



Macroporous silica for concentration of nitroenergetic targets

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ABSTRACT

Hierarchical organosilicate sorbents were synthesized which possess structure on two length scales: macropores of approximately 1 μm lined by mesopores (35–45 Å). The incorporation of macropores provides enhanced flow-through characteristics over purely mesoporous materials, thereby reducing back pressure when used in column formats. Materials of this type with varied surface groups were applied to the adsorption of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) in both batch and column formats. The results presented here demonstrate the potential of these materials for application as solid phase extraction materials for the pre-concentration of nitroenergetic targets from aqueous solutions. The structural and binding characteristics of the materials have been evaluated and preliminary data on the impact of complex matrices is provided.

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1. Introduction

RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and TNT (2,4,6-trinitrotoluene) as well as their associated breakdown products are present in the soil and groundwater at many U.S. Department of Defense testing and training facilities. Many of these compounds are suspected or confirmed carcinogens, and there is concern regarding their ecological impact. Monitoring the presence of such contaminants in the environment is challenging due to the rapid diffusion of targets into the surrounding matrix. Pre-concentration of targets is often necessary to provide levels that are detectable by currently available technologies. In addition, it is often desirable to remove non-target analytes

from samples to prevent their interference with evaluation of targets.

Solid phase extraction (SPE) involves absorbing targets onto a functionalized solid support. Desorption of target is accomplished either through a thermal process or through elution from the support using a solvent. The absorption of targets may be through non-selective, semi-selective, or more specific binding mechanisms. Solid phase microextraction (SPME) is one example of this technique [2–5]. SPME uses chemically modified silica fibers with thermal desorption. The surface area of the sorptive material is low in these systems, and exhaustive extraction of targets generally requires prohibitively long incubation times [5]. Some efforts have focused on increasing the surface area available to this technique [6]. Other efforts have focused on reducing the fragile character of SPME fibers through the use of metals rather than silica [7]. Semi-permeable membrane devices (SPMD) represent another type of SPE material. SPMDs are passive integrative sampling devices that are often used to provide a time-weighted average concentration of contaminants. Like polyethylene (PEDs) and polyoxymethylene (POMs) devices, sorption occurs through partitioning [8–15]. The insensitivity of this approach to short-term variations in concentration can be either an advantage or disadvantage depending on the particular water monitoring application. Equilibration of these devices with environmental conditions often requires days to weeks.

Our efforts in developing SPE materials have focused on periodic mesoporous organosilicas (PMOs) which are hybrid

Abbreviations: SPE, solid phase extraction; SPME, solid phase microextraction; SPMD, semi-permeable membrane devices; PEDs, polyethylene devices; POMs, polyoxymethylene devices; PMOs, periodic mesoporous organosilicas; DEB, 1,4-bis(trimethoxysilyl)benzene; BTE, 1,2-bis(trimethoxysilyl)ethane; PTS, phenyltrimethoxysilane; TMB, mesitylene; BET, Brunauer–Emmett–Teller; BJH, Barrett–Joyner–Halenda; MM1, hierarchical sorbent material; P10, hierarchical sorbent material with surface terminal phenyl groups.

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organic/inorganic materials synthesized by condensing organic-bridged multifunctional silanes around surfactant micelles [16–19]. The materials possess high surface areas with the rugged character of silicates and the binding characteristics expected of organic functional groups. We have previously described the synthesis of ordered and semi-ordered organosilicate materials and their application to the adsorption of nitroenergetic compounds [20]. These materials were synthesized through co-condensation of 1,4-bis(trimethoxysilylethyl)benzene (DEB) and 1,2-bis(trimethoxysilyl)ethane (BTE) in the presence of Brij[®]76 micelles. We were able to demonstrate enhanced order through the use of co-condensation as well as enhanced selectivity through the use of a templating process involving the incorporation of 3,5-dinitrobenzoyl modified Brij[®]76. The modified surfactant provided a target-like structure in contact with the pore walls during condensation. The study focused on optimizing components of the synthesis to provide ordered, semi-selective sorbents for application to 2,4,6-trinitrotoluene (TNT) and dinitrotoluene (DNT) targets in aqueous samples.

While the materials developed in the previous study provided the desired binding characteristics, application of the sorbents was limited by the structural characteristics. The particle sizes in the PMO powders are small resulting in dense packing within a column; there may be poor interconnectivity between the pores throughout a given particle; the pore sizes within the particles are on the order of 30 Å. These aspects combine to produce poor performance in a column format due to the generation of high back pressures. The use of a column format is desirable when designing a system for in-line pre-concentration of targets. One method for reducing the back pressure is to mix these materials with sand or other materials of a controlled larger particle size. This allows for application in column formats; however, it also reduces the capture surface area in the column. In addition, the PMO materials eventually compact to the end of the column resulting in increasing back pressure. In order to address the high back pressures generated by the sorbents, we combined lessons learned through the development of the mesoporous sorbents with a method for the synthesis of monolithic organosilicates employing Pluronic P123 to template the mesostructures. This new method produces a hierarchical material with mesopores organized within macropores. The larger pores provide reduced pressure and increased connectivity and flow. The mesostructure provides the desired high concentration of binding sites. Here, we describe the hierarchical materials and demonstrate their potential for application to the pre-concentration of nitroenergetic targets for the enhancement of detection applications.

2. Experimental

2.1. Reagents

Phenyltrimethoxysilane (PTS), 1,4-bis(trimethoxysilylethyl)benzene (DEB) and 1,2-bis(trimethoxysilyl)ethane (BTE) were obtained from Gelest, Inc. (Tullytown, PA). NaOH, HCl, 3,5-dinitrobenzoyl chloride ($\geq 98\%$), dichloromethane ($\geq 99.5\%$), magnesium turnings (98%), p-cresol (pCr), and p-nitrophenol (pNP) were purchased from Sigma–Aldrich (St. Louis, MO). The activated charcoal used here for comparison purposes was purchased from Sigma–Aldrich (catalog #05113). Nitrogen sorption for this product was used to determine a BET surface area of 905 m²/g and a BJH pore volume of 0.432 cm³/g. Pluronic P123 (referred to here as P123) was a gift from BASF (Mount Olive, NJ). 2,4,6-Trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), nitroglycerin (NG), and 2,4-dinitrotoluene (DNT) were purchased from Cerilliant (Round Rock, TX). Water was deionized to 18.2 M Ω cm using a Millipore Milli-Q UV-Plus water purification system. Artificial sea water was prepared using sea

salts as directed by the supplier (Sigma–Aldrich). Pond water samples were collected from a park in Alexandria, VA, USA.

2.2. Materials synthesis and imprint template

Synthesis of the hierarchical material referred to as MM1 was accomplished using a variation on our previously reported technique [20,21]: 1.66 g P123 was combined with 0.24 g 3,5-dinitrobenzoyl modified P123 (described below) and dissolved with 0.2 g mesitylene (TMB) in 6 g of 0.1 M HNO₃ with stirring at 60 °C. The stirring solution was allowed to cool to room temperature, and a siloxane mixture consisting of 7.84 mmol total bis-silane (BTE+DEB at a molar ratio of 1 to 1) was added drop wise. The reaction mixture was stirred until homogeneous and transferred to a culture tube which was sealed tightly and heated at 60 °C overnight (approximately 18 h). A white gel formed during this period. The tube was unsealed and heated at 60 °C for 2 days followed by incubation at 80 °C for an additional 2 days. The product, in the form of a white monolith, was refluxed three times in ethanol for at least 12 h to extract P123. This process broke the monolith producing a powder. The powder was collected by suction filtration, rinsed with ethanol and water, and dried at 100 °C. Synthesis of a sorbent material with terminal phenyl groups (P10) and no imprint employed a similar protocol using variations on the constituent concentrations. Pluronic P123 (1.9 g) was dissolved with 0.55 g mesitylene (TMB) in 7.5 g of 0.1 M HNO₃. Phenyltrimethoxysilane was incorporated into the material to provide enhanced functionality through the use of a siloxane mixture consisting of 7.84 mmol total silane with a BTE:DEB:PTS molar ratio of 50:40:10.

The imprint template for the materials was prepared by esterification of Pluronic P123 with 3,5-dinitrobenzoyl chloride. This was accomplished as follows [20]: 8 g P123, 1.27 g 3,5-dinitrobenzoyl chloride, and magnesium turnings were added to 60 mL dichloromethane and refluxed for 2 h. The solution was shaken with 60 mL 2% aqueous NaHCO₃. The organic phase was collected and evaporated to yield the yellow, derivatized surfactant.

2.3. Characterization methods

A Micromeritics ASAP 2010 was used for N₂ sorption experiments performed at 77 K. Prior to analysis, samples were degassed to 1 μ m Hg at 100 °C. Standard methods were applied to the calculation of characteristics. Surface area was determined by use of the Brunauer–Emmett–Teller (BET) method; pore size was calculated by the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the isotherm; total pore volume was calculated by the single point method at relative pressure (P/P_0) 0.97. Thermogravimetric analysis was performed using a TA Instruments Hi-Res 2950 Thermogravimetric Analyzer under a N₂ atmosphere; temperature was ramped 5 °C/min to 800 °C. Powder X-ray diffraction patterns were obtained with a Rigaku high-resolution powder diffractometer with 18 kW CuK α radiation derived from a high-power Rigaku rotating anode X-ray generator.

Conducting carbon tape was used to mount samples on SEM stubs for imaging by scanning electron microscopy (SEM). Sputter coating with gold under argon was accomplished using a Cressington 108 auto sputter coater for (duration 60 s). Scanning electron micrographs of the samples were collected using a LEO 1455 SEM (Carl Zeiss SMT, Inc., Peabody, MA). For imaging via transmission electron microscopy (TEM), samples were deposited onto a holey carbon grid (200 mesh copper, SPI, West Chester, PA) and viewed under an energy filtering transmission electron microscope (LIBRA 120 EFTEM, Carl Zeiss SMT, Peabody, MA) operated at 120 kV. Zero Loss, brightfield, energy filtered (EF) TEM images were captured on a bottom-mounted, digital camera (KeenView, Olympus SIS, Montvale, NJ).

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