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SHORT CONTENTS

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EFFECT OF FINE PARTICLE AND NUTRIENT ADDITION ON THE ACTIVATED SLUDGE PROCESS

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ABSTRACT

Twelve laboratory scale activated sludge reactors were operated for a 140-day period treating unbleached kraft pulp mill effluents. Data were taken on reactor feed and effluent BOD, COD, TOC, SS, and VSS. Measurements were also made on reactor activated sludge settling characteristics. The results describe the effect of fine particles (calcium carbonate and kaolin), inorganic nutrient addition (N and P), hydraulic retention time, food-to-microorganism (F/M) ratio, sludge retention time (SRT), and reactor pH on reactor performance. The best organic (BOD, COD, and TOC) removals were obtained for reactors operated at a very low F/M ratio or very high SRT. Also, low F/M ratio reactors had sludge yields significantly less than reactors operated at conventional F/M ratios. CaCO$_3$ proved to be a very beneficial addendum to an activated sludge reactor. A CaCO$_3$ sludge typically had superior coagulating properties compared with kaolin and no-particle sludges. Also, CaCO$_3$ proved to be a very good pH buffer, obviating the pH fluctuations observed in kaolin and no-particle reactors.

INTRODUCTION

The activated sludge process is widely used to provide secondary treatment for both municipal and industrial wastewater effluents. Though innumerable modifications of the process exist, basically the process involves contacting of a wastewater influent with a settleable mass of microorganisms (activated sludge) in an aeration basin. The microorganisms metabolize the organic and inorganic materials contained in the wastewater and convert them to carbon dioxide, water, cell energy, and biomass. Air or pure oxygen is supplied to the aeration basin to provide the oxygen necessary for microbial catabolism and to mix the contents of the aeration basin. The activated sludge-wastewater mixture (mixed liquor) then flows to a sedimentation basin where the activated sludge is separated from treated effluent. Normally, most of the separated sludge is recycled back to the aeration basin with a small portion wasted in order to maintain the desired biological solids concentration within the aeration basin.

The goals of activated sludge process treatment should be as follows: (1) achieve required removals of conventional pollutants (BOD, SS) and (2) minimize the production of waste biological sludge. All would recognize the importance of achieving required reductions of conventional pollutants with

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the activated sludge process in order to comply with NPDES permits. However, few operators consider the possibility of reducing waste biological sludge production via process operational modifications. Reducing the production of waste biological sludge would lower the cost of waste sludge handling, treatment, and disposal and lessen the environmental impact of sludge disposal. However, most activated sludge processes are operated such that sludge production is close to the maximum possible. This is because operators feel constrained to operate the activated sludge process at a food-to-microorganism (F/M) ratio of 0.2-0.5 lb BOD/lb MLSS-day or a sludge retention time (SRT) of 5-15 days. These conditions normally (but not necessarily) yield a sludge that settles and compacts well in clarification. However, these conditions also ensure that copious amounts of biological sludge will be produced per pound of BOD removed.

Our experience in the treatment of unbleached kraft pulp mill wastewaters in bench scale reactors indicates that operation of an activated sludge process at a higher F/M ratio or lower SRT than stated above is often detrimental. These conditions often result in the formation of a bulking or filamentous sludge and the production of a low-quality effluent. On the other hand, our experience in operating activated sludge reactors at very low F/M ratios or very high sludge retention times has been very positive. A low process F/M ratio or high SRT maximizes soluble organic removals and minimizes biological sludge production. Also, a low F/M ratio or high SRT process sludge often has excellent settling characteristics. It therefore seems that an activated sludge process should be operated at the lowest possible F/M ratio or highest possible SRT in order to optimize process performance and minimize sludge disposal costs.

Unfortunately, achieving a very low F/M ratio or very high SRT in a conventional activated sludge process presents some practical problems. For example, a low process F/M ratio means a high concentration of activated sludge must be maintained in the aeration basin. This in turn means a high solids loading rate is exerted on the secondary clarifier or sedimentation basin. The sludge must have unusually good settling characteristics. Its settling velocity must be greater than the clarifier upflow velocity in order to be successfully separated from the treated effluent. Also, it must thicken and compact well in sedimentation to avoid excessive recycle pumping rates. Activated sludge settling velocity, however, diminishes dramatically as concentration increases, making it difficult to clarify a highly concentrated sludge. Also, unless a low F/M sludge thickens substantially better than a normal F/M sludge, it is likely that sludge recycle pumping rates must be increased to maintain a high aeration basin biological solids level. Unfortunately, as sludge recycle rates are increased, the concentration of biological sludge in the underflow diminishes. This further aggravates the problem of maintaining a high aeration basin biological solids concentration. Fortunately, there are several approaches to solving these practical problems that will be discussed in the following sections.

Effect of fine particle addition on the activated sludge process

One method of obtaining an activated sludge with superior settling characteristics is to add fine particle materials of high specific gravity to the sludge. Results presented in a previous paper (1) show that the addition of inexpensive fine particle materials of $CaCO_3$ and kaolin to an activated sludge can yield substantial improvements in its zone settling velocity and 30-minute compaction density. Table 1 gives the physical properties and cost of the kaolin and $CaCO_3$ particles used in our experimental research program as stated by the manufacturers. It is critical that only particles within a very narrow size range be added to the aeration basin. Particles that are too coarse will not be successfully suspended and will eventually sediment on the bottom of the aeration basin. Extremely fine particles that are not successfully bound up with the biological sludge will exit the process during clarification.

Table 1 Fine particle materials used in high rate fixed film activated sludge process experimental reactors

Calcium Carbonate ($CaCO_3$)

Average diameter: 10 μ Specific gravity: 2.71
90% finer than: 30 μ Cost: $17.50/ton
90% coarser than: 2.2 μ

Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

Average diameter: 21 μ Specific gravity: 2.63
86.1% finer than: 35 μ Cost: $100-150/ton
84.5% coarser than: 15 μ

The following equation describes the settling velocity of a spherical particle according to Stoke's Law:

$$V_p = \frac{g}{18v} (S_p - 1) d_p^2 \qquad (1)$$

where

V_p – particle settling velocity (cm/sec)
g – gravitational constant (981 cm/sec^2)
v – water kinematic viscosity (cm^2/sec)
S_p – particle specific gravity
d_p – particle diameter (cm)

Table 2 gives V_p values based on this equation that shows the variation of particle settling velocity with size when particle specific gravity is 2.70. Most secondary clarifiers have upflow velocities in the range of 85-170 cm/hour (500-1000 gpd/ft^2). Therefore, particles with diameters greater than 25 μ should be successfully captured if not bound up with the biological sludge.

Our experience with the kaolin product (see Table 1) indicates that it is fairly easy to suspend. Nevertheless, we would not recommend the addition of a particle material that is coarser than this product. Particle-dosed sludges are very dense, and some sediment accumulation on the bottom of an aeration basin is to be expected. Addition of very coarse particles at high particle dosages aggravates the sediment accumulation problem.

Table 2 Stoke's Law settling velocities of fine particles with a 2.70 specific gravity

Diameter (μ)	Settling Velocity (cm/hour)	Settling Velocity (gal/day-ft^2)
1	0.33	2
5	8.3	49
10	33.2	196
15	74.8	440
20	132.9	783
25	207.7	1223
30	299.0	1762

Fine particles whose settling velocities are less than the clarifier upflow velocity can be safely added to the aeration basin if intimately mixed with the activated sludge and if the coagulating properties of the sludge are good. Even so, extremely fine particles are difficult to coagulate, and we do not recommend the addition of fine particles less than 5 μ. In this regard, the $CaCO_3$ product we are using does contain a substantial percentage of particles with sizes less than 5 μ. We have experienced losses of these extremely fine particles in our experimental reactors on many occasions after initial dosing. However, losses depend on the ability of the sludge to coagulate the extremely fine particles. Addition of a suitable coagulation agent to an activated sludge (e.g., alum, bentonite, or organic polymers) may substantially reduce losses of extremely fine particles after initially dosing an aeration basin.

Fine particles of high specific gravity improve sludge settling characteristics because they increase the effective specific gravity of the biomass flocs. The specific gravity of dry biomass solids is in the range of 1.25-1.30 (2,3). Biomass, however, contains considerable amounts of intracellular and extracellular bound water that lowers the overall specific gravity of the floc. Bound water will be no less than 80-85% of the floc volume (2) and can constitute a much higher percentage of the floc volume. Floc specific gravity would be 1.06 when the floc contains 80% water by volume and dry biomass solids specific gravity is 1.3. If it contains 95% water by volume, its specific gravity would be 1.015. Since floc settling velocity is proportional to ($S_p - 1$), it is apparent that floc sizes must be large in order to settle at a reasonable rate. Incorporating fine particle materials of high specific gravity into the floc should greatly increase its settling velocity. As an example, suppose 10% of the floc volume is occupied by fine particles. Assume the specific gravities of the particles and biomass dry solids are 2.7 and 1.3, respectively, and the biomass normally contains 95% water by volume. In this case, the particle-biomass floc will settle 12.2 times faster than a biomass floc of equal diameter. The ratio of weights of particle to _dry_ biomass solids (P/B ratio) would be 4.6.

Though the addition of fine particle materials to an activated sludge can greatly improve its settling characteristics, it is also critical that an activated sludge flocculate well. Equation (1)

shows that floc settling velocity is proportional to the square of floc diameter. Therefore, addition of coagulating chemicals to an activated sludge process may be of substantial benefit. The addition of both fine particles and coagulating chemicals to an activated sludge should yield a biological sludge of superior settling characteristics.

It is, of course, possible for a biological sludge to normally have excellent coagulating properties and be of high specific gravity. In this case, fine particle and coagulating chemical addition will be of little benefit. Fine particles and coagulating chemicals are, however, substances which can be used to improve activated sludge settling characteristics as needed.

Effect of fine particle addition on waste sludge production

An apparent problem with fine particle addition to an activated sludge process is that it increases the mass of sludge solids requiring ultimate disposal. The mass of sludge solids requiring disposal would definitely increase if biomass production were the same both before and after fine particle addition. For example, suppose an operator operates his aeration basin to maintain a particle-to-biomass weight ratio of 2 and wasted sludge such that 0.5 lb biological SS were produced per pound of BOD removed. In this case, 1 lb of fine particle solids would also be wasted per pound of BOD removed, resulting in an overall yield of 1.5 lb solids produced/lb BOD removed. If the operator's sludge yield were normally 0.5 lb biological SS/lb BOD removed without particle addition, he would have to dispose of 3 times the mass of sludge solids when dosing with fine particles. Though this seems like a highly undesirable situation, the total sludge volume going to thickening and dewatering unit operations will nevertheless be less for the fine particle sludge. Though its sludge solids mass is considerably greater, the fine particle sludge should thicken better during secondary clarification than a no particle sludge. Indeed, the primary reason for adding fine particles to the sludge is to get a sludge with a higher biological solids concentration in the underflow during secondary clarification.

Therefore, the total sludge mass (including water) of sludge entering thickening and dewatering unit operations will be less for a fine particle sludge. The mass and volume of activated sludge requiring ultimate disposal depends on its dewatering capabilities. Activated sludge normally can be dewatered on a vacuum filter to 20% solids at a rate of 2.5-3.5 lb/ft^2-hour (3). This means for every pound of biological sludge solids to be disposed of, 4 lb of water must also be disposed of. A fine-particle sludge that can also be dewatered to 20% biological solids content will contain 1 lb biological sludge, 2 lb fine particles, and 4 lb water if the P/B ratio is 2. Therefore, the total mass of solids requiring ultimate disposal would be only 40% higher for the fine-particle sludge in this instance. The volume of the fine particle dewatered sludge would be only 16% greater than the no particle dewatered sludge in this instance if particle specific gravity is 2.7.

The mass of fine particle sludge requiring ultimate disposal can actually be less in this example if it dewaters better than a no particle sludge. A fine particle sludge that can be dewatered to a biological solids concentration of 25%, will have less total sludge mass to be disposed of than a no particle sludge that can be dewatered to a biological solids concentration of only 15%, even though the fine particle sludge contains 2 lb of fine particles per pound of biological solids.

The point of this discussion is that fine particle addition to an activated sludge process will not necessarily increase the volume and mass of sludge requiring ultimate disposal even if the rate of biological solids production from an activated sludge process is the same both before and after fine particle addition. Much depends on the dewatering capabilities of a fine particle dosed activated sludge compared with a no particle dosed sludge. Unfortunately, we have not performed experiments to see if there are differences but hope to investigate this point.

The effect of sludge retention time on biological solids production

An activated sludge process can be operated to reduce the rate of waste sludge production. Essentially this involves increasing the biological solids residence time of the process such that a more complete oxidation of the biodegradable organic materials entering the process occurs. It is, in fact, possible to operate an activated sludge process without wasting any biological sludge. Gaudy and co-workers (4,5) demonstrated this fact in operating a bench scale extended aeration activated sludge reactor for several years on a glucose feed. The reactor effluent was routinely centrifuged, with all biological solids returned to the reactor. No biological sludge was therefore wasted except small samples taken for measurement purposes. The reactor was very successful in removing the organic nutrient with the biological solids content of the reactor rising or declining slowly from one pseudo-steady state concentration level to another.

In our studies, we have noticed a very definite relationship between activated sludge reactor sludge retention time (SRT) and the amount of biological solids produced (g biological solids produced/g organic nutrient consumed). Material balances of organic nutrient and sludge for an activated sludge reactor yields the following relationship at steady state:

$$1/SRT = Yo \ (F/M)o \qquad (2)$$

where

SRT - biological sludge retention time (g biological sludge in process/g biological sludge leaving process/ day)

Yo - overall sludge yield (g biological sludge leaving process/g organic nutrient consumed)

(F/M)o - overall food-to-microorganism ratio (g organic nutrient consumed/day - g biological sludge in process)

A mathematical model, described by Pirt (6), gives the relationship between Yo and SRT

$$1/Yo = a \ SRT + b \qquad (3)$$

where a and b are constants. Combining Eq. (2) and (3) yields the following familiar relationship

$$1/SRT = Ym \ (F/M)o - k_D \qquad (4)$$

where

Ym - maximum overall growth yield (= 1/b)
k_D - endogeneous decay coefficient (= a/b)

Later plots of 1/Yo vs. SRT and 1/SRT vs. (F/M)o will be presented for some of the data generated in our studies on activated sludge treatment of unbleached kraft mill effluents. Values of the constants a, b, Ym, and k_D will be given at that time.

Equation (3) states that to obtain a zero sludge wastage process with no biological solids appearing in the effluent, the SRT must be infinite. Equation (4), however, states that it is possible to obtain an infinite SRT at a finite food-to-microorganism ratio, (F/M)o. In fact, (F/M)o = k_D/Ym in this instance. A real process, however, will omit biological solids in the effluent. Yo will be finite for this reason. The SRT of a zero sludge wastage process will be

$$SRT = \frac{1}{aYo} - \frac{b}{a} \qquad (5)$$

where Yo is the overall sludge yield based on effluent losses. In most instances, the SRT must be extremely high (months to years) to operate a process without sludge wastage and have acceptably low effluent biological suspended solids losses.

The potential benefit of fine particle addition to an activated sludge process is that it may help to achieve the low (F/M)o ratios in a conventional process necessary for a zero or near-zero sludge wastage process. Many of our results show that very low (F/M)o ratios can be achieved even without fine particle addition. The ability to achieve a very low process (F/M)o ratio depends strongly on the process organic loading rate (g organic loaded/ L reactor volume-day). For example, doubling the loading rate of the process, means that the concentration of sludge in the aeration basin must also double to maintain the same (F/M)o, Yo, and SRT. There is a limit on how highly concentrated the aeration basin sludge can become. We have successfully maintained, however, up to 20,000 mg/L of biological VSS in our reactors - approximately 10 times the concentration normally maintained in aeration basins.

If there is not a concern in limiting biological sludge production in an activated sludge process, maintaining a high aeration basin biological solids concentration has another substantial benefit. At a given (F/M)o ratio, doubling the biological VSS of the reactor doubles the allowable organic loading rate. A reactor that contains 20,000 mg/L of biological VSS can process 10 times more wastewater feed than a reactor of the same size with only 2000 mg/L of biological VSS. If fine particle addition can increase the allowable concentration of aeration basin biological solids, it is a low cost method of increasing the capacity of the process.

Oxygen transfer in a total oxidation activated sludge process

A concern in converting a conventional activated sludge process to a total oxidation process is that the aeration capacity of the process must also be increased. It is true that a total oxidation process will consume more oxygen than a conventional process since a higher proportion of the organic materials that enter the process are oxidized to carbon dioxide and water. Up to 50% more oxygen might need to be transferred in a total oxidation process compared with a conventional process.

While it is true that more oxygen needs to be transferred to a total oxidation process mixed liquor, it is not necessarily true that aeration capacity needs to be increased in converting a conventional activated sludge process to a total oxidation process. This is because aeration equipment typically transfers only a fraction of the oxygen applied to the mixed liquor. This fraction varies depending on the type and efficiency of the aeration equipment employed but is usually in the range of 0.05-0.4 lb O_2 transferred/lb O_2 applied. A total oxidation process will have a higher activated sludge respiration rate and concentration than a conventional process. These factors can influence the oxygen mass transfer rate. Albertson and Di Gregorio (7) provide evidence that the oxygen mass transfer rate increases dramatically with activated sludge respiration rate in field scale aeration basins. Our own observations indicate that highly concentrated sludges affect bubble hold up time and size. Research needs to be performed, however, to explicitly define the effects of sludge concentration and respiration rate on the oxygen mass transfer rate.

Effects of nutrient addition on the activated sludge process

Many pulp and paper mill wastewaters are deficient in either available nitrogen or phosphorus or both. Therefore, inorganic chemicals containing N and P are often added to the wastewater feed to an activated sludge process. Typically, sufficient N and P is added to yield 5 'b N and 1 lb P for every 100 lb BOD removed. Work by C. N. Sawyer and co-workers (8-10) on the treatment of rag-rope, cotton-kiering, and brewery industrial wastewaters showed that the maximum average nitrogen requirement was 5-6 lb and the maximum average phosphorus requirement was 0.8-1.0 lb per 100 BOD removed. The critical average nitrogen requirement was 3-4 lb and the critical average P requirement was 0.5-0.7 lb per 100 lb BOD removed. Adding N and P at or above the critical requirement was shown to achieve satisfactory stabilization of the industrial wastewaters without a decrease in the rate of BOD removal. Adding N and P above the maximum requirement caused N and P leakage to the effluent. It would appear that less N and P can be added to a conventional activated sludge process than the normally recommended dosages of 5 lb N and 1 lb N per 100 lb BOD removed.

The actual N and P added should be based on the N and P content of the activated sludge leaving the process. Enough N and P should be added to make up for this loss. A high SRT process would require considerably less N and P addition than a normal SRT process since considerably less biomass is being produced in a high SRT process.

An activated sludge process treating a nitrogen and phosphorus limited waste could be operated as follows. Depending on whether N or P is the more critically deficient nutrient, N or P would be added to achieve a N to P ratio equal to that of the sludge. This ratio would normally be 5:1. The process would then be run at a sludge wastage rate such that the pounds of N and P leaving in the biological sludge is equal to that entering the process. This practice would ensure that no N and P is being leaked into the effluent and the mass of biological sludge produced is minimized.

Internal clarification region in an activated-sludge aeration basin

In an activated sludge process, little or no separation of the activated sludge from the treated effluent occurs within the aeration basin. This is the primary function of the secondary clarifier. Normally, almost all of the separated sludge is returned to the aeration basin with only a small fraction wasted. To reduce the amount of sludge pumped back to the aeration basin, it would appear beneficial to achieve some degree of sludge separation within the aeration basin itself. Ideally, the secondary clarifier would be used only to further clarify a wastewater effluent: to capture suspended solids that inadvertently escape the aeration basin. A secondary clarifier whose primary function was to clarify a biological treated effluent could be designed with a higher upflow velocity than a clarifier whose primary function was to thicken a separated activated sludge. The thickening function generally governs the design of an activated sludge process clarifier.

Both reaction of the activated sludge with wastewater and separation of the treated sludge with the effluent can be achieved in a single vessel. We routinely employ activated sludge reactors that perform both the reaction and clarification functions in our experimental research studies. Figure 1 illustrates the Davis-Swisher activated sludge reactor (11) that has been used in several previous studies by the senior author (1, 12,13,14). This apparatus consists of aeration (~ 290 mL) and settling (~ 40 mL) sections interconnected by 10-mm tubing. Air is introduced near the bottom of the aeration section and serves to both aerate the microbial suspension and pump settled sludge from the settling section back into the aeration zone. Though the apparatus is very easy to operate and maintain, problems arise whenever a very dense or highly filamentous activated sludge is contained in the apparatus. A very dense sludge is difficult to circulate and a filamentous sludge tends to plug the small diameter reactor tubing. Figure 2 illustrates an apparatus designed by the authors that eliminates these difficulties. The apparatus also consists of aeration (~ 500 mL) and settling (~ 50 mL) sections like the Davis-Swisher reactor. The reactor has a 5.08-cm (2

inch) ID reaction tube and a 2.54-cm (1 inch) ID clarification tube. The liquid height in the apparatus is 25.4 cm (10 inches). Baffles were inserted in the reaction section, as shown, to help direct sparged air bubbles away from the clarification section. Some air bubbles would, however, inevitably ascend into the clarification section. A baffle was inserted in the clarification section, dividing it into an upper and lower half. The air bubbles ascend into the upper half, maintaining quiescent conditions in the lower half. Results using this apparatus in the treatment of unbleached kraft pulp mill effluent will be presented later.
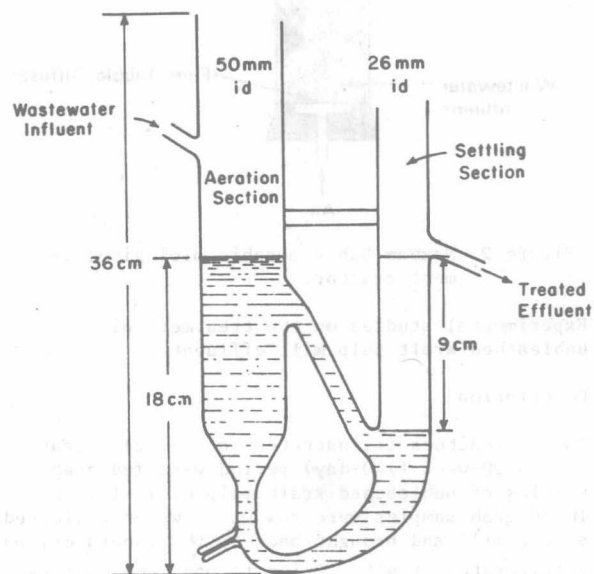

Figure 1 Davis-Swisher aerobic biological treatment reactor.

An aeration basin can be baffled in an arrangement similar to that shown in the apparatus in Fig. 2 to create a clarification section within the basin. The concentration of activated sludge that can be maintained in the aeration basin would be a strong function of the activated sludge settling characteristics and clarification section upflow velocity. As activated sludge concentration increases, its settling velocity decreases. As long as the activated sludge settling velocity is less than the clarification section upflow velocity, it will remain in the aeration basin. When the sludge settling velocity is less than the clarification section upflow velocity, the sludge blanket will rise in the clarification section and solids will be discharged in the aeration basin effluent. Effluent solids will be discharged until the aeration basin activated sludge concentration diminishes to the level where the sludge settling velocity is less than the clarification upflow velocity. Solids emitted in the effluent are captured by the secondary clarifier. These captured solids constitute the waste sludge, though this sludge could be recycled to the aeration basin in situations where the aeration basin is discharging large amounts of solids due to hydraulic surges.
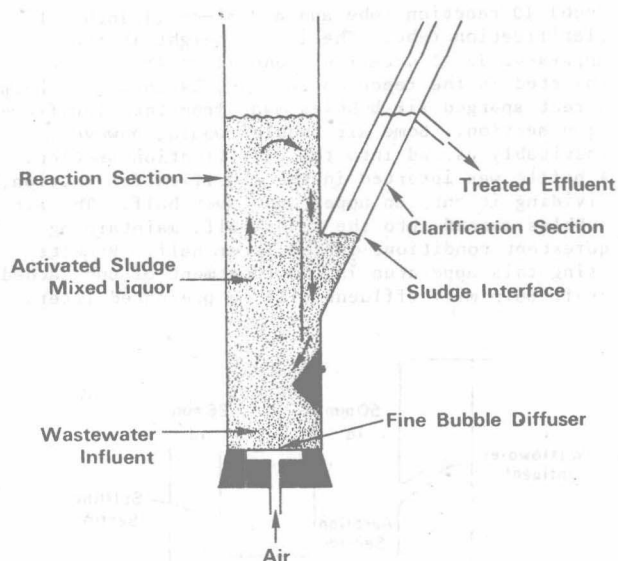
Figure 2 Maxham-Dubey aerobic biological treat-
ment reactor.

**Experimental studies on the treatment of
unbleached kraft pulp mill effluents**

Description

Twelve reactors (illustrated in Fig. 2) operated
over a 20-week (140-day) period were fed grab
samples of unbleached kraft pulp mill effluent.
These grab samples were raw waste-water collected
at the mill and brought back to the laboratory and
refrigerated at 4°C. Prior to use, the samples
were allowed to sediment in 50-gallon containers.
Feeds were prepared daily by decanting a portion of
the wastewater above the sediment layer and then
adding N and P nutrient solutions and dilution tap
water. Table 3 presents measured values for BOD,
COD, TOC, color, TSS, TVSS, NH_3-N, TKN, and total P
for the wastewater samples as they entered the
biological treatment reactors. Measured values for
BOD, COD, and TOC were made on samples filtered
through glass fiber filters and therefore represent
filterable values. Since the SS and VSS content of
the wastewater feeds was low, filterable BOD, COD,
and TOC values would be only slightly less than
total values.

If a feed had N and P nutrients added, the dos-
age was 267 mg NH_4Cl/L (70 mg NH_4-N/L) and 84.3 mg
K_2HPO_4/L (15 mg PO_4-P/L). Nutrient addition was
therefore well in excess of actual requirements.
All feeds were alkaline and were adjusted with HCl
to a pH below 10.0 if necessary. Sample 16 had an
unusually high pH, and a large amount of HCl was re-
quired to neutralize it. It is suspected that this
effluent emanated from the recausticizing area of
the mill. Samples 15 and 16 had unusually high COD/
TOC ratios, indicating that a substantial portion of
the COD was due to reduced inorganic species.

During the 20-week period over which the reac-
tors were operated, Sample 13 was fed during the
first 5 weeks; Sample 14 was fed during weeks 6-10;
Sample 15 was fed during weeks 11-14; and Sample 16

was fed during weeks 15-20. Reactors 1-3 were
operated at a hydraulic residence time (HRT) of
approximately 32 hours; reactors 4-6 were operated
at a HRT of approximately 16 hours, and reactors
7-9 were operated at a HRT of approximately 7 hours
during the entire 20-week period. Reactors 10-12
were operated at a HRT of approximately 3 hours
during the first 10 weeks of the study. During the
last 10 weeks of the study, reactors 10, 11, and 12
were operated at HRT's of approximately 32, 16, and
7 hours, respectively.

Table 3 Unbleached kraft pulp mill effluent feeds
to aerobic biological treatment reactors
(all units in mg/L unless noted; standard
deviations given in parentheses)

	Sample Number			
	13	14	15	16
sBOD$_5$	341(11)	409(12)	711(52)	766(73)
sCOD	1089(40)	960(23)	1363(30)	1336(66)
sTOC	384(7)	296(4)	252(7)	218(14)
Color	--	771(17)	490(99)	73(6)
TSS	27(15)	26(6)	31(9)	25(29)
TVSS	14(8)	13(4)	20(6)	13(17)
NH_3-N[a]	--	--	9.5	56.9
TKN[a]	--	--	15.2	58.7
Total P[a]	--	--	0.4	0.04
Parts tap water/ parts feed	3/1	1/1	None	None
BOD/COD ratio	0.31	0.43	0.52	0.57
COD/TOC ratio	2.84	3.24	5.41	6.13

[a]Concentration in sample before N and P nutrients
added.

During the first 10 weeks of the study period,
all reactors had N and P nutrients added to the
wastewater feed. During the last 10 weeks of the
study period, only reactors 10, 11, and 12 had N
and P nutrients added to the wastewater feed.
Table 3 shows that samples 15 and 16 were highly
deficient in P. Sample 15 was slightly deficient
in N; Sample 16 contained excess N.

Reactors 1, 4, and 7 were dosed with fine par-
ticles of kaolin (see Table 1 for physical proper-
ties) to maintain a reactor total suspended solids
concentration in the range of 100-150 g/L. Reactors
3, 6, and 9 were likewise dosed with fine particles
of $CaCO_3$. Reactors 10 and 12 were dosed with fine
particles of kaolin and $CaCO_3$, respectively, during
the first 10 weeks of the study period. For the
last 10 weeks of the study period, the particle-
dosed sludges were removed from reactors 10 and 12
with no particle sludges added. Reactors 2, 5, 8,
and 11 did not have particles added. All reactors
upon start-up were seeded with sludges that were
well acclimatized to unbleached kraft mill
effluents.

Reactors 1-12 were operated with no intentional
sludge wastage except for 10 mL/week needed to
determine reactor SS and VSS levels. Based on this
rate of sludge wastage, reactor SRT would be ~ 1
year. However, actual reactor SRT's were typically
much lower than this due to effluent solids losses.

The intention was to obtain as high a reactor SRT and biological solids concentration as possible. Reactors 10-12 were operated with intentional sludge wastage during the last 10 weeks of the study period to yield a SRT of 5-15 days in accordance with conventional operational practice.

The entire volume of effluent discharged from a reactor was collected in a container placed in a 4°C refrigerator next to the reactors. The composited reactor effluents were collected weekly with the following measurements made: volume, pH, TSS, TVSS, sBOD, sCOD, and sTOC. Though refrigeration of the samples helped preserve effluent organic values, some deterioration probably occurred during storage. Daily measurements were made on reactor pH, DO, and temperature. Weekly measurements were made on reactor MLSS, MLVSS, sludge zone settling velocity (ZSV), and 30-minute sludge settled volume. Measurements of ZSV and 30-minute settled volume were taken in situ by turning off the sparged air to the reactor. These measurements were therefore not performed in accordance with standard methods (15). All other measurements, however, were performed in accordance with standard methods (15).

The experimental results of this study are presented in Tables 4-8 and in Fig. 3-16. Discussion of these results will follow.

Table 4 Summary of data for M-D reactors fed unbleached kraft pulp mill effluents (Samples 13, 14, 15, and 16) for 140-day period[a]

| | Reactor Number | | |
	1 Kaolin	2 No Particles	3 CaCO₃
Hydraulic residence time (hours)	31.9(4.9)	34.6(4.6)	33.2(6.6)
Clarifier upflow velocity (cm/hour)	3.4(0.5)	3.3(0.5)	3.4(0.6)
Temperature (°C)	25.2(1.7)	25.2(1.6)	25.2(1.6)
Dissolved oxygen (mg/L)	5.5(2.0)	6.5(1.0)	6.2(1.1)
MLSS (g/L)	122.6(13.8)	6.2(1.3)	92.3(30.5)
Biol. MLVSS (g/L)[b]	6.9(2.0)	5.1(0.9)	11.4(3.7)
Ash/biol. VSS ratio	15.9(7.6)	0.23(0.08)	7.4(2.3)
Zone settling velocity (cm/hour)	217(105)	226(99)	14(6)
30-minute settled biol. MLVSS (g/L)	21.5(5.1)	28.8(11.4)	19.2(8.8)
Total particle dosage (g/L reactor)	190.7	0	245.7
Total particle dosage (g/L effluent)	1.77	0	2.34
Total particles wasted (g/L reactor)[c]	42.6	0	92.5

[a]Standard deviations given in parentheses.
[b]Same as MLVSS for CaCO₃ and no particle reactors. For kaolin-dosed reactor, value estimated assuming kaolin has 12% and biological sludge 90% volatile content.
[c]Particles wasted from reactor due to sampling and effluent losses divided by reactor volume.

Table 5 Summary of data for M-D reactors fed unbleached kraft pulp mill effluents (Samples 13, 14, 15, and 16) for 140-day period[a]

| | Reactor Number | | |
	4 Kaolin	5 No Particles	6 CaCO₃
Hydraulic residence time (hours)	15.7(2.2)	16.0(2.6)	17.5(3.1)
Clarifier upflow velocity (cm/hour)	7.2(1.0)	6.8(0.9)	6.7(1.1)
Temperature (°C)	25.2(1.6)	25.2(1.5)	25.2(1.5)
Dissolved oxygen (mg/L)	4.8(1.9)	5.4(1.3)	4.6(1.8)
MLSS (g/L)	127.0(22.1)	8.9(1.7)	84.0(34.0)
Biol. MLVSS (g/L)[b]	7.9(2.7)	7.1(1.7)	12.0(b.0)
Ash/biol. VSS ratio	15.0(5.9)	0.29(0.22)	7.3(3.8)
Zone settling velocity (cm/hour)	215(140)	298(151)	25(31)
30-minute settled Biol. MLVSS (g/L)	25.4(7.5)	38.6(20.0)	23.3(15.7)
Total particle dosage (g/L reactor)	233.9	0	333.5
Total particle dosage (g/L effluent)	1:07	0	1.87
Total particles wasted (g/L reactor)[c]	68.8	0	216.0

[a]Standard deviations given in parentheses.
[b]Same as MLVSS for CaCO₃ and no particle reactors. For kaolin-dosed reactor, value estimated assuming kaolin has 12% and biological sludge 90% volatile content.
[c]Particles wasted from reactor due to sampling and effluent losses divided by reactor volume.

Effect of fine particle addition on activated sludge settling characteristics

Tables 4-8 present data on reactor operational parameters and activated sludge characteristics. The data given in Tables 4-6 for HRT, clarifier upflow velocity, MLSS, biological MLVSS, ash/biological VSS ratio, zone settling velocity, and 30-

minute settled biological MLVSS are the averages of 20 weekly values taken over the 140-day study period. In Tables 7 and 8, averages of 10 weekly values are given for 70-day study periods. Reactor temperature and dissolved oxygen measurements were performed daily, and the values given in Tables 4-8 are averages of these values over the given study period.

Table 6 Summary of data for M-D reactors fed unbleached kraft pulp mill effluents (Samples 13, 14, 15, and 16) for 140-day period[a]

| | Reactor Number | | |
	7 Kaolin	8 No Particles	9 CaCO₃
Hydraulic residence time (hours)	7.20(1.33)	7.28(1.22)	7.08(1.17)
Clarifier upflow velocity (cm/hour)	15.2(2.1)	15.4(1.9)	15.2(2.0)
Temperature (°C)	25.7(1.6)	25.4(1.6)	25.2(1.6)
Dissolved oxygen (mg/L)	5.5(3.6)	5.0(3.0)	5.4(3.0)
MLSS (g/L)	113.6(31.5)	8.1(3.6)	53.9(28.2)
Biol. MLVSS (g/L)[b]	11.1(3.05)	6.6(3.2)	9.2(5.1)
Ash/biol. VSS ratio	9.1(5.0)	0.30(0.30)	7.2(6.8)
Zone settling velocity (cm/hour)	174(157)	142(207)	194(258)
30-minute settled Biol. MLVSS (g/L)	32.0(9.8)	16.0(9.3)	25.2(8.6)
Total particle dosage (g/L reactor)	487.6	0	647.7
Total particle dosage (g/L effluent)	1.02	0	1.34
Total particles wasted (g/L reactor)[c]	243.5	0	461.2

[a]Standard deviations given in parentheses.
[b]Same as MLVSS for CaCO₃ and no particle reactors. For kaolin-dosed reactor, value estimated assuming kaolin has 12% and biological sludge 90% volatile content.
[c]Particles wasted from reactor due to sampling and effluent losses divided by reactor volume.

Table 7 Summary of data for M-D reactors fed unbleached kraft pulp mill effluents (Samples 13 and 14) for 70-day period[a]

| | Reactor Number | | |
	10 Kaolin	11 No Particles	12 CaCO₃
Hydraulic residence time (hours)	3.31(0.27)	3.13(0.16)	3.45(0.42)
Clarifier upflow velocity (cm/hour)	33.6(2.7)	33.4(1.7)	32.6(3.6)
Temperature (°C)	24.5(1.2)	23.8(1.2)	24.6(1.2)
Dissolved oxygen (mg/L)	2.6(2.4)	3.5(3.2)	3.6(3.0)
MLSS (g/L)	71.4(26.5)	9.0(1.8)	30.4(12.9)
Biol. MLVSS (g/L)[b]	8.6(3.1)	7.5(1.5)	6.7(1.2)
Ash/biol. VSS ratio	6.76(2.81)	0.19(0.06)	3.55(1.84)
Zone settling velocity (cm/hour)	62(26)	19(6)	37(24)
30-minute settled Biol. MLVSS (g/L)	19.2(5.3)	11.5(2.9)	14.4(1.8)
Total particle dosage (g/L reactor)	410.3	0	576.6
Total particle dosage (g/L effluent)	0.80	0	1.17
Total particles wasted (g/L reactor)[c]	296.5	0	464.6

[a]Standard deviations given in parentheses.
[b]Same as MLVSS for CaCO₃ and no particle reactors. For kaolin-dosed reactor, value estimated assuming kaolin has 12% and biological sludge 90% volatile content.
[c]Particles wasted from reactor due to sampling and effluent losses divided by reactor volume.

Table 8 Summary of data for M-D reactors fed unbleached kraft pulp mill effluents (Samples 15 and 16) for 70-day period

| | Reactor Number | | |
	10 No Particles	11 No Particles	12 No Particles
Hydraulic residence time (hours)	32.9(4.1)	13.1(2.2)	7.9(1.7)
Clarifier upflow velocity (cm/hour)	3.42(0.40)	8.25(1.66)	14.64(2.42)
Temperature (°C)	25.8(1.6)	25.9(1.6)	25.9(1.6)
Dissolved oxygen (mg/L)	6.1(1.4)	5.8(2.5)	5.6(2.9)
MLSS (g/L)	1.94(1.04)	3.51(2.22)	3.78(2.46)
MLVSS (g/L)	1.40(0.62)	3.01(1.87)	3.14(2.32)
Ash/biol. VSS ratio	0.39(0.33)	0.17(0.12)	0.16(0.16)
Zone settling velocity (cm/hour)	332(208)	205(128)	151(107)
30 minute settled sludge conc. (g biol. VSS/L)	10.2(5.3)	18.7(10.8)	14.3(4.9)

Sludge characteristics for particle and no particle reactors at a given HRT were different. In nearly all cases, the particle-dosed reactors were able to maintain a higher average biological solids concentration than the no particle dosed reactors. CaCO₃ was particularly effective in concentrating reactor biological solids at high reactor HRT's. The better coagulating properties of the CaCO₃ sludges compared with kaolin and no particle sludges was responsible for this difference. CaCO₃ effluents were characteristically sparkling clear, whereas kaolin and no particle reactor effluents were often highly turbid due to dispersed bacterial growth.
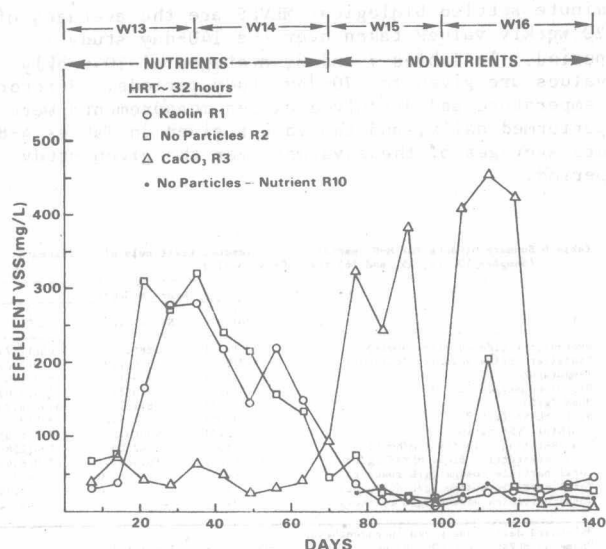
Figure 3 Weekly composited effluent volatile suspended solids (VSS) concentrations of reactors fed unbleached kraft pulp mill wastewaters.
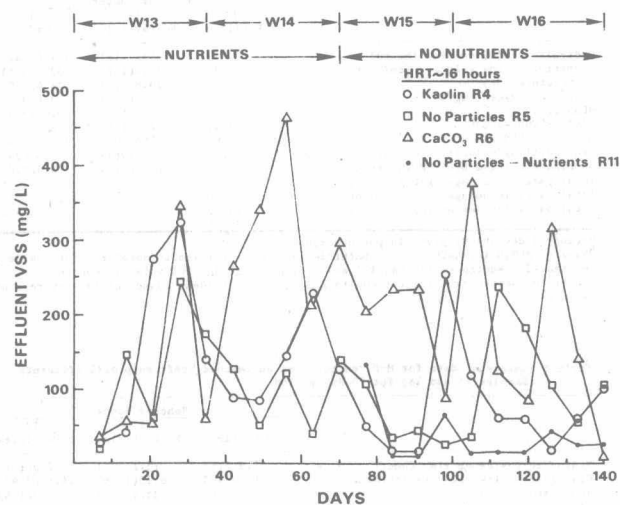

Figure 4 Weekly composited effluent volatile suspended solids (VSS) concentrations of reactors fed unbleached kraft pulp mill wastewaters.

Though the particle-dosed reactors had higher biological VSS levels, they did not necessarily have better sludge settling characteristics. For reactors operated at HRT's of ~ 16 and ~ 32 hours, the no particle sludges had higher zone settling velocities and higher 30-minute settled sludge biological solids concentrations than particle dosed reactors. All sludges at these HRT's, however, had very good settling characteristics. The CaCO₃ sludges had zone settling velocities substantially below the kaolin and no-particle reactors. This is primarily because of its substantially higher reactor biological VSS concentration. The zone settling velocity of a sludge declines sharply as biological solids concentration increases.
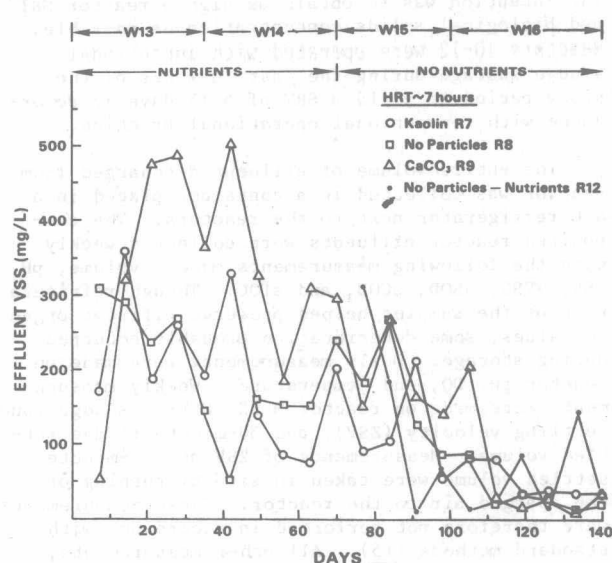

Figure 5 Weekly composited effluent volatile suspended solids (VSS) concentrations of reactors fed unbleached kraft pulp mill wastewaters.
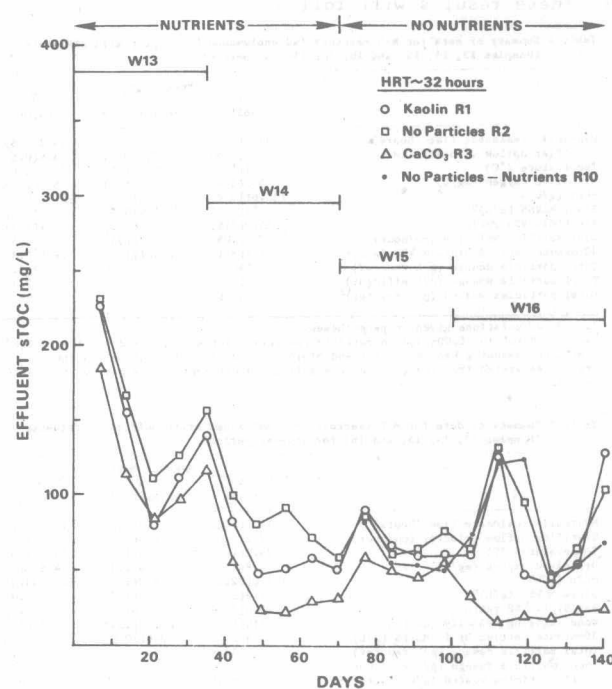

Figure 6 Weekly composited effluent total organic carbon (TOC) concentrations of reactors fed unbleached kraft pulp mill wastewaters.

For reactors operated at HRT's of ~ 3 and 7 hours, the particle-dosed reactors had higher zone settling velocities and 30-minute settled sludge biological solids concentrations than no particle sludges. The results indicate that fine particle addition helps to concentrate biomass in an activated sludge reactor. There is more benefit,

however, in dosing a highly loaded reactor than a low loaded reactor. A low loaded reactor, operated at a low F/M ratio, will normally have a sludge with excellent settling characteristics. Previous results (1) show that the best results are obtained by adding fine particles to sludges that are normally filamentous or bulking in nature.
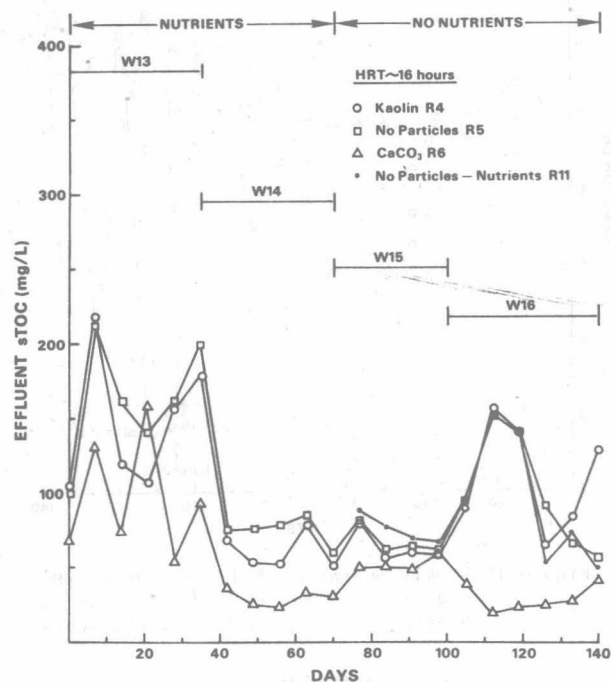
Figure 7 Weekly composited effluent total organic carbon (TOC) concentrations of reactors fed unbleached kraft pulp mill waste-waters.

The particle-dosed reactors in this study had very high particle-to-biomass weight ratios. The ash/biological VSS ratios given in Tables 4-7 are approximately equal to the particle-to-biomass weight ratios. The reactors were dosed periodically during the 140-day study period in an attempt to maintain a total reactor SS content greater than 100 g/L at all times. Substantial losses of particles occurred in reactors 3, 6, 7, 9, 10, and 12 due to sludge carry-over losses, which were measured. This carry-over of solids occurs when sludge settling velocity is less than the clarifier section upflow velocity, causing a rising of the sludge blanket in the clarifier section and eventual discharge of solids into the effluent. Figures 3-5 show the variation in effluent VSS emissions for the reactors. Most of these solids would be easily captured in a secondary clarifier.

Reactors 1, 2, 4, and 5, which were operated at very low F/M ratios, also had high VSS losses on occasion. These losses were due primarily to a dispersed biological growth rather than a sludge solids carry-over, since the sludge settling velocity was much less than the clarifier upflow velocity. This is a much more serious problem since these solids would not be successfully captured in a secondary clarifier. The CaCO3-dosed reactors 3

and 6 did not have this particular problem due to the superior coagulating properties of the CaCO3 sludges. Unfortunately, the CaCO3 product we were using (see Table 1) had a very substantial portion of very fine particle materials. At the high dosages we were employing, the very fine particles did appear in the reactor effluent immediately after dosing. After this initial washout period, however, effluent clarity was very good.
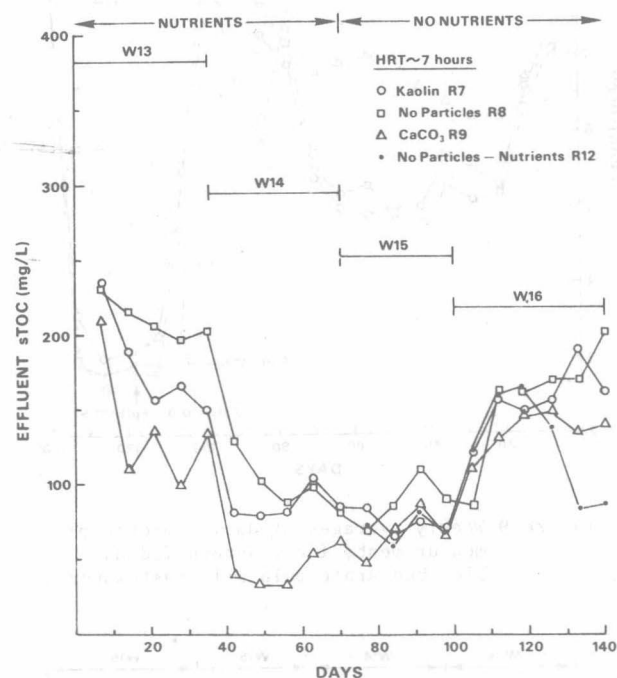
Figure 8 Weekly composited effluent total organic carbon (TOC) concentrations of reactors fed unbleached kraft pulp mill waste-waters.

The actual concentration of particles in the particle-dosed reactors may have been substantially higher than the measured values of MLSS given in Tables 4-8 indicate. Total particle dosages based on liters of reactor and effluent volume are given in these tables. Also given is the total particles losses due to sampling wastage or effluent losses. The total particle dosage (g/L reactor) minus the total particles wasted (g/L reactor) should be approximately equal to the reactor MLSS minus biological MLVSS. In all cases, the measured reactor particle concentration is less than what should have been present. This may have been the result of sampling errors. The particle sludges were very dense, and there may have been a substantially higher concentration of particles at or near the bottom of the reactors than at the sampling point near the middle of the reactor. Therefore, measured MLSS values may be lower than the actual reactor concentration. Also, very fine particles may not have been captured during the SS test procedure. Dissolution of the fine particle materials, particularly CaCO3, may also have been responsible for the losses.
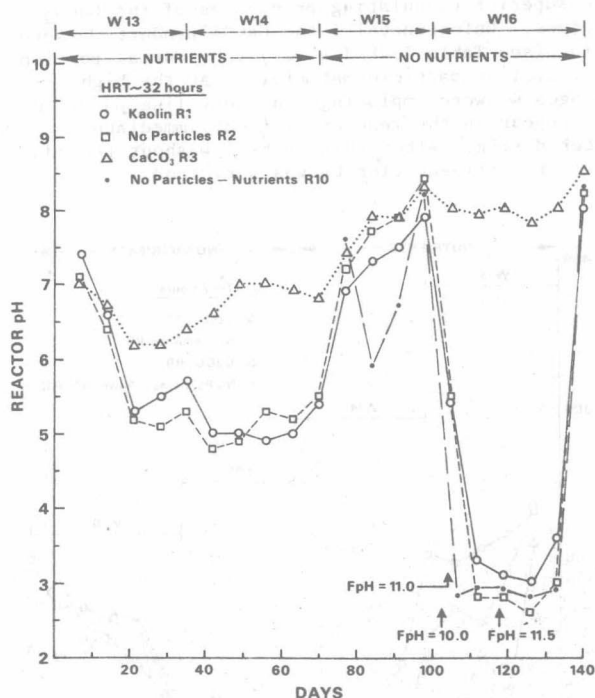
Figure 9 Weekly averages of daily reactor pH measurements for reactors fed un- bleached kraft pulp mill wastewaters.
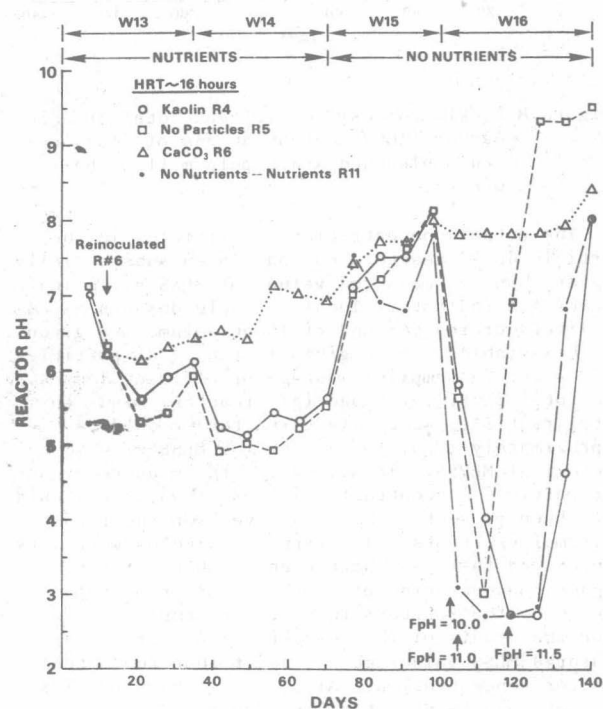

Figure 10 Weekly averages of daily reactor pH measurements for reactors fed un- bleached kraft pulp mill wastewaters.
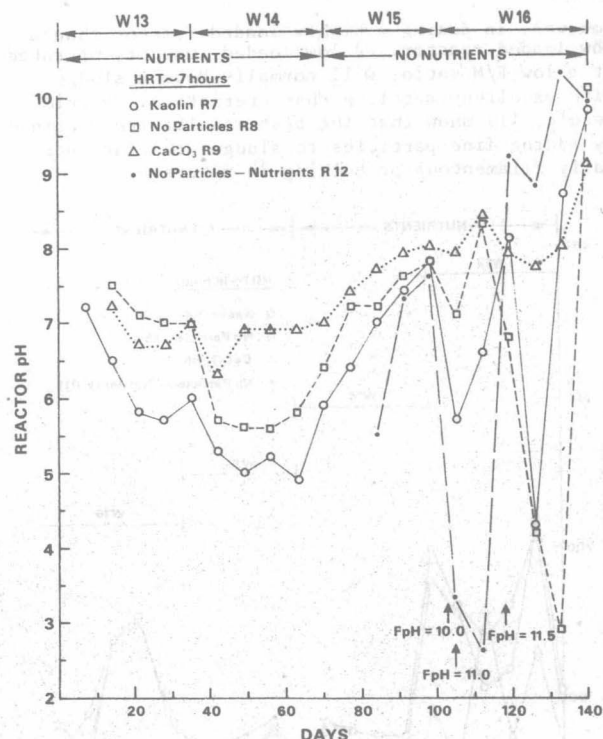

Figure 11 Weekly averages of daily reactor pH measurements for reactors fed un- bleached kraft pulp mill wastewaters.
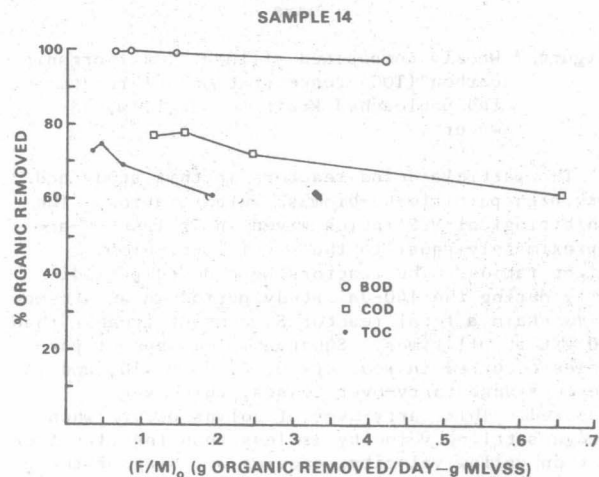

Figure 12 Variation in percent organic removal (BOD, COD, and TOC) with overall food-to- microorganism ratio $(F/M)_o$ for no-particle reactors fed unbleached kraft pulp mill wastewater (Sample 14).

Organic removals

During the course of the 140-day study period, four different unbleached kraft pulp mill effluents were fed to the reactors whose BOD, COD, TOC, SS, and VSS values are given in Table 3. It was expected that the extent of organic removal would depend on the wastewater sample fed, since the samples ema- nated from different parts of the mill. This was

in general the case as Fig. 6-8 indicate. Effluent TOC is plotted vs. time for the twelve reactors. Values of effluent BOD and COD were also taken but are not presented. BOD removal percentages were often greater than 99% when inorganic N and P was added to the feed and reactor pH was stable (except at very high reactor F/M ratios when a slight decline occurred). Reactor COD removal percentages closely paralleled TOC removal percentages.
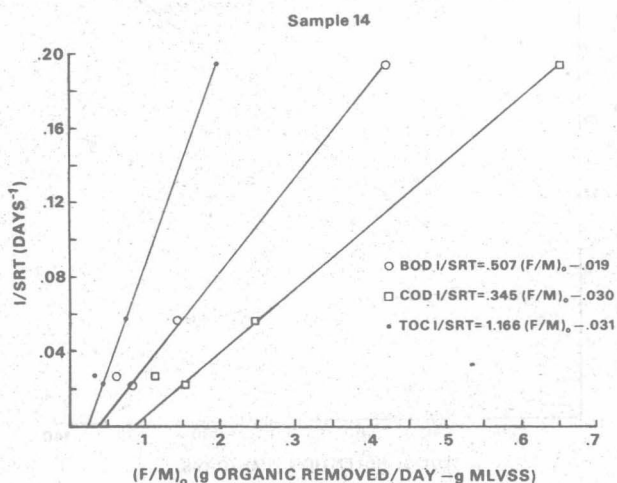

Sample 14

$$O\ BOD\ I/SRT = .507\ (F/M)_o - .019$$
$$\square\ COD\ I/SRT = .345\ (F/M)_o - .030$$
$$\bullet\ TOC\ I/SRT = 1.166\ (F/M)_o - .031$$

Figure 13 Correlations of reactor solids retention time (SRT) to reactor overall food-to-microorganism ratio $(F/M)_o$ for no-particle reactors fed unbleached kraft pulp mill wastewater (Sample 14).

Figures 6-8 show that reactor TOC values fluctuated considerably during the course of the study for all reactors. The greatest stability in these values occurred when wastewater Samples 14 and 15 were added. In all cases, the $CaCO_3$-dosed reactors yielded the lowest effluent TOC values, with the kaolin-dosed reactors often yielding lower effluent TOC values than the no particle dosed reactors. Several factors may have been responsible for these differences in TOC removals. Figures 9-11 present data for weekly averages of daily reactor pH values. Since the wastewater feeds entering the reactors were unbuffered, the reactor pH values depended on the original buffering capacity of the feed and extent of biological activity. Reactor pH fluctuated for the kaolin and no particle dosed reactors. The pH of the $CaCO_3$-dosed reactors remained relatively stable due to the buffering characteristics of $CaCO_3$. This buffering ability may have been a key factor in the ability of the $CaCO_3$ reactor to remove more TOC from the effluent. Also, the biological solids concentration in the $CaCO_3$ reactors was greater at HRT's of ~ 16 and 32 hours, possibly resulting in greater removals due to lower F/M ratios compared with kaolin and no-particle reactors. The fact that the kaolin and no-particle reactors had similar pH values and yet the kaolin reactor had better TOC removals would support the argument that this was due to the lower F/M ratios of the kaolin-dosed reactors.
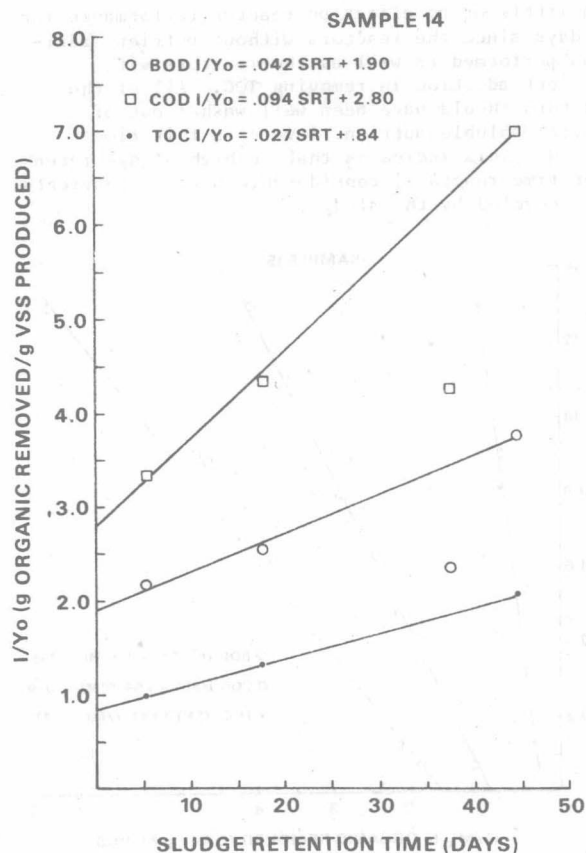

SAMPLE 14

$$O\ BOD\ I/Yo = .042\ SRT + 1.90$$
$$\square\ COD\ I/Yo = .094\ SRT + 2.80$$
$$\bullet\ TOC\ I/Yo = .027\ SRT + .84$$

Figure 14 Correlations of reactor biomass yield (Yo) to reactor solids retention time (SRT) for no particle reactors fed unbleached kraft pulp mill wastewater (Sample 14).

Another explanation for the good performance of the $CaCO_3$ reactors in removing TOC was that a considerable portion of the TOC was adsorbed by the $CaCO_3$ and removed with the sludge. Undoubtedly all three factors - stable reactor pH, low F/M ratio, and organic adsorption on $CaCO_3$ - were responsible to some degree for the superior performance of the $CaCO_3$ reactors. Only further research can uncover the dominant mechanisms.

Effect of nutrient addition on the activated sludge process

During the last 70 days of the study period, no N and P nutrients were added to the feed of reactors 1-9. Reactors 10-12 had excess N and P nutrients added and were operated with sludge wastage to yield a sludge retention time of 5-15 days. Unfortunately, wastewater Sample 16 caused the pH of both kaolin and no particle reactors to plummet to the 2-4 range. This obscured the results obtained during that period.

When wastewater Sample 15 was fed to the reactors, the pH of all reactors was in the 7-8 range and should not have been a factor in determining performance. Effluent TOC values for the reactors (see Fig. 6-8) show that N and P nutrient addition

had little or no effect on reactor performance for 28 days since the reactors without nutrient addition performed as well as the reactors with nutrient addition in removing TOC. All of the reactors should have been well washed out of initial soluble nutrient levels in this time period. This indicates that in high sludge retention time reactors, considerable N and P nutrients are recycled by the sludge.
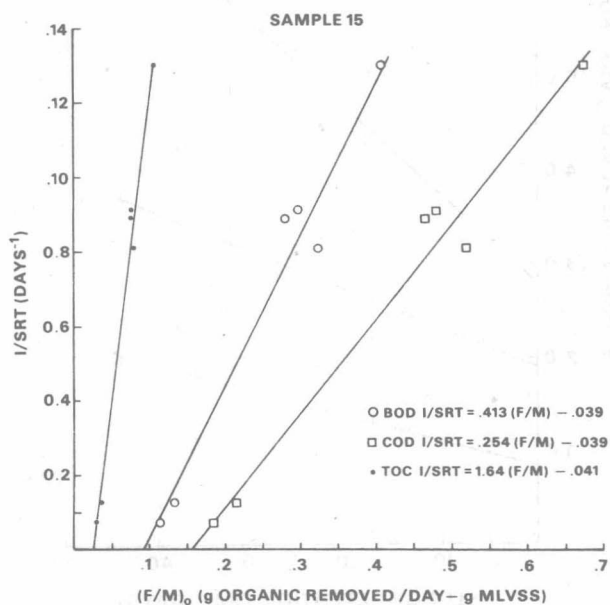

Figure 15 Correlations of reactor solids retention time (SRT) to reactor overall food-to-microorganism ratio (F/M)o for no-particle reactors fed unbleached kraft pulp mill wastewater (Sample 15).

When wastewater Sample 16 was fed to the reactors, the pH of all reactors, except for the CaCO₃ reactors, plummeted to very low levels. This was probably responsible for poor TOC removals in those reactors. Sample 16 was initially highly alkaline, with a pH of 12.3. This feed required considerable acid addition for neutralization. At first, the pH of the feed was lowered to 10.0. Because of low reactor pH, the feed pH was raised to 11.0 and then to 11.5 (see Fig. 8-10). At a feed pH of 11.5, the pH of the reactors rose to very high levels.

The results show that despite pH fluctuations, the reactors still removed organic materials to some extent. For reactors operated at HRT's of ~ 16 and 32 hours, results indicate that initial pH shocks are a more dominant factor in determining reactor organic removals than a low pH per se. It seemed that once the reactor pH stabilized at low level, the organisms acclimated and TOC removals were respectable. For reactors operated at a HRT of ~ 7 hours, the reactor pH fluctuated considerably for reactors 7-9. No stabilization of pH occurred, and these reactors had poor organic removals. Reactor 12, however, had much better TOC removals once the pH stabilized in the 9-10 range. Again, these results confirm the notion that while pH fluctuations are detrimental to reactor organic

removal ability, very high or very low reactor pH values are not detrimental per se. These results contradict the widely held belief that the pH of activated sludge reactors must be maintained in the range of 6.5-8.0 for good organic removals.
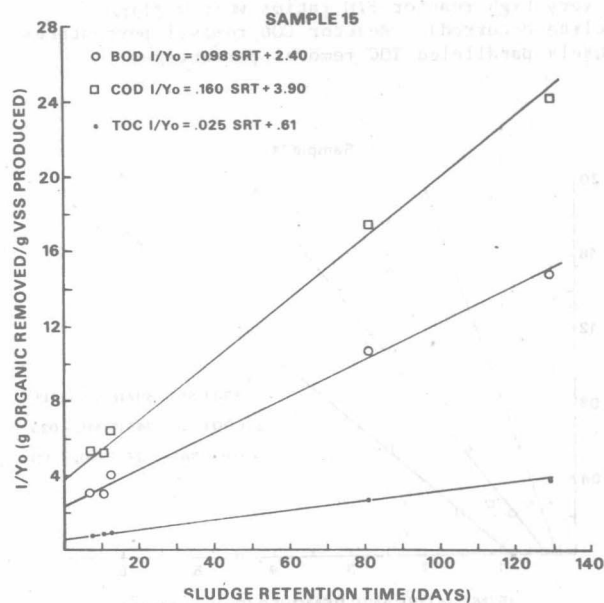

Figure 16 Correlations of reactor biomass yield (Yo) to reactor solids retention time (SRT) for no-particle reactors fed unbleached kraft pulp mill wastewater (Sample 15).

The poor organic removals for CaCO₃ reactor 9 fed wastewater Sample 16 were probably due to the lack of P nutrient. The pH of this reactor was relatively stable and probably was not a factor in determining reactor TOC removal. This reactor had a heavy washout of sludge in the course of its operation. Therefore the sludge probably contained little adsorbed P that could be recycled to the sludge organisms. The TOC removals for CaCO₃ reactors 3 and 6 remained very good, however, during the entire 70 days of operation with no N and P nutrients added to the feed.

Effect of food-to-microorganism ratio on reactor organic removal

It can be shown from material balances for an activated sludge process that 1/SRT is equal to the sludge specific growth rate. The Monod model (16), given below, is widely used to predict the soluble organic concentration of a wastewater as a function of sludge specific growth rate:

$$\mu = \mu_m \frac{S}{K_S + S} \qquad (6)$$

μ - sludge specific growth rate (day^{-1})
μ_m - sludge maximum specific growth rate (day^{-1})
S - organic concentration (g/L)
K_S - Monod model constant (g/L)