**Experimental assessment and modelling of nitrate utilisation for primary sludge**

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Abstract

Electron acceptor utilisation potential of filtered primary sludge under anoxic conditions was experimentally investigated. Major kinetic and stoichiometric parameters were assessed by means of model evaluation of nitrate profile obtained in batch reactors. ASM1, modified for endogenous decay, and ASM3 were used for model simulation. Both models provided consistent interpretation of experimental data. ASM1 yielded $\mu_H$ and $Y_{HD}$ values of 6.1 d$^{-1}$ and 0.64 g cell COD(g COD)$^{-1}$ respectively for heterotrophic anoxic growth. The corresponding storage mechanism associated with ASM3 could be characterised by a $k_{STO}$ of 13 g COD (g COD d)$^{-1}$ and a $Y_{STO}$ of 0.78 g COD(g COD)$^{-1}$. The high $k_{STO}$ value suggests re-evaluation of the concept of readily biodegradable substrate as defined in ASM3 and tested in the study.

Keywords

ASM3; COD fractions; Endogenous Decay Model (EDM); nitrate utilisation; primary sludge; storage

Introduction

A significant COD removal is achieved in the primary settling of domestic sewage. The soluble fraction of primary sludge represents a potential of an additional organic carbon source for nutrient removal, where needed. This potential is obtained by hydrolysis and conversion of particulate COD into more easily biodegradable components through limited fermentation (Münch and Koch, 1999; Orhon et al., 2001). Little is known about the character of this fraction. Its nutrient removal potential needs to be expressed in a way that can be readily interpreted by process kinetics applicable to activated sludge systems.

In this context, this study reports the results of an experimental evaluation on the electron utilisation potential of filtered primary sludge under anoxic conditions. The study is designed to model and interpret nitrate utilisation rate (NUR) resulting from the biodegradation of filtered primary sludge in batch reactors. Significant kinetic and stoichiometric coefficients are determined in accordance with ASM1, modified for endogenous decay (EDM), and ASM3.

Materials and methods

Primary sludge was obtained, over a period of four months, from the Ataköy plant, a small wastewater treatment facility in Istanbul. Sludge samples were withdrawn from the underflow line of the primary clarifier operated with a hydraulic detention time of 1.5 hours. In the plant, primary sludge withdrawal was usually performed in a way to allow an average of 0.7 days for sludge detention time. COD was determined, for both centrifuged and filtered sludge samples passed through 0.45 µm membrane filters, in accordance with Standard Methods (APHA, 1998). Centrifugation of sludge was performed for five minutes at 10,000 rpm. The readily biodegradable COD content of the centrifuged sludge supernatant was determined in 1 l aerobic batch reactors on a respirometric basis (Ekama et al., 1986). Biomass was seeded from fill and draw reactors acclimatised to domestic sewage and operated under 24-h aerobic/24-h anoxic conditions, for a sludge age of 15 days. OUR levels were monitored by using a WTW OXIDIGI 550 oxygen meter. Nitrate ($S_{NO}$) profiles were determined.
obtained in 1-l volume anoxic reactors. Nitrite and nitrate-nitrogen analyses were performed on filtered samples, using a CHEMLAB autoanalyser. All laboratory experiments were conducted at room temperature (18–20°C).

Testing of the experimental data was performed by means of sensitivity analysis and model simulation, using the AQUASIM computer program developed by the Swiss Federal Institute for Environmental Science and Technology. ASM1 (Henze et al., 1987) modified for endogenous decay (EDM) (Orhon and Artan, 1994) and ASM3 (Gujer et al., 1999) were used for model evaluations.

**Results and discussion**

**COD fractionation**

COD content of centrifuged (C_{T1}) and filtered (S_{T1}) primary sludge was determined on 4 different samples reflecting different characteristics of incoming raw sewage and plant operation. The readily biodegradable COD fractions (S_{S1}) were calculated using specific OUR experiments, in accordance with the method defined by Ekama et al. (1986), using a heterotrophic yield value, Y_H, of 0.67 g cell COD (g COD)^{-1} previously computed for the same sewage. Similarly, for the soluble inert COD concentration, S_{I1}, an S_{I}/S_{T} ratio of 0.1 was adopted, as no specific measurements were made in this study for this purpose (Orhon et al., 1997). The soluble slowly biodegradable COD, S_{H1}, was computed from mass balance. The resulting COD fractionation is outlined in Table 1, together with the average data of the same domestic sewage (Avcıoğlu et al., 2001).

Inspection of the data in Table 1 reveals the following characteristics related to the quality of filtered primary sludge. (i) Both centrifuged and filtered COD vary in a wide range, depending on the quality of the influent and the performance of primary settling. (ii) The centrifuged primary sludge represents an average organic carbon potential of 1,300 mg l^{-1} COD, around three times that of domestic sewage. (iii) The filtered primary sludge has an average COD of 600 mg l^{-1}, five times more than the total soluble COD of domestic sewage, a clear indication of the solubilisation of particulate COD during settling. (iv) An average readily biodegradable COD, S_{S1}, of 285 mg l^{-1}, with an S_{I}/S_{T} ratio of 0.47, is associated with filtered primary sludge. These values, compared with S_{S1} = 20 mg l^{-1} and S_{I}/S_{T} = 0.15 characterising domestic sewage, show the magnitude of hydrolysis achieved in the settling tank, converting both particulate and soluble COD into readily biodegradable components.

**Nitrogen utilization rate experiments**

Nitrate utilization potential of filtered primary sludge samples was experimentally tested in anoxic batch reactors. The tests were started, as shown in Table 2, with initial soluble COD concentrations in the range of 95–330 mg l^{-1} and corresponding F/M ratios of 0.27–0.36 mg COD (mg VSS)^{-1}. The S_{NO} profiles obtained were evaluated by model simulation using EDM and ASM3, to identify appropriate values of significant model coefficients. Since these two models exhibit different characteristics in terms of processes and parameter

<table>
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<th>Run no</th>
<th>C_{T1} (mg COD l^{-1})</th>
<th>S_{T1}</th>
<th>S_{S1}</th>
<th>S_{I1}</th>
<th>S_{H1}</th>
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<tr>
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<td>395</td>
<td>175</td>
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<tr>
<td>2</td>
<td>2,300</td>
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<tr>
<td>3</td>
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<td>265</td>
<td>115</td>
<td>120</td>
<td>30</td>
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<tr>
<td>4</td>
<td>1,825</td>
<td>710</td>
<td>370</td>
<td>270</td>
<td>70</td>
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<td>360</td>
<td>130</td>
<td>20</td>
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</table>
definition, the main purpose was to investigate the compliance of experimental data with the model simulations using justifiable and consistent parameter values.

Sensitivity analyses. Prior to simulation studies sensitivity analyses were performed for both models, in order to assess the individual effects of kinetic and stoichiometric coefficients on S\text{NO} profiles. The results obtained for run 3 are illustrated in Figure 1 and Figure 2, for EDM and ASM3 respectively. For EDM, Y\text{HD} was found to exert a significant impact on the whole S\text{NO} profile while \( \mu_H \) was sensitive to a less extent between 1–2 hours. The other coefficients did not impose appreciable impact on S\text{NO} utilization. For ASM3, sensitivity analysis was performed for the recently introduced parameters, namely, the storage yield, Y\text{STOD}, the maximum storage rate, k\text{STO} and the saturation coefficient for storage, K\text{STO}, besides Y\text{HD} and \( \mu_H \). Among these parameters, Y\text{STOD} was dominantly effective on the entire electron acceptor consumption profile. Secondary effects were observed for k\text{STO} in the first phase and for Y\text{HD} in the second phase. \( \mu_H \) and K\text{STO} were observed to exert opposite but negligible effects.

Model calibration and validation with EDM. Model simulation was initiated using the generally adopted values of the coefficients in ASM1, except for \( \mu_H \) and Y\text{HD}. EDM could well be calibrated and validated with all the experimental data as in Figure 3, for an average \( \mu_H \) value of 6.1 d\(^{-1}\), comparable with the default value reported in the literature for acetate and domestic sewage (Avcıoğlu et al., 2001). Similarly, the appropriate Y\text{HD} could be defined with an average value of 0.64 g cell COD(g COD\(^{-1}\))\(^{-1}\), varying in a narrow range of 0.62–0.66 g cell COD(g COD\(^{-1}\))\(^{-1}\). The rates of hydrolysis used (k\text{HS} = 3 g COD(g CODd)\(^{-1}\); K\text{XS} = 0.01 g COD(g COD\(^{-1}\))\(^{-1}\) are similar to the rates reported by Orhon et al. (1999) for soluble hydrolyzable COD.

Model calibration and validation with ASM3. Similarly, model calibration and validation with ASM3 was performed for Y\text{STOD} and k\text{STO}, since nitrate utilization rate is mainly sensitive to biochemical storage kinetics. Values of other coefficients were adopted as suggested in ASM3. Figure 4 reflects a perfect fit of the experimental S\text{NO} profile from run

<table>
<thead>
<tr>
<th>Run No</th>
<th>F/M (mg COD (mg VSS)(^{-1}))</th>
<th>S\text{S1}</th>
<th>S\text{S2}</th>
<th>S\text{S3}</th>
<th>S\text{S4}</th>
<th>S\text{T1}</th>
<th>S\text{T2}</th>
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<td>175</td>
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<tr>
<td>4</td>
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<td>50</td>
<td>35</td>
<td>10</td>
<td>95</td>
<td>85</td>
<td>10</td>
<td></td>
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</table>

Table 2: Initial COD fractions of filtered primary sludge reactors in accordance with EDM and ASM3

Figure 1 The results of sensitivity analysis for run no 3 for EDM

Figure 2 The results of sensitivity analysis for run no 3 for ASM3
no 4. For four different runs $Y_{STD}$ and $k_{STO}$ values of 0.78 g COD (g COD)$^{-1}$ and 12–14 g COD (g COD d)$^{-1}$ were used. It should be noted that $Y_{STD}$ defined for filtered primary sludge matches well with the suggested level in ASM3. The $k_{STO}$ of 12–14 g COD (g COD d)$^{-1}$ is higher than its counterpart suggested in ASM3. It agrees well however, with the value of 12 g COD (g COD d)$^{-1}$ adopted by Koch et al. (2000) for the calibration of municipal sewage, and slightly higher than 10 g COD (g COD d)$^{-1}$ found to characterise acetate utilization under anoxic conditions in a parallel study (Avcıoğlu et al., 2001). The high $k_{STO}$ value may also be partly attributed, as an alternative explanation, to the assumption in model evaluations, defining all soluble COD, except the inert fraction, as readily biodegradable (Table 2), potentially increasing substrate to be readily converted into storage compounds. The resulting nitrate utilization can only be explained using a higher conversion rate (Avcıoğlu et al., 2001).

Conclusions
Filtered primary sludge incorporates a substantially higher electron utilisation potential through solubilisation of particulate COD and its further hydrolysis into readily biodegradable components. Nitrate utilisation profile provides a sensitive basis of evaluation for either anoxic heterotrophic growth or biochemical storage kinetics, depending on the model used. For filtered primary sludge, EDM defines $Y_{HD}$ and $\mu_H$ values generally accepted in the literature for simple compounds and domestic sewage. The biochemical storage kinetics as defined in ASM3 involves a $k_{STO}$ level of 12–14 g COD (gCOD.d)$^{-1}$, more than twice higher than the originally suggested value. The high storage rate observed can be explained by challenging the validity of the original guess on the value of $k_{STO}$ or the concept of COD fractionation introduced by ASM3.

Acknowledgements
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References


