Title: Spent Coffee Ground Biochar for enhanced removal of very small microplastics (1-5 µm) from polluted water: a quaternary treatment approach

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1. Introduction

Incessant production of plastics in modern times have led to the accumulation, fragmentation, and subsequent transformation of these synthetic polymers into microplastic waste. Microplastics (MP) (5 mm - 1 µm) are commonly present in municipal wastewater [1] where they enter through various sources connected to the sewage network and can be subsequently discharged to receiving surface water bodies if not properly removed, eventually entering the aquatic systems [2]. The effective control of microplastic pollution is contingent upon the development of versatile and sustainable removal technologies that can be applied on a large scale. Various technologies have been employed to remove microplastics from polluted waters, including but not limited to filtration, coagulation, and adsorption. Among these, adsorption has recently aroused great interest in pollutant removal, with biochar derived from renewable biomass emerging as one of the most promising adsorbents. Biochar is regarded as a low-cost and eco-friendly substitute for activated carbon, serving as a valuable by-product for the safe disposal of various feedstock materials, and its unique porous structure and active vacant sites offer extensive potential for the immobilisation of microplastic spheres [3].
The present study investigates a new, promising and sustainable approach for the remediation of MPs from polluted water using biochar derived from spent coffee grounds (SCG). A column filled with SCG biochar underwent filtration tests with short contact time, ideally suited as a quaternary treatment of wastewater. To assess the efficacy of biochar in removing MPs, the influence of various factors was investigated, including MP size, presence of solids in the aqueous matrix, and capacity for accumulation over time. Micrometric scale polystyrene particles ranging from 1-5 µm were used in the experimental tests as they represent the very small size range that tends to escape conventional wastewater treatments at full-scale, primarily due to limited settleability and surface interactions. To overcome the difficulties of detecting small MPs with size around 1 µm naturally present in polluted water, traceable microspheres were spiked into water and secondary-treated sewage effluent, and subsequently enumerated with flow cytometry (FCM).

2. Characterisation of SCG biochar

Spent coffee grounds underwent pyrolysis in a N_2-purged vertical furnace across a temperature range of 300-550°C, with a 1-h holding time. These grounds, inherently characterised by high purity, demonstrated a high potential for the production of biochar, yielding an average of 30%. Microscopically, the surface of SCGs granules appears coarse and homogeneous (Figure 1A), showcasing a uniform and well-graded structure. Instead, the SCG-derived biochar displayed a sponge-like morphology with enhanced porosity (Figure 1B). Active sites of the porous structure form via the rapid release of volatile substances from the initial biomass, with higher pyrolysis temperatures consequently enhancing carbon content, aromaticity, and surface area.

A B

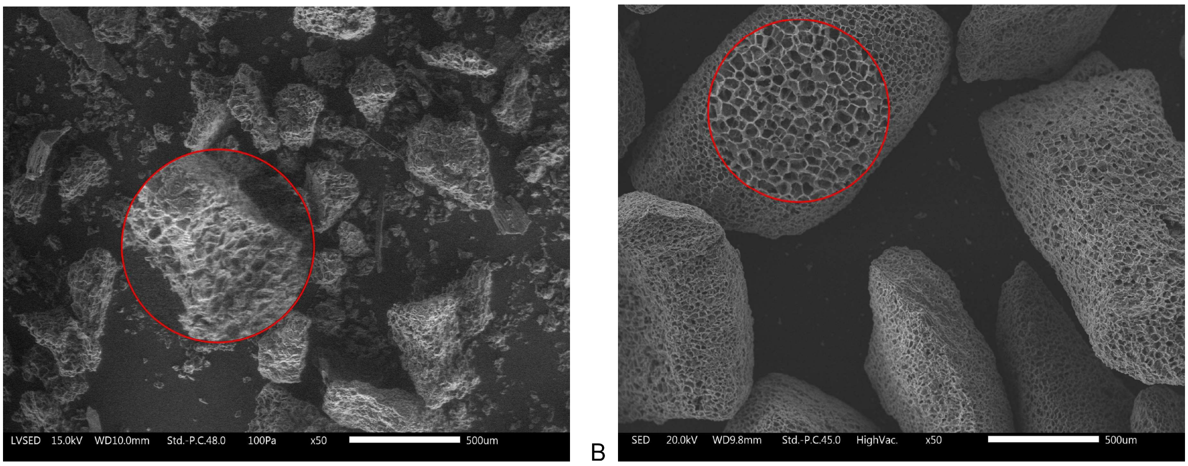

Figure 1. SED images of (A) unheated SCG at 50x magnification and (B) SCG biochar (450°C, N_2) at 50x.

3. *Filtration column tests* with SCG biochar

A layer of biochar with depth of 40 mm was packed into a cylindrical column measuring 80 mm in length and 18 mm in diameter. Biochar was positioned between two 20 mm-layers of sand to avoid loss of biochar, which has a grain size larger than 125 µm. To account for sand interference, a second column made up of 80 mm of sand was used in parallel as a control. At the end of the tests, biochar was extracted from the column and samples underwent scanning electron microscope (SEM) imaging.

3.1. Influence of MP size

Working suspensions of polystyrene microspheres (Fluoro Max microplastics, 1% solid, Thermo Fisher, USA) ranging in size from 1 to 5 µm in deionized water were prepared (Table 1). Aliquots of these suspensions were systematically injected into both biochar and sand filtration columns. Effluents were collected over time and MPs were subsequently enumerated by FCM.

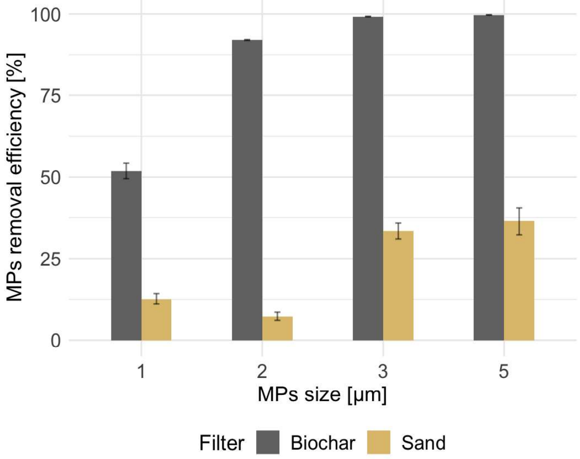

Table 1. MP concentrations in effluents from biochar and sand filter as a function of MP size

MP size	MPs applied	MPs in the effluent	
		Biochar filter	**Sand filter**
[µm]	[No. part/µL]	[No. part/µL]	[No. part/µL]
1	2488	1197 ± 59	2174 ± 42
2	1967	156 ± 2.6	1826 ± 24
3	546	4.5 ± 0.4	364 ± 13
5	264	0.9 ± 0.1	191 ± 35

Figure 2. Removal efficiency of MPs in biochar and sand filtration columns as a function of MP size (1, 2, 3, 5 µm).

SCG biochar demonstrates notably greater effectiveness in removing MPs compared to the sand filter (Figure 2). Larger MPs are easily trapped within the biochar pores, leading to a high removal capacity (92.1%, 99.2% e 99.7% for MPs sized at 2, 3, 5 µm, respectively). Conversely, 1 µm-sized MPs prove more demanding to remove (51.2% efficiency), posing significant challenges to filtration systems.

3.2. 1-µm MP removal from secondary-treated effluent

The most challenging MPs with a fixed size of 1 µm were suspended in both deionized water (DW) and secondary-treated wastewater (WW) at a constant concentration of 2500 particles/µL. The two filters (biochar and sand filters) were subjected to repeated application of these MP suspensions to assess their efficacy in retaining 1-µm MPs in complex water matrices. Remarkably, the biochar filter demonstrated a slight enhancement in filtration capacity when exposed to treated wastewater (Figure 3). This can be attributed to aggregation, wherein the 1-µm MPs tend to adhere or be entrapped on other solids present in the matrix. This aggregation facilitates the removal of MPs, thereby improving overall filtration efficiency.

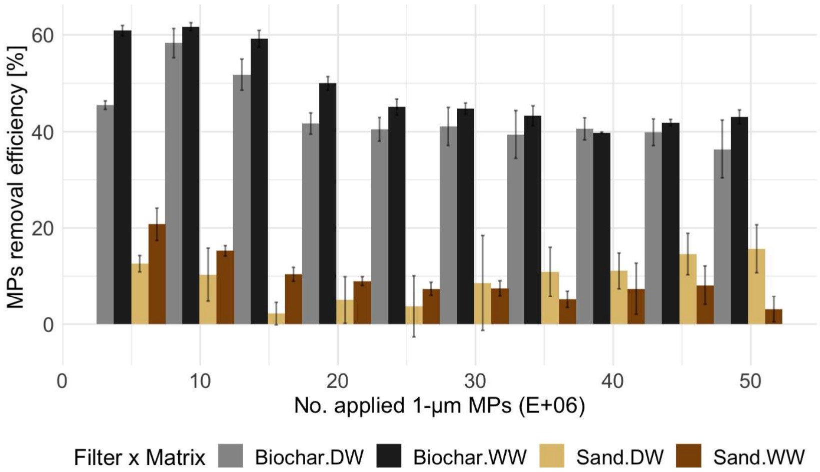

Figure 3. 1-µm MPs removal efficiency of biochar and sand filter as a function of the water matrix.

3.3. 1-µm MP cumulative retention

The assessment of cumulative 1-µm MPs retention by biochar and sand filtration columns bridges lab findings to real-scale applications. The accumulation capacity per gram of biochar rises steadily with applied particles (Figure 4), showing no plateau or saturation, and most importantly, no MP desorption over time. Notably, the sharper slope in the latter segment of the biochar curve indicates enhanced efficacy of the biochar filter in trapping MPs in presence of the wastewater matrix, underscoring its promising applicability in wastewater remediation.

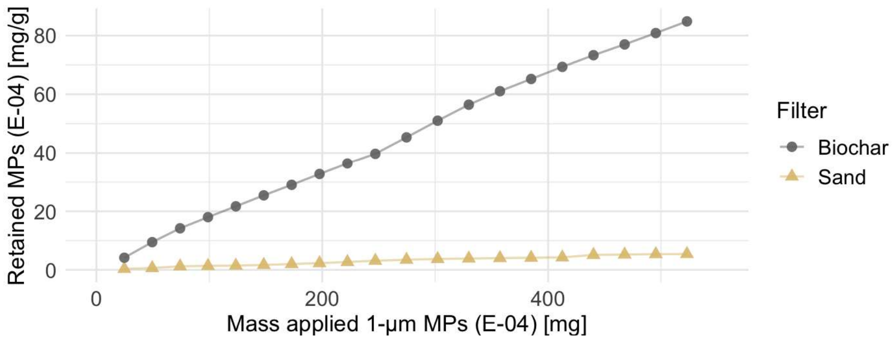

Figure 4. 1-µm MPs cumulative retention per gram of biochar and per gram of sand.

4. Microscopic observation of the adsorbed MPs

MPs were found to be both trapped within the porous structure of biochar (Figure 5A), entangled by flaky biochar particles which exhibited colloidal properties (Figure 5B) and stuck in the gaps between the filter particles (Figure 5C, D), further contributing to their immobilisation.

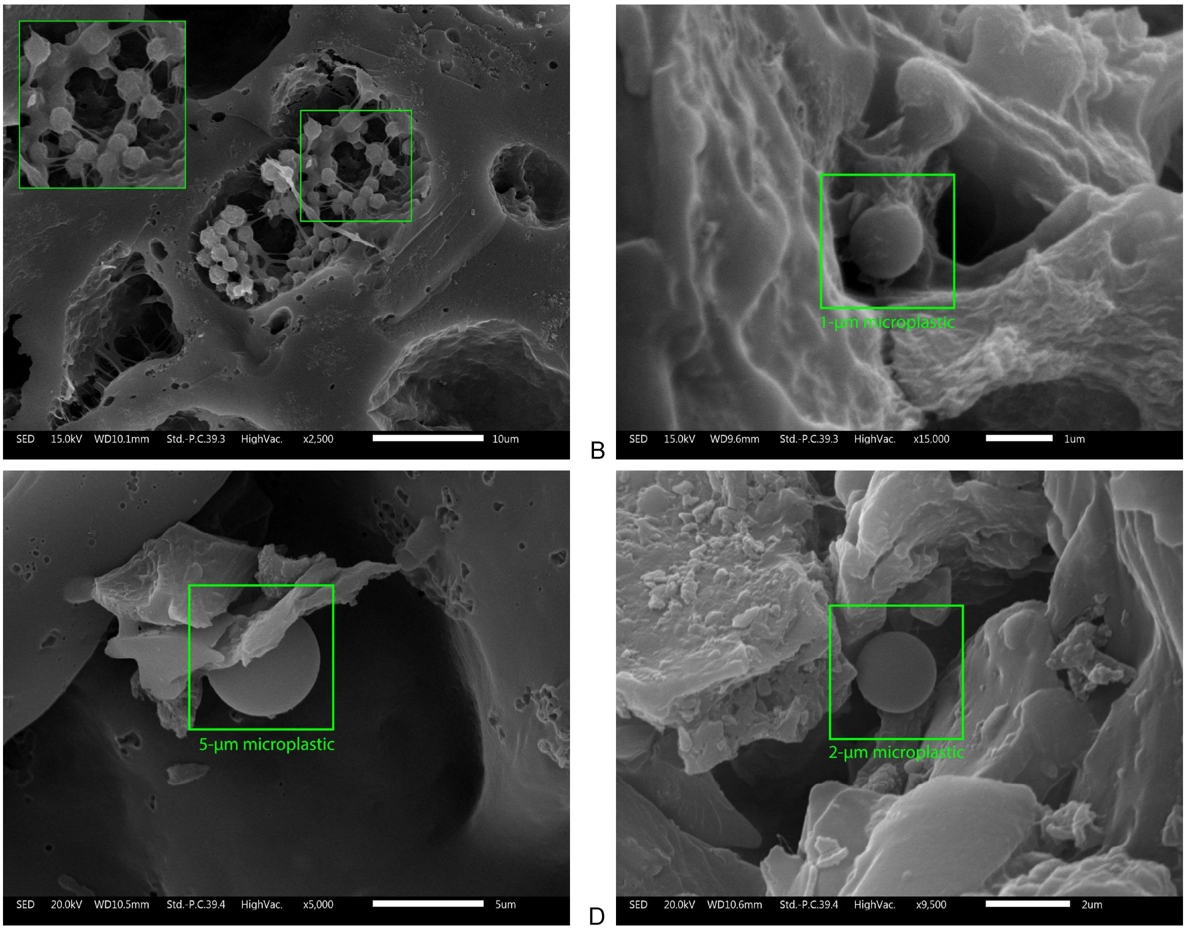

Figure 5. SED images of SCG biochar with microplastics (A) trapped, (B) entangled and (C,D) stuck.

5. Conclusions

The substantial accumulation capacity of MPs per gram of biochar highlights its potential for large-scale application in quaternary treatment of wastewater. Presently, there is limited research on MP concentration in influent and effluent wastewater, especially in the 1–10 μm range, which shows extremely large variation compared to MPs with size from 10 μm to 1 mm [4]. In this study, biochar demonstrated its ability to accumulate at least 8.5 mg MPs/kg biochar, equivalent to 1E+10 1-μm particles. These findings collectively highlight the potential of SCG biochar as a sustainable, cost-effective technology for remediating small microplastics from wastewater.

References

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