Design of a modular green tile coupled to Fenton-like processes for decentralised urban runoff treatment

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Abstract
An innovative train of technologies comprising a modular green tile as nature-based solution (NBS) and an Advanced Oxidation Process (AOP) (Fenton and solar photo-Fenton (SPF)), was evaluated for the removal of Polycyclic Aromatic Hydrocarbons (PAH) and Microplastics (MP) in urban runoff. To maximise pollutants removal, the green tile design was optimised through column and leaching experiments by studying the adsorption effect of biochar and the retention capacity of two grass species. In parallel, different Fe^{2+}/H_2O_2 ratios were tested to optimise Fenton and SPF performance using a Compound Parabolic Collector (CPC) to maximise sunlight irradiation. The results showed that both AOP and biochar were more effective for low molecular weight (LMW) PAHs, whereas high molecular weight (HMW) PAHs were more effectively retained by the plant species. Additional column assays were performed to assess MP retention by biochar showing good retention results.

Keywords (maximum 6 in alphabetical order)
Advanced Oxidation Process; Nature-Based Solutions; Microplastics; PHA urban runoff; Solar photo-Fenton.

INTRODUCTION
The removal of microplastics and hydrocarbons from urban runoff has received significant attention in recent years due to growing awareness of their adverse environmental impacts[1]. Urban runoff typically contains a complex mixture of particulate matter, including microplastics (from tire wear, road paint, and litter) along with hydrocarbons (from vehicle emissions, oil leaks, and fuel combustion)[2]. Current treatment approaches for these contaminants involve various strategies, including physical filtration, chemical processes, and biological treatments, which are expensive, complex, or ineffective technologies. This study aims to develop a cost-effective train of technologies capable of removing at least 90% of the MP and PAHs from urban runoff. The proposed treatment system integrates a modular green tile (NBS) with a Fenton/SPF (AOP) to achieve enhanced removal efficiencies for both classes of pollutants.

MATERIALS AND METHODS

Reference material and quantification methods
Experiments were carried out using synthetic urban runoff prepared by diluting the EPA 610 Polynuclear Aromatic Hydrocarbons Mixture analytical standard (Sigma-Aldrich) following the method proposed by Kargar et al. (2020)[3]. An initial concentration of 100 µg ΣPAHs/L and 300 µg ΣPAHs/mL was set to evaluate NBS and AOPs, respectively. A two-stage gas chromatography method based on i) a dispersive liquid-liquid microextraction method for sample preparation, and ii) gas chromatographic-mass spectrometric analysis, was used to follow individual PAH concentrations throughout the assays. To evaluate MP removal by the proposed NBS, a synthetic urban runoff solution was prepared by diluting a MP capsule (commercial fluorescent polystyrene microspheres of 10 µm diameter, Magsphere Inc) with $4{,}77 \times 10^7$ MP/mL, in ultrapure water, up to a concentration of 1070 MP/mL. MP quantification was performed by an optical microscope with UV light, counting all fluorescent spheres contained in 1.6 µm fiberglass filters used to filter sample aliquots of 5 mL.

Nature-Based Solution: Green tile design and experiments
The green tile comprises two layers: 1) substrate layer with biochar produced from woody trees

(from LivingChar), selected due to its good adsorption and filtration capacity for PAHs[4] and MP[5], and 2) a vegetative layer with *Festuca arundinacea* and *Poa pratensis* in roll grass format since, according to literature, they have potential to retain and absorb PAHs in their roots and leaves[6]. Biochar efficiency, in terms of PAH and MP retention, was assessed performing column experiments. For PAH, 8L of the PAH synthetic solution were filtered through a column filled with biochar (100g in 25cm height), recirculating the volume 3 times (at 160 mL/min) to analyse adsorption-desorption dynamics. PAH concentration was determined after each filtration step. For MP, the operational conditions were used, pumping 8L of the MP synthetic solution through 3 identical biochar columns to assess retention without recirculation. In both cases, samples were taken and analysed by triplicate. Leaching experiments were also performed to assess PAHs retention by plants. Roll grass samples were placed in aluminium trays, evaluating two irrigation regimes for 21 days: 1) Group 1 was irrigated 5 days/week, 2 days with PAHs solution and 3 days with tap water (high water availability scenario) and 2) Group 2 was only irrigated 2 days/week with the PAHs solution (water scarcity scenario). In both groups, a blank tray was set and irrigated only with tap water, and 5 replicates were prepared. The leachate after each irrigation was analysed in terms of PAHs concentration, and plants growth was assessed taking daily pictures and comparing green/yellow leaves.

Advanced Oxidation Processes: Fenton and SPF set-up and experiments
The experimental set-up consisted of a 5 L tank (where the Fenton reagents were mixed) connected to a CPC of 1 borosilicate tube with an inclination of 42º (local latitude) and an irradiated volume of 0.3 L. The recirculation flow (600 mL/min) between the feeding tank and the CPC was ensured by a peristaltic pump, and a Metal Halide Lamp was used to simulate the solar radiation. The set-up was also equipped with temperature, pH probes and a radiometer to record the incident radiation. The initial concentration of H_2O_2 was varied between the stoichiometric dose (ST) to fully oxidise the initial organic matter in terms of chemical oxygen demand, half and a quarter of ST, while keeping constant the initial concentration of the catalyst to the maximum dischargeable value (Fe^{2+}= 10 mg/), the pH to the optimal value (2.8) and the incident radiation to the average value in summertime time in the mediterranean area (4 mW cm^{-2}). Once the best-performing H_2O_2 initial concentration and oxidation time were identified, the effect of reducing the Fe^{2+} concentration to 5 mg/L was also studied. Experiments lasted for 15 min (Fenton) + 180 (SPF), analysing individual PAHs concentrations throughout the reaction time.

RESULTS

Green tile
Only 5 of the 16 PAHs were adsorbed in more than 95% (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene) after the first filtration with the biochar column, although this number increased to 11 and 13 after the second and third recirculation, respectively. Benzo[ghi]perylene, indeno[c,d]pyrene, and dibenz[a,h]anthracene, that are HMW PAH, were retained up to 70%. Regarding MP filtration, an average retention of 76,36±1.69% was obtained under the studied conditions. Leaching assays showed that plants from Group 1 (with higher water availability) grew up slightly more than those from Group 2 (with water stress) but similarly to blanks, showing more effect to water availability than PAH toxicity under the studied conditions. Water scarcity also resulted in a better PAH retention in Group 2 compared to Group 1. The PAH analysis showed very similar retention results in the two groups, 77% in Group 1 and 75,5% in Group 2 (in average), and no significative differences were found in the replicates and in the 6 lixiviation assays for each PAH.

Advanced Oxidation Processes

Varying the H_2O_2 initial concentration showed a general trend where higher H_2O_2 concentrations resulted in higher removal efficiency. However, since half of the stoichiometric dose (0.5xST) allowed reaching >95% degradation for all the PAHs, it was selected as the best performing concentration. Reducing the initial concentration of the catalyst led to a slight decrease of performance for most of the PAH. Regarding the oxidation time, a maximum of 195 minutes (15 min of Fenton+180 min of SPF) was required to degrade all PAHs. However, as can be observed in Table 1, the PAH with less aromatic rings and molecular weight, were removed during the first 15 minutes of Fenton reaction (F), and most of them were almost completely removed in the first 60 min of the SPF reaction, being the dibenz[a,h]anthracene, chrysene, b[k] fluoranthene, indeno[c,d]pyrene, and b[g,h,i]perylene the most refractory ones.

Table 1 Degradation efficiency (D) and corresponding oxidation time (t) obtained for each PAH, varying the H_2O_2 and Fe^{2+} initial concentrations.

Assays	**1**		**2**		**3**		**4**	
H_2O_2	**ST**		**0.5xST**		**0.25xST**		**0.5xST**	
Fe^{2+} (mg/L)	**10**		**10**		**10**		**5**	
	D (%)	**t (min)**	**D (%)**	**t (min)**	**D (%)**	**t (min)**	**D (%)**	**t (min)**
Naphthalene	100%	15^{F}	98%	15^{F}	98%	30^{SPF}	99%	15^{F}
Acenaphthylene	100%	15^{F}	96%	15^{F}	95%	30^{SPF}	100%	15^{F}
Acenaphthene	100%	15^{F}	97%	15^{F}	97%	30^{SPF}	96%	15^{F}
Fluorene	100%	15^{F}	100%	15^{F}	98%	30^{SPF}	99%	15^{F}
Phenanthrene	98%	15^{F}	100%	15^{F}	99%	30^{SPF}	97%	15^{F}
Anthracene	99%	15^{F}	99%	15^{F}	100%	30^{SPF}	99%	15^{F}
Fluoranthene	96%	15^{F}	98%	15^{F}	97%	30^{SPF}	99%	15^{F}
Pyrene	98%	15^{F}	98%	15^{F}	98%	20^{SPF}	98%	15^{F}
B[a]Anthracene	95%	75^{SPF}	98%	75^{SPF}	97%	195^{SPF}	96%	75^{SPF}
Chrysene	96%	135^{SPF}	96%	135^{SPF}	94%	195^{SPF}	96%	135^{SPF}
B[b]Fluoranthene	96%	45^{SPF}	97%	45^{SPF}	95%	135^{SPF}	95%	45^{SPF}
B[k] Fluoranthene	100%	135^{SPF}	98%	135^{SPF}	93%	195^{SPF}	98%	135^{SPF}
B[a]Pyrene	95%	75^{SPF}	96%	75^{SPF}	91%	195^{SPF}	95%	75^{SPF}
Indeno[c,d]Pyrene	98%	135^{SPF}	95%	135^{SPF}	91%	195^{SPF}	97%	135^{SPF}
DB[a,h]Anthracene	95%	195^{SPF}	95%	195^{SPF}	71%	195^{SPF}	88%	195^{SPF}
B[g,h,i]Perylene	98%	135^{SPF}	97%	135^{SPF}	78%	195^{SPF}	95%	135^{SPF}
Average	**98%**	**66**	**97%**	**66**	**93%**	**108**	**96%**	**66**

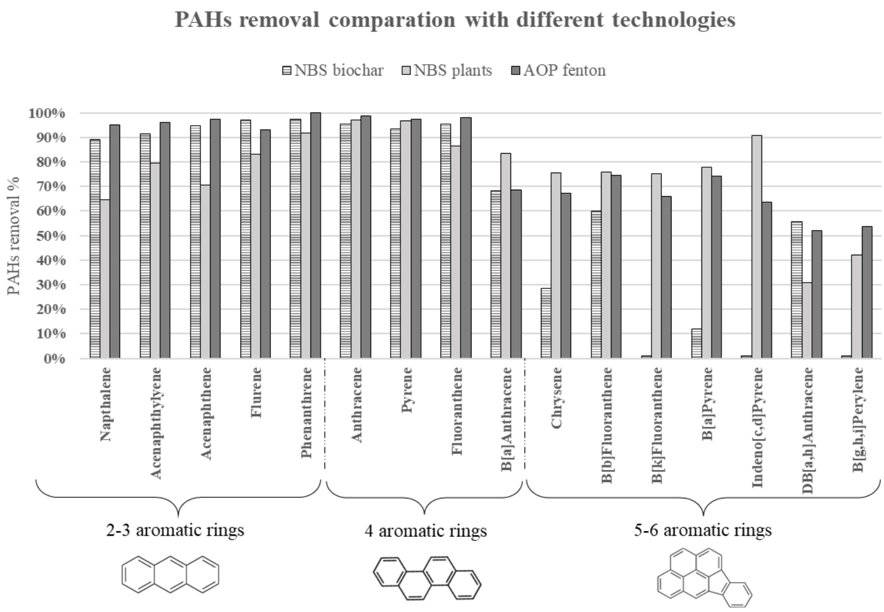

Figure 1. PAHs removal (%) obtained for each component of the proposed combined technology.

Figure 1 shows the promising results achieved for most of the PAH, even under the simplest treatment scenario (biochar column without recirculation and 15 min of Fenton without irradiation).

CONCLUSION AND DISCUSSION

The proposed technologies achieved overall PAH removal, although HMW PAHs were more challenging to eliminate by AOP and biochar adsorption. Higher adsorption efficiencies were expected (in comparison with LMW) due to the higher hydrophobicity of these compounds suggests[7]. However, biochar structure has not been yet assessed and the dominance of micropores vs mesopores may be hindering retention of HMW PAHs[8]. In contrast, higher retention of HMW PAHs was achieved by the plants with no remarkable effect in the plant's vigor. However, in this case, their retention behaviour could not be easily related to molecular weight (in contrast with some literature[6]) and further analysis of roots and leaves will be performed to reveal the real retention mechanism that occurred within the plant and rhizosphere.

Although the investigated technologies per separate did not reach 90% of retention/degradation for all the contaminants, their combination is expected to achieve this goal. In the next future, experiments using real urban runoff (with, for example, real MPs instead of microspheres) will be performed.

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