

Electronic Supplementary Information

Supercritical fluid technology as a new strategy for the development of semi-covalent molecularly imprinted materials

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Morphological, physical and mechanical characterization of the synthesized materials

The morphology of the synthesized copolymers and corresponding hybrid membranes was characterized using scanning electron microscopy (SEM) in a Hitachi S-2400 instrument, with an accelerating voltage set to 15 kV. For cross-section analysis the membrane samples were frozen and fractured in liquid nitrogen. Samples were mounted on aluminum stubs using carbon tape and were gold/platinum coated.

Specific surface area and pore diameter of the polymeric particles were determined by N₂ adsorption according to the BET method. An accelerated surface area and porosimetry system (ASAP 2010 Micromeritics) was used under nitrogen flow.

The contact angle of the membranes was measured with Millipore water droplets in a KSV Goniometer model CAM 100 at room temperature. The water flux of the membranes was determined using a 10 mL filtration unit (Amicon Corp., model 8010) with an effective area of 4.1 cm². All the experiments were carried out varying the applied hydrostatic pressure from 0 to 5 bar.

The tensile properties of the membranes were tested by dynamic mechanical analysis (DMA) with a tensile testing machine (MINIMAT firm-ware v.3.1) at room temperature. The samples were cut into 5 mm × 15 mm strips. The length between the clamps was set at 5 mm and the speed of testing was set to 0.1 mm.min⁻¹. A full scale load of 20 N and maximum extension of 35 mm were used. Measurements were performed with dried membranes. Load extension graphs were obtained during testing and converted to stress-strain curves. The Young's modulus determined and other characteristic parameters concerned with the properties of the materials are in Table 1.

Table 1. Physical and mechanical properties of the copolymers synthesized and corresponding hybrid membranes prepared

Analysis	Material			
	NIP	MIP	PMMA NIP	PMMA MIP
<i>Nitrogen Porosimetry</i>				
BET surface area (m ² .g ⁻¹)	58.2	49.5	-	-
Pore volume (cm ³ .g ⁻¹)	0.07	0.06	-	-
Average pore diameter (nm)	5.0	4.6	-	-
<i>Contact Angle</i> (°)	-	-	81.6	97.1
<i>Young's Modulus</i> (MPa)	-	-	0.34	0.55
<i>Water Flux</i> (L.m ⁻² .h ⁻¹ .bar ⁻¹)	-	-	25.8	8.8

Analyte adsorption quantification

The amount of analytes adsorbed by the matrices was assessed through Equation 1 where [S] corresponds to the amount of analyte bound, C_0 represents the initial molar concentrations of the analyte, C_t corresponds to the concentrations at predetermined time intervals, V represents the volume of the solution and W corresponds to the weight of the polymeric sample.

$$[S] = \frac{(C_0 - C_t) \cdot V}{W} \quad \text{Equation (1)}$$

The samples collected were quantified by UV spectroscopy at 275, 248 and 278 nm for BPA, PRO and EE, respectively. All the experiments were carried out in duplicates.

Scatchard Equation

Data of equilibrium adsorption experiments were processed using the Scatchard equation, where K_a is the association constant, B_{max} the apparent maximum binding capacity, C_e represents the free concentration of substrate in equilibrium and B corresponds to the amount of BPA bound to the polymer.

$$\frac{B}{C_e} = -B \cdot K_a + B_{max} K_a \quad \text{Equation (2)}$$

Table 2 - Binding constants for MIP and NIP as calculated by the Scatchard equation.

Polymer	High-affinity binding sites		Low affinity binding sites	
	$K_a \times 10^5 (M^{-1})$	$B_{max} (\mu\text{mol.g}^{-1})$	$K_a \times 10^5 (M^{-1})$	$B_{max} (\mu\text{mol.g}^{-1})$
<i>MIP</i>	9.9	39.7	0.88	133.6
<i>NIP</i>	-	-	0.40	74.5