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An On-Line Respirographic Biosensor for the Characterization of Load and Toxicity of Wastewaters

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Abstract: A respirographic biosensor is presented that is capable of monitoring the waste load and potential toxicity of wastewaters, both off-line in a laboratory or on-line at the wastewater treatment plant. The principles of the sensors' operation have been developed and implications of the design choices evaluated. Short term BOD values were obtained every 30 min. The linear dynamic range spanned concentrations differing by a factor of 5000. This range could be expanded by a factor of 10 by adjusting the aeration rate of the bioreactor in the sensor. The response time for toxicity detection was approximately 1 h. The use in the sensor of activated sludge from the plant concerned ensured relevant toxicity information was obtained. To check the condition of the sludge, an independent respiration measurement is proposed. When a significant activity change is observed, the sludge in the sensor must be replaced. The presence of oxido-reduction chemicals can cause interferences that may lead to measurement errors. Based on a difference in reaction kinetics, their presence can be assessed and the effect eliminated. Both on-line and laboratory applications in the chemical industry are presented. Special emphasis is given to the usefulness of the sensor data for waste management of production divisions. On-line assessment of load variations and hydrogen peroxide spills are given as illustrations of the implementation of the sensor on the treatment plant. Attention is drawn to the potential application of the data for process control and improved performance of the treatment plant.

Key words: wastewater treatment, biosensor, on-line monitoring and control, mass transfer.

1 INTRODUCTION

Whereas computers are now commonly introduced for automation and control in many industrial processes, biological wastewater treatment systems still mainly rely on manual control essentially influenced by the personal expertise of the plant manager/operator.[1] Thus far, the follow-up has largely been based on empirical principles, rather than on systematic monitoring and control of key process variables.

In recent years process performance has become an economic reality in view of the standards and important levies imposed by government legislation. This has resulted in an increasing demand on the installed treatment facilities and upgrade paths have become an important area of research.[2] In general, two approaches to achieve the goal of increased removal capacity can be distinguished. One approach is to invest in new process units, e.g. aeration tanks and settlers, whereas the alternative approach is to increase reliability and efficiency. An improved control capability based on adequate on-line data should allow use of the capacity of the treatment plant in a more optimal way. In this paper, a sensor is presented that aims at providing the

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TABLE 1
Characteristics of Existing Sidestream Respirographic Biosensors used in Wastewater Treatment Systems

Reference	*Oxygen supply*		*Flow regime*		*Key variable*	
	Closed	*Open*	*Batch*	*Continuous*	*Sludge*	*Water*
Vernimmen *et al.*[14]	x		x			x
Clarke *et al.*[10]	x			x	x	
Köhne[11]	x			x		x
Aidun and Smith[7]	x		x		x	
Sekine *et al.*[8]	x		x		x	
Sollfrank and Gujer[12]	x			x	x	
Spanjers and Klapwijk[13]	x			x	x	
Drtil *et al.*[9]	x		x		x	
Farkas[15]		x	x			x
Blok[16]		x	x			x
Ros *et al.*[17]		x	x			x
Vanrolleghem *et al.*[18]		x	x			x
Vasel *et al.*[19]		x	x			x

information necessary to run existing facilities at higher loadings, coping with important disturbances through improved process control.

Due to the long response time (incubation takes 5 days at 20°C), the traditional method for determining biological oxygen demand (BOD) cannot be used for on-line control of wastewater treatment facilities and is merely a long term performance evaluation instrument. Alternatives which rely on physicochemical quantities such as chemical oxygen demand (COD), total organic carbon (TOC) or input flow rates have been widely used. However, the relevance of the information obtained is rather restricted and can only be relied upon on the premise that the wastewater composition is approximately constant.

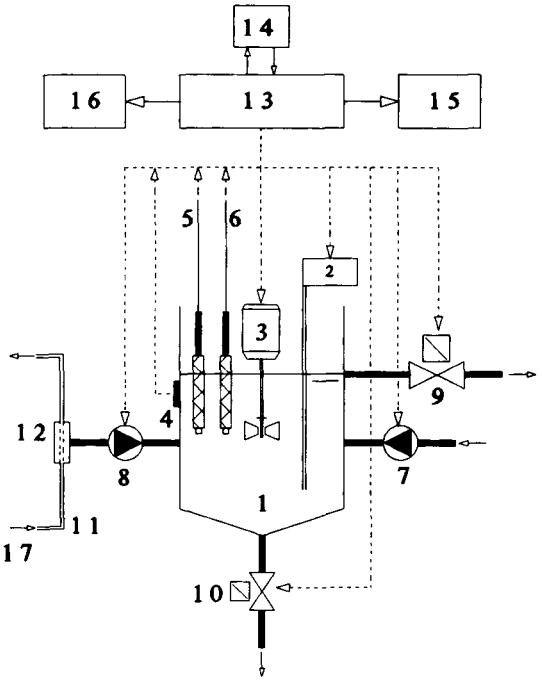
In-situ methods for on-line monitoring of the oxidation process all focus on the identification of the dissolved oxygen (DO) dynamics as recorded by a DO probe placed in the aeration tank. A number of authors have dealt with the problem of combined control/estimation schemes.[3–6] These studies have resulted in appropriate procedures for the introduction of the necessary excitation of the aeration rate, ensuring good identifiability of the bioprocess within the limits imposed by the DO control.

In contrast to these estimation schemes based on in-situ DO electrode outputs, most respirographic sensors are installed on sidestreams providing sludge and/or wastewater to the device. Table 1 summarizes the characteristics of a number of devices described in the literature. All sludge-centred systems are of the closed type, i.e. characterized by the absence of external oxygen supply, yielding more sensitive respiration measurements. In such systems the central idea is to obtain the respiration rate from a DO mass balance of the respiration chamber. Two approaches have been developed to measure the drop in DO. In one type, a stopped-flow batch-wise procedure is used to obtain a decreasing DO versus time profile from which the oxygen uptake rate is readily calculated.[7–9] In the other, continuous flow approach, a difference in two DO readings after a certain retention time in the respiration chamber is used to calculate the oxygen uptake rate.[10–12] An important problem of this arrangement concerns reliability since two probes are prone to fouling, drift, etc. A rather elegant solution proposed by Spanjers and Klapwijk[13] is based on a reversing flow mode that allows use of the same electrode in both the inlet and outlet of the respiration vessel.

In the case of systems that focus on input wastewaters, the respiration rate caused by the presence of wastewaters is rather high. As a result, either important dilution[11] or small sample sizes[14] are necessary to allow measurement of the respiration rate in closed systems. In all other cases, aeration is necessary to provide the required oxygen, resulting in open systems that are easier to operate because larger sample sizes can be applied.[15–19]

A new development is the application of microbial sensors as BOD probes. Except in one case,[20] these sensors consist of a DO electrode in which the membrane is replaced with a sandwich membrane containing different types of biocatalysts. Immobilization of activated sludge[21–23] has been found to be a tedious task with problems of result reproducibility. Pure culture BOD-probes are, however, much easier to manufacture but lack the broad substrate specificity of an activated sludge community. Yeasts, in particular, have been studied.[24–26]

In this paper, an open, batch operation input flow-



1. Reactor (10dm³ sludge)
2. Aerator
3. Stirrer
4. Temperature sensor
5. DO electrode
6. pH electrode
7. Calibration pump
8. Sample pump
9. Decantation valve
10. Sludge outlet valve
11. Bypass
12. Filter system (0.5mm)
13. Microprocessor
14. Display / Keyboard
15. Computer (PC)
16. Printer
17. Wastewater

Fig. 1. Scheme of the respirographic biosensor.

centred respirographic sensor is presented that is able to determine:

—the BOD of wastewater
—the toxicity of the test sample towards the sludge
—the specific activity of the biological sludge

The industrial device is a microprocessor controlled biosensor called RODTOX, acronym for Rapid Oxygen Demand and TOXicity Tester.

2 HARDWARE CONFIGURATION OF THE BIOSENSOR

The biosensor (RODTOX, KELMA NV, Niel, Belgium) consisted of three main parts (Fig. 1): a biological section, the microprocessor with accessories and software and an electronic section that interfaced the first two parts.

The biological unit consisted of a reactor vessel, filled with 10 dm^3 of activated sludge taken from the wastewater treatment plant at which the device was installed. Under normal operating conditions, the mixed liquor was subject to constant aeration of 15 $dm^3\ min^{-1}$ and temperature controlled at $25 \pm 0{\cdot}1°C$. DO and pH-electrodes were installed in the cover of the bioreactor. The steady-state DO concentration (see below) was 6–9 mg $O_2\ dm^{-3}$ and pH was normally maintained at $7{\cdot}0 \pm 0{\cdot}2$. These values could be tuned to specific requirements.

Wastewaters and calibration substrates were introduced with precision membrane pumps (sample sizes ranged from 2 to 500 cm^3). Wastewaters were supplied through a fast loop. A coarse (0·5 mm) tangential filter in this fast loop bypass line protected the pumping system from clogging.

The respirometric data were constantly analysed by the microprocessor. The whole of the apparatus was designed to operate on crude wastewaters at the treatment site.

3 GENERAL PRINCIPLES

3.1 Estimation of wastewater load (stBOD)

The DO mass balance in an activated sludge filled reactor vessel is governed by an oxygen supply and biological oxygen uptake process. Respiration can be sub-divided into endogenous (OUR_{end}) and exogenous (OUR_{ex}, substrate degradation induced) oxygen uptake rates. The DO can therefore by expressed as follows:

$$\frac{dc}{dt} = K_L a(c_s - c) - OUR_{end} - OUR_{ex} \qquad (1)$$

When aeration takes place in the absence of substrate, the DO concentration will reach a steady state, reflecting the equilibrium between oxygen transfer and endogenous respiration:

$$\frac{dc}{dt} = 0 = K_L a(c_s - c_e) - OUR_{end} \qquad (2)$$

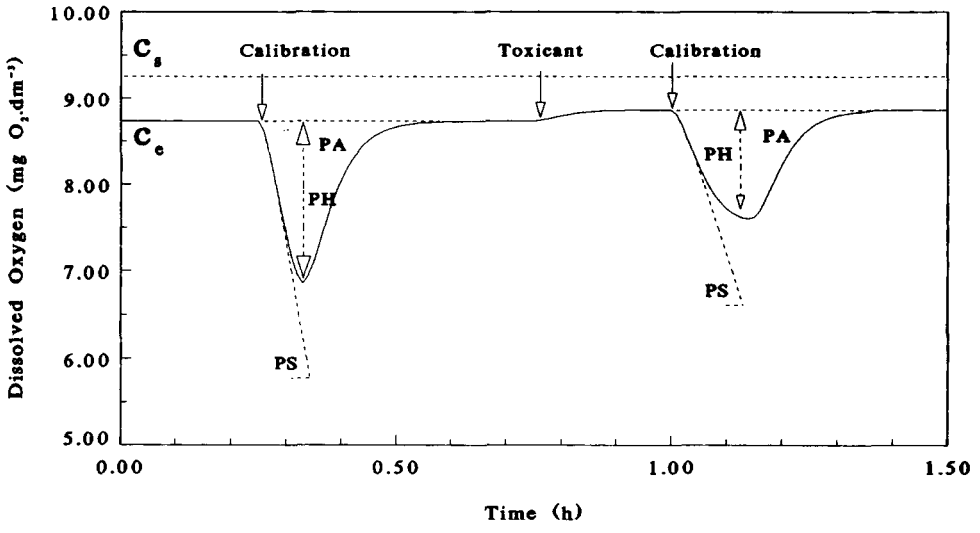


Fig. 2. Typical DO profiles ('respirograms') obtained after injections of a pulse of wastewater (PS: peak slope, PH: peak height, PA: peak area, c_s: saturation DO, c_e: equilibrium DO).

From this, the difference between the equilibrium concentration (c_e) and the saturation level (c_s) multiplied by the volumetric mass transfer coefficient (K_La) reflects the OUR_{end}. Substituting OUR_{end} by K_La (c_s-c_e) in eqn (1) results after rearrangement in:

$$\frac{dc}{dt} = K_La(c_e - c) - OUR_{ex} \tag{3}$$

Addition of a biodegradable substrate to the mixed liquor causes the DO level to decrease due to exogenous respiration. When the substrate is oxidized completely, OUR_{ex} returns to zero. Due to continuous aeration, the DO concentration will increase until the steady state is again reached. Figure 2 shows the resulting DO profiles, termed respirograms.

These respirograms are characterized by three parameters calculated from the DO data, namely the peak slope (PS), peak height (PH) and peak area (PA). By comparing the respirographic parameters of the calibration respirogram with the ones obtained from a sample injection, insights can be gained in the biodegradation characteristics of the sample.

The peak slope gives an indication of the degradation rate of the waste. This is a measure particularly useful for toxicity assessment (see below). From the two other characteristics, estimates of the wastewater load can be obtained. Based on the knowledge of the BOD_5^{20} content of the calibration solution, the sample BOD_5^{20} can be derived using the following formula:

$$BOD^{20}_{5\,sample} = \frac{P_{sample}}{P_{calibration}} BOD^{20}_{5\,calibration} \tag{4}$$

with P either peak height or peak area. Peak height gives a first waste load estimate in less than 10 min after injection of the sample while the peak area is obtained within 20–40 min.

The BOD_5^{20} value is defined as the amount of oxygen consumed during the degradation of substrates. Since part of the substrate is not oxidized but incorporated in new biomass, the yield coefficient is a factor that influences a BOD measurement. Since a sludge–substrate interaction can occur in different ways (for example, with different biomass yields), for eqn (4) to hold, the calibration substrate should resemble the composition of the samples. When the composition of the waste is approximately known, a representative synthetic medium can be composed. When unknown, actual wastewater can be collected, stored, analysed for BOD_5^{20} content and subsequently used as calibration substrate.

There is discussion in the literature as to whether BOD_5^{20} measurements are relevant for process control of wastewater treatment systems (see e.g. Spanjers *et al.*[27]). The short-term (stBOD)BOD value, i.e. the amount of oxygen consumed within the time constraints of a plant, is believed to be more relevant to plant control, while BOD_5^{20} values relate more to the processes in receiving waters. Since the measurements obtained from the sensor presented are based on 30 min experiments, these data should be interpreted as stBOD. Correlation with BOD_5^{20} is useful, but was not a goal pursued with this device. Therefore eqn (4) should be rewritten as:

$$stBOD_{sample} = \frac{P_{sample}}{P_{calibration}} stBOD_{calibration} \tag{5}$$

Integration of eqn (3) over a respirogram (assuming K_La is constant within the short time interval of a respirogram) leads to:

$$c(t) - c(0) = K_La \int_0^t (c_e - c(t))\,dt - \int_0^t OUR_{ex}(t)\,dt \tag{6}$$

By definition stBOD is the amount of oxygen consumed

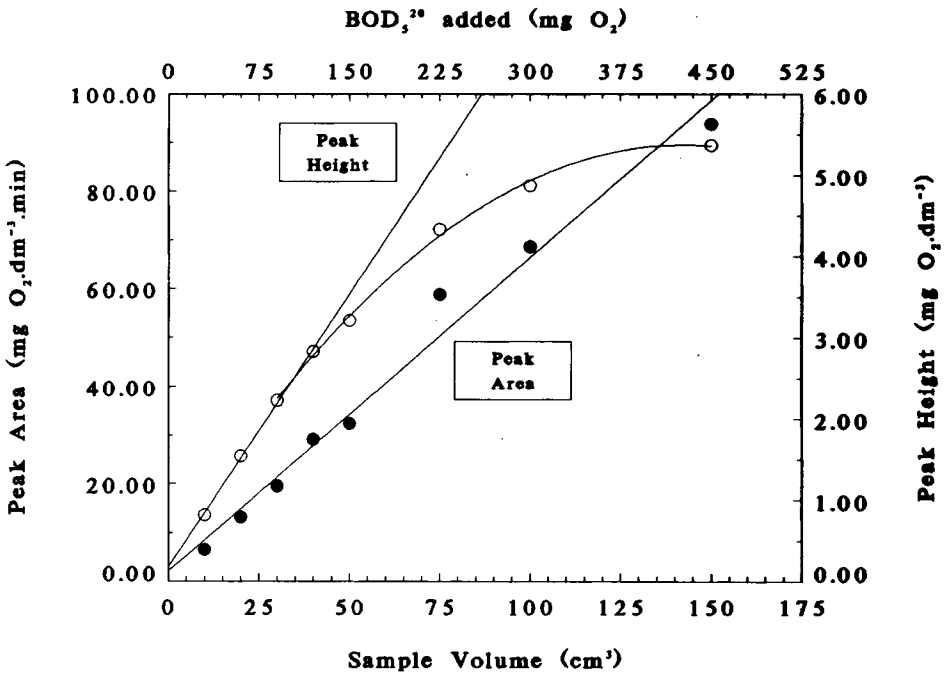


Fig. 3. Evaluation of the linearity of respirogram peak area (●) and height (○) as a function of the amount of waste injected.

for degradation of readily biodegradable substrates and equals the integral of the latter. Since the DO concentration at the end of a respirogram is equal to the initial value, $c(t) - c(0) = 0$ and as a result:

$$0 = K_L a \times \text{PA} - \text{stBOD} \qquad (7)$$

which states that the amount of stBOD is proportional to the area of the respirogram multiplied by the volumetric mass transfer coefficient.

Equation (7) has a number of consequences with respect to the operational characteristics of the respirographic biosensor. Firstly, this equation expresses the linear dependence of the peak area on the amount of waste injected. The range of stBOD concentrations where this linear relationship was valid was verified with a number of wastewaters. In Fig. 3, the results for an industrial wastewater are given. For this concentrated wastewater (3000 mg BOD_5^{20} dm^{-3}) from the chemical industry, linearity for peak area was maintained at least up to an injection volume of 150 cm^3. Linearity was not checked for higher sample injection volumes because respirograms then became too lengthy. From these experiments, linearity of peak area versus waste content held within an operating range of 25 to 500 mg BOD_5^{20} injected.

For comparison, the evolution of peak heights as function of injected volume is also illustrated in Fig. 3. As discussed, peak heights can give a first estimate of the waste load of the wastewater on the basis of eqn (5). However, the range of linearity is smaller since the peak height is saturating as injection volume increases.

A second consequence of eqn (7) is that the peak area is inversely proportional to the volumetric mass transfer coefficient. With dynamic re-aeration experiments under different aeration regimes (0 up to 2·5 vvm)[28] the aeration system in the biosensor device was shown to allow $K_L a$ values ranging between 0·03 and 0·30 min^{-1}. Therefore, for the same amount of stBOD injected, eqn (7) predicts a 10-fold increase in peak area when changing the air supply from minimum to maximum flow rate.

Figure 4 summarizes the results of an experiment in which respirograms were recorded under different aeration conditions (air flow rates of 1·0, 1·5, 2·0 and 2·5 $dm^3\ dm^{-3}\ min^{-1}$), each time with an injection of 200 mg COD as acetic acid. Each respirogram is preceded with a transient provoked by the change in aeration conditions. When DO had reached the steady state, the stBOD injection was performed. In Table 2, the peak areas and heights obtained are summarized, illustrating their dependence on aeration conditions. Also evident from the results listed in the table is that a lower aeration efficiency was reflected in longer respirograms since more time elapsed before DO returned to the baseline level.

The $K_L a$ in the sensor may be adjusted for optimum performance. Two applications are given to illustrate this.

In view of the fact that the time a respirogram took to finish depended on the $K_L a$ value, the measuring frequency may be increased by increasing the aeration efficiency.

Secondly, in a situation where diluted wastewaters are monitored, the measurable concentration range under normal operating conditions (maximum sample volumes of 500 cm^3 and aeration rates of 1·5 vvm, corresponding to a $K_L a$ of approx. 0·15 min^{-1}) was situated between 50 and 1000 mg BOD_5^{20} dm^{-3}. Lower concentrations could not be measured reliably because the peak became

TABLE 2
Dependence of the Respirographic Peak Parameters on the Air Flow Rate in the Sensor's Bioreactor

Peak parameter	*Aeration conditions (vvm)*				
	1·5	*2·5*	*1·0*	*2·0*	*1·5*
Peak area (mg O_2 dm^{-3} min)	32·65	19·09	49·07	25·65	31·01
Peak height (mg O_2 dm^{-3})	5·76	5·09	6·13	5·48	5·79
Peak length (min)	20·6	17·3	32·3	18·4	19·8

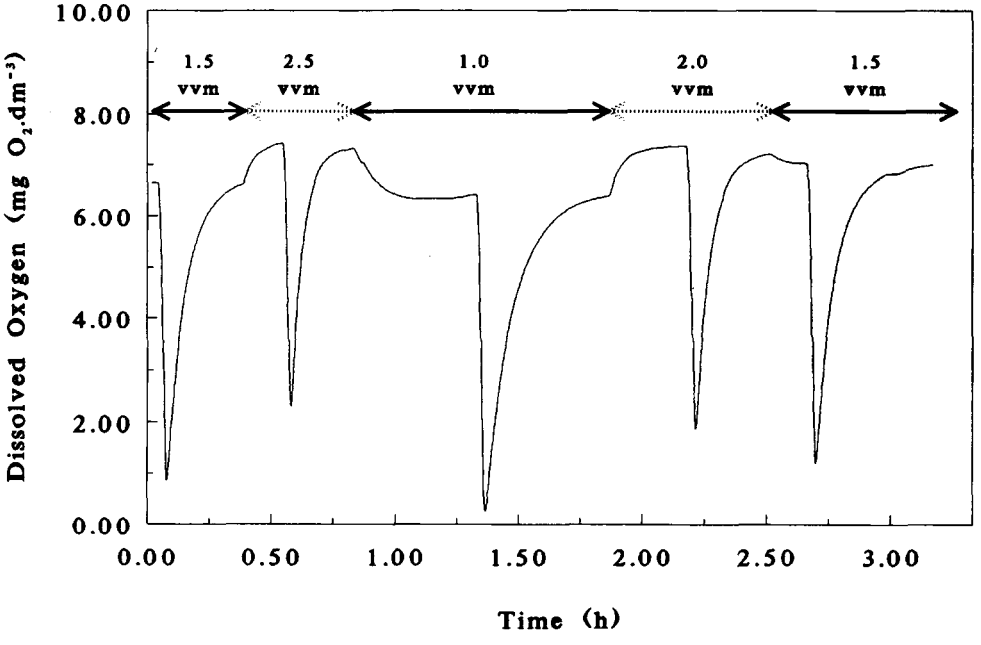


Fig. 4. Respirograms obtained in the biosensor under different aeration conditions (1·0, 1·5, 2·0 and 2·5 vvm). Respirograms are the result of an injection of 100 mg BOD_5^{20}. The new steady-state DO was obtained before the sample was injected.

insignificant compared with the DO data noise. A reduction of the air flow rate to a K_La of 0·03 min^{-1} alleviated this, resulting in an inversely proportional shift in the concentration range to 10 to 200 mg BOD_5^{20} dm^{-3}. The lower concentration corresponded to an initial reactor concentration of only 0·5 mg BOD_5^{20} dm^{-3} (0·5 dm^3 sample × 10 mg BOD_5^{20} dm^{-3}/10 dm reactor) and still gave rise to a measurable respirogram.

Clearly, the operating range can be allocated using the air flow rate as an adjustable system parameter allowing a 10-fold span. With an inherent concentration range up to 20 times the lowest concentration and a pumping range that spans a factor of 250, the sensor can accommodate wastewaters containing between 10 and 500 000 mg BOD_5^{20} dm^{-3}.

3.2 Toxicity testing

Evaluation of wastewater toxicity towards the activated sludge in the biosensor was based on a comparison of the respirographic parameters of calibration respirograms before (t_1) and after (t_2) the addition of the potentially toxic wastewater sample (Fig. 2). The % inhibition of the peak slope, peak height and peak area may be calculated using:

$$\%I = \frac{P_{calibration}(t_1) - P_{calibration}(t_2)}{P_{calibration}(t_1)} \quad (8)$$

with P equal to one of these peak parameters. Subsequently, these inhibition percentages may be evaluated against predefined limits and the result used to activate alarm signals.

In Fig. 5, a typical sequence of calibration respirograms is given, in this case with copper intoxication. Between each calibration, four wastewater samples were injected with increasing copper concentrations. As a result, the peak parameters changed. Table 3 illustrates that peak slope was the most sensitive parameter. This is acceptable from a biological point of view because the peak slope reflects the biodegradation rate of the substrate and is therefore indicative of the sludge degradation capacity. This result is also advantageous since the peak slope is

TABLE 3
Influence of Copper Intoxication on Respirographic Characteristics Recorded in the Biosensor

Peak parameter	*Wastewater copper concentration (mg dm^{-3})*			
	0	*1·0*	*2·0*	*4·0*
Peak slope (mg O_2 dm^{-3} min^{-1})	0·57	0·44	0·19	0·02
Peak height (mg O_2 dm^{-3})	2·20	1·81	0·80	0·38
Peak area (mg O_2 dm^{-3} min)	18·63	16·68	17·04	17·51
Baseline c_e (mg O_2 dm^{-3})	7·22	7·20	7·45	7·63
Peak length (min)	20·1	22·9	36·3	64·0

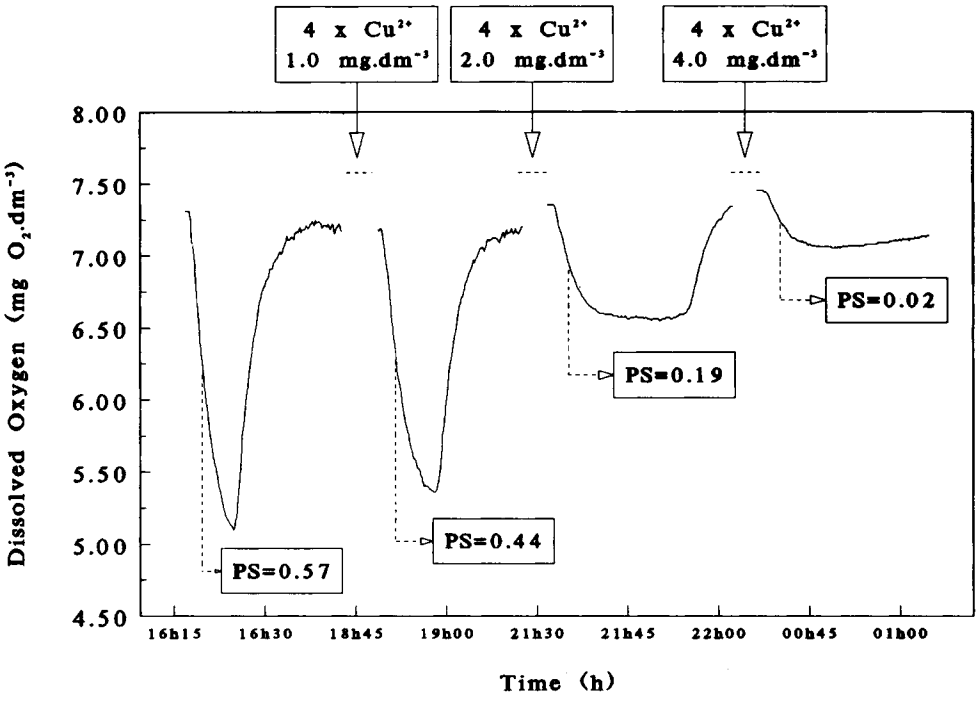


Fig. 5. Respirograms observed under copper intoxication with a copper-containing wastewater. The copper concentration increased gradually during the experiment from 1 ppm to 4 ppm. Four injections were performed between calibrations.

the first parameter available after initiation of the calibration. Therefore, inhibition can be assessed within 2–4 min. From the results in Fig. 5, peak height could also be used as a toxicity indicator. However, for other calibration mixtures tested, the effect was less pronounced (results not shown).

In the example of Fig. 5, peak area remained unchanged until complete inhibition of the sludge occurred, a typical feature of this respirographic parameter since the peak area reflects the amount of substrate oxidized by the sludge and not the condition of the sludge. Toxicity will affect the peak area only when the degradation capacity of the sludge with respect to one or more wastewater components is lost completely. An application of this phenomenon is the use of a binary calibration substrate consisting of a carbon source and ammonium to check the viability of nitrifying organisms in the sludge. If the nitrifiers are inhibited completely, this will be reflected by a change in peak area proportional to the amount of Nitrogen oxygen demand (NOD) present in the calibration liquid.

An important factor for toxicity detection is the response time. From the principle presented above, the response time is clearly dependent on the calibration frequency. With a typical respirogram length of 30 min and a normal operating mode of four to six wastewater samples between calibrations, a worst case scenario would result in a response time of 2 h (4 × 30 + 4 min) to 3 h. However, this can be decreased to 1 h in two ways. Firstly, the calibration frequency may be increased, but this would be at the expense of stBOD measurements and therefore not recommended. The second method

does not require a decrease in the number of measurements between calibrations and is based on the on-line interpretation of the baseline DO (c_e). The central principle is that the endogenous respiration rate is also affected if the sludge is intoxicated. As eqn (2) shows, the baseline reached at the end of the respirogram will be shifted proportionally to a toxicity-induced change in OUR_{end}. Detection of this can be used to set off an alarm. However, before the alarm is activated, a verification test is performed, consisting of an enforced calibration respirogram that allows assessment of the inhibition of the sludge within minutes.

Two types of effects on the baseline have been found experimentally. A decrease in OUR_{end} has been mainly observed, giving rise to an upward shift of c_e (see eqn (2)). This phenomenon is also apparent in Fig. 5; the corresponding c_e values have been compiled in Table 3. In some instances, an increase in endogenous respiration due to metabolic uncoupling by a toxic component of wastewater can lead to a baseline drop. This effect has been observed in the presence of 1 ppm of pentachlorophenol. Observation of this phenomenon will also induce a calibration test to confirm toxicity.

The sensitivity of respirographic toxicity detection is typically as follows: pentachlorophenol, 1 ppm; Hg^{2+}, Cu^{2+}, CN^-, 3,5-dichlorophenol, 10 ppm; *o*-cresol, 100 ppm; toluene, 1000 ppm.

3.3 Activity measurement

For toxicity testing, but equally important for reliable wastewater load assessment, the sludge used in the sensor should be as close as possible in activity and composition to that in the wastewater treatment plant. Regular replacement of the sludge in the bioreactor may be employed, but results in an interruption of normal operation. More efficient is to quantify the activity of the sludge present in the sensor and check the value regularly. The sludge must be replaced only when a significant deviation is observed.

Although the calibration respirograms are useful in reflecting the sludge condition, an independent respirographic measure was sought. Since calibration gave a regular check on exogenous (substrate induced) respiration, an obvious choice was to look at endogenous respiration as an additional sludge characteristic.

In the proposed method, the air supply is interrupted and DO will decrease according to eqn (1) as a result of the cellular respiration with OUR_{ex} and K_La being zero. The slope of the curve obtained equals OUR_{end}, the measure of sludge activity. Stirring must be continued during the activity test to prevent drifting of the DO probe as a result of the stagnant liquid film building up around the electrode tip. When a certain DO drop is reached (typically 2 mg O_2 dm^{-3}), aeration is started and, after reaeration of the mixed liquor, the sensor can return to normal operation. The time taken for such a test is approximately 30 min.

3.4 Detection of oxidizing and reducing agents

In any measurement technique based on the interpretation of biologically-induced oxygen uptake, the occurrence of purely chemical oxidation or reduction reactions may have detrimental effects on deduced variables such as toxicity or stBOD. Wastewater components, such as hydrogen peroxide and reduced sulphur compounds, will give rise to erroneous results if their presence is not taken into account.

The method developed to assess the presence of oxido-reduction reagents was based on the difference in reaction rate between chemical reactions and biologically-catalysed reactions. Figure 6 illustrates that injection of a wastewater containing 111 mg H_2O_2 dm^{-3} resulted in an almost instantaneous increase in the DO concentration. Here, the effect of the peroxide was superimposed on the biological oxygen consumption which would otherwise have given a respirogram following the dashed line in Fig. 6. After an initial increase in DO, the effect of peroxide continues for approximately 3 min. During this period, eqn (1) is not valid to describe the DO balance since oxygen was also supplied from the peroxide. In the case of reducing compounds, eqn (1) is otherwise affected since oxygen uptake is no longer due only to biological reactions, a significant part being a result of chemical reactions.

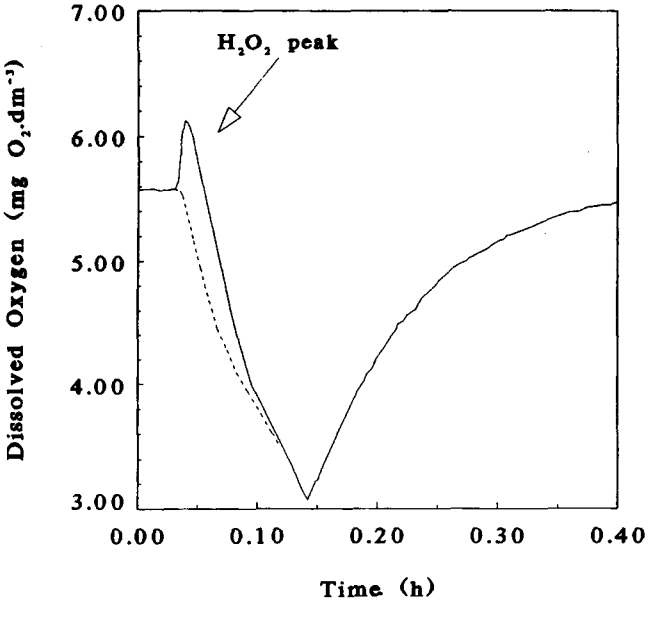


Fig. 6. Effect of the presence of hydrogen peroxide on respirograms, obtained with a wastewater containing 111 ppm H_2O_2. The dashed line illustrates how the respirogram would have been in the absence of the peroxide.

4 APPLICATIONS OF THE SENSOR

The system can be used in a laboratory environment or in a wastewater treatment plant for on-line input wastewater characterization.

4.1 Laboratory applications

Firstly, the sensor may be used for the testing of biodegradability and toxicity of new chemicals. For the assessment of toxicity, Kong *et al.*[29] proposed a fast method for the estimation of the IC_{50}, i.e. the toxicant concentration where the activated sludge is 50% inhibited. This method has been validated and compared well to the Microtox method.[29]

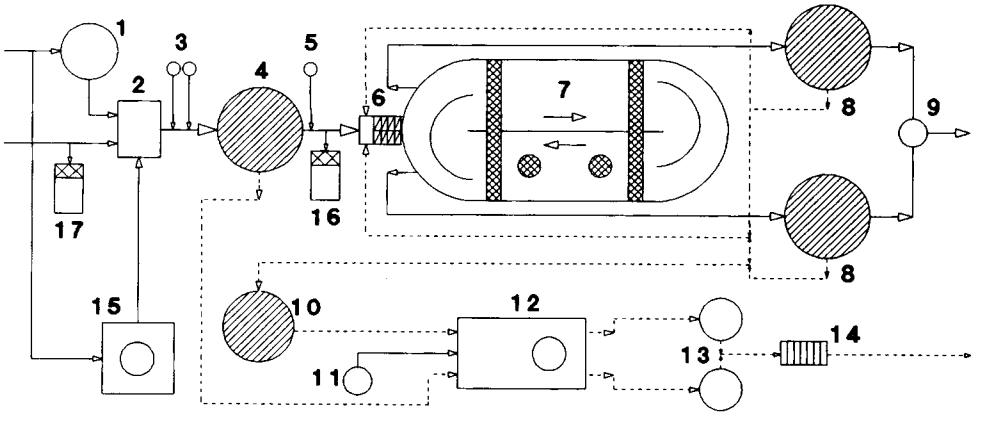
The environmental department of Esso Belgium is using the sensor to overview potential dangers of different wastewater sources and chemicals such as cleaning agents, paints and fire extinguishers (regularly used for training). For each of these a toxicity card is produced that includes toxicity data obtained on the basis of respirographic tests. The cards are subsequently distributed within the production facilities to all personnel concerned.

In another application, Degussa Antwerpen has decided to use the sensor to define the responsibility of the different production divisions for their respective waste discharges. The operating costs and part of the investment costs of the centralized wastewater treatment plant are paid by the production divisions in proportion to their discharges. To obtain the necessary objective data, samples are taken regularly at the different discharge points. The stBOD values obtained, together with flow information and other wastewater characteristics (suspended solids, COD, nitrogen load) are subsequently used to calculate the invoice of each division.

4.2 On-line implementation in the wastewater treatment plant

The importance of a correct choice of the site of installation for the sensor within a treatment plant is illustrated with an example from the chemical industry.

Figure 7 summarizes the wastewater treatment facility for the different production plants operating at Degussa in Antwerp. The wastewater is collected through two different channels, one of which transports a wastewater with approximately constant composition to the treatment facility. Being a concentrated wastewater, this supply route uses a buffer tank (1500 m^3) to equalize load variations to the treatment process. A calamity basin with a volume of 6000 m^3 can be used in case of overload or toxicity problems. After the 600 m^3 equalization basin and pH adjustment, flocculant addition and primary settling occurs. Water is then pumped into the surface aerated basin (11000 m^3) where carbon oxidation, nitrification and denitrification occur. Two parallel clarifiers (2 × 1570 m^3) produce the final effluent and return sludge. Waste sludge



1. COD Buffer Tank
2. Equalization Basin
3. pH Control Equipment
4. Primary Clarifier
5. P-dosing Unit
6. Archimedes Screws
7. Aeration Basin
8. Secondary Clarifier
9. Effluent Tank
10. Sludge Thickener
11. $FeCl_3/CaCO_3$ dosing Unit
12. Sludge Conditioning
13. Sludge Buffer Tank
14. Sludge Filter Press
15. Calamity Basin
16. RODTOX 1
17. RODTOX 2

Fig. 7. Flowsheet of a full-scale chemical wastewater treatment facility (Degussa Antwerpen). The biosensors are installed to monitor the raw wastewater and also the equalized and pretreated input wastewater of the aeration basin.

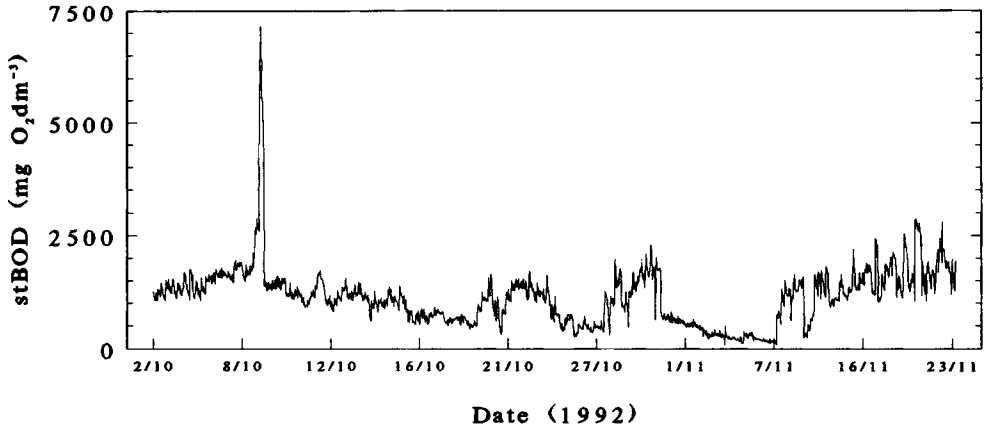


Fig. 8. Operational data (1808 respirograms) collected by the biosensor sampling the input of the aeration basin. The stBOD values ranged between 70 and over 7000 mg dm^{-3} with a mean load of 1120 mg dm^{-3}.

is thickened and combined with primary sludge for further dewatering.

An initial respirographic sensor was installed in mid-1991 at the effluent of the primary settler. In Fig. 8, a seven week operational data record of this system is presented (1808 respirograms). Large variations in the stBOD loading can be observed (1120 $\pm$ 630 mg O_2 dm^{-3}) which may be correlated with changes in the batch productions occurring in the firm. As the loading of the treatment plant increases due to the expansion of the production facilities, a more optimal use of the installed capacity will be required to achieve the required (increasing) effluent quality. Data records as shown may assist in an improved scheduling of batch productions with respect to the loading of the plant.

In a number of chemical processes, hydrogen peroxide is used and discharged in high concentrations. Typically, a background of 20 ppm H_2O_2 is observed in the input wastewater. This amount is not detrimental to plant performance, but, occasionally, important peroxide spills occur, e.g. when a batch process fails. In Fig. 9, the hydrogen peroxide content of the wastewater is displayed for a period of one month during which such an event took place (in the night of Tuesday, October 27th). Nine hours before the off-line measurement took place by the plant operator, the biosensor had activated an alarm for the presence of oxidizing compounds in the wastewater (at 22h02, see Table 4). As soon as the importance of the spill had been acknowledged, the wastewater was diverted to the calamity basin to protect the sludge. The next step consisted of tracking the source and of evaluating the size of the spill. Only when this information was available (by Monday, November 2nd), was the wastewater released gradually to the treatment plant in

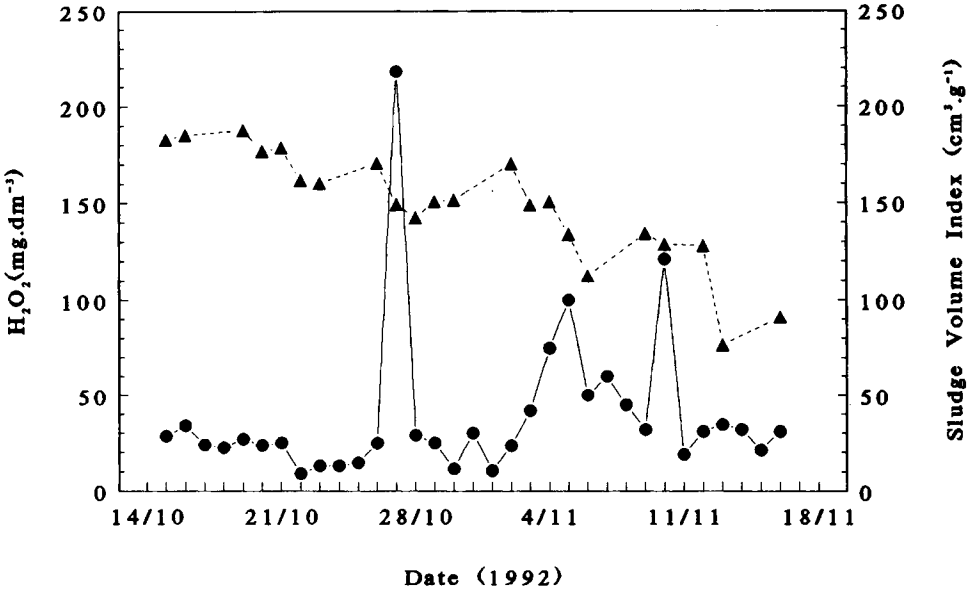


Fig. 9. Off-line hydrogen peroxide (●) and SVI (▲) measurements performed when a peroxide spill was detected with the respirographic biosensor.

TABLE 4
Printout of the Biosensor Showing Alarms Given at an Industrial Site During the Week of an Important Hydrogen Peroxide Spill in October 1992

Date	*Time*	*Alarm Text*
23.10	20.20	Slowly biodegr. compounds in prev. sample
25.10	06.42	Slowly biodegr. compounds in prev. sample
27.10	00.21	Slowly biodegr. compounds in prev. sample
	14.08	Slowly biodegr. compounds in prev. sample
	18.47	Slowly biodegr. compounds in prev. sample
	22.02	Abnorm increase of DO level Oxid. or toxic compounds
	22.39	Abnorm increase of DO level Oxid. or toxic compounds
	23.17	Abnorm increase of DO level Oxid. or toxic compounds
28.10	00.09	Oxid alarm
	01.00	Oxid alarm
	01.38	Oxid alarm
	02.14	Oxid alarm
	02.50	Oxid alarm
	03.27	Oxid alarm
	04.02	Oxid alarm
30.10	01.10	Oxid alarm
	14.06	No baseline found
31.10	04.22	Oxid alarm

such a way that toxicity thresholds were not exceeded. The sensor occasionally reported on the presence of oxidizing compounds during this period (November 3rd–11th). The effect of this toxic waste spill was restricted in terms of removal efficiency, since no deterioration could be observed from the off-line data on COD, ammonia and nitrate in the effluent. However, an improvement in the settling characteristics (as determined by the sludge volume index, SVI) could be correlated with the presence of sub-inhibitory peroxide concentrations. The SVI values summarized in Fig. 9 illustrate this phenomenon. Microscopic inspection of the sludge revealed a decrease in filament abundance as a result of 'peroxide burning'.[30]

An increasing demand for laboratory tests as described above resulted in periodic interruptions of the on-line monitoring of the input wastewater by the first sensor installed. Also, monitoring of the wastewater upstream of the equalization basin may lead to improvement of the load variation control system and would assist in early toxicity detection. As a result, a second respirographic sensor was implemented in the beginning of 1993 (item 17 in Figure 7). At present, studies are going on to use the information provided by both sensors for the control of the COD buffer tank so as to minimize load variations. In a first stage the flow rate out of the buffer tank is controlled manually, but an automated control system seems a logical step for the future.

5 CONCLUSIONS

A respirographic biosensor has been presented that is fit for implementation on a sidestream of the input wastewater. The sensor has an inherently large dynamic range for short term BOD measurements (0·01–500 g stBOD dm^{-3}). Toxicity assessment was based on a reference activity test which allowed clear separation of toxic effect from load variations. The response time for toxicity detection was typically 2 h, but severe intoxications were detected more readily.

A separate test is proposed to check the condition of the sludge in the sensor which allows minimization of the number of sludge replacements required to keep the sludge in the sensor as representative of the treatment plants' sludge. Interferences by oxido-reduction chemicals in the wastewater can be eliminated.

The sensor's potential for improved waste management and control of treatment plant performance has been illustrated with applications in the laboratory and on the treatment plant.

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NOTATION

BOD_5^{20}	Biochemical oxygen demand (mg O_2 dm^{-3})
C	Dissolved oxygen (mg O_2 dm^{-3})
c_e	Steady-state dissolved oxygen (mg O_2 dm^{-3})
c_s	Saturation dissolved oxygen (mg O_2 dm^{-3})
COD	Chemical oxygen demand (mg O_2 dm^{-3})
DO	Dissolved oxygen (mg O_2 dm^{-3})
%I	Percentage Inhibition
K_La	Volumetric mass transfer coefficient (min^{-1})
NOD	Nitrogen oxygen demand (mg O_2 dm^{-3})
OUR_{end}	Endogenous oxygen uptake rate (mg O_2 dm^{-3} min^{-1})
OUR_{ex}	Exogenous oxygen uptake rate (mg O_2 dm^{-3} min^{-1})
PA	Respirogram peak area (mg O_2 dm^{-3} min)
PH	Respirogram peak height (mg O_2 dm^{-3})
PS	Respirogram peak slope (mg O_2 dm^{-3} min^{-1})
RODTOX	Rapid Oxygen Demand and TOXicity tester
stBOD	Short-term biochemical oxygen demand (mg O_2 dm^{-3})
SVI	Sludge volume index (dm^3 g^{-1})
TOC	Total organic carbon (mg C dm^{-3})

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