65 APPLICATION OF A HYBRID RESPIROMETRIC TECHNIQUE TO THE CHARACTERIZATION OF AN INDUSTRIAL WASTEWATER

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INTRODUCTION

Respiration rate is a most sensitive variable for characterization of the activated sludge process and the associated removal and degradation of the biodegradable matter from wastewater.[1-7] Carefully designed respirometric experiments can provide us with wastewater characteristics such as the concentrations of readily degradable substrate and hydrolysable matter but also with activated sludge characteristics such as maximum specific growth rates and decay coefficients.

Measurement of the respiration rate of activated sludge has been the subject of many studies and consequently many techniques have been developed; even so, they rely on only a few principles.[8] Two frequently applied principles are used in respirometers: one (denoted E-principle) is based on parameter estimation from dissolved oxygen (DO) measurements and the other (denoted D-principle) is based on measuring the difference between DO concentrations.

The E-principle calculates the respiration rate from the mass balance of dissolved oxygen in an open aerated respiration vessel.[9,10] To this end, the oxygen mass-transfer coefficient and the saturation DO concentration under operating conditions have to be known. To obtain these coefficients, Vanrolleghem[10] developed a dedicated estimation method in which the temporary disturbance of the DO concentration, obtained after addition of substrate, is used to obtain the oxygen transfer coefficients.

The D-principle is based on the measurement of the DO concentrations at the inlet and at the outlet of a closed respiration vessel through which the activated sludge is continuously pumped. The respiration rate is calculated from the difference of the DO concentrations and the residence time in the respiration vessel.[11,12]

Vanrolleghem and Spanjers[13] compared the above principles for determining the short-term biochemical oxygen demand (BODst) of wastewater. They concluded that both principles can be used for this purpose but that a significant difference exists between the BODst values obtained with both principles. They could not give an explanation for this difference and proposed, *inter alia*, to apply the E-principle to the DO data of the other principle. This paper describes such a combination of the two principles and the application of this hybrid technique to the characterization of an industrial wastewater.

THE HYBRID RESPIROMETRIC TECHNIQUE

Figure 1 shows a scheme of a possible setup for the application of the hybrid technique. Two vessels are used of which one is open and aerated and the other is closed. Activated sludge is circulated through both vessels and the dissolved oxygen (DO) concentration is measured in each

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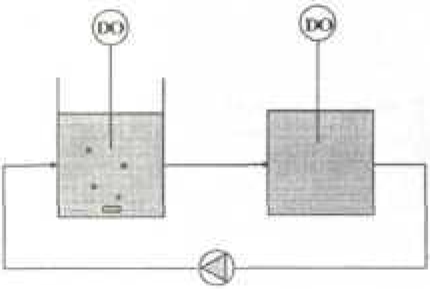

Figure 1. Scheme hybrid technique.

vessel. The respiration rate of the activated sludge in the system is equal if both vessels are mixed well and if the DO concentration is not-limiting. Figure 2 shows that, after the addition of a substrate to the aerated vessel, the DO concentrations in both vessels first decrease and, after substrate is oxidized, return to the original level. Because in the aerated vessel oxygen is continuously supplied, the oxygen concentration is always higher than that in the closed vessel. By applying the E-principle to the DO measurements in the aerated vessel, the respiration rate of the activated sludge in the system can be obtained. Simultaneously, the respiration rate can also be obtained by applying the D-principle to both DO measurements. The two respirometric principles combined here have already been described elsewhere[10,12,13] and will only be shortly summarized.

The E-Principle

In this principle a temporary disturbance of the DO concentration in the aerated vessel (on the left in Figure 1) is used to estimate the respiration rate. The disturbance caused by the addition of a wastewater sample or by switching off and on the aeration can be used for this purpose. In the first approach, the oxidation of the substrate results in an increase of the respiration rate causing the DO concentration to decrease (upper curve in Figure 2). From the moment the substrate is oxidized, the respiration rate becomes constant and the remaining part of the dissolved oxygen curve can be considered as a reaeration curve. Several methods can be used to estimate the oxygen transfer coefficients from a reaeration curve. The inherent problem is to determine when the substrate is oxidized and the respiration rate becomes constant or, in other words, from what time instant the DO data obey a first order reaeration process. For the estimation, Vanrolleghem[10] uses a technique in which a moving window nonlinear regression of a first order reaeration model is applied to the data. The initial point of the window yielding the best fit is considered as the starting point of the reaeration curve from which the coefficients can be calculated. Once the oxygen transfer coefficients are estimated, the respiration rate can be calculated using the DO mass balance in the aerator. Because the coefficients may change from one sample to another, they are estimated each time a sample is added.

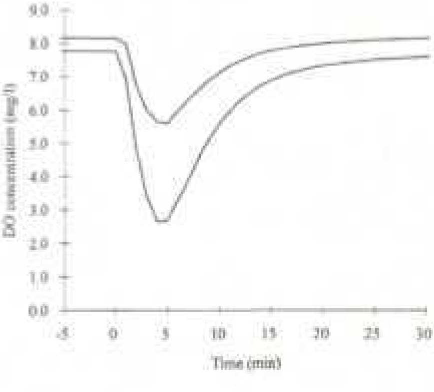

Figure 2. Dissolved oxygen concentration in aerated vessel (upper curve) and closed vessel (lower curve). Abrupt decrease indicates the addition of wastewater.

When the E-principle is combined with the D-principle to compose the hybrid technique, a modification in the calculation of the respiration rate must be made: the DO mass balance in the aerator is extended with a term to account for the circulation over the closed vessel, so that the total mass balance can be written:

$$\frac{dS_{O1}}{dt} = K_La(S_{O*} - S_{O1}) - \frac{Q}{V_1}(S_{O1} - S_{O2}) - R_1 \qquad (1)$$

Since the circulation flow Q and the open vessel volume V_1 are known process constants and the DO concentrations in the open vessel S_{O1} and in the closed vessel S_{O2} are measured, this modification does not affect the E-principle.

The D-Principle

This principle uses a closed, completely mixed vessel (on the right in Figure 1) through which activated sludge is continuously pumped. The DO concentrations in the sludge entering the vessel S_{O1} and in the sludge leaving the vessel S_{O2} are measured. The respiration rate is then calculated on the basis of the DO mass balance over the respiration vessel:

$$\frac{dS_{O2}}{dt} = -\frac{Q}{V_2}(S_{O2} - S_{O1}) - R_2 \qquad (2)$$

If the volumes of the conduits are negligible and both vessels are ideally mixed, then two probes as indicated in Figure 1 will provide the necessary information. Spanjers[12] uses one and the same probe, located at either side of the closed vessel, to measure DO concentration of the sludge entering and of the sludge leaving the vessel. This is realized by alternating the flow direction through the vessel by using a reversible pump or a set of four solenoid valves. A consequence of this method is that the measuring frequency is limited by the response time of the probe. Another consequence of using one probe is that at a specific time instant only one measurement is available: either the DO concentration of the sludge entering the vessel or the DO of the sludge leaving the vessel. Given these discrete time measurements, the DO mass balance is solved by interpolation and by approximation of the time derivative with finite differences. When the D-principle is combined with the E-principle to compose the hybrid technique there is no requirement for modification in the calculation of the respiration rate.

CHARACTERIZATION OF ACTIVATED SLUDGE AND WASTEWATER

In this paper respiration measurements obtained with both principles are used to characterize a wastewater and the corresponding activated sludge. For such a characterization it is necessary to adopt some model of the wastewater and the biokinetic process. Here we consider a substantially simplified version (Table I) of the model proposed by Henze et al.[14] The model includes the following assumptions (see also [2,7]):

Table I. Process Model for the Characterization of Activated Sludge and Wastewater (See Nomenclature for explanation of symbols)

Component → Process ↓	S_S	X_R	X_{BH}	S_O	Process Rate
Growth	$-\frac{1}{Y_H}$		1	$\frac{-(1-Y_H)}{Y_H}$	$\mu_{mH}\frac{S_s}{K_s+S_s}X_{BH}$
Decay			−1	$-(1-f_I)$	b_HX_{BH}
Rapid hydrolysis	1	−1			k_RX_R

- only heterotrophic growth
- no DO-limitation and no denitrification
- first-order hydrolysis
- decay is associated with endogenous oxygen consumption.

To create the mass balances for each component within the measuring unit the reaction rates r_C should be combined with the flow terms for each vessel:

$$\frac{dC_1}{dt} = -\frac{Q}{V_1}(C_1 - C_2) + r_{C1} \tag{3}$$

$$\frac{dC_2}{dt} = -\frac{Q}{V_2}(C_2 - C_1) + r_{C2} \tag{4}$$

where C denotes the concentration of a component. In the case of S_O an extra term for the oxygen transfer should be included and the oxygen reaction rate $-r_O$ equals R (Equation 1). The reaction rates are formulated by summing the products of the stoichiometric coefficients and the process rate expressions, as explained by Henze et al.[14] Because R $(=-r_O)$ is linked to all the variables and it is the only variable that can be measured, the respiration rate is the most suitable variable to obtain information on the processes and components in the biokinetic model. Therefore, to characterize wastewater and sludge the respirometric response of the biomass on the addition of wastewater should be measured. The parameters (kinetic parameters and initial concentrations of degradable matter) can then be obtained by fitting the model to the respirometric measurement time series. Not all the parameters can be uniquely estimated from only respiration rate.[7] In this paper we assume values for f_I and Y_H of zero and 0.64, respectively. Moreover, we assume that all the activated sludge VSS consists of heterotrophic biomass and that the COD of this biomass is 1.48 g COD per g VSS.[15] For studies with the aim to obtain kinetic parameters it is necessary to work at low substrate to biomass ratio.[16] Therefore, in this study, we strived to keep this ratio as low as possible but high enough to allow accurate measurement of the respirometric response.

MATERIALS AND METHOD

The measuring unit consisted of a commercially available respiration meter (RA-1000 Manotherm, The Netherlands) connected to a laboratory-scale aeration tank, the total system having an activated sludge content of 1-2 liter (see also the scheme in Figure 1). The respiration meter, based on the D-principle, uses one and the same probe to measure the DO concentration of the sludge entering a closed respiration vessel and of the sludge leaving the vessel. The respiration rate was obtained according to the standard procedure with the RA-1000. The DO concentration of the sludge entering the closed vessel was considered equal to the DO in the aeration tank and was used to assess the respiration rate according to the E-principle. For this purpose the method to obtain the oxygen transfer coefficients, as described by Vanrolleghem,[10] was expanded with a mass balance of DO over both vessels to account for oxygen uptake in the closed vessel. Both respiration measurement series were fed into a parameter estimator using the model in Table 1 completed with the mass balances of the two vessels (Equations 3 and 4).

The measurements were commenced by transferring activated sludge to the measuring unit and starting the respirometer. When the endogenous respiration rate was reached and observed to be constant for at least 10 minutes, a sample was added to the open vessel. This was repeated several times with raw and filtered wastewater. If necessary, nitrification was suppressed by adding 3–27 mg allylthiourea (ATU) per liter activated sludge. To check whether nitrification occurred, a known amount of ammonium was added and the respirometric response to the addition was observed.

Sludge and wastewater were sampled from an industrial plug flow plant treating the effluent of a potato starch mill (Veendam, The Netherlands). The loading of this plant is typically 0.05 to 0.10 g $g^{-1}day^{-1}$ on COD basis. Prior to input to the aeration tank the influent is enriched with nutrients. This water was used in the experiments. Part of the wastewater samples was filtered over 0.45 μm membranes. Analysis for COD, Kjeldahl, and ammonium yielded the following values: 2055 g m^{-3}, 84 gN m^{-3}, and 6.7 gN m^{-3}, respectively, for the raw wastewater and 1735 g m^{-3}, 77 gN m^{-3}, and 6.6 gN m^{-3}, respectively, for the filtered wastewater. The MLVSS of the sludge used in the experiments was 3.3 to 3.9 g per liter.

RESULTS

The addition of ammonium generated a respirometric response that remained when nitrification inhibitor (ATU) was added. We conclude that nitrification was absent and that the respirometric response was caused by the oxidation of stored organic substrate because of the addition of ammonium. Several samples of raw and filtered wastewater were added to activated sludge whether or not in the presence of ATU. Some additions were repeated. The sludge was replaced once with fresh sludge from the same sample. Respiration rate time series obtained with the two principles were used to estimate activated sludge process model parameters according to the model in Table I. Table II shows the wastewater characteristics, derived from the estimated initial concentrations, and Table III the characteristics of the sludge-wastewater interaction. As an example, Figure 3 shows that respirograms obtained with the two principles applied on the same DO data set correspond reasonably well.

The results of the parameter estimation show some inconsistency among the values for S_S and X_R, irrespective of the respirometric principle, sludge sample, and wastewater sample (Table II). However, the total short-term biochemical oxygen demands (sum of S_S and X_R, multiplied by $(1 - Y_H)$) are quite invariable. This suggests that, for the given dataset, the optimizer was not capable of discriminating between S_S and X_R. In attempting to work at low substrate to biomass ratios, we added small amounts of wastewater to the sludge which resulted in subsaturated condi-

Table II. **Wastewater Characteristics. D and E Denote D-Principle and E-Principle, Respectively. *Sludge 1 and 2 Indicate Two Identical Portions from One Sludge Sample.* Results in One Cell are Repetitions and Are Expected to be Reproductions.**

		S_S (mgCOD l^{-1})		X_R (mgCOD l^{-1})		S_S+X_R (mgCOD l^{-1})	
Wastewater	Sludge	D	E	D	E	D	E
Raw	1	290	471	483	461	773	932
	1	330	100	447	655	777	755
	2	0	415	759	439	759	854
Raw+ATU	1	240	180	504	588	745	768
	2	0	285	753	543	753	828
Filtered	2	0	223	762	567	762	790
Filtered+ATU	1	350	118	422	590	772	707
	1	326	82	434	600	760	681
	2	0	88	727	674	727	762

Table III. **Characteristics Sludge-Wastewater Interaction. See also Description of Table II.**

		μ_{mH} (day^{-1})		K_S (mgCOD l^{-1})		k_R (day^{-1})		b_H (day^{-1})	
Wastewater	Sludge	D	E	D	E	D	E	D	E
Raw	1	2.4	1.4	4.2	3.14	432	229	0.09	0.08
	1	2.5	1.1	3.9	0.24	357	498	0.09	0.09
	2	4.9	1.3	19.8	2.70	569	240	0.08	0.07
Raw+ATU	1	2.6	1.1	4.4	0.22	472	420	0.09	0.09
	2	3.7	1.2	9.5	1.20	481	268	0.08	0.08
Filtered	2	4.3	1.4	15.9	2.00	547	308	0.08	0.07
Filtered+ATU	1	2.3	1.1	3.6	0.21	285	452	0.09	0.10
	1	2.3	1.1	3.5	0.20	305	492	0.09	0.10
	2	3.1	1.1	6.2	0.36	433	327	0.08	0.08

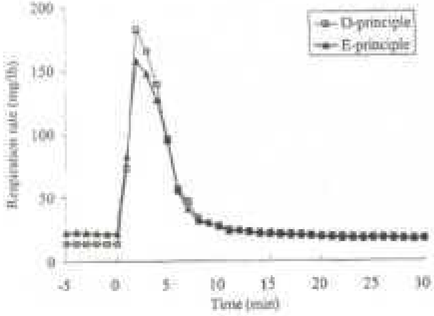

Figure 3. Addition of 60 mL raw wastewater to 1.41 liter activated sludge. Comparison of respiration rates obtained with the two different principles.

tions. This is demonstrated by the absence of a plateau in the respirogram (e.g., Figure 3). At low concentrations of S_S and X_R, the degradation kinetics of S_S and X_R (Monod and first order, respectively) become less distinctive. Nevertheless, objective model selection criteria[17] showed that the model applied here was significantly better than a model with only one substrate. Both principles do not show significant variation in $(S_S + X_R)$ values of the different kinds of wastewater: the absence of an effect of ATU indicates that nitrification did not occur, and similar values for raw and filtered wastewater suggest that the hydrolyzable matter is soluble.

On an average, the E-principle generated slightly higher values for $(S_S + X_R)$ (Table II) and lower values for μ_{mH} and K_S (Table III) than the D-principle. This is partly because the degradable matter is not instantaneously distributed over the two vessels upon addition of wastewater to the open vessel. The model, however, assumes that the wastewater is simultaneously added to both vessels. The effect of this delay on the parameter estimates is amplified by the low overall concentrations of S_S and X_R due to the small substrate to biomass ratio applied. The hydrolysis coefficient k_R is less sensitive to the delay because when hydrolysis becomes the limiting process, the distribution of degradable matter over the two vessels is completed. The same holds to a greater extent for b_H, which is estimated when all the degradable matter has disappeared and the respiration rate only changes slowly.

DISCUSSION

The primary purpose of the study was to combine two respirometric principles to obtain a hybrid respirometric technique that incorporates the advantages of both principles. The advantage of the E-principle is that it allows a high measuring frequency. The D-principle has the advantage that the respiration rate can be obtained directly from the DO measurements. It has been shown that the two principles can easily be implemented in the hybrid technique. A minor modification to the data interpretation of the E-principle is necessary to account for the circulation over the closed vessel.

To investigate the performance of the new technique, it was applied to the characterization of an industrial wastewater-activated sludge combination. Since two independent respiration measurements were simultaneously obtained from the same experiment, a straightforward evaluation of the results is possible. The disagreement between the two principles may be explained from the effect of the addition of the sewage to only one vessel. The same effect may also explain the difference between the short-term BOD values of both principles as reported in previous work.[13] Different behavior of the DO-probes, as suggested in that work as a possible cause, is eliminated in the hybrid technique. Because for some parameters, each principle produced different parameter estimates for duplicate measurements, explicit conclusions cannot be drawn from the results. A possible explanation for these differences is the low substrate to biomass ratio applied. This is supported by the good agreement among b_H values that are less sensitive to this ratio. Further work should concentrate on the elimination of the mixing effect and on the proper choice of the substrate to biomass ratio. Since the primary purpose was to develop and try the hybrid technique, no absolute value should be given to the biokinetic parameters obtained in this study.

The hybrid technique is particularly useful for studies of wastewater-activated sludge interaction, biodegradation, and toxicity. The two respirometric outputs can be averaged or the difference can be used to check the performance of the two measurements. For biokinetic characterization, the E-principle allows the determination of model parameters on only DO measurements, once the oxygen transfer coefficients are estimated. The equipment described here was designed for laboratory applications. However, if wastewater additions and sludge refreshments are automated, it would also be applicable in full-scale treatment plants.

In the measurements described here only one single DO probe was used to measure both the DO concentration in the open and in the closed vessel by changing the flow direction. The advantage of this construction is that it is simple and reliable since only one DO probe has to be maintained and calibrated. However, if probes are carefully maintained and calibrated, introduction of a second DO probe in the open vessel (on the left in Figure 1) and maintaining the periodic reversement of the flow would provide an additional check on the DO in the open vessel and thus on the assessed respiration rate. Regardless, if the periodic reversement of the flow is employed, a continuous diagnosis of the probe condition can be obtained by using the technique described by Spanjers and Olsson.[18]

The E-principle described here requires a temporary disturbance of the DO concentration in the aerated vessel to estimate the oxygen transfer coefficients, after which the respiration rate can be calculated. This disturbance was caused by an addition of wastewater. An alternative method that might be used to obtain the respiration rate is the one where the estimator is part of an adaptive controller for the DO concentration in the aeration vessel.[19, 20] In this estimator the response on a continuous excitation of the DO by manipulating the air flow rate is used to simultaneously estimate K_La and respiration rate.

CONCLUSIONS

It has been shown that the two principles can easily be implemented in the hybrid technique. Only a minor modification to the E-principle is necessary to account for the circulation over the closed vessel. Respirograms obtained with the two principles correspond reasonably well. However, when the respiration rate is used to determine biokinetic model parameters, there is some disagreement between the results. This can be explained by the low substrate to biomass ratio used in the experiments and by a mixing effect. These factors have less effect on the decay coefficient that shows consistent values. There are several possibilities to develop the technique further.

NOMENCLATURE

b_H	decay coefficient (day^{-1})
C	concentration of a component in the process model (COD m^{-3})
f_I	fraction of inert particulate matter (-)
K_La	oxygen mass-transfer coefficient (h^{-1})
k_R	hydrolysis coefficient (day^{-1})
K_S	half-saturation coefficient (gCOD m^{-3})
Q	circulation flow (l h^{-1})
R	oxygen respiration rate (gO$_2$m^{-3}h^{-1})
r_C	reaction rate of a component (gCODm^{-3}h^{-1})
S_O	dissolved oxygen concentration (g m^{-3})
S_S	concentration readily degradable substrate (gCOD m^{-3})
V	volume (m^3)
X_{BH}	concentration heterotrophic biomass (gCOD m^{-3})
X_R	concentration hydrolyzable matter (gCOD m^{-3})
Y_H	yield coefficient (-)
μ_{mH}	maximum specific growth rate (day^{-1})
$1,2$	index relative to open vessel and closed vessel, respectively

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