Monitoring biological wastewater treatment processes: recent advances in spectroscopy applications

Abstract Biological processes based on aerobic and anaerobic technologies have been continuously developed to wastewater treatment and are currently routinely employed to reduce the contaminants discharge levels in the environment. However, most methodologies commonly applied for monitoring key parameters are labor intensive, timeconsuming and just provide a snapshot of the process. Thus, spectroscopy applications in biological processes are, nowadays, considered a rapid and effective alternative technology for realtime monitoring though still lacking implementation in fullscale plants. In this review, the application of spectroscopic techniques to aerobic and anaerobic systems is addressed focusing on UV Vis, infrared, and fluorescence spectroscopy. Furthermore, chemometric techniques, valuable tools to extract the relevant data, are also referred. To that effect, a detailed analysis is performed for aerobic and anaerobic systems to summarize the findings that have been obtained since 2000.

1 Introduction

The arrival of new technologies and products over the past decades, promoted not only progress but several environmental problems. It is known that living organisms activities, urban demand, domestic consumption and industrial operations, including washing, rinsing, and cleaning equipments, generate high amounts of effluents. From the above, the industry activities are the most prominent factor of water contamination, exceeding the environment regenerative capacity and selfpurification, causing imbalances in the aquatic ecosystems when an appropriate treatment is not taken into account. Thus, environmental concerns, associated with sustainable development, led to the appearance of restrictive legislation, limiting the levels of contaminants discharge in watercourses. Generally, effluents are composed by organic and inorganic substances, including nutrients and aromatic compounds, and feasible treatments are commonly required.

Aerobic systems are, nowadays, frequently established in wastewater treatment plants (WWTPs) worldwide, with conventional activated sludge (CAS) systems, a classical technology, still adopted for its convenience and simplicity (Tandoi et al. 2006). However, these systems are also prone to be affected by a multiplicity of malfunctions, as reported by Mesquita et al. (2016). In addition, the use of membrane bioreactors (MBR) has been increasingly

applied in WWTP over the years, providing many advantages over CAS, such as a small footprint and high effluent quality (Van de Staey et al. 2015). On the other hand, despite extensive research efforts, the fouling process still remains one of the main problems and concerns of MBR research within the academic community (Krzeminski et al. 2012). Aerobic processes are quite dependent on the operating conditions, and, therefore, can be unstable, particularly when subjected to changes in the environment. This, in turn, leads to a negative effect on the bacterial metabolic activity and consequently on the process efficiency. On the basis of these considerations, the sequencing batch reactor (SBR) technology has been increasingly developed taking into account the early experiences gained with CAS systems. SBRs which are flexible systems where both nutrients and organic matter (OM) are removed in the same unit, have been arising with a variety of several attractive properties presented elsewhere (Tchobanoglous et al. 2003).It is wellknown that in flocculent activated sludge systems, like CAS, the sludge aggregation is essential for the solid/ liquid separation, and poor sludge aggregation leads to an increase in the effluent turbidity and biomass washout (Li and Yuan 2002; Bitton 2005; Jenkins et al. 2003). An attractive lowcost and lowfootprint alternative to the flocculent CAS process for WWT is the aerobic granular sludge (AGS) (Lou et al. 2014). AGS systems have been developed in SBRs and have demonstrated excellent settling capabilities, due to their selfimmobilization formation process, which increases their density (Adav et al. 2008). Nevertheless, several key factors have been already described as responsible for the loss of the structural longterm stability (Liu and Liu 2006; Tay et al. 2002; Zheng et al. 2006; Lemaire et al. 2008).

In the past few years, with the increase of contaminants complexity, anaerobic technology also emerged as a means to improve WWT. Indeed, anaerobic digestion (AD) is commonly used as a pretreatment of agrofood industrial wastewaters containing high levels of biodegradable organic compounds. As Alves et al. (2009) points out, AD should be applied to concentrated effluents allowing energy production and nutrient redistribution. However, a posttreatment step is quite always necessary in order to meet the required discharge criteria in surface waters.

Monitoring biological systems is an important task for the performance enhancement of WWT processes.

The increasing demand for biological processes technologies requires the development of adequate monitoring and control techniques. Several physical, chemical and operational parameters are generally monitored in WWTP for assessing wastewater and sludge quality, being of the utmost importance to meet the required discharged values. However, most traditional methodologies for determining these parameters are costly, labor intensive and timeconsuming, and a few may even present environmental risks associated to end products. Therefore, a preferable alternative would be to continuously monitor the key variables within the process and to use this information to make educated decisions. Thus, a great deal of attention has been recently given to different monitoring strategies to help clarifying the behavior of WWT biological processes. Moreover, it is known that waste sludge is a byproduct of the biological processes, and its treatment and disposal represents up to 50% of the running operating costs of a WWTP (Guo et al. 2014). Thus, it is quite imperative to also monitor the waste sludge posttreatment which generally includes stabilization, drying or composting stages.

Recently, high significance has been attributed to the technological evolution and advances in spectroscopic methods to investigate complex samples. In fact, over the last years, spectroscopic techniques have gained a relevant interest within the biotechnology field. With these technologies, absorption, reflectance, transmission, or vibrational properties of chemical species can be measured in order to determine the concentration or composition of a sample. Once implemented, and optimized, these methods are fast, nondestructive and user friendly, allowing rapid inference of the process state.

Furthermore, spectrometry combined with multivariate statistical analysis has been shown to be a valuable tool for monitoring physicochemical parameters associated to water quality, being the analysis performed without the need of any special reagent or solvent, both offline and online, with potential to be applied in situ or inline. Among the spectroscopy techniques, ultraviolet visible (UV Vis), infrared (IR), and fluorescence (FLC) have lately attracted substantial attention in WWT monitoring. It should be noticed, though, that other spectroscopy techniques (Raman spectroscopy, NMR spectroscopy, Terahertz spectroscopy) are distinguished by specific

applications and implementations which are beyond the scope of this article.

In conclusion, this review outlines recent progresses in UV Vis, IR and FLC spectroscopy, related to WWT monitoring. An indepth analysis is performed to summarize the many new findings that have been obtained in the last years, and future developments for the application of spectroscopy techniques in WWT biological processes.

2 Monitoring aerobic and anaerobic systems

Traditionally, the biochemical oxygen demand (BOD5), chemical oxygen demand (COD) (including filtered and dissolvedDCOD), turbidity, total organic carbon (TOC) (including dissolved organic carbonDOC), and volatile fatty acids (VFA) are considered key monitoring parameters and have been widely employed for assessing the wastewater quality in aerobic and anaerobic systems. In the particular case of AD systems, the monitoring of alkalinity, biochemical methane potential (BMP), gas production rate and hydrogen sulfide (H2S) production (Pontoni et al. 2015) is also essential for the evaluation of a good performance. Furthermore, BOD5, COD, and TOC have also been used to characterize various complex compositions known as OM, and namely dissolved organic matter (DOM). DOM is a heterogeneous mixture of aromatic, amino and aliphatic organic compounds containing oxygen, nitrogen and sulfur functional groups (Chen et al. 2003). However, the above parameters do not provide information on the composition of the DOM, and in addition, their analysis is rather tedious and time consuming, and sometimes requires expensive equipment and instrumentation (Janhom et al. 2009).

Additionally, in recent years, the development of new and more sensitive methods of analysis has made possible the detection of other potentially harmful contaminants, globally referred to as emerging contaminants, and present in trace amounts, in both aerobic and anaerobic systems. The most common methods include the use of gas chromatographymass spectrometry (GC MS) and/or liquid chromatographymass spectrometry (LC MS). Traditionally, these chromatography techniques, coupled with mass spectrometry, have been used for the identification and quantification of trace compounds (Aguera et al. 2006;

AfonsoOlivares et al. 2012; Feng et al. 2015). However, this methodology typically requires extensive offline sample preparation, and since the compounds of interest are generally present at trace levels, the sample preparation method requires a prior concentration step. It is known that MS always requires the use of GC and LC equipments, thus difficult to implement online (in situ or inline) towards the monitoring of WWT. Thus, the present review will focus on the use of fast, nondestructive and user friendly spectroscopic techniques (UV Vis, IR and FLC) without extensive sample preparation, thus not encompassing MS spectroscopy.

Total solids (TS), volatile solids (VS), suspended solids (SS), comprising total suspended solids (TSS) and volatile suspended solids (VSS) have been of utmost significance for monitoring purposes. Total nitrogen, including nitrate, nitrite, and ammonia and phosphorus concentration is also widely assessed, reflecting the extent of nitrification, denitrification, and phosphorus removal processes. The sludge quality and stability, which can be related to the extracellular polymeric substances (EPS) matrix role, is also an important factor to take in consideration, but still not implemented in real WWTP.

Globally, the wastewater quality is generally assessed using physical, chemical and microbiological tests. However, these parameters depend on expensive, labor intensive and/or timeconsuming methods, offering only snapshots of moments in time, which makes them unsuitable for realtime monitoring (Carstea et al. 2016). Direct and rapid measurements of the parameters previously presented would provide close monitoring of WWTP quality and allow for a realtime process diagnosis and control. Thus, in the next sections, the most promising and recent available spectroscopic techniques for aerobic and anaerobic processes monitoring are described. Figure 1 provides brief information about the evaluated parameters in the biological processes for each spectroscopy technique discussed in this review.