Electrical conductivity as a state indicator for the start-up period of anaerobic fixed-film reactors

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Abstract: The aim of this work was to analyse the applicability of electrical conductivity sensors for on-line monitoring the start-up period of an anaerobic fixed-bed reactor. The evolution of bicarbonate concentration and methane production-rate in the system was analysed. Strong linear relationships between electrical conductivity and both bicarbonate concentration and methane production-rate were observed. On-line estimations of the studied parameters were carried out in a new start-up period by applying simple linear regression models, which resulted in a good concordance between both observed and predicted values. Electrical conductivity sensors were identified as an interesting method for monitoring the start-up period of anaerobic fixed-film reactors due to its reliability, robustness, easy operation, low cost, and minimum maintenance compared with the currently used sensors.

Keywords: Anaerobic fixed-film reactor; electrical conductivity; start-up

INTRODUCTION

Methane production represents the main challenge for anaerobic digestion (AD) of waste. Nowadays, high effort has been focussed on the study of high-rate systems that use self-immobilised biomass (e.g. up-flow anaerobic sludge blanket (UASB), expanded granular sludge blanket (EGSB) or fixed-bed bioreactors), where both hydraulic retentions time (HRT) and solid retention time (SRT) are uncoupled. However, anaerobic fixed-film reactors usually require of a long start-up time, which is critical to obtain a successful process performance (Escudié et al., 2011). Optimising the start-up time is a key challenge in order to maximise the economic benefits of an anaerobic process. Hence, due to the high complexity and instability of AD processes, the development of an advanced monitoring system is required for successfully start-up, stabilise and optimise an anaerobic fixed-film reactor (von Sachs et al., 2003).

Electrical conductivity is defined as the ability of a solution to conduct electrical current and is directly proportional to its ions concentration. Therefore, conductivity measurements could suppose a big challenge for monitoring and control AD processes, where ions concentration is mainly affected by both volatile fatty acids (VFA) and bicarbonate concentration: two of the most reliable indicators of the AD process performance (Olsson et al., 2005). Electrical conductivity sensors are robust, simple to maintain and to perform, and should involve long life-spans and minimal investment costs, which are some of the main factors that must be taken into account for on-line monitoring techniques in full-scale applications (Aceves-Lara et al., 2012).

The main objective of this work was to analyse the applicability of electrical conductivity sensors for on-line monitoring the start-up period of an anaerobic fixed-bed reactor fed with raw industrial winery wastewater. Bicarbonate concentration and
methane production were analysed, and strong linear relationships between these parameters and electrical conductivity were observed. Theoretical calculations of both bicarbonate concentration and methane production from the on-line electrical conductivity measurements were carried out in a new start-up period, assessing the feasibility of electrical conductivity sensors for monitoring the start-up period of this AD process.

MATERIALS AND METHODS
Pilot plant description and operation
This study was carried out in a continuous anaerobic fixed-bed reactor of 0.358 m$^3$ total volume fed with raw industrial winery wastewater (WWW) from local cellars located in the area of Narbonne (France). The support media (Cloisonyl: 180 m$^2$ m$^{-3}$ specific surface) fills 0.034 m$^3$, leaving the resting 0.324 m$^3$ of effective volume. In order to control the temperature when necessary, the anaerobic reactor is jacketed and connected to a water heating system. The reactor includes a pH PID-controller that feeds NaOH (30%) when necessary.

On-line monitoring
The on-line equipment used in this work consists of: 1 conductivity-temperature transmitter located in the recycling pipe; 1 flow-rate indicator transmitters for the WWW fed-pump; 1 gas flow-rate indicator transmitter (electromagnetic floater-based sensor) and 1 on-line CH$_4$/CO$_2$ sensor (Ultramat 22P Siemens), both located in the biogas discharging pipeline; and 1 on-line titrimetric sensor (Anaerobic Control Analyser AnaSense®, AppliTek S.L.) for the measurements of VFA and bicarbonate.

Sampling and off-line measurements
Besides the on-line monitoring, biogas composition (CH$_4$, CO$_2$, O$_2$, H$_2$S and N$_2$) was determined off-line using a Gas Chromatograph equipped with a Thermic Conductivity Detector (GC-TCD, Perkin Elmer®, Clarus 480 Gas Chromatograph), and VFA composition was determined by Gas Chromatography (Perkin Elmer®, Clarus 580 Gas Chromatograph).

RESULTS AND DISCUSSIONS
Since ions conductivity is sensitive to temperature, electrical conductivity was corrected to 25°C (G$_{25}$) as proposed by Colombié et al. (2007). During a first start-up period of the anaerobic fixed-bed reactor increasing organic loading rates (OLRs) were applied, and the evolution of G$_{25}$, bicarbonate concentration and methane production-rate was evaluated.

For an established G$_{25}$ operating range (0.5 mS cm$^{-1}$ < G$_{25}$ < 4 mS cm$^{-1}$), a linear regression (R$^2$ coefficient of 0.89) between both bicarbonate concentration and G$_{25}$ was observed (Equation 1).

\[ (Bic - Bic_0)_{est} = \alpha_{Bic/G} \cdot (G - G_0)_{25} \]  

Where $Bic$ is the bicarbonate concentration (mmol L$^{-1}$); $Bic_0$ is the reference bicarbonate concentration (mmol L$^{-1}$); $(Bic - Bic_0)_{est}$ is the estimated change in the bicarbonate concentration; $(G - G_0)_{25}$ is the measured change in G$_{25}$; and $\alpha_{Bic/G}$ is the regression coefficient (38.63 mmol cm L$^{-1}$ mS$^{-1}$).

Equation 1 highlights the possibility of using electrical conductivity sensors for on-line monitoring the bicarbonate concentration during the start-up period of an anaerobic fixed-film reactor. However, the use of these sensors could only be appropriate when operating at stable VFA levels because electrical conductivity is...
proportional to the total ion concentration, thus VFA and bicarbonate cannot be considered as independent variables at the same time.

For an established Bic operating range (20 mmol L\(^{-1}\) < Bic < 60 mmol L\(^{-1}\)), a linear regression (\(R^2\) coefficient of 0.87) between both bicarbonate concentration and methane production-rate was also observed (Equation 2).

\[
(Q_{\text{CH}_4} - Q_{\text{CH}_4,0})_{\text{est}} = \alpha_{Q_{\text{CH}_4}/\text{Bic}} \cdot (\text{Bic} - \text{Bic}_0)
\]  
(2)

Where \(Q_{\text{CH}_4}\) is the specific methane production-rate (L\(_{\text{CH}_4}\) d\(^{-1}\) L\(^{-1}\)); \(Q_{\text{CH}_4,0}\) is the reference specific methane production-rate (L\(_{\text{CH}_4}\) d\(^{-1}\) L\(^{-1}\)); \((\text{Bic} - \text{Bic}_0)\) is the change in the bicarbonate concentration; \((Q_{\text{CH}_4} - Q_{\text{CH}_4,0})_{\text{est}}\) is the estimated change in the specific methane production from the measured bicarbonate concentration; and \(\alpha_{Q_{\text{CH}_4}/\text{Bic}}\) is the regression coefficient (0.014 L\(_{\text{CH}_4}\) mmol\(^{-1}\) d\(^{-1}\)).

Equation 2 predicts the necessity of achieving suitable bicarbonate concentrations to successfully start-up an anaerobic fixed-film reactor. On the other hand, an increasing dispersion of the monitored methane production-rate was observed for bicarbonate concentrations higher than 60 mmol L\(^{-1}\). Above this value it was assumed that the process was completely started-up, thus methane production depended on different operating conditions.

For an established \(G_{25}\) operating range (1.2 mS cm\(^{-1}\) < \(G_{25}\) < 2.1 mS cm\(^{-1}\)), a linear regression (\(R^2\) coefficient of 0.84) between both \(G_{25}\) and methane production was observed (Equation 3).

\[
(Q_{\text{CH}_4} - Q_{\text{CH}_4,0})_{\text{est}} = \alpha_{Q_{\text{CH}_4}/G} \cdot (G - G_0)_{25}
\]  
(3)

Where \(\alpha_{Q_{\text{CH}_4}/G}\) is the regression coefficient (0.546 L\(_{\text{CH}_4}\) cm d\(^{-1}\) L\(^{-1}\) mS\(^{-1}\)).

Equation 3 predicts that suitable anaerobic biofilm stability for methane production is obtained when the system conductivity achieves suitable values (\(G_{25}\) values higher than 1.2 mS cm\(^{-1}\)). This value established the minimum starting-up time (20 days in our work) required to develop a functional and stable anaerobic biomass consortium. In this respect, a minimum \(G_{25}\) value of around 1 mS cm\(^{-1}\) was identified as the minimum value that predicted a suitable bicarbonate concentration to achieve a proper performance of anaerobic biomass consortia.

Finally, in order to validate the feasibility of electrical conductivity sensors for monitoring the start-up period of this AD process, the obtained simple regression models were used to estimate both bicarbonate concentration and methane production-rate in two new start-up periods (from day 0 to day 16 and from day 16 to day 28). Figure 1a shows the evolution of \(G_{25}\), the experimentally measured bicarbonate concentration, and the estimated bicarbonate concentration. Figure 1b shows the evolution of \(G_{25}\), the experimentally measured methane production-rate, and the estimated methane production-rate. As can be observed in the figure, linear regression models were enough to successfully predict the bicarbonate concentration (\(R^2\) coefficient of 0.91) and the methane production-rate (\(R^2\) coefficient of 0.81) from the measured electrical conductivity.
The results shown in this work keep electrical conductivity as a possible state indicator for the start-up period of an anaerobic fixed-film reactor. It is important to highlight that electrical conductivity sensors are included in the so-called low-cost sensors group, presenting not only low acquisition and maintenance costs, but also reliable on-line measurement, sensitivity, and robustness.

CONCLUSIONS

Linear relationships between electric conductivity and both bicarbonate concentration and methane production-rate were observed. The obtained linear relationships successfully predicted both bicarbonate concentration and methane production-rate from on-line electrical conductivity measurements. This highlighted the possibility of using electrical conductivity sensors as a cheap and simple method for on-line monitoring the start-up period of an anaerobic fixed-film reactor.

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