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Emerging applications of EEM-PARAFAC for water treatment: a concise review / Sciscenko, I.; Arques, A.; Mico, P.; Mora, M.; Garcia-Ballesteros, S.. - In: CHEMICAL ENGINEERING JOURNAL ADVANCES. - ISSN 2666-8211. - 10:(2022). [10.1016/j.cej.2022.100286]

Availability:

This version is available at: 11583/2992198 since: 2024-09-04T09:44:14Z

Publisher:

Elsevier

Published

DOI:10.1016/j.cej.2022.100286

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Emerging applications of EEM-PARAFAC for water treatment: a concise review

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ARTICLE INFO

Keywords:

Advanced oxidation processes
Chemometrics
Emerging contaminants
Fluorescent by-products
Organic matter

ABSTRACT

In this work, the application of EEM-PARAFAC (fluorescence excitation-emission matrix-parallel factor analysis) in water treatment processes, has been summarized. First, its most common use, the characterization and monitoring of dissolved organic matter (DOM) along freshwater ecosystems, drinking and wastewater treatment plants (DWTP and WWTP, respectively), was reviewed. In particular for DWWT/WWTP, the effect towards the different DOM fractions after adsorption, coagulation, biological/chemical processes or tertiary treatments (e.g. advanced oxidation processes), as well as the PARAFAC components scores (i.e. fluorescence intensity) correlation with disinfection by-products formation, were reported. On the other hand, barely for the first time, we also reviewed the emerging uses of EEM-PARAFAC focused on water treatment studies, such as, the simultaneous analysis of several fluorescent CECs degradation (with the concomitant formation of major by-products), the use of PARAFAC components scores decay to estimate certain CECs removals, the correlation of reactive oxygen species formation with the specific DOM fractions originating them, or even the study of interactions between DOM with other water constituents. Therefore, this study aims to extend the uses of this economical, reagentless and low time-consuming tool to obtain further insight into fluorescent compounds during water treatment processes, mainly to: i) tentatively elucidate structural modifications of target analyte (DOM or CECs), ii) obtain semi-quantitative data on parent pollutants and by-products variation, and iii) investigate the plausible mechanistic aspects which are involved.

1. Introduction

Complex sample analysis containing several chemical compounds constitutes one of the most important challenges in analytical chemistry. The difficulty scales up when the user tries to measure in a cost-efficient way and simultaneously, all the analytes from a sample, those being at low concentrations and in presence of interferences. In this regard, fluorescence spectroscopy is a sensitive and non-destructive method widely used for the analysis of complex samples in several scientific fields. Among the advantages of this methodology it can be mentioned its low cost, the fast response that provides, and none, or simple, sample

preparation [1]. For instance, in the food industry, fluorescence can be very useful towards qualitative and quantitative analysis of aminoacids, vitamins, nucleic acids or polyphenols [2], as well as quality assurance assays for the denomination of origin verification for products such as wine [3], oil [4] or honey [5]. Regarding water treatment applications, fluorescence spectroscopy has been mostly applied at drinking water and wastewater treatment plants (DWTP and WWTP, respectively) to characterize and monitor the different types of dissolved organic matter (DOM) [6,7].

The three-dimensional plot, fluorescence excitation-emission matrix (EEM), is of particular importance towards water samples

Abbreviations: AOPs, American Joint Committee on Cancer; CECs, contaminants of emerging concern; DBP, disinfection by-products; DOM, dissolved organic matter; DWTP, drinking water treatment plant; EEM, fluorescence excitation-emission matrix; FA, fulvic acid; HPLC, high performance liquid chromatography; HLS, humic like substances; NOM, natural organic matter; PARAFAC, parallel factor analysis; PCA, principal component analysis; SBO, soluble bio-based substances; TOC, total organic carbon; COD, chemical oxygen demand; BOD, biological oxygen demand; Try-L, tryptophane like substances; Ty-L, tyrosine like substances; UV254, ultraviolet absorbance at 254 nm; WWTP, wastewater treatment plant.

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<https://doi.org/10.1016/j.cej.2022.100286>

Received 31 December 2021; Received in revised form 7 March 2022; Accepted 10 March 2022

Available online 11 March 2022

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characterization, as it can be considered as its fingerprint (see example in Figure 1). In fact, traditionally, the different DOM compounds emitting within a EEM were identified and quantified based on the visible peak-picking method, where characteristic fluorescence peaks were selected from defined regions [8,9]. However, this procedure might be only useful for samples containing few fluorophores. When several analytes are present, also in presence of fluorescent interferences, the strong signal overlapping requires the application of more sophisticated mathematical treatments for their analysis. In this sense, multivariate analysis exhibits the ability to simultaneously measure several components in the presence of uncalibrated fluorophores (second-order advantage), and without requiring a separative method (e.g. chromatography) [10]. Diverse methods have been tested for EEM signal deconvolution, such as Artificial Neural Networks, Principal Component Analysis (PCA) and PARAllel FACtor analysis (PARAFAC), being the latter the most commonly employed [11,12].

Briefly, the idea behind PCA is to generate new variables, $C_1, \dots, C_i, \dots, C_N$, these being linear combinations from the original ones (Eq. 1). This process allows achieving dimensionality reduction, therefore, simplifying the data set analysis. Each of the linear combination coefficients, c_{i1}, \dots, c_{iN} , are called “loadings” and the projected data on C_1, \dots, C_N , “scores”. The linear combinations are made in a way where C_1 will be in the direction where the variance of the projected data is maximized, followed by C_2 (orthogonal to C_1), and so on. Therefore, there will be a certain number of the newly constructed variables which will accumulate the relevant information of the system in decreasing order, being the last linear combinations only describing the noise or interferences. The new variables describing the system are called Principal Components. Mathematically, the Principal Components are the eigenvectors from the covariance matrix. To each eigenvector, the belonging eigenvalue provides the data-set variance amount from that particular Principal Component [13].

$$C_i = c_{i1}X_1 + c_{i2}X_2 + \dots + c_{iN}X_N \quad (1)$$

PARAFAC is a N-way method, being N the system's dimensionality. Differently from PCA, PARAFAC remains with its multivariate structure. For EEM analysis, data will be decomposed with three trilinear elements, a_{if} , b_{jf} and c_{kf} as stated by Eq. 2.

$$x_{ijk} = \sum_{f=1}^F a_{if}b_{jf}c_{kf} + e_{ijk} \quad (2)$$

From Eq. 2, there will be a given number of I total samples whose fluorescence was determined in a certain range of J emission and K

excitation wavelengths. X_{ijk} will be the data point corresponding to the i^{th} sample, j^{th} emission and k^{th} excitation wavelengths, respectively, and with a variability not considered by the model, e_{ijk} . Therefore, if it is considered that dataset contains a number F of fluorophores (being F named as the number of PARAFAC components—or factors—), a_{if} will be directly proportional to the concentration of the f^{th} component in the i^{th} sample, b_{jf} an estimate of its emission spectrum, and c_{kf} the estimate of its excitation spectrum, being $f = 1, \dots, F$ [14–16].

The major advantage of PARAFAC is its solution uniqueness, which is obtained through the Alternating Least Squares algorithm. According to the chosen number of PARAFAC components, this algorithm will give certain initial loadings to two of the three trilinear elements, calculating with least-squares the loadings for the remaining element. Therefore, the model is improved with each iteration until it is reached convergence in a global minimum [17].

The right number of factors/components to model the dataset can be chosen according to different possible criteria (main drawback of the method), being always mandatory to have chemical consistency. The two most accepted algorithms that can usually help choosing the correct number of factors are the split-half analysis method and core consistency diagnostic [15]. Moreover, unavoidable interferences such as the inner filter effect or light scattering must be corrected during model pre-processing [14], as well as normalizing each EEM to its total signal since not all the fluorophores in the dataset might have the same fluorescence intensity, due to quantum yield or concentration differences, reflected on a lower statistical weight when performing the PARAFAC analysis. In addition, it is important to consider the matrix effect, since fluorescence can be seriously altered with pH changes or by the presence of inorganic species (mainly cations due to coordination complexes formation). For this reason, sample preparation might include the use of buffer solutions to analyse the whole dataset at fixed pH, as well as removing inorganic interferences. This is particularly important when dealing with samples from Advanced Oxidation Processes (AOPs) reactions, such as Fenton, where there is a significant amount of iron that can be chelated by the fluorophore(s) and abrupt pH changes occur [18,19].

Noteworthy, PARAFAC requires a solid programming background a major drawback which has been overcome with several published free-access graphical user interfaces [1,20], allowing inexperienced users to run the complex equations managed by softwares such as MATLAB®, but with a user-friendly graphical interface. Moreover, even though it is usually claimed that PARAFAC datasets should contain more than 50 samples, there are also published approaches to reduce this number to just a few (e.g. < 10 samples) by introducing the missing chemical variability, such as employing solid-phase extraction permeates, which

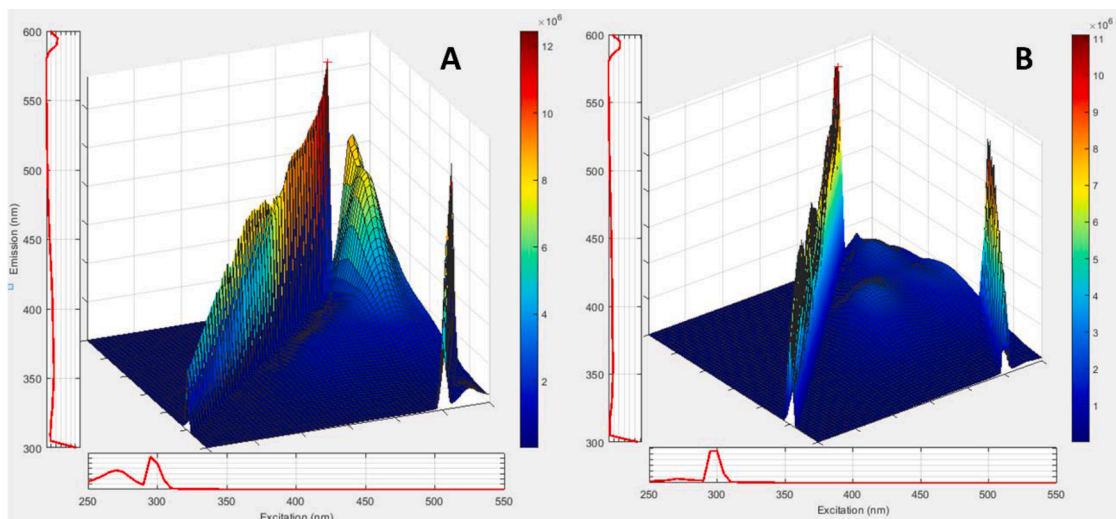


Figure 1. EEM examples from samples taken from a WWTP at its: A) inlet, and B) outlet (tertiary treatment, chlorination).

uses already established protocols and the extraction sorbents are economical [21].

In the last 10 years, 308 Scopus-indexed journal and conference papers were published with searched terms “PARAFAC” and “water treatment”. As shown in Figure 2, this trend is growing, thus representing the fast uptake of a technique that was introduced to the organic matter and water research fields ca. 20 years ago [14,22].

In this paper, we review all the potential uses being actually explored of EEM-PARAFAC tool in water treatment, not only revising the ones within DWTP/WWTP facilities and freshwater ecosystems [12,23–25], but also including the emerging ones, such as the analysis of fluorescent contaminants of emerging concern (CECs) degradation by AOPs or the correlation between reactive oxygen species formation with DOM fractions.

2. Monitoring of DOM in DWTPs and WWTPs

Natural organic matter (NOM) can be defined as the mixture of complex macromolecules excreted by algae, plants or animals, or generated by their decomposition. These substances are ubiquitously present in the environment (e.g. soil, groundwater, rivers or oceans) playing vital roles in the carbon cycle and exerting a high influence in aqueous ecosystems [26]. Although its composition is highly variable, NOM basically consists of a complex mixture of humic and fulvic acids (which account for ca. 50% of total amount), carbohydrates, proteins or low molecular weight organic acids. NOM can be classified as particulate organic matter and DOM, if it is retained or not in 0.45 µm pore size filters, respectively [27]. Towards water treatment analysis implications, the most relevant NOM fraction to focus on is the dissolved one.

DOM is involved in the generation of genotoxic and carcinogenic disinfection by-products (e.g. trihalomethanes or haloacetic acids) by chlorine-based reagents [28], microorganism proliferation [29], or even enhancement of membrane fouling [30], all of which result in an overall increase of water production costs. Besides, it can also interact with pollutants through its hydroxyl, carboxyl or amino moieties, modifying their mobility. This is of particular importance for heavy metals, since implicates the risk of their re-dissolution [26]. Therefore, as mentioned in previous section, DOM monitoring is of paramount importance in water treatment facilities.

Up to date, the methods most commonly used for DOM monitoring within DWTP and WWTP are based on non-specific parameters, such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD) or ultraviolet absorbance at 254 nm (UV₂₅₄), which provide limited information on the nature of the organic matter that is present and the changes that it might suffer during the treatment [31]. EEM provides complementary information to TOC or UV₂₅₄ and remains relatively simple, economic and fast. For instance, an important advantage of EEM vs. UV₂₅₄, is that while the latter is not able to differentiate between compounds with similar absorption spectra,

variations in EEM are most likely to be appreciated. Moreover, substances with significant absorption at 254 nm, (e.g. high concentration of NO₃[−]) can give misinterpretations of DOM content [27].

Several works intending to popularize EEM-PARAFAC within DWTP and WWTP have been published during the last 15 years, demonstrating to be useful towards DBP formation trends prediction [23,32], detect changes in the composition of DOM during abrupt weather changes [31, 33], or combining it with machine learning towards online monitoring [34,35].

2.1. DOM composition in DWTPs and WWTPs

The concentration and composition of DOM are highly variable depending on the origin of water uptake and treatments that have been applied, being especially true when comparing samples from WWTP and DWTP [24]. However, the DOM fractions differ in quantity, being all of them usually present in both cases. Figure 3 summarizes the fluorescence regions for generally identified types of DOM within the aforementioned facilities, these being: protein-like, including tyrosine and tryptophan like substances (Ty-L and Try-L, respectively), microbial humic-like (MH), humic-like (HLS) and fulvic acid (FA).

For the sake of quantitative comparisons between studies, Murphy et al., 2014, developed an open-access online library of published organic fluorescence spectra, called “Openfluor” [37], where the obtained PARAFAC components can be compared with those from another works, offering the user a more accurate sample characterization beyond comparisons based on raw data.

Knowing the regions where a target DOM emits is an outstanding advantage of EEM-PARAFAC over other more traditional analytical methods such as TOC or UVA₂₅₄, since each fraction of DOM can be individually tracked; furthermore this measurement requires low sample volumes (ca. 3 mL). Therefore, the user can better understand the effects of the different treatment steps based on the behavior of the obtained scores (i.e. fluorescence intensity) for each PARAFAC component, which might afterwards improve the efficiency of the treatment plant.

On the other hand, water sources for DWTP are usually natural aquatic environments, and hence, DOM from soil or plant decomposition origin –HLS– predominates [38], whereas WWTP is enriched by matter derived from microbial activity [39]. In fact, fluorescence intensity ratio between Try-L and HLS is a parameter used for fast classification of water origin. Try-L/HLS ratio decreases from the inlet to the outlet of a WWTP, and it is utterly lower when analysing samples coming from river or potable water [8]. In line with these statements, Goffin et al. obtained good correlation between Try-L component scores with biological oxygen demand ($r^2 = 0.839$, $p < 0.0001$) and chemical oxygen demand ($r^2 = 0.825$, $p < 0.0001$) within a WWTP [40,41], being these correlations poor or moderate when replacing Try-L scores for HLS ones. Moreover, Sorensen et al., 2018, proposed that Try-L fluorescence signal can be easily used as a fast and continuous indicator of drinking water faecal pollution, or cross-connections between potable and reclaimed water systems, due to its correlation with thermotolerant coliforms (e.g. *E. coli*) [42]. However, according to authors, threshold for Try-L detection seems to be still high and further efforts to improve the sensitivity of these assays are still needed.

2.2. Effects of treatment processes on fluorescent DOM

According to previous works, the efficiency of adsorption (mainly with granular activated carbon) and coagulation steps in WWTP towards DOM, is between 20 to 50% [24,38,43,44]. Particularly for the coagulation step, each reagent might be more selective towards a certain DOM fraction than other. In this sense, a study comparing three coagulants, FeCl₃, polyaluminum chloride and Al₂(SO₄)₃, showed that the first two were able to remove predominantly protein-like components (Ty and Try-like), whereas Al₂(SO₄)₃ exhibited a better performance mainly

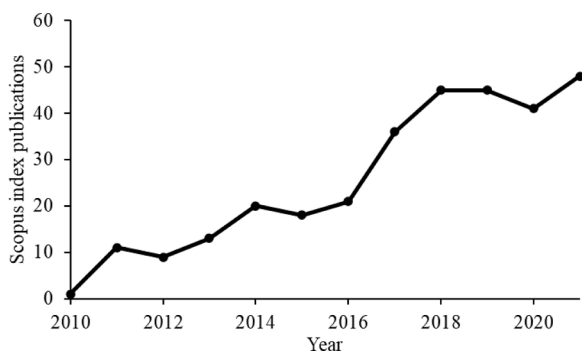


Figure 2. Number of publications in Scopus (<https://www.scopus.com>) with searched terms “PARAFAC” and “water treatment” in the last 10 years.

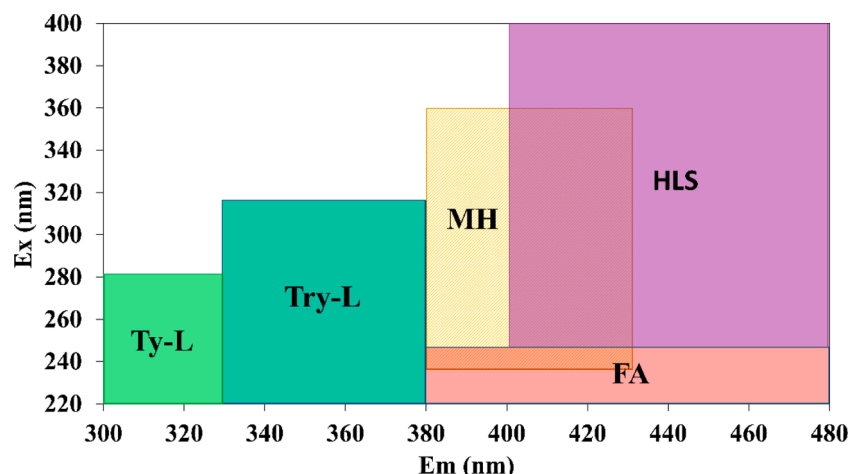


Figure 3. Typical emitting regions of fluorescent DOM within from DWTP/WWTP systems: Ty: tyrosine-like (Ty); tryptophan-like (Try); microbial humic-like (MH); humic-like (HLS), fulvic acids (FA). Based on [23,25,36].

towards HLS [45]. In line with these statements, in DWTP (with higher predomination of HLS than Try-L, as mentioned above), $\text{Al}_2(\text{SO}_4)_3$ exhibits better results as a coagulant than other analogous chemicals [23].

Regarding the biological treatments of WWTP (e.g. anaerobic-anoxic-oxic process, sequencing batch reactor, or membrane bioreactor), protein-like components shown from moderate (20-50%) to high elimination (>80%), moderate for HLS and very low for MH [24]. On another hand, it has been also observed that biological and chemical treatments were able to reduce the scores from Try-L substances, but with a concomitant increment of HLS component scores [23]. This might indicate that one type of DOM can be transformed into another, and/or the generated by-products exhibit analogous EEM fingerprint as other types of DOM, thus increasing the scores of the other fluorophore due to impossible/poor signal deconvolution.

2.3. Tracking DOM changes when employing advanced oxidation processes

Towards future wastewater discharges directives and use of reclaimed water [46,47], tertiary treatments are needed to be coupled to the secondary ones within WWTPs. Chemical-oxidative processes can induce important changes in organic substances, and hence, in chromophore moieties, resulting in a signal decay and/or EEM fingerprints shape changes. The previously introduced AOPs, are technologies where highly reactive species (e.g. hydroxyl radical, HO^\bullet) are generated “*in situ*”, and are able to oxidize organic pollutants, being the reaction thermodynamic and kinetically favoured; therefore, these reactive radicals can degrade, in a short period, practically every organic substance [48]. Among AOPs, it can be mentioned the Fenton(-like) ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$) and photo-Fenton(-like) (Fenton with UV or sunlight irradiation) processes, electrooxidation, $\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{UV}$, Cl_2/UV or heterogeneous photocatalysis (mainly TiO_2/UV). Detailed information about these and many other AOPs can be found elsewhere [49–51].

AOPs commonly decreases the fluorescence intensity of DOM fractions; however, as mentioned in the previous section, PARAFAC components scores enhancement is also likely observed. Due to the complex and varied molecular structures of DOM, as well as the multiple parallel reactions that might be occurring, there is still a great discrepancy between reported results.

When studying the effect of ozonation alone, TiO_2/UV and the combination of these two, $\text{O}_3/\text{TiO}_2/\text{UV}$, significant differences in fluorescence signals of DOM were observed. When applying O_3 , an overall fluorescence reduction was observed. The same happened when using the combined treatment, $\text{O}_3/\text{TiO}_2/\text{UV}$, observing even a faster reduction of the overall fluorescence. However, when using TiO_2/UV , there was a selective enhancement of certain substances emitting at shorter

wavelengths, probably due to donating groups bonding (e.g. hydroxylation of aromatic rings) [52]. Similarly, another study observed a reduction of the score values of one PARAFAC component with the proportional increment of another one after oxidation with TiO_2/UV [53].

Świetlik and Sikorska, 2004, studied the fluorescence changes of hydrophilic and hydrophobic HLS after the treatment with O_3 and ClO_2 , and observed differences according to the type of HLS as well as the employed oxidant. After ozonation of hydrophobic HLS, its EEM fingerprint maximum exhibited a marked red-shift (i.e. towards higher wavelengths), which they attributed to the formation reaction intermediates exhibiting substituents such as hydroxyl, carbonyl and carboxyl ($-\text{OH}$, $-\text{C}=\text{O}$ and $-\text{CO}_2\text{H}$), whereas for hydrophilic ones, a slight blue-shift was observed. On the other hand, with ClO_2 treatment, both HLS fractions, hydrophobic and hydrophilic, showed a marked blue-shift, which was attributed to their cleavage into molecules with smaller molecular weight, that decreases the degree of electron delocalization of the π -electron system [54].

3. EEM-PARAFAC applied to fluorescent contaminants of emerging concern degradation studies

Due to a partial degradation within conventional WWTP, a large number of scientific papers have pointed out the presence of chemicals from anthropogenic sources in lakes, rivers and oceans all over the globe, such as personal care products, pharmaceuticals, food additives and/or pesticides [55–58]. The so-called CECs, are present in concentrations that vary from $\text{ng} - \mu\text{g/L}$, reaching, in some extreme cases, the level of mg/L . The real ecological damage that the continuous release of these chemicals have into the environment is still unknown, although many of them proved to be hazardous even at low concentrations [59, 60]. In addition to this, the hazards of CECs are also dependent on a large and complex set of interactions with other CECs and/or compounds commonly found in water bodies, such as NOM, anions and metals [58,61]. In fact, CECs frequently undergo adsorption on organic matter particles, representing a challenge to the analytical determination of these pollutants in water [62]. Moreover, reaction by-products that arise from CECs partial degradations within WWTPs could exhibit even higher toxicity than the parent compound [63].

Although CECs discharge could be decreased with more sustainable consumption habits, it is recognized that, for instance, pharmaceuticals are commodities of the vital need for human health; hence, their excretion is unlikely to stop in the future. A performance improvement in the WWTPs is required to achieve satisfactory CECs and microbiological content abatement. In this regard, the aforementioned AOPs

treatment arises as a remarkable alternative to enhance the quality of the effluent and ensure safe disposal.

Recent studies have investigated the possibility of employing EEM-PARAFAC as a visual tool for the monitoring of fluorescent CECs evolution along degradation processes. Sgroi et al., 2017, selected ten WWTPs with different secondary treatments, measured the concentration of eleven CECs by HPLC-MS at the inlet and at the outlet, and compared these results with the fluorescence decay of the different DOM fractions [64], founding that: i) CECs exhibiting average removals higher than 70% (particularly, triclosan, caffeine and ibuprofen) presented good correlations (coefficient of determination, $R^2 \geq 0.8$) with the fluorescence decay from Ty-L and Try-L substances; ii) HLS component scores decay trend was significantly related to the one of CECs with moderate elimination (between 30% and 70%, being atenolol, naproxen and gemfibrozil); iii) recalcitrant CECs (average removal < 30%, being sulfamethoxazole, sucralose and carbamazepine) could not be correlated with any DOM fraction. Therefore, it was demonstrated that a given DOM fraction removal percentage can provide an analogous estimation for some CECs elimination. In conclusion, by only measuring and analysing EEMs, the user might predict the removal degree of certain CECs (at least those with high to moderate removals) without requiring expensive equipment. Most recently, the same authors extended this approach by correlating the influent PARAFAC scores decay by granular activated carbon [65] and AOPs [66], with the analogous CECs elimination for each process.

DOM interactions with other water constituents were also reported employing EEM. For instance, Berkovic et al., 2013, studied the interaction between FA and Hg^{2+} [67]; Caram et al., 2018, when employing waste-derived soluble bio-based substances (SBO) as a low-cost iron-chelating agent to extend photo-Fenton efficiency at mild pH conditions, observed an interaction between the SBO and the target CEC, thiabendazole [68], whereas, in the same research line than the latter, García-Ballesteros et al., 2017, observed that the PARAFAC components associated to HLS fraction of SBO where the responsible of Fe(III) chelation at pH 5 and 7, and not the Try-L ones [69]. In fact, only the scores from the components associated to HLS fractions were sensitive to irradiation (increased), and not the ones of the Try-L, evidencing the ligand to metal charge transfer transition (resulting in the Fe(III) reduction into Fe(II), which is not chelated) from the HLS-Fe(III) complexes.

Another interesting approach recently gaining momentum, is tracking fluorescent CECs removal with this technique. According to our knowledge, the first work to use this strategy was published by Carabajal et al., 2017, where the degradation of the heavy-polycyclic aromatic hydrocarbons benzo[a]pyrene, dibenz[a,h]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene and benz[a]anthracene by Fenton reaction was reported [70]. The work demonstrated that the fluorescence signal decay of the five parent pollutants (also in presence of other non-calibrated fluorescence interferences) can be easily measured in a fast way, without any separation method or complex sample preparation, and being able to detect concentrations below the $\mu g/L$ range.

In this regard, Sciscenko et al. recently studied the degradation of fluoroquinolones (antibiotics) by different AOPs, employing EEM-PARAFAC to obtain parent pollutants and by-products kinetics, as well as deducing the plausible molecular structures of the reaction intermediates [19,71]. When degrading a single fluoroquinolone, enrofloxacin, EEM-PARAFAC analysis showed that 4 components belonged to formed by-products, and another one to enrofloxacin and enrofloxacin-like (by-products with analogous EEM than the parent pollutant) compounds. Most importantly, an excellent agreement between PARAFAC components scores with the antibiotic activity decay was observed, indicating that this technique could be a fast methodology to estimate when a fluorescent CEC reactive site (the environmentally relevant moiety to get rid of) is actually oxidized. This strategy was afterwards extended to the degradation of a mixture of three fluoroquinolones, being the PARAFAC algorithm able to deconvolute

–besides from the generated by-products– the three CECs, even though the corresponding fingerprints were highly overlapped one with another. In Figure 4 it is shown the scores behaviour of the PARAFAC components associated to the aforementioned 3 fluoroquinolones plus the ones corresponding to a major photoproduct when employing H_2O_2 /sunlight [19].

In line with these CECs degradation analysis approach, we can also mention the following studies: degradation of phenolic compound mixtures, commonly found in food processing industry by AOPs [72,73]; pentachlorophenol (pesticide) transformation into phenol by zerovalent iron [74]; EEM fingerprint changes analysis of anthracene during its photodegradation [75]. Moreover, although it was not orientated to water treatment, another interesting work was performed by Villarruel et al., 2019, where, exploring the behavior of harmaline (alkaloid) during its irradiation in water at aerobic and anaerobic conditions, they have tentatively proposed the molecular changes produced on the compound according to the deconvoluted fluorescence signals, obtaining different PARAFAC models for each studied condition [76].

Finally, EEM-PARAFAC has been recently proposed to explain the specific DOM fractions responsible for reactive oxygen species (i.e. 1O_2 , HO^\bullet or $O_2^{\bullet-}$) formation during the irradiation of river samples [77], resulting to be the quinonic-like compounds (emitting within the region of HLS, Figure 3). Therefore if the DOM content is enriched by quinonic-like substances, under irradiation, reactive oxygen species formation should be considerable, which might lead to indirect-photolysis of some CECs, as well as DOM itself.

4. Conclusions

In this short review, the classical and emerging uses of EEM-PARAFAC in water treatment have been reviewed. For its conventional use, the most relevant works characterizing and monitoring DOM in freshwater ecosystems, WWTP and DWTP were mentioned. In this context, important correlations between the PARAFAC components associated to the different DOM fractions with chemical and biological oxygen demand, or DBP formation, have been found. One of the major drawbacks, namely the difficult mathematical treatment of data, is overcome by the development of graphical user-friendly interfaces, and, thus, an exponential application of this methodology could be expected.

Even though there is still scarce literature of EEM-PARAFAC applied on CECs, further efforts are meant to evaluate the applicability of this tool to gain further insight into the behaviour of fluorescent emerging pollutants towards AOPs and to correlate it with detoxification of the

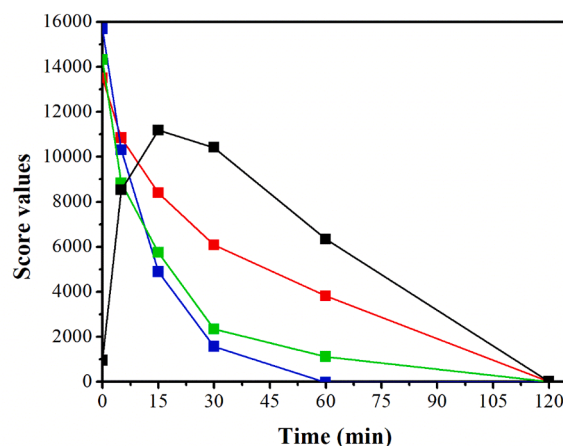


Figure 4. PARAFAC components evolution during the degradation of three fluoroquinolones with H_2O_2 /simulated sunlight in ultra-pure water at initial pH 7.0. Red, green and blue lines correspond to parent pollutant fluorescence decay and the black one to a major intermediate being formed and afterwards consumed. Results were taken from Sciscenko et al. 2021 [19].

effluents. It is also important to remark the low detection limits of fluorescence, within the ng – µg/L range, that can be reached without complex sample preparation. Overall, PARAFAC allows the use of a spectrofluorometer, a low-cost equipment, to obtain a quick picture of major trends occurring when chemical oxidation is applied to fluorescent CECs within a complex aqueous matrix. Hence, this could be an alternative for sophisticated methods, such as HPLC-MS, when the detailed identification of every single component in a sample is not required.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 765860 (AQUALity). The paper reflects only the authors' view and the Agency is not responsible for any use that may be made of the information it contains. The authors wish to also thank the Spanish Ministry of Science, Innovation and Universities (MCIU) for funding under the CalypSol Project (Reference: RTI2018- 097997-B-C32). Sara García-Ballesteros wish to thank the Valencian government for her post-doctoral fellowship (APOSTD2019).

References

- [1] P. Micó, S. García-Ballesteros, M. Mora, R. Vicente, A.M. Amat, A. Arques, EEMlab: A graphical user-friendly interface for fluorimetry experiments based on the drEEM toolbox, *Chemom. Intell. Lab. Syst.* 188 (2019) 6–13, <https://doi.org/10.1016/j.chemolab.2019.03.001>.
- [2] J. Christensen, L. Nørgaard, R. Bro, S.B. Engelsen, Multivariate autofluorescence of intact food systems, *Chem. Rev.* 106 (2006) 1979–1994, <https://doi.org/10.1021/cr050019q>.
- [3] D. Airado-Rodríguez, I. Durán-Merás, T. Galeano-Díaz, J.P. Wold, Front-face fluorescence spectroscopy: A new tool for control in the wine industry, *J. Food Compos. Anal.* 24 (2011) 257–264, <https://doi.org/10.1016/j.jfca.2010.10.005>.
- [4] E. Guzmán, V. Baeten, J.A.F. Pierna, J.A. García-Mesa, Evaluation of the overall quality of olive oil using fluorescence spectroscopy, *Food Chem.* 173 (2015) 927–934, <https://doi.org/10.1016/j.foodchem.2014.10.041>.
- [5] L. Lenhardt, R. Bro, I. Zeković, T. Dramićanin, M.D. Dramićanin, Fluorescence spectroscopy coupled with PARAFAC and PLS DA for characterization and classification of honey, *Food Chem.* 175 (2015) 284–291, <https://doi.org/10.1016/j.foodchem.2014.11.162>.
- [6] D. Palma, M. Sleiman, O. Voldoire, A. Beauger, E. Parlanti, C. Richard, Study of the dissolved organic matter (DOM) of the Auzon cut-off meander (Allier River, France) by spectral and photoreactivity approaches, *Environ. Sci. Pollut. Res.* 27 (2020) 26385–26394, <https://doi.org/10.1007/s11356-020-09005-7>.
- [7] E. Cohen, G.J. Levy, M. Borisover, Fluorescent components of organic matter in wastewater: Efficacy and selectivity of the water treatment, *Water Res.* 55 (2014) 323–334, <https://doi.org/10.1016/j.watres.2014.02.040>.
- [8] R.K. Henderson, A. Baker, K.R. Murphy, A. Hambly, R.M. Stuetz, S.J. Khan, Fluorescence as a potential monitoring tool for recycled water systems: A review, *Water Res.* 43 (2009) 863–881, <https://doi.org/10.1016/j.watres.2008.11.027>.
- [9] P.G. Coble, Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.* 51 (1996) 325–346, [https://doi.org/10.1016/0304-4203\(95\)00062-3](https://doi.org/10.1016/0304-4203(95)00062-3).
- [10] A.C. Olivieri, Practical guidelines for reporting results in single- and multi-component analytical calibration: A tutorial, *Anal. Chim. Acta.* 868 (2015) 10–22, <https://doi.org/10.1016/j.aca.2015.01.017>.
- [11] N.M. Peleato, R.L. Legge, R.C. Andrews, Neural networks for dimensionality reduction of fluorescence spectra and prediction of drinking water disinfection by-products, *Water Res.* 136 (2018) 84–94, <https://doi.org/10.1016/j.watres.2018.02.052>.
- [12] L. Li, Y. Wang, W. Zhang, S. Yu, X. Wang, N. Gao, New advances in fluorescence excitation-emission matrix spectroscopy for the characterization of dissolved organic matter in drinking water treatment: A review, *Chem. Eng. J.* 381 (2020), 122676, <https://doi.org/10.1016/j.cej.2019.122676>.
- [13] J.N. Miller, J.C. Miller, *Estadística y Quimiometría para Química Analítica*, Pearson Educación S.A., 2002.
- [14] K.R. Murphy, C.A. Stedmon, D. Graeber, R. Bro, Fluorescence spectroscopy and multi-way techniques. PARAFAC, *Anal. Methods* 5 (2013) 6557, <https://doi.org/10.1039/c3ay41160e>.
- [15] R. Bro, H.A.L. Kiers, A new efficient method for determining the number of components in PARAFAC models, *J. Chemom.* 17 (2003) 274–286, <https://doi.org/10.1002/cem.801>.
- [16] R. Bro, PARAFAC. Tutorial and applications, *Chemom. Intell. Lab. Syst.* 38 (1997) 149–171, [https://doi.org/10.1016/S0169-7439\(97\)00032-4](https://doi.org/10.1016/S0169-7439(97)00032-4).
- [17] M. Porcel, Aplicación de técnicas quimiométricas para el desarrollo de nuevos métodos cinético-espectrofotométricos de análisis, Universitat Autònoma de Barcelona, 2001. <http://hdl.handle.net/10803/3118>.
- [18] I. Sciscenko, A. Arques, Z. Varga, S. Bouchonnet, O. Monfort, M. Brigante, G. Mailhot, Significant role of iron on the fate and photodegradation of enrofloxacin, *Chemosphere* 270 (2021), 129791, <https://doi.org/10.1016/j.chemosphere.2021.129791>.
- [19] I. Sciscenko, H. Thị Mỹ Hằng, C. Escudero-Onate, I. Oller, A. Arques, Fluorescence Spectroscopy and Chemometrics: A Simple and Easy Way for the Monitoring of Fluoroquinolone Mixture Degradation, *ACS Omega* 6 (2021) 4663–4671, <https://doi.org/10.1021/acsomega.0c05370>.
- [20] S.J. Mazivila, S.A. Bortolato, A.C. Olivieri, MVC3.GUI: A MATLAB graphical user interface for third-order multivariate calibration. An upgrade including new multi-way models, *Chemom. Intell. Lab. Syst.* 173 (2018) 21–29, <https://doi.org/10.1016/j.chemolab.2017.12.012>.
- [21] U.J. Wünsch, K. Murphy, A simple method to isolate fluorescence spectra from small dissolved organic matter datasets, *Water Res.* 190 (2021), <https://doi.org/10.1016/j.watres.2020.116730>.
- [22] C.M. Andersen, R. Bro, Practical aspects of PARAFAC modeling of fluorescence excitation-emission data, *J. Chemom.* 17 (2003) 200–215, <https://doi.org/10.1002/cem.790>.
- [23] L. Yang, J. Hur, W. Zhuang, Occurrence and behaviors of fluorescence EEM-PARAFAC components in drinking water and wastewater treatment systems and their applications: A review, *Environ. Sci. Pollut. Res.* 22 (2015) 6500–6510, <https://doi.org/10.1007/s11356-015-4214-3>.
- [24] W. Shi, W.-E. Zhuang, J. Hur, L. Yang, Monitoring dissolved organic matter in wastewater and drinking water treatments using spectroscopic analysis and ultra-high resolution mass spectrometry, *Water Res.* 188 (2021), 116406, <https://doi.org/10.1016/j.watres.2020.116406>.
- [25] K.R. Murphy, A. Hambly, S. Singh, R.K. Henderson, A. Baker, R. Stuetz, S.J. Khan, Organic matter fluorescence in municipal water recycling schemes: Toward a unified PARAFAC model, *Environ. Sci. Technol.* 45 (2011) 2909–2916, <https://doi.org/10.1021/es103015e>.
- [26] K.M.G. Mostofa, C. Liu, M.A. Mottaleb, G. Wan, H. Ogawa, D. Vione, T. Yoshioka, F. Wu, Dissolved Organic Matter in Natural Waters, in: K.M.G. Mostofa, T. Yoshioka, A. Mottaleb, D. Vione (Eds.), *Biogeochemistry*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013, pp. 1–137, https://doi.org/10.1007/978-3-642-32223-5_1.
- [27] J.A. Leenheer, J.P. Croué, Characterizing aquatic dissolved organic matter, *Environ. Sci. Technol.* 37 (2003) 18A–26A, <https://doi.org/10.1017/S003822200003672>.
- [28] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D.M. DeMarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research, *Mutat. Res. - Rev. Mutat. Res.* 636 (2007) 178–242, <https://doi.org/10.1016/j.mrrev.2007.09.001>.
- [29] L.A. Weinrich, P.K. Jjemba, E. Giraldo, M.W. LeChevallier, Implications of organic carbon in the deterioration of water quality in reclaimed water distribution systems, *Water Res.* 44 (2010) 5367–5375, <https://doi.org/10.1016/j.watres.2010.06.035>.
- [30] S.K.L. Ishii, T.H. Boyer, Behavior of reoccurring parafac components in fluorescent dissolved organic matter in natural and engineered systems: A critical review, *Environ. Sci. Technol.* 46 (2012) 2006–2017, <https://doi.org/10.1021/es2043504>.
- [31] A.D. Pifer, S.L. Cousins, J.L. Fairey, Assessing UV- and fluorescence-based metrics as disinfection byproduct precursor surrogate parameters in a water body influenced by a heavy rainfall event, *J. Water Supply Res. Technol. - AQUA.* 63 (2014) 200–211, <https://doi.org/10.2166/aqua.2013.122>.
- [32] B.F. Trueman, S.A. Macisaac, A.K. Stoddart, G.A. Gagnon, Prediction of disinfection by-product formation in drinking water: Via fluorescence spectroscopy, *Environ. Sci. Water Res. Technol.* 2 (2016) 383–389, <https://doi.org/10.1039/c5ew00285k>.
- [33] R.G.M. Spencer, L. Bolton, A. Baker, Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations, *Water Res.* 41 (2007) 2941–2950, <https://doi.org/10.1016/j.watres.2007.04.012>.
- [34] C.W. Cuss, S.M. McConnell, C. Guéguen, Combining parallel factor analysis and machine learning for the classification of dissolved organic matter according to source using fluorescence signatures, *Chemosphere* 155 (2016) 283–291, <https://doi.org/10.1016/j.chemosphere.2016.04.061>.
- [35] R. Xu, J. Cao, G. Feng, J. Luo, Q. Feng, B. Ni, F. Fang, Fast identification of fluorescent components in three-dimensional excitation-emission matrix fluorescence spectra via deep learning, *Chem. Eng. J.* (2021), 132893, <https://doi.org/10.1016/j.cej.2021.132893>.
- [36] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence Excitation-Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter, *Environ. Sci. Technol.* 37 (2003) 5701–5710, <https://doi.org/10.1021/es034354c>.
- [37] K.R. Murphy, C.A. Stedmon, P. Wenig, R. Bro, OpenFluor- An online spectral library of auto-fluorescence by organic compounds in the environment, *Anal. Methods* 6 (2014) 658–661, <https://doi.org/10.1039/c3ay41935e>.

- [38] M. Vera, S. Cruz, M.R. Boleda, J. Mesa, J. Martín-Alonso, S. Casas, O. Gibert, J. L. Cortina, Fluorescence spectroscopy and parallel factor analysis as a dissolved organic monitoring tool to assess treatment performance in drinking water trains, *Sci. Total Environ.* 584 (585) (2017) 1212–1220, <https://doi.org/10.1016/j.scitotenv.2017.01.184>.
- [39] J. Li, L. Wang, J. Geng, S. Li, Q. Yu, K. Xu, H. Ren, Distribution and removal of fluorescent dissolved organic matter in 15 municipal wastewater treatment plants in China, *Chemosphere* 251 (2020), 126375, <https://doi.org/10.1016/j.chemosphere.2020.126375>.
- [40] A. Goffin, S. Guérin, V. Rocher, G. Varrault, Towards a better control of the wastewater treatment process: excitation-emission matrix fluorescence spectroscopy of dissolved organic matter as a predictive tool of soluble BOD5 in influents of six Parisian wastewater treatment plants, *Environ. Sci. Pollut. Res.* (2018) 25, <https://doi.org/10.1007/s11356-018-1205-1>.
- [41] A. Goffin, S. Guérin-Rechdaoui, V. Rocher, G. Varrault, An environmentally friendly surrogate method for measuring the soluble chemical oxygen demand in wastewater: use of three-dimensional excitation and emission matrix fluorescence spectroscopy in wastewater treatment monitoring, *Environ. Monit. Assess.* (2019) 191, <https://doi.org/10.1007/s10661-019-7570-5>.
- [42] J.P.R. Sorensen, A. Baker, S.A. Cumberland, D.J. Lapworth, A.M. MacDonald, S. Pedley, R.G. Taylor, J.S.T. Ward, Real-time detection of faecally contaminated drinking water with tryptophan-like fluorescence: defining threshold values, *Sci. Total Environ.* 622 (623) (2018) 1250–1257, <https://doi.org/10.1016/j.scitotenv.2017.11.162>.
- [43] R. Guillosoy, J. Le Roux, A. Goffin, R. Mailler, G. Varrault, E. Vulliet, C. Morlay, F. Nauleau, S. Guérin, V. Rocher, J. Gaspéri, Fluorescence excitation/emission matrices as a tool to monitor the removal of organic micropollutants from wastewater effluents by adsorption onto activated carbon, *Water Res* 190 (2021), 116749, <https://doi.org/10.1016/j.watres.2020.116749>.
- [44] N. Moona, K.R. Murphy, M. Bondelind, O. Bergstedt, T.J.R. Pettersson, Partial renewal of granular activated carbon biofilters for improved drinking water treatment, *Environ. Sci. Water Res. Technol.* 4 (2018) 529–538, <https://doi.org/10.1039/c7ew00413c>.
- [45] Y. An, Z. Zhou, W. Qiao, W. Pan, Z. Chen, Simultaneous removal of phosphorus and dissolved organic matter from a sludge: In situ reduction process effluent by coagulants, *RSC Adv* 7 (2017), <https://doi.org/10.1039/c7ra08054a>.
- [46] L. Alcalde-Sanz, B.M. Gawlik, Minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge, 2017, <https://doi.org/10.2760/887727>. Luxembourg.
- [47] A. Pistocchi, C. Dorati, B. Grizzetti, A. Udias, O. Vigiak, M. Zanni, Water quality in Europe : effects of the Urban Wastewater Treatment Directive, 2019, <https://doi.org/10.2760/303163>. Luxembourg.
- [48] J.J. Pignatello, E. Oliveros, A. McKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84, <https://doi.org/10.1080/10643380500326564>.
- [49] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Grnajak, Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, *Catal. Today* 147 (2009) 1–59, <https://doi.org/10.1016/j.cattod.2009.06.018>.
- [50] M.A. Oturan, J.-J. Aaron, Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review, *Crit. Rev. Environ. Sci. Technol.* 44 (2014) 2577–2641, <https://doi.org/10.1080/10643389.2013.829765>.
- [51] P. Calza, V.A. Sakkas, C. Medana, C. Baiocchi, A. Dimou, E. Pelizzetti, T. Albanis, Photocatalytic degradation study of diclofenac over aqueous TiO₂ suspensions, *Appl. Catal. B Environ.* 67 (2006) 197–205, <https://doi.org/10.1016/j.apcatb.2006.04.021>.
- [52] C.S. Uyguner, S.A. Suphandag, A. Kerc, M. Bekbolet, Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques, *Desalination* 210 (2007) 183–193, <https://doi.org/10.1016/j.desal.2006.05.043>.
- [53] Q.V. Ly, H.C. Kim, J. Hur, Tracking fluorescent dissolved organic matter in hybrid ultrafiltration systems with TiO₂/UV oxidation via EEM-PARAFAC, *J. Memb. Sci.* 549 (2018) 275–282, <https://doi.org/10.1016/j.memsci.2017.12.020>.
- [54] J. Świetlik, E. Sikorska, Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone, *Water Res* 38 (2004) 3791–3799, <https://doi.org/10.1016/j.watres.2004.06.010>.
- [55] B.F. da Silva, A. Jelic, R. López-Serna, A.A. Mozeto, M. Petrovic, D. Barceló, Occurrence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain, *Chemosphere* 85 (2011) 1331–1339, <https://doi.org/10.1016/j.chemosphere.2011.07.051>.
- [56] R. Binetti, P. Calza, G. Costantino, S. Morgillo, D. Papagiannaki, Perfluoroalkyl substance assessment in turin metropolitan area and correlation with potential sources of pollution according to the water safety plan risk management approach, *Separations* 6 (2019), <https://doi.org/10.3390/separations6010017>.
- [57] I.T. Carvalho, L. Santos, Antibiotics in the aquatic environments: A review of the European scenario, *Environ. Int.* 94 (2016) 736–757, <https://doi.org/10.1016/j.envint.2016.06.025>.
- [58] B. Petrie, R. Barden, B. Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring, *Water Res* 72 (2015) 3–27, <https://doi.org/10.1016/j.watres.2014.08.053>.
- [59] R.N. Carvalho, L. Ceriani, A. Ippolito, Development of the first Watch List under the Environmental Quality Standards Directive water policy, 2015. <https://doi.org/10.2788/101376>.
- [60] T. Brodin, J. Fick, M. Jonsson, J. Klaminder, Dilute Concentrations of a Psychiatric Drug Alter Behavior of Fish from Natural Populations, *Science* (80-.). 339 (2013) 814–815. <https://doi.org/10.1126/science.1226850>.
- [61] S.H. Ruiz, S. Wickramasekara, L. Abrell, X. Gao, B. Chefetz, J. Chorover, Complexation of trace organic contaminants with fractionated dissolved organic matter: Implications for mass spectrometric quantification, *Chemosphere* 91 (2013) 344–350, <https://doi.org/10.1016/j.chemosphere.2012.11.059>.
- [62] X. Van Doorslaer, J. Dewulf, H. Van Langenhove, K. Demeestere, Fluoroquinolone antibiotics: An emerging class of environmental micropollutants, *Sci. Total Environ.* 500 (501) (2014) 250–269, <https://doi.org/10.1016/j.scitotenv.2014.08.075>.
- [63] T. Kosjek, E. Heath, M. Petrović, D. Barceló, Mass spectrometry for identifying pharmaceutical biotransformation products in the environment, *Trends Anal. Chem.* 26 (2007) 1076–1085, <https://doi.org/10.1016/j.trac.2007.10.005>.
- [64] M. Sgroi, P. Roccaro, G.V. Korshin, V. Greco, S. Sciuto, T. Anumol, S.A. Snyder, F. G.A. Vagliasindi, Use of fluorescence EEM to monitor the removal of emerging contaminants in full scale wastewater treatment plants, *J. Hazard. Mater.* 323 (2017) 367–376, <https://doi.org/10.1016/j.jhazmat.2016.05.035>.
- [65] M. Sgroi, T. Anumol, P. Roccaro, F.G.A. Vagliasindi, S.A. Snyder, Modeling emerging contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing components of dissolved organic matter, *Water Res* 145 (2018) 667–677, <https://doi.org/10.1016/j.watres.2018.09.018>.
- [66] M. Sgroi, T. Anumol, F.G.A. Vagliasindi, S.A. Snyder, P. Roccaro, Comparison of the new Cl₂/O₃/UV process with different ozone- and UV-based AOPs for wastewater treatment at pilot scale: Removal of pharmaceuticals and changes in fluorescing organic matter, *Sci. Total Environ.* 765 (2021), 142720, <https://doi.org/10.1016/j.scitotenv.2020.142720>.
- [67] A.M. Berkovic, F.S. García Einschlag, M.C. Gonzalez, R. Pis Diez, D.O. Mártire, Evaluation of the Hg²⁺ binding potential of fulvic acids from fluorescence excitation-emission matrices, *Photochem. Photobiol. Sci.* 12 (2013) 384–392, <https://doi.org/10.1039/c2pp25280e>.
- [68] B. Caram, S. García-Ballesteros, L. Santos-Juanes, A. Arques, F.S. García-Einschlag, Humic like substances for the treatment of scarcely soluble pollutants by mild photo-Fenton process, *Chemosphere* 198 (2018) 139–146, <https://doi.org/10.1016/j.chemosphere.2018.01.074>.
- [69] S. García-Ballesteros, M. Costante, R. Vicente, M. Mora, A.M. Amat, A. Arques, L. Carlos, F.S.G. Einschlag, Humic-like substances from urban waste as auxiliaries for photo-Fenton treatment: a fluorescence EEM-PARAFAC study, *Photochem. Photobiol. Sci.* 16 (2017) 38–45, <https://doi.org/10.1039/C6PP00236F>.
- [70] M.D. Carabajal, J.A. Arancibia, G.M. Escandar, Excitation-emission fluorescence-kinetic data obtained by Fenton degradation. Determination of heavy-polycyclic aromatic hydrocarbons by four-way parallel factor analysis, *Talanta* 165 (2017) 52–63, <https://doi.org/10.1016/j.talanta.2016.12.030>.
- [71] I. Sciscenko, S. García-Ballesteros, C. Sabater, M.A. Castillo, C. Escudero-Oñate, I. Oller, A. Arques, Monitoring photolysis and (solar photo)-Fenton of enrofloxacin by a methodology involving EEM-PARAFAC and bioassays: Role of pH and water matrix, *Sci. Total Environ.* 719 (2020), 137331, <https://doi.org/10.1016/j.scitotenv.2020.137331>.
- [72] S. García-Ballesteros, M. Mora, R. Vicente, R.F. Vercher, C. Sabater, M.A. Castillo, A.M. Amat, A. Arques, A new methodology to assess the performance of AOPs in complex samples: Application to the degradation of phenolic compounds by O₃ and O₃/UV-A-Vis, *Chemosphere* 222 (2019) 114–123, <https://doi.org/10.1016/j.chemosphere.2019.01.015>.
- [73] S. García-Ballesteros, M. Mora, R. Vicente, C. Sabater, M.A. Castillo, A. Arques, A. M. Amat, Gaining further insight into photo-Fenton treatment of phenolic compounds commonly found in food processing industry, *Chem. Eng. J.* 288 (2016) 126–136, <https://doi.org/10.1016/j.cej.2015.11.031>.
- [74] L. Santos-Juanes, F.S. García Einschlag, A.M. Amat, A. Arques, Combining ZVI reduction with photo-Fenton process for the removal of persistent pollutants, *Chem. Eng. J.* 310 (2017) 484–490, <https://doi.org/10.1016/j.cej.2016.04.114>.
- [75] A.B. Prevot, P. Avetta, D. Fabbri, E. Montoneri, A. Morales-Rubio, M. De La Guardia, Ecofriendly in-line process monitoring: A case study. Anthracene photodegradation in the presence of refuse-derived soluble bio-organics, *Anal. Bioanal. Chem.* 404 (2012) 657–664, <https://doi.org/10.1007/s00216-012-5961-3>.
- [76] F. Villarruel, M.P. Denofrio, F.A.O. Rasse-Suriani, F.S. García Einschlag, T. Schmidt De León, R. Erra-Balsells, F.M. Cabrerizo, Light-induced full aromatization and hydroxylation of 7-methoxy-1-methyl-3,4-dihydro-2H-pyrido[3,4-b]indole alkaloid: Oxygen partial pressure as a key modulator of the photoproducts distribution, *J. Photochem. Photobiol. B Biol.* 199 (2019), 111600, <https://doi.org/10.1016/j.jphotobiol.2019.111600>.
- [77] D. Palma, E. Parlanti, M. Sourzac, O. Voldoire, A. Beauger, M. Sleiman, C. Richard, Fluorescence analysis allows to predict the oxidative capacity of humic quinones in dissolved organic matter: implication for pollutant degradation, *Environ. Chem. Lett.* (2020), <https://doi.org/10.1007/s10311-020-01137-z>.