

## Wastewater Treatment in an Offline Storage Tank

### Introduction

Each year in the United States, 850 billion gallons of untreated combined wastewater and 3-10 billion gallons of untreated sanitary wastewater overflow in the environment (EPA 2004). These waters contaminate their receiving waters with dangerously high pathogen concentrations, as well as high concentrations of nutrients and Biochemical Oxygen Demand (BOD), which contribute to eutrophication and fish kills. Such overflows occur because the amount of wastewater in the sewer system exceeds the capacity of the wastewater treatment plant (WWTP). Several cities, such as Montreal and Cleveland, have installed systems that store this excess water in either off-line storage basins/tanks or in-line storage until the WWTP is able to treat it (Schutze et al. 2002, EPA 1999a, Thomas et al. 2004, Duchesne et al. 2004).

Once the wastewater is stored, it may be possible to treat the wastewater in situ below the WWTP effluent standards for total suspended solids (TSS), fecal coliform, BOD, ammonia, and phosphorus. Currently, there is no single in-situ treatment method that treats all of these parameters, but rather a combination of treatment technologies is required. Disinfection can be achieved through chlorination, ozonation, ultraviolet light treatment, and electrochemical disinfection (Freese and Noziak 2004, Metcalf and Eddy 2003). The addition of chemical coagulants to the stored water will promote the settling out of the TSS, which may also contain particulate BOD (Field and O'Connor 1997). It is still very difficult to increase the removal of soluble BOD beyond normal biological process. The addition of extracellular enzymes may be able to accomplish just this.

Enzymes are defined as substances that alter a reaction's rate and/or a reaction's activation energy without being present in the reaction products (Uhlir 1998). They lower the activation energy required for breaking certain bonds in organic molecules, making the resulting molecules more biodegradable. The microbes can consume these molecules more easily, decreasing the amount of electrons required for energy production and increasing the amount of electrons available for microbial synthesis. More microbes are produced, which allows for more soluble BOD to be consumed.

The most important aspect of in-situ treatment is time. The treatment must be completed quickly in order to keep the water from becoming septic. Also, the storage areas need to be emptied as quickly as possible in preparation for the next storm event (EPA 1999b). If possible, the treatment process should last only a few hours, with one day being the maximum storage time.

### Objective

This model examines the impact of extracellular enzymes on wastewater stored in an off-line storage tank when the amount of dissolved oxygen (DO) in the water is and is not the limiting factor. The objective of the model is to determine whether enzymes help or hinder BOD oxidation under these conditions. The model simulates what occurs in the tank during a one day period.

The degradation of BOD consumes DO and cannot continue without it. However, simplified microbial models, such as those used for activated sludge systems and chemostats, often use the BOD as the rate-limiting substrate instead of DO. These models work well when DO is abundant, but that is not the case for storage tanks. This

model uses enzymes to convert non-biodegradable Chemical Oxygen Demand (COD) to BOD, but DO limitations may limit the ability of the biomass to grow and consume the additional BOD<sup>1</sup>.

### Process Model

This model focuses on a typical rectangular storage tank that measures 2.5m x 2.5m x 1000m for a period of 24 hours. Wastewater enters the tank from several input pipes spread out along the length of the tank, with a combined inflow rate of 5000 m<sup>3</sup>/d and no outflow (see figure 1a). This distributed input creates an internal mixing within the tank, making the water in the tank essentially homogenous. The volume of water in the tank and the depth of the water in the tank increase linearly to 5,000,000 L and 2m, respectively, after 24 hours. The wastewater influent contains 150 mg/L of BOD, 150 mg/L of COD, 120 mg/L of TSS, 5 mg/L of active biomass, 4 mg/L of DO (when applicable), and 1 mg/L of enzymes (when applicable). It is assumed that there is no inert biomass entering the system or produced in the system. It is also assumed that no soluble microbial products are formed in the system. The tank itself behaves as a semi-batch reactor (SBR). On the bottom face of the tank, there is a biofilm, which behaves as a completely mixed biofilm reactor (CMBR). The water surface is open to the atmosphere, which allows for some DO transfer from the atmosphere to the wastewater (see figure 1b).

*Is this meant to represent a mixed rather than a batch reactor?*

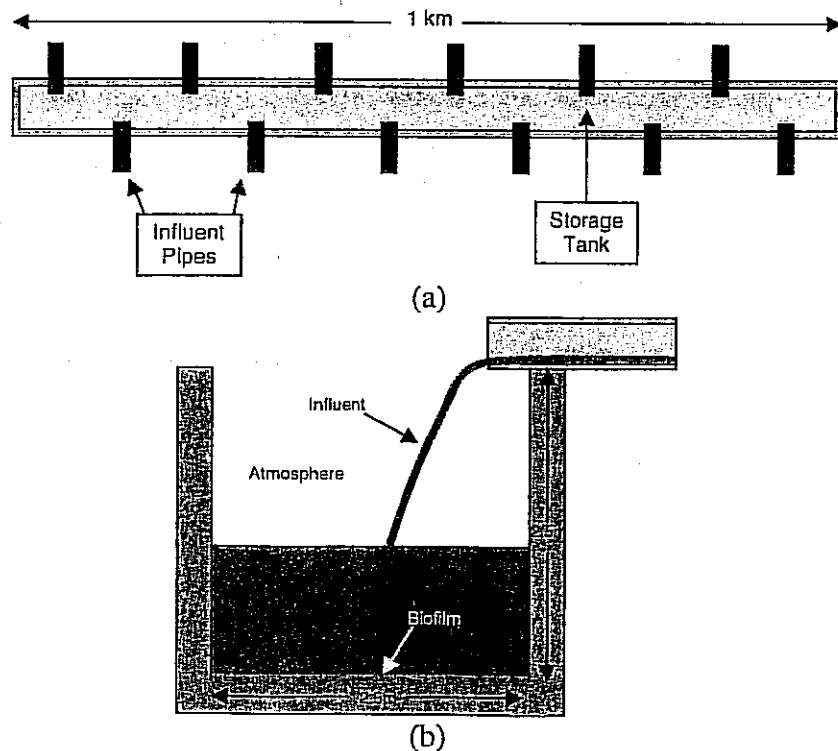


Figure 1. (a) Plan view of the storage tank. (b) Cross sectional view of the storage tank.

<sup>1</sup> Note: The non-biodegradable COD will simply be referred to as COD for the remainder of the paper.  
 Note: It is assumed that the tanks that are not limited by the DO supply will act as if there is a continual excess of DO.  
 Note: A system without enzymes may also be referred to as the "control."

Conceptually, there are three compartments connected by diffusive links in this model (the atmosphere, the SBR, and the CMBR), although only the SBR and CMBR were actually created within the model (see figure 2). The atmosphere's function is to continually saturate the water surface with DO. Instead of creating a link between the SBR and the atmosphere, the DO at the water surface is defined automatically to be at the saturation level by the SBR compartment. The tank is assumed to be held at a constant 13°C, which is a typical temperature within sewerlines in the Midwest. At this temperature, the partial pressure of oxygen in the atmosphere is 0.2095 atm and the Henry's constant is  $3.49 \times 10^4$  atm/mol fraction. This results in a saturation level of 10.58 mg DO/L for the tank. Since the tank is open to the environment, the amount of oxygen in the air will not change and neither will the DO saturation level. It is assumed that the internal mixing in the tank creates a mixing velocity equivalent to 0.5 m/s. The rate of oxygen transfer from the saturated water to the rest of the tank is modeled as:

*seems high for a closed tank*

$$\frac{d(DO_{sat} - DO)}{dt} = 1.016^{T-20} \left( \frac{3.9\sqrt{v}}{d^{1.5}} \right) (DO_{sat} - DO), \text{ where } \rightarrow \text{ refs ?}$$

- DO<sub>sat</sub> = Saturation DO (mg/L)
- DO = DO in the tank (mg/L)
- t = time (d)
- T = temperature (°C)
- v = mixing velocity (m/s)
- d = depth in the tank (m)

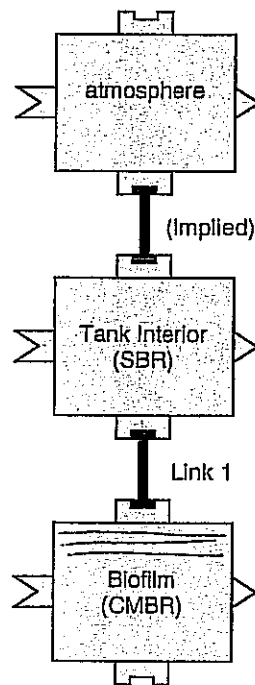


Figure 2. Schematic of the model's compartments and links.

seems low, should be  $q_{max} = 9/d$

seems low for a tower, maybe ok for an exhaust tank

7.7

The biofilm in the model has an initial thickness of 10  $\mu\text{m}$  and an initial biomass density of 20,000  $\text{mg}/\text{m}^3$ . It is contained in a 4.0 cm thick bulk volume with the link connected to the biofilm base. For simplicity's sake, it was assumed that no biomass attached or detached from the biofilm. This not normally the case in the environment, but it is assumed that the attachment would roughly balance the detachment. Attachment and detachment, therefore, should have played only a minimal role in the biofilm development. The biofilm receives BOD, COD, enzymes (when applicable), and DO (when applicable) from the SBR, but does not appear to release any significant species back to the SBR. It is assumed that these species do not undergo any conversion during this transfer and that each exchange coefficient equals 1. Once these species enter the biofilm, it is assumed that all of them have a boundary layer resistance of 0.0001 d/m and a pore diffusivity of  $6.4 \times 10^{-5} \text{ m}^2/\text{d}$ . The conversation factors, exchange coefficients, boundary layer resistances, and pore diffusivities are selected to give a general picture of what is occurring within the system, but further honing is required to achieve a more accurate model.

There are a number of processes that occur within the SBR and the CMBR. It is assumed that BOD oxidation, biomass formation and decay, enzymatic conversion of COD to BOD (when applicable), and the conversion of enzymes to BOD (when applicable) occurred in both compartments. However, it also is assumed that the hydrolysis of TSS to COD and BOD and the transfer of oxygen from the atmosphere to the stored water only occur in the SBR compartment. The model is designed so that 20% of the TSS will hydrolyze to soluble BOD and 20% will also hydrolyze to soluble COD. Two of the processes, BOD oxidation and biomass formation, are dependent on the DO concentration in the water. When oxygen consumption is included, these process rates are multiplied by the DO in the water divided by the difference between the saturation DO and the current DO in the water. This multiplier ensures that these processes will slow down when the DO concentration decreases and stop when the DO becomes zero. Table 1 lists the model processes, their corresponding rates, and the rate multipliers for the various species in the system. Table 2 lists the variables and their descriptions, values, and units.

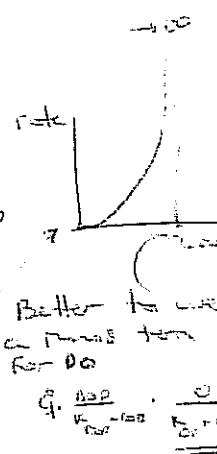


Table 1. The model processes, rates, and rate multipliers.

Process	Description	Rate	X_a	BOD	COD	DO	TSS	Enz.
BOD_ox_without_O2	BOD oxidation without O <sub>2</sub> transfer	$q_{max} * X_a * BOD / (BOD + K)$		-1				
BOD_ox_with_O2	BOD oxidation with O <sub>2</sub> transfer	$q_{max} * X_a * BOD / (BOD + K) * O2_{water} / (DO_{sat} - O2_{water})$		-1		-Y?		
COD_to_BOD	Conversion of COD to BOD with enzymes	$K_{COD\_to\_BOD} * Enz\_conc$		-1	1			
decay_without_O2	Decay rate of biomass without O <sub>2</sub> transfer	$b * X_a$	-1			-1.42		
decay_with_O2	Decay rate of biomass with O <sub>2</sub> transfer	$b * X_a$	-1			-1.42		
enzymes	Conversion of	$b_{enzymes} * Enz\_conc$		1				-1

*Handwritten notes and scribbles at the bottom right of the page.*

to_BOD	enzymes to BOD						
O2_transfer	Transfer of O <sub>2</sub> from atmosphere to water	$K_{O2\_transfer}*(DO_{sat}-O2\_water)$				1	
TSS_to_BOD_COD	hydrolysis of TSS to COD and BOD	$TSS*K_{TSS}$		1 0.2	1 0.2		-2
X_a_without_O2	Production of active biomass without O <sub>2</sub> transfer	$q_{max}*X_a*Y*BOD/(BOD+K)$	1				1
X_a_with_O2	Production of active biomass with O <sub>2</sub> transfer	$q_{max}*X_a*Y*BOD/(BOD+K)*O2\_water/(DO_{sat}-O2\_water)$	1				1

Table 2. The model variables.

Variable	Description	Value	Units
b	Decay rate of biomass	0.15	1/d
BOD	BOD concentration		mg/L
BOD_influent	Influent BOD	150	mg/L
b_enzymes	Decay rate of enzymes	6	1/d
COD	Concentration of COD		mg/L
D	Diffusivity within the biofilm	$6.4 \times 10^{-5}$	m <sup>2</sup> /d
depth	Depth in the reactor		m
DO_sat	Saturation DO for the water	10.58	mg/L
Enz_conc	Enzyme concentration in the reactor		mg/L
input_enzymes	Influent enzymes	10	mg/L
K	Half maximum rate concentration	20	mg/L
K_COD_to_BOD	Rate constant for conversion of COD to BOD	50	mg COD/ mg enz - d
K_O2_transfer	Rate coefficient for oxygen transfer	See DO equation	1/d
K_TSS	TSS hydrolysis conversion factor	0.2	mg BOD or COD/ mg VSS-d
L_f	Biofilm thickness		m
mixing_vel	Velocity of water in the tank due to mixing	0.5	m/s
nonBOD_COD_influent	COD influent	150	mg/L
O2_atmos	Oxygen concentration in the atmosphere	0.2095	atm
O2_water	DO concentration in the water		mg/L
O2_water_in	DO concentration in the influent	4	mg/L
pipe_length	Reactor length	1000	m
pipe_width	Width of the square reactor	2.5	m
Q	Inflow rate	5,000,000	L/d
q_max	Maximum specific rate of substrate Utilization	10	g BOD/ g VSS - d
TSS	TSS concentration		mg/L

Do the units match

TSS <sub>in</sub>	Influent TSS concentration	120	mg/L
V	Reactor volume		L
X <sub>a</sub>	Active biomass		mg/L
X <sub>a</sub> <sub>in</sub>	Influent active biomass		mg/L
X <sub>f</sub>	Biofilm cell density	40,000	mg/m <sup>3</sup>
Y	True yield	0.5	g VSS/ g BOD

Initial conditions?

$D = 0.12 = 1.5 \text{ day}^{-1}$   
 $COD_{in} = 150 \text{ mg/L}$

## Results

The model is run under four sets of conditions:

- Without enzyme addition and DO not being the limiting factor.
- With enzyme addition and DO not being the limiting factor.
- Without enzyme addition and DO being the limiting factor.
- With enzyme addition and DO being the limiting factor.

For the SBR component of the model, the parameters of interest are BOD, COD, TSS, and active biomass concentration, particularly how they change over time. Results for each set of conditions are shown in figure 3.

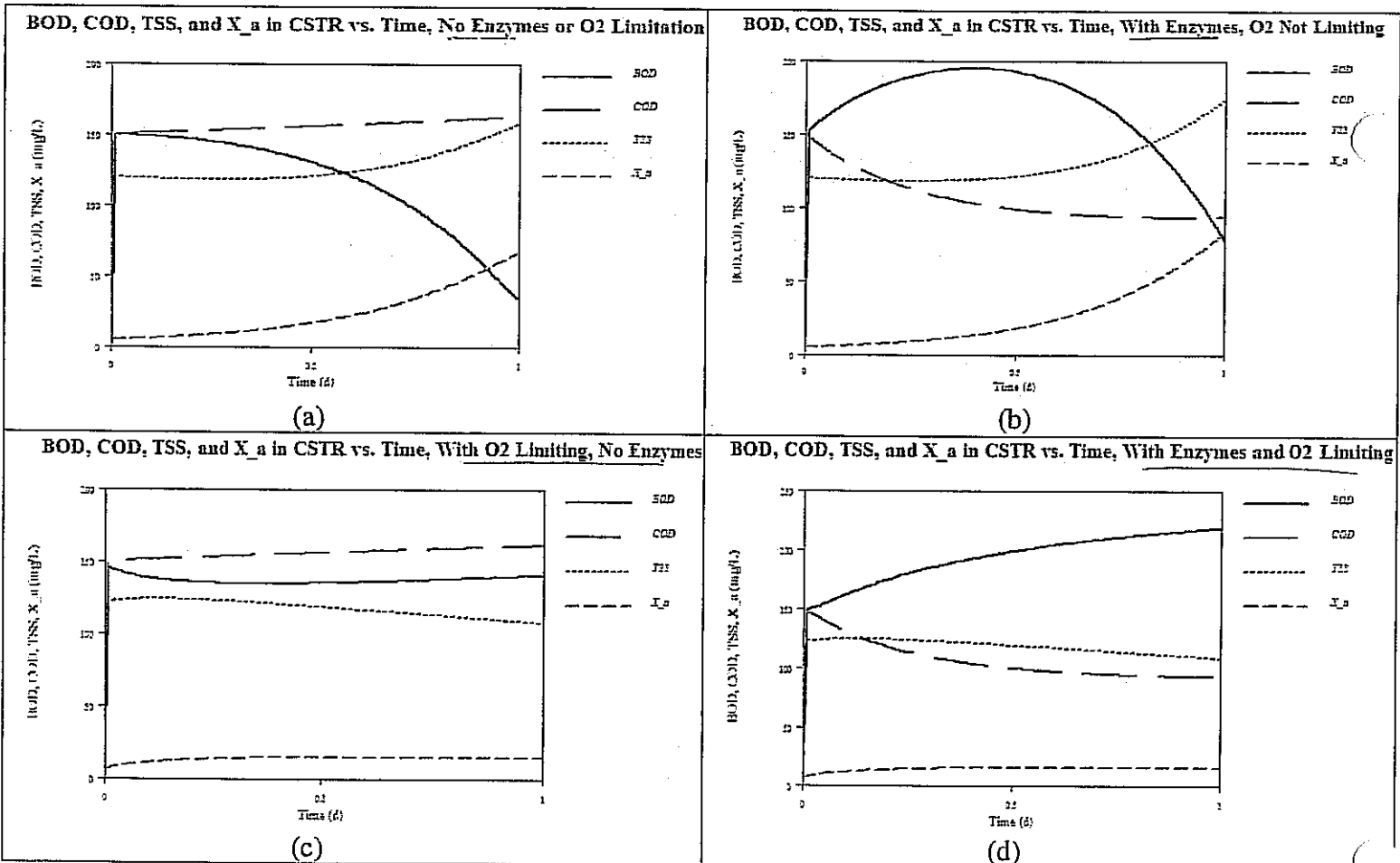


Figure 3. The changes in BOD, COD, TSS, and active biomass ( $X_a$ ) over time for the SBR when (a) no enzymes are present and DO is not the limiting factor, (b) enzymes are present and DO is not the limiting factor, (c) no enzymes are present and DO is the limiting factor, and (d) enzymes are present and DO is the limiting factor.

It appears that the addition of enzymes to the wastewater actually increases the amount of BOD in the system both when the DO level is limiting and when it is not. This contradicts the belief that enzymes will lower the final BOD. However, when oxygen is not the limiting factor, the enzymes increase the final active biomass concentration from 67.3 mg/L in the control to 84.1 mg/L. This indicates that the rate of BOD consumption at the end of the simulation is greater for the system with enzymes than for the control. If the model simulated more than 24 hours, the BOD concentration in the system with enzymes may fall very quickly below that of the control. This increase in biomass also increases the TSS to above that in the control, meaning that more coagulant may be required in order to control the TSS concentration. The enzymes are very effective in reducing the COD, should that be required.

When DO is the limiting factor, the system completely changes. The final concentration of active biomass in the system only slightly increases when enzymes are added (from 14.4 mg/L to 14.6 mg/L). This means that the enzymes only slightly increase the BOD oxidation ability of the system; however, the enzymes continue to transform the COD to BOD. The result is that the BOD concentration in the enzyme enhanced system greatly increases from 150 mg/L to 218.1 mg/L, while the BOD concentration in the system without enzymes actually decreases from 150 mg/L to 140.5 mg/L. Once again, the enzymes are very efficient in reducing COD.

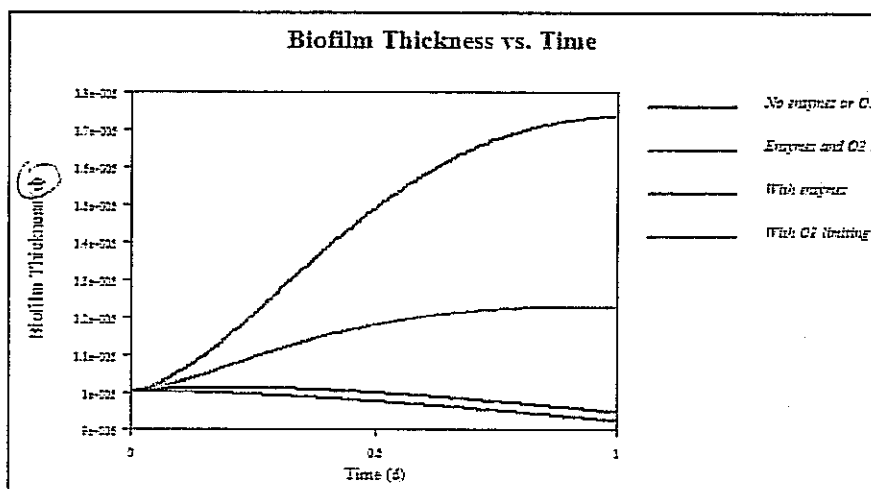


Figure 3. Biofilm thickness vs. time for each set of conditions.

For the CMBR, the parameters of interest are the BOD concentration in the bulk volume, the BOD concentration in the biofilm matrix, and the biofilm thickness. In all condition sets, the BOD concentrations in the bulk volume are very similar to those in the biofilm matrix, which is probably due to the very low boundary layer resistance between the two. Figure 3 shows how each set of conditions impacts the biofilm thickness, and figure 4 shows how the BOD concentrations change under each condition set.

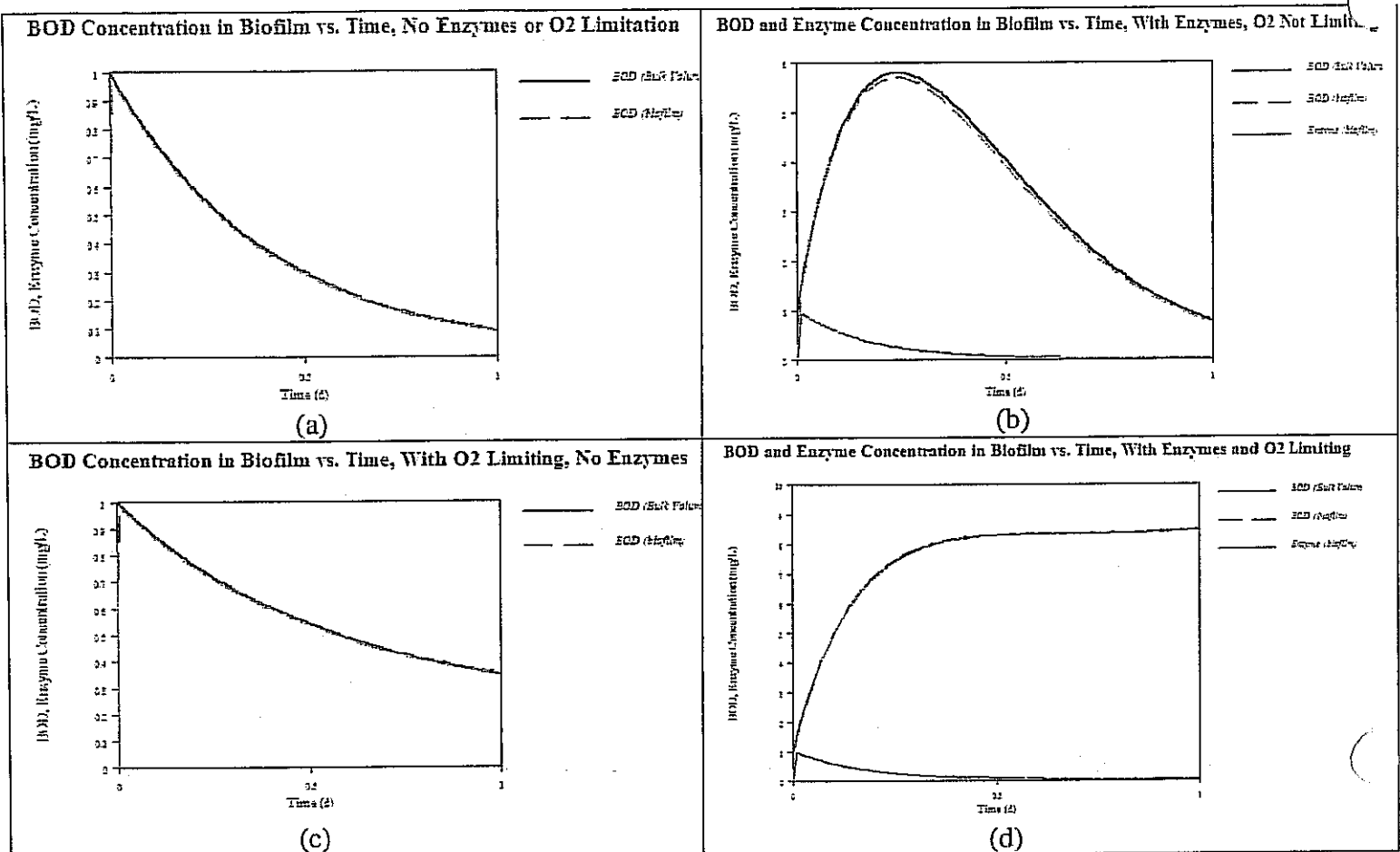


Figure 3. The changes in BOD in the bulk volume, BOD in the biofilm matrix, and enzyme concentration in the biofilm matrix over time for the CMBR when (a) no enzymes are present and DO is not the limiting factor, (b) enzymes are present and DO is not the limiting factor, (c) no enzymes are present and DO is the limiting factor, and (d) enzymes are present and DO is the limiting factor.

When the DO is not the limiting factor, the BOD concentration in the control steadily decreases from 1.0 mg/L to 0.09 mg/L. When enzymes are present in the mixture, the BOD concentration increases to nearly 6 mg/L, but then results in a net decrease. However, the biofilm thickness for the system with the enzymes is nearly twice that of the control ( $1.734 \times 10^{-5}$  m compared with  $9.43 \times 10^{-6}$  m) after 24 hours. This means that the enzyme-enhanced biofilm possesses a higher potential for further BOD oxidation in the future.

Even when the DO is the limiting factor, the enzyme treated system is able to form a thicker biofilm than the control ( $1.222 \times 10^{-5}$  m compared with  $9.2 \times 10^{-6}$  m). Despite this fact, the BOD concentration in the enzyme system continually increased and leveled off at 8.45 mg/L, while the control saw a continual decrease to 0.35 mg/L.

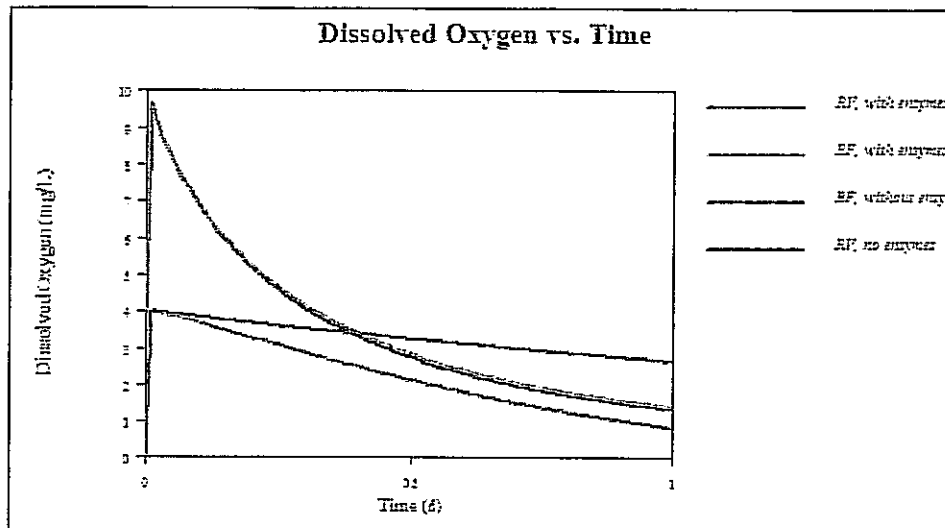


Figure 5. The DO concentrations vs. time for the reactor volume (RV) and the biofilm matrix (BF) for systems with and without enzymes added.

The DO concentration in the reactor volume appears to be independent of the presence of enzymes, even though the BOD concentrations in the biofilm-enhanced system are much greater. This indicates that the BOD consumption rate is the same for both systems and that this rate is probably at the maximum consumption rate for this particular system. The DO concentration in the control biofilm after 24 hours is 3.3 times that of the biofilm with enzymes (2.61 mg/L compared to 0.78 mg/L). The DO concentration in the control biofilm is still relatively high, indicating that it still has the potential for further BOD consumption.

### Summary and Conclusion

An AQUASIM model was created to simulate the impact of the addition of extracellular enzymes on the degradation of wastewater in an off-line storage tank during one day. The system was simulated under oxygen rich and oxygen limited conditions. In both conditions, the addition of enzymes actually increased the final BOD and TSS concentrations in the reactor volume and biofilm matrix, while reducing the COD concentrations. The enzymes also increased the active biomass concentration and biofilm thickness in all cases. This indicates that the enzyme enhanced systems may have a greater BOD consumption potential should the reactions last for more than 24 hours. It is important to remember that these results hold only for this particular model, which is based on assumed values. If the maximum specific rate of substrate utilization or the true yield is increased or the half maximum rate concentration is decreased, then this model will behave completely differently. This model does demonstrate that the addition of enzymes must be done in a very careful and controlled manner if they are to aid treatment instead of hindering it. ✓

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