# **Supporting Information**

## Phenol-formaldehyde polymeric network to generate organic

### aerogels: synthesis, physicochemical characteristics

### and potential applications

Halyna Zubyk,<sup>a</sup> Olena Mykhailiv,<sup>a</sup> Anthony N. Papathanassiou,<sup>b</sup> Bogdan Sulikowski,<sup>c</sup> Elzbieta

Zambrzycka-Szelewa,<sup>a</sup> Michael Bratychak,<sup>d</sup> Marta E. Plonska-Brzezinska\*<sup>a</sup>

<sup>a</sup> Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland. \*E-mail: mplonska@uwb.edu.pl

<sup>b</sup> National and Kaposdistrian University of Athens, Physics Department, Panepistimiopolis, GR 15784 Athens, Greece

<sup>c</sup> Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Cracow, Poland

<sup>c</sup> Lviv Polytechnic National University, 12, St. Bandera str., 79013 Lviv, Ukraine

#### **Characterization Methods**

The films were imaged by secondary electron scanning electron microscopy (SEM) using a FEI Tecnai S-3000N (Tokyo, Japan). N<sub>2</sub> gas adsorption measurements were performed using a Micromeritics apparatus (ASAP2020 - automatic sorption analyser, Micromeritics Corp., USA) at -196°C. Prior to gas adsorption analysis, all samples were degassed at 350°C and 10  $\mu$ mHg vacuum for 20 h to remove any adsorbed species.

<sup>10</sup>B and <sup>11</sup>B solid-state MAS NMR spectra were acquired at 53.7 and 160.47 MHz on a Bruker Avance III 500 MHz WB spectrometer, operating at a magnetic field of 11.7 T. <sup>11</sup>B MAS NMR spectra were recorded with short single-pulse excitations of 0.4  $\mu$ s (250 kHz) and repetition times of 0.1 - 1 s. The samples were spun in zirconia rotors at 12 kHz. Typically, 8192 transients were acquired for each spectrum. Short pulses were used in order to obtain quantitative spectra.<sup>[64]</sup> <sup>11</sup>B chemical shifts are reported in ppm from external 1 M boric acid solution. In order to estimate the magnitude of quadrupolar effects, a supplementary <sup>11</sup>B MAS NMR spectrum of the 3B-CNOs sample was measured at 96.2 MHz, using the Tecmag Apollo console operating at a magnetic field of 7.0 T. The spinning speed was equal to 11 kHz, and a single 2  $\mu$ s RF excitation pulse was used, which corresponded to the 45° flip angle for the liquid. 1000 scans were accumulated with a repetition time of 1 s.

The room temperature Raman spectra in the range between 100 and 3500 cm<sup>-1</sup> were investigated with a Renishaw Raman InVia Microscope equipped with a high sensitivity ultra-low noise CCD detector. The radiation from an argon ion laser (514 nm) at an incident power of 1.15 mW was used as the excitation source. Raman spectra were acquired with 3 accumulations of 10 s each, 2400 l mm<sup>-1</sup> grating and using a 20x objective. The Fourier Transform Infrared (FTIR) spectra were recorded in the range between 4000 and 100 cm<sup>-1</sup> with a Nicolet 6700 Thermo Scientific spectrometer at room temperature under a N<sub>2</sub> atmosphere. The spectra were collected at a resolution of 4 cm<sup>-1</sup>, apodized with a triangular function, and a zero-filling factor of 1 was applied. All the spectra were corrected with conventional software in order to cancel the variation of the analyzed thickness with the wavelength.

#### Sorption of Solvent and Oils

To determine the sorption capacities of solvents and oils, a cylindrical piece of the as-prepared AGs was immersed into solvent or oil (pump oil) until it was completely saturated with the liquid adsorbate. Around 200 mg of AGs was weighed and immersed in 2 mL of oil or organic solvents in 5 mL water. After 15 min, the sample was drained for 2 min. Thereafter, the wet sample was weighted (M2). The weight ratio (sorption capacity, Q (g/g)) of absorbed oil/organic solvent to the original AG samples was calculated using Eq. (1). For each adsorbate, the adsorption test was repeated several times (minimum 5) and the average adsorption capacity was recorded.

$$Q = (M_2 - M_1)/M_1$$
 (1)

#### **Desorption and repeatability**

After oil/organic solvents/dyes sorption, AGs were soaked in water/acetone/ethanol several times in 1 h for desorption (ultrasonic bath). After desorption, AGs were weighed again to calculate the removal ratio and then dried at 60 °C before the next cycle of adsorption. For the repeatability test, at least three AGs were used to gain the average value.

#### **Calculation of AG Density**

The density of AGs was determined from the mass weight divided by the volume. The avargade values of data were used. The volumes (V) of cylindrical shaped AG was calculated based on Eq below:

$$V = \pi (2/d)^2 h$$
 (2)

where d refers to the diameter of AG monoliths, and h represents the height of AG monoliths. The densities  $(\rho, g/cm^3)$  were calculated from Eq. 3:

$$\rho = m/V \tag{3}$$

m refers to the mass of AGs obtained by the precision balance (METTLER TOLEDO ML204).

### **Figures and Tables**



Figure S1. Deconvolution of the <sup>1</sup>H MAS NMR spectrum of AG2. (Goodness of fit R = 98.66 %)



**Figure S2.** Organic aerogel before (1) and after (2-4) immersion in 15% H<sub>2</sub>SO<sub>4</sub> and 15% KOH. The stability of AG1 (a, b) and AG2 (c, d) in aqueous solution of 15% H<sub>2</sub>SO<sub>4</sub> (2a, 2c, 3a, 3c, 4a, 4c, 5a, 5c) and 15% KOH in (2b, 2d, 3b, 3d, 4b, 4d, 5b, 5d).



**Figure S3.** SEM images of AG1 after immersion in aqueous solution of 15% H<sub>2</sub>SO<sub>4</sub> (a-c) and 15% KOH (d-f) during 180 h.



**Figure S4.** SEM images of AG2 after immersion in aqueous solution of 15% H<sub>2</sub>SO<sub>4</sub> (a-c) and 15% KOH (d-f) during 180 h.



**Figure S5.** Effect of contact time on percent removal of (a) pump oil and (b) Cu(II) and Mn(II) by AG1 and AG2.

Table S1. Quantitative compositions of resins.

Components	Amount (% mass) <sup>a</sup>		
	Resins and derived AG (AG1)	Resins and derived AG (AG1)	
PhF resin <sup>b</sup>	26	25	
PhF resin with methacrylate groups <sup>b</sup>	36	33	
Bisphenol A diglycidyl ether <sup>c</sup>	38	33	
4-vinylpyridine <sup>d</sup>	-	9	
Hexamethylenetetramine <sup>e</sup>	12	11	
10% KOH in water $(mL)^{f}$	1	1.5	
Isopropanol (mL) <sup>g</sup>	1	1	

<sup>a</sup> without hexamethylenetetramine; 10% KOH in water and isopropanol;

<sup>b</sup>PhF resins were synthesized according to a known method with slight modifications (Strap, G.; Astakhova, O.; Lazorko, O.; Shyshchak, O.; Bratychak, M; *Chemistry & Chemical Technology* **2013**, 7 (3), 279–287) and Bratychak M., Strap G., Astakhova O., Shyshchak O.; *Chemistry & Chemical Technology* **2013**, 7 (2), 153-159. All chemical were used of analytical reagent grade as received: phenol ( $\geq$ 99%, Sigma-Aldrich), formaldehyde (36-38% pure p.a., POCH), oxalic acid ( $\geq$ 99.0%, Sigma-Aldrich), glycidyl methacrylate ( $\geq$ 97%, Sigma-Aldrich), KOH ( pure p.a., POCH).

<sup>c</sup> $\geq$ 95.0% (HPLC), Sigma-Aldrich; <sup>d</sup>95%, Sigma-Aldrich; <sup>e</sup> $\geq$ 99.5%, Sigma-Aldrich; <sup>f</sup> pure p.a., POCH; <sup>g</sup> pure p.a., POCH.

Table S2. Deconvolution of the <sup>1</sup>H MAS NMR spectrum of AG2 (cf. Fig. SI1).

Chemical shift $\delta_{1H}$	Content
(ppm from TMS)	(%)
13.4	2.3
8.2	29.6
7.1	8.7
5.3	23.3
1.8	36.1

Aerogel	pH	Sorption capacity for Cu(II)	Sorption capacity for Mn(II)
		(mg/g)	(mg/g)
AG1-1	1.3	0	0
AG1-2	2.0	0.017	0
AG1-3	3.0	0.268	0
AG1-4	4.0	0.694	0
AG1-5	5.0	0.754	0.506
AG2-1	1.3	0	0
AG2-2	2.0	0.248	0.091
AG2-3	3.0	0.534	0.081
AG2-4	4.0	0.534	0.331
AG2-5	5.0	0.833	1.736

**Table S3.** Sorption capacity of 0,03 g AGs towards Cu(II) and Mn(II) as a function of pH.