An environmentally-friendly surrogate method to measure the soluble chemical oxygen and the biochemical oxygen demand in wastewater: use of three-dimensional excitation and emission matrix fluorescence spectroscopy for wastewater treatment monitoring

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The regulatory context in the field of urban wastewater treatment has evolved considerably in the last two decades by presenting a significant increase in the requirements on the water quality returned to the receiving environment. In this context, the main French agglomerations conducted a policy of construction and modernization of sanitation facilities. While these intensive technologies make it possible to maintain a high quality of treatment, their management requires a high level of technical and scientific expertise and an adapted metrology. Improvement of online monitoring and characterization of sewage dissolved organic matter (DOM) is one of the ways considered to optimize control and management of treatment facilities (Carstea et al., 2016; Goffin et al., 2018). However current methods used to characterize DOM quality, like biological oxygen demand in five days (BOD_5) or chemical oxygen demand (COD), are laborious, time consuming (few hours to several days) and are not applicable to monitor organic matter *in situ*. In the context of MOCOPEE research program (www.mocopee.com), this study aims to assess the use fluorescence spectroscopy in order to monitor and to optimize process efficiency in wastewater treatment plants (WWTP).

Excitation-emission matrix (EEM) Fluorescence spectroscopy coupled to PARAFAC analysis was used on a 62 domestic sewage samples dataset from the “Seine Centre” WWTP (240,000 m^3/day; sewage from the western Paris basin) in Paris, France. All samples were collected at different hours in order to highlight temporal variation (daily and hourly) of DOM fluorescence during April 2015 and between June and July 2016. Soluble COD and BOD_5 measurements were also made directly after sampling. Since the PARAFAC approach cannot be used *in situ* at the moment, a "peak-picking" approach based on the maximum fluorescence intensity localization of PARAFAC components highlighted, has been applied to all 62 samples from the "Seine Centre" WWTP. Finally, in order to take into account the variability of influents between different WWTPs, the possibility of transposing the first prediction models of soluble COD and soluble BOD_5 was tested for a second set of 83 sewage samples from six Paris WWTPs (Marne Aval WWTP: 75,000 m^3/day; Seine Morée WWTP: 50,000 m^3/day; Seine Centre WWTP: 240,000 m^3/day; Seine Grésillons WWTP: 300,000 m^3/day, Seine Valenton WWTP: 600,000 m^3/day, Seine Aval WWTP: 1,700,000 m^3/day).

A six PARAFAC components model was obtained based on a 69 sewage samples: three components were related to humic substances-like components and three others were related to protein-like components. Fluorescence signature of sewage DOM from Seine Centre WWTP was mainly composed of protein-like components, which exhibit the highest fluorescence intensities and humic substances-like components showed the lowest fluorescence intensity. The soluble COD of wastewater can be predicted via a simple linear model with the tyrosine-like component scores (r^2=0.829; p<0.0001; n=62). The soluble BOD_5 can be predicted by a multiple linear model with various fluorescence indices (r^2=0.863; adjusted r^2=0.857; p<0.0001; n=62). Since the PARAFAC methodology cannot currently be automated (to date), prediction models based on the location of fluorescence maximums (Ex-Em) of the identified PARAFAC components have been developed. The Pearson determination coefficient obtained for the prediction of soluble COD is 0.825 (p<0.0001; n=62). For soluble BOD_5, it is 0.803; with an adjusted r^2 of 0.792; (p<0.0001; n=62). Thus, the potential for *in situ* application of these prediction models has been successfully demonstrated for sewage from the western Paris basin ("Seine Centre" WWTP influent). These models were generalized to sewage from the entire Paris basin (6 Paris WWTPs; n=83). A Pearson determination coefficient of 0.785 (p<0.0001; n=83) was obtained for soluble COD and for soluble BOD_5, a Pearson determination coefficient of 0.846 with an adjusted r^2=0.839 (p<0.001; n=83) were obtained.

Use of EEM fluorescence spectroscopy coupled with PARAFAC allowed to better characterize temporal variability of sewage DOM quality and quantity. A six fluorescent components model showed useful information about sewage fluorescent DOM quality. The peak-picking method highlighted, derived from the PARAFAC components identified above, is simple, easy to automate and applicable to the operational area of wastewater treatment for high-frequency and ecological online monitoring of soluble COD and soluble BOD_5 in order to reduce the energy costs of WWTPs (chemical reagents, pumping and aeration) and to better control treatment processes. The models highlighted by this study can also be used for fast, simple and inexpensive laboratory measurement.

Keywords: wastewater dissolved organic matter; wastewater monitoring; fluorescence spectroscopy; biochemical oxidation demand; chemical oxidation demand.

References

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