



## Periodic Mesoporous Organosilicas as adsorbents for the organic pollutants removal in aqueous phase



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### ABSTRACT

Heavy organic pollutants such as pesticides and pharmaceuticals are found in wastewater and are difficult to remove by microporous adsorbents because of their large size. Mesoporous organosilicas as potential adsorbents for removal of heavy organic pollutants from aqueous phase are investigated. Propylsulfonic acid-functionalized mesoporous silica (SBA-15-SO<sub>3</sub>H) and propylsulfonic acid-functionalized periodic mesoporous benzene-silica (Ph-PMO-SO<sub>3</sub>H) are prepared by co-condensation method. Textural and structural characterizations are conducted by X-ray diffraction, N<sub>2</sub> physisorption, solid state NMR spectroscopy, elemental analysis and confirmed the structural integrity of the materials. Material adsorption behaviors are studied in pesticide, mesosulfuron methyl (MM), removal from aqueous phase. For all the materials, adsorption kinetics are well described by a pseudo-second order model indicating the chemisorption of the MM molecules via acid–basic interaction of the neutral form. Sorption isotherms are S-shape isotherms and can be well fitted by the Freundlich model. Ph-PMO-SO<sub>3</sub>H exhibits higher sorption rate (8.95 mg g<sup>-1</sup> h<sup>-1</sup>) and better sorption capacity (9.70 mg g<sup>-1</sup>) than the mesoporous silica SBA-15-SO<sub>3</sub>H (4.16 mg g<sup>-1</sup> h<sup>-1</sup>, 9.4 mg g<sup>-1</sup>). Furthermore, Ph-PMO-SO<sub>3</sub>H has also the best MM abatement rates in aqueous phase up to 95% for initial concentrations ranging from 4 to 10 ppm than microporous acidic zeolite (HFAU) (~70%) and mesoporous silica SBA-15-SO<sub>3</sub>H (~70%). The phenyl groups in sulfonic PMO material seem to enhance organic pollutant adsorption capacity either by reducing wall hydrophilicity or by favoring the interaction with MM phenyl rings.

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### 1. Introduction

Periodic Mesoporous Organosilicas (PMOs) were synthesized for the first time by three different teams in 1999 [1–3]. This is a class of mesostructured organic–inorganic hybrid nanomaterials wherein the organic moieties are totally incorporated in the walls [4,5]. The inorganic and organic moieties placed alternately along the mesopore walls make PMOs more hydrophobic and stable in water than pure organized silicas (MCM-41 or SBA-15). In addition, PMOs can be functionalized with various organic groups in order to be used in aqueous phase as heterogeneous catalysts or adsorbents [6]. Propylsulfonic acid functionalized phenylene-PMO (Ph-PMO-SO<sub>3</sub>H) has shown a considerable stability when applied as heterogeneous catalyst in aqueous phase medium [7,8] and catalytic activities higher than that of mesoporous silica SBA-15-SO<sub>3</sub>H [7]. The remarkable catalytic activity of these materials was also

observed in the literature on many reactions [9–11]. Only a few references were found in the literature concerning the use of adsorptive properties of PMOs for the removal of organic pollutants in aqueous phase [12–14]. In addition, the molecules studied in these papers are molecules with a relatively small size that easily adsorb on zeolites or activated carbons which are efficient adsorbents and less expensive than the PMOs. However, the removal by adsorption of bulky molecules in the aqueous phase is a challenge. Unlike microporous solids, which do not allow efficient and rapid adsorption of such molecules, mesoporous materials are well adapted for bulky molecule removal. However, the use of conventional silica (MCM-41 or SBA-15) is not recommended because of their high hydrophilicity due to the high superficial silanol density which induce preferential water adsorption and their few number of efficient adsorption sites. The grafting of hydrophobic and adsorption active sites is therefore necessary to use these materials. In the present work, we propose to study the removal by adsorption of mesosulfuron-methyl as model of a bulky organic pesticide, (Fig. 1).

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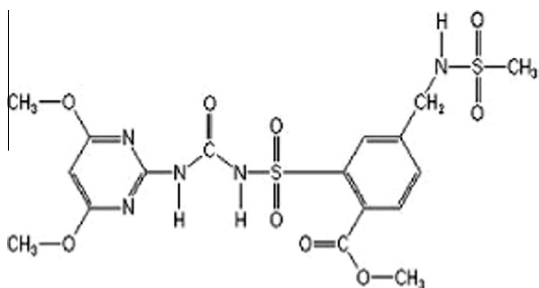


Fig. 1. Mesosulfuron-methyl structure.

The mesosulfuron-methyl (MM) is a compound from the sulfonyleurea family. Compound from this family are typically used as pesticides [15] and as medical agents in the treatment of diabetes [16]. Similarly to sulfonyleurea, MM is a weak acid ( $pK_a = 4.3$ ) and is more persistent in neutral and weakly acid media [17]. These compounds can be found in the natural media and their impact on the human health is not very well known. Furthermore, sulfonyleurea derivative used as pesticides are bulky molecules which cannot be adsorbed on microporous adsorbent such as zeolites. In the present work we propose a comparison of mesosulfuron sorption behavior on the Ph-PMO, Ph-PMO-SO<sub>3</sub>H (containing propylsulfonic acid groups), SBA-15 and propylsulfonic acid functionalized SBA-15-SO<sub>3</sub>H. We particularly investigate the sorption kinetics and capacities as well as the sorption mechanism of MM on the different materials.

## 2. Experimental section

### 2.1. Chemicals

Tetraethyl orthosilicate (TEOS), 1,2-bis(triethoxysilyl)ethane (BTEE), 3-mercaptopropyltrimethoxysilane (MPTMS, 95%), Pluronic® 123 (P123) and octadecyltrimethylammonium bromide (ODTAB), were obtained from Aldrich and used without any further purification. Methanol (HPLC-grade), mesosulfuron-methyl (MM), absolute ethanol, HCl, NaOH, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> – all of analytical grade were also purchased from Aldrich. 1,4-bis(triethoxysilyl)benzene (BTEB) was synthesized via Grignard reaction and distilled in vacuum as reported by Shea et al. [18]. Deionized water was used throughout the synthesis and adsorption processes.

### 2.2. Materials preparation

#### 2.2.1. Synthesis of SBA-15 and SBA-15-SO<sub>3</sub>H

SBA-15 and SBA-15-SO<sub>3</sub>H materials were prepared via one-pot synthesis method using TEOS or a mixture of TEOS with MPTMS, respectively, as precursors. P123 was used as structure directing agent under acidic conditions following the procedure reported by Margolese et al. [19]. For each 4.0 g of the template, the molar composition of each mixture was  $x$  TEOS: (0.041 –  $x$ ) MPTMS: 0.24 HCl: 6.67 H<sub>2</sub>O, where  $x = 0.041$  for SBA-15 and 0.0369 for SBA-15-SO<sub>3</sub>H.

The oxidation of the mercaptopropyl groups to propyl sulfonic groups was achieved by reaction with H<sub>2</sub>O<sub>2</sub>.

#### 2.2.2. Synthesis of PMO and PMO-SO<sub>3</sub>H

Both Ph-PMO and Ph-PMO-SO<sub>3</sub>H were prepared following the procedure described in Refs. [4,5] and [7,20], respectively. The oxidation of mercaptopropyl to sulfopropyl acid groups was performed using HNO<sub>3</sub> as described in [20].

### 2.3. Physico-chemical characterizations

Nitrogen adsorption measurements were performed at –196 °C on gas adsorption system ASAP 2000 (Micromeritics). Prior to measurements, samples without propyl sulfonic were outgassed under secondary vacuum at 300 °C for 12 h while those functionalized with propyl sulfonic were outgassed at a lower temperature (200 °C) to avoid deterioration of the sulfonic group. The BET equation was used to calculate the surface area of the samples at relative pressures between 0.01 and 0.30 and the pore size distribution was obtained from the desorption branch of the N<sub>2</sub> adsorption isotherms using Barret–Joyner–Halenda (BJH) approach.

Powder small-angle X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker AXS D5005 X-ray diffractometer, equipped with a monochromatic CuK<sub>α</sub> radiation ( $\lambda = 1.54184 \text{ \AA}$ ) and operating at 30 mA, 40 kV. Scanning rate of 0.025° s<sup>–1</sup> and step size of 10 s was used for each XRD pattern between 0° and 15° 2 $\theta$  angle.

<sup>29</sup>Si and <sup>13</sup>C solid-state NMR spectra were recorded on (9.4 T) Bruker AVANCE400 spectrometer at 79.49 and 100.62 MHz, respectively. <sup>29</sup>Si magic-angle spinning (MAS) NMR spectra were collected using 40° pulses, 5 kHz spinning rate and 60 s delay. <sup>29</sup>Si cross-polarization magic-angle spinning (CP MAS) NMR spectra were collected using 4  $\mu$ s <sup>1</sup>H  $\pi/2$  pulse; 8 ms contact time 5 kHz spinning rate and 5 s recycle delays. <sup>13</sup>C CP MAS NMR spectra were collected with a 4  $\mu$ s <sup>1</sup>H  $\pi/2$  pulse, 1 ms contact time, 6 kHz spinning rate and 4 s recycle delay.

Thermal gravimetric-differential thermal analysis (TGA-DTA) was performed in platinum crucibles using a SDT Q600 microbalance (TA Instruments) from 30 up to 900 °C under nitrogen atmosphere (50 mL min<sup>–1</sup>) at a heating rate of 2 °C min<sup>–1</sup>.

The acidic strength of the functionalized samples was measured by titration with KOH as described in Ref. [20]. In a typical procedure, 0.03 g of the solid was suspended in 20 ml of 0.1 M KCl. The result suspension was stirred at room temperature for 30 min and then titrated in drops against 0.01 M KOH.

The FT-IR quantification of both Lewis and Brønsted acid sites on the functionalized samples were carried out on FT-IR NEXUS Thermo – Nicolet under secondary vacuum. Prior to the measurement, the thin pellets made from the samples were pre-treated overnight at 200 °C under secondary vacuum. After collecting the reference spectra, pyridine was adsorbed onto the samples up to 2 mbar pressure and ambient temperature. Secondary vacuum was performed to remove physisorbed pyridine molecule and FT-IR spectra were collected at 50, 150 and 200 °C. The amount of Lewis and Brønsted sites present were calculated using Eq. (1).

$$Q_{te} = \frac{A_S}{\epsilon m} \times 1000 \text{ (}\mu\text{mol g}^{-1}\text{)} \quad (1)$$

where  $Q_{te}$ , the quantities in  $\mu\text{mol g}^{-1}$  of the Brønsted sites;  $A$  is the area of the  $\nu_{19b}$  of the pyridinium adsorbed species,  $\epsilon$  is the molar absorption coefficient of the corresponding vibrator, 1.67  $\text{cm}^2 \mu\text{mol}^{-1}$  as given by Emeis [21] and  $m$  is the mass of the pellet in mg.

### 2.4. Adsorption studies

Batch adsorption technique was employed for both kinetic and equilibrium studies. For equilibrium studies, 40 mg of adsorbent was added into a number of sealed glass flasks containing 20 mL of MM solution of different concentration (4–20 mg L<sup>–1</sup>) and stirred for 120 h at 25 °C until equilibration. The pH of the initial solution of MM is fixed to 6 with adding few  $\mu$ L of 1 M NaOH solution. The pH remains almost constant during all the sorption experiment (2% decrease). Samples were collected (20  $\mu$ L and filtered through 0.45  $\mu$ m (X200 NYL) syringe filters. The residual concentration of the pesticide in the filtrate was analyzed with a HPLC

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