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Transport and retardation of microplastic in biochar

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ABSTRACT

Microplastic is an emerging contaminant of concern. Presence of microplastic at significant level in aquatic and soil environments has been reported in recent studies; which highlights the microplastic pollution as a global environmental challenge. Recent studies have shown that biochar; which is a product of pyrolysis of biomass, presents promising properties as a carbonaceous absorbent for managing various contaminants. We will present the results of a series of experimental investigations on the removal of microplastic spheres (microbeads) by biochar and the interactions between microbeads and biochar. Filtration properties of biochar samples produced at three different temperatures from corn straw and a hardwood biochar show significant capacity for the removal and immobilisation of 10 μm diameter microplastic spheres. Biochar samples showed high immobilisation (95% removal efficiency) whilst 60-80% of microplastic particles were retained in sand under same experimental conditions. The microscopic examination of the samples that were retrieved after the leaching tests revealed that the microplastic spheres were immobilised through three morphologically controlled mechanisms (or combinations of those) which are conceptualised to be stuck, trapped and entangled mechanisms whilst the microplastic spheres would only stuck in the sand.

Keywords: microplastic, biochar, emerging contaminants, sand filter, water treatment.

1 INTRODUCTION

The growing evidence of the extensive presence of microplastic in water, soil and air has generated public concerns on potential risks to the environment and human health. Microplastic has been found in soil, water bodies, food, and living organisms, highlighting the widespread threat of such emerging pollution. Approximately 80% of microplastic particles in the environment are released from factories, wastewater treatment plants (WWTPs), and urban sewage outlets (Ritchie & Roser, 2020). Although most WWTPs can effectively remove significant proportion of microplastic particles in wastewater (Ziajahromi et al., 2017), there is significant volume of wastewater and the non-biodegradable nature of plastic would make the situation challenging (Enfrin et al., 2019). A pathway for microplastic to aquatic environment from WWTPs is through the outflow water from tertiary treatment system. The importance and effectiveness of tertiary treatment processes for microplastic removal in WWTPs are highlighted in various case studies (Talvitie et al., 2017). Sand filters, which are widely used as a tertiary treatment process in WWTPs are known for their low cost and easy maintenance (de Oliveira Cruz et al., 2018). The adsorption efficiency of sand filters in WWTPs can be improved by adding adsorbents including carbonaceous materials such as activated carbon. A potential adsorbent that has gained attention in recent years is biochar, which is a carbonaceous porous material from the pyrolysis of biomass.

Biochar is commonly used in agriculture as a soil amendment. It has been found that biochar has promising properties to be used as an adsorbent to remove and retain a wide range of contaminants (e.g. Rajabi et al., 2021). Biochar's ability to remove pollutants from wastewater has made it a popular subject (Inyang & Dickenson, 2015). The ability of biochar to adsorb contaminants also overlaps with an important pathway for microplastic to soil environment which is because of the use of sewage sludge in agriculture. There is limited understanding of the ability of biochar to retain and immobilize microplastic particles.

This paper presents an investigation on the interaction of microplastic spheres (micorbeads) with biochar that aims to develop a fundamental understanding about the governing mechanisms of the removal. This paper follows our pioneering study (Wang et al., 2020) that suggested high potential of biochar to remove microplastic. Microbeads, which are spherical microplastic particles sourcing mainly from personal care and cosmetic products, are present in influent and effluent water from wastewater treatment plants at a size range from < 63 µm to 2000 µm (Estahbanati and Fahrenfeld, 2016). Tong et al. (2020) reported the transport of plastic particles within the size range of 0.02 to 2 µm in sand and biochar. Such sizes of microplastic particle are similar to colloids (0.001 µm to 1 µm) with regards to their transport behaviour, (Jonasz & Fournier, 2007). The surface charges of these particles play a critical role in their interactions with surfaces, as the influence of the pore system decreases in importance (Bhattacharjee, 2016). We look at larger size particles (10 µm) to reveal structural interactions between the particle and pore/surface system.

The incorporation of biochar into sand filters has the potential to enhance the removal efficiency of sand filters in tertiary treatment systems and minimize microplastic pollution release to environment (Wang et al., 2020; 2022). This is particularly relevant for upgrading existing wastewater treatment plants, as alternatives such as membranes are costly, energy-intensive, and difficult to implement, especially in the Global South. In addition, there is growing interest in understanding the transport and fate of microplastic in agriculture soil (significant quantity of microplastic is introduced to the soil by the sewage sludge as a fertiliser). The existing applications of biochar in agriculture soil can provide a level of natural retardation of microplastic. Understanding of the interactions between microplastic and biochar is limited. This paper presents an investigation on the filtration properties of microplastic spheres in four different types of biochar, three of which were from corn straw and one from hardwood feedstock. A leaching column system was designed to test the efficiency of microplastic sphere removal by biochar and sand filters. The immobilisation mechanisms are analysed based on systematic microscopic examinations.

2 MATERIALS AND METHOD

2.1 Biochar and silica sand

Two biochar types were used in this study: corn straw (C300, C400, C500) and hardwood, produced by the pyrolysis and open fire stove methods (sourced externally from commercial suppliers). Silica sand was sourced from Garside Sands in the UK. The particle size was measured according to BS-1377-2 and the particle size distributions are shown in Figure 1, with a median size of 0.6-0.7mm. Density was determined using the miniature pycnometer method, and the total specific surface area was calculated using the EGME method. Table 1 shows the physical and chemical properties of the biochars.

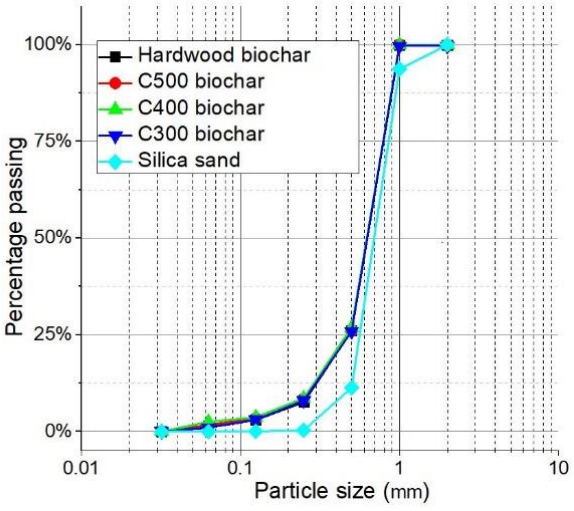


Figure 1. *Particle size distributions of sand and biochars.*

ESEM tests were performed using a FEI Quanta 650 FEGSEM, with elemental analysis conducted using an Oxford Instrument EDX and analyzed with AZtec®. Surface roughness was measured with a Keyence X200K microscope, and Zeta potential was determined using a Zetasizer from Malvern

Instruments at the Geoenvironmental Engineering Laboratory at the University of Manchester. Biochar materials were composed of carbon and oxygen with traces of silicon due to soil particles, as shown in Table 2. Details of the ESEM analyses are presented in Wang et al. (2020), highlighting the pore system's morphology. The porous structure of the biochars studied are shown in *Figure 2*.

Table 1. *Physical properties of biochar samples.*

Biochar	SSA by EGME m^2/g	Particle Density Mg/m^3	Bulk density Mg/m^3
C300	808.3±81.9	1.32	0.06
C400	609.0±83.5	1.23	0.08
C500	177.5±16.3	1.21	0.12
Hardwood	292.8±69.3	1.31	0.41

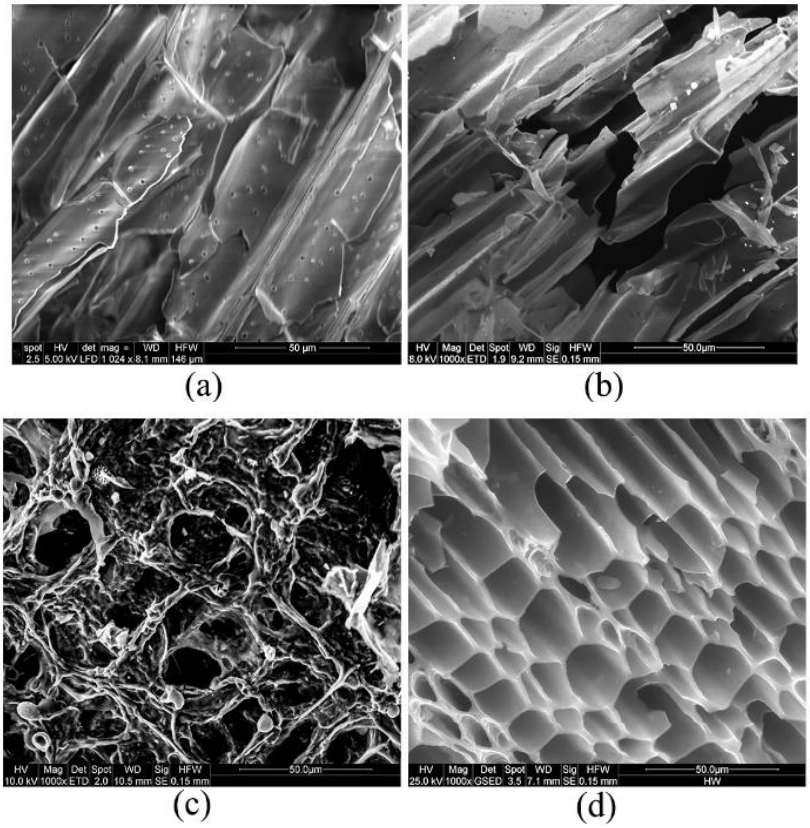


Figure 2. *Surface morphology of the biochars in this research: C300 (a), C400 (b), C500 (c) and Hardwood (d).*

Table 2. Elemental contents of biochar and sand (w/w %).

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

2.2 Leaching column tests

In this research, we used 10 µm polystyrene microspheres at a high concentration of 1.6×10^8 particles per litre in distilled water with a pH of 7.56. The concentration of microplastic in the solution was measured using a Neubauer improved counting chamber. To evaluate the removal of microplastic spheres by biochar and sand, leaching column experiments were designed and used. The biochar samples were packed in cylindrical columns between two layers of silica sand, as shown in Figure 2, and a constant flow rate of 180 ml/h was used to inject the inflow solution. The breakthrough curves were monitored, and the ability of biochar for retaining the captured particles was examined by flushing the system with distilled water after certain pore volumes of microplastic injection. The experiments were carried out at room temperature (25±1°C) and the details are summarized in Table 3. The samples were collected from a location near the water inlet of the filter inside the column for SEM imaging and were analysed without prior treatment. During imaging, the stage temperature was set to 5°C, and the chamber pressure was between 5.0-6.2 Torr. The pore water was removed gently by vaporization until the microplastic particles and filter surface were visible.

Figure 3. *The leaching column (left) designed and used in this study.*

Table 3. *Details of the leaching column tests.*

Filter system	Weight (g)	Height (cm)	Diameter (cm)	Pore volume (ml)	Flow rate (ml/h)	Hydraulic conductivity (m/s)
C300	2.9	7.0	3.0	47.28	180.0	5.41×10^{-5}
C400	4.1			46.14		7.13×10^{-5}
C500	6.0			44.49		7.84×10^{-5}
Hardwood	21.0			34.89		3.72×10^{-5}
Silica sand	110.0	10.0		31.40		1.34×10^{-3}

3 RESULTS AND DISCUSSION

3.1 Microplastic spheres retentions and stability

Figure 4 presents the findings of leaching experiments conducted on biochar and sand filters. In the first three pore volumes, where 1.6×10^8 particles/l of a microplastic suspension were injected, the removal efficiency was calculated as the concentration difference divided by the initial concentration. The release rate was determined by dividing the residual concentration in the effluent by 1.6×10^8 particles/l to determine the leakage potential for the subsequent pore volumes, where distilled water was supplied.

The results showed that the C400 and C500 filters had no leakage from the third to the 10th pore volume, with 100% removal and 0% release for the C500 filter. In contrast, the silica sand, hardwood, and C300 filters showed 6.85%, 0.23%, and 0.1% of the total retained microplastics escaping from the first three pore volumes during the 3rd to 10th pore volumes. The biochar filters demonstrated better removal efficiencies than sand filters, and the C500 filter was the most effective.

In the water flume tests, hardwood biochar showed a higher immobilization than that of sand filter. The sand filter released more microplastics with an increase in water velocity, while the biochar filter retained more than 95% of the microplastics as shown in Figure 5. All samples were alkaline, and the biochar filter's effluent was found to be more alkaline than that of the sand filter due to the erosion of small biochar particles from the filter. The Zeta potential of biochar samples and microplastic were measured by Zetasizer. It was found that the Zeta potential is -36.97mV for C300, -40.70mV for C400, -35.47mV for C500, and -32.70mV for Hardwood, while the Zeta potential of microplastic was found to be -54.67mV. Therefore, the presence of biochar and microplastic in pure water would result in alkaline water as shown by Wang et al. (2020).

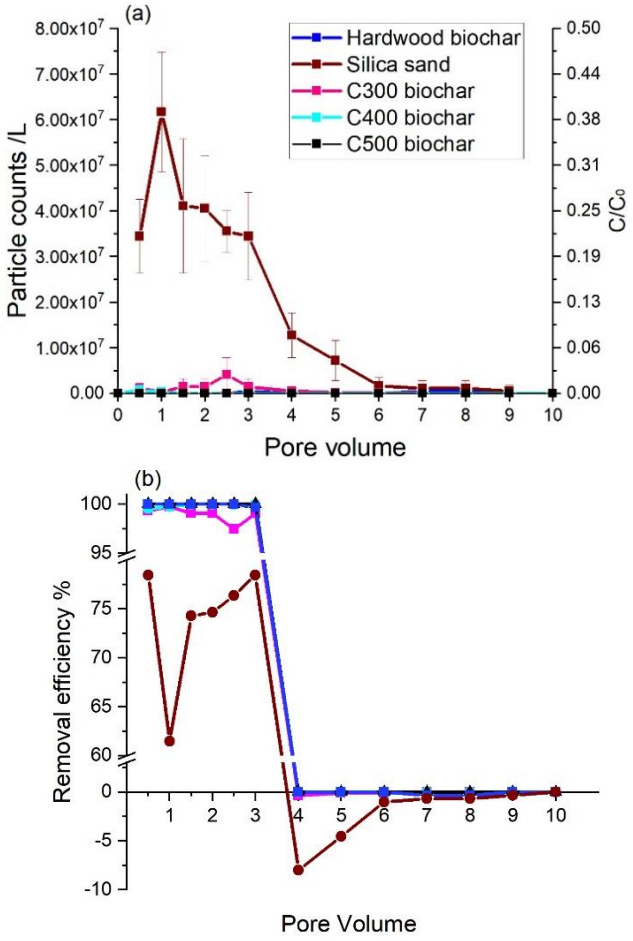
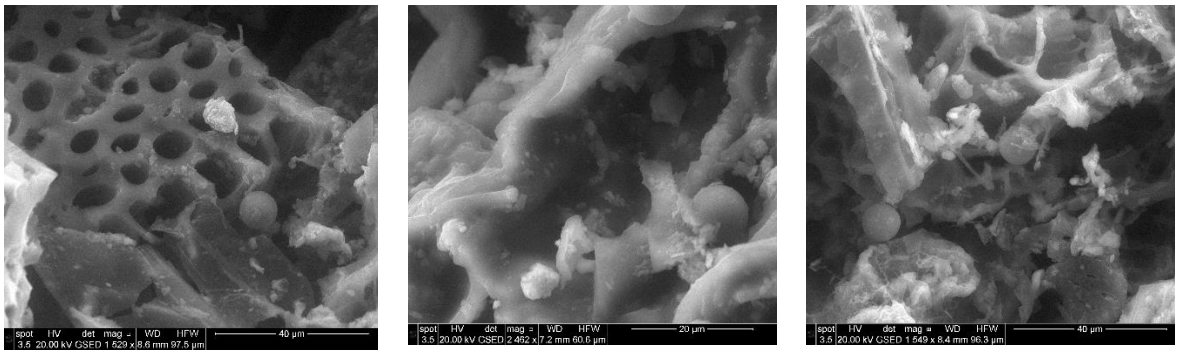


Figure 4. *The breakthrough curves (a) and removal efficiency (b) of microplastic spheres at different pore volumes.*

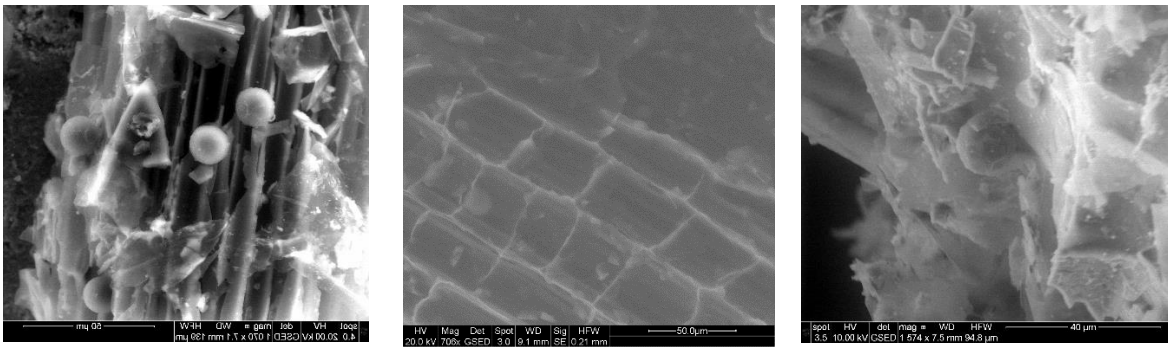
3.2 Immobilisation mechanisms

The microplastic particles used in this study were 10 µm in size, which is larger than colloids in size. At such sizes of particles, the potential effects related to surface interactions that can be observed at colloidal sizes, such as the effects of ionic strength, Zeta potential, and van der Waals forces, are negligible. This allows observing the effects of the pore system on microplastics. Following the leaching column experiments, the biochar and sand samples were examined using ESEM to obtain a better understanding of the retention mechanisms of microplastics in biochar and sand. A number of ESEM observations of MP interactions with different biochars are presented in Figure 5.

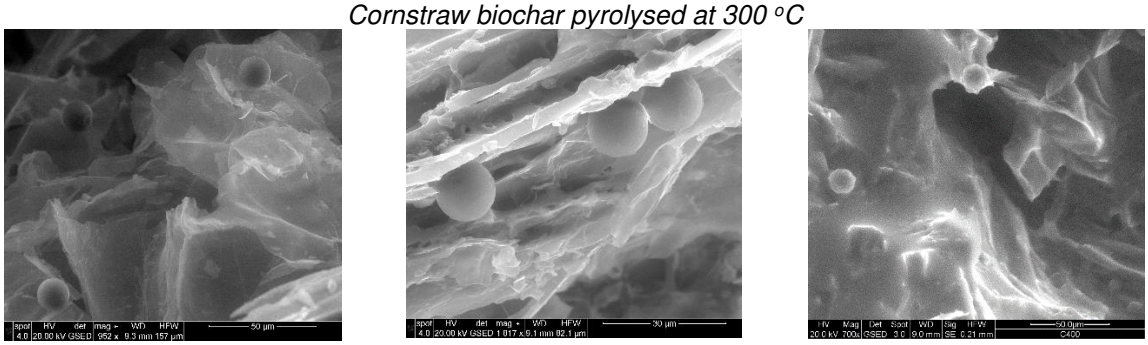
The ESEM observations revealed that there are a combination of three mechanisms for particle interactions with biochar which are categorised based on their nature of interactions into 'Stuck', 'Trapped', and 'Entangled', as depicted in Figure 5. The particles 'Stuck' in biochar are those located in the interstices between biochar particles smaller than the MP's size. The 'Trapped' particles are those present in the pore system due to mechanisms unique to filters with a porous structure, such as activated carbon and biochar. The 'Entangled' particles refers to those microplastics tangled with small biochar chips and grains. A combination of two or three of these mechanisms can retain particles.



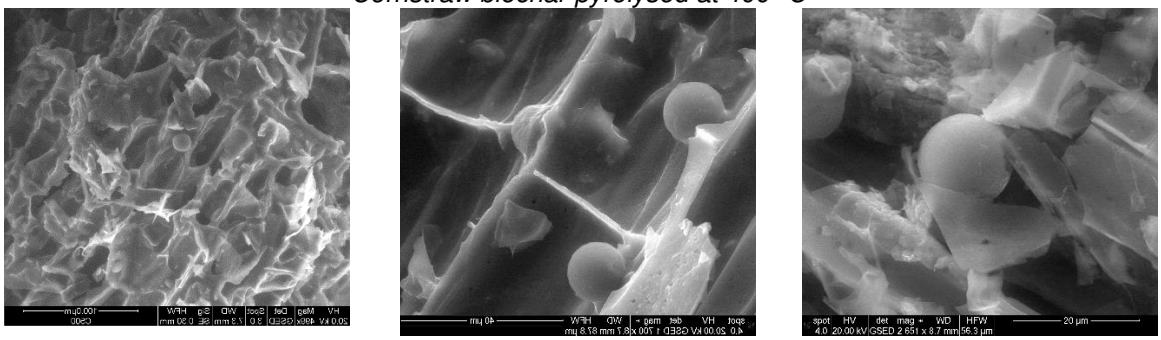
Hardwood biochar



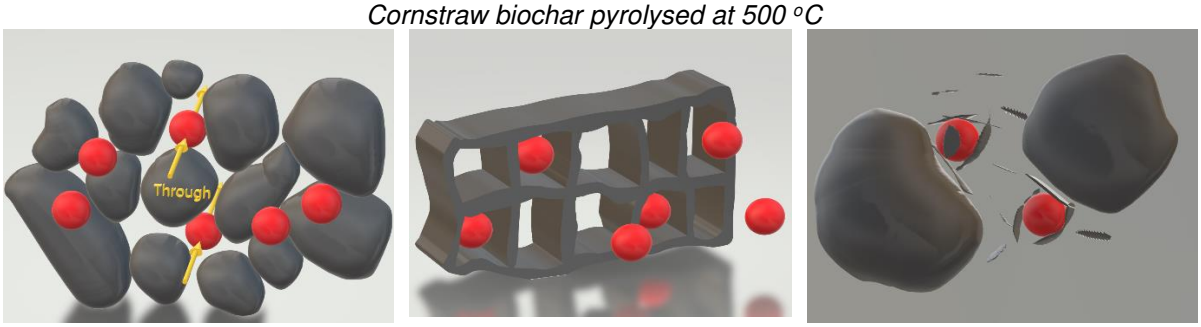
Cornstraw biochar pyrolysed at 300 °C



Cornstraw biochar pyrolysed at 400 °C



Cornstraw biochar pyrolysed at 500 °C



MPs become "Stuck" between or by the particles.

MPs are "trapped" in pores of individual particles.

MPs become "entangled" by fine partcicles.

Figure 5. *Three mechanisms of interactions between biochar and microplastic spheres observed in ESME.*

The removal efficiency of sand for microplastics depends on the size of the sand particles and microplastic particles. The ESME results presented in Figure 6 show that the interaction between microplastic spheres and sand particles is mainly in the form of stocking particles at surfaces (Wang et al., 2020).

Biochar demonstrated higher retention capacity for microplastics than sand due to the specific porous structure and surface characteristics that enable three mechanisms described above retains particles. The "honeycomb" and "loofah" structures in hardwood biochar and C500 biochar, respectively, are believed to be cause of stronger retention compared with other biochars studied here. (Wang et al., 2020).

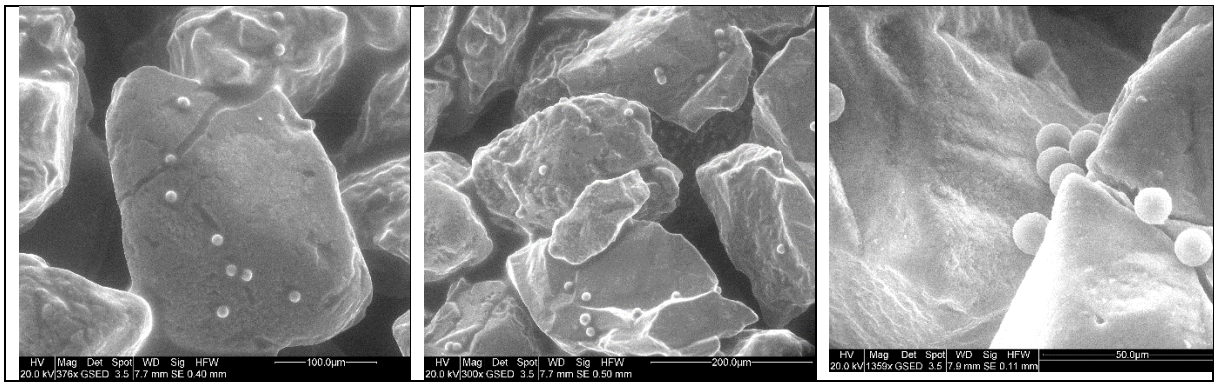


Figure 6. *Interactions between sand and microplastic spheres observed in ESME.*

4 CONCLUSIONS

The results of a series of leaching column tests and ESEM examinations of four types of biochar and sand were presented in this paper. The results showed that biochar is highly effective in filtering the microplastic spheres, with removal efficiencies of at least 95% compared to 60-80% for sand. We showed that less than 0.5% of the microplastics retained by the biochar were released during backwashing with distilled water, which was significantly lower than the 6.85% release rate observed in sand. Using electron scanning microscopy, three different mechanisms for microplastic association with biochar filters were observed on the adsorbent surfaces, micropores, and inclusions of the biochar: "stuck," "trapped," and "entangled." The "trapped" and "entangled" mechanisms are believed to contribute to the higher removal efficiencies achieved by biochar compared to similarly sized sand filters. This study provides fundamental insights into the transport of microbeads in biochar and highlights the strong potential of biochar for use in tertiary treatment systems in wastewater treatment plants. By improving the performance of rapid sand filters in removing microplastics, biochar has the potential to increase the efficiency of tertiary systems and provide a low-cost, low-maintenance solution to minimize the release of microplastics in wastewater treatment plant effluent.

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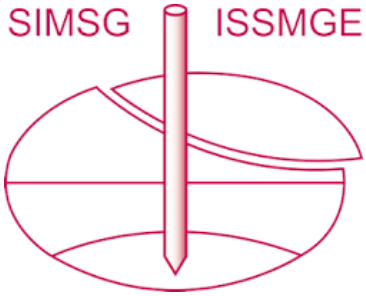

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