

## Supplementary Information

### Removal of Ammonium from Wastewater with Geopolymer Sorbents Fabricated via Additive Manufacturing

*Giorgia Franchin, Janne Pesonen, Tero Luukkonen\*, Chengying Bai, Paolo Scanferla, Renata Botti, Sara Carturan, Murilo Innocentini, Paolo Colombo*

Dr. G. Franchin, P. Scanferla, Dr. R. Botti  
Department of Industrial Engineering, University of Padova, 35131 Padova, Italy

J. Pesonen  
Sustainable Chemistry, University of Oulu, FI-90014 Oulu, Finland

Corresponding author:

Dr. T. Luukkonen  
Fibre and Particle Engineering, University of Oulu, FI-90014 Oulu, Finland  
Pentti Kaiteran katu 1, 90570 Oulu  
E-mail: [tero.luukkonen@oulu.fi](mailto:tero.luukkonen@oulu.fi)

Dr. C. Bai  
College of Material Science and Chemical Engineering, Harbin Engineering University, 150001 Harbin, China

Dr. S. Carturan  
Legnaro National Lab, National Institute for Nuclear Physics (INFN), 35020 Legnaro, Italy

Prof. M. Innocentini  
Course of Chemical Engineering, University of Ribeirão Preto, 14096-900 Ribeirão Preto, SP (Brazil)

Prof. P. Colombo  
Department of Industrial Engineering - University of Padova, Via Marzolo 9, 35131 Padova, Italy  
and  
Material Science and Engineering Department, The Pennsylvania State University, 16801 State College, PA (USA)

Keywords: geopolymer; additive manufacturing; direct ink writing; ammonium removal; wastewater

### **Ink preparation and feeding of the DIW setup (as reported in [1])**

The geopolymer ink comprised metakaolin (Argical 1200S, Imerys S.A.) as an aluminosilicate source, and an alkaline solution of sodium silicate (SS2942, Ingessil S.r.l.), sodium hydroxide (NaOH, Sigma–Aldrich) and distilled water. The compositions of the metakaolin and of the sodium silicate are summarized in Table S 1.

<b>Reagent</b>	<b>SiO<sub>2</sub> (%wt)</b>	<b>Al<sub>2</sub>O<sub>3</sub> (%wt)</b>	<b>Na<sub>2</sub>O (%wt)</b>	<b>H<sub>2</sub>O (%wt)</b>
Argical 1200S	55	39	< 1	/
SS2942	28.4	/	9.8	61.9

*Table S 1. Composition of the metakaolin and soluble silicate solution in use.*

First, a solution of sodium silicate, sodium hydroxide and water was prepared with the following molar ratios: SiO<sub>2</sub>/Na<sub>2</sub>O = 1.4, H<sub>2</sub>O/Na<sub>2</sub>O = 13. The solution was prepared at least 24 h in advance and was stored at 4 °C. The composition of the alkaline solution is reported in Table S 2.

<b>SS 2492 (%wt)</b>	<b>NaOH (%wt)</b>	<b>H<sub>2</sub>O (%wt)</b>
78.4	11.1	10.5

*Table S 2. Composition of the alkaline solution.*

Polyethylene glycol with an average molecular weight of 1000 g/mol (PEG 1000, Sigma-Aldrich) was added to the solution under mechanical stirring at 500 rpm for 5 min at room temperature. Metakaolin powder was then added to the solution under mechanical stirring at 1000 rpm for 10 min at room temperature. The composition of the ink is reported in Table S 3.

<b>Argical 1200S (%wt)</b>	<b>Alkaline solution (%wt)</b>	<b>PEG (%wt)</b>
37.3	57.7	5.0

*Table S 3. Composition of the ink.*

After mixing, the ink was transferred into a plastic syringe, which served as a pressurized vessel for feeding the DIW device. Each syringe can contain up to 30 mm<sup>3</sup> of ink and could be printed for ~ 1.5 – 2 h before setting.

## Attenuated total reflection Fourier-transformed infrared (ATR - FTIR) spectroscopy before and after the washing procedure

Infrared spectra were obtained by ATR - FTIR spectroscopy (6200 FTIR spectrometer equipped with ATR Pro One diamond prism, Jasco Inc.). Absorption spectra were determined for fine powders from printed structures before and after washing procedure on 4000–500  $\text{cm}^{-1}$  range; they are reported in Figure S 1.

Although PEG main absorption peak at  $\sim 1100 \text{ cm}^{-1}$  (corresponding to C-O stretching) is masked by the geopolymer peak at the same wavenumbers (Si-O stretching), it can be observed that those at  $\sim 1470$  and  $\sim 1370 \text{ cm}^{-1}$  (corresponding to C-H bending) and that at  $\sim 2870 \text{ cm}^{-1}$  (C-H stretching) decrease in washed samples, meaning that a significant amount of PEG is released during the washing procedure. Such decrease is in agreement with the value of SSA measured after washing, which increases from 3.7 to  $12.2 \text{ m}^2/\text{g}$ : as the PEG leaves the geopolymer structures, more and smaller mesopores can be accessed providing for higher SSA values and higher sorption capacity.

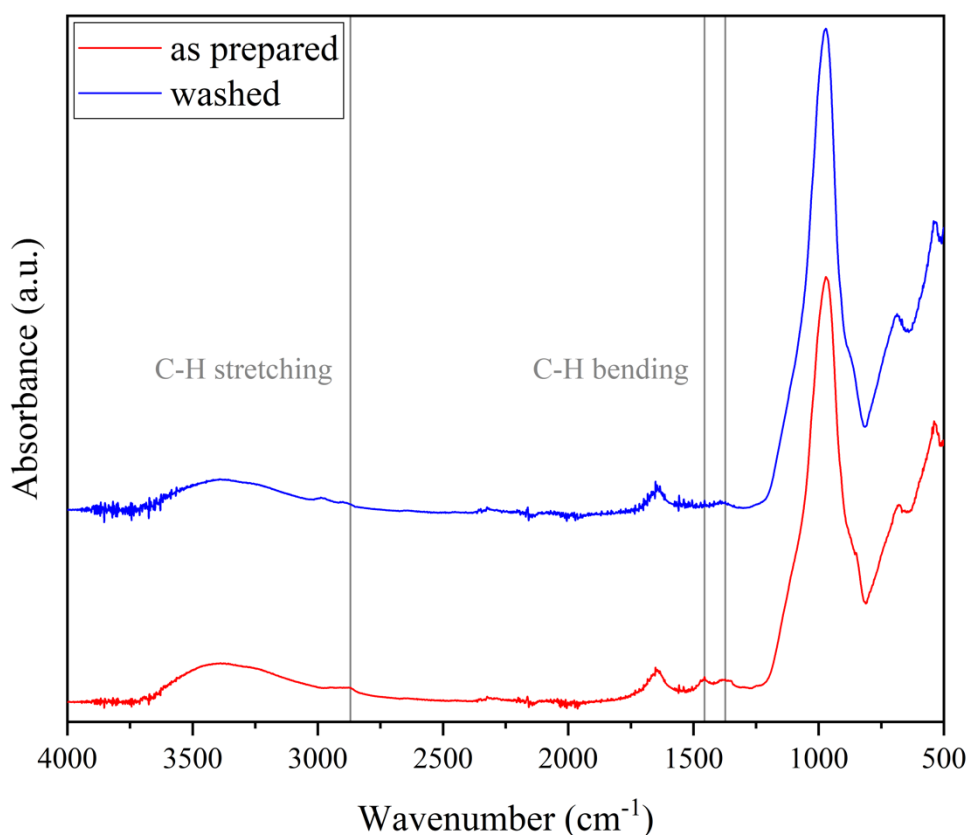


Figure S 1. ATR FTIR absorption spectra before and after the washing procedure. Peaks corresponding to PEG's organic bonds are highlighted.

## Description of the permeability apparatus and determination of $k_1$ and $k_2$ parameters

Experimental evaluation of permeability was carried out in a laboratory-made apparatus schematized in Figure S 2, with tests performed in steady-state regime with dry airflow at room conditions ( $T \sim 25^\circ\text{C}$  and  $P_0 = P_{\text{atm}} \sim 1 \text{ bar}$ ).

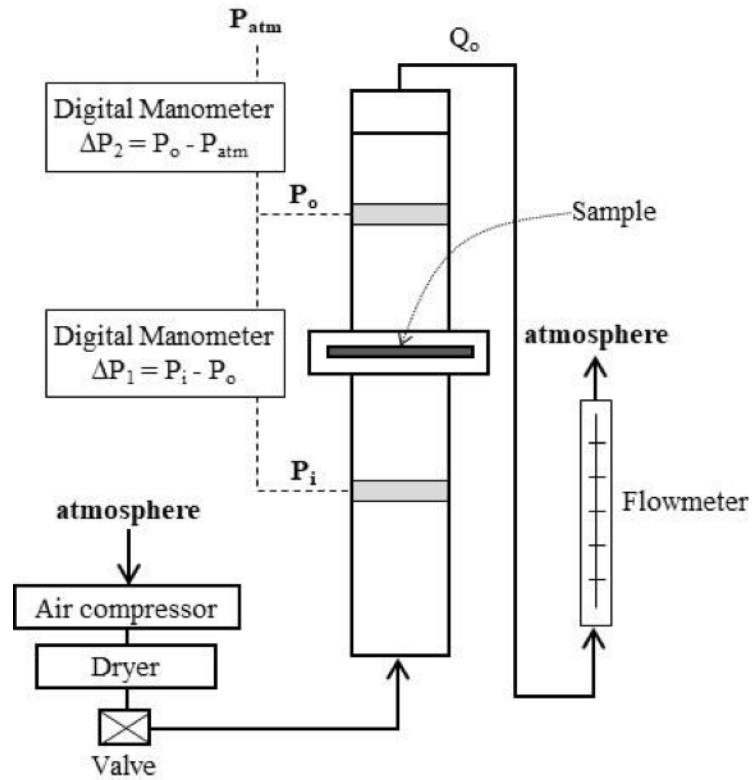


Figure S 2. Schematics of the permeability apparatus.

2 printed lattices were used for permeation tests with airflow. Each sample was sealed within a cylindrical sample holder with a circular flow area ( $A_{\text{flow}}$ ) of  $172 \text{ mm}^2$ . The pressure gradient across the specimen  $\Delta P$  was measured by a digital manometer (Sper Scientific 840083), in response to variations in the air volumetric flow rate  $Q$  controlled by a needle valve and measured with a rotameter open to the atmosphere. Flow rate ( $Q$ ) was corrected to the value at sample exit ( $Q_0$ ) and finally converted to superficial velocity by  $v_s = Q_0/A_{\text{flow}}$ .

The collected data set ( $\Delta P$  and  $v_s$ ) for each test was fitted according to Forchheimer's equation [39]:

$$\frac{\Delta P}{L} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^2 \quad (1)$$

where  $L$  = length of the medium,  $\mu$  = viscosity of the fluid (here:  $1.84 \cdot 10^{-5}$  Pa·s) and  $\rho$  = density of the fluid (here:  $1.18$  kg/m<sup>3</sup>).

The influence of the stacking length on the permeability of the produced lattice sorbents was experimentally assessed by measuring the pressure drop through two samples stacked along the air flow direction (1+2). Results indicate that surface effects were not significant for the printed lattices. The parabolic relationship was confirmed through the high-quality fitting of Forchheimer's equation (correlation coefficient  $R^2 > 0.99$  in all cases), observed in Figure S 3. The individual permeability coefficients retrieved from the airflow curves in Figure S 3 are given in Table S 4.

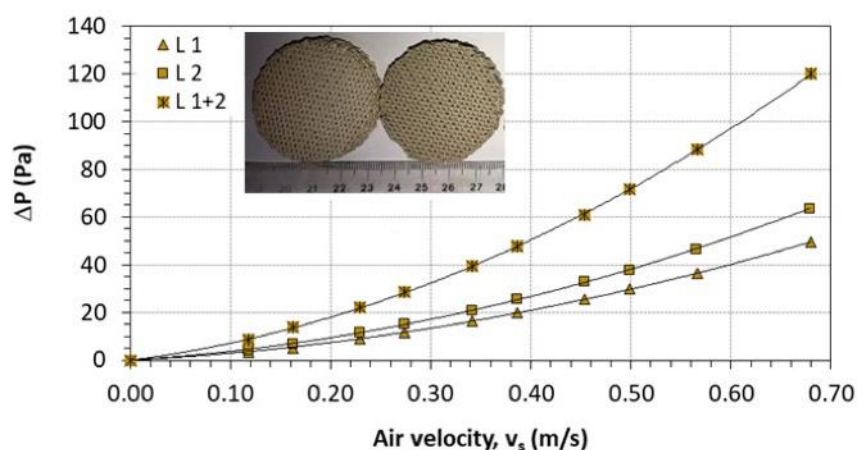


Figure S 3. Pressure drop curves for lattice samples.

Sample	L (mm)	$k_1(10^{-9} \text{ m}^2)$	$k_2 (10^{-4} \text{ m})$
L1	10.1	8.40	1.51
L2	9.05	6.05	1.06
L1+2	19.15	6.60	1.20

Table S 4. Lengths and permeability coefficients of the lattice samples.