Rapid Preparation of Electrospun Nanofibre Sponges through Supercritical CO_2 Drying

Supporting Information

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Preparation of nanofibre sponges by the CPD process.

The slurry as explained in the experimental part was poured into the mould specially made for this purpose (Figure S1). The mould had an inner diameter of 3 cm and a height of 2.1 cm. A polyacrylonitrile mesh was placed on the bottom and top of the mould to prevent fibres from flowing through the system. The polyacrylonitrile mesh was fixed with a metal grid attached to the bottom with 4 screws and to the top with 4 magnets. The mould was designed to have the same height and volume as the moulds supplied by Leica Microsystem. A mould with twice the size was also made.

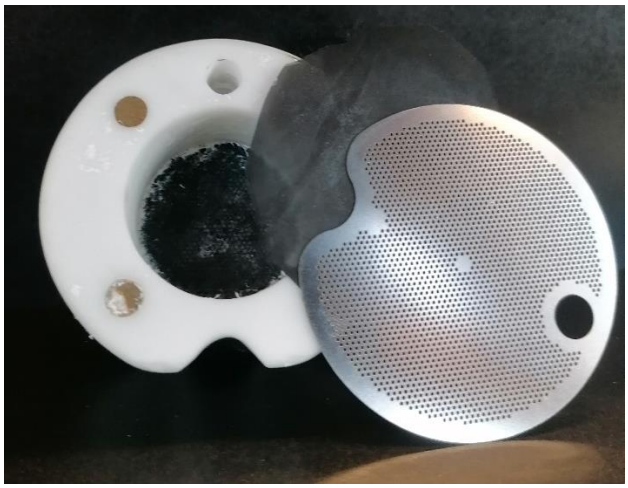

Figure S1: Mould for the production of CPD sponges. A mould with twice the size was also made.

As an alternative to the presented method, a previously weighed amount of single short dry nanofibres was added to the mould and suspended in situ with a 1:1 solution of ethanol and acetone. However, this method resulted in the formation of larger nanofibre clusters and aggregates.

Air permeability

Air permeability was measured using an FX 3300 LabAir IV air permeability tester (TEXTest AG, Switzerland) with a differential pressure between 1250 and 2500 Pa. Sealing was achieved by radial compression based on ISO 7231:2023. Instead of using square samples, the cylindrical sponges were inserted into a thermal shrinking tube coated with vacuum grease that was then shrunk to a mean diameter of approx. 16.3 mm (ε_r = 30 %) and fixed on a metal tube to fit to the air permeability tester, Figure S2.

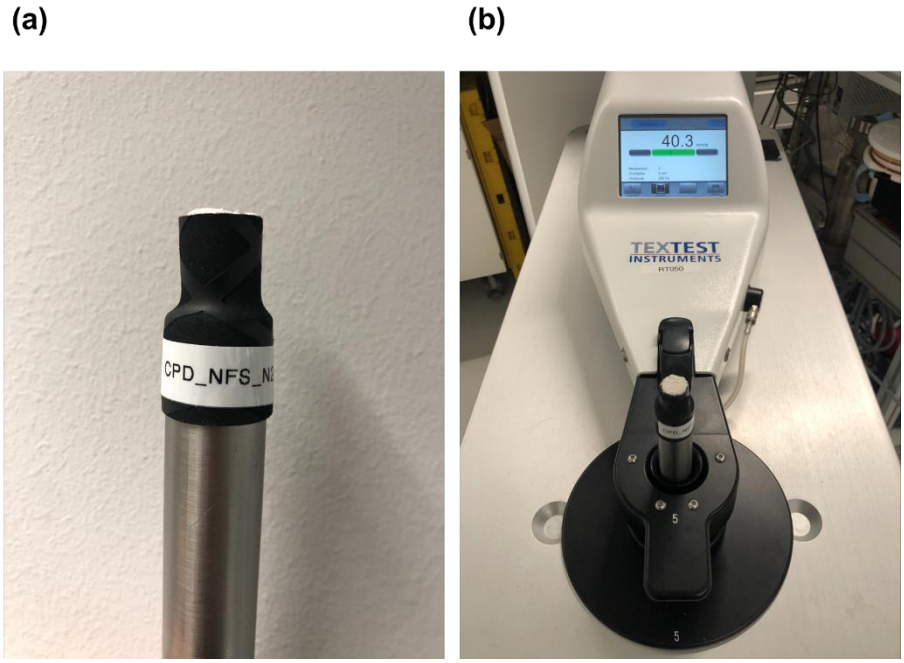

Figure S2: (a) Radially compressed nanofibre sponge (NFS) sealed through a thermal shrinking tube and mounted on a metal tube. (b) FX 3300 LabAir IV air permeability tester measuring the NFS.

Filtration

The filtration setup shown in Figure S3 consisted of a 1-liter tank with an overflow that was continuously fed from a reservoir by a peristaltic pump (LabDos EasyLoad, HiTec Zang, Germany). Constant hydrostatic pressure was maintained by the overflow level. The sponges were connected to the bottom of the apparatus and fixed using heat shrink tubing. The sponges were compressed to 30 % of their original diameter. The filtration rate was monitored using a Mettler Toledo PB8001-S/FACT balance with serial readout to Matlab® (R2021b, Natick, Massachusetts: The MathWorks Inc.).

A suspension of microplastics $\gamma = 1$ g L^{-1} and a suspension of Arizona Test Dust (ISO 12103-1, A2 ATD, 68-76 % silica) $\gamma = 10$ g L^{-1} were used for filtration. Before each filtration, distilled water was allowed to flow through the sponges to pre-wet them and determine their water flow rates.

Samples were taken during the filtration to measure turbidity offline using a TN-100 portable turbidimeter from Eutech Instruments. The turbidity was used to calculate the filtration efficiency.

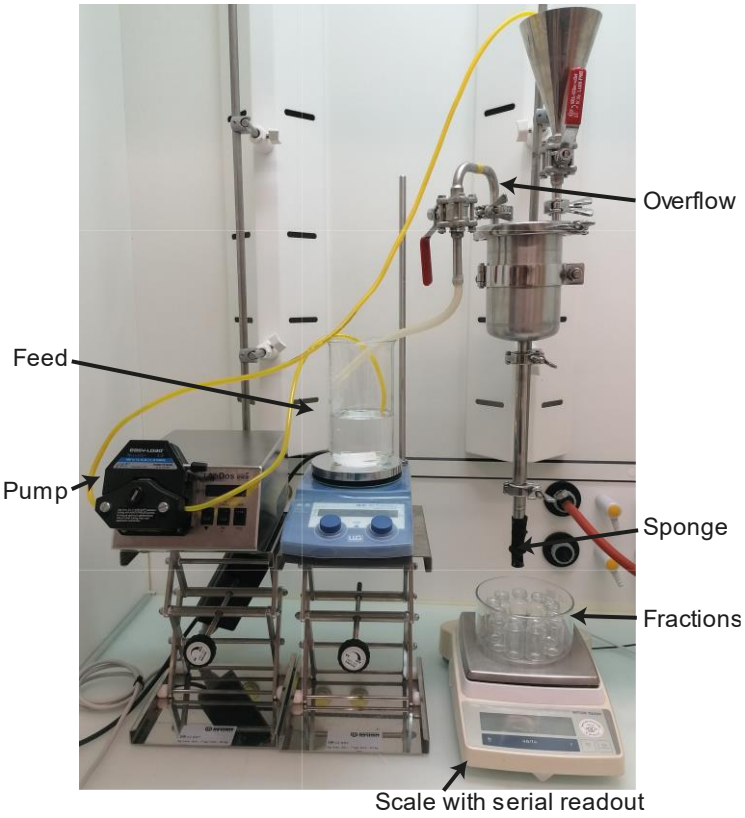

Figure S3: Apparatus used for the filtration tests.

Fibre length

The fibre length of the suspended nanofibres was determined from SEM images (Figure S4) from at least 100 individual fibres using the open source software ImageJ [1]. In general, the short fibres were fully separated (Figures S4a to S4l) with only few entangled fibres (Figures S4m to S4o).

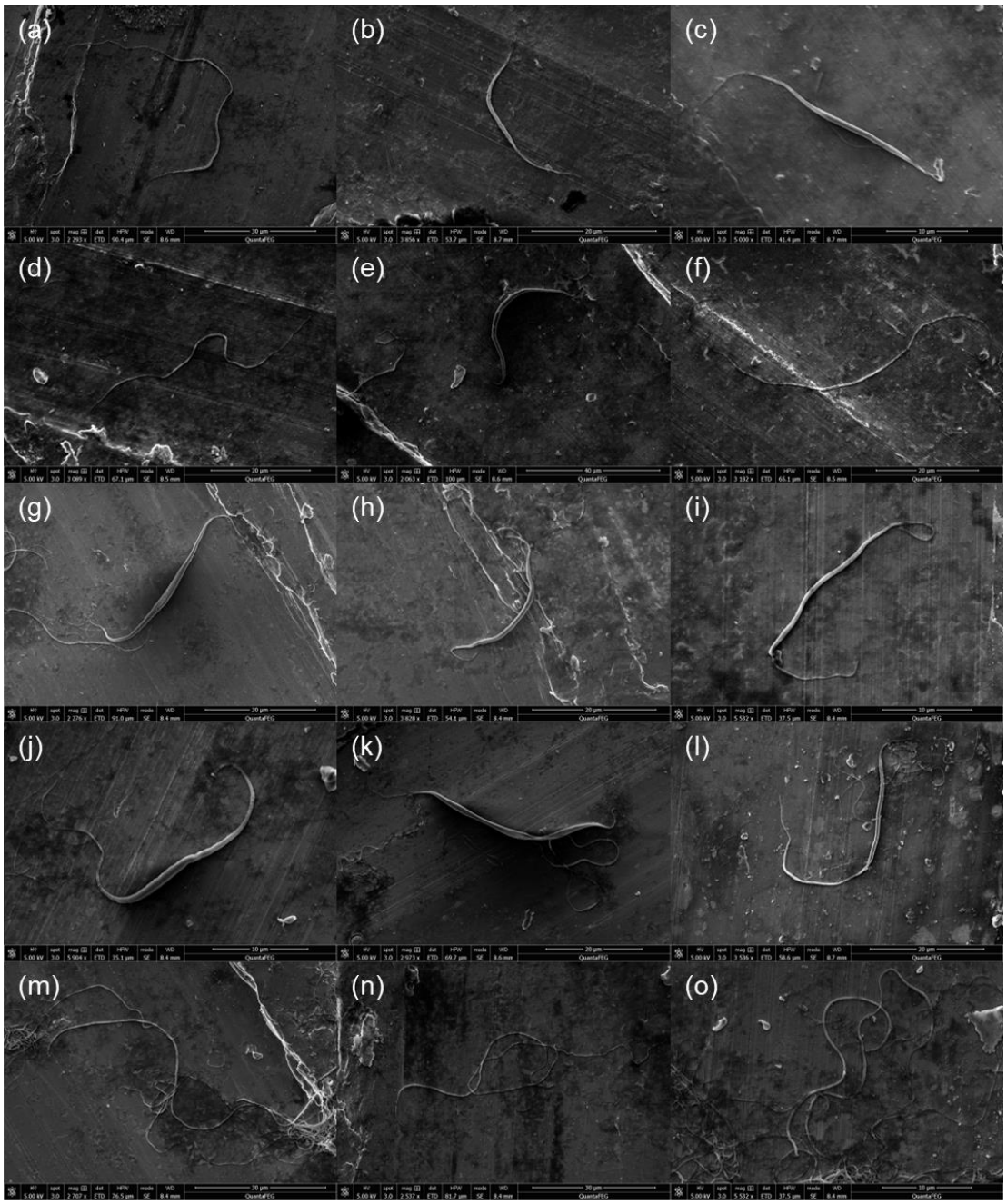

Figure S4: Typical SEM images of the suspension of short PA6 nanofibres recorded from dried samples. Scale bar between 10 and 30 µm.

DSC

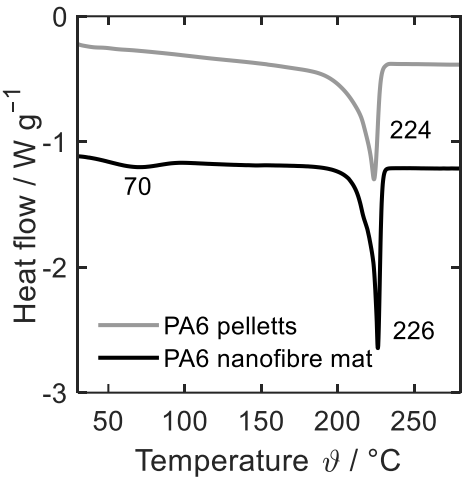

Figure S5: DSC curves recorded between 30 °C and 280 °C for PA6 pellets and a PA6 nanofibre mat (shifted by –1 W g^{-1}). Note the characteristic peak at 70 °C for the electrospun nanofibre mat, that is missing in the PA6 pellets.

FTIR

The IR spectra (**Fehler! Verweisquelle konnte nicht gefunden werden.**) the sponges prepared with freeze-drying and CPD showed the same bands with the same intensity. The principal band observed were 1539 (Amide II, C-N stretch and C(O)-N-H bend combination), 1637 (Amide I), 2865 and 2930 (CH_2, symmetric and antisymmetric stretching), 3070 (N-H stretching), and 3290 (hydrogen bonded N-H stretching). The peaks are typical for PA6, confirming the absence of contaminants [2].

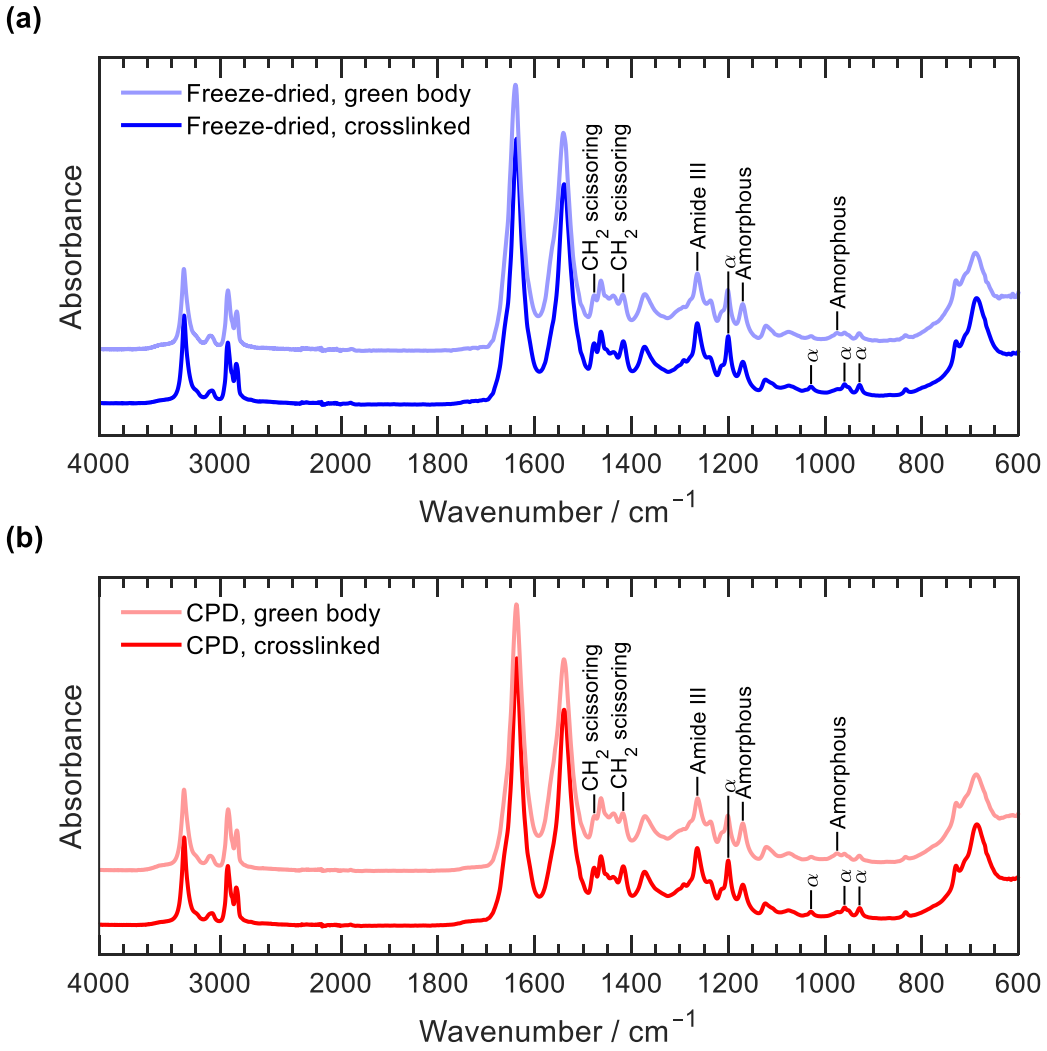

Figure S6: Infrared spectra recorded between 600 and 4000 cm^{-1} for freeze-dried (a) and CPD sponges (b) before (green body) and after crosslinking (crosslinked).

TGA

TGA (Figure S7) confirmed the absence of other materials, as only a single decomposition segment was observed at around 330 °C.

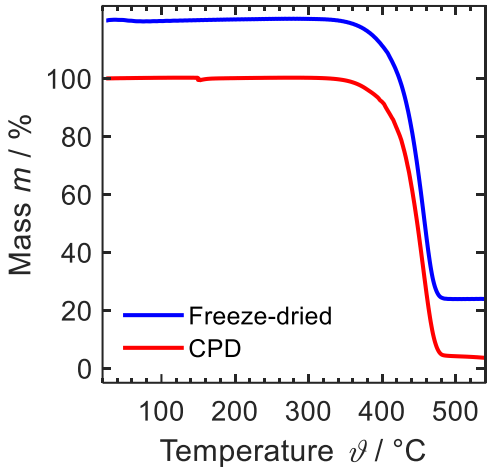

Figure S7: TGA curves recorded between 25 °C and 550 °C for freeze-dried (shifted by + 20 %) and CPD sponges.

Particle size distribution of the test suspensions

Microplastics had a mass median diameter (MMD) of 4.92 µm with a span of 1.08, and the Arizona Test Dust particles had an MMD of 8.07 µm with a span of 4.57. The particle size distributions are shown in Figure S5. The span was calculated using the following equation

$$\text{span} = \frac{d(x,0.9) - d(x,0.1)}{d(x,0.5)}$$

where $d(x, 0.9)$ represents the particle size d containing 90 % of the volume.

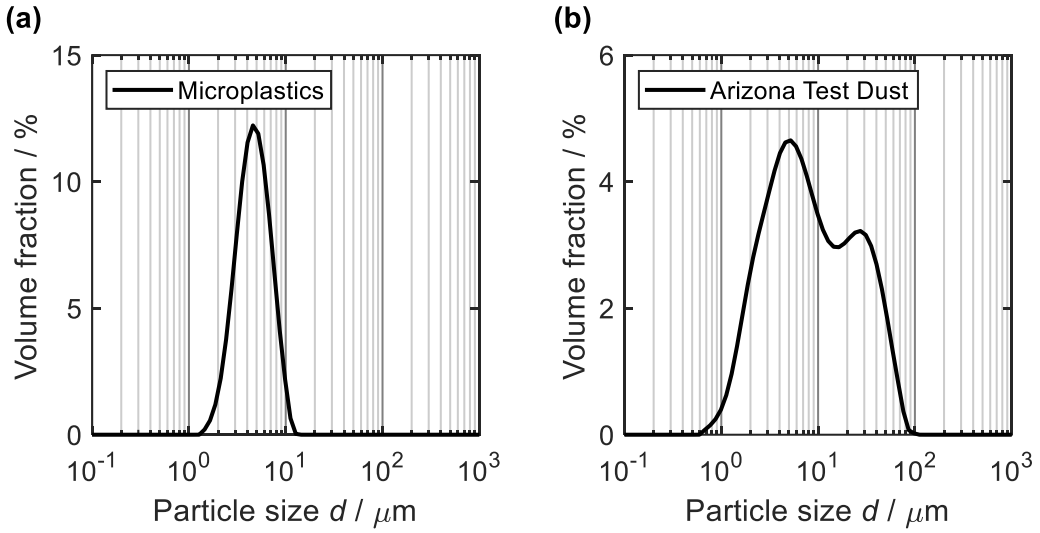

Figure S8: Particle size distribution of microplastics (a) and Arizona Test Dust (b) suspensions, used for the filtration test with the nanofibre sponges.

Filtration efficiency of the Arizona Test Dust

The filter cross sections and flow rate for the filtration of the Arizona Test Dust suspension with freeze-dried and CPD-processed nanofibre sponges are shown in Figure S9.

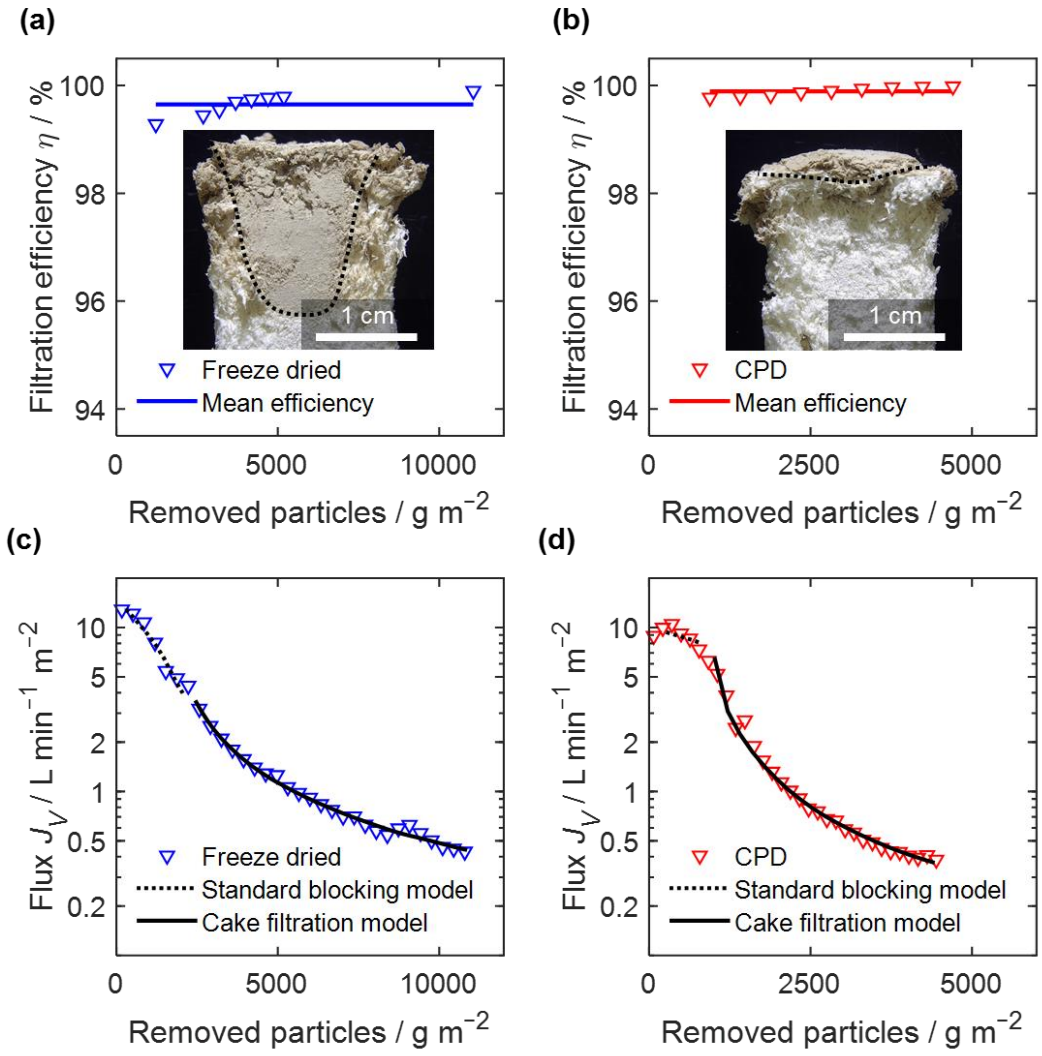

Figure S9: Filtration efficiency of Arizona Test Dust (a, b) and volumetric flux for (c, d) freeze-dried sponges (a, c) and CPD-processed sponges (b, d) in terms of particles removed per unit area; insets in (a) and (b) show cross sections of sponges after filtration with penetration front indicated (dashed lines); dashed and solid lines in (c) and (d) are fitted blocking models for initial filtration (standard blocking) and final filtration (cake filtration).

References

1 W. S. Rasband, ImageJ U. S. National Institutes of Health, Bethesda, Maryland, USA 1997.

2 J. Pocket, Crystallinity in Linear Polyamides: a Study using Melt Blending with Small-Molecule Diluents. *Ph. D. Thesis*, University of South Australia, Australia 2004.