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UV spectra analysis for water quality monitoring in a fuel park wastewater treatment plant

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Abstract

In the context of the high application potentials for on-line measurements in wastewater quality monitoring, UV spectroscopy has received recent attention. In the present work UV spectrophotometric analyses were coupled to principal component analysis (PCA) and cluster analysis (CA) to characterize samples taken from a fuel park wastewater treatment plant and to attempt preliminary contaminant identification in the treated wastewater. The score plot resulting from PCA identified two different groups of spectra, one including the influents to the biological reactor and the other the treated wastewater samples. Among the latter, weekday and weekend samples could be further distinguished. The same groups of samples were identified in a dendrogram from CA. The score plot and the dendrogram also allowed the tentative identification of employed process chemicals (lubricant and detergents) as residual contaminants in the treated effluent.

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1. Introduction

The recent trends on environmental protection indicate that, in the immediate future, regulators in Europe will probably increase their demands towards wastewater treatment activities and require better information regarding the treatment processes (Scott, 1999). The compliance assessment of legal discharge requirements is the main driving force for wastewater quality monitoring (Jacobsen, 1999), but knowledge on the quality and quantity of the influents to a wastewater treatment plant is essential for its design and operation. Furthermore, the ability to monitor parameters containing critical information on the treatment process is very important for research and development (R&D). However, the available wastewater quality moni-

toring technologies have several drawbacks in what concerns the control of the treatment systems (Pouet et al., 1999). In addition to sampling and sample storage problems, the standard analytical methods currently used do not allow real-time control of the phenomena influencing the wastewater treatment plant operation. Thus, the use of on-line sensors has been proposed for better wastewater quality monitoring (Namieśnik, 2000). However, due to the complex matrix and generally hostile environment in which these measurements have to be performed, the lack of accurate, cost-effective and resistant sensors has been the main reason for the slower automation progress of wastewater treatment systems when compared to other industrial processes (Lynggaard-Jensen, 1999).

In view of the high potential for the development and application of on-line measurements in wastewater quality monitoring (Clement and Yang, 2001), this is an area where the application of UV spectroscopy can lead to very useful results (Jacobsen, 1999), particularly in countries

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like Portugal, where many wastewater treatment systems are still at an implementation stage. UV spectroscopy is a fast and simple method that has been used as a complementary approach for wastewater quality evaluation and organic matrix composition identification (Thomas et al., 1999; Vaillant et al., 2002). However, most of the reported wastewater UV spectrophotometric applications are based on visual observation and direct comparison of the UV spectra (Suryani et al., 1995; Roig et al., 2002; Roig et al., 2003). On the other hand, multivariate statistical methods are frequently used in exploratory data analysis to obtain environmental knowledge, mainly through principal component analysis (PCA) (Christensen et al., 2004; Peré-Trepat et al., 2004). Multivariate monitoring approaches based on PCA received considerable attention in different contexts (Miletic et al., 2004). However, for the particular case of wastewater quality monitoring, only a few cases have been reported (Rosen and Lennox, 2001; Miettinen et al., 2004).

In the present work UV spectrophotometric analyses were coupled to simple chemometric techniques (PCA and CA) in order to characterize samples taken from a fuel park wastewater treatment plant (WWTP) without using further analytical information and also to evaluate wastewater quality through attempted contaminant identification.

2. Methods

2.1. WWTP description and sampling strategy

Companhia Logística de Combustíveis (CLC) is a Portuguese logistic fuel company responsible for the exploration of the multi-product pipeline existing between the Sines oil refinery and the Aveiras fuel park. The activities of CLC involve the transport, storage and expedition of gaseous and liquid fuels for its customers, who are its own shareholders. This company received a safety, quality and environmental certification in 2004 and is responsible for the distribution of around 50% of all the fuels consumed in Portugal.

Wastewaters generated at the Aveiras fuel park include domestic effluents and oily sewage. The latter is composed of liquid effluents with high hydrocarbon content due to occasional spills and of aqueous effluents with detergents and lubricants, mainly from the gas cylinder washing zone. During the washing operation the empty gas cylinders are placed in a carousel and transported through the washing machine where they are sprayed with detergent and water. Lubricants are used in order to improve the mobility of the cylinders in the carousels. During this transport, detergent and water drain from the cylinders and wash away part of the lubricant into the wastewater line.

The domestic and oily sewage streams are treated in the CLC WWTP (Fig. 1), which can be divided in three main areas: the wastewater collection sumps (S1 and S3), the tilted plate interceptor (TPI) and the biological reactor

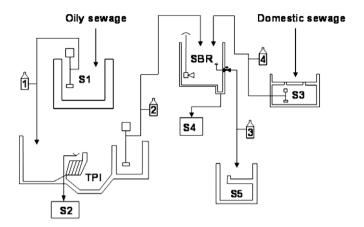


Fig. 1. Simplified scheme of the CLC WWTP including the four selected sampling points (1). S1 – oily sewage sump; S2 – oil sump; S3 – domestic sewage sump; S4 – sludge sump; S5 – treated wastewater sump; TPI – tilted plate interceptor; SBR - biological sequencing batch reactor.

(SBR). The oily sewage is collected in the oily sewage sump (S1) and flows via a skimmer to the TPI unit, which separates oil from water. The oil is collected in the oil sump (S2) and the TPI effluent is pumped into the biological reactor (SBR). The domestic sewage is collected in the domestic sewage collection sump (S3) and is also pumped into the biological reactor (SBR). The biological reactor is an activated sludge Sequencing Batch Reactor running in 24-h cycles consisting of four main steps: TPI effluent and domestic sewage feed, aeration, biomass settling and treated effluent discharge. The excess sludge built up during successive SBR cycles is pumped into the sludge sump (S4) and the treated effluent is discharged into the treated wastewater sump (S5). The four selected sampling points in the WWTP lines are indicated in Fig. 1.

2.2. Spectra acquisition and data set

UV spectra of wastewater samples were acquired (single scan) in a UV–Vis Hitachi 150–20 spectrophotometer (Tokyo, Japan) between 190 and 300 nm (1 nm of wavelength increment) in a quartz cell of 10 mm path length, after appropriate dilution. This dilution was performed with distilled water in order to overcome signal saturation in the UV region (absorbance values above 2 AU). The data set used in the present study was composed of 62 spectra of samples collected over a period of 2 months, and of 111 variables (wavelengths of the UV spectra).

2.3. Principal component analysis

The main objectives of principal component analysis (PCA) are the transformation of the original data's coordinate system into a more relevant one and the reduction of the original system dimension through the use of a limited number of the principal components (PC's) which reflect the inherent structure of the data. A principal component model is an approximation to a given data matrix

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