COD AND NITROGEN MASS BALANCES IN ACTIVATED
SLUDGE SYSTEMS

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Abstract—COD and nitrogen balances were performed on four different types of laboratory-scale activated sludge system: aerobic, anoxic, anoxic-aerobic and anaerobic-anoxic-aerobic (biological excess phosphorus removal systems). The systems included a variety of configurations, with differing wastewater characteristics and operating parameters. The results suggest that good COD balances are to be expected in aerobic and anoxic-aerobic systems. Systems incorporating anaerobic zones exhibit low COD balances (less than 80%). Fermentation in the anaerobic zone apparently is implicated in this "loss" of COD. The consequences of the COD "loss" include both a significant decrease in oxygen requirements and in sludge production compared to aerobic or anoxic-aerobic systems. Possible mechanisms for the loss of COD and areas which require further study are discussed.

Key words—activated sludge, mass balances, COD, TKN, nitrification, denitrification, biological excess phosphorus removal (BEPR), fermentation, anaerobic stabilization

INTRODUCTION

Current understanding of activated sludge system behaviour has developed from observations on operating systems. These have been full-scale plants, pilot plants and laboratory-scale experimental systems. There is a fundamental requirement if conclusions drawn from analysis of experimental data are defensible; namely, that data gathered from the experimental system are reliable. Mass balances provide one way of checking the reliability of the data. Surprisingly this is seldom done, most likely because gathering the data to conduct these balances may necessitate additional sampling and monitoring of the experimental system, beyond that regarded as necessary for addressing a particular research problem. Also, in certain cases it may not be feasible to gather the required data; for example, on a full-scale plant with dynamic influent loading.

Two balances which often can be applied to experimental data are for chemical oxygen demand (COD) and nitrogen (N). In addition to reflecting the validity of experimental data, results of mass balance calculations can also be used to investigate process behaviour, leading to an improved understanding of the underlying mechanisms.

This paper reviews the results of COD and nitrogen mass balances on laboratory-scale activated sludge systems with a range of configurations, operating parameters and influent wastewater characteristics.

In the discussion of results, emphasis is on nutrient removal systems. In the biological excess phosphorus removal (BEPR) systems investigated in this study, the results of COD balances suggest the possibility of fermentative processes occurring in the anaerobic zone, leading to a "loss" of COD from the system.

DATABASE FOR COD AND NITROGEN MASS BALANCES

Comprehensive data are required to perform COD and N mass balances. The data set includes information on operating parameters (flows, recycle rates, sludge wastage, etc.), influent and effluent concentrations of COD, TKN and nitrate, as well as the concentration of nitrate in each reactor, the oxygen utilization rate(s) and the volatile suspended solids (VSS) concentration of the waste sludge. In addition, the COD/VSS ratio and the TKN/VSS ratio should also be reported.

The complete data set seldom is available for systems which receive a time-varying (i.e. dynamic input of flow and/or concentration. Also, for dynamic systems, it is necessary to consider accumulation terms in mass balance calculations; this complicates the procedure considerably. All of the systems considered in this paper were operated under "steady state" conditions as far as is practical. That is, the systems each received a fixed influent volume per day at a constant rate, and the composition of the influent was nearly uniform from day to day. Also, a fixed volume of mixed liquor was removed.
from the systems each day to maintain a constant sludge age (SRT, MCRT). Where municipal wastewater was used as influent, the influent was prepared by diluting high-strength wastewater to a target COD concentration for the duration of each study. Because the wastewater was drawn from the same source, the composition (TKN/COD ratio, unbiodegradable fractions, etc.) remained reasonably constant.

An important aspect regarding steady-state data is that the system necessarily should be operated for an extended period (3-4 sludge ages) to ensure attaining a "steady" operating condition. Even under this condition there will be fluctuations in the values of monitored parameters from day to day. Therefore it is essential that data used in mass balances should be averages obtained over an extended period after attaining steady state. This will account for small fluctuations in response. Also, averaging over an extended period avoids the necessity to include accumulation terms in mass balance calculations. In the mass balances reported here the steady-state data were gathered in this manner.

Data from five sources for four different types of activated sludge system were used in this investigation:

- aerobic systems—Schroeter et al. (1982)
- anoxic only systems—McClintock et al. (1988)
- anoxic-aerobic systems—Arkley and Marais (1981)

**COD MASS BALANCES ON EXPERIMENTAL DATA**

The premise of a COD balance is that it should be possible to account for the COD entering an activated sludge system via the influent in the following fractions:

- COD (unfiltered) leaving the system in the effluent
- COD incorporated into the sludge mass through cell synthesis, enmeshment or absorption, leaving the system in the sludge wastage stream
- COD oxidized (i.e. the electrons which are transferred from the organic material to the electron acceptor). In purely aerobic systems this fraction can be estimated from the oxygen utilization rate (after deducting the oxygen required for nitrification). In systems incorporating anoxic zones (that is, where nitrate is present but oxygen is not), it is also necessary to account for COD oxidized through denitrification.

The assumption here is that any COD loss due to volatilization of organics is negligible. Also, it is assumed that denitrification under aerobic conditions is not significant. These aspects are discussed later.

In systems incorporating denitrification, the mass of COD oxidized through denitrification can be accounted for by estimating the equivalent amount of oxygen which would have been needed if oxygen had been the electron acceptor instead of nitrate. It has been proposed that denitrification is essentially a four step process (Payne, 1981).

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow N_2\text{O} \rightarrow N_2 \\
2e^- + 2\text{NO}_3^- + 2\text{H}^+ & \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} \\
e^- + \frac{1}{2}\text{NO}_3^- + \frac{1}{2}\text{H}^+ & \rightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{H}_2\text{O} \\
2e^- + 2\text{NO}_2^- + 2\text{H}^+ & \rightarrow 2\text{N}_2\text{O} + 2\text{H}_2\text{O} \\
\end{align*}
\]

The net reaction is obtained by combining the four equations:

\[
10e^- + 2\text{NO}_3^- + 12\text{H}^+ \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}
\]

or equivalently,

\[
e^- + \frac{3}{4}\text{NO}_3^- + 3\text{H}^+ \rightarrow \frac{3}{2}\text{N}_2 + \frac{3}{2}\text{H}_2\text{O}
\]

Similarly, the half reaction for the reduction of oxygen is given by:

\[
e^- + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}^+ \rightarrow \frac{1}{2}\text{H}_2\text{O}
\]

The above two equations imply that the transfer of one electron equivalent requires the reduction of 1/4 mol of oxygen or 1/5 mol of nitrate, i.e.:

\[
\frac{1}{4} \text{ mol nitrate} \equiv \frac{1}{5} \text{ mol oxygen}
\]

\[
\frac{3}{4} \text{ g NO}_3^- - \text{ N} \equiv \frac{3}{5} \text{ g oxygen}
\]

\[
1 \text{ mg NO}_3^- - \text{ N} \equiv 2.86 \text{ mg oxygen}
\]

The assumption here is that nitrate denitrified is converted to nitrogen gas (N₂), and that there is no release of intermediates (NO₂, NO, N₂O). If intermediates were released the factor of 2.86 would be lower.

A detailed description of the COD mass balance procedure is described in the Appendix.

**NITROGEN MASS BALANCES ON EXPERIMENTAL DATA**

In general, nitrogen enters the system in the form of organic N or ammonia. The influent TKN gives a measure of the amount of these compounds present. If the system is nitrifying, the majority of the influent TKN is converted to nitrate. If the system includes unaerated zones, then denitrification will result in the conversion of a portion of the nitrate to nitrogen gas (or the intermediates discussed above). Nitrogen leaving the system in the gaseous form can be estimated by performing a
Fig. 1. Aerobic system configuration utilized by Schroeter et al. (1982).

Fig. 2. Anoxic system configuration utilized by McClintock et al. (1988).

nitrate balance on the unaerated reactors. A fraction of the influent TKN is also utilized in cell synthesis, leaving the system in the sludge wastage system. Therefore, it should be possible to account for the mass of nitrogen in the influent in the following fractions:

- effluent TKN (unfiltered)
- effluent nitrate
- TKN of the waste sludge
- nitrogen converted to gaseous nitrogen through denitrification (if the system includes unaerated zones).

As with the COD balance, aerobic denitrification is not considered here. A significant amount of aerobic denitrification in a system would result in low COD and N balances.

A detailed description of the nitrogen mass balance procedure is described in the Appendix.

### AEROBIC SYSTEMS

Schroeter et al. (1982) operated four pairs of aerobic lab-scale systems at temperatures of 12 and 20°C. The systems were operated at sludge ages of 3, 8 and 20 days; two systems were operated at the 3 day sludge age for reasons discussed later. The influent consisted of domestic wastewater, diluted with tap water to a concentration of 500 mgCOD/l. All systems were single reactor systems as shown in Fig. 1.

The results of mass balances for COD and N for the Schroeter et al. (1982) systems are listed in Table 1. The results are very good for all systems, regardless of whether nitrification was occurring (systems at the 3 day sludge age and 12°C were not nitrifying; all other systems nitrified fully). As the nitrogen balances are close to 100%, it is unlikely that aerobic denitrification occurred in these systems to a significant extent.

Initially only one system was operated at a 3 day sludge age; however, the COD balance obtained at 12°C was poor (81.7% versus N balance of 97.4%). Examination of the system indicated that inadvertent aeration due to turbulence at the reactor surface was the cause, leading to underestimates of the oxygen utilization rate. When the problem was remedied (by using a smaller stirrer paddle) two systems were operated in parallel and very good COD and N balances were obtained for both. This highlights the need for careful attention to experimental detail, and the utility of mass balances in checking the validity of experimental data.

### ANOXIC ONLY SYSTEMS

McClintock et al. (1988) operated lab-scale single reactor aerobic and anoxic systems in parallel at five different sludge ages. The 3 day sludge age systems were operated as flow through systems; systems at longer sludge ages were operated as single reactor systems with a baffle inserted to separate the mixed liquor zone from the sludge settling zone. Functionally the systems are shown schematically in Fig. 2. All systems received a synthetic sewage (primarily bactopeptone), with nitrate and oxygen supplied in excess to the anoxic and aerobic reactors, respectively. Unfortunately, as oxygen utilization rates were not reported, COD balances cannot be conducted on the aerobic systems.

Results of mass balances for COD and N for the McClintock et al. (1988) systems are listed in Table 2. COD balances on the anoxic systems ranged from approx. 95 to 85%, with a decreasing trend with increasing sludge age (except for the 15 day system); nitrogen balances are reasonable for all systems. (It should be noted that the data from the 15 day anoxic system is questionable as solids production in this system was reportedly greater than that for the 15 day aerobic system, while

<table>
<thead>
<tr>
<th>System</th>
<th>Sludge age (d)</th>
<th>N balance (%)</th>
<th>COD balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>100.2</td>
<td>99.6</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>100.2</td>
<td>99.7</td>
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<td>8</td>
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<td>99.6</td>
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<tr>
<td>4</td>
<td>20</td>
<td>99.2</td>
<td>99.4</td>
</tr>
</tbody>
</table>
the other anoxic systems were observed to produce approx. 40% less solids than the corresponding aerobic systems. Comparing these COD balance results with those for the Schroeter et al. (1982) aerobic systems, it appears that completely anoxic systems (especially at longer sludge ages) may exhibit poorer balances.

In considering possible explanations for the lower COD balances in anoxic systems, it is useful to consider the assumptions made in performing a COD balance on an anoxic system. The implicit assumption with an oxygen equivalence factor of 2.86 for nitrate denitrified is that denitrification is complete. If denitrification intermediates such as nitric oxide (NO) or nitrous oxide (N₂O) were released to the atmosphere, fewer electrons would be transferred per unit nitrate denitrified, and the equivalence factor would be lower than 2.86. If this were the case, the actual COD balance would be even lower than that calculated using a factor of 2.86. As these anoxic systems tend to have low COD balances, it seems unlikely that the release of denitrification intermediates is a major factor; therefore other possible causes for the lower COD balances should be considered (these are discussed later).

**ANOXIC-AEROBIC SYSTEMS**

Arkley and Marais (1981) operated lab-scale aerobic, pre-denitrification and post-denitrification systems. All systems were operated at a 20 day sludge age with municipal wastewater as influent. System 1 (operated as a control) was a single reactor aerobic system (Fig. 1). Systems 2, 3 and 4 were two-in-series reactor configurations operated in three possible modes: (i) both reactors aerated; or (ii) first reactor unaerated (pre-denitrification); or (iii) second reactor unaerated (post-denitrification). The pre- and post-denitrification system configurations are shown in Fig. 3. Data for the experimental study were reported for a number of phases corresponding to different operating modes. For example, System 2 was operated sequentially in a post-denitrification, a pre-denitrification and a fully aerobic mode in phases I, II and III, respectively (see Table 3). Table 3 also lists the unaerated volume (or mass) fractions for phases with unaerated reactors.

An important feature of the data is the nitrate concentration in the unaerated reactor in systems operated in the pre-denitrification mode. For System 2 (phase II, with an unaerated volume fraction of 0.4) the nitrate concentration in the unaerated reactor was approx. 14 mgN/L; that is, the reactor was anoxic. For System 4 (phases II and IV, with a larger unaerated volume fraction of 0.7) the nitrate concentration in the unaerated reactor was essentially zero; that is, the reactor was anaerobic.

Results of mass balances for COD and N for the Arkley and Marais (1981) systems are listed in Table 3. Balances were performed only for those phases where the systems appeared to be at steady state. The following features are evident:

- COD balances on completely aerobic systems average approx. 95%
- the pre-denitrification system with an anoxic reactor (as opposed to anaerobic) exhibits a COD balance close to 100% (96.9%—System 2, phase II)
- the post-denitrification system with an anoxic reactor (as opposed to anaerobic) also exhibits a COD balance close to 100% (97.7%—System 2, phase I)
Table 3. COD and nitrogen mass balances for aerobic and anoxic-aerobic systems [data from Arkley and Marais (1981)]

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Type</th>
<th>Unequated N balance (%)</th>
<th>COD balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>Aerobic</td>
<td>0</td>
<td>99.0</td>
</tr>
<tr>
<td>1</td>
<td>II</td>
<td>Aerobic</td>
<td>0</td>
<td>93.4</td>
</tr>
<tr>
<td>1</td>
<td>III</td>
<td>Aerobic</td>
<td>0</td>
<td>99.4</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>Post-denitrification</td>
<td>0.40</td>
<td>99.2</td>
</tr>
<tr>
<td>2</td>
<td>II</td>
<td>Predenitrification</td>
<td>0.40</td>
<td>102.3</td>
</tr>
<tr>
<td>2</td>
<td>III</td>
<td>Predenitrification</td>
<td>0.40</td>
<td>102.3</td>
</tr>
<tr>
<td>3</td>
<td>III</td>
<td>Predenitrification</td>
<td>0.40</td>
<td>102.3</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>Predenitrification</td>
<td>0.70</td>
<td>102.1</td>
</tr>
<tr>
<td>4</td>
<td>III</td>
<td>Predenitrification</td>
<td>0.70</td>
<td>102.1</td>
</tr>
<tr>
<td>4</td>
<td>IV</td>
<td>Predenitrification</td>
<td>0.70</td>
<td>102.1</td>
</tr>
</tbody>
</table>

- the pre-denitrification systems which maintained essentially anaerobic conditions in the unaerated reactor both exhibit COD balances below 80% (System 4, phase II and IV)
- the operating mode for System 4 sequentially was changed from pre-denitrification to fully aerobic and then returned to pre-denitrification in phases II, III and IV, respectively. The nitrate concentration in the unaerated reactor for phases II and IV achieved a steady-state value of zero. The COD balance changed from 77.3 to 98.1 to 74.2% as the operating mode changed
- nitrogen balances for all phases average close to 100%

These observations suggest that COD balances for both aerobic and anoxic-aerobic systems should be close to 100%. However, when an anaerobic condition exists in the system, the calculated COD balance is significantly lower; this phenomenon is discussed later.

**ANAEROBIC–ANOXIC–AEROBIC SYSTEMS**

Wentzel *et al.* (1990) provide comprehensive data for 30 lab-scale nutrient removal systems treating municipal wastewater. These systems varied in configuration, reactor sizes, recycle ratios, influent flowrates and were operated over a range of sludge ages from 3 to 21 days. There were five basic configurations as shown in Fig. 4: Phoredox, 3-stage Bardenpho, Johannesburg, University of Cape Town (UCT), and the modified UCT (MUCT) configuration. Data were reported for each system for a number of different batches of influent wastewater (denoted by a letter appended to the system number in Table 4). In addition, Wentzel *et al.* (1989) reported data for four different lab-scale enhanced culture BEPR systems with acetate as influent. The enhanced cultures (greater than 90% polyP organisms) were developed using modified Bardenpho and UCT systems operated at sludge ages of 7.5, 10 and 20 days.

![Fig. 4. NDBEPR system configurations for which Wentzel *et al.* (1989, 1990) reported data.](image-url)
Mass balances for COD and N were conducted on the data sets for which all the relevant data were reported; in certain instances VSS data were omitted and it was not possible to calculate balances. In certain of the remaining cases for the mixed culture systems treating municipal wastewater, the validity of the data was questionable. This was generally reflected by very poor N balances; for example, balances of 200% output N compared to input N. Those data sets were not considered here. Table 4 presents results of COD and N mass balance calculations for the mixed culture systems with N balances between 90 and 110%, as well as the enhanced culture systems. The following observations are noted:

- COD balances on the BEPR systems treating municipal wastewater are generally substantially lower than those for the non-BEPR systems described earlier (some systems show balances below 70%)
- the average of the COD balances for the mixed culture BEPR systems with municipal wastewater as influent is only 78%
- COD balances for the enhanced culture systems with acetate as influent are all close to the average of 91% for these systems
- N balances for both the mixed culture and the enhanced culture BEPR systems are close to 100%

These results suggest that the presence of an anaerobic zone may lead to an appreciable reduction in the calculated COD balance for systems with a fermentable substrate (such as domestic wastewater).

### DISCUSSION

The following points summarize the results for COD and N balances conducted on the four types of activated sludge systems:

- COD balances on the completely aerobic systems are close to 100%
- COD balances on the anoxic only systems range from 95 to 85%, possibly with a decreasing trend as the sludge age increases
- the anoxic-aerobic systems which did not exhibit anaerobic conditions show COD balances close to 100%, while those in which the unaerated reactor nitrate concentration dropped to zero have balances less than 80%
- the average of the COD balances for the mixed culture BEPR systems with municipal wastewater as influent is only 78%. The average for the enhanced culture BEPR systems with acetate as influent is 91%
- nitrogen balances for all systems are close to 100%. This would indicate that nitrogen loss through denitrification under aerobic conditions was not significant for these systems.

The most significant finding is that for systems incorporating anaerobic zones (i.e. BEPR systems) the COD balances, averaging less than 80%, do not account for a substantial portion of the influent COD.

This apparent "loss" of COD in BEPR systems with anaerobic zone has been reported previously, for example, by Burke et al. (1986) in a study on short

<table>
<thead>
<tr>
<th>System Type*</th>
<th>Sludge age (d)</th>
<th>N balance (%)</th>
<th>COD balance (%)</th>
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<tr>
<td>Systems with municipal wastewater as influent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a Phoredox</td>
<td>3</td>
<td>93.9</td>
<td>79.4</td>
</tr>
<tr>
<td>1b Phoredox</td>
<td>3</td>
<td>109.8</td>
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<td>Enhanced culture systems with acetate as influent</td>
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<td>4 Bardenpho</td>
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<tr>
<td>Averages</td>
<td></td>
<td>97.8</td>
<td>90.7</td>
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</tbody>
</table>
sludge age BEPR systems. Bordacs and Tracy (1988) observed that the presence of an anaerobic zone leads to as much as a 30% reduction in oxygen requirements compared to a conventional aerobic process. However, the study was based on the assumption that the reduction in oxygen consumption is due to the retention of organic storage products (such as PHB) by the polyP organisms, and COD measurements were not made. Dold (1990) noted that, unless COD loss associated with anaerobic fermentation was taken into account, BEPR activated sludge models over predict both oxygen consumption rates in aerated zones of BEPR systems and volatile suspended solids production.

A requisite for BEPR is the presence of an anaerobic zone which allows the polyP organisms to sequester short chain fatty acids (SCFA) such as acetate. These SCFAs are stored by the organisms in the form of PHB until an electron acceptor is available. The stored PHB is then used for growth and P uptake. Generally the influent waste contains only a very low concentration of SCFA; therefore the SCFA necessary for BEPR must be produced within the system, likely in the anaerobic reactor through a fermentative process. The production of SCFA under anaerobic conditions has been observed by Meganck et al. (1985). It was noted that significant numbers of the bacteria Aeromonas hydrophila, a facultative organism capable of utilizing some sugars and alcohols under anaerobic conditions, were present in sludge from a lab-scale BEPR system. Production of SCFA in the anaerobic zone of BEPR systems presumably results from the fermentation of the “complex” readily biodegradable COD in the influent (i.e. the SCFA are produced via the oxidation of the influent complex readily biodegradable COD using an internally supplied organic compound as the oxidizing agent). This hypothesis is supported by the work of Bordacs and Chiesa (1989) who used radio-labelled substrates (glucose and acetate) to track the carbon flow in phosphorus accumulating cultures. Results indicated that a greater percentage of the labelled carbon was converted to carbon dioxide under anaerobic conditions when glucose was the labelled substrate compared to acetate (12 and 2%, respectively).

The “loss” of COD in BEPR systems most likely is associated with the fermentation process occurring in the anaerobic zone. However, a full understanding of the fermentation behaviour does not exist. It has been suggested that the COD “loss” is due to release of gaseous fermentation products (excluding carbon dioxide which does not have a COD).

Burke et al. (1986) suggested that generation of hydrogen gas occurs during the acidogenesis process in the anaerobic reactor. Many facultative organisms have been documented that are capable of fermenting glucose to produce hydrogen and carbon dioxide gases (Stanier et al., 1976). Among these are some species of the genus Aeromonas, mentioned earlier as one of the organisms found to occur in significant numbers in BEPR pilot plants (Meganck et al., 1985; Malnou et al., 1984).

A possible alternative to hydrogen as a gaseous COD loss would be generation of methane during fermentation. For the systems investigated in this study, theoretically methane production should not have been possible due both to the temperature at which these pilot plant systems were operated (20°C), and the fact that methanogenic bacteria are obligate anaerobes (Stanier, 1976) and would not likely survive the anaerobic/aerobic sequencing. However, this possibility should not be ignored as methanogenic bacteria capable of tolerating low oxygen concentrations have been documented (Grady and Lim, 1980).

An alternative theory to explain the significant disappearance of COD in BEPR systems is the hypothesis that fermentation in the anaerobic reactor results in the production of volatile compounds, which are then released from the system under aerobic conditions. The production of volatile compounds (such as ethanol, acetic acid and other volatile fatty acids) under oxygen limited conditions has been documented for a number of facultative organisms (Stanier et al., 1976; Vollbrecht, 1982). A recent study by Wable and Randall (1992) proposed that this is a more probable mechanism for COD loss than that of hydrogen or methane generation. However, the volatilization mechanism seems unlikely as these readily biodegradable components should be removed from solution prior to the aerated zone.

Aside from the observations on BEPR systems treating municipal wastewater, this study has identified two additional aspects which require further research:

- results from anoxic only systems indicate that COD “loss” occurs to a limited extent in these systems; this may also be associated with fermentation. Generally the perception is that fermentation should not occur in anoxic zones of activated sludge systems. However, fermentation has been observed in the presence of nitrate in pure culture studies (Hadjipetrou and Stouthamer, 1965; Stouthamer and Bettenhausen, 1972)
- in the enhanced culture systems with acetate as influent the COD balances do not account for approx. 10% of the input COD. Fermentation in these systems should be minimal. The COD “loss” possibly is associated with the process of PHB formation.

CONCLUSIONS

The results of this study suggest that while good COD balances are to be expected in aerobic
and aerobic-anoxic systems, systems incorporating anaerobic zones (i.e. BEPR systems) tend to exhibit low COD balances (less than 80%). This "loss" of COD apparently is associated with the fermentation processes occurring in the anaerobic zone of BEPR systems treating municipal wastewater. Whether this COD loss is a direct result of fermentation (through the generation of gas which evolves during the actual fermentation process), or an indirect result (through the production of volatile compounds which are released from the system under aerated conditions), remains to be determined.

Irrespective of the reason(s) for the COD "loss", this phenomenon has significant implications with regards to reduced aeration costs and sludge production in BEPR versus conventional activated sludge systems. If the causes of this loss of COD can be determined, it may be possible to design and/or operate systems so as to maximize COD loss thereby reducing the cost of aeration and sludge treatment/disposal.

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REFERENCES


APPENDIX

COD and N Balance Calculations

1. Nomenclature

\[ Q = \text{average influent flowrate (l/d)} \]
\[ q = \text{average wastage flowrate (l/d)} \]
\[ S_{in} = \text{total influent COD (mgCOD/l)} \]
\[ S_{e} = \text{total effluent COD (mgCOD/l)} \]
\[ j = \text{COD/VSS ratio (mg COD/rag VSS)} \]
\[ j_{l} = \text{mixed liquor volatile suspended solids of waste stream (mg VSS/l)} \]
\[ j_{O} = \text{total oxygen utilization rate (mg O/l/h)} \]
\[ M_{O} = \text{mass of oxygen consumed for nitrification (mg O/d)} \]
\[ V_{re} = \text{volume of aerobic reactor (litres)} \]
\[ N_{N} = \text{average influent TKN (mg N/l)} \]
\[ N_{e} = \text{average effluent TKN (mg N/l)} \]
\[ N_{a} = \text{average effluent nitrate (mg NO3-N/l)} \]
\[ N_{at} = \text{average aerobic nitrate (mg NO3-N/l)} \]
\[ N_{N,anox} = \text{average anoxic nitrate (mg NO3-N/l)} \]
\[ N_{N,anox} = \text{average anaerobic nitrate (mg NO3-N/l)} \]
\[ j_{s} = \text{nitrogen fraction of waste sludge (mg N/l)} \]
\[ s = \text{settler underflow recycle ratio with respect to influent flowrate} \]
\[ r = \text{anoxic mixed liquor recycle ratio} \]
\[ a = \text{nitrified/aerobic mixed liquor recycle ratio} \]
\[ M_{den, anox} = \text{mass of nitrate denitrified in the anoxic zone (mg N/d)} \]
\[ M_{den, anox} = \text{mass of nitrate denitrified in the aerobic zone (mg N/d)} \]
\[ M_{den, T} = \text{mass of nitrate denitrified in the system (mg N/d)} \]
\[ M_{COD, eff} = \text{mass of COD in the system effluent (mg COD/d)} \]
\[ M_{COD, wastage} = \text{mass of COD in the wastage stream (mg COD/d)} \]
\[ M_{COD, eff} = \text{mass of COD oxidized under aerobic conditions (mg COD/d)} \]
\[ M_{COD, denote} = \text{mass of COD oxidized through denitrification (mg COD/d)} \]
\[ M_{COD, total} = \text{mass of COD oxidized in the system (mg COD/d)} \]
(II) Denitrification calculations

In nitrifying systems with unaerated zones, in order to perform both COD and N balances, the mass of nitrate which is denitrified in each of the unaerated reactors must be determined from mass balance on nitrate. Referring to Fig. A1, for a UCT type system, the mass of nitrate entering the anoxic reactor per day is given by:

\[ M_{\text{N, in}} = aQN_{\text{N,in}} + sQN_{\text{N,in}} + (1 + r)QN_{\text{N,answer}} \]

Similarly, the mass of nitrate leaving the anoxic reactor is determined from mass balance on nitrate. Referring to Fig. A1, for a UCT type system, the mass of nitrate entering the anaerobic reactor (assuming no nitrate in the influent), this implies that 14 mg NH₄-N require 64 mg oxygen, or equivalently, if x mg 1 of NO₃-N are formed, then 4.57x mg O₂ are consumed. In a purely aerobic system, the mass of nitrate formed is given by the product of the influent flowrate and the effluent nitrate concentration \( N_{\text{Ne}} \). For systems incorporating denitrification, the mass of nitrate formed is given by:

\[ \text{mass nitrate formed} = M_{\text{denit,in}} + QN_{\text{N,Ne}} \]

Thus the mass of oxygen consumed due to nitrification \( MO_N \) is given by:

\[ MO_N = (M_{\text{denit,in}} + QN_{\text{N,Ne}})4.57 \]  

Therefore the total mass of COD oxidized per day under aerobic conditions \( M_{\text{COD,aer}} \), is given by:

\[ M_{\text{COD,aer}} = O_1 V_{\text{aer}} 24 - MO_N \]

Although equation (A6) represents a simplification of the actual reactions mediated by the nitrifying organisms *Nitrosomonas* and *Nitrobacter*, the error introduced by this simplification should be minimal (Grady and Lim, 1980).

(III) COD balance calculations

To perform a COD balance on a system, it is necessary to estimate the mass of COD in the effluent, the COD of the waste sludge, and the amount of COD oxidized. If the effluent COD is known, the mass of COD in the effluent is simply:

\[ M_{\text{COD,eff}} = QS_T \]  

Similarly, if the volatile suspended solids concentration of the waste sludge \( X_v \), is known, then by assuming a value 2 of 1.48 mg COD/mg VSS for \( f_{CV} \), the mass of COD wasted is given by:

\[ M_{\text{COD,wa}} = qX_v f_{CV} \]

Ideally, the COD/VSS ratio \( f_{CV} \) should be determined experimentally for a particular sludge; however, the value of 1.48 mg COD/mg VSS has been shown to be a good approximation over a range of sludge ages and wastewater characteristics (Schroeter *et al.*, 1982).

In a purely aerobic system, the amount of COD oxidized is determined from the oxygen utilization rate, after deducting the oxygen required for nitrification. This can be done by assuming the somewhat simplified relationship:

\[ \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \]  

Equation (A6) implies that 1 mol of ammonia requires 2 mol of oxygen to form 1 mol of nitrate. Taking molecular weights into account, this implies that 14 mg NH₄-N require 64 mg oxygen, or equivalently, if x mg 1 of NO₃-N are formed, then 4.57x mg O₂ are consumed.

In systems incorporating unaerated zones, the mass of COD oxidized through denitrification must also be taken into account in the COD balance. This is done by using the equivalence factor of 2.86 outlined earlier. Thus if \( M_{\text{denit,T}} \) is the total mass of nitrate denitrified per day, then the total COD consumed through denitrification is given by:

\[ M_{\text{COD,deni}} = 2.86M_{\text{denit,T}} \]

Therefore the total amount of COD oxidized in a system incorporating both nitrification and denitrification, is given by:

\[ M_{\text{COD,oxid}} = M_{\text{COD,deni}} + M_{\text{COD,aer}} \]

\[ = 2.86M_{\text{denit,T}} + O_1 V_{\text{aer}} 24 - (M_{\text{denit,T}} + QN_{\text{N,Ne}})4.57 \]  

The total amount of "output" COD can therefore be determined from the sum of \( M_{\text{COD,eff}} \), \( M_{\text{COD,wa}} \) and \( M_{\text{COD,oxid}} \) using equations (A4), (A5) and (A10), as well as the estimate for \( M_{\text{denit,T}} \) obtained from mass balances on nitrate around the unaerated reactors (as described earlier for the UCT system), i.e.:

\[ \text{output COD} = M_{\text{COD,eff}} + M_{\text{COD,wa}} - M_{\text{COD,oxid}} \]
The total mass per day of "input" COD is given by the product of the influent flowrate and the influent COD, i.e.:

\[
\text{input COD} = QST_i
\]

Thus the % COD balance is given as:

\[
\% \text{ COD balance} = \left( \frac{\text{output COD}}{\text{input COD}} \right) \times 100
\]

(IV) Nitrogen balance calculations

To perform a nitrogen balance on a system, it is necessary to estimate the mass of nitrate in the effluent, the mass of effluent TKN (unfiltered), the mass of TKN in the waste sludge and the nitrogen loss through denitrification.

In terms of the variables defined earlier, the mass of nitrate in the effluent \(M_{N,N,\text{eff}}\) is given by:

\[
M_{N,N,\text{eff}} = QN_{N,\text{eff}} \tag{A13}
\]

Similarly, the mass of TKN in the effluent \(M_{N,T,\text{eff}}\) is given by:

\[
M_{N,T,\text{eff}} = QN_{T,\text{eff}} \tag{A14}
\]

To estimate the mass of N in the waste sludge, a value for \(f_N\), the nitrogen fraction of the sludge, must be assumed. Experimental evidence suggests a value of 0.1 mg N/mg VSS is reasonable over a range of sludge ages (WRC, 1984); however, ideally \(f_N\) should be determined experimentally for a particular system and set of operating parameters. Given a value for \(f_N\), the mass of N in the waste sludge \(M_{N,\text{was}}\) is calculated from:

\[
M_{N,\text{was}} = qX_v f_N \tag{A15}
\]

In Section II the method was outlined for estimating the mass of NO\(_3\)-N which is denitrified in the unaerated reactors. For a UCT system, \(M_{\text{denit},\text{unaer}}\) is calculated using equations (A1), (A2) and (A3).

The total output N is therefore the sum of \(M_{N,N,\text{eff}}\), \(M_{N,T,\text{eff}}\), \(M_{N,\text{was}}\) and \(M_{\text{denit},\text{unaer}}\), which can be calculated using equations (A13), (A14) and (A15), as well as the estimate for \(M_{\text{denit},\text{reaer}}\) obtained from a mass balance on nitrate, i.e.:

\[
\text{output N} = M_{N,N,\text{eff}} + M_{N,T,\text{eff}} + M_{N,\text{was}} + M_{\text{denit},\text{reaer}} \tag{A16}
\]

The total mass per day of input N is given by the product of the influent flowrate and the influent TKN (assuming zero nitrate in the influent), i.e.:

\[
\text{input N} = QN_{T_i} \tag{A17}
\]

Therefore the % N balance is given as:

\[
\% \text{ N balance} = \left( \frac{\text{output N}}{\text{input N}} \right) \times 100
\]

Using System 6a from Wentzel et al. (1990) as an example, the following section outlines the mass balance procedure.

(V) COD and N balances—example calculations

The data necessary for performing N and COD balances for System 6a are listed in Table A1. System 6a is a UCT configuration with two aerobic reactors, one anoxic and one anaerobic reactor as shown.

Denitrification calculations. The mass of NO\(_3\)-N denitrified in the anaerobic reactor is given by equation (A1):

\[
M_{\text{denit},\text{anaer}} = 402.5 \text{ mg N/d}
\]

The mass of NO\(_3\)-N denitrified in the anaerobic reactor is obtained from equation (A2):

\[
M_{\text{denit},\text{anaer}} = 12.5 \text{ mg N/d}
\]

The total mass of NO\(_3\)-N denitrified in the system is the sum of \(M_{\text{denit},\text{anaer}}\) and \(M_{\text{denit},\text{reaer}}\) given by equation (A3):

\[
M_{\text{denit},T} = 415 \text{ mg N/d}
\]

COD balance calculations. From equation (A4), the mass of COD in the effluent is:

\[
M_{\text{COD,eff}} = 1000 \text{ mg COD/d}
\]

The mass of COD in the waste sludge is calculated using equation (A5):

\[
M_{\text{COD,was}} = 3649 \text{ mg COD/d}
\]

Using equation (A10), and the value for \(M_{\text{denit},T}\) calculated above, the mass of COD oxidized is:

\[
M_{\text{COD,reaer}} = 3899 \text{ mg COD/d}
\]

The total output COD is the sum of the above three terms [or equation (11)]:

\[
\text{output COD} = 8548 \text{ mg COD/d}
\]

Applying equation (12) gives:

\[
\text{input COD} = 12,750 \text{ mg COD/d}
\]

Therefore, the % COD balance is given by:

\[
\% \text{ COD balance} = \frac{\text{output COD}}{\text{input COD}} \times 100 = 67.0\%
\]

The results of the COD balance for System 6a are shown in Table A2.

Nitrogen balance calculations. Referring to equation (A13), the mass of NO\(_3\)-N in the effluent is:

\[
M_{N,N,\text{eff}} = 263 \text{ mg N/d}
\]

From equation (A14), the mass of TKN in the effluent is:

\[
M_{N,T,\text{eff}} = 100 \text{ mg N/d}
\]

Table A2. COD balance calculations for System 6a [data from Wentzel et al. (1990)]

<table>
<thead>
<tr>
<th>Input COD (mg COD/d)</th>
<th>Output COD (mg COD/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QST_i 12.750</td>
<td>M_{\text{COD,eff}} 1000</td>
</tr>
<tr>
<td>M_{\text{COD,reaer}} 3649</td>
<td></td>
</tr>
<tr>
<td>M_{\text{COD,was}} 3899</td>
<td></td>
</tr>
<tr>
<td>Total 12.750</td>
<td>Total 8548</td>
</tr>
<tr>
<td>% COD balance = 67.0%</td>
<td></td>
</tr>
</tbody>
</table>

Table A1. Steady-state data for the four-reactor UCT System 6a [data from Wentzel et al. (1990)]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>Anaerobic</th>
<th>Anoxic</th>
<th>Aerobic</th>
<th>Aerobic</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/l)</td>
<td>510</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>40</td>
</tr>
<tr>
<td>TKN (mg N/l)</td>
<td>42</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4</td>
</tr>
<tr>
<td>NO(_3) (mg N/l)</td>
<td>0.0</td>
<td>0.5</td>
<td>1.5</td>
<td>9.4</td>
<td>10.6</td>
<td>10.5</td>
</tr>
<tr>
<td>OUR (mg/l/h)</td>
<td>--</td>
<td>--</td>
<td>78</td>
<td>43</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>VSS (mg/l)</td>
<td>--</td>
<td>2100</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2100</td>
</tr>
</tbody>
</table>
Table A3. Nitrogen balance calculations for System 6a [data from Wentzel et al. (1990)]

<table>
<thead>
<tr>
<th>Input N (mg N/d)</th>
<th>Output N (mg N/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{N_T}$ 1050</td>
<td>$M_{N_{waste}}$ 263</td>
</tr>
<tr>
<td>$M_{N_{TC}}$ 100</td>
<td>$M_{N_{raw}}$ 247</td>
</tr>
<tr>
<td>$M_{down,T}$</td>
<td>415</td>
</tr>
<tr>
<td>Total 1050</td>
<td>Total 1024</td>
</tr>
</tbody>
</table>

% N balance = 97.5%

The mass of N leaving with the waste sludge is given by equation (A15):

$$M_{N_{waste}} = 247 \text{ mg N/d}$$

The total output N is then calculated by summing the above values, together with $M_{down,T}$ calculated earlier [i.e. equation (A16)], giving:

$$\text{output N} = 1024 \text{ mg N/d}$$

Equation (A17) is used to calculate the total input N:

$$\text{input N} = 1050 \text{ mg N/d}$$

Therefore the % N balance is given by:

$$\% \text{ N balance} = \left( \frac{\text{output N}}{\text{input N}} \right) \times 100$$

$$= \left( \frac{1024}{1050} \right) \times 100$$

$$= 97.5\%$$

The results of the nitrogen balance for System 6a are shown in Table A3.