Adsorption in the Activated Sludge Process

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Abstract

Investigations into the phenomenon of storage of substrate in the activated sludge process indicate that this phase is preceded by an adsorption phase, which requires the expenditure of energy. Incorporation of the adsorption mechanism into the general model of the activated sludge process by Ekama and Marais (1977) allowed the reinstatement in their model of the widely accepted Monod formulation for nitrification. Application of the modified model to processes with imposed dynamic loading conditions operated at long and short sludge ages gave improved predictions of the process response variables, i.e. oxygen consumption rate, effluent total Kjeldahl nitrogen (TKN) and nitrate concentrations.

Introduction

Ekama and Marais (1977) presented a generalized dynamic model for the activated sludge process, including nitrification. Their model incorporated storage of energy on the organism mass as an essential prerequisite to synthesis of new cell material. By including the storage phase the model yielded predictions of oxygen utilization rates much closer to those observed experimentally than predicted by models not including a storage phase. However, certain inconsistencies were observed. In experimental activated sludge units receiving a daily cyclic square wave loading, i.e. a 12 hour feed period followed by a 12 hour no-feed period, a precipitous decrease of the oxygen utilization rate was observed at the moment the feed terminated, a behavioural pattern which was observed at both 2,5 and 20 days sludge age.

The experimental units were operated at 20°C and nitrification occurred even in the units operated at 2,5 days sludge age, so that the oxygen consumption rates observed were the sum of two independent oxygen requirements, that for nitrification and that for carbonaceous material degradation.

The discontinuous behaviour observed in the oxygen consumption rate was not predicted at low sludge ages by either the carbonaceous material degradation kinetic theory incorporating storage of COD, or the nitrification kinetic theory under square wave loading conditions. Ekama and Marais (1977) eventually concluded that this sudden decrease in oxygen consumption rate can be explained if it is accepted that the ammonia fraction of the influent total Kjeldahl nitrogen (TKN) is only 20%, that the organic bound fraction is converted to saline ammonia at a slow rate and that saline ammonia is nitrified virtually instantaneously. Their hypothesis can be criticised on two points:

1. It presumes that the current ammonia test actually converts some of the organic bound nitrogen to saline ammonia, i.e. the test was suspected to overestimate the true ammonia value.
2. Instantaneous conversion of saline ammonia to nitrate implies the rejection of the widely accepted Monod based kinetic formulation for nitrification.

Although the application of the hypothesis to dynamic loading conditions gave good correlation between the predicted and observed oxygen utilization rates over wide ranges of sludge ages, loading conditions and process configurations, the exclusion of Monod kinetics and the suspicion cast on a well established chemical test cannot be accepted unless very powerful supporting evidence can be presented.

Two observations have led to a reassessment of the hypothesis. Reviewing the contact-stabilization process, an important aspect of this process is the adsorption of colloidal organic matter onto the organism mass. In the model of Ekama and Marais (1977) the adsorption phenomenon is not quantitatively incorporated *per se* – storage is accepted but the mechanism by which storage occurs is not delineated. This aspect would be of minor importance insofar as the predictive power of the model is concerned, provided the adsorption mechanism is not energy consuming. However, there is evidence that the biological adsorption does, in fact, require the expenditure of energy.

In a study of biological denitrification Stern and Marais (1974) concluded that denitrification in the primary anoxic reactor using sewage as the influent energy source, takes place in three sequential phases. In the first phase (NO_3-N) is reduced at a high rate over a short interval of time, ranging from 1 minute at high sludge concentrations to 5 minutes at low sludge concentrations. In the second phase (NO_3-N) is reduced at a rate approximately 10 percent of the initial rate and the reaction persists for 5 to 40 minutes. In the third phase denitrification ceases (Fig. 1). They found that the first phase of denitrification appeared to be linked to a phase of rapid COD removal – the reaction time to termination of the rapid phase of soluble COD removal and reaction time to termination of the first phase of denitrification showed good correlation. They suggested that the disappearance of the COD from the liquid may be due to some form of biological sorption.

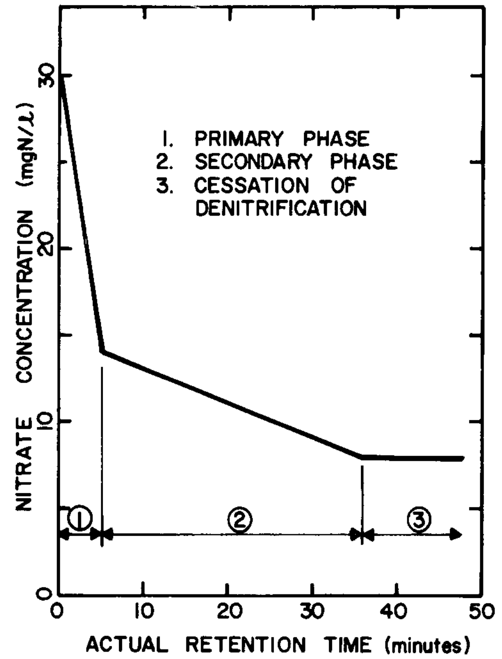

Figure 1
Characteristic features of biological denitrification in a primary plug flow anoxic reactor using sewage as the influent energy source (After Stern and Marais, 1974)

Subsequently Wilson and Marais (1976), from a detailed investigation into the initial phase of biological denitrification in the primary anoxic reactor, established that the initial phase of denitrification and the phase of rapid removal of COD were linked by a biological adsorption mechanism. They concluded that the nitrate reduction observed was due to nitrate serving as the electron acceptor for the energy requirements during adsorption. Their measurements showed that approximately 7% of the COD that disappeared from the liquid phase was utilized as energy for adsorption.

It can be postulated that in the aerobic activated sludge process there will also be an expenditure of energy for the adsorption of COD, that the adsorption occurs very rapidly so that a sudden termination of influent energy should show a correspondingly rapid decrease in the oxygen utilization rate. The hypothesis implies that the discontinuity in oxygen consumption rate when feeding ceases is a behavioural characteristic of heterotrophic carbonaceous energy degradation activity and is independent of autotrophic nitrification activity. This hypothesis is contrary to the original hypothesis of Ekama and Marais (1977).

This paper deals with an investigation to establish the cause of the precipitous decrease in oxygen consumption rate at the instant of feed termination.

Conceptual Framework

In order to test the hypothesis that the precipitous decrease in the total oxygen consumption rate at feed termination is due to the cessation of an energy requirement for adsorption of influent energy, it is necessary to devise an experimental procedure in which the dynamic response of the autotrophic nitrifying organisms and the heterotrophic carbonaceous material degrading organisms can be observed independently. At 20°C and at sludge ages greater than 2 days in the presence of adequate oxygen concentrations, activated sludge processes nitrify virtually completely unless inhibitory chemicals are present in the influent. The experimental oxygen consumption rates measured in activated sludge processes are therefore the sum of two independent metabolic oxygen requirements, that for carbonaceous material degradation and that for nitrification. In order to establish which of these two oxygen requirements is the cause of the precipitous decrease in the oxygen demand at the instant of feed termination, it is necessary to investigate the dynamic behaviour of the two oxygen requirements as independently as possible.

Using the normal conventional activated sludge process the dynamic behaviour of the oxygen demand for carbonaceous material degradation can be isolated by feeding an influent having a low TKN concentration, i.e. just sufficient for cell production. A square wave of this influent is fed to the plant. Under these conditions the variation in measured oxygen consumption rate will reflect principally the behaviour of this variable associated with carbonaceous material degradation. The dynamic behaviour of the oxygen demand for nitrification can be isolated by feeding the influent with a low TKN concentration on a continuous basis, and superimposing on this feed, a square wave of saline ammonia addition. The variations in measured oxygen consumption rate will reflect principally the response of this variable associated with nitrification.

If the unit in which the dynamic behaviour of the carbonaceous material degradation kinetics is observed, manifests the precipitous decrease in oxygen consumption rate, while the other unit, in which the dynamic behaviour of nitrification is observed, does not show such discontinuous behaviour, it can be concluded that the observed discontinuous behaviour is due to the adsorption of COD. If however, the precipitous decrease in the oxygen consumption rate is observed only in the latter unit and not in the former, then the original hypothesis of Ekama and Marais (1977) is valid. If a step change is observed in the oxygen consumption rate in both units, then it is possible that both hypotheses contribute to explain the behaviour.

These concepts were utlized in the experimental procedure.

Experimental procedure

An influent with a low TKN concentration was prepared as follows. The pH of unsettled domestic sewage was raised with a 50% sodium hydroxide solution to 10,5 and was then passed through an ammonia stripping column with a liquid to air ratio of about 1,2 ℓ/m³. After ammonia stripping, the pH was reduced to 7,5 using 5N hydrochloric acid and the buffering capacity was improved by adding 250 mg/ℓ sodium bicarbonate. Approximately 1 200 litres of sewage were treated and it was found that the ammonia concentration was reduced from 25 mgN/ℓ to 10 mgN/ℓ and the TKN was reduced from 48 mgN/ℓ to 21 mgN/ℓ.

Two laboratory scale activated sludge units were operated using the treated domestic sewage as influent. In the first unit (unit C) the dynamic behaviour of the carbonaceous material removal was observed under conditions in which nitrification has a negligible effect; this unit was fed in a square wave, with a feed period of 12 hours followed by a 12 hour period during which no feeding occurred. In the second unit (unit N) the dynamic behaviour of nitrification was observed while the effects of the carbonaceous material removal were held constant; this was achieved by feeding the treated domestic sewage on a continuous basis serving as a steady input of nutrient for the heterotrophs in the activated sludge in conjunction with a square wave feed (consisting of a 12 hour period of saline ammonia addition followed by a period of 12 hours during which no saline ammonia was added) which serves as the dynamic load on the nitrifiers in the process. A small volume (~0,5ℓ) of strong ammonium chloride (600 mgN/ℓ) was fed dropwise over the 12 hour feed intervals being equivalent to 25 mgN/ℓ of treated domestic sewage added. It was necessary to use small volumes of concentrated ammonia to cause minimal changes in the hydraulic retention time resulting from the 20 litres influent flow. The process parameters for the two units are given in Table 1.

TABLE 1

EXPERIMENTAL UNITS PROCESS PARAMETERS

Parameter	Unit C	Unit N
State	Cyclic carbonaceous, negligible nitrification	Steady state carbonaceous, cyclic nitrification
Chemical ammonia added	–	~25 mgN/ℓ*
Influent COD (mg/ℓ)	350	350
Volume feed (ℓ/d)	20	20
Sludge age (d)	10; 2,5	10; 2,5
Volume of reactor (ℓ)	6,5	6,5
Temperature	19-20	19-20
pH	7,7	7,4
D.O. Level (mg0/ℓ)	1,5-2,0	1,5-2,0

*Chemical ammonia added for a 12-hour period per ℓ influent applied during the 12-hour period.

TABLE 2

AVERAGES OF PROCESS VARIABLES MEASURED* IN UNITS C AND N OPERATING AT 10 AND 2,5 DAYS SLUDGE AGE, DURING THE INVESTIGATION

Process Variable		Unit C		Unit N	
		$R_s = 10$	$R_s = 2,5$	$R_s = 10$	$R_s = 2,5$
COD (mg/ℓ)	Influent	389	357	389	357
	Reactor	47,0	–	42,0	–
	Effluent	39,3	42,3	37,3	34,6
MLVSS		3204	1065	3005	1156
(mg/ℓ)	Reactor				
MLSS		4263	1385	3988	1436
TKN (mgN/ℓ)	Influent	20,3	21,4	20,3	21,4
	Reactor	–	–	–	–
	Effluent	4,2	4,6	6,8	6,9
NH_3 (mgN/ℓ)	Influent	10,9	9,1	10,9	9,1
	Reactor	0,0	–	0,5	–
	Effluent	0,0	0,4	0,3	1,7
NO_3 (mgN/ℓ)	Influent	0,0	0,0	0,0	0,0
	Reactor	12,5	–	27,5	–
	Effluent	13,0	8,1	27,8	19,2
NO_2 (mgN/ℓ)	Influent	0,0	0,0	0,0	0,0
	Effluent	1,5	0,5	1,5	0,8

*Test methods for the determination of the variables are given in Appendix A.

Both units were first operated at a sludge age of 10 days and were run for a period of about 1,5 sludge ages to allow dynamic steady state conditions to be established. The process variables were monitored daily over this period and for a subsequent period of five days (half a sludge age). The averages of the process variables monitored over the five day period are given in Table 2. The two units were then tested over a 10 hour period, which was selected so that the sampling was done from 3 hours before to 7 hours after feed termination. Special attention was given to the oxygen consumption rate in the two units at the instant of COD or ammonia feed termination. The results of this 10 hour test are shown in Figure 2, (Test 1). It is evident that in both units the oxygen consumption rate rapidly decreased after the cessation of feed of COD or ammonia. At a sludge age of 10 days nitrification is rapid (under Monod's hypothesis) and storage of COD is low, so that both units should show a rapid decrease in the oxygen consumption rates. This test was not therefore conclusive and it was decided to shorten the sludge age such that storage of COD will be significant and the rate of nitrification slow.

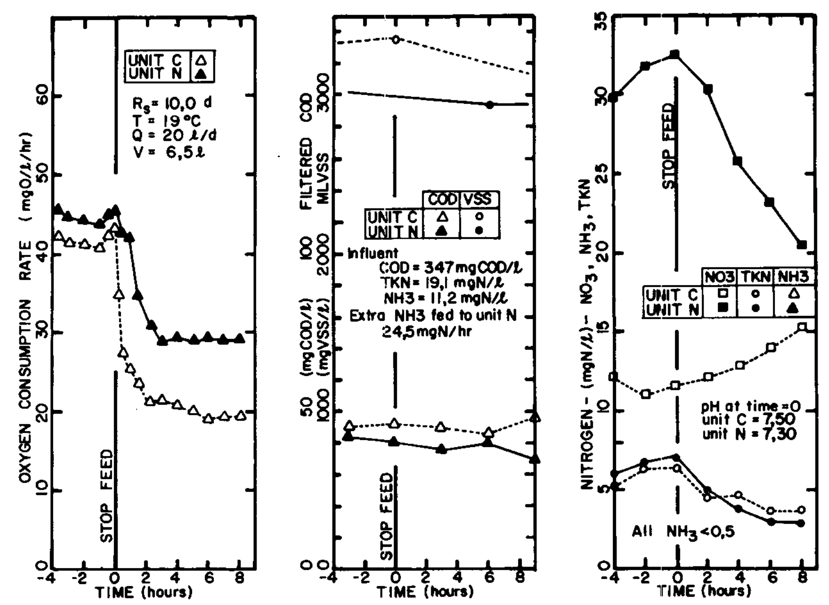

Figure 2

Experimental response waves observed in both Unit C and N during the 10-hour testing period at 10 days sludge age. (Test 1) Unit C has a square wave COD feed, Unit N has a constant COD feed and a square wave ammoniacal nitrogen feed.

Both units were changed to 2,5 days sludge age by wasting 40% of the mixed liquor from the units during the feed period. The waste sludge was abstracted from the reactor in an automatic semi-discontinuous fashion by pumping at a high rate for about 2 minutes every half hour. The input loading conditions of COD and ammonia to the units were left unchanged (Table 3). The units were operated for three days to allow dynamic steady state conditions to develop. The two units were then tested over the 10-hour period on four consecutive days.

The loading pattern on the carbonaceous material cyclically fed unit (unit C) remained the same for all four 10-hour testing periods (Tests 2 – 5), i.e. the unit C received a cyclic square wave addition of influent which had a low nitrogen concentration. The results observed in unit C served as the basis for comparing of the results of the experiments on unit N.

The loading *pattern* on the ammonia cyclically fed unit (unit N) remained unchanged during three 10-hour testing periods (Tests 2 – 4), i.e. unit N received a constant feed of sewage with a low nitrogen concentration, but with a cyclic square wave ammonia feed superimposed. In Tests 2 and 3 in unit N, ammonia was fed at a rate of 24 mgN/h over the 12-hour period (Figs. 3 and 4) and in Test 4, at a rate of 13,7 mgN/h (Fig. 5). In the last 10-hour test (Test 5), the loading pattern on unit N was changed to the same cyclic influent feed pattern as on unit C, i.e., a square wave form, *except* the influent was spiked with an additional 20 mgN/ℓ of ammônia (Fig. 6).

A summary of the different conditions on units C and N during the five 10-hour tests is given in Table 3 and the average of the process variable measurements in Table 2.

The different ammonia loading patterns on the ammonia cyclically fed unit (unit N) were designed specifically to investigate whether or not the precipitous decrease in oxygen consumption rate was in any way related to nitrification kinetics. The hypothesis for making this decision was as follows:

TABLE 3

LOADING CONDITIONS ON CARBONACEOUS MATERIAL CYCLICALLY FED UNIT (UNIT C) AND AMMONIACAL NITROGEN CYCLICALLY FED UNIT (UNIT N) DURING 10-HOUR TESTING PERIODS 1 TO 5

Test Number	R_s	Unit C	Unit N
Test 1	10	Square wave* COD addition of influent with low N concentration.	Constant COD feed with low N influent + square wave NH_4 addition, (24mgN/h for 12 h).
Test 2	2,5	Square wave* COD addition of influent with low N concentration.	Constant COD feed with low N influent + square wave NH_4 addition, (24mgN/h for 12 h).
Test 3	2,5	Square wave* COD addition of influent with low N concentration.	Constant COD feed with low N influent + square wave NH_4 addition, (24mgN/h for 12 h).
Test 4	2,5	Square wave* COD addition of influent with low N	Same as above except NH_4 fed at 13,7 mgN/h over 12 h.
Test 5	2,5	Square wave* COD addition of influent with low N concentration.	Square wave*COD addition of influent with a high N concentration.

*Square wave consists of a 12-hour period of feeding followed by a 12-hour period during which no feeding occurs.

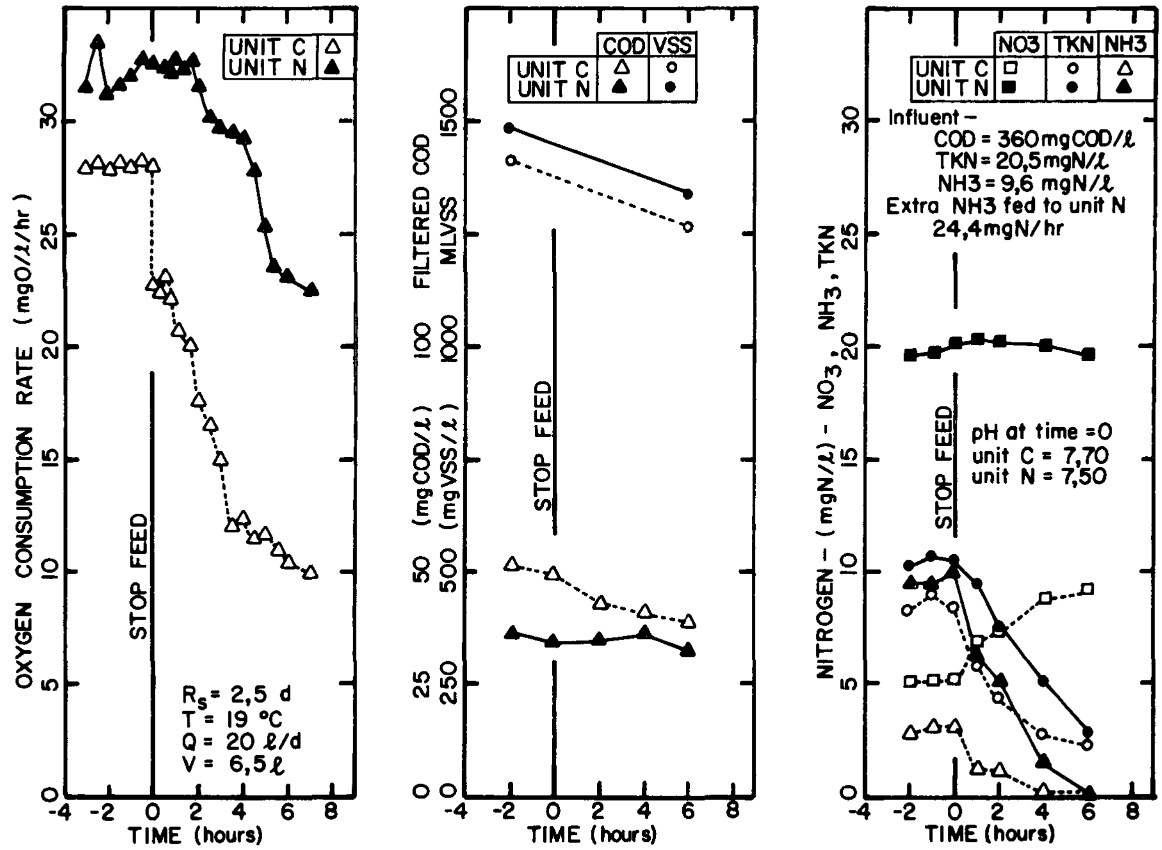

Figure 3
Experimental response waves observed in both Unit C and N during the first 10-hour testing period at 2,5 days sludge age. (Test 2) Unit C has a square wave COD feed, Unit N has a constant COD feed and a square wave ammoniacal nitrogen feed.

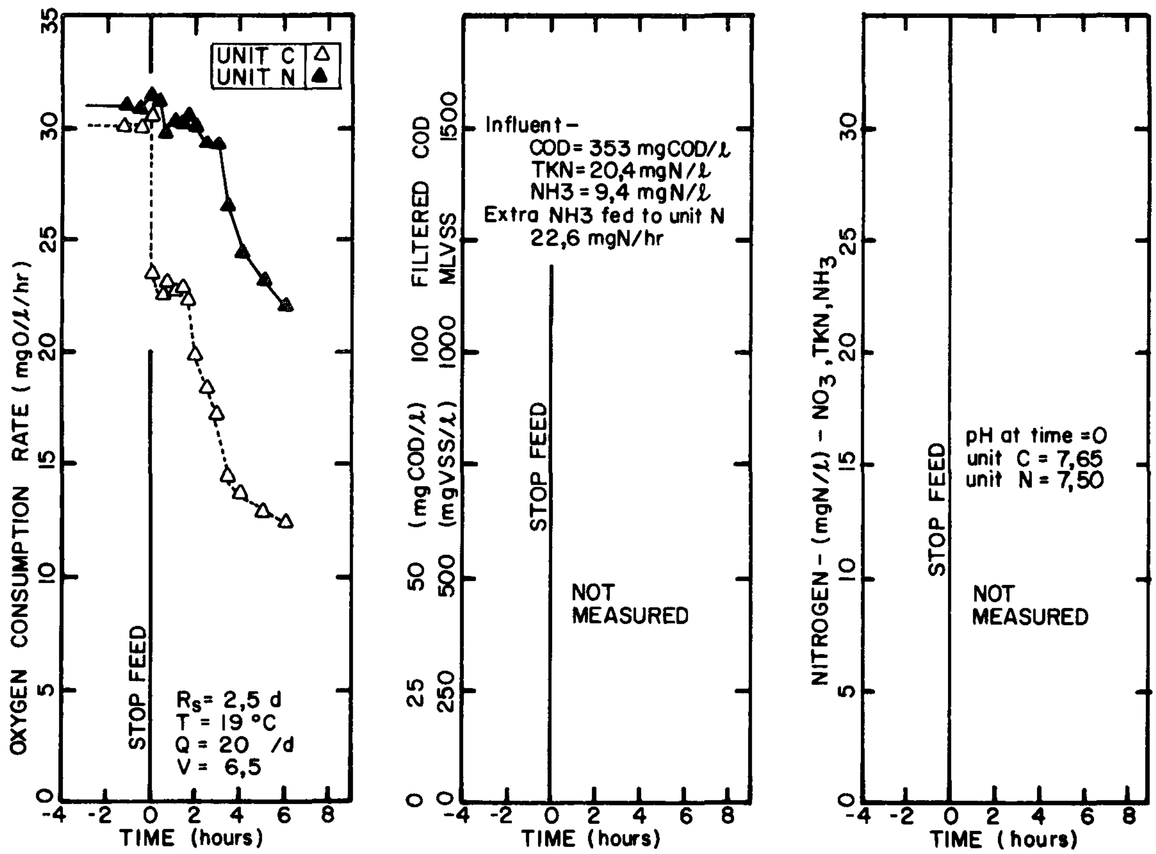

Figure 4
Experimental response waves observed in both Unit C and N during the second 10-hour testing period at 2,5 days sludge age. (Test 3) Unit C has a square wave COD feed, Unit N has a constant COD feed and a square wave ammoniacal nitrogen feed.

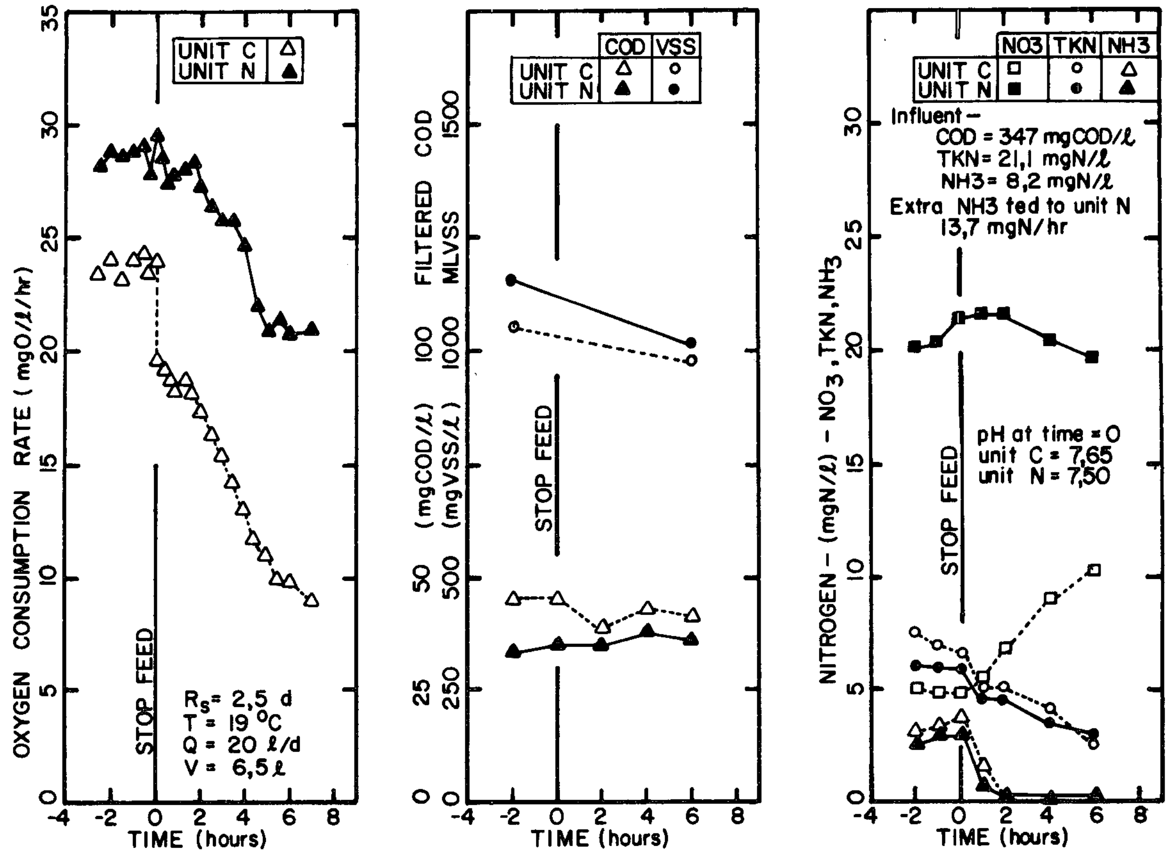

Figure 5
Experimental response waves observed in both Unit C and N during the third 10-hour testing period at 2,5 days sludge age. (Test 4) Unit C has a square wave COD feed, Unit N has a constant COD feed and a square wave ammoniacal nitrogen feed.

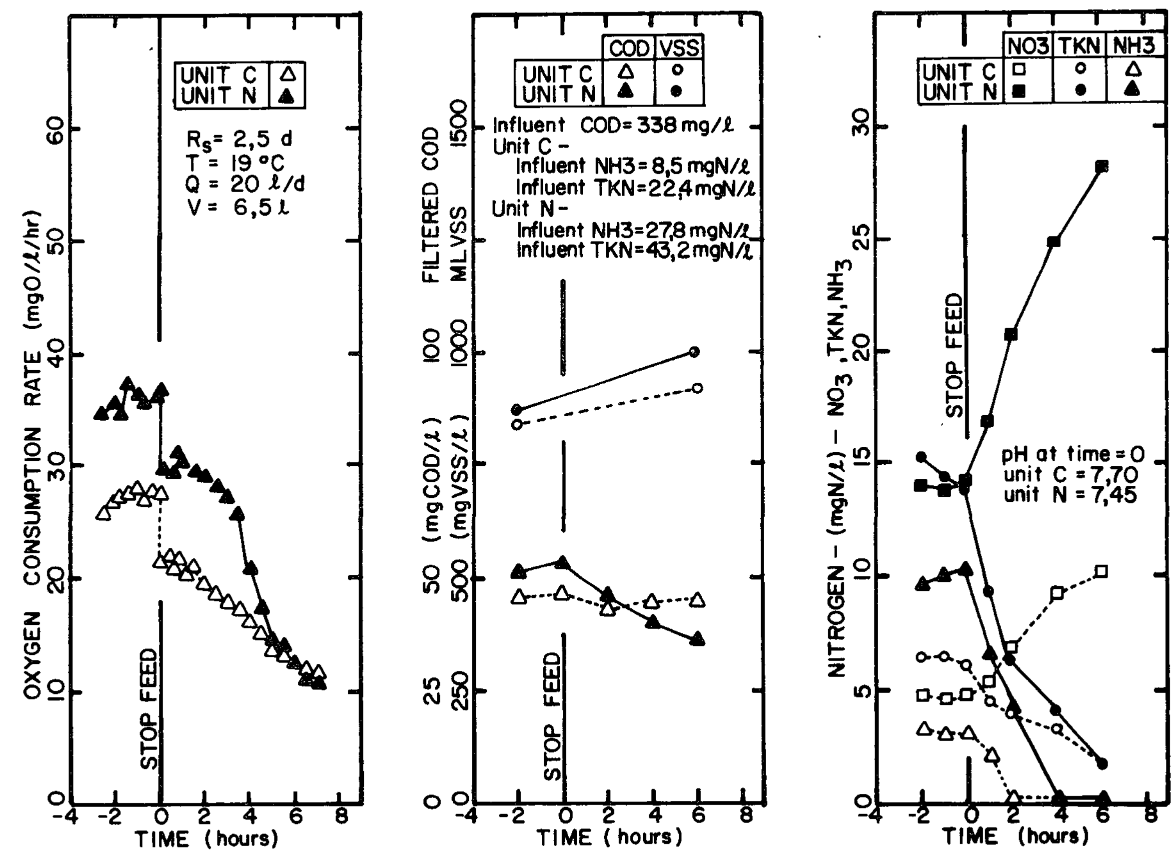

Figure 6
Experimental response waves observed in both Unit C and N during the fourth 10-hour testing period at 2,5 days sludge age. (Test 5) Units C and N have a square wave COD feed, but the influent to Unit N was spiked with 20 mgN/ℓ ammonia.

In unit N, if no significant jump in oxygen consumption rate occurs at termination of the nitrogen feed (Tests 2 to 4, Figs. 3 to 5), but a jump occurs in unit C which receives nitrogen sufficient only for synthesis, then the jump is *not* due to nitrification, but due to COD adsorption. This hypothesis will be substantiated if in Test 5, Fig. 6, (in which both units receive the same cyclic COD feed, but the influent to unit N contains a high nitrogen concentration), the jump in oxygen consumption rate is the same.

Results

By comparing the total oxygen consumption rates in Tests 2 to 4 on the units operating at 2,5 days sludge age (Figs. 3 to 5), it can be seen that the unit receiving the cyclic load of carbonaceous material with negligible nitrification (unit C) was the only one that showed a step change in the oxygen consumption rate at the instant of feed termination. Unit N receiving the cyclic feed of ammonical nitrogen, with the carbonaceous material feed kept constant showed *no* step change in the total oxygen consumption rate at the instant the feed period of ammonical nitrogen terminated.

In Test 5, Fig. 6, the step changes in oxygen consumption rate in units C and N were the same. The difference in the average oxygen consumption rates measured over 2,5 h before feed termination and 1,5 h after feed termination was 5,9 mg0/ℓ/h in unit C and 6,0 mg0/ℓ/h in unit N.

These observations are in accordance with the hypothesis that the precipitous decrease in oxygen consumption rate at feed termination is due to energy requirement for the adsorption of carbonaceous material and is not a behavioural characteristic of nitrification.

The general behaviour characteristics during all the 10-hour tests, while the two units were operated at 2,5 and 10 days sludge age, can be explained in terms of the adsorption hypothesis with its associated energy requirement and the Monod based formulation for nitrification as follows:

Carbonaceous degradation kinetics

The longer the sludge age, the lower will be the food to active micro-organism ratio. Marais and Ekama (1976) present the following relationship for steady state conditions:

$$F/MX_a = SUR_a = (1/R_s + b)/Y$$

where

F/MX_a = Food to active organism mass ratio (mg COD/mg VSS/d)

SUR_a = Substrate utilization rate in terms of the active organism concentration (mg COD/mg VSS/d)

R_s = Sludge age (d)

b = Endogenous respiration rate (d^{-1})
= 0,24 /d at 20°C

Y = Specific yield coefficient (mg VSS/mg COD)
= 0,43

$$\therefore F/MX_a(R_s = 10): F/MX_a\ (R_s = 2{,}5) = 1{,}0: 1{,}88$$

Under dynamic steady state conditions of loading the F/MX_a ratio varies with the load and the active mass concentration, although the latter remains relatively constant over a cycle. Generally the higher the F/MX_a ratio, the higher will be the level of COD storage and the greater will be the energy for adsorption relative to the total carbonaceous oxygen requirement. With high active mass concentrations and small masses of stored COD, the conditions encountered at the longer sludge ages, the stored COD is rapidly utilized. Therefore at the instant of carbonaceous material feed termination, the total oxygen consumption rate shows a precipitous decrease, followed by a rapidly decreasing total oxygen consumption rate as the stored COD is metabolized until approximately 2 hours after the instant of feed termination the oxygen consumption rate levels off at that value associated with endogenous respiration.

The magnitude of the precipitous step decrease in the total oxygen consumption rates is difficult to determine as it merges with the stage of rapidly decreasing total oxygen consumption rate to such an extent that the two stages are observed as one continuous decrease in the oxygen consumption rate. The rapid decrease in the rate continues until that value associated with endogenous respiration is reached.

In contrast, the behaviour of the oxygen consumption rate at 2,5 days sludge age observed in the carbonaceous material cyclically fed unit (unit C) differs substantially from that observed at 10 days sludge age (compare Fig. 2 and Fig. 3). At the instant of carbonaceous material feed termination at 2,5 days sludge age, a precipitous step change in the oxygen consumption rate was observed (Figs. 3 – 6). The oxygen consumption rate then continued for 1,5 to 2 hours at a rate approximately 90% of that measured prior to feed termination. This was followed by a period of approximately 5 hours during which the total oxygen consumption rate gradually decreased until, fairly abruptly, the rate steadied at that value associated with endogenous respiration. This behaviour subsequent to feed termination made it possible to determine relatively accurately the size of the step change in the oxygen consumption rate and therefore the fraction of energy required for the adsorption and storage of carbonaceous material. It also indicated that the storage of COD achieved such a high level that stored nutrient was available to sustain the high rate of synthesis for 1,5 to 2 hours after the instant of feed termination. It further indicated that the rate of utilization of stored material was a function of the stored material remaining – as the stored nutrient was depleted a concomitant reduction took place in the oxygen consumption rate. True endogenous respiration took place only after the stored material was completely metabolized.

Nitrification kinetics

The behaviour of the total oxygen consumption rate observed in the ammoniacal nitrogen cyclically fed unit (unit N) operating at 10 days sludge age also showed a rapidly decreasing total oxygen consumption rate after the instant of ammoniacal nitrogen feed termination similar to that of unit C (Fig. 2), although for the first half hour the decrease in the rate observed in unit N was substantially lower than that observed in unit C during the same period. However, this difference could not be regarded as proof of the hypothesis of an energy requirement for the adsorption of COD.

It has been generally agreed that the rate of nitrification is dependent, *inter alia,* on the concentration of nitrifying organisms. With high concentrations of nitrifying organisms, a condition usually found at longer sludge ages, the nitrification rate is therefore extremely rapid. This observation is substantiated from an inspection of the data measured during the 10 hour test performed on the ammoniacal nitrogen cyclically fed unit (unit N) while operated at 10 days sludge age (Fig. 2). The ammonia concentration in the reactor remained at less than 0,5 mgN/ℓ irrespective of whether the concentration was measured during the feed period of ammoniacal nitrogen or during the period during which no extra ammonia was added. This indicated that the extra ammonia fed to the unit during the period of ammoniacal nitrogen addition was nitrified rapidly. Therefore the rapid decrease in the total oxygen consumption rate after the instant of ammoniacal nitrogen feed termination results from a rapid decrease in the nitrification oxygen consumption rate.

In contrast, the behaviour of the total oxygen consumption rate at 2,5 days sludge age observed in the ammoniacal nitrogen cyclically fed unit (unit N) differs from that observed at 10 days sludge age (compare Fig. 2 and Fig. 3). At 2,5 days sludge age, a sludge age only about 20% longer than the minimum sludge age for nitrification, the concentration of nitrifying organisms is very low, resulting in a slow nitrification rate. The slow nitrification rate can be observed from the ammonia concentrations measured in the reactor. During the period in which ammoniacal nitrogen was added to the unit, nitrification proceeded so slowly that there was an increase in the ammonia concentration in the reactor, the concentration being about 10 mgN/ℓ just before the termination of the ammoniacal nitrogen feed period. After the ammoniacal nitrogen feed period, nitrification continued at virtually the same rate as during ammoniacal nitrogen feed period, causing a decrease in the ammonia concentration in the reactor, which in turn, results in the total oxygen consumption continuing at the same rate before and after the instant of ammoniacal nitrogen feed termination (Figs. 3, 4 and 5).

Energy Requirements for Adsorption

Before finally accepting the hypothesis of COD adsorption and its associated energy requirement, it was necessary to check whether or not domestic sewage, stored at 4°C for a period of up to two weeks has an immediate dissolved oxygen requirement without the presence of a bacterial mass. This was tested on two different domestic sewages as follows:

The dissolved oxygen was measured in the cold domestic sewage and was found to be zero. One litre of clean tap water at room temperature (± 20°C) was aerated in a 3 litre container until the dissolved oxygen concentration recorded was 8,8 mg0/ℓ. The aeration was then stopped and while still continuously recording the dissolved oxygen concentration, one litre of the domestic sewage was added to the saturated tap water. The dissolved oxygen concentration decreased immediately to 5,25 mg0/ℓ and thereafter decreased slowly until 30 minutes later the reading was 4,50 mg/ℓ. A similar behaviour was observed during the second test, indicating that there is no immediate dissolved oxygen requirement by domestic sewage without the presence of a bacterial mass.

Accepting the hypothesis that there exists an energy requirement by the bacterial mass for the adsorption and storage of carbonaceous material, the mass of energy required to store a unit mass of carbonaceous material (COD) can be calculated from the size of the step change in the total oxygen consumption rate as the discontinuity is independent of nitrification. Taking the difference between the averages of the total oxygen consumption rates measured over approximately 2,5 hours before and 1,5 hours after feed termination, the average step change measured was 6,12 mg0/ℓ/h. The flow rate of biodegradable COD per unit reactor volume is:

$$q_{COD} = (S_i - S)Q/V$$

where

Q = Feed rate (ℓ/h) = 1,67 (20 ℓ in 12 hours)
V = Volume of reactor (ℓ) = 6,5

The average biodegradable COD, $(S_i - S)$ was approximately 305 mg COD/ℓ,

i.e.

$$q_{COD} = 305.1{,}67/6{,}5 = 78{,}1 \text{ mg COD/ℓ/h}$$

Therefore the percentage energy required for adsorption and storage is

6,12.100/78,1 = 7,8%

This value compares very well with the value of 7% found in the work on the adsorption phase in biological denitrification by Wilson and Marais (1976). The fact that such similar values of the percentage energy required for adsorption are obtained under aerobic conditions, in which oxygen is the final electron acceptor and under anoxic conditions in which nitrate is the final electron acceptor, seems to support the general validity of the adsorption hypothesis.

Model Verification

The mathematical model of Ekama and Marais (1977) was modified to incorporate the results obtained in this investigation. The formulations for nitrification in accordance with the Monod equation of specific growth rate of *nitrosomonas* were reinstated in the model. Adsorption energy requirements were incorporated on the basis that 7% of the COD disappearing from the liquid to the storage phase is required to provide energy for storage, an identical mass of oxygen is utilized for this purpose. The influent TKN fractions of ammonia and organic bound nitrogen were taken as those measured experimentally, i.e. approximately 80% free and saline ammonia and 20% organic bound nitrogen. The mathematical model was then applied to predict the response in all the experimental 24-hour intensive tests reported by Ekama and Marais (1977). The theoretically calculated and experimentally measured responses of two of these tests are shown in Figs. 7 and 8 which correspond to Figs. 6 and 31 in the paper by Ekama and Marais (1977). A comparison of previous and present simulations with experimental data indicates a significant improvement in the predictive capabilities of the modified mathematical model, in the oxygen consumption rate, TKN and nitrate responses at both 2,5 and 20 days sludge ages.

The modified model, unaltered in its basic kinetic formulations, has been applied to series configurations of the activated sludge process under constant and dynamic loading conditions and also the contact-stabilization activated sludge process. In all these processes the modified model appeared to simulate the behaviour adequately. Application of the model to these processes will be considered in detail in a later paper.

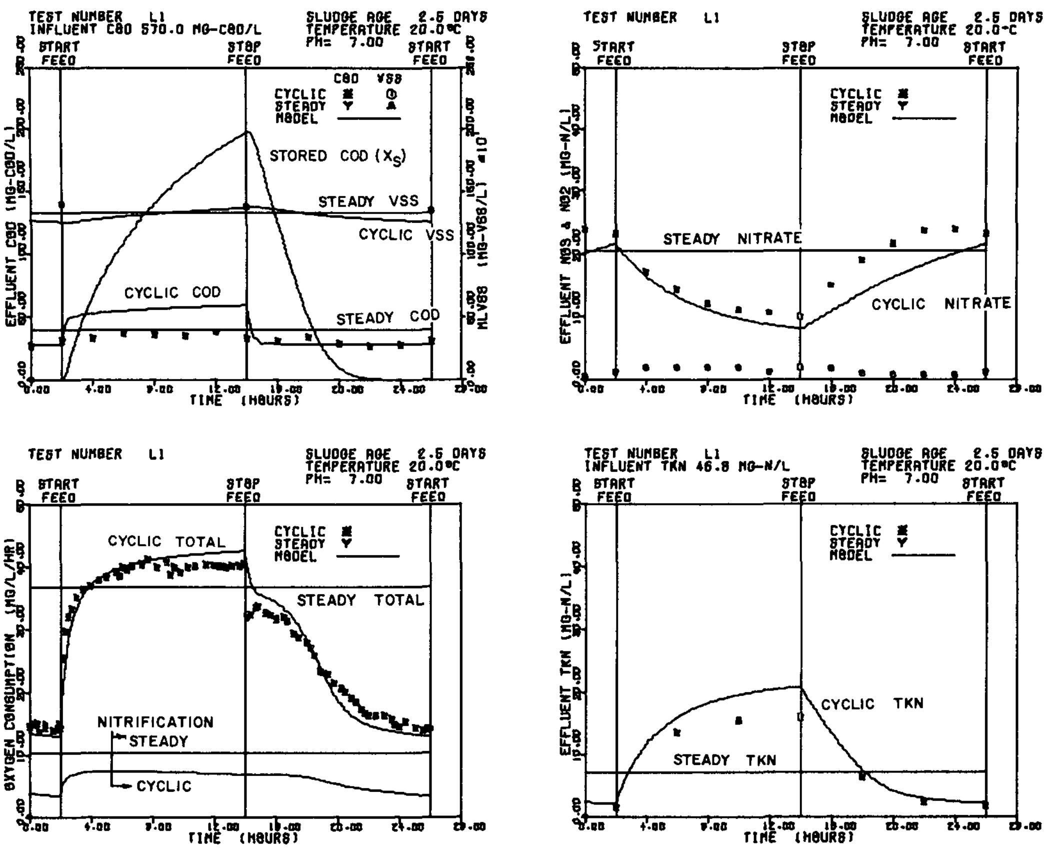

Figure 7

Comparison of experimental and theoretical response waves in a square wave cyclically loaded activated sludge unit operated at 2,5 days sludge age, pH = 7,00 and temperature 20°C

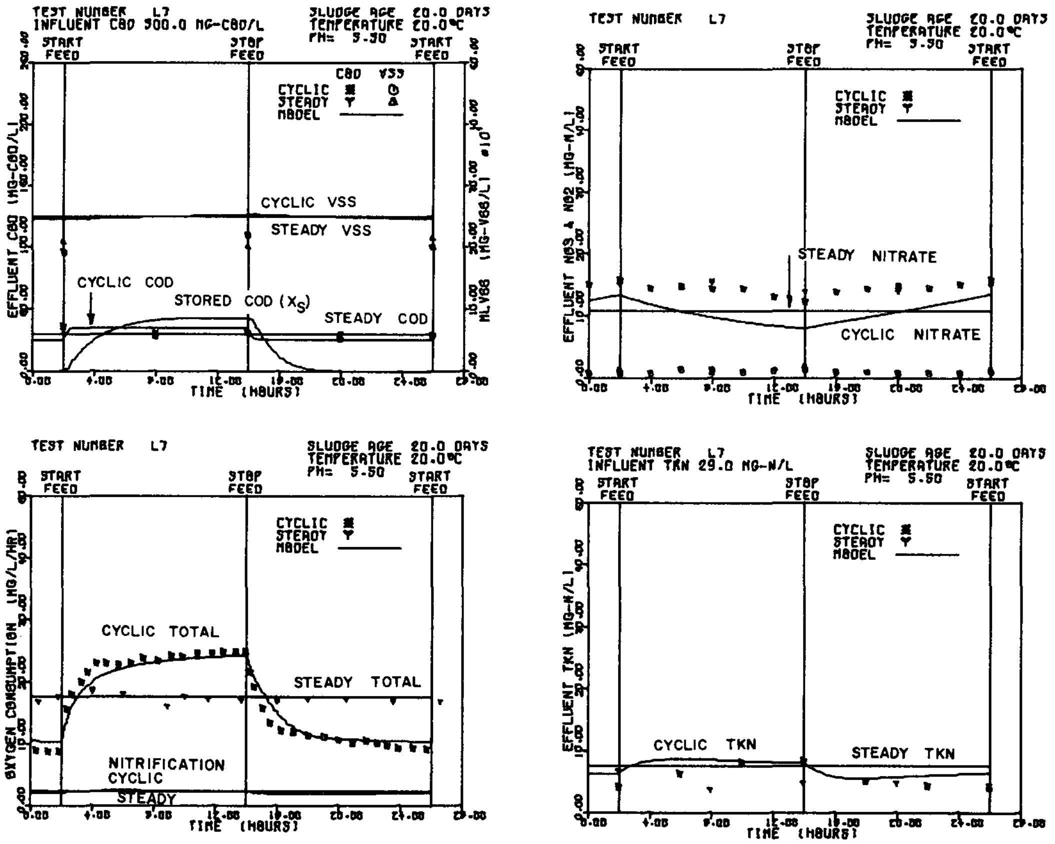

Figure 8

Comparison of experimental and theoretical response waves in a square wave cyclically loaded activated sludge unit operated at 20 days sludge age, pH = 5,50 and temperature 20°C

Conclusion

By incorporating an energy requirement for the adsorption of substrate in the mathematical model for the completely mixed activated sludge process presented by Ekama and Marais (1977), it has been found possible to reinstate the widely accepted nitrification kinetic equation based on formulation for specific growth rate and to accept the experimentally measured nitrogen fractions of the influent TKN, thereby resolving the inconsistencies of their original model.

Appendix A

Test methods

All tests, other than influent and effluent tests, were conducted on centrifuged supernatant samples, except in the measurement of MLSS and MLVSS. The methods for measuring the COD, TKN and NH_3 concentrations are those described in "Standard Methods for the Examination of Water And Wastewater" (1971). The MLSS and MLVSS concentrations were determined from the solids accumulated in the bottom of the centrifuge tube as follows: The supernatant was decanted carefully so that no solids were lost. The solids were then washed onto a clean and dry evaporating dish, the weight of which was recorded, with distilled water. The sample was then dried at 105°C for 24 hours, cooled in a desiccator and weighed. The sample was then ignited at 550°C for 20 minutes, cooled in desiccator and weighed.

The nitrite and nitrate concentrations were measured by the auto-analyser, automated method. The testing methods followed are given in Technicon Auto-Analyser Methodology: these are Industrial Methods 33.68 and 35.69W.

Temperature was measured with a mercury bulb thermometer graduated in 0,1°C divisions. The dissolved oxygen concentration was measured with a Yellow Springs Oxygen Probe. The probe was calibrated as follows: The probe was immersed in a jar containing clean tap water. The jar contents, having been well aerated and stirred, were allowed to achieve a constant dissolved oxygen concentration. Because the jar contents were so well aerated it was assumed that the water achieved saturation with respect to dissolved oxygen when this concentration no longer increased. The value of the saturated dissolved oxygen concentration was read from tables for the respective temperature and pressure. The probe was first zeroed and then, while immersed in the jar contents, calibrated to that value taken from the tables.

Oxygen consumption rate was measured as follows: The dissolved oxygen concentration in the aeration tank was raised from the general operating concentration of about 2 to 3 mg/ℓ up to 6 to 7 mg/ℓ. Aeration was then stopped and the change in dissolved oxygen concentration was recorded with time for about six minutes, while the aeration tank was still being fed and well stirred. The total oxygen consumption rate was given by the slope of line (usually linear) of the dissolved oxygen concentration versus time plot.

The COD and TKN tests on the influent and effluent were done on unfiltered samples. Occasionally the influent was tested for NO_3-N and NO_2-N concentrations, these were always found to be less than 0,1 mg/ℓ.

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