxygen and phenol, respectively; K_{O_2} and K_p are the half-saturation Monod constants; K_I is an inhibition constant; K_{max} is a kinetic coefficient; β is the concentration of microorganisms in the bed, which is determined from the film density and geometry; and γ is a stoichiometric coefficient. Diffusion and reaction of phenol and oxygen within the film are governed by:

$$\frac{\partial C_p}{\partial t} = D_p\left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r}\frac{\partial C_p}{\partial r}\right) - R_{phenol}, \tag{5}$$

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2}\left(\frac{\partial^2 C_{O_2}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{O_2}}{\partial r}\right) - R_{O_2}, \tag{6}$$

with boundary conditions:

$$r = \text{outer radius of film; } C_p,\ C_{O_2} = \text{bulk phase concentrations ;} \quad (7)$$

$$r = \text{inner radius of film; } \frac{\partial C_p}{\partial r} = \frac{\partial C_{O_2}}{\partial r} = 0 \ . \quad (8)$$

The initial conditions and concentration profiles within the film are steady state values prior to the phenol pulse. The parameters D_p and D_{O_2} are the diffusivities of phenol and oxygen, respectively, in the film. These equations are used to calculate phenol and oxygen concentration profiles in the film and provide the reaction kinetics term for the reactor model, which is the material balance in Eq. (2). An oxygen balance is also needed:

$$V_T \frac{dC_{O_2}}{dt} = Q(C_{O_2}{}_{in} - C_{O_2}{}_{out}) + K_La(C^*_{O_2} - C_{O_2}) - R_{O_2}V_{FB} \ , \quad (9)$$

where $K_La(C^*_{O_2} - C_{O_2})$ is the rate of transfer of oxygen from the gas to the liquid. The equations are solved numerically.

Several model simulation results are compared with experimental data in Figs. 8 and 9. Figure 8 illustrates the time trajectories of the phenol concentration and the reaction rate. The curves are obviously qualitatively similar to the experimental results in Fig. 6. Figure 9 shows a simulation using similar experimental conditions to Fig. 7. Recall that the data in Fig. 7 showed inhibition of the reaction rate. The phenol concentration trajectories are in excellent agreement with the experimental values. Parameters used in the simulation are shown in Table 7.

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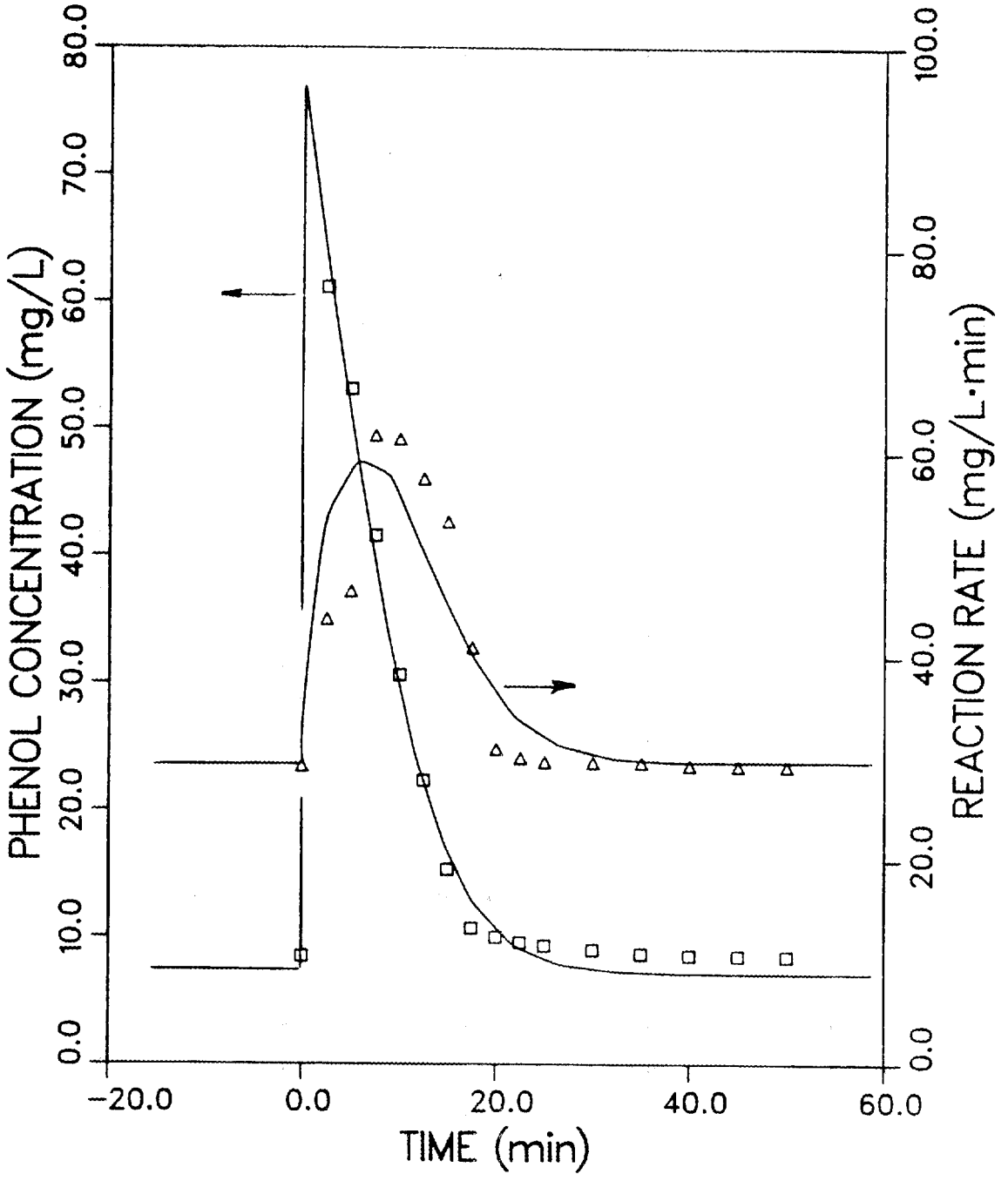

Fig. 8. Comparison of simulation results (———) and experimental data for phenol concentration (□) and reaction rate (Δ).

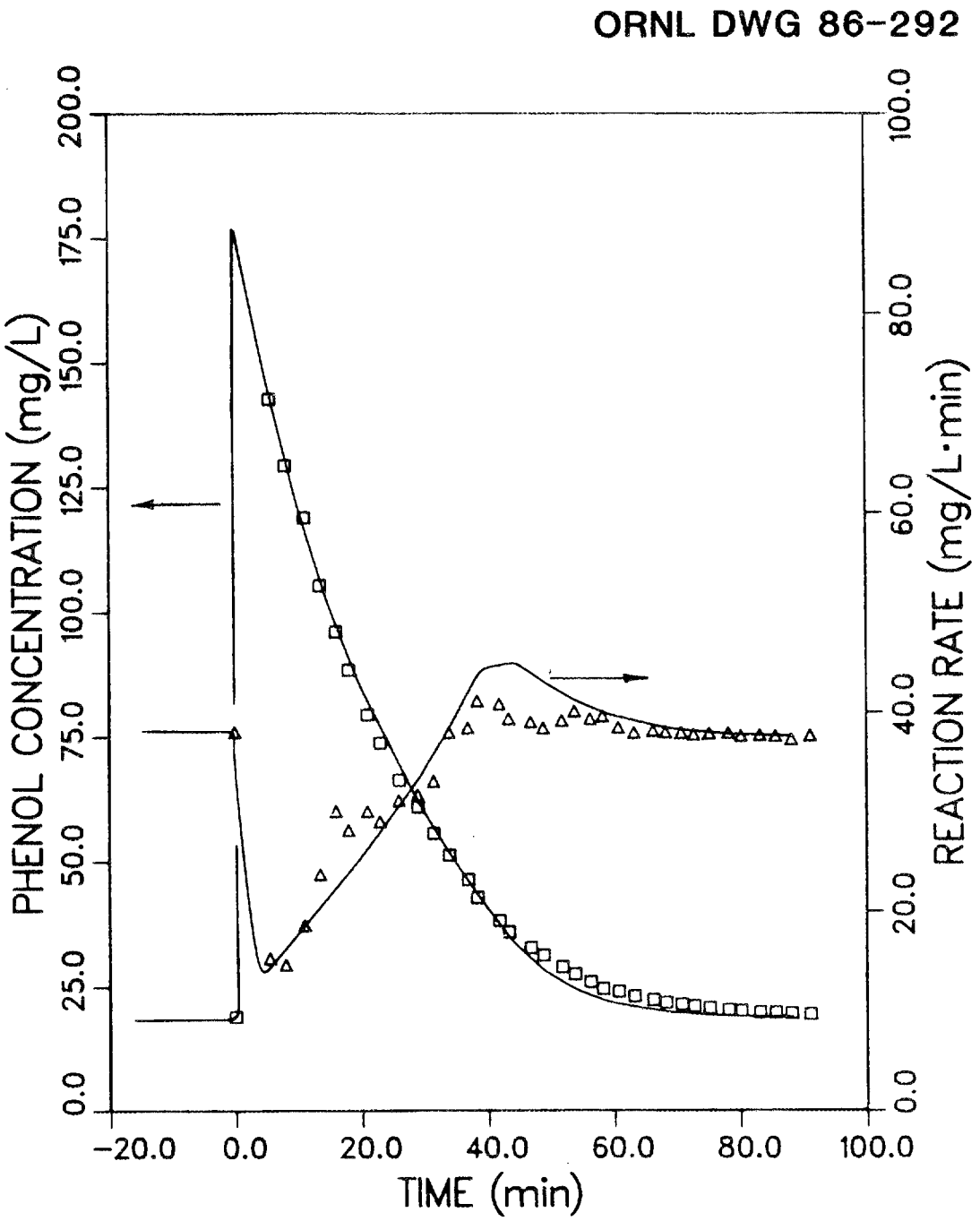

Fig. 9. Comparison of simulation results (———) and experimental data for phenol concentration (□) and reaction rate (Δ).

Table 7. Typical parameter values used in the dynamic model

Parameter	Value
Coal particle radius	2.2×10^{-2} cm
Biofilm thickness	8.8×10^{-3} cm
Biofilm density	1.019 g/cm^3
Settled bed volume	24 cm^3
Total system volume	360 cm^3
Residence time	17 min
Influent phenol concentration	65 mg/L
Influent oxygen concentration	1.0 mg/L
Phenol pulse	50 mg/L
$C^*_{O_2}$ (pure oxygen)	40 mg/L
K_La	0.01 s^{-1}
D_p	2.75×10^{-6} cm^2/s
D_{O_2}	6.25×10^{-6} cm^2/s
K_p	1.0 mg/L
K_{O_2}	0.1 mg/L
K_I	60 mg/L
K_{max}	8.0 mg phenol/g cells•min
γ	1.4 g oxygen/g phenol

This dynamic model appears to do an excellent job of reproducing the experimental data under conditions of pH control. However, the oscillations observed without pH control have not been obtained in the simulations. We do not yet understand the cause of the oscillations, nor have

we been able to induce oscillations in the model using inhibition functions and other pH-dependent parameters.

6. PROCESS STATUS AND EVALUATION

The fluidized-bed bioreactor is a proven technology in several applications and is growing in use. Large pilot plant equipment constructed and tested at ORNL[7] is now in use at the Portsmouth Diffusion Plant, operated by Goodyear Atomic, for biodenitrification of wastewaters. The Feed Materials Production Center at Fernald, Ohio, operated by National Lead of Ohio, is presently constructing a similar process, which is scheduled for startup in 1986. The Dorr-Oliver Corporation has a fluidized-bed bioreactor technology for wastewater treatment.[18,19] Similar technology has been proposed for wastewater treatment at shale oil plants.[1]

Process development work has been carried out at ORNL for 3.5 years to assess the utility of fluidized-bed bioreactors for biooxidation of coal gasification wastewaters. This particular work has built on the previous successful development of biodenitrification at ORNL[7] and on earlier work on treatment of coal conversion wastewaters.[20] Both synthetic wastewaters, formulated according to Singer et al.[21] and actual wastewaters from the Holston Army Ammunition Plant and the METC have been treated. The focus of these studies has been on treatability of these wastewaters, demonstration of long-term stable operation of the fluidized-bed bioreactors, and reaction-rate kinetics. This work has been done using laboratory-scale bioreactors having a 5-cm ID and a 150-cm height (Fig. 1), and bench-scale equipment.

The technical status of the process, additional development needs, and an economic evaluation are summarized in Sect. 6.1.

6.1 TECHNICAL STATUS

Process development studies at ORNL have led to the following observations:

1. The fluidized-bed bioreactor will operate continuously and remain stable over long periods of time. Continuous stable operation has been achieved experimentally for periods of months. Prolonged pulses or spikes of organics may cause temporary inhibition of biological activity, but the activity returns within 1 to 2 d. Similarly, biological activity picks up quickly after downtimes with no carbon substrate and no hydraulic flow. This quick response is superior to the response of suspended growth systems.
2. Startup procedures are straightforward. The bioreactor is operated at total recycle for several days to one week, at which time self-sustaining films are established on the coal particles. Inocula derived from two different commercial preparations have been used successfully.
3. Monohydric and substituted phenols in actual wastewaters are easily degraded. The rate depends on the biofilm loading and characteristics (thin, dense films are best). Typical volumetric degradation rates are 10 mg/(L bed•min) with real wastewater at 25 to 30°C. Under controlled conditions and special efforts to maintain high concentrations of dissolved oxygen, rates of 20 and 100 mg/(L bed•min) have been obtained with actual and synthetic wastewaters, respectively.

4. Dissolved organics in addition to phenols are degraded, as evidenced by decreases in COD and TOC. The identity of these compounds is not known.
5. High-strength wastewater (50% process condensate wastewater) can be treated successfully after stripping to remove ammonia and sulfides. The reaction rate appears to be reduced slightly compared with more dilute wastewaters; however, the distinction between this effect and dependence on dissolved oxygen is not yet resolved.
6. High-strength wastewater appears to slow the growth of biofilms and hence reduce the sludge for ultimate disposal. Sludge production appears to be comparable to that for suspended growth systems, such as activated sludge.

6.2 RESEARCH AND DEVELOPMENT NEEDS

Several potential problems have been identified that need to be resolved before this technology is fully ready for commercialization for biotreatment of coal gasification wastewaters. In addition, several new opportunities have arisen for further process improvement that could further increase the attractiveness and value of this process. These issues are addressed in this section.

1. Maintenance of sufficient dissolved oxygen in the liquid phase to allow maximal reaction rates is a significant problem. The demand for oxygen is high. On a mass basis, approximately one gram of oxygen is needed per gram of phenols to be degraded. Thus, the oxygen demand rate is ~10 g/(L bed•min), which is difficult to supply when the solubility of oxygen is only ~40 mg/L (or less) at a partial

pressure of 1 atm. It is probable that oxygen will need to be supplied throughout the fluidized bed, by sparging or other means; presaturation of the feed will probably not be sufficient. Various means to improve oxygen transfer and increase availability can be proposed. However, realistic study of these means will require operation at a larger scale than the bioreactors used to date. This issue is particularly important because the overall degradation rate is quite sensitive to maintaining sufficient oxygen.

2. Occasional foaming and clumping of the bioparticles have been experienced. Foaming can be controlled in the laboratory bioreactors with the use of antifoam compounds. Clumping of the bioparticles, which leads to a loss of fluidization and severe channeling of liquid, was circumstantially related to buildup of unknown chemicals in the bioreactor. The problem could be solved by removing the agglomerated material and flushing the fluidized bed briefly with process water. These phenomena need to be investigated in larger-scale equipment.
3. Quantities and characteristics of sludge need to be examined in larger equipment. Although no particular problems were experienced, the laboratory equipment was too small to assess these features adequately. Similarly, the need for additional treatment of the water for removal of suspended solids should be considered further.

Several opportunities for substantial improvements in the fluidized-bed process have become apparent. Implementation of these concepts will require R&D but offer improved performance and flexibility in the "next generation" of bioreactors.

1. Physical characteristics of the biofilms, probably related to biological characteristics, appear to be related to biological activity. Denser biofilms, presumably containing more microorganisms and less "glue," are more active. It is not known how to favor and promote such films. Circumstantial evidence suggests, not surprisingly, that environmental conditions such as nutrient levels play a role. There is much to be learned about biofilms to enable an engineering design approach.
2. Genetic engineering techniques now offer the opportunity to produce microorganisms with metabolic capabilities to degrade specific wastes. This can be done under controlled conditions in laboratory flasks. However, use of these new microorganisms in open bioreactor systems for treatment of actual wastewaters requires the completion of further experimental and conceptual/modeling work.
3. New types of biocatalysts are being developed that immobilize the microorganisms within porous matrices such as alginate and carrageenan gels. These support materials offer mild immobilization and protection from the environment for the microorganisms, while substrates and products can diffuse in and out easily. These concepts may prove useful in wastewater treatment in particular applications.

6.3 ECONOMICS

An economic analysis was conducted[10] in which the fluidized-bed bioreactor process was compared with a conventional activated sludge process outlined by other investigators.[2] This comparison indicated that the fluidized-bed process might require half the capital investment as

well as half the operating costs of an activated sludge process. The principal reason for these lower costs is the higher reaction rate in the fluidized bed, which requires smaller reactor volume. The conceptual process flowsheet is shown in Fig. 10.

The key issues governing the costs for the fluidized-bed process were (1) the strength of the wastewater to be treated, which affects reactor volume and recycle requirements; and (2) the reaction rate. Technical progress during the past year has helped to resolve uncertainties in the former, but the latter remains uncertain.

The process design called for treatment of 50% strength wastewater in the front end of the biotreatment process. The technical feasibility of this strategy was verified (see Sect. 2.4). At this time, it is believed that this strategy is the proper course. The economic calculations thus remain the same as reported last year.

The process design was based on a phenols degradation rate of 20 mg/(L bed•min) in the major bioreactors exclusive of the polishing bioreactor. Efforts to determine the minimum requirements for dissolved oxygen and demonstrate degradation rates of 20 mg/(L bed•min) with actual wastewater have been inconclusive to date. This degradation rate has been achieved in small bioreactors with plenty of dissolved oxygen. However, it is clear that maintaining sufficient oxygen in larger (and commercial) bioreactors will not be a trivial matter. Neither is it obvious that it will be impossible to do so. Therefore, the economic picture remains uncertain. More development work with larger-scale equipment and innovative oxygen supply methods is needed to resolve this issue.

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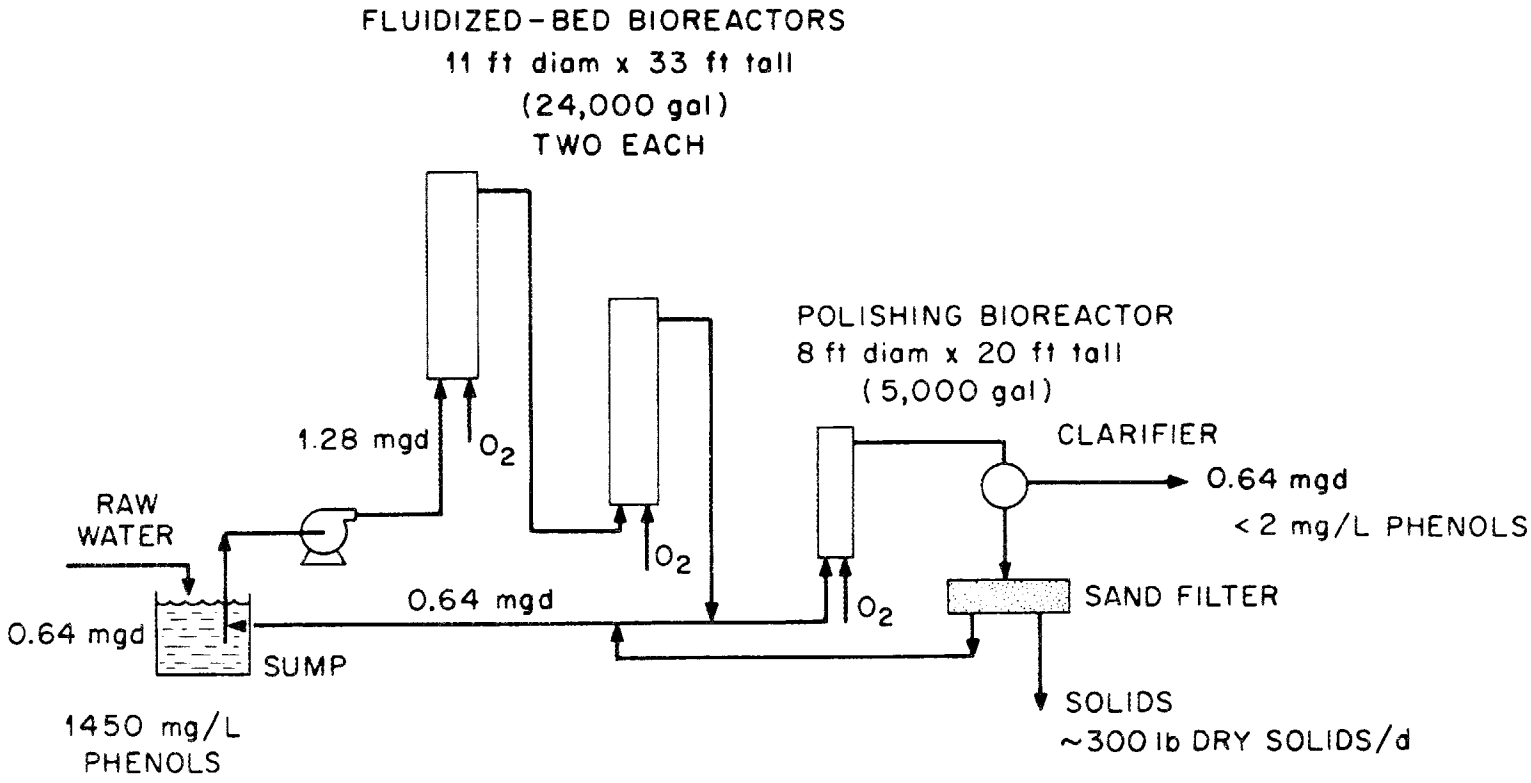

Fig. 10. Conceptual flowsheet for a fluidized-bed bioreactor process.

7. ACKNOWLEDGMENTS

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8. REFERENCES

1. I. Frankel and M. Drabkin, "Wastewater Treatment Systems for Synthetic Fuels Plants Based on Peat and Oil Shale," Environ. Prog. 4(1), 39-43 (1985).

2. R. D. Neufeld, C. Moretti, F. Ali, and J. Paladino, Pretreatment and Biological Digestion of METC Stirred Fixed Bed Gas Producer Wastewaters, DOE/ET/14372-7, September 1981.

3. J. W. Patterson and P. S. Kodukala, "Biodegradation of Hazardous Organic Pollutants," Chem. Eng. Prog., 48-55 (April 1981).

4. H. Kobayashi and B. E. Rittmann, "Microbial Removal of Hazardous Organic Compounds," Environ. Sci. Technol. 16 (3), 170A-183A (1982).

5. R. G. Luthy, "Treatment of Coal Coking and Coal Gasification Wastewaters," J. Water Pollut. Control Fed. 53(3), 325-39 (1981).

6. E. J. Bouwer, "Secondary Utilization of Trace Halogenated Organic Compounds in Biofilms," Environ. Prog. 4(1), 43-45 (1985).

7. J. F. Walker, C. W. Hancher, R. K. Genung, B. D. Patton, and M. Kowalchuk, "Biological Treatment of Nitrate Wastewater Using Fluidized-Bed Bioreactors," Biotechnol. Bioeng. Symp. No. 11, 415-25 (1981).

8. A. L. Rivera, "Heavy Metal Removal in a Packed-Bed, Anaerobic Upflow (ANFLOW) Bioreactor," J. Water Pollut. Control Fed. 55(12), 1450-56 (1983).

9. K. J. Kennedy, M. Muzar, and G. H. Copp, "Stability and Performance of Mesophilic Anaerobic Fixed-Film Reactors During Organic Overloading," Biotechnol. & Bioeng. 27, 86-93 (1985).

10. G. W. Strandberg, R. M. Worden, J. D. Hewitt, and T. L. Donaldson, Fixed-Film, Fluidized-Bed Bioreactors for Biooxidation of Coal Conversion Wastewaters: Progress Report for the Period October 1, 1983-September 30, 1984, ORNL/TM-9395, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., March 1985.

11. T. L. Donaldson, G. W. Strandberg, J. D. Hewitt, and G. S. Shields, "Biooxidation of Coal Gasification Wastewaters," Environ. Prog. 3, 248-53 (1984).

12. T. L. Donaldson, G. W. Strandberg, J. D. Hewitt, and G. S. Shields, Fixed Film Fluidized-Bed Bioreactors For Biooxidation of Coal Conversion Wastewaters: Progress Report for the Period October 1, 1982-September 30, 1983, ORNL/TM-9031, Union Carbide Corp. Nuclear Div., Oak Ridge Natl. Lab., April 1984.

13. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association, Washington, D.C., 1975, pp. 580-81.

14. L. B. Yeatts, Jr., G. B. Hurst, and J. E. Caton, "Determination of Hydroxybenzenes in Fossil Fuel-Derived Liquids and in Associated Process Waters," Anal. Chim. Acta 151, 349-58 (1983).

15. Wastewater Analysis Handbook, Hach Chemical Company, Loveland, Colo., 1978, pp. 371-80.

16. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association, Washington, D.C., 1975, pp. 383-86.

17. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.

18. P. M. Sutton, "Fluidized Bed Finds New Application in Wastewater Treatment," Pollut. Eng. 13(2), 38-40 (1981).

19. H. Melcer, S. Nutt, I. Marvan, and P. Sutton, "Combined Treatment of Coke Plant Wastewater and Blast Furnace Blowdown Water in a Coupled Biological Fluidized Bed System," J. Water Pollut. Control Fed. 56(2), 192-98 (1984).

20. D. D. Lee, C. D. Scott, and C. W. Hancher, "Fluidized-Bed Bioreactor for Coal-Conversion Effluents," J. Water Pollut. Control Fed. 51, 974-84 (1979).

21. P. C. Singer, J. C. Lamb III, and F. K. Pfaender, Treatability and Assessment of Coal Conversion Wastewater: Phase 1, EPA-600/7-79-248, University of North Carolina, Chapel Hill (1979).

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