Transformation products formed by tertiary treatment process: strategies for tentative identification in real effluents and water matrices

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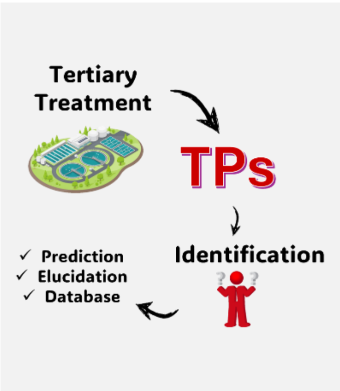

The presence of CECs in environment creates the need of new tertiary treatment processes to degrade these compounds. However, some of these treatment processes can be responsible for generating different TPs when complete mineralization is not achieved. Some of these TPs may represent risk for environment and human health and, because of that, their identification is necessary. Three different approaches to evaluate tentatively the presence of TPs in effluents and water matrices, their advantages and disadvantages were discussed in this study: i) prediction of TPs; ii) elucidation by classical method and, iii) purpose-built databases. After analyzing all the analytical strategies, it is clear that each one has its strengths and limitations and to carry out a comprehensive study, the use of any of these strategies makes it possible to increase the safety of the treated water evaluated.

Introduction

CECs (Contaminants of Emerging Concern) are commonly found in the environment at concentrations levels of ng L^{-1} and μg L^{-1} [1,2]. Even at trace levels, exposure to mixtures of CECs can represent risks to aquatic ecosystems and human health [3]. Different tertiary treatment methods have been explored to remove CECs from wastewater, as Advanced Oxidation Processes (AOPs) [4] and, despite achieving high degradation rates of the original compounds, complete mineralization of CECs is not achieved, resulting in the formation of Transformation Products (TPs). TPs often are non-biodegradable and can possess high toxicity [5].
The presence of TPs in treated and water matrices, sometimes at concentrations exceeding those of the original compounds, is becoming increasingly prevalent [6]. Analytical standards for these TPs are generally unavailable commercially and represents a significant challenge for their identification. Thus, different strategies to provide tentatively identification of TPs in effluents and water matrices are necessary, specially due to the importance of assessing TPs together with the original compounds to ensure security of water treated.

Material and Methods

To make possible the tentative identification of TPs formed by different tertiary wastewater treatment processes, three different methods used by researchers worldwide were discussed, as well as their advantages and disadvantages: i) prediction of TPs; ii) elucidation by classical elucidation method and, iii) purpose-built database strategy.

Results and Discussion

Tentative identification and evaluation of TPs in treated effluent or water matrices, especially after AOPs treatment processes is undeniable. However, as each compound responds differently to each treatment, it is important to know which TPs can be formed. The lack of analytical standards makes this work even more difficult, as well as makes necessary to use chemical analysis techniques to allow the separation of TPs coexisting in the effluent or treated water (e.g. liquid chromatography) and their tentative identification with relevant information (e.g. high resolution mass spectrometers - HRMS as analyzers). In this context, LC-HRMS systems have the following main positive characteristics: no restrictions on the type and quantity of compounds analyzed simultaneously; high sensitivity in full scan mode; and highly specific and abundant structural information. Conversely, this tool demands a more labor-intensive data processing and very well formed analysts to perform this processing. The tentative identification of TPs, especially in effluents and water matrices can be done by the use of some strategies described followed:
The first strategy was based in the prediction of TPs formed by tertiary wastewater treatment processes by computational tools and software that apply algorithms to simulate reaction pathways based on chemical structures of the compound and the main mechanism of degradation. Different TPs prediction systems are available, as BioTransformer [7]. However, the main information presented in this kind of tool is about metabolism pathway, and just a little part of the data related to TPs, especially from tertiary treatment processes. The advantages of this proposal identification method are low cost, since it uses computational tools, no need of experimental analysis and possibility of a rapid predictive screening analysis in real aqueous samples. Predictions present some disadvantages: limited accuracy especially considering complex pathways,

a lack in some reaction's mechanism, and just a small part of predictions consider tertiary treatment process as AOPs.

The second strategy for TPs elucidation is via the classical method. This methodology uses a non-target approach where, during the degradation process, aliquots in different degradation times are taken and analyzed by HRMS. Identification of TPs are made by appearance and disappearance of chromatographic peaks. After identifying some possible TP, the analyst considers the structure of the original compound and HRMS information provided by the software, as exact mass of the possible TP, fragmentation profile, double bond equivalence (DBE), and isotopic profile, as can be seen in an example shown in Figure 1 [8]. The advantages of this approach are the high specificity and reliability to identify new TPs and the possibility, in the most cases, of proposing the TP structure based on fragmentation profile. However, this strategy has also disadvantages, because it is a high time-consuming and labor-intensive process, requires analyst skills, demands high cost (since experiments are needed), and, when TPs are formed in low concentrations, they may be not detected or demand the use of pre-concentration techniques before instrumental analysis to increase the possibility of their detection.

Elucidating TPs can be a challenging task. In this regard, the third monitoring strategy employs purpose-built databases containing hundreds of TPs, and it has been gaining attention, becoming a very promising search tool [9]. This strategy proved to be a dynamic tool, requiring constantly updated, whenever new information about new TPs and their fragments are available in the literature, is therefore characterized as a study in constant evolution. Purpose-built databases may include experimental data, computational predictions, and literature reviews information. The advantages of this approach include its accessibility, comprehensive coverage, and potential for rapid tentatively identification of TPs. However, the potential of database depends on the quality and completeness of the data input, and there may be limitations in published studies. It is not possible to tentatively identified new TPs (not yet published).

The use of purpose-built database strategy is the easier way to provide tentative identification of TPs formed by tertiary treatment process.

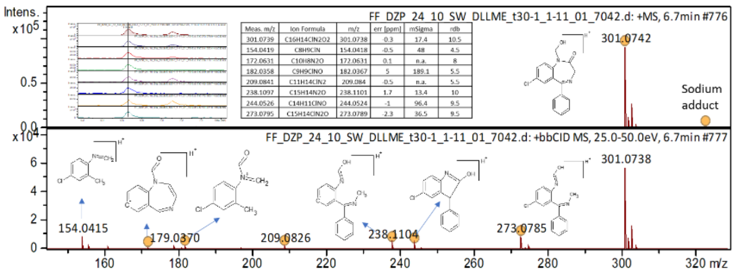

Figure 1. Example of elucidation of TP *via* classical method

Conclusions

As it was possible to see, the prediction of TPs, the elucidation *via* classical method, and the use of purpose-built databases represent three analytical strategies for identifying TPs formed during tertiary wastewater/water treatments. Each method has its strengths and limitations, and researchers could select the approach more appropriate for their purpose.

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