Addressing recalcitrant pharmaceuticals at the WWTP effluent using nature-based solutions

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Introduction

Concern for the aquatic environment is nowadays causing an increased awareness of the presence of emerging micropollutants (EMs), especially recalcitrant pharmaceuticals (rPHA), in wastewater (WW) (Hejna et al., 2022). In the context of the Proposal of Directive of the European Parliament an updated set of requirements for all wastewater treatment plants (WWTP) will apply with goal to remove chosen EMs and PHA(Directive (EU) 2024/3019, 2024). Multiple studies confirmed the presence of PHA and personal care products (PCP) in the WWTP effluent due to its resistance to biological treatment step at the traditional mechanical-biological WWTP. Effects on the environment on the fauna, esp. aquatic organisms are increasing. Effects of individual substances and their mixtures (so called cocktail effect) can vary and are tested by various ecotoxicological tests(Li et al., 2019).

Materials and methods

A comprehensive analysis of 140 pharmaceuticals was conducted by ALS Czech Republic, with validation performed using effluent from the ozonation unit to ensure data reliability. The influent originated from the Blansko WWTP, allowing comparison with upcoming EU legislation.

Four NBS modules were installed: a constructed wetland (CW), a granular activated carbon (GAC) filter, and two trickled biofilters – gravel (GF) and gravel-biochar (GBF). Except for the GAC filter, housed separately, all modules operated in IBC containers (0.78 m³, 1.2 m² surface area, 0.65 m filter layer). The GAC filter, in a smaller unit (0.13 m³, 0.2 m² flow area), contained Hydraffin CC 8x30 granular activated carbon (0.6–2.36 mm, 530 $kg \cdot m^{-3}$ density, 1150 $m^2 \cdot g^{-1}$ BET surface). The CW medium consisted of hardwood biochar (16–32 mm) and gravel (8–16 mm) in a 50:50 ratio, with Common reed (Phragmites australis) planted at a density of 1 per 0.15 m². A geotextile and a 0.1 m gravel layer prevented clogging. The CW operated with vertical gravitational flow at 0.8 $l \cdot min^{-1}$ (960 $mm \cdot day^{-1}$) in operational mode, reduced to 30% in non-operational mode. The biofilters (GF and GBF) had identical setups for comparability, with GF containing only gravel (8–16 mm) and GBF using the same biochar-gravel mix as CW. Both were irrigated via misting nozzles.

NBS sampling occurred at five points: the storage tanks (ST), where effluent from ozonation (3–5 $mg \cdot l^{-1}$ ozone) was stored during unit downtime, and at the outflows of GAC, CW, GBF, and GF. Samples were collected every 20 minutes for over two hours, pooled for analysis, and transported to ALS within 24 hours under controlled conditions. Pharmaceuticals and metabolites were analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) with quadrupole detection, using solid-phase extraction (SPE) to concentrate analytes and eliminate interference. Ecotoxicity was assessed via Vibrio fischeri bioluminescence. Total organic carbon (TOC) and total nitrogen (TN) were measured per Czech standards using IR spectrometry at the AdMaS Research Centre(ČSN EN ISO 20236, 2022).

Results and discussion

When evaluating the additional pharmaceutical removal by nature-based solutions (NBS), the efficiency of preceding treatment processes must first be considered. In this case, these include a municipal wastewater treatment plant (WWTP) serving over 10,000 PE and an ozonation unit operating at 3–5 $mg \cdot l^{-1}$ ozone. The WWTP achieved pharmaceutical removal rates of 22–60%, with a median of 51%, while the ozonation unit enhanced removal to 58–88%. The subsequent application of NBS led to further reductions in pharmaceutical (IND) concentrations across all modules.

The removal efficiency of NBS varied significantly, ranging from 15% to 88% depending on the filtration method. The trickled gravel filter with biomass (GF) exhibited the lowest performance, removing 15–35% of pharmaceuticals, with a median efficiency of 30.7%. The other three filtration systems demonstrated significantly higher removal rates. The granular activated carbon (GAC) filter achieved the highest efficiency, with removal ranging from 70–88% (median: 83.2%). Constructed wetlands (CW) followed closely, with removal between 69–85% (median: 82.4%), while the gravel bed filter (GBF) achieved 71–82% removal (median: 79.8%). These findings indicate that the GAC filter is the most effective method for pharmaceutical removal. However, its higher acquisition and operational costs must be considered, making CW and GBF viable, cost-effective alternatives with nearly comparable performance.

In addition to pharmaceutical removal, CW also contributed to the degradation of total nitrogen (TN), likely due to plant activity. Among the tested methods, the GAC filter again performed best, removing 95–98% of TN (median: 96.4%), followed by CW, which achieved 80–93% removal (median: 84.8%). Given the upcoming EU directive mandating at least 80% pharmaceutical removal and stricter TN limits, both GAC and CW emerge as effective solutions. While GAC offers superior performance, CW presents a more economically sustainable option for meeting future regulatory requirements.

Conclusion

The completed study showed that the current conventional WWTPs are technologically unable to achieve a reduction of PHAs below the level required by EU Directive proposal. As a part of the measurement, the average removal rate of the monitored pharmaceuticals by the WWTP itself ranged from 22–60%. Based on the current data, it may be inferred that municipal wastewater treatment plants (WWTPs) will need to implement further levels of purification, exceeding ten thousand population equivalents (PE), to comply with upcoming regulatory standards. The main aim of this work was to determine the efficacy of various nature-based solutions (NBS) for the additional removal of PHAs. In this study, the removal rate of target PHAs achieved by NBS varied between 15–88%, depending on the given technology. Granular activated carbon (GAC) showed the best results among NBS, with an average removal rate of 70–88%. However, the economically more efficient option, constructed wetland (CW), reached an additional removal rate of 68–85%. In the instance of TN, GAC meets the stricter restrictions set by the legislation with a median value of 96.4%, whereas CW meets them with a median of 84.8%.

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