

Sensors for Anaerobic Digestion: An overview

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ABSTRACT

New and existing technologies for the monitoring of anaerobic digestion processes are presented. Emphasis is given to the way these sensors can provide insight in the ongoing (bio-)processes. Attention is drawn to a number of practical problems associated with the use of sophisticated sensors in the harsh (dirty) conditions of wastewater treatment processes. The use of autocalibration and built-in sensor checks, cleaning systems and the recent implementation of reliable sample preparation units is illustrated.

INTRODUCTION

Control of wastewater treatment plants relies on four building blocks: 1) insight in the process as summarized in a proper process model; 2) sensors that provide on-line data; 3) adequate control strategies and 4) actuators that implement the controller output. Recently it was emphasized that, "in general, sensors are the weakest part of the chain in real-time process control of wastewater treatment plants" (Harremoës et al., 1993). Note, however, that this statement exists since the sixties... Although the chain itself has strengthened considerably during this period -with significant breakthroughs in control theory and ever increasing sensor capabilities- the wastewater treatment problem itself evolved as well. Demands on water quality become more and more stringent, requiring more advanced treatment systems able to comply with (lowering) standards not only for organic carbon, but also for nitrogen and phosphorous levels. Hence, increasingly complex treatment systems must be run and yield ever increasing effluent water quality. Sensor technology has tried to catch up with the higher demands. However, at this stage an important barrier for the widespread acceptance of new sensors is that existing wastewater treatment plants were not designed for their use in real-time control systems. This is clearly exemplified in the lack of manipulable variables and actuators. Moreover, the fact that plant design was done in such a way that the effluent quality could be guaranteed without advanced control strategies (that rely on the new monitoring equipment) has resulted in overdimensioned plants. Hence, although at this stage effluent criteria may still be reached by these systems, the implementation of some new sensor technology seems unavoidable as criteria become more stringent or increasing waste loads must be treated (Barnard & Crowther, 1993). For outdated treatment plants that need considerable upgrading investments, the use of new monitoring equipment should be regarded as a valuable alternative to increased reactor volumes.

In this paper some evolving technologies are reviewed. The potential use and the practical experience gained so far will be presented. Attention will be drawn to the basic problems associated to the use of sensors (Harremoës et al., 1993): reliability, fouling, calibration and for some of them, sampling techniques. Although maintenance in the harsh environment of "waste" water will always be of concern, the new sensors are particularly sensitive and at this time require skilled personnel spending an important amount of time "maintaining" the systems in operation.

GENERAL PURPOSE SENSORS

Central to all wastewater treatment plants are flowing water, solids and gases. The physical properties of the three phases are worth monitoring and since these measurements are not specific for any biological process, these variables are treated separately in this section. Sensors measuring characteristics specific to anaerobic digestion processes will be discussed in the next section.

Temperature

This is a classic measurement, typically with a thermistor. It is a rather important variable for anaerobic digesters where temperature control is often implemented (for mesophilic or thermophilic operation).

Pressure

Pressure measurements are traditional on wastewater treatment plants as well, especially for alarm functions in aeration and anaerobic digesters.

Liquid Level

Common principles used to monitor water levels are: floats with an internal electric switch; conductivity switches; (differential) pressure transducers; capacitance measurements and ultrasonic level detection. The two first techniques are only useful for on/off level detection and mostly serve alarm functions. Differential pressure and ultrasonic equipment give a continuous signal, the latter being more precise but also sensitive to foam.

Flow of Liquid/Gas

Instruments for the monitoring of gas and liquid flows are ubiquitous in wastewater treatment. Harremoës et al. (1993) give an extensive overview of liquid flow measurement techniques and point to the importance of proper installation for guaranteed accuracy. Measurements are based on the change in water level (see above) as a result of an obstacle in the water flow path (Venturi principle). In addition, electromagnetic and ultrasonic sensors are applied.

For gas flow measurements recurrence is made to rotameters and, less common, thermal mass flow meters. As biogas formation rate is one of the most commonly monitored variables in anaerobic digestion processes these gas flow sensors are very often part of digester instrumentation. Presence of hydrogen sulphide in the gas and the explosive character of biogas ask for precautions.

pH

It is normal practice to install pH electrodes in a treatment plant. Immersion of these probes in "sticky" sludge has encouraged the development of different cleaning strategies: hydraulic (water spray), mechanical (brush), chemical (rinsing with cleaning agent) or ultrasonic cleaning. With these techniques longer periods without maintenance can be attained. Harremoës et al. (1993) state that poor or no automatic cleaning may cause problems. Self-diagnosis has been integrated in advanced systems. In the more simple implementations, sensors are duplicated and their readings compared. More sophisticated setups include automated checks of the impedance of the diaphragm and the glass electrode, while tests performed during (automatic) calibration may point to other sensor deficiencies.

Although pH is a variable that is important in all biological processes, its value is especially critical in anaerobic digestion where important quantities of protons are released, eventually leading to acidification and process failure (Hawkes et al., 1992). Hence, its measurement and control are important. However, in the case of wastewaters with high buffering capacity, pH measurements may be rather insensitive to indicate process changes and are therefore not advisable for process supervision and control. In such cases they may be replaced with bicarbonate measuring systems (Di Pinto et al., 1990; Hawkes et al., 1993) (see below).

Conductivity

Sensors measuring conductivity are used to monitor influent composition changes (Teichgräber, 1993). Subject to fouling as well, these sensors should be equipped with cleaning systems. Moreover, as the principle of the measurement requires a voltage over the electrodes, an alternating current is essential to eliminate electrode polarisation.

Chemical Oxygen Demand (COD)

One of the most intensively monitored variables in wastewater treatment plants is the chemical oxygen demand. Using standardized laboratory analyses, the performance of most plants w.r.t. their carbon removal efficiency is determined.

A few attempts have been made to automate the two-step laboratory procedure which consists of: 1) 2 hr digestion in bichromate solution and 2) backtitration or colorimetric quantification of the residual oxidans. Two types of implementations have resulted, batch systems on the one hand and flow-through continuous COD monitors on the other. In the different setups that have evolved, several modifications have been made to the original methods in view of their on-line use. Digestion is shortened (typically 0.5 h instead of 2 h) to improve sample throughput and response time (Korenaga et al., 1990, Meredith, 1990). The titration end-point may be determined potentiometrically instead of using an indicator that is determined with a colorimeter. Also direct absorbance measurement as in some laboratory methods has been proposed for low range COD measurements (Korenaga et al., 1990). More important changes concern the digestion method applied. Meredith (1990) proposes not to use bichromate as an oxidizing agent, but to use hydrogen peroxide coupled to UV light to produce ozone in situ. After oxidation the surplus oxygen is monitored by means of a DO probe, giving the COD-content of the sample. Pilz and Werner (1988) present an electrochemical COD (ECOD) sensor in which the oxidative power is generated by a PbO₂ anode to which a high potential is applied.

Experience with a number of these sensors in the authors' laboratory has shown that sensors using chemical oxidation are subject to important clogging problems due to the formation of crystals of the oxidation chemicals on the one hand, and the presence of particulate matter in the sample on the other hand. The ECOD system showed potential but the relation between ECOD and laboratory COD-values was not constant and depended on the type of wastewater. Especially the rate of oxidation of the components in the sample affected the ECOD-reading substantially since a retention time in the reactor of only 5 minutes is maintained. Clogging problems were also noticed by Korenaga et al. (1990) and Meredith (1990). Hence, it must be advised to apply only prefiltered samples to the measuring devices.

Total Organic Carbon (TOC)

The central principle of a TOC measurement is to convert organic carbon to CO₂ and measure this product in the evolving gas phase, typically with an infrared off-gas analyser. Two principles exist for the conversion to carbon dioxide: In the one, a high temperature (650-800 °C) catalytic conversion is imposed, while in the other case persulphate is added to the sample where UV light promotes the oxidation of organic matter at moderate temperatures. Both methods have drawbacks. For the former method salts can produce a melt on the catalytic surface, inhibiting its proper operation. For the persulphate method, incomplete oxidation can occur when the pH of the sample is too low or when turbidity in the sample decreases penetration of the UV light. Stephenson et al. (1981) mention that potassium persulphate crystals can plague operation and that care must be taken to remove humidity from the gas stream prior to introduction in the gas analyser. For both types particulate matter is to be avoided because the retention time in the reaction chamber is insufficient to allow complete combustion. Moreover clogging may be a problem. Prefiltration of the samples seems therefore essential for proper operation. Some drawbacks inherent to the method are that the inorganic carbon present in the sample must be stripped first, potentially resulting in the loss of volatile organics. Also, one measures organic carbon (an important variable to characterise the load), but no information is obtained with respect to the oxidation state of the carbon. In addition, no data on the biodegradability of the waste water is given. Remark that the same holds true for the COD measurement (Londong, 1992). However, if the composition of the wastewater is rather constant, one can calibrate for these effects. Since the method is fast (5-10 min response time) and reliable if low-salt and particulate-free samples are provided, TOC can be advocated as a good monitoring parameter.

UV-absorbance

Many wastewater components absorb UV light. Already in the early fifties measurement of UV absorbance was introduced to assess the quality of an effluent (Dobbs et al., 1972). Optical methods have the advantage to be rather inexpensive and not to require reagents or preparation of the sample. Moreover, in the last decade fibre optic technology has made significant progress enabling remote and multi-point measurement (MacCraith et al., 1993). Different studies have illustrated the high correlation between UV absorption and TOC-content of samples (Dobbs et al., 1972). They state however that turbidity should not exceed a certain limit if the correlation is to be useful and propose the use of filtration units. MacCraith et al. (1993) performed similar studies but eliminated turbidity interference using newer technologies. Like TOC-measurements, UV-absorption methods require constant sample composition to predict actual loads to the treatment plant.

Turbidity/Suspended Solids

Probably one of the most important variables in digestion processes is the suspended solids concentration (SS). On the one hand, SS partially determine effluent quality where small concentrations are desired in order 1) not to loose too much of the slow growing biomass and 2) not to load subsequent stages with particulate COD. On the other hand, high concentrations are wanted in the reactor for high biocatalytic activity in the system. Monitoring SS is mainly based on turbidity. Three measuring principles have found application: optical measurements, absorption of ultrason and gamma rays. The latter two are mounted in high solids systems (> 10g/l). With the advent of sensitive light detectors, sensors were developed capable of automating the measurement of optic effects in an illuminated sample. Although it is impossible to make a direct calculation of the dry weight concentration from any "optical density" measurement, the systems can provide reasonable estimates if regularly calibrated.

Different principles have been brought to practice, based on the different phenomena occurring when a sample with (biomass) particles is illuminated. Part of the light is absorbed, another part is allowed to pass the sample (transmission), and, finally, light scattering in all directions occurs. Scattering is not homogeneous with the angle: forward scattering is the more pronounced, while backscattering is the least effective. The scattering over 90° gives light intensities between both extremes; its measurement is also known as nephelometry. Depending on the solids concentration, one or the other light measurement will be the more beneficial. Scattering techniques are preferred for low solids samples, typically effluent turbidity, while light absorption is favoured in case mixed liquor concentrations are to be measured. Back-scattering is also rather advantageous in high solids systems where absorption may be too high to allow its measurement, all light being absorbed! A workaround for absorption monitoring consisting of shortening the light path is practically impossible due to the associated fouling problems.

Measurement errors are typically 5-10%, which is in the same order of magnitude as the standard dry weight measurement (Andersen & Wagner, 1990). Problems that need attention are the following. Gas bubbles may contribute significantly to light scattering. The effect can be reduced by proper sensor location and filtering of the bubble-induced noise. Also, with a special optical construction both forward scattering and transmission can be measured. The ratio between both allows to eliminate scattered light not originating from the particles or bubbles in the light path (Sonnleitner et al., 1992). Colour in the water may contribute to the light absorption and should be eliminated from the measurement. Pulsating IR-light instead of white light helps eliminating this interference. Again, fouling is a major concern. Probes with holes or long "legs" are more prone to blocking than, for instance, backscatter sensors where light source and detector are at the same side of the sample (Andersen & Wagner, 1990). Equipping the sensors with a regularly performed "gas check" allows automatic detection of a minute build-up of film on the optics, allowing to ask for operator intervention (Watts et al., 1990). To decrease the fouling problem, different remedies are available. Location of the turbidity monitors in a highly turbulent region and sensors equipped with automatic cleaning devices, e.g. wipers or pistons, will decrease operator attendance time (Thomsen & Nielsen, 1992; Harremoës et al., 1993). A rather ingenious setup of the optical system makes the measurement insensitive to a number of sensor deficiencies such as light source weakening, aging of the detector and film build-up on the optics. The four-beam setup as this construction is termed performs this compensation by evaluating four different light beams. For more details reference is made to Vanrolleghem & Verstraete (1993).

Ultrafiltration

In the previous sections the need for prefiltered samples has been stressed, e.g. in the cases of COD and TOC monitors. A submerged pump transfers sludge through a (cross-flow) membrane filter where particulate free filtrate is obtained. It is advisable to equip the submerged pump with a shredder to prevent problems caused by the presence of rope and threads in the sludge (Andersen & Wagner, 1990). Also, it is important to use low-angle pipe bends and smooth narrowings in the pipe diameter to decrease the chance of pipe clogging. In principle, sufficient pumping capacity (typically 100 l/min) guarantees the self-cleaning properties of cross-flow filters due to the high shear forces that result (Thomsen & Nielsen, 1992).

Ultrafiltration (UF) membranes with a cut-off molecular weight of 20000 are typically applied. The life of a cross-flow filter is approx. 1 year (Thomsen & Nielsen, 1992) but regular cleaning is necessary. To maintain sample flow to the analysers a setup with two UF units is preferred. Using built-in filtrate flow meters or pressure drop measurements, automated switching of the active unit and activation of the cleaning program has been implemented. Typically the membranes need to be cleaned every 1 to 4 weeks. Cleaning strategies consist of an air blow or a hypochlorite chemical treatment.

ANAEROBIC DIGESTION SPECIFIC MONITORING EQUIPMENT

The anaerobic digestion is characterized by the complete mineralization of organic material into gaseous products such as H₂, CH₄, CO₂ and H₂S. The production of this biogas occurs in a two-step process where methanogenesis depends on the intermediates produced in the preceding acidification stage. Both processes must be geared to one another to prevent accumulation of the (volatile fatty) acids produced in the first step. Imbalance will eventually lead to process failure due to the inhibitory effects of these products at high concentrations and the pH-drop they induce (Anderson & Yang, 1992b). Measurement of the intermediates and the final gaseous products is therefore of great interest.

Gaseous Products (H_2 , CH_4 , CO_2 , H_2S)

Although a biogas flow measurement will give an indication of the overall activity of the reactor and has been used frequently as such, more specific techniques have been developed to monitor gas composition. A typical lab-scale method consists of a combination of flow measurements in a setup where one or more of the constituents is trapped in a washing bottle. The ratio of the flows before and after the bottle is representative of the gas composition. For instance, an alkaline washing bottle will trap all CO_2 and H_2S and lets CH_4 pass. More specific gas analysers monitor the content of a component directly. Typically, infrared absorption measurements are used to determine carbon dioxide and methane, while specific hydrogen analysers have been developed based on electrochemical cells (Mathiot et al., 1992; Pauss et al., 1993). Escoffier et al. (1992) trap H_2S before the entrance of the biogas into the hydrogen monitor. Hydrogen sulphide measurement in the gas phase may be performed by monitoring the reaction of sulphide with a Pb-strip. Subsequently, the black PbS that is produced, is quantified by colorimetry. A major problem associated with monitoring systems based on gas analysis is that it is not straightforward to predict the corresponding concentrations in the liquid phase which, after all, represent the organism's environment. Pauss et al. (1993) mention that often the dissolved hydrogen concentration is calculated from the biogas composition under the assumption of equilibrium between gas and liquid phase (Henry's law):

$$[H_2]^* = K_H p_{H_2}$$

where $[H_2]^*$ is the dissolved hydrogen concentration in equilibrium with the gaseous partial pressure (mole/l), p_{H_2} the gaseous hydrogen partial pressure (Pa) and K_H Henry's constant (mole/l.Pa). To calculate the liquid concentration correctly, however, mass transfer should also be considered:

$$\frac{d[H_2]}{dt} = k_L a ([H_2]^* - [H_2]) + r_{H_2}$$

with $k_L a$ the mass transfer coefficient (/h) and r_{H_2} the hydrogen production rate (mole/l.h). This equation expresses that a discrepancy will exist between the exact dissolved hydrogen concentration $[H_2]$ and the one calculated under the equilibrium assumption $[H_2]^*$. Moreover, this discrepancy will be more pronounced as the production rate increases and the mass transfer coefficient decreases. Pauss and Guiot (1993) give hydrogen mass transfer coefficients for digesters ranging between 0.04 and 0.4 h^{-1} . These low mass transfer efficiencies lead to supersaturation of the liquid ($[H_2] > [H_2]^*$). The authors observed that hundred-fold underestimations of the dissolved hydrogen concentration were obtained when calculated from biogas composition measurements. Therefore, gas composition measurements should only be used with great care, especially under dynamic conditions.

Recently, immersible sensors were developed to measure dissolved hydrogen concentration directly in the liquid phase down to partial pressures of 1 Pa. Pauss et al. (1993) evaluated these and report their reliable use and long-term stability. Here too, fuel cells are the heart of the sensor. Strong and Cord-Ruwisch (1995) describe the use of an inexpensive amperometric dissolved hydrogen probe to determine the onset of digester failure by substrate overloading. The measuring principle is based on the oxidation of hydrogen at a platinum black electrode at an adjusted potential. The current flowing to the electrode is directly related to the hydrogen concentration in the bulk liquid.

Membrane inlet mass spectrometry (Heinzle, 1992) is another method to directly measure a large number of dissolved gases and volatile compounds. Hence, this sensor set-up can also be used for VFA measurement, but correction for pH effects is necessary as the concentration of the undissociated form is measured. The MS-membrane probe response is often linear over very large concentration ranges. For application of thin membranes - that are required for sufficiently fast response and high sensitivity - the analyzer should be protected because of the rather high risk of membrane rupture. A fast safety shut-off system including fast pressure measurement must be installed. A pilot application of a batch anaerobic digester was reported in Heinzle (1992).

The measurement of dissolved carbon dioxide is described in the next section. As far as known to the authors, no direct on-line measurement of hydrogen sulphide in the liquid phase has been reported.

Bicarbonate Alkalinity

The incentive to measure the dissolved carbon dioxide and bicarbonate content of the mixed liquor originates from the fact that imbalance of anaerobic digestors (due to accumulation of volatile fatty acids) cannot easily be detected on the basis of pH-measurements, especially when the alkalinity of the mixed liquor is high (Rozzi, 1991; Hawkes et al., 1992). Indeed, in such systems, alkalinity must be destroyed to a large extent before pH drops significantly. Since the alkalinity is mainly due to the bicarbonate buffer, it has been proposed since the early sixties that its measurement can be used in control strategies for anaerobic digesters (McCarty, 1964). However, only recently automated bicarbonate monitors have been developed and applied in practice (Di Pinto et al., 1990; Hawkes et al., 1993).

Two basic principles have been used to assess bicarbonate alkalinity. First, titrimetry can be applied. It consists of titrating the sample down to a pH of 5.1 in a first step, followed by a further titration down to pH 3.5. This two-step titration allows to determine the bicarbonate content with a correction for the volatile fatty acids present (Anderson & Yang, 1992a). However, interferences with other weak acid/base organic couples cannot be excluded. As an alternative, titration and back titration methods have been proposed (Powell & Archer, 1989). Such setups are less prone to these interferences since the back titration provides a CO_2 -free blank.

The second method is based on quantifying the gaseous carbon dioxide evolving from the sample as it is acidified. The volume of gas may be measured in two different ways. Di Pinto et al. (1990) measure the overpressure in a closed constant volume vessel, while Hawkes et al. (1993) measure the produced gas volume with a sensitive gas flow meter. The latter principle allows continuous measurement while the former method and the titration methods require intermittent sampling.

Calorimetry

All biological activity is characterized by the production of heat. Athermal or even endothermic growth processes are unthinkable as they would violate the second law of thermodynamics (von Stockar & Marison, 1989). Measurement of heat production in so-called calorimeters therefore provides direct insight in the biological processes. Moreover, since heat dissipation is a universal feature, calorimetry can be applied to any bioprocess. Calorimeters have essentially followed the developments in temperature measurements. Different setups have been devised but it is beyond the scope of this paper to detail their design (Jolicoeur & Beaubien, 1986; von Stockar & Marison, 1989). For on-line monitoring of wastewater treatment preference should be given to flow calorimeters. Such devices are installed on a bypass fast loop and do not require special adaptations of the reactor the calorimeter is attached to. As an alternative, the heat balance of the reactor can be applied to calculate the biological heat production (van Kleeff et al., 1993). Here, all heat flows in and out of the reactor must be known, including for instance heat transfer through reactor walls, heat loss with the (gas and liquid) mass flows across the reactor boundaries, mechanical heat input and heat exchange with the temperature control system. A systematic overview of such heat balances is given in van Kleeff et al. (1993). These authors also focus attention to the problems inherent to this type of "whole reactor calorimetry": changes in heat transfer coefficients as a result of wall growth or changing hydrodynamic conditions. They also point to the precautions to be taken when the heat balance is used under dynamic conditions.

Fluorescence

A number of essential intermediates in bioreactions are characterized by fluorescence at particular wavelengths. A first group of fluorophores consist of the reduced forms of NAD(P)H. These electron carriers are widespread among living cells and since the early eighties attempts have been made to determine their level in microbial cultures (Sonnleitner et al., 1992). Most applications are found in aerobic systems, but Peck and Chynoweth (1992) report on experiments in which NADH fluorescence allows to detect digester instability due to substrate overload and inhibitory compounds. Moreover, it was found that this variable, among the different variables tested (VFA, pH, biogas flow), gave the first indication of imbalance.

A second fluorescing intracellular compound is the electron carrier coenzyme F_{420} that is unique to methanogens. Although still some discussion remains whether F_{420} is a good indicator of methanogenic activity (Colleran et al., 1992), probes have been developed to allow its quantification (Peck & Chynoweth, 1992). At this stage further study is required for a proper interpretation of the F_{420} signal, eventually leading to a direct measurement of the physiological state of methanogens.

Fluorosensors are built around two optical fibres, one bringing the excitation light into the culture, the other carrying the fluorescence light to the detector. For NAD(P)H measurement, excitation and fluorescence wavelengths are 351 and 460 nm respectively. For F_{420} monitoring the respective wavelengths are 406 and 465 nm (Peck & Chynoweth, 1992). Again, since these sensors are built as immersion probes, they will be subjected to fouling of the optical surfaces and probe design should take this into account (Peck & Chynoweth, 1992).

Often these fluorosensors have been advertised as biomass sensors. It is, however, important to note that the fluorescence measured is indicative of the metabolic state of the culture and can only be used to determine biomass concentrations if the physiological state of the culture remains constant (Sonnleitner et al., 1992).

Volatile Fatty Acids (VFA)

Volatile fatty acids are the most important intermediates in the anaerobic digestion process. Moreover, since their accumulation may lead to process failure due to the pH-drop they induce and their inhibitory effects in acid form. (Anderson & Yang, 1992b). VFA concentrations have been monitored for a long time as process performance indicators. However, few on-line sensors have been implemented. The most advanced instrumentation consists of a gas chromatograph or mass spectrometer coupled to a sample preparation unit, but so far no full-scale applications for this method have been reported (Rozzi, 1991; Heinzle, 1992). More robust techniques are based on titrimetry. To eliminate the interference of the titration with the bicarbonate buffer, either two-step titration or titration and back titration have been proposed (Anderson and Yang, 1992a). Both methods provide information on both the bicarbonate and VFA content of the sample. The ratio of these variables gives an idea of the relative amount of buffer capacity which is still left to neutralize VFA and can be used to control anaerobic sludge digestion (Rozzi, 1991).

Ammonium

Inorganic reduced nitrogen can become a problem at high concentrations and raised pH due to the toxic character of ammonia. Hence, some interest may grow in monitoring this compound in anaerobic digestion. Two approaches are available for ammonium monitoring; ion-selective electrodes (ISE's) and automated wet chemistry methods.

Ion-selective electrodes ISE's that use an electrochemical reaction to monitor the concentration of specific compounds such as Cl^- , Na^+ , F^- , CN^- , S^{2-} are also the preferred measuring principle for NH_4^+ (Thomsen & Nielsen, 1992; Harremoës et al., 1993). The method consists of increasing the sample pH to 11, converting all NH_4^+ into NH_3 which is quantified by the gas-sensitive electrode. The limited operating problems concern clogging and gas bubble retention under the electrode tip (Andersen & Wagner, 1990; Aspegren et al., 1993). In addition, recalibration may be necessary and hydroxide poisoning of the electrode must be prevented (Aspegren et al., 1993). The importance of a thermostated measuring cell is also stressed (Teichgräber, 1993). Response times are typically 15 minutes, including sample pretreatment (Thomsen & Nielsen, 1992).

Automated Wet Chemistry Methods: Since the advent of reliable sample preparation units, a lot of efforts have been devoted to the automation of typical laboratory methods for on-line use in wastewater treatment plants. Two implementations exist: batch-wise chemical analysis and continuous flow-through systems based on the flow injection analysis (FIA) principle. In both cases chemicals are added to the sample and after some reaction time the coloured products are quantified colorimetrically. Advantages of the FIA over the batch systems are the small sample size, low reagent use (Pedersen et al., 1990) and high

sample throughput (Isaacs et al., 1992). The narrow tubings, however, lead to frequent clogging problems and high maintenance needs (Isaacs, personal communication). Two colorimetric methods have been implemented in automated ammonia analysers. Pedersen et al. (1990) use a gas diffusion unit through which ammonia is transported in a weak pH-buffer with a pH-indicator. The ammonia gas causes a pH-increase that is accompanied with a colour change. Thomsen & Nielsen (1992) describe the more traditional method that consists of producing an indophenol blue compound the intensity of which is proportional to the amount of NH_4^+ present in the sample. It is generally accepted that the colorimetric method is less reliable compared to the ISE method (Harremoës et al., 1993). Moreover, response times for batch chemical analysis are rather long compared to electrodes.

NEW DEVELOPMENTS AT THE UNIVERSITY OF GENT

In this section a number of sensor developments at two laboratories of the University of Gent (Laboratory of Microbial Ecology and BIOMATH) are reviewed. Although initially developed for the monitoring of activated sludge processes, it is suggested here also to apply these measuring principles in the context of anaerobic digesters.

In-Sensor-Experiments

During the last five years research has mainly focused on the use of special monitoring systems in which dedicated experiments are conducted in down-scaled versions of the monitored reactor systems). These experiments have been termed *In-Sensor-Experiments* (Vanrolleghem, 1994). The experimental conditions in the reactor system incorporated in the device are such that relevant information can be obtained on the supervised system. Originally developed for activated sludge processes, more specifically based on respirometry, the In-Sensor-Experiment concept is now also being applied for anaerobic digestion monitoring, mainly for overload and toxicity detection (Rozzi, these proceedings; Grijspeerdt et al., 1995).

Titrimetry

Recent research has resulted in a titrimetric sensor for the simultaneous monitoring of different compounds of interest -also in anaerobic digesters- such as ammonia, bicarbonate and VFA's (Van Vooren et al., 1995). In contrast to the titrimetric methods mentioned above, a titration is carried out over the whole pH-range (3-10). Next, the buffer capacity, i.e. the amount of acid/base needed per unit of pH change, is calculated. These data are then subjected to model-based interpretation, providing estimates of the concentrations of the different compounds of interest (Van Vooren et al., 1995). The response time is approx. 30 minutes and sensitivity is in the ppm-range.

Settling properties

Biomass separation is an important unit process in wastewater treatment, also in anaerobic digestion systems. It is therefore surprising that relatively little attention is paid to on-line instrumentation of this important unit process. Probably this is due to the lack of fundamental insights in the determining factors, e.g. flocculation and granulation. Two recent studies are worth mentioning, i.e. the development of a settlometer and the use of automated image analysis.

The settlometer study aims to automate the manual procedures for sludge volume and settling rate determination. Biomass is supplied to a settling cylinder and after an optional mixing step, the interface between clarified water and sludge bed is followed with a moving optical system (Vanrolleghem et al., 1995). An important prerequisite for automation and long-term use of the test is that the cylinder walls must be kept clean to ensure the proper operation of the optical scanning. Typical solutions include a moving piston that drives the sample out of the cylinder at the end of the batch settling experiment, cleaning the walls at the same time. Alternatively a brush or wiper is rotating in the cylinder. Although a number of systems have been developed that allow to monitor complete batch settling curves, no use is being made of all information recorded during the settling experiment. Vanrolleghem et al. (1995) have added more elaborate data analysis based on model-based interpretation of the complete settling curve.

The increasing capabilities and decreasing investment costs of image analysis systems has lead to a recent surge of developments in the field of processing microscopic images (Adams & Thomas, 1988). Interpretation of such images is especially interesting with respect to a better insight in the settling properties of anaerobic biomass, e.g. granulation. Grijspeerdt and Verstraete (1995) have developed an on-line set-up to obtain images of activated sludge that are fit for further processing. At this stage form factors and size distributions can be deduced automatically from the raw images taken in a flow-through microscopic viewing chamber. In the frame of granulation studies the system has been applied on an off-line basis to determine frequency distributions of granule size and the changes thereof.

CONCLUSIONS

A review of existing and new sensor technology for anaerobic digesters was presented. Developments are many and increasingly sophisticated sensors are proposed in an attempt to provide the necessary information. A lot of evaluation work is still to be done in order to prove 1) the reliability of the developed instruments and 2) the applicability of the information they provide in automatic control systems. Practical experience with the devices in full-scale plants will allow to improve their reliability, decrease the maintenance requirements and promote the confidence in the sensors. Consequently they will be accepted for automation of treatment plants, eventually leading to increased plant performance and reduced running costs.

REFERENCES

- Adams H. and Thomas C. (1988) The use of image analysis for morphological measurements on filamentous organisms. *Biotechnol. Bioeng.*, 32, 707-712.
- Andersen K.L. and Wagner P. (1990) Testing on-line monitors for ammonia, orthophosphate and suspended solids in activated sludge treatment plants. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 667-675.
- Anderson G.K. and Yang G. (1992a) Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. *Water Environ. Res.*, 64, 53-59.

- Anderson G.K. and Yang G. (1992b) pH control in anaerobic treatment of industrial wastewater. *J. Environ. Eng.*, 118, 551-567.
- Aspegren H., Nyberg U. and Andersson B. (1993) Integration of on-line instruments in the practical operation of the Klagshamn wastewater treatment plant. In: *Proceedings Workshop on Modelling, Monitoring and Control of Wastewater Treatment Plants*. Med. Fac. Landbouww. Univ. Gent, 58, 2019-2028.
- Barnard J.L. and Crowther R. (1993) Instrumentation in biological nutrient removal plants. In: *Proceedings 6th IAWQ Workshop on ICA of Water and Wastewater Treatment and Transport Systems*. Banff, Canada, June 17-19 1993.
- Colleran E., Concannon F., Golden T., Geoghegan F., Crumlish B., Killilea E., Henry M. and Coates J. (1992) Use of methanogenic activity tests to characterize anaerobic biodegradability and determine toxicity thresholds against individual anaerobic trophic groups and species. *Wat. Sci. Tech.*, 25(7), 31-40.
- Di Pinto A.C., Limoni N., Passino R., Rozzi A. and Tomei M.C. (1990) Anaerobic process control by automated bicarbonate monitoring. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 51-58.
- Dobbs R.A., Wise R.H. and Dean R.B. (1972) The use of ultra-violet absorbance for monitoring the total organic carbon of water and wastewater. *Wat. Res.*, 6, 1173-1180.
- Escoffier Y., Ehlinger F., Coudert J.P., Leyris J.P. and Moletta R. (1992) On-line monitoring and control of a fluidised bed anaerobic digester. In: *Proceedings 6th Forum Applied Biotechnology*. Med. Fac. Landbouww. Univ. Gent, 57, 1614.
- Grijpsperdt K. and Verstraete W. (1995) A sensor for the secondary clarifier, based on image analysis. In: *Proceedings IAWQ specialized conference on Sensors in Waste Water Technology*. Copenhagen, Denmark, October 25-27 1995. (in Press).
- Grijpsperdt K., Müller, Aivasidis, Wandrey, Guwy, Hawkes, Van Der Schueren, Verstraete, di Pinto and Rozzi (1995) Development of an integrated process control system for a multi-stage wastewater treatment plant - Part I: Sensor Technology. In: *Proceedings Workshop Modelling, Monitoring and Control of Wastewater Treatment Processes*. Med. Fac. Landbouww. Univ. Gent, 60/4b, 2459-2466.
- Harremoës P., Capodaglio A.G., Hellström B.G., Henze M., Jensen K.N., Lynggaard-Jensen A., Otterpohl R. and Soeberg H. (1993) Wastewater treatment plants under transient loading - Performance, modelling and control. *Wat. Sci. Tech.*, 27(12), 71-115.
- Hawkes F.R., Guwy A.J., Rozzi A.G. and Hawkes D.L. (1993) A new instrument for on-line measurement of bicarbonate alkalinity. *Wat. Res.*, 27, 167-170.
- Hawkes F.R., Rozzi A., Black K., Guwy A. and Hawkes D.L. (1992) The stability of anaerobic digesters operating on a food-processing wastewater. *Wat. Sci. Tech.*, 25(7), 73-82.
- Heinzle E. (1992) Present and potential applications of mass spectrometry for bioprocess research and control. *J. Biotechnology*, 25, 81-114.
- Isaacs S.H., Zhao H., Soeberg H. and Kümmel M. (1992) On the monitoring and control of a biological nutrient removal process. In: *Proceedings Workshop Modelling, Monitoring and Control of the Activated Sludge Process*. Med. Fac. Landbouww. Rijksuniv. Gent, 57, 2199-2208.
- Jolicoeur C. and Beaubien A. (1986) Microcalorimetric studies of microbial metabolism and inhibition: bases for in vitro toxicity evaluation. In: *Toxicity Testing using Microorganisms*, Vol I. Eds. Dutka B. and Bitton G., CRC Press, Florida. 115-151.
- Korenaga T., Takahashi T., Moriwake T. and Sanuki S. (1990) Water quality monitoring system using a flow-through sensing device. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 625-631.
- Londong J. (1992) Strategies for optimized nitrate reduction with primary denitrification. *Wat. Sci. Tech.*, 26(5-6), 1087-1096.
- MacCraith B., Grattan K.T.V., Connolly D., Briggs R., Boyle W.J.O. and Avis M. (1993) Cross comparison of techniques for the monitoring of total organic carbon (TOC) in water resources and supplies. *Wat. Sci. Tech.*, 28(11-12), 457-463.
- Mathiot S., Escoffier Y., Ehlinger F., Couderc J.P., Leyris J.P. and Moletta R. (1992) Control parameter variations in an anaerobic fluidised bed reactor subjected to organic shockloads. *Wat. Sci. Tech.*, 25(7), 93-101.
- McCarty P.L. (1964) Anaerobic waste treatment fundamentals. Part two. Environmental requirements and control. *Publ. Wks*, 95, 123-126.
- Meredith W.D. (1990) Recent innovations in instrumentation for sewage treatment plant monitoring and control. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 699-703.
- Pauss A. and Guiot S.R. (1993) Hydrogen monitoring in anaerobic sludge bed reactors at various hydraulic regimes and loading rates. *Water Environ. Res.*, 65, 276-280.
- Pauss A., Guiot S., Dochain D. and Perrier M. (1993) Hydrogen as a key-parameter for the monitoring and control of methane producing processes. In: *Proceedings Workshop on Modelling, Monitoring and Control of Wastewater Treatment Processes*. Med. Fac. Landbouww. Univ. Gent, 58, 2011-2017.
- Peck M.W. and Chynoweth D.P. (1992) On-line fluorescence-monitoring of the methanogenic fermentation. *Biotechnol. Bioeng.*, 39, 1151-1160.
- Pedersen K.M., Kümmel M. and Soeberg H. (1990) A real time measurement system for an activated sludge wastewater treatment plant. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 171-178.
- Pilz U. and Werner M. (1988) Ein potentiostatisches Verfahren zur empfindlichen Bestimmung des chemischen Sauerstoffbedarfs (CSB). *Z. Wasser-Abwasser-Forsch.*, 21, 203-208.
- Powell G.E. and Archer D.B. (1989) On-line titration method for monitoring buffer capacity and total volatile fatty acid levels in anaerobic digesters. *Biotechnol. Bioeng.*, 33, 570-577.
- Rozzi A. (1991) Alkalinity considerations with respect to anaerobic digesters. In: *Proceedings 5th Forum Applied Biotechnology*. Med. Fac. Landbouww. Rijksuniv. Gent, 56, 1499-1514.
- Sonnleitner B., Locher G. and Fiechter A. (1992) Biomass determination. *J. Biotechnol.*, 25, 5-22.
- Stephenson J.P., Luxon E.G., Monaghan B.A. and Gillespie R.G. (1981) Evaluation of instruments for continuous activated sludge monitoring. *Wat. Sci. Tech.*, 13(10-11), 721-728.
- Strong G.E. and Cord-Ruwisch R. (1995) An in situ dissolved-hydrogen probe for monitoring anaerobic digesters under overload conditions. *Biotechnol. Bioeng.*, 45, 63-68.
- Teichgräber B. (1993) Control strategies for a highly loaded biological ammonia elimination process. *Wat. Sci. Tech.*, 28(11-12), 531-538.
- Thomsen H.A., Nielsen M.K. (1992) Practical experience with on-line measurements of NH₄, NO₃, PO₄, redox, MLSS and SS in advanced activated sludge plants. In: *Proceedings HYDROTOP92, The City and The Water*. Marseille, France. Vol. 2, 378-388
- van Kleeff B.H.A., Kuenen J.G. and Heijnen J.J. (1993) Continuous measurement of microbial heat production in laboratory fermentors. *Biotechnol. Bioeng.*, 41, 541-549.
- Vanrolleghem P.A. (1994) The adaptive sensor concept: On-line modelling of the activated sludge process with optimal In-Sensor-Experiments. In: *Proceeding 3rd IEEE Conference on Control Applications, Session on Environmental Process Control*. Glasgow, UK, August 24-26 1994. 1017-1022.
- Vanrolleghem P.A. and Verstraete W. (1993) On-line monitoring equipment for wastewater treatment processes: State of the art. In: *Proceedings TI-KVIV Studiedag Optimalisatie van Waterzuiveringsinstallaties door Procescontrole en -sturing*. Gent, Belgium, October 21 1993. 1-20.
- Vanrolleghem P.A., Van der Schueren D., Krikilion G., Grijpsperdt K., Willems P. and Verstraete W. (1995) On-line quantification of settling properties with In-Sensor-Experiments in an automated settlometer. In: *Proceedings IAWQ Specialized Conference on Sensors in Waste Water Technology*. Copenhagen, Denmark, October 25-27 1995. (in Press).
- Van Vooren L., Willems P., Ottoy J.P., Vansteenkiste G.C. and Verstraete W. (1995) Automatic buffer capacity based sensor for effluent quality monitoring. In: *Proceedings IAWQ Specialized Conference on Sensors in Waste Water Technology*. Copenhagen, Denmark, October 25-27 1995. (in Press).
- von Stockar U. and Marison W. (1989) The use of calorimetry in biotechnology. *Adv. Biochem. Eng. Biotechnol.*, 40, 93-136.
- Watts J.B., Evans K. and Molloy A. (1990) A wastewater/water process monitoring system allowing operational control - Developed by an operational manager. In: *Advances in Water Pollution Control*. Ed. Briggs R., Pergamon Press, London. 143-154.