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Review

Fluorescence spectroscopy for wastewater monitoring: A review

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ABSTRACT

Wastewater quality is usually assessed using physical, chemical and microbiological tests, which are not suitable for online monitoring, provide unreliable results, or use hazardous chemicals. Hence, there is an urgent need to find a rapid and effective method for the evaluation of water quality in natural and engineered systems and for providing an early warning of pollution events. Fluorescence spectroscopy has been shown to be a valuable technique to characterize and monitor wastewater in surface waters for tracking sources of pollution, and in treatment works for process control and optimization. This paper reviews the current progress in applying fluorescence to assess wastewater quality. Studies have shown that, in general, wastewater presents higher fluorescence intensity compared to natural waters for the components associated with peak T (living and dead cellular material and their exudates) and peak C (microbially reprocessed organic matter). Furthermore, peak T fluorescence is significantly reduced after the biological treatment process and peak C is almost completely removed after the chlorination and reverse osmosis stages. Thus, simple fluorometers with appropriate wavelength selectivity, particularly for peaks T and C could be used for online monitoring in wastewater treatment works. This review also shows that care should be taken in any attempt to identify wastewater pollution sources due to potential overlapping fluorophores. Correlations between fluorescence intensity and water quality parameters such as biochemical oxygen demand (BOD) and total organic carbon (TOC) have been developed and dilution of samples, typically up to ×10, has been shown to be useful to limit inner filter effect. It has been concluded that the following research gaps need to be filled: lack of studies on the on-line application of fluorescence spectroscopy in wastewater treatment works and lack of data processing tools suitable for rapid correction and extraction of data contained in fluorescence excitation-emission matrices (EEMs) for real-time studies.

Contents

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1. Introduction

Environmental monitoring is applied to determine the compliance with ambient and discharge standards and to identify areas with persistent issues for timely and effective remediation (Cahoon and Mallin, 2013). Wastewater quality assessment is an essential part of environmental monitoring due to the high anthropogenic impact of treated and untreated discharges on water bodies (Suthar et al., 2010). There are two important aspects of wastewater quality monitoring: the first concerns the detection of pollution events for early warning and rapid remedial responses of water bodies, while the second aspect relates to wastewater treatment works where quality monitoring is required for process control and compliance with regulations at the effluent discharge point (Bourgeois et al., 2001; Michael et al., 2015; Rehman et al., 2015).

The quality of wastewater is generally assessed using physical, chemical and microbiological tests. Among these techniques, reliance is often placed on biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) (Bourgeois et al., 2001; Bridgeman et al., 2013). However, these global parameters depend on expensive or time-consuming methods, offering only snapshots of moments in time (Bourgeois et al., 2001; Chong et al., 2013; Yang et al., 2015a), which makes them unsuitable for online monitoring. Research conducted almost two decades ago (Ahmad and Reynolds, 1995; Tartakovsky et al., 1996; Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999) has shown that fluorescence spectroscopy could be used for wastewater quality assessment as a tool for discharge detection in natural water systems and for process control in wastewater treatment plants (WwTPs). Fluorescence is the release of energy in the form of light when molecules or moieties, named fluorophores, are excited with a high-energy light source (Lakowicz, 2006; Reynolds, 2014). The technique has been suggested for its multiple advantages: it is fast, inexpensive, reagentless, requires little sample preparation, is highly sensitive and non-invasive (Reynolds, 2003; Hudson et al., 2007; Cao et al., 2009; Henderson et al., 2009; Hambly et al., 2010; Murphy et al., 2011; Chong et al., 2013; Yang et al., 2015a). According to Reynolds (2002) fluorescence monitoring could provide rapid feedback, allowing dynamic, high spatial and temporal resolution studies.

In the past decades, more studies have proved the potential of fluorescence spectroscopy as a monitoring and detection tool in natural and engineered systems. This technique has been used successfully to characterize organic matter in seawater (Coble et al., 1990; Coble, 1996; Conmy et al., 2004; Drozdowska, 2007), freshwater (Baker, 2001; McKnight et al., 2001; Spencer et al., 2007b; Carstea et al., 2009) or estuarine water (Huguet et al., 2009). Also, it has been used to monitor riverine organic matter and diesel pollution (Downing et al., 2009; Carstea et al., 2010), evaluate drinking water treatment processes (Bieroza et al., 2009; Cumberland et al., 2012; Shutova et al., 2014) or detect pesticides (Ferretto et al., 2014). Fluorescence spectroscopy has been used to assess the quality of raw sewage and effluents (Baker, 2001; Boving et al., 2004; Pfeiffer et al., 2008), industrial (Santos et al., 2001; Borisover et al., 2011; Li et al., 2015), or farm (Baker, 2002b; Old et al., 2012) discharges into natural systems. Moreover, recent studies on short and long-term fluorescence monitoring along the WwTPs process train have been undertaken, to determine the potential of the technique for treatment processes control (for example, (Murphy et al., 2011; Bridgeman et al., 2013; Cohen et al., 2014; Ou et al., 2014; Singh et al., 2015). Although considerable work has been done so far in this field, there are still issues with regard to the "matrix effects", as reviewed by Henderson et al. (2009), or with fouling (Reynolds, 2002) that must be overcome to allow application of the technique in WwTPs.

Other reviews proved the potential of applying fluorescence spectroscopy to water quality monitoring (Hudson et al., 2007; Henderson et al., 2009; Fellman et al., 2010; Ishii and Boyer, 2012; Yang et al., 2015b). However, none of them focused only on wastewater, which requires a specific discussion due to its complexity in composition and impact on the environment. Moreover, a growing number of studies are published each year on the application of fluorescence spectroscopy to wastewater quality evaluation, proving its scientific and industrial importance. In this paper, we review the current progress in applying fluorescence spectroscopy to assess wastewater quality. The technique's capabilities as a detection and early warning tool of pollution with treated or raw wastewater from different sources are discussed. Also, its potential for process control in WwTPs is presented.

2. Fluorescence assessment of wastewater components

2.1. *Organic matter fluorescence assessment*

The most common methods of recording fluorescence spectra for wastewater are excitation–emission matrices (EEM) and synchronous fluorescence spectra (SFS). EEMs represent fluorescence contour maps, which comprise a series of repeated emission scans recorded in a range of excitation wavelengths (Coble, 1996). SFS are obtained by scanning simultaneously both excitation and emission monochromators at a fixed wavelength interval between them (Patra and Mishra, 2002; Reynolds, 2003). For many years, since the mid-1970s, SFS were preferred as a multidimensional technique for the analysis of complex solutions, because it provided better peak resolution, compared to emission spectra, and faster recording time than EEMs (Ryder, 2005). However, the improvement of instrumentation allowed researchers to obtain fast, high-resolution EEM collection, which increased the method popularity in the research community. In addition, EEMs offer varied possibilities of data interpretation, from simple peak-picking and Fluorescence Regional Integration to the more complex Parallel Factor Analysis (PARAFAC) and Self-Organizing Maps. Among these methods, peak-