On-line measurements of COD, TOC, VFA, total and partial alkalinity in anaerobic digestion processes using infra-red spectrometry

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Abstract This paper describes the use of a Fourier Transform Infra-Red (FT-IR) spectrometer as an on-line sensor to measure Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Volatile Fatty Acids (VFA), and Partial and Total Alkalinity (PA and TA) in anaerobic digestion processes for the treatment of industrial wastewaters. Comparison with manual off-line analysis and with an on-line industrial TOC analyser and an on-line titrimetric sensor (for the measurements of VFA, TA and PA) are provided to demonstrate the interest of spectral analysis in the mid infra-red domain for the monitoring of anaerobic digestion processes. In order to further illustrate the advantages of using such a technique, on-line measurements recorded during an accident of the pH regulation in the input (pH in the reactor went above 11 and biomass activity stopped) are shown. They demonstrate that, if carefully performed, the calibration can be extended outside its range while being still compatible with requirements of wastewater treatment processes.

Keywords Anaerobic digestion; mid infra-red; on-line sensors; spectrometry

Introduction

Despite the large interest in anaerobic digestion processes (i.e. high capacity to degrade difficult substrates at high concentrations, very low sludge production, low energy requirements and possibility for energy recovery through methane combustion,…), many industrial companies are still reluctant to use them in practice, probably because of the counterpart of their efficiency: they can become unstable under some circumstances.

Indeed, disturbances like variations of the process operating conditions can lead to a destabilisation of the process due to accumulation of intermediate toxic compounds resulting in biomass elimination and several weeks to several months are then necessary for the reactor to recover (see, for example, Steyer et al., 2000). During this period, no treatment can be performed by the unit. It is therefore a great challenge for instrumentation and control sciences to make this process more reliable and usable at industrial scale. The first step is to be able to follow dynamically the key process variables (i.e. using on-line sensors with a small enough sampling period). However, as already emphasised by many authors in the literature : “sensors are the weakest part of the chain in real-time process control of wastewater treatment plants” (Harremoës et al., 1993).

Dealing specifically with anaerobic digestion processes, a review of existing technologies was presented by (Vanrolleghem, 1995). This review highlighted that, even though non-specific on-line sensors (e.g. temperature, pH, pressure, liquid/gas flows) are available on the market, they are not informative enough to efficiently control anaerobic digestion processes. This could be partly solved using sensors in the gas phase (e.g. H₂, CH₄, CO₂ and H₂S) but a major problem is that it is not straightforward to predict the corresponding concentrations in the liquid phase which, after all, represent the organism’s environment. On the other hand, there exist dedicated sensors for measurements of COD, TOC, VFA and alkalinity but they are mainly based on automated standardised laboratory analyses and they usually only provide single component measurements. As a consequence, there are
still many scientific studies at lab scale and validation at the industrial scale to be performed concerning instrumentation of anaerobic digestion processes.

This paper goes in that direction describing the use of a Fourier Transform Infra-Red (FT-IR) spectrometer in the mid infra-red range as an on-line multi-parameter sensor (i.e. one unique equipment to provide on-line measurements of COD, TOC, VFA, PA and TA). The paper is organised as follows. First, the principle of FT-IR spectrometry is briefly presented. The anaerobic digestion process and wastewater used are then shortly described before detailing experimental results obtained for one year of on-line implementation. Finally, some perspective and conclusions are drawn from this experience.

**Principle of fourier transform infra-red spectroscopy**

The foundations of modern Fourier Transform Infra-Red spectroscopy were laid in the latter part of the 19th century when the physicist A.A. Michelson constructed an interferometer (Michelson, 1891). Since then, many advances in technology and in computers made infra-red spectrometers reliable and available at a reasonable price (Perkins, 1986). FT-IR spectrometry is based on the fact that each compound has a unique absorbance pattern, in terms of band shape and band position in the infrared absorption spectrum. By comparing a sample spectrum with the reference spectra for compounds of interest, the composition of the sample can be identified using the Beer–Lambert law. The concentration of each compound is then related to the height of its absorbance band.

This technique has been shown to be of interest for many fields of application (see for example Demirgian and Erickson, 1990; Hall *et al*., 1991; Mao and Demirgian, 1995) for monitoring of incinerator emissions in the gas phase but, to our knowledge, no application was developed for on-line measurements in the mid infra-red range in the liquid phase of WWTPs in general and in anaerobic digestion processes in particular.

**The anaerobic digestion process**

The wastewaters used in the present study are raw wine distillery effluents, whose characteristics are depicted in Table 1. The reactor is an up-flow fixed bed reactor with a total volume of 0.982 m³. The following available measurements are available on-line (i.e. every two minutes): input and recirculation liquid flow rates, pH, temperature, pressure, gas flow rate, CO₂, CH₄ and H₂ gas composition, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Volatile Fatty Acids (VFA), bicarbonate concentrations and partial and total alkalinity (PA and TA). More information about this process can be found in Steyer *et al*. (2002).

An ultrafiltration membrane (Tami Industries) enables a clear sample to be taken from the reactor. Total Organic Carbon (TOC) is first measured from this clear sample by an on-line Zellweger analytics autoTOC 1950, the measurement range of which is 0 to 2,000 mg/l. An on-line automatic titrimetric sensor developed in our laboratory is also

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
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</thead>
<tbody>
<tr>
<td>Total COD (g/l)</td>
<td>[12–34]</td>
</tr>
<tr>
<td>Soluble COD (g/l)</td>
<td>[7.6–31]</td>
</tr>
<tr>
<td>Volatile Fatty Acids (g/l)</td>
<td>[1.5–10]</td>
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<tr>
<td>Total Suspended Solids (g/l)</td>
<td>[2.4–10]</td>
</tr>
<tr>
<td>Volatile Suspended Solids (g/l)</td>
<td>[1.2–5.4]</td>
</tr>
<tr>
<td>Phenol (mg/l)</td>
<td>[90–275]</td>
</tr>
<tr>
<td>pH</td>
<td>[4.5–5.2]</td>
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connected to allow the on-line acquisition of bicarbonate and VFAs concentrations and of partial and total alkalinity. Finally, a mid infra-red spectrometer (Avatar 380 FT-IR from the Nicolet company modified in our laboratory to remove temperature effects in particular) working in the range 2–10 µm is connected to the ultrafiltration module. Results obtained using this equipment are detailed in the following.

**Results**

To obtain quantitative results from an FT-IR spectrometer, a collection of reference spectra is necessary for each component that is targeted for measurements. This work can be time-consuming but is critical to the quality of the measurements. Indeed, the best quantitative results would be obtained by calibrating the spectrometer with a large set of samples prepared for known concentrations. However, it is widely recognised that the spectrum of a liquid mixture is not a linear combination of single-component spectra since there are interactions between the compounds involved (especially in complex liquids like wastewaters) and the energy levels of the molecules of these compounds are altered from those of single compounds.

As a consequence, the calibration procedure has to be conducted while driving the process in the different operating conditions that will be faced when operating the FT-IR spectrometer on-line. Several experiments were thus first carried out off-line to determine the calibration curve. Figure 1 shows for example the calibration results obtained for COD, TOC and VFA. The collected reference spectra were then used to create a mathematical model that will predict the quantities of the components of interest in the unknown samples. To this end, different multivariate calibration methods are available in the literature (Haaland and Thomas, 1988) and, because it is superior for multi-component analysis, we decided to use the partial least squares (PLS) technique.

Given these calibration results (linearity of the calibration and good reproducibility in particular), the on-line implementation was decided. In order to check the validity and the precision of the FT-IT spectrometer, on-line measurements were compared to those provided by the TOC analyser and the titrimetric sensor. An example of results obtained in September 2000 after step changes of the organic loading rate (i.e. step changes of the influent flow rate at $t \approx 55$ and 75 h and change of the input concentration at $t = 100$ h while changing vinasses) is shown in Figure 2. As can be seen, the measurements are very close to those of well admitted sensors in the wastewater field. And for almost a year now, the same quality of results has been obtained – using the same calibration – proof of the adequacy and reliability of this instrumentation technique.

However, one of the major drawback of infra-red spectroscopy recognised in the literature is that the calibration mainly depends on the liquid characteristics. This is true but a careful and appropriate calibration can be extended outside of its range while being valid with regards to the specific requirements of the wastewater field. As an illustration, results

**Figure 1**  Calibration curves for COD, TOC and VFA obtained from off-line analysis and comparison with results provided by spectra from the FT-IR spectrometer
shown in Figure 3 were obtained 7 months later with the same calibration as the one described in Figure 1 and used on-line in Figure 2. What happens then is that, after few changes of the influent liquid flow rate to analyse the dynamic evolution of the process (see until $t \approx 85$ h where results very much comparable to those of Figure 2 were obtained), a major problem appeared in the regulation of pH in the input. Indeed, due to a wrong human intervention, pH in the input reached almost 14. A safety rule was automatically activated to decrease the feed flow of the process down to 5 l/h but it was not sufficient to avoid the pH in the reactor reaching 11. This very rapidly affected the micro-organism activity (see the drop of the biogas flow rate for example). At $t = 100$ h, we introduced water in the

![Figure 2](https://iwaponline.com/wst/article-pdf/45/10/133/424729/133.pdf)

**Figure 2** An example of on-line measurements after a step change in the influent flow rate

![Figure 3a](https://iwaponline.com/wst/article-pdf/45/10/133/424729/133.pdf)

**Figure 3a** Process evolution after an pH accident in the feeding loop
reactor at 15 l/h to decrease the pH and at $t = 120$ h, we fed the process with diluted wastewater. As can be seen, the process was highly overloaded with COD in the output close to 12 g/l and VFA concentration close to 5 g/l.

**Discussion**

Two quite remarkable points can be drawn from this accident.

- First, it can be seen that, after few hours of disconnection of the ultrafiltration loop, because clogged, between $t = 100$ and 115 h, the FT-IR spectrometer provided accurate and reliable results outside of its calibration range. In addition, the liquid characteristics changed a lot (because of the problem with the pH, part of the biomass was lost and, for a while, the process could be considered as a VFA producing and accumulating process with very low COD degradation).

- These results also demonstrated the very good ability of anaerobic digestion processes to recover from an important accident. This is due, of course, to the fact that a fixed bed reactor was used and biofilm systems are more robust than CSTR. But instrumentation also provided us with more insight – in real time – of the consequences of the accident and the process could recover in about 5 days (see the re-start of biogas production about 100 hours after the pH accident) as compared with almost a month in (Steyer et al., 2001) when the same problem appeared. Re-inoculation was then also decided whereas here, no new sludge was added.
An additional advantage of using FT-IR technology is that it does not require any chemical to be added and thus the operation cost of the spectrometer is null (compared to the one requested by the TOC analyser, for example, that is about 4,000 euros a year, just for buying the chemicals).

Finally, it has to be highlighted that the FT-IR spectrometer is very simple to use and to maintain. As an illustration, for one year it has been installed on-line on the process, only few cleanings of the cell where the sample is introduced were needed. And this cleaning procedure could be very easily performed automatically at industrial scale. No other action was carried out on the spectrometer which, for one year, required lower maintenance efforts than those spent for pumps, pipes and even pH probes.

**Conclusion**

As illustrated, infra-red spectrometry is a very powerful approach that, in addition, does not require any chemicals to perform the measurements and that is very reliable over time. Moreover, calibration, which is sometimes said to be a limitation, can be extended – with care though – if carefully performed.

In a more general perspective, it has to be said that this technique still requires the sample to be taken to the instrument and the ultrafiltration loop can be considered as a limiting step. However, the multi-billion dollar optical fibre communications market – with associated mass production of optical and optoelectronical devices – expanding since the 1980s has paved the way for new generations of optical sensors and measurements techniques (Scully, 1997). It might then soon become reality that optical based sensors like the FT-IR spectrometer used in the present study are of common use in the WWTP field. However, coupling of optical fibres with mid infra-red spectrometer in our range of interest (2 to 10 µm) is not yet easy even though optical fibres have been developed for the mid infra-red region, based on fluoride (0.5 to 5 µm), chalcogenide (1 to 6 µm) and silver halide (3 to 15 µm).

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**References**