Quaternary treatments in the upgrading of wastewater treatment plants: micropollutant removal and operation reliability

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Abstract. The recent revised Urban Wastewater Treatment Directive (UWWTD) requires the implementation of quaternary treatments (QT) for large wastewater treatment plants (WWTPs) and for small ones placed in risk areas in order to reduce micropollutants (MPs) content. The current study compares the operation reliability and the removal efficiencies of the twelve MPs listed in the UWWTD of several consolidated technologies acting as a QT. The reliability evaluation is based on a risk assessment resulting from: (*i*) identification of the failure modes for each component of the different treatment trains and their related consequences; (*ii*) score assignment of the expected likelihood of occurrence (L) of each failure mode and the magnitude (M) of the corresponding effects to the final effluent quality, equipment, worker health and environment; (*iii*) estimation of the risk (R) of each failure mode (R = L x M); and (iv) ranking and identification of the most critical risks (highest R). Data on removal efficiencies are collected from literature. Ozonation followed by granular activated carbon is the QT with the highest number of very high risks, and the most difficult MPs to be removed are candesartan and irbesartan (slightly lower than 80%).

Keywords: micropollutants, operation reliability, quaternary treatment, removal efficiency, risk assessment

1. Introduction

The traditional urban WWTPs normally consist of pre-treatments, primary sedimentation and a biological step based on the conventional activated sludge process (CAS) with afinal disinfection (if requested). As these treatments are inefficient in removing MPs (the so-called contaminants of emerging concern), the recently revised UWWTD, (EU Directive 2024/3019) requires the implementation of a QT in large WWTPs (with a population equivalent of 150,000 or more) and in small ones (with 10,000 population equivalent or more) discharging into an area where the concentration and accumulation of MPs may pose a risk to the environment and human health. A removal percentage of 80% is requested for at least 6 of the indicator MPs listed in the UWWTD. The QT implies an upgrading of the existing secondary treatment and/or the adoption of an end-of-pipe step.

In this context, the current study investigates CAS or membrane bioreactor (MBR) with powdered activated carbon (PAC) added to the biological tank , and different end-of-pipe treatments (namely, granular activeted carbon filter GAC, ozonation chamber O_3 and ultrafiltration unit UF). Specifically, this study compares their efficiency in removing the MPs listed in the UWWTD and their operation reliability through a risk assessment that analyses each treatment component in order to identify and prioritize potential failure modes, along with their associated effects on equipment, final effluent quality, plant workers health and the environment.

2. Material and methods

2.1. Quaternary treatment technologies under study

The treatment configurations investigated in the present study involve CAS and MBR (Table 1). The QTs considered are: UF as a CAS post-treatment (*I*), PAC added to the bioreactor (*II* and *V*); GAC as a post treatment (*III* and *VI*), ozonation O_3 followed by GAC (*IV*). All CAS configurations include a disinfection (DIS), achieved by means of NaClO addition or UV irradiation.

2.2. Removal efficiency evaluation

The MPs listed in UWWTD include 8 very easily treated compounds (amisulprid, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, venlafaxine) and 4 easily disposed substances (benzotriazole, candesartan, irbesartan, mixture of 4-methylbenzotriazole and 5-methylbenzotriazole). For each of the QTs of Table 1, the removal achieved for the listed MPs was collected from literature.

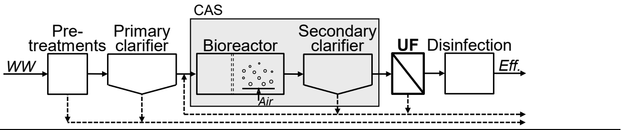
2.3. Operation reliability

The risk assessment starts with the identification of the failure modes of the main components of the different treatment steps (i.e. pipes, valves, pumps, sensors, PAC dosage etc..) and their main potential effects on the equipment, the final effluent quality, the worker health and the environment. Then, according to WHO (2022), the study assigns a score to the expected likelihood of occurrence L (1–5), and the magnitude of the effects M (1, 2, 4, 8, and 16) of each failure mode: the higher the expected likelihood of occurrence and the magnitude, the higher the score.

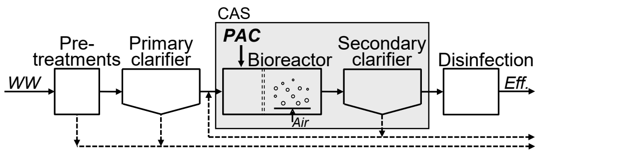
Table 1. The treatment configurations considered in the study

Treatment configuration

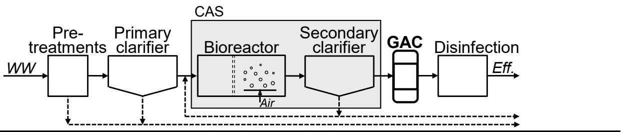
I CAS → **UF** → DIS



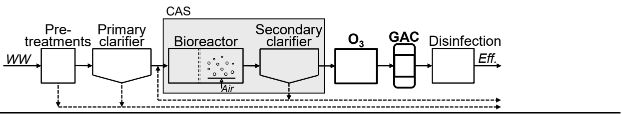
II (CAS + **PAC**) → DIS



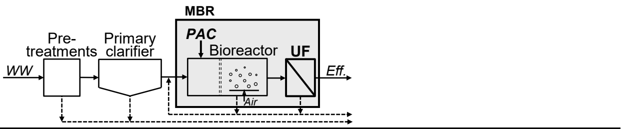
III CAS → **GAC** → DIS



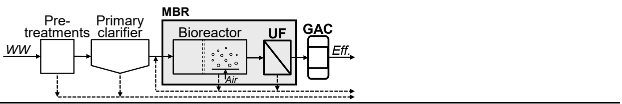
IV CAS → **O_3** → **GAC** → DIS



V **(MBR + PAC)**



VI **MBR → GAC**



The product of the two scores leads to the estimation of the risk R associated to each failure mode and ranging from 1 to 80. Failure modes are then ranked according to the decreasing R values. In agreement with WHO (2022), the risk for a failure is low if $R < 6$; medium if $6 \leq R \leq 12$; high if $12 < R \leq 32$ and very high if $R > 32$. The failure modes with the highest values of R are the most critical for the QT under study. A risk reduction requires an evaluation of how to reduce the occurrence of the failures or how to mitigate the effects.

3. Results and discussion

Figure 1 reports the number of failure modes with R > 32 (very high risk) for the different configurations. It emerges that CAS → O_3 → GAC → UV is the sequence with the highest number of critical failure modes, but, according to Bourgin et al. (2018) and Gutierrez et al. (2021), it is also able to guarantee the highest removal efficiencies for the twelve MPs listed in the recent UWWTD (only for irbesartan and candesartan the removal is slightly lower than 80 %). MBR → GAC and MBR + PAC present the lowest numbers of failure modes with R = 48 and limiting the analysis to the available literature (Gutierrez et al., 2021), they are able to guarantee 80 % removal for some of the MPs listed in the UWWTD. The consequences of failure modes with the highest risks refer to the equipment and/or the final effluent quality, only one refers to the working staff (sequences *IV* due to the ozonation step).

4. Conclusion

The risk assessment here applied to the different QT configurations highlights the most critical failure modes and suggests where to check the available safety measures and if it is necessary to add new ones in order to reduce the risks. To complete the comparison of the different QTs from a technical point of view, further values of removal efficiencies for the MPs listed in the UWWTD must be collected, according to the sampling requirements of the directive as well as an economic evaluation of the different sequences.

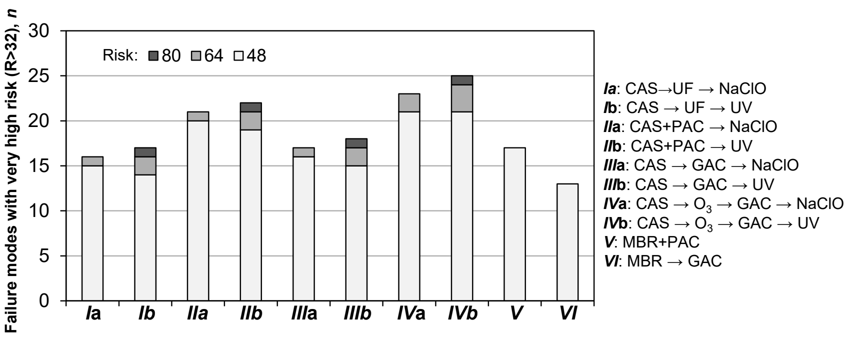


Figure 1. Failure modes corresponding to very high risk for the different configurations

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