Experimental Assessment of the Degradation of "Unbiodegradable" Organic Solids in Activated Sludge

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ABSTRACT: In current process models activated sludge consists of biodegradable and unbiodegradable organic fractions. Recent evidence suggests that this approach may not be accurate because some of this "unbiodegradable" material may indeed be degradable. To improve sludge production predictions, it is important to know to what extent the "unbiodegradable" organic fraction is degradable. Assuming that volatile suspended solids (VSS) is a measure of the sum of biodegradable and unbiodegradable organic solids and the integral of the oxygen uptake rate (OUR) is representative of the biodegradable organics, the combination of these measurements can be used to predict the change of unbiodegradable organic solids within an aerobic digestion batch experiment. This procedure was used to estimate degradation rates of "unbiodegradable" VSS between 0.006 to 0.029 d^{-1}. The advantage of the proposed method is that the degradation rate can be determined directly based on measurements and relies on a limited number of assumptions. *Water Environ. Res.*, **88,** 272 (2016).

KEYWORDS: activated sludge, decay, VSS, OUR, unbiodegradable organic compounds.

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Introduction

The prediction of sludge production and oxygen consumption in water resource recovery facilities (WRRFs) is a main objective of structured mathematical activated sludge models (ASMs) (Henze et al., 2000). However, sludge production is not only the result of solids accumulation and microbial growth on soluble substrate. It is also strongly influenced by concomitant aerobic biodegradation of organic solids. To elucidate the magnitude and characteristics of biodegradation in activated sludge, this paper deals with the experimental assessment of the degradation rate of formerly defined "unbiodegradable" organic solids in activated sludge.

In practice, the total mass of organic compounds in activated sludge mixed liquor suspended solids (MLSS) is measured as volatile suspended solids (VSS). However, to make this measurement usable for mass balances in activated sludge modeling, the VSS is converted into chemical oxygen demand (COD) units using eq 1:

$$X_{ORG} = VSS \cdot i_{cv} \quad (\text{mg COD/L}) \tag{1}$$

where X_{ORG} (in mg COD/L) represents particulate organic material and i_{cv} (in mg COD/mg VSS) is the COD content of the organic material.

Organic material in activated sludge models is regarded to be either biodegradable (X_{DEG}) or unbiodegradable (X_U) (see Figure 1 column A).

$$X_{ORG} = X_{DEG} + X_U \quad (\text{mg COD/L}) \tag{2}$$

The exponential decrease of X_{DEG} during aerobic digestion batch experiments means that biodegradation of X_{DEG} follows first order reaction kinetics (Metcalf and Eddy, 2004). Hence, X_{DEG} can be regarded as a homogenous substrate even if biologically X_{DEG} is the sum of many different organic substances like cell plasma, cell membrane, cell internal stored material like PHA or glycogen, and extracellular polymeric substances. In contrast, it is assumed that X_U is truly unbiodegradable and cannot be degraded biologically even at a slow rate.

However, comprehensive mechanistic activated sludge models (Dold et al., 1980; Marais et al., 1976) are based on a further fractionation of organic material. Ordinary heterotrophic organisms (X_{OHO}) are assumed to be the main organism group in active biomass in activated sludge and the majority of X_{OHO} is assumed to be biodegradable but there is also an unbiodegradable portion that is termed endogenous residue $X_{U,E}$ and is determined by eq 3:

$$X_{U,E} = f_{U,E} \cdot X_{OHO} \quad (\text{mg COD/L}) \tag{3}$$

where $f_{U,E}$ is the endogenous residue fraction of X_{OHO}. Consequently, X_{DEG} is the degradable subset of X_{OHO}:

$$X_{DEG} = (1 - f_{U,E}) \cdot X_{OHO} \quad (\text{mg COD/L}) \tag{4}$$

The ultimate biodegradable fraction (f_{DEG}) of X_{ORG} is determined with eq 5:

$$f_{DEG} = \frac{(1 - f_{U,E}) \cdot X_{OHO}}{X_{ORG}} \tag{5}$$

The endogenous residue fraction $f_{U,E}$ of X_{OHO} is assumed to be constant within typical municipal sludge and its value in the literature ranges from 0.15 to 0.23 (Ramdani et al., 2010). The magnitude and availability of $X_{U,E}$ in the MLSS (see Figure 1, column B) is mainly determined by the degradation of X_{OHO}, the so-called decay process which includes death, lysis, and predation by active biomass (van Loosdrecht et al., 1999). The

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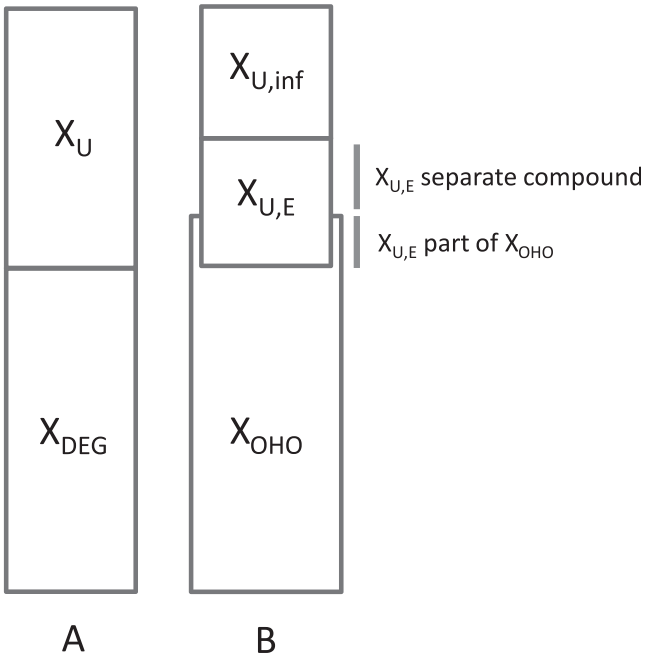

Figure 1—Major organic activated sludge components

decay of X_{OHO} is characterised by a constant first order rate parameter (b_{OHO}) (Gujer et al., 1999; Henze et al., 1987).

It is notable that the majority of the degradable material in the MLSS of an activated sludge process is associated with X_{OHO}, as the biodegradable organic material from the wastewater influent ($X_{DEG,inf}$) is assumed to be a very small fraction in activated sludge MLSS at a sludge retention time (SRT) of more than 3 days.

Another significant component of the activated sludge MLSS is the accumulated unbiodegradable solids fraction ($X_{U,inf}$) that entered the system in the influent. These solids accumulate in the mixed liquor depending on the influent loading and SRT of the system. Both fractions, the unbiodegradable endogenous residue $X_{U,E}$ and the influent unbiodegradable organic solids $X_{U,inf}$, contribute to the unbiodegradable activated sludge component X_U.

$$X_U = X_{U,E} + X_{U,inf} \quad (\text{mg COD/L}) \qquad (6)$$

Considering these three activated sludge components, X_{ORG} is given by eq 7 and visualized in Figure 1, column B:

$$X_{ORG} = X_{OHO} + X_{U,E} + X_{U,inf} \quad (\text{mg COD/L}) \qquad (7)$$

The existing ASM framework is based on experimental research within system boundaries between SRTs of 3 and 20 days. In this range, sludge production predictions are quite accurate (Henze et al., 2000; Menniti et al., 2012). However, outside of that SRT range (i.e., in membrane bioreactor [MBR], oxic settling anaerobic sludge process [OSA], and Cannibal systems) there seem to be deficiencies in the model predictions with regard to sludge production. In particular the phenomenon of "zero sludge production" as reported in Rosenberger et al. (2002), Pollice et al. (2004), and Laera et al. (2005) indicates that the degradation of organic material obviously cannot be explained with a single decay process. Therefore, recent research has focused on degradation processes in activated sludge and has addressed two basic assumptions of activated sludge modeling that have survived for more than four decades.

The first assumption is the unbiodegradable characteristics of X_U. Nowak et al. (1999) observed a mismatch between full-scale and pilot-scale sludge production measurements with simulation results using ASM1 and proposed a degradation process for "very slowly degradable organic material". In a similar way, Lubello et al. (2009) found an overprediction of sludge production with ASM1 running pilot-scale MBRs and introduced a hydrolysis process for the unbiodegradable particulate organics. First order kinetics was used and the rate constant q_U was determined in a range of 0.012 to 0.014 d^{-1}. Spérandio et al. (2013), using 30 references from long SRT systems, showed that the sludge production in these systems could be explained if a first order degradation rate of 0.007 d^{-1} for X_U was applied. This is in agreement with Ramdani et al. (2012) who found a range for q_U of 0.006 to 0.007 d^{-1} using pilot-scale MBR systems fed only soluble COD. Interestingly Jones et al. (2009) showed in long-term anaerobic batch experiments that X_U is further degradable even in an anaerobic environment with a first order degradation rate of 0.0075 d^{-1}. The research so far does not indicate whether the process of degradation depends on the SRT of the system directly and, therefore, it is not yet clear when the degradation of X_U starts to become significant and detectable. Except for the Ramdani et al. (2012) study, there is little information about the specific characteristics of X_U and no information about the quality of the degradable fraction of X_U. Recently, Ruiken et al. (2013) found that cellulosic material from toilet paper is a significant contributor to the particulate material in activated sludge and is partially biodegradable.

However, the obtained rates for q_U are so small that the data used for comparative prediction have to be very accurate for the validation of the model. In particular the experimental determination of the X_{OHO} degradation rate as a constant parameter with a value of 0.24 d^{-1} (Fenu et al., 2010; Gujer et al., 1999; Ramdani et al., 2010) is a crucial point for the model prediction and, therefore, led to challenge the second assumption.

Secondly, it is assumed in the ASMs that the decay of X_{OHO} is independent of the substrate supply and, therefore, independent of the metabolic activity and the SRT of an activated sludge system, respectively. In a previous study (Friedrich and Takács, 2013) it was shown that the decay rate of X_{OHO} decreases with decreasing activity of X_{OHO} expressed as the specific initial oxygen uptake rate with respect to X_{ORG}. The decay rate b_{OHO} was derived from an OUR profile of an aerobic digestion batch experiment. The procedure was based on the exclusion of an initial high OUR decrease resulting from the consumption of stored organic material X_{STOR}.

The first assumption that X_U is unbiodegradable, led to the VSS-based method for the determination of b_{OHO} using aerobic digestion batch experiments (Ramdani et al., 2010). It was suggested that the VSS degradation profile ends at the truly unbiodegradable VSS_U. This suggestion is crucial, because if VSS_U is degradable even at a low rate (Figure 2a) or the VSS_U detection is inaccurate (Figure 2b), the decay rate b_{OHO} would be significantly lower.

However, if the VSS degradation profile is uncertain for the determination of the degradable fraction of the MLSS in the

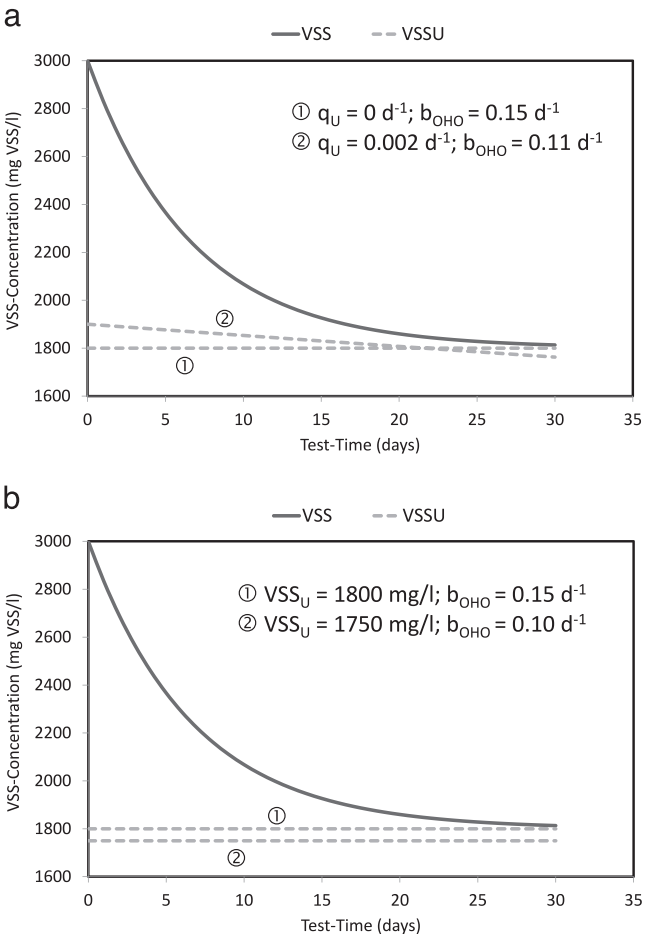

Figure 2—(a) b_{OHO} for decreasing VSS_U; (b) b_{OHO} for a lower VSS_U estimate.

course of an aerobic digestion batch experiment, this information can be provided by a simultaneously recorded endogenous OUR profile. The VSS measurement represents both the biodegradable and the unbiodegradable VSS fraction. In contrast, the integral of the OUR over the course of aerobic degradation stands only for the biodegraded VSS in COD units.

Therefore, it is promising to combine the VSS and OUR measurements of an aerobic digestion batch experiment for the extraction of the unbiodegradable organic fraction of the MLSS and to investigate whether this fraction is constant in the course of this experiment or not.

Material and Methods

Origin and Characterisation of Activated Sludge. The activated sludge for the aerobic digestion batch experiment was drawn from the return sludge of six different full-scale activated sludge WRRFs ranging from 15,000 to 600,000 population equivalents situated in the Northeast of Germany. The characteristic properties are summarized in Table 1.

As a result of the higher accuracy of the OUR measurements in comparison to the available data for SRT calculations, the initial specific OUR in mg O_2/(g VSS·d) of the activated sludge sample rather than the SRT was used to describe the loading state of the particular activated sludge.

Table 1—Characteristics of activated sludge used in aerobic digestion batch experiments (spOUR = specific OUR with respect to VSS).

Test	TSS (mg/L)	VSS (mg/L)	VSS/TSS (%)	OUR(0) [mg O_2/(L·h)]	spOUR(0) [mg O_2/(g VSS·h)]
A	4310	2830	68	13.8	3.2
B	4140	3020	74	20.3	4.9
C	3940	3040	77	14.5	3.7
D	3320	2663	80	25.8	7.8
E	4040	2810	69	20.4	5.0
F	3950	3060	77	17.5	4.4

With the exception of the sludge from plants C and D, the WRRFs are equipped with a primary settler. The sludge samples from plants D and E were strongly influenced by industrial coffee-processing wastewater. Before the experiment, the sludge samples were diluted with effluent. The time from sampling to the start of the experiment was not longer than 1.5 hours.

Experimental Setup and Analytical Methods. The experimental setup comprised an OUR reactor and VSS reactor (see Figure 3). As the activated sludge in the 2.5-L reactor of the respirometer (OUR reactor) had to remain closed to the surrounding atmosphere, it was not possible to take VSS samples from this reactor without establishing an open water surface. For this reason, an open VSS sampling reactor (VSS reactor) with a volume of 15 L was simultaneously and identically operated to the OUR reactor. The VSS was measured in the first week every day and afterwards at increasing intervals of 2 to 5 days. The OUR value that belonged to a VSS measurement was taken from the computed and logged OUR measurements of the respirometer. At the end of the experiment, the VSS in the two parallel reactors was "similar", so identical degradation was assumed.

The dissolved oxygen concentration in the OUR reactor as well as in the VSS reactor was operated between 4 and 6 mg O_2/L. The reactor temperature was controlled by controlling the room temperature to 20 °C.

To check the quality of the experiment, a COD balance was performed using the following relationship:

$$\begin{aligned}\text{COD-Balance} = {} & \text{COD}_{\text{start}} - \text{COD}_{\text{end}} - \text{COD}_{\text{loss}} \\ & - \text{Integral OUR}_{\text{e}} \\ & - (\text{NO}_3\text{-N}_{\text{end}} - \text{NO}_3\text{-N}_{\text{start}}) \cdot 4.57 \end{aligned} \quad (8)$$

where COD_{start} and COD_{end} are the COD concentrations of the activated sludge at the beginning and the end of the batch experiment, respectively. OUR_e is the endogenous oxygen uptake rate that was recorded throughout the experiment. The COD loss is obtained by collecting the total suspended solids (TSS) that was sticking to the sidewalls of the glass ball on top of the OUR reactor. On average, this loss was 2% of the initial TSS. NO_3-N_{start} and NO_3-N_{end} are the nitrate concentrations at the beginning and at the end of the batch experiment, respectively. As a result of anoxic sample transportation, the nitrate in the sample at the beginning of the experiment was zero. The electron equivalence of the NH_3 to NO_3^- conversion in nitrification is 4.57.

Further details on the operation of the respirometer as well as the execution of the aerobic digestion batch experiment and the

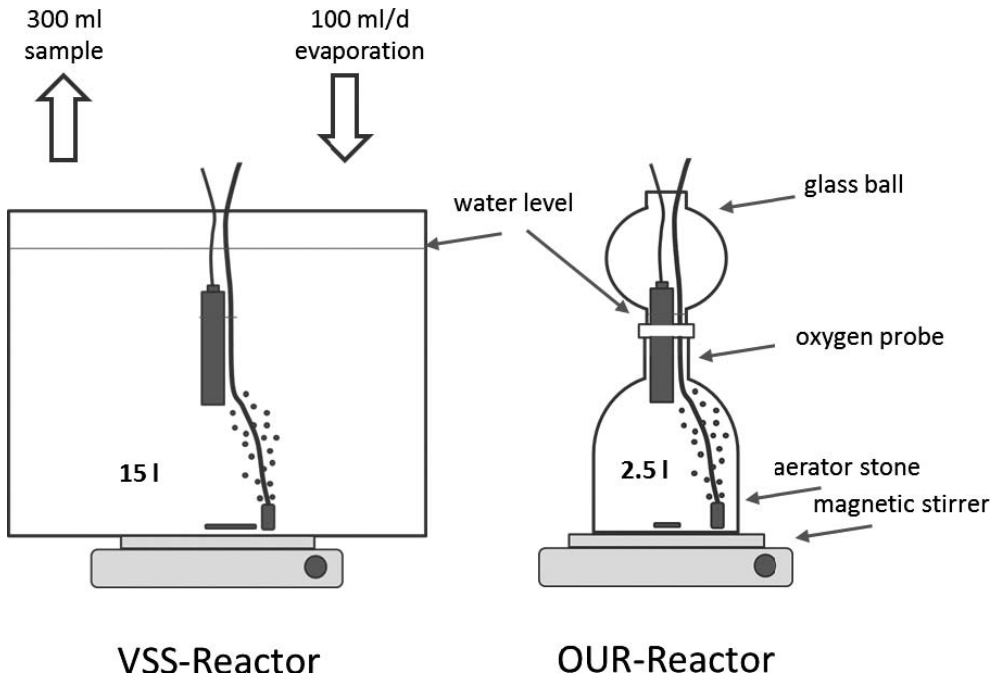

Figure 3—Experimental setup.

analytical methods are described in a previous research (Friedrich and Takács, 2013).

Method for the Estimation of X_U. For the assessment of X_U, the OUR and the VSS measurements had to be combined as indicated above. As Friedrich and Takács (2013) suggested, the OUR profile of the aerobic digestion batch experiments can be modeled with eq 9:

$$OUR(t) = OUR_{STOR}(t) + OUR_{OHO}(t) + OUR_{NO3}(t) \quad [mg\ O_2/(L{\cdot}h)] \tag{9}$$

OUR_{STOR} was observed at the beginning of the aerobic digestion batch experiment with a degradation time of 1 to 5 days. Friedrich and Takács (2013) assumed that this activity was the result of the degradation of stored organic material X_{STOR}. The reaction rate (q_{STOR}) of this process was comparatively high (usually $> 1.0\ d^{-1}$) and the reaction was modeled with first order reaction kinetics according to eq 10 as a simultaneous reaction to the degradation of X_{OHO}:

$$OUR_{STOR}(t) = q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR}\cdot t} \quad [mg\ O_2/(L{\cdot}h)] \tag{10}$$

OUR_{OHO} represents the respiration rate resulting from the degradation of X_{OHO} and, therefore, corresponds to the actual decay process. The decay rate b_{OHO} is relatively low in comparison to q_{STOR}. The decay process is modeled with first order reaction kinetics according to eq 11:

$$OUR_{OHO}(t) = (1 - f_{U,E}) \cdot X_{OHO}(0) \cdot b_{OHO} \cdot e^{-b_{OHO}\cdot t} \quad [mg\ O_2/(L{\cdot}h)] \tag{11}$$

As no nitrification inhibitor was used in any of the experiments, OUR_{NO3} due to the oxidation of the nitrogen fraction of the degraded biomass (f_N) to nitrate by nitrifiers had to be accounted for. This is modeled with eq 12.

$$OUR_{NO3}(t) = 4.57 \cdot f_N \cdot (1 - f_{U,E}) \cdot b_{OHO} \cdot X_{OHO}(0) \cdot e^{-b_{OHO}\cdot t} \quad [mg\ O_2/(L{\cdot}h)] \tag{12}$$

The combination of eqs 10 to 12 yields:

$$OUR(t) = q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR}\cdot t} + b_{OHO} \cdot (1 + 4.57 \cdot f_N) \cdot (1 - f_{U,E}) \cdot X_{OHO}(0) \cdot e^{-b_{OHO}\cdot t} \quad [mg\ O_2/(L{\cdot}h)] \tag{13}$$

Rearranging eq 13 results an expression for the degradable fraction of the ordinary heterotrophic biomass X_{OHO}:

$$\frac{OUR(t) - q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR}\cdot t}}{b_{OHO} \cdot (1 + 4.57 \cdot f_N)} = (1 - f_{U,E}) \cdot X_{OHO}(0) \cdot e^{-b_{OHO}\cdot t} \quad (mg\ COD/L) \tag{14}$$

There is a consensus that X_{OHO} dominates the degradable fraction of X_{ORG} and is, therefore, regarded to represent X_{DEG} according to eq 2 in terms of $X_{ORG} - X_U$.

$$\frac{OUR(t) - q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR}\cdot t}}{b_{OHO} \cdot (1 + 4.57 \cdot f_N)} = X_{DEG}(t) = X_{ORG}(t) - X_U(t) \quad (mg\ COD/L) \tag{15}$$

Rearranging eq 15 leads to an equation that expresses X_U by parameters that nearly all can be derived directly from the aerobic digestion batch experiment.

$$X_U(t) = X_{ORG}(t) - \frac{OUR(t) - q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR}\cdot t}}{b_{OHO} \cdot (1 + 4.57 \cdot f_N)} \quad (mg\ COD/L) \tag{16}$$

The OUR(t) is measured directly. The heterotrophic decay rate b_{OHO}, the degradation rate of stored organic material q_{STOR}, as well as the fraction of stored organic material $X_{STOR}(0)$ are

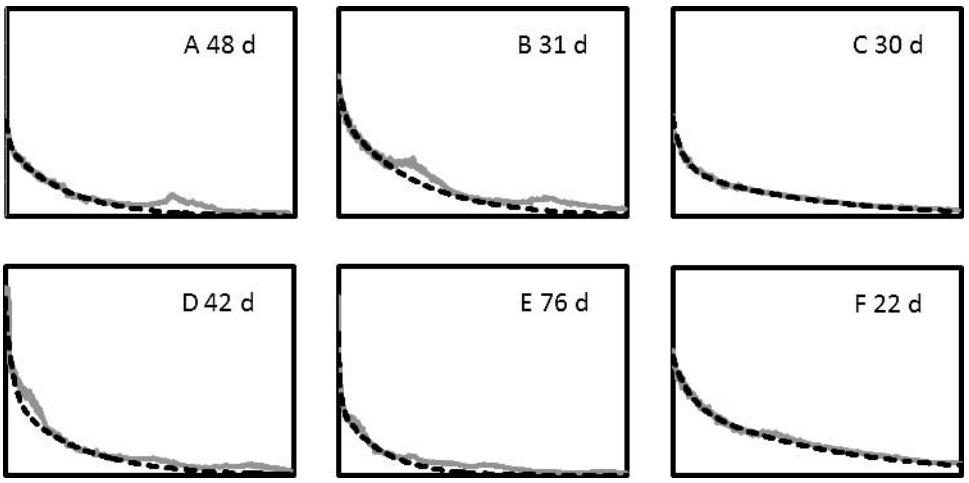

Figure 4—Respirograms of aerobic digestion batch tests with OUR measured (solid line) and OUR modeled (dashed line); T = duration of experiment; maximum of Y-axis is OUR = 30 mg O_2/(L·h).

derived from the respirogram of the first 5 days by nonlinear regression parameter estimation.

All the nitrogen that is released in the course of biodegradation of X_{DEG} will be nitrified during the aerobic digestion batch experiment. Therefore, the nitrogen fraction of the degraded biomass can be measured by relating the nitrate nitrogen at the end of the experiment to the degraded VSS in terms of COD. However, it should be noted that this is a rough assumption, as X_{DEG} is the sum of different degradable compounds and it is likely that the nitrogen content of these different compounds might be different, too (Lee et al., 2003).

To determine X_{ORG}, the VSS is measured. However, eq 16 cannot be used directly, as X_{ORG} consists of at least two different fractions, X_{DEG} and X_U, respectively. The COD content of these fractions is likely to be different from each other (Spérandio et al., 2013). With respect to this experiment, the COD content for X_{DEG} ($i_{CV,DEG}$) was measured directly by relating the integral of OUR to the degraded VSS over the time of the experiment. At the end of the experiment, $i_{CV,U}$ can be measured directly using standard methods for the COD and VSS analysis. In this study, the COD of the MLSS was not measured. A value of $i_{CV,U} = 1.55$ mg COD/mg VSS was used as the most likely value based on literature (Spérandio et al., 2013).

The following procedure for the assessment of $X_U(t)$, $X_{DEG}(t)$, and $X_{ORG}(t)$ was applied:

1. Calculation of $X_{DEG}(t)$ with eq 15.
2. Calculation of $VSS_{DEG}(t)$ by:

$$VSS_{DEG}(t) = \frac{X_{DEG}(t)}{i_{CV,DEG}} \quad (\text{mg VSS/L}) \tag{17}$$

3. Calculation of $VSS_U(t)$ by:

$$VSS_U(t) = VSS(t) - VSS_{DEG}(t) \quad (\text{mg VSS/L}) \tag{18}$$

4. Calculation of $X_U(t)$ by:

$$X_U(t) = VSS_U(t) \cdot i_{CV,U} \quad (\text{mg COD/L}) \tag{19}$$

Combining eqs 15 to 19 yields an expression for the direct determination of $X_U(t)$:

$$X_U(t) = \left[VSS(t) - \frac{OUR(t) - q_{STOR} \cdot X_{STOR}(0) \cdot e^{-q_{STOR} \cdot t}}{i_{CV,DEG} \cdot [b_{OHO} \cdot (1 + 4.57 \cdot f_N)]}\right] \cdot i_{CV,U} \quad (\text{mg COD/L}) \tag{20}$$

In comparison to an integrated modeling approach for $X_U(t)$ estimation, this procedure has the potential to identify $X_U(t)$ in the course of an aerobic digestion batch experiment with a limited number of assumptions.

However, this approach does not supply information about the buildup of $X_{U,E}$ within the degradation time of the experiment, because it considers the total $X_{U,E}$ inside and outside of the active biomass from the beginning. Activated sludge models simulate $X_{U,E}$ after release from active biomass. The value of $X_U(t)$ in this work is basically the result of the balance of VSS(t) and OUR(t) measurements.

Results and Discussion

Characteristics of Respirograms. The respirograms of the aerobic digestion batch experiments are displayed in Figure 4 and their estimated parameters are summarized in Table 2. The test time was between 22 and 76 days and, therefore, sufficiently long to detect the initial fast OUR decline that is associated with the degradation of stored material X_{STOR} and the subsequent exponential OUR decrease resulting from the degradation of X_{OHO} only.

The COD balance of the experiments was in the range of 99.5 to 103.7% and the reliability of the test data can be assumed as good.

Sludge A had the highest degradation rate q_{STOR} but the lowest fraction of stored material X_{STOR}. The decay rate b_{OHO} as well as the $OUR(0)_{OHO}$ were moderate, so that the sludge could be regarded as low loaded. The SRT of this sludge was between 20 and 25 days.

Sludge B had the highest decay rate b_{OHO} and the highest $OUR(0)_{OHO}$. The SRT was in a range of 10 to 12 days, so that this sludge could be regarded as comparatively high loaded.

Table 2—Results of the aerobic digestion batch experiments.

Test	Test-time (d)	COD-bal. (%)	f_N (g N/g COD)	$i_{cv,DEG}$ (g COD/g VSS)	q_{STOR} (1/d)	X_{STOR} (mg COD/L)	b_{OHO} (1/d)	X_{OHO} (mg COD/L)	$OUR_e(0)$ [mg O_2/(l·h)]	$OUR_{OHO}(0)$ [mg O_2/(l·h)]	f_{DEG} (%)
A	49	101.9	0.050	1.45	2.09	39	0.100	2509	13.8	8.3	47
B	31	100.7	0.059	1.45	1.00	100	0.129	2650	20.3	11.4	47
C	30	103.7	0.064	1.47	1.00	172	0.077	2260	14.5	5.8	39
D	42	101.3	0.058	1.42	1.00	330	0.100	2700	25.8	9.0	55
E	76	101.2	0.048	1.43	1.90	130	0.093	2650	20.4	8.2	51
F	22	99.5	0.051	1.40	0.85	180	0.094	2719	17.5	8.5	48

However, its X_{OHO} fraction is very close to the lower loaded sludge A.

Sludge C, in contrast to sludge B, had the lowest decay rate and the lowest $OUR(0)_{OHO}$. From the operators' reports, it was estimated that the SRT was in the range of 70 to 80 days. Even if f_{DEG} is comparatively low, it is still close to that of sludge A and B, taking the high SRT into account. The N content of sludge C in comparison to the other types of sludge is rather high. This is notable because sludge C was already aerobically digested to a very large extent. However it should be mentioned that approximately 80% of the COD load to this plant originates from a slaughterhouse processing wastewater.

Sludge samples D and E were from different plants, but both were fed more or less regularly with coffee-processing wastewater. They showed a high OUR(0) that was not consistent with their decay rates, which were moderately low. This discrepancy made it hard to find an estimate for X_{OHO}.

Sludge F was again a moderately loaded sludge with an SRT of at least 15 days. Its characteristics were similar to sludge A, but had a slightly higher estimated X_{OHO} concentration.

Biomass Concentration Profiles. The results of the procedure to determine X_U, X_{DEG}, and X_{ORG} are summarized in Table 3 and displayed as biomass concentration profiles for the examples of tests D and E in Figures 5a and 5b, respectively. In all experiments, X_U at the end of the experiment was smaller than the initial $X_U(0)$ concentration. But the development of the $X_U(t)$ curve is not homogeneous and can be divided in two sections.

The first section lasts for 4 to 18 days, depending on the experiment. During this time, X_U is either increasing or randomly going up and down. It is believed that this behavior does not reflect reality in terms of the true variation in $X_U(t)$. A factor that cannot be evaluated with sufficient certainty is the respiratory activity of protozoa. For instance, in test B, a mass development of the rotifer Lecane was observed and could be directly related to the first irregular OUR increase, but an associated higher VSS decrease could not be measured. Looking at tests D and E, it is also possible that a substrate fraction that was not included in the model of eq 9 disturbed the match of VSS and OUR within the applied approach. Furthermore, it is possible that the formation of soluble microbial products as described in the literature (Xie et al., 2012; Xie et al., 2013) led to a reduction of VSS without concomitant oxygen consumption. However, the magnitude of this phenomenon seems to be below the accuracy of the TSS measurements and not likely to occur in the course of a degradation experiment as conducted in this study. Alternatively, inadequate assumptions like a constant

Table 3—Initial biomass concentration and degradation rate of X_U.

	Initial concentration			X_U decrease		
Test	$X_{ORG}(0)$ (mg COD/L)	$X_U(0)$ (mg COD/L)	$X_{DEG}(0)$ (mg COD/L)	From (d)	q_U (d^{-1})	R^2 –
A	4246	2210	2036	18	0.011	0.685
B	4518	2153	2365	7	0.008	0.780
C	4615	2838	1778	14	0.006	0.947
D	3917	1626	2291	9	0.029	0.982
E	4177	2045	2131	10	0.009	0.959
F	4495	2179	2316	4	0.015	0.922

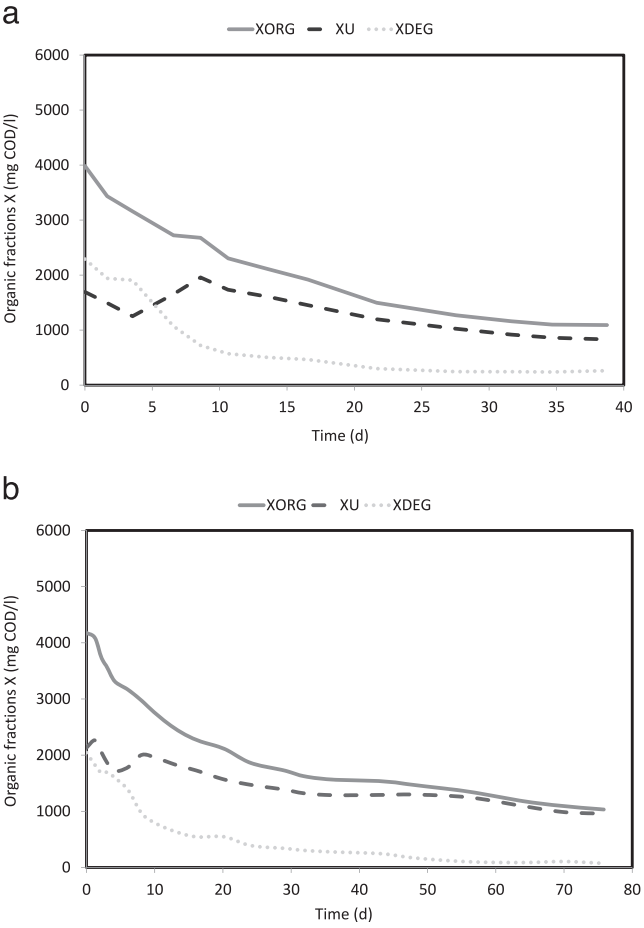

Figure 5—Profile of (a) organic fractions test D; (b) organic fractions test E.

$i_{CV,DEG}$ and a constant f_N could lead to nonhomogenous behavior of the X_U graph evolution.

The second section showed a decrease of X_U. It is arguable whether the degradation characteristics of X_U follows first order reaction kinetics, because it is unlikely that X_U will be sufficiently homogenous. However, this simplest approach provides an opportunity to compare the results of this study with the work of other researchers (Lubello et al., 2009; Ramdani et al., 2012; Spérandio et al., 2013).

The first order rate parameter q_U was determined by linearization of X_U during the second section in a range of 0.006 d^{-1} to 0.029 d^{-1} (see Table 3). These results are in the order of magnitude as reported in the literature and confirm the suggestion of Nowak et al. (1999) and the results of Spérandio et al. (2013) and others to introduce a degradation process into aerobic activated sludge models for the degradation of X_U. The rather low R^2 values (especially for tests A and B) show that X_U is either not sufficiently homogenous or that microbial activity changed due to adaption of active biomass to the advancing starvation. This is illustrated very well in the respirogram of test E in Figure 5b, where a slight OUR increase and subsequent decrease after more than 40 days of digestion time points to the completion of the degradation of a certain part of X_U, which obviously leads to limited microbial growth. The lowest X_U degradation rate was observed in test C. The degradation kinetics of X_U of this sludge could be measured as a true exponential OUR decrease and, consequently, R^2 for linearization of X_U was relatively high. This is important to note because sludge C was already aerobically stabilized to a very large extent. Possibly at such high SRTs X_U with regard to degradability tends to become homogenous.

Conclusions

The VSS of activated sludge includes a biodegradable fraction X_{DEG} that is mainly associated with active biomass and an "unbiodegradable" fraction X_U. Furthermore, the integral of the OUR is representative of the biodegradable fraction X_{DEG}.

This study has shown that it is possible to combine VSS and OUR measurements in the course of an aerobic digestion batch experiment to generate information about the degradation of X_U.

It could be shown for six different types of activated sludge that after a certain time X_U decreases until the end of the experiment. It is assumed that active biomass adapts to the severe starvation conditions with the advancing batch experiment by producing hydrolytic enzymes that support the X_U degradation.

The degradation rate q_U was estimated in the range of 0.006 d^{-1} to 0.026 d^{-1}. These experimentally produced values are consistent with the values in the literature, which were the result of simulation studies using existing ASMs.

However, more research is needed to distinguish between the degradation of "unbiodegradable" material from the influent and from bacterial decay ($X_{U,inf}$ and $X_{U,E}$). Moreover, it is of interest whether there is an influence of the SRT on the degradation characteristic of X_U.

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