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DOI:
10.1016/j.watres.2020.116165

Document Version
Accepted author manuscript

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
Water Research

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Filtration of Microplastic Spheres by Biochar: Removal Efficiency and Immobilisation Mechanisms

Ziheng Wang¹, Majid Sedighi²*, Amanda Lea-Langton³

¹PhD Student, Department of Mechanical, Aerospace and Civil Engineering, School of Engineering, The University of Manchester, Manchester, M13 9PL, United Kingdom.
²Senior Lecturer, Department of Mechanical, Aerospace and Civil Engineering, School of Engineering, The University of Manchester, Manchester, M13 9PL, United Kingdom.
³Lecturer, Department of Mechanical, Aerospace and Civil Engineering, School of Engineering, The University of Manchester, Manchester, M13 9PL, United Kingdom.

*Corresponding author; email:majid.sedighi@manchester.ac.uk

Abstract

Extensive presence of microplastic pollution in the aquatic environment has recently been identified as a critical global challenge. A large proportion of the microplastic in aquatic environments originates from the effluent discharges from wastewater treatment plants and urban runoff. We present an experimental study on the removal of microplastic spheres using biochar as potential low-cost material for integration in sand filter systems to improve their efficiency for removing microbeads in wastewater treatment plants. Based on the results of a series of filtration tests and microscopic characterisation, the major mechanisms of interactions between the microplastic spheres and biochar and immobilisation processes are presented.

The results of leaching column tests on three biochar samples produced at three different temperatures from corn straw and a hardwood biochar are compared. The results show that the biochar filters provide significant capacity for the removal and immobilisation of 10 μm diameter microplastic spheres (above 95%) which is much larger than that of similar grain-sized sand filter studied. The extensive ESEM microscopic examination on the samples retrieved after the leaching tests show that the microplastic spheres were immobilised through three morphologically controlled mechanisms which are conceptualised to be ‘Stuck’, ‘Trapped’ and ‘Entangled’ whilst the microplastic spheres only ‘Stuck’ in sand filter. The
presence of abundant honeycomb structures and thin chips to the high removal and immobilisation capacity of corn straw biochar produced at 500 °C and the hardwood biochar. In this study, we demonstrate that biochar can offer extensive potential for immobilisation of microplastic spheres (microbeads). This capacity can in principle be investigated and utilised to improve the efficiency of sand filters to remove microplastic in wastewater treatment plants.

**Keywords:** microplastic, biochar, morphology, immobilisation, porous media, wastewater.
1. Introduction

The alarming extent of microplastics presence in the aquatic environment has recently attracted global attention to the potential health and environmental issues, as well as the research need for developing sustainable solutions to reduce its emission and release to the aquatic environment. Although the toxicological impacts of microplastic pollution to the living organisms and human health are yet to be explored (Barboza et al., 2018), the World Health Organisation recognises the microplastic pollution in aquatic environment to be an urgent global problem. The potential impact of primary microplastic sourcing from industrial detergents (Qi et al., 2020) is of particular concern with regards to their toxic potential (Jaikumar et al., 2019).

The production and release of microplastic particles in numerous forms and from various anthropogenic activities to the aquatic environment is significant and still growing (Miranda et al., 2019). It is estimated that approximately 80% of the microplastic in ocean originates from land-based sources which are mainly related to the effluent discharges of sewage, wastewater treatment plants and urban runoff (Ritchie and Roser, 2020). Sewage systems are a major pathway of microplastic transportation (Zhang and Chen, 2020); despite the fact that WWTPs have shown to be able to retain the majority of microplastic particles. Although the importance of sewer overflow on microplastic transport has only limited study (Siegfried et al., 2017), it has been found that the sewer overflow can be an important pathway for the transport of microplastic during heavy precipitations (Mak et al., 2020). The overflow from WWTPs sewer and municipal drainage can facilitate the transport of microplastics to the aquatic environment (Ó Briain et al., 2020). Recent studies provide evidence of enhanced microplastic release after rainy days into rivers due to municipal sewer overflow (Cheung et al., 2019, Chen et al., 2020).

Studies on microplastics in the influent and effluent of waste water treatment plants (WWTPs) reveal that the efficiency of primary, secondary and tertiary treatment processes to remove/retain microplastic particles is mostly above 90% (Ziajahromi et al., 2017, Conley et al., 2019, Talvitie et al., 2017a) and majority of microplastic particles in the effluent remains
in the sludge (Ngo et al., 2019). Despite the high efficiency of the treatment systems in WWTP
to remove the majority of microplastic prior to the discharge to aquatic environment, the
quantity microplastic particle released is still of great concern due to the significant volume of
wastewater treated on a daily base (Enfrin et al., 2019, Long et al., 2019). Improving the
effectiveness of microplastic removal is therefore of high importance to minimise the release
of microplastics.

Case studies reported highlight the importance and effectiveness of the tertiary treatment
processes in removing microplastic (Talvitie et al., 2017b). Rapid sand filters (as part of the
last stage of the tertiary treatment) present a high efficiency and potential for removing
microplastic particles at a reasonable scale. In an examination of a number of WWTPs in
Finland, the efficiency of rapid sand filter to remove the microplastic from the effluent of
secondary treatment stage was found to be 97% (Talvitie et al., 2017a). A similar study on
different tertiary treatment systems of WWTPs (coagulation plus either of the final stage
treatments including ozone, membrane disc-filter and rapid sand filtration) in South Korea, has
shown that the removal efficiencies for all treatment systems are larger than 98.9%, although
the rapid sand filter demonstrated the lowest removal efficiency compared to the other two
methods (Hidayaturrahman and Lee, 2019).

In this paper, we present an investigation on filtration characteristics of biochar for removing
sphere-shape microplastic particles. The aim of this research was to develop a fundamental
understanding required for assessing the capacity and potential of biochar for integration within
the conventional sand filter technology. Microbeads (spherical shape microplastic particles)
mostly originate from personal care and cosmetics products at sizes varying (in diameter) from
<63 µm to 2000 µm in the influent and effluent of WWTPs (Estabbanati and Fahrenfeld, 2016).
Hidayaturrahman and Lee (2019) have shown that the microbeads comprise the highest
percentage of the composition of microplastic particles (with regards to the shape) present in
the effluents from the different tertiary treatments system. Due to the smooth surface of
microbeads, lower adsorption capacity of microbeads in sand filter is expected compared with
that of irregular shape particles of microplastic (e.g. fibres, fragments, films and sheets) (Ding et al., 2020).

Rapid sand filters are a feasible treatment technology with favourable characteristics including minimum maintenance and energy usage (Mutemi et al., 2020) in comparison with alternative solutions such as membrane-based filtration, which consumes a significant amount of energy (half of the total energy consumption in water treatment process) (Wang et al., 2020).

Rapid sand filters integrated with activated carbon have been shown to offer an enhanced adsorption capacity; improving the competitiveness of sand filter in comparison with other methods (e.g. membranes), which offer a higher removal efficiency of various contaminants (Kalmykova et al., 2014). Biochar is a carbonaceous material and widely utilised in agriculture to improve the soil properties with significant economic added value (Oni et al., 2020). It has been shown that replacing activated carbon can fully or partially by biochar (Kah et al., 2017) significantly reduce the process cost (including regeneration cost) while maintaining a similar level of removal efficiency in WWTPs. Due to the high adsorption capacity of biochar, the low cost of the pyrolysis process to manufacture biochar and the extensive potential for the local production (using locally available feedstock), the application of biochar in water/wastewater treatment systems has received an increasing attention (Inyang and Dickenson, 2015).

Despite the fact that a wealth of knowledge on adsorption of various chemicals on biochar has been developed (Dai et al., 2019), research on potential use of biochar in removing microplastic is only at the very early stages of development. The microstructure of biochar contains pores at varying scales ranging from 50 μm to less than 1 nm. The complex and multiscale structure provides an ideal porous structure for the removal of turbidity from water (Marcus et al., 2014). In this paper we look at whether such capacity can be utilised for the removal of microplastics. We present a fundamental investigation into mechanisms of interactions between biochar and microplastic spheres.

With regards to the size, microplastic is categorised as particles down to 0.1μm (Sobhani et al., 2020) (smaller sizes are categorised as nanoplastics). Studies on microplastic in WWTPs are
mostly refer to the particles larger than 10 μm (Rajala et al., 2020). It is recognised that smaller size microplastic is more likely to break through the WWTPs (Mintenig et al., 2017). The transport of plastic particles ranging between 0.02 μm and 2 μm in sand and biochar has recently been reported (Tong et al., 2020). This range of microplastic sizes (0.02 μm-2 μm) is close to colloid sizes (0.001 μm-1 μm) (Jonasz and Fournier, 2007) for which the magnitude and polarity of surface charge can play critical role in governing the interactions between the particles and surfaces whilst the pore system effects become less prominent and visible (Bhattacharjee, 2016). However, understanding of potential retardation and immobilisation of microplastic particles by biochar through its complex microstructure and pore system is largely unknown. We present an experimental investigation that aims to develop a fundamental understanding of the underlying mechanisms of immobilisation of microplastic spheres in biochar for potential applications as a low cost, low maintenance porous filter for microplastic. The inclusion of biochar in rapid sand filter has the potential to increase the removal efficiency of the tertiary treatment system. This is important for upgrading existing WWTPs to minimise the discharge of microplastic as alternative methods (e.g. membrane) can be expensive, energy demanding and difficult to be implemented; especially in Global South.

Microplastic spheres with 10 μm diameter were selected to study in this research to develop an understanding of the effects of morphology of pore system and the extent the porous system can play to immobilise the microplastic spheres. This size was of microplastic particles (10 μm) was chosen to eliminate the potential impact of surface charges on removal to be able to focus on morphology and pore system effects. Filtration characteristics of uniform microplastic spheres in four different types of biochars (three biochars from pyrolysis of corn straw and 1 biochar from hardwood feedstock) are presented. Hemocytometer analysis (also known as ‘counting chamber’ in medical science) was adopted in this research to measure the concentrations of microplastics and determine the removal efficiency. We present the results of an extensive microscopic characterisations based on Environmental Scanning Electron Microscope (ESEM) which allows the filters to be imaged without pre-treatment.
2. Materials and methods

A leaching column system was designed and developed to measure the removal efficiency of microplastic sphere by biochar and sand filters. The immobilisation mechanisms were analysed from the perspective of morphology through microscopic examination.

2.1 Biochar and silica sand

Two types of biochar have been selected and used in this study which are corn straw biochar and hardwood biochar. The corn straw biochar was acquired from the Nanjing Zhironglian Technology Company (based in China). The biochar samples were manufactured through slow-pyrolysis process of biomass at three different temperatures. The biochar samples from the corn straw used are manufactured at 300°C, 400°C and 500°C (labelled as C300, C400 and C500 in this work which represent the pyrolysis temperature 300°C, 400°C and 500°C, respectively). The hardwood biochar was purchased from the Oxford Charcoal Company (based in the UK). The biochar had been produced through a traditional open fire stove method as a by-product of charcoal rather than a fixed temperature method. The silica sand used in this study was acquired from Garside Sands from the resourced based at Leighton Buzzard in Bedfordshire (UK).

The particle size distribution tests were carried out based on BS-1377-2 (RDB, 1990). The biochar samples were mildly ground and mixed into the same particle size distribution to obtain $d_{50}$ around 0.6-0.7 mm which is similar to that of sand. Figure 1 presents the particle size distribution of sand and biochar samples.

The density was measured by small pycnometer method according to BS-1377-2 (RDB, 1990). The specific surface area of the samples was measured using Ethylene Glycol Monobutyl Ether (EGME) method to obtain the total specific surface area (SSA). This method has been reported to be successfully used for measuring the SSA in biochar in other studies (Günal et al., 2018, Laird et al., 2010, Arthur et al., 2015).
Figure 1. Particle size distribution of biochar samples and sand used in this study.

A summary of physical and chemical properties of the biochars used in this study is presented in Table 1.

Table 1. Physical properties of biochar samples

<table>
<thead>
<tr>
<th>Biochar</th>
<th>SSA by EGME m²/g</th>
<th>Particle Density Mg/m³</th>
<th>Bulk density Mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>C300</td>
<td>808.3±81.9</td>
<td>1.318</td>
<td>0.059</td>
</tr>
<tr>
<td>C400</td>
<td>609.0±83.5</td>
<td>1.226</td>
<td>0.083</td>
</tr>
<tr>
<td>C500</td>
<td>177.5±16.3</td>
<td>1.208</td>
<td>0.121</td>
</tr>
<tr>
<td>Hardwood</td>
<td>292.8±69.3</td>
<td>1.312</td>
<td>0.413</td>
</tr>
</tbody>
</table>

2.2 Microscopic characterisation

The Scanning Electron Microscope (SEM) examination were carried out by FEI Quanta 650 FEGSEM. The elemental data was generated by Oxford Instrument Energy Dispersive X-ray detector (EDX) and analysed by AZtec®. The X-ray powder diffractometer (XRD) measurement was carried by the PANalytical's X'Pert Pro, Malvern Instruments, and the crystalline phases were identified by Highscore®. The crystalline phase candidates were selected based on previously reported phases in biochar (Singh et al., 2017). The surface
roughness was measured by Keyence X200K 3D Laser Microscope. The Zeta potential was measured by Zetasizer Nano ZS, Malvern Instruments. All microscopic characterisation tests have been carried out by the facilities at the University of Manchester.

The main content of the four biochar species was found to be amorphous carbon from the XRD results (Table 2) (Singh et al., 2017) and high elemental content of carbon (Table 2). As shown in the elemental map (from Figure S1 to Figure S4 in Appendix A), the structure of biochars used consist of carbon and oxygen, while silicon was also detected at minor scale, due to the presence of soil particle in the corn straw and wood (Table 3). The full results of characterisation by EDX and XRD are presented in the supplementary information.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C300</th>
<th>C400</th>
<th>C500</th>
<th>Hardwood</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>70.0</td>
<td>81.3</td>
<td>68.7</td>
<td>84.7</td>
<td>6.01</td>
</tr>
<tr>
<td>O</td>
<td>18.7</td>
<td>11.7</td>
<td>19.1</td>
<td>14.1</td>
<td>46.69</td>
</tr>
<tr>
<td>N</td>
<td>3.1</td>
<td>3.7</td>
<td>2.2</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>2.6</td>
<td>0.3</td>
<td>1.8</td>
<td>0.2</td>
<td>0.08</td>
</tr>
<tr>
<td>Ca</td>
<td>2.4</td>
<td>0.8</td>
<td>2.0</td>
<td>0.5</td>
<td>0.09</td>
</tr>
<tr>
<td>Mg</td>
<td>1.3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>1.2</td>
<td>0.2</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>0.2</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>0.2</td>
<td>1.1</td>
<td>3.4</td>
<td>-</td>
<td>31.41</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>3.13</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

| Crystalline phases of the biochar and sand materials used. |
|-------------|-------------|-------------|-------------|-------------|-------------|
| C300        | SiO2, Na(AlSi3O8), KCl |
| C400        | SiO2, Na(AlSi3O8), KCl |
| C500        | SiO2, Na(AlSi3O8), KCl |
| Hardwood    | SiO2, Ca(C2O4)(H2O), K2SO4, CaCl2, Na2Mg(SO4)2(H2O)4, Na2CO3, KNO3, CaCO3 |
| Silica sand*| SiO2, Al2O2, Fe2O3, CaO, K2O, Na2O, MgO, P2O5, Cr2O3 |

* Information provided by the supplier.
The ESEM results for different biochar samples used in this study are presented in Figure 2 which shows the morphology of pore system. The microstructures of biochar can be categorised as ‘rind’, ‘chip’, ‘loofah’ and ‘honeycomb’ for the samples studied. Biochar possess a complex heterogeneous porous system at microscopic length scale.

The main reasons for the difference in morphology are the difference in the biomass feedstock and the pyrolysis temperature. The organic matter of the wood cells is normally removed by the gasification process (Hagemann et al., 2018) and the hard cytoderm remained, forming a honeycomb structure as shown in Figure 2g. However, the corn straw do not have secondary growth by the production of concentric annual rings so the majority of areas at the cross section was occupied by pith (Fosket, 1994) which cannot survive the pyrolysis process. Therefore, the corn straw biochar exhibited layered shape consisting of epidermis cytoderm and vascular bundle.

With regards to the effects of pyrolysis temperature, from 300°C to 400°C (Figure 2a-c), the microstructure surface and the thickness of layers become smoother and the layers become thinner. It is observed that from 400°C to 500°C (Figure 2c-e), the relatively weaker components were removed which resulted in high pore system. As shown in Table 1, the specific surface area (SSA) decreases with the increase of pyrolysis temperature. This phenomenon can be explained by the results of surface roughness in Table 4 where the Developed Interfacial Area Ratio ($S_{dr}$) values have the same trend as the SSA.

Table 4. Surface roughness of biochar and sand.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>$S_a$</th>
<th>$S_z$</th>
<th>$S_{pc}$</th>
<th>$S_{dr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg</td>
<td>SD</td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>C300</td>
<td>12.0</td>
<td>3.2</td>
<td>159.3</td>
<td>45.6</td>
</tr>
<tr>
<td>C400</td>
<td>7.4</td>
<td>2.3</td>
<td>106.3</td>
<td>22.3</td>
</tr>
<tr>
<td>C500</td>
<td>4.1</td>
<td>2.5</td>
<td>59.7</td>
<td>35.4</td>
</tr>
<tr>
<td>Hardwood</td>
<td>4.1</td>
<td>2.2</td>
<td>48.9</td>
<td>21.3</td>
</tr>
<tr>
<td>Sand</td>
<td>2.8</td>
<td>1.3</td>
<td>31.2</td>
<td>15.5</td>
</tr>
</tbody>
</table>

* Arithmetical Mean Height (µm); † Maximum Height (µm); ‡ Arithmetic Mean Peak Curvature (1/mm); Developed Interfacial Area Ratio; ** Average (n=12); †† Standard deviation.
Figure 2. Microstructure and morphology of the pore system of biochar samples: ‘Rind’ in C300 (a, b), ‘Chip’ in C400 (c, d), ‘Loofah’ in C500 (e, f) and ‘Honeycomb’ in Hardwood.
2.3 Microplastic solution/suspension

In this study 10 \( \mu m \) polystyrene microsphere (from Thermo Scientific™) was selected and used. The concentration of microplastics in sewage varies site to site and from less than 1 to several 10,000s of particles per litre (Sun et al., 2019). For example, the presence of a wide range of both light and heavy density microplastic particles in sewage sludge (approximately from 2000 to 51,000 particles per kg of sewage) has been reported in an investigation in Spain (van den Berg et al., 2020). In the study reported by van den Berg et al. (2020), the smallest particles accounted were found to be larger than 50 \( \mu m \); noting the fact that the smaller particles present at higher concentrations (Marcus et al., 2014). We have focused on microbeads as they represent the highest possibilities of escape from sand filters due to absence of surface interactions (Ding et al., 2020). We have selected a high concentration of a uniform microspheres suspension at 1.6\( \times \)10\(^8\) (±0.2) particles per litre of solvent to be able to readily detect how the system retain the particles. It is recognised that this concentration does not necessarily represent a specific field concentration. The solvent used is distilled water and the pH of the solution used is 7.56. The concentration of the suspension was measured by Neubauer improved counting chamber (haemocytometer) (Randolph, 1944, Wen et al., 2021). The concentration of particles in each sample was measured 6 times and the average values are reported. The microplastic spheres have similar sizes with the cells (the object that counting chamber is designed for). The microplastic spheres were distinguishable from biochar particles due to their distinctive regular and shapes.

2.4 Leaching column tests

To investigate the removal efficiency of microplastic spheres by different biochar filters, a series of leaching column experiments were carried out. The breakthrough curves of each biochar filter were first measured. The experiments were followed by flushing the system by distilled water to assess the stability of microplastic particles trapped or adsorbed in the system. The filter was initially dry and flushed with the solution after the emplacement in the system. The biochar samples with 70 mm length where packed in 100 mm length and 30 mm diameter
cylindrical columns. The sample was sandwiched between two layers of silica sand each at 15
mm length as shown in Figure 3. The packing process was carefully conducted to ensure
minimum mixing between sand and biochar can happen during the process.

The inflow solution was injected from the bottom of the cell by a peristaltic pump at constant
flow rate 180 ml/h. A manometer was placed between the inlet of column and the outlet of
pump to monitor the water pressure/head. The hydraulic conductivity of filter system was then
calculated using the pressure gradient and flow rate in equation (1). For the case of sand filter,
the 70 mm biochar filter bed was replaced by silica sand (the same sand used as supporting
material in biochar filter). The operation conditions are summarised in

Table 5.

\[ Q = k i A \]  

(1)

where, \( Q \) is the flow rate (L\(^3\)/T), \( k \) is the hydraulic conductivity (L/T), \( i \) is the hydraulic
gradient (L/L) and \( A \) is the cross-section area.

The ingress of microplastic suspension consisted of 3 pore volume injections. This was then
followed by flooding the system by distilled water for up to 10 pore volume. The tests were
carried out at ambient temperature (25 ± 1 °C).

At the end of the leaching tests, the biochar/sand filters were removed from the column and
samples were taken for the SEM imaging under the ESEM mode of imaging. The samples were
collected from near the inlet and transferred to the ESEM holder without any treatment prior
to imaging. Inside the chamber, the stage temperature was set at 5 °C and chamber pressure
was 5.0-6.2 Torr (0.67-0.83kPa). All images were taken at 6.2 Torr. The pore water in the
biochar and sand was gently removed by vapouring at 5.0 Torr until the microplastic particles
and filter surface showed up.
Figure 3. Schematic of the leaching column setup designed and used in this study.

Table 5. Operating conditions of the leaching column tests.

<table>
<thead>
<tr>
<th>Filter system</th>
<th>Weight (g)</th>
<th>Height (cm)</th>
<th>Diameter (cm)</th>
<th>Pore volume (ml)</th>
<th>Flow rate (ml/h)</th>
<th>Initial concentration (N/l)</th>
<th>Hydraulic conductivity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C300</td>
<td>2.9</td>
<td></td>
<td></td>
<td>47.28</td>
<td></td>
<td></td>
<td>5.41×10⁻⁵</td>
</tr>
<tr>
<td>C400</td>
<td>4.1</td>
<td>7.0</td>
<td>3.0</td>
<td>46.14</td>
<td></td>
<td></td>
<td>7.13×10⁻⁵</td>
</tr>
<tr>
<td>C500</td>
<td>6.0</td>
<td></td>
<td></td>
<td>44.49</td>
<td>180.0</td>
<td>1.6 (±0.2)×10⁸</td>
<td>7.84×10⁻⁵</td>
</tr>
<tr>
<td>Hardwood</td>
<td>21.0</td>
<td></td>
<td></td>
<td>34.89</td>
<td></td>
<td></td>
<td>3.72×10⁻³</td>
</tr>
<tr>
<td>Silica sand</td>
<td>110.0</td>
<td>10.0</td>
<td></td>
<td>31.40</td>
<td></td>
<td></td>
<td>1.34×10⁻³</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1 Column tests: Microplastic spheres retentions and stability

Figure 4a-b show the concentration of microplastic measured in the effluent for biochar and sand. The average of 6 measurements is reported (n = 6). The results show that apart from the silica sand filter, the concentration of microplastic has significantly dropped after filtering with the biochar. Biochar C500 demonstrates the highest removal capacity where almost no microplastic was detected during the tests whereas C300 provides the lowest removal capacity.
among the 4 types of biochars tested in this research. Data are presented in a semi-log coordinate in Figure 4b to demonstrate that less than 1% of initial concentration of microplastic was found in both C400 and Hardwood filters' effluent which is below the detection limit of the experimental method adopted.

The removal efficiencies of the 5 filters tested are shown in Figure 4c. In the first 3 pore volumes where $1.6 \times 10^8$ particles/l microplastic suspension was injected, the removal efficiency was calculated by dividing concentration difference (retained by filter) by initial concentration. For the following pore volumes that distilled water was supplied, the release rate was calculated by dividing the residual concentration in effluent by $1.6 \times 10^8$ particles/l to demonstrate leakage potential in the same figure.

Figure 4. Concentrations of microplastic particles measured in the effluent.
Both C400 and C500 showed no leakage from 3 to 10 pore volumes. However, 6.85%, 0.23% and 0.1% of total retained microplastic in first 3 pore volumes escaped during 3-10 pore volumes for Silica sand, Hardwood and C300 respectively. The results are compatible with those by Tong et al. (2020) where sand filter released more micro- and nano-plastic particles than the biochar filter. The effluent concentration decreased with the pore volume and eventually decreased at a level which was under the detection limit at 10\textsuperscript{th} pore volume. This indicates that the leakage rate of decreased and particles inside the filters remained in place. Biochar filters showed better removal efficiencies than that of sand filters and C500 filter was the best showed 100% removal and 0% releasing.

![Figure 5. The removal efficiency of microplastic spheres at different pore volumes.](image)

As shown in Figure 6, all samples were found to be alkaline. Sand, biochar and microplastic have negative Zeta potential value (Table S1, Appendix B) which is as the result of the negative surface charges. Therefore, the hydrogen ions in the distilled water are adsorbed on the surface of particles, so that the concentration of hydroxide ions is higher than that of hydrogen ions, and the solution becomes alkaline. The effluents from biochar filters were found to be more alkaline than those of sand filter because small biochar particles eroded from filter.
In order to obtain a better understanding of the immobilisation process in the filters studied, the results from the sand filter and the biochar filters are further analysed with the Herzig-Leclerc-LeGoff model (HLL) which is a class filter model for collide transport (Logan, 2001). This model describes the transported of particles which are sieved by the solid porous fabric and as the result porosity can decrease and possible clogging of the porous medium may occur (deep bed model assumptions) (Logan, 2001). A simplified form of this model is used which assumes a steady state flow (the case applicable to the leaching experiments here); and an equilibrium state of filtration where capacity of filter is not reached (nor the flow is clogged). In addition, it is assumed that the dispersion of particles plays a negligible effect of the overall transport process (i.e. advection is the dominant transport mechanism). Accordingly; the variation of particle concentrations can be describe by the analytical solution to the HLL model (Logan, 2001):

$$C(x, t) = C_0e^{-\lambda x}$$  \hspace{1cm} (2)
where \( C(x, t) \) is the concentration (particles/L); \( x \) is the distance from inlet boundary (cm), \( t \) is time (min), \( C_0 \) is the inlet concentration which is \( 1.6 \times 10^8 \) (particles/L) for the experiments in this study. \( \lambda \) represents the filter coefficient (cm\(^{-1}\)).

The concentration of immobilised particles; \( \sigma(x, t) \), per unit volume of the filter medium (particles/L) can be described by (Logan, 2001):

\[
\sigma(x, t) = \lambda v C_0 e^{-\lambda x \left( t - \frac{x \theta}{v} \right)}
\]

where \( v \) is the discharge flow rate (cm/min) which is calculated by Darcy’s law and is constant for the case of leaching experiments. \( \theta \) is porosity and for the cases of experiments presented in this work; total volume of immobilised microplastic particles is less than 0.025% of total pore volume. Therefore, the change of porosity is negligible.

Figure 7 presents the variations of microplastic concentration in the domain calculated using Eq. 2 for the case sand filter and C300 biochar filter. The average concentration of the outlets from experimental results were used to obtain the value of filter coefficient (\( \lambda \)). The values of filter coefficient (\( \lambda \)) for C300 and sand filter are 0.59 cm\(^{-1}\) and 0.13 cm\(^{-1}\), respectively. A range of values for \( \lambda \) removal of PVC particles (1.3 \( \mu \)m) in sand filters is 0.06-0.14 cm\(^{-1}\) (Herzig et al., 1970). It is noted that our experimental data indicate that removal efficiencies of Hardwood, C400 and C500 biochar approaches 100%. Therefore, the filtration curve (green dashed lines in Figure 7) plunged below the detection limit in the middle of the filter. Although, C300 represents the lowest removal efficiency among all biochars, the filter coefficient for C300 is 4.5 times larger than that of sand filter.

Figure 8 presents the variations of immobilised particles for the sand and C300 biochar filter for different pore volumes calculated based on Eq. 3. The porosity of sand and biochar used in the calculation are given in Table 5. At a given distance from the inlet boundary (2 cm; arbitrary chosen), the variations of the concentration of immobilised particles varies linearly with time; providing a constant rate
of $3.68 \times 10^8$ particle/L per min for the C300 biochar and $1.56 \times 10^8$ particle/L per min for sand filter. The removal rate of biochar filter for microplastics is 2.36 times that of sand filter with similar size, and if converted to unit mass of filter, it is more than 10 times.

![Filtration curve of sand](image)

Figure 7. Variations of concentration of microplastic inside the filters calculated by the HLL model and calibrated based on the outflow concentrations.

A large difference between the values of filter coefficient for C300 biochar and sand was obtained which indicate that for obtaining an equal removal efficiency of 7cm C300 biochar filter, the length of sand filter should be extended from 7 cm to 34 cm. It is noted that the particle sizes distributions for the sand and biochars used in this study are very similar. It is therefore anticipated that certain macroscopic porous characteristics of the materials are similar (e.g. porosity, tortuosity). Both sand and biochar are negatively charged; hence the polarity of the filter medium is similar. The structure difference is reflected in surface roughness, as stated in Table 4, and SEM/ESEM images (Figure 2). It is therefore concluded that the main reason for the considerably higher retentions is the existence of additional retardation mechanisms than surface interactions; governed by microscopic and pore structure. We provide in the next
section, a series of microscopic examination which provide insight into the governing mechanisms of retardation of microplastic in the pore system.

![Graph](image)

Figure 8 Theoretical variations of $\sigma$ in the domain at different pore volumes.

### 3.2 Microscopic examination of microplastic spheres in biochar and sand

The Biochar and sand filter samples were analysed by the use of ESEM after the leaching column experiments were completed. The aim was to develop an understanding of retention mechanisms of microplastics in biochar and sand. In general, the surface morphology of biochar is more complex and fluctuant than that of sand. This can be observed from Figure 9 to Figure 13 as shown by the $S_a$ and $S_z$ values in Table 4. For the case of sand filter, microplastic particles were mainly found adhered onto clean surfaces (Figure 13), whereas in biochar filters, the microplastic particles were entangled by small biochar chips and grains as shown in Figure 9b-c and Figure 12c. From the images obtained, the microplastic particles in the sand filter were likely to be more mobile than those in the biochar filter due to the clean surface of sand.
Figure 9. ESEM images of C300 biochar filter; the area under higher beam energy is shown in green box (larger visible depth); blue arrow shows the spotted microplastic particles.
By adjusting the beam energy at the ESEM process, the microplastic particles which are not immediately visible and locate underneath the biochar particles were identified. Examples are presented in Figure 9 and Figure 10d which reflect the behaviour on the hollow structure fabric of biochar. In addition, some microplastic particles were found in the pores which are slightly larger than that of microplastic particles, as shown in Figure 11a-b and Figure 12c-d.
Figure 11. ESEM images of C500 biochar filter (red square – local zoom in; blue arrow – spotted microplastic particles.)
Figure 12. ESEM images of Hardwood biochar filter; red square – local zoom in; green square – area under higher beam energy (larger visible depth); blue arrow – spotted microplastic particles.
Figure 13. Sand surface before the leaching test (a, c) and after the test with microplastic particles attached to the surfaces (b, d).

### 3.3 Immobilisation mechanisms of microplastic particles in biochar

Previous studies have shown that microplastic particles (with 1μm diameter) can be trapped in pine chip biochar by the large internal space of biochar (Abit et al. (2014). In this study, the microplastic particles used are larger in size (10 μm) than previous studies (Abit et al., 2014, Tong et al., 2020). The reason was to eliminate the effects associated with surface interaction with colloid size such as ionic strength, Zeta potential, van der Waals forces to be able to observe the pore system effects. As described earlier, the surface effects have small effects for interaction between the 10-μm microplastic particles and porous system of biochar. As shown in Figure 14, three categories of particles retained in the system by different mechanisms/modes of microplastic immobilisation were observed from ESEM images which
are classified and introduced as ‘Stuck’, ‘Trapped’ and ‘Entangled’. It can be observed that the microplastic particles were only Stuck in the sand filter while all three modes of interactions were found to exist in relation to microplastic spheres retained in biochar samples.

The first type of particles retained in the porous system is Stuck in the pore system which describe a mechanism by which the microplastic particles are retained in the gaps between the filter particles which are smaller than the particle size. In other words, the porous system acts as a sieve. This explains why smaller microplastic dominated in effluent of water treatment plants while large particles were stuck (Talvitie et al., 2017a). Therefore, the removal efficiency of sand filter for microplastic particles depends on the size of sand particles and the size of plastic particles.

The particles can also be ‘trapped’ in the pore system which is by a mechanism that only exists in the filter with porous structure such as the activated carbon and biochar. Plastic particles may enter the pores with slightly larger size and lose their mobility when the water flow happens at slow rate in the pores smaller than 30 μm (Downie, 2011). This phenomenon is observed mostly in Hardwood biochar and C500 biochar because of the ‘honeycomb’ and ‘loofah’ structures.

The entrapped particles exist at much larger number in biochar system than sand (Abit et al., 2014). Although there are microscopic holes on sand surface in Figure 13b), there is rarely a hole adequately deep to provide restriction for microplastic spheres against water flow. This mechanism could also explain the reason why C300 filter showed relatively low removal efficiency. C300 is the closest biochar to the original corn straw in terms of microstructure and the honeycomb structure is not the primary structure for the cases of C300.

Biochar contains many flaky shaped particles which can relatively easily detach themselves from the main particles or those may exist originally among the particles. Such flaky shapes particles exist especially in C300 and C400 as shown in Figure 2a-d. Although relatively large biochar particles and plastic particles do not exhibit the properties of colloidal particles, flaky particles do. It was observed that microplastic particles were likely entangled by small particles.
or chips as shown in Figure 9b-c and Figure 12b. Since both biochar and polystyrene particles’
surfaces are negatively charged (El-Gholabzouri et al., 2006, Hong et al., 2019, Yang et al.,
2017), the force between the two would be Van der Waals force. Entangled microplastic
particles would be immobilised due to increase of size, or microplastic particles would be
wrapped and attached on filter bed. Furthermore, based on interaction volume theory (Kanaya,
1972, Goldstein, 2018), the thickness of entangled flaky biochar can be estimated by changing
the beam energy of SEM as shown in Figure 15.

The visible depth under SE detector is similar with that of BSE detector because secondary
electron class 2 (SE2) and secondary electron class 3 (SE3), which are generated by BSE,
account for the majority of total SE (Peters, 1982). Furthermore, depth where 90% of BSE
occurs which is 0.285 Kanaya-Okayama range ($R_{K-O}$) (Goldstein, 2018) can be taken as visible
depth. $R_{K-O}$ can be calculated by:

$$R_{K-O} = 27.6\left(\frac{A}{Z^{0.89} \rho}\right)E_0^{1.67}$$  \hspace{1cm} (2)

where, $A$ is the atomic weight (g/mol), $Z$ stand for the atomic number, $\rho$ is the density
(g/cm$^3$) and $E_0$ is the incident beam energy (keV).

Therefore, the thickness of biochar chips attached on microplastic particles can be estimated
by adjusting beam energy until the chips become transparent.

The results showed that the thickness mostly ranged from 2 μm to 0.5 μm or even thinner. From
the results of the leaching column tests and in terms of immobilisation of microplastic, the
retardation efficiencies of biochars can be summarised and ranked as: C500>C400>Hardwood>C300>Silica sand. From analysing the immobilisation mechanisms,
C300 has less ‘honeycomb’ structure while the biochar chips are relatively thick (>2 μm)
indicating less effect by the van der Waals forces which have resulted in less immobilisation
by the ‘Trapped’ and ‘Entangled’ mechanisms, respectively. As for Hardwood, it has the most
abundant ‘honeycomb’ structure. However, thin chips were rarely found. C500 could be the
best balance so all three immobilisation mechanisms were realised during the column transport tests resulted in the best performance.

Figure 14. Three mechanisms for microplastic immobilisation – ‘Stuck’ (a); ‘Trapped’ (b); ‘Entangled’ (c), corresponding ESEM images – sand filter (d, g); biochar filter (e, f, g) and optical microscope image (i).
Figure 15. Illustration of the interaction volume theory utilised for detecting microplastic and calculating biochar chip thickness (a); same area under SEM at beam energy of 10 KeV (b) and 20 KeV (c).

Sphere-shaped microplastic particles are only one type of microplastic; but represent a category of sizes which are likely to be more easily escape from tertiary treatment (including from rapid sand filter). While it is recognised that the shape and surface properties of microplastic in aquatic environment (e.g. rivers or industrial effluents) may differ from the microplastic spheres used in this study, the study presented provides critical knowledge on potential use of biochar as a microplastic filter and mechanisms of interactions. It is, however, recognised that
further research on real-world microplastic systems effluents of primary and secondary WWTS would be required to provide further confidence on the efficiency of technology.

Absence of wide spread use of high standard and advanced WWTPs (due to the cost) in global South has been reported which provide the base for integration of low cost/low maintenance technologies. (Nansubuga et al., 2016). In this paper, we demonstrated that biochar is a promising porous material for the removal of microbeads, and we envisage that the potential integration in rapid sand filters can provide techno-economically feasible solution to enhance the capacity of WWTPs; especially as a solution for the global south.

Biochar manufacturing is a mature and well-known process. Biochar is affordable and widely used in agriculture activities. The price of biochar in comparison with activated carbon is very low. For example, in this study, the corn straw biochar is produced at a rate of 350 kg/h in each production line (based on communications with the supplier based in Nanjing, China). The price of the high-quality corn biochar used in this study is 564 USD per ton while the price of activated carbon (in the same geographical location) is 2524 USD per ton. The straw feedstock is in principle an agriculture waste with no added value for the farmers and reduce the carbon emission associated with burning the straw waste (Chalco Vera et al., 2017). Utilisation of agriculture waste in the form of biochar and for various applications (including in wastewater treatment) can create local economic values.

The costly process of regeneration of activated carbon in integrated sand filters can considerably add to the overall maintenance cost of the system. With regards to regeneration, the traditional biochar regeneration methods would be applicable for the case of applications in microplastic treatment (i.e. adsorbate decomposition and adsorbate desorption). The decomposition through thermal regeneration has been recommended and widely used in industry which represents a cost-effective process (Román et al., 2013). Alternative potential approach for regeneration is desorption such as dispersing and collecting by magnet (Tong et al., 2020). It is noted that the gross cost of feedstock can be close to shipping cost where the feedstock is agricultural wastes and regeneration may not represent the most feasible options.
The results of the research presented outline the potential use of biochar in microplastic removal. It is recognised that further research on various aspects of such application is required to demonstrate the technical and economic feasibility.

4. Conclusions

We presented the first experimental study on filtration characteristics and performance of biochar for immobilisation of uniformly graded microplastic spheres based on a series of leaching tests and microscopic examination of four types of biochars and sand. The main conclusions drawn from this work are as follows:

- For all biochars analysed, the removal efficiency of the filter to microplastic spheres is higher than 95% and substantially larger than that of sand (60-80%). Only less than 0.5% of the retained microplastic particles in biochars were found to be released when the samples were flushed back with distilled water. The retention behaviour was found to be significantly higher than that measured for sand (6.85%). The filter coefficient for biochar is at least 4.5 times larger than that of sand by application of Herzig-Leclerc-LeGoff model (HLL) model under steady state flow.

- Using a detailed ESEM microscopic examination, microplastic particles were found to be retained on the surfaces, pores and underneath of the biochar chips for all biochar filters which are associated with three mechanisms of ‘Stuck’, ‘Trapped’ and ‘Entangled’ are identified, controlling the fate of microplastic spheres in biochar. The ‘Trapped’ and ‘Entangled’ immobilisation mechanisms provide the biochar a high removal efficiency than that of similar-sized sand filter.

- This study highlights a strong capacity and potential for biochar to be used for improving the performance of rapid sand filter to remove microplastic and in particular microbeads in tertiary treatment systems of WWTPs. Such capacity can in principal offer low cost/low maintenance
solutions to improve the efficiency of tertiary systems and minimize the release of microplastic from outflow of WWTPs.

Contributors

Z Wang (ZW) extended the concept, co-designed the programme of study and conducted the experiments, analysed data and co-drafted the manuscript. M Sedighi (MS) proposed the original idea and developed the concept, supervised the research work presented and ZW, co-designed the experimental programme and co-analysed the results, co-drafted the original manuscript with ZW. A Lea-Langton (ALL) co-supervised ZW, reviewed the manuscript, contributed in the discussions of the results and co-edited the manuscript.

Acknowledgement

The authors gratefully acknowledge the financial support provided for the project Lotus by the University of Manchester’s Research England GCRF QR Allocation. M Sedighi acknowledges the financial support by The British Academy/Newton Fund through the project Socio-technical solutions to water security challenges in urban areas and post-disaster scenarios. Z Wang acknowledges the financial support by the Department of Mechanical, Aerospace and Civil Engineering at the University of Manchester in the form of a PhD Scholarship. The authors thank the technical support from the Electron Microscopy Centre of The University of Manchester through the training provided to Z Wang by Dr P Hill and Dr M Nikiel for the ESEM imaging and analysis reported here. The authors also thank the staff in the Department of Materials at the University of Manchester for the access provided to the XRD Facility and their assistance.
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Appendix A. SEM-EDX analysis

Figure S1 Electron image (left) and Elemental map (right) of C300

Figure S2 Electron image (left) and elemental map (right) of C400
Figure S3 Electron image (left) and elemental map (right) of C500

Figure S4 Electron image (left) and elemental map (right) of Hardwood
### Appendix B. Electrical properties of surfaces

Table S1 Zeta potentials, electrical mobility and conductivity of biochar and microplastic sphere suspension.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Zeta Potential (mV)</th>
<th>Electrical mobility (m²/Vs×10⁻⁸)</th>
<th>Conductivity (mS/cm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Avg</td>
<td>SD</td>
<td>Avg</td>
<td>SD</td>
</tr>
<tr>
<td>C300</td>
<td></td>
<td>-36.97</td>
<td>0.62</td>
<td>-2.90</td>
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<tr>
<td>C400</td>
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<td>-3.19</td>
<td>0.049</td>
</tr>
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<td>-2.78</td>
<td>0.033</td>
</tr>
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<tr>
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<td>1.82</td>
<td>-4.29</td>
<td>0.14</td>
</tr>
</tbody>
</table>

* Mean value (n=3); † Standard deviation