Self-reporting materials: Dual use for porphyrin-embedded sorbents

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ABSTRACT

A previous effort demonstrated the utility of porphyrin functionalized organosilicate sorbents in the removal of phosgene. The current study sought to characterize the spectrophotometric response of the sorbents during their application to determine the potential for dual use in both removal of phosgene and reporting on phosgene exposure. The effort is intended as a first step toward using the materials for self-reporting or residual life indication. An ethane bridged silica was functionalized using deuteroporphyrin IX 2,4 bis-ethylene glycol. Several metalloporphyrin variants were generated based on this porphyrin functionalized sorbent, and fluorescence characteristics were evaluated in the prior to and following exposure to phosgene. Reflectance characteristics and changes upon target exposure were also evaluated. Cu, Mg, and Zn sorbents showed the most significant changes upon exposure to phosgene. The reflectance characteristics of these sorbents were evaluated across a range of loading levels for sorbent columns to the point of complete target breakthrough. The results indicate the possibility for reflectance or visual inspection based end-of-life indication for these sorbents.

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1. Introduction

In 2009, a memorandum for record (MFR) was released by the Toxic Industrial Chemical/Toxic Industrial Material (TIC/TIM) Task Force [2] focusing on ocular and inhalation hazards in an operational environment. The document provides a list of 16 compounds prioritized based on toxic hazard and the likelihood of an encounter. Phosgene is one of the compounds identified by this document in which it is classified as a self-polymerizer (reactive monomer). While phosgene is well known as a World War I era chemical warfare agent, it is also widely used in industrial and pharmaceutical chemical processes. This availability results in a greater threat than that presented by more toxic compounds that are not utilized by civilian processes. Current NIOSH recommendations indicate the use of self-contained breathing apparatus for persons working in areas of potential exposure. The warfighter, however, utilizes cartridge-based air purifying respirators for protection against chemical exposure. This method can be effective provided the cartridges have not exceeded their service life as a result of the contaminants encountered, the concentration levels of those contaminants, breathing rates, etc. Improvements in cartridge based systems including active residual life indicators and regenerable or catalytic cartridge materials are of ongoing interest.

In a previous report, we demonstrated the use of metalloporphyrin embedded organosilicate sorbents for the capture and photocatalytic removal of phosgene [3]. The nature of the metalloporphyrins used to provide affinity and catalytic activity within the organosilicate materials makes them ideally suited to a spectrophotometric reporting application. The porphyrin component of the construct offers a highly conjugated macrocycle with strong, sensitive spectrophotometric characteristics. These characteristics as well as the interaction characteristics of porphyrins can be varied through altering the porphyrin structure and through incorporation of metal atoms at the central coordination site. Varying the coordinated metal ion has been shown to significantly impact the sensitivity of spectrophotometric characteristics to the presence of ammonia, for example [4]. The structure of the porphyrin or phthalocyanine has also been shown to impact both response to ammonia and the reversibility of that response [5,6].

Porous organosilicates offer a number of features owing to their structural and chemical composition. Their silicate nature makes them rugged and stabile. The materials are suitable for application across a wide range of temperatures, are not subject to swelling/contracting due to changes in humidity, and are tolerant to a number of solvents. As a result, porous organosilicates have been utilized in a wide range of catalysis and sensing applications [7–9] as well as in the capture and detection of gases [10,11]. Here, their high surface area and large interconnected pore volume provide an ideal scaffold for immobilization of porphyrin moieties. Selectivity in the porous materials can be altered through changing the polysilsesquioxane precursors utilized or through grafting

onto the sorbent surfaces. Coordinated metals within a structure, for example, have been used for detection of nitric oxide [10,12] and carbon monoxide [13]. The silica component of these materials provides structural rigidity while the organic groups offer control over the interaction of the scaffold with targets [14–16]. The wetting properties of a sorbent, for example, can be altered through selection of the bridging groups. The materials utilized in the current study, combine controlled mesoporosity (2–50 nm) with macroscale texture (>50 nm) to improve access to the mesopore volume, which is advantageous to diffusion dependent applications [17–19]. The macropores also provide improved flow through the sorbents (reduced pressure drop).

We have previously reported on our efforts directed at combining the materials characteristics provided by organosilicate scaffolds with the optical and catalytic properties of porphyrins [6,14,16,20]. Those efforts took varied approaches to scaffold design. For larger liquid targets, the scaffold provided high binding capacity and selectivity for the targets [14,16,20]. For light gases, we utilized the scaffold as purely that and incorporated binding sites through grafting onto the scaffold surface [3,6,21]. This study details the spectrophotometric response characteristics of DIX-modified sorbents with varied metal coordination to phosgene with a view toward demonstrating their potential for dual use in both removal of phosgene and in self-reporting of the sorbent condition. Both fluorescence and reflectance analysis are discussed.

2. Experimental

Deuteroporphyrin IX 2,4 bis-ethylene glycol (DIX) was obtained from Frontier Scientific, Logan, UT. Pluronic®P123 was generously donated by BASF. Mesitylene (1,3,5-trimethylbenzene or TMB), 3-aminopropyltrimethoxysilane (APS) and 1,2-bis(trimethoxysilyl)ethane (BTE), tryptamine, and phosgene (20% in toluene) were purchased from Sigma–Aldrich (St. Louis, MO). 1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide (EDC) was purchased from Pierce Chemical Company (Rockford, IL). Chemicals were used as received. Water was deionized to $18.2\,M\Omega\,cm$ using a Millipore Milli-Q UV-Plus water purification system.

2.1. Material synthesis and porphyrin incorporation

Our preparation method for the materials using Pluronic P123 in acidic media has been described elsewhere [18,21]. Briefly, 1.9 g Pluronic P123 and 0.3 g TMB were dissolved in 9.5 g 0.1 M HNO$_3$ with stirring at 60 °C. When the solution had cooled to room temperature, a precursor mixture of 2.12 g BTE and 0.025 g APS was added drop-wise. The reaction mixture was stirred until homogeneous and heated in a sealed tube overnight at 60 °C. The tube was unsealed and heated at 60 °C for 2 d, and then 80 °C for 2 d. The product in the form of a white monolith was refluxed three times in 1 M HCl in ethanol for at least 12 h to extract the surfactant, a process that resulted in breaking up the monolith to a powder. The powder was collected by suction filtration, rinsed with ethanol and water, and dried at 110 °C. Morphological characterization for this sorbent has been reported previously [3,6]. Prior to metalloporphyrin functionalization, the amine-functionalized material had a surface area of 925 m^2/g, a pore volume of 0.72 cm^3/g, and an average pore diameter of 62 Å. Metalloporphyrin functionalization resulted in a surface area of 425 m^2/g, a pore volume of 0.31 cm^3/g, and an average pore diameter of 62 Å.

Porphyrin incorporation into the amine-functionalized sorbent was accomplished using EDC coupling chemistry. The organosilicate material (1 g) was placed in a solution of 5 mM EDC and 0.6 mM porphyrin in 100 mM MES buffer (2-(N-morpholino)ethanesulfonic acid; total volume 50 mL). The solution was incubated overnight with agitation and collected by vacuum filtration. It was then rinsed with ethanol and water. Metals were incorporated into the porphyrin-functionalized material by refluxing the sorbent in a solution of 1 mM metal salt in deionized water overnight. Metal salts used were copper (II) chloride (CuDIX), cobalt (II) acetate (CoDIX), magnesium chloride hexahydrate (MgDIX), europium (II) chloride (EuDIX), iron (II) chloride (FeDIX), zinc chloride (ZnDIX).

2.2. Target interaction

The fluorescence response of the sorbents to phosgene was determined in 96-well plate format with a Tecan XSafire monochromator-based microplate reader (2 nm resolution). Emission wavelengths were selected to be those providing maximum fluorescence intensities for the given porphyrin. Fluorescence spectra of the porphyrin-functionalized materials (5 mg of dry powder) were collected prior to and following target exposure. Difference spectra are calculated as the point-by-point subtraction of the pre-exposure spectrum from the post-exposure spectrum. Fluorescence measurements were completed in triplicate in order to verify the capture of representative behaviors for the materials.

In order to evaluate reflectance characteristics for the materials, scanned images were used. Sorbent materials (50 mg, ±2 mg) were packed in borosilicate glass Pasteur pipettes using glass wool as frits. Phosgene exposure was accomplished batch wise through application of indicated quantities in 50 mL ambient air volumes with flow through the column and into an impinger solution (detailed below) at 15 mL/min. For collection of reflectance spectra by scanner, porphyrin-embedded materials packed in Pasteur pipettes were exposed to ambient air (100 mL) to equilibrate with experimental conditions. Columns were placed on the surface of a Canon CanoScan N670U flatbed scanner with a control swatch for color profile verification. Images were collected for the columns before and after exposure to phosgene and after a final air purge. The scanned images were analyzed using Adobe Photo-Shop CS3 Extended (version 10.0.1). Control swatch color profile did not vary between images. Average RGB (red, green, and blue) color values across each sample obtained using Adobe Photoshop CS3 are reported here [14]. Reflectance experiments were repeated in duplicate to insure that representative behavior was captured for the materials.

2.3. High performance liquid chromatography

Analysis of phosgene concentrations was accomplished using an adaptation of a published protocol. An impinger solution of 1 mg/mL tryptamine in acetonitrile was prepared and aliquoted into scintillation vials (20 mL each). Impinger solutions were prepared fresh on the day during which they were used. Control samples (50 mL) were bubbled through the impinger solution, and five point calibration curves were prepared identically each day. All samples were allowed to dry completely (on a 90 °C hotplate) and resuspended in 8 mL acetonitrile. Acetic acid (200 μL, 1% in acetonitrile) was added to the acetonitrile, and the sample was incubated for 30 min at room temperature. Water (100 μL) was then added to the sample, and it was incubated for an additional 30 min. The sample was then diluted with the HPLC mobile phase by a factor of 10 and filtered prior to HPLC analysis (0.2 μm PTFE syringe filter). HPLC analysis was completed using a Shimadzu High Performance Liquid Chromatography system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC) coupled to a fluorescence detector (RF10-AxL). The stationary phase was a 250 mm × 4.6 mm Waters Symmetry C18 (5 μm) analytical column. The mobile phase was