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Electrochemical detection of TNT with in-line pre-concentration using imprinted diethylbenzene-bridged periodic mesoporous organosilicas

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ABSTRACT

We examined the adsorption and release of TNT using diethylbenzene-bridged (DEB) periodic mesoporous organosilica sorbents under varying conditions. The sorbents were applied for in-line target pre-concentration in conjunction with an electrochemical flow cell containing a glassy carbon electrode. Square wave voltammetry was employed for TNT detection. TNT sample volumes between 2 and 480 mL at concentrations ranging from 0.5 to 500 ppb were passed through the DEB sorbents (imprinted or not imprinted for TNT) at pH 6 (sodium acetate) or at pH 7.4 (PBS). Release of target was accomplished using solvent mixtures of methanol/water with sodium acetate as electrolyte or acetonitrile/water with PBS components as electrolyte. Under these conditions, the TNT was released in <200 μL of the solvent mixture, and pre-concentration factors of >3000 can be achieved when using large volumes of trace TNT samples. When sample volumes of 2 mL were utilized, the sensing system gave a linear response between 20 and 500 ppb with an estimated limit of detection of 13 ppb. When pre-concentrating 480 mL of sample in either buffered solution or seawater, detection of 0.5 ppb TNT was achieved with a signal to noise ratio of 20.

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1. Introduction

Electrochemical detection schemes benefit from the inherent advantages of electrochemical transducers that use simple instrumentation and have the ability to incorporate the detection element into integrated circuitry [1,2]. These advantages have been utilized for the direct electrochemical detection of certain types of explosives such as 2,4,6-trinitrotoluene (TNT) since nitroaromatic compounds are easily reduced. Current electrochemical techniques for TNT detection include the use of liquid chromatography or capillary electrophoresis with carbon [3] and gold electrodes [4–6]. Typical detection limits for these methods are between 10 and 80 ppb. Square-wave voltammetry employing activated carbon fiber electrodes or screen-printed carbon electrodes offers limits of detection (LOD) at 25 ppb [7] and 100 ppb [8], respectively. Using adsorptive stripping voltammetric measurements with carbon nanotube-modified glassy carbon electrodes, LODs of 0.6 ppb have been reported with good precision using a deposition time of 10 min [9]. Recently, we reported using interdigitated electrode arrays (IDA) for amplified detection of TNT using redox cycling and achieved an LOD of 6 ppb [10]. Modified electrodes employing, for example, a porphyrin polymer have been shown to provide similar detection limits (8 ppb) [11].

A major obstacle to application of electroanalytical techniques in a fielded platform is their limited sensitivity. For homeland security and military needs in particular, rapid detection of trace levels of explosives can provide warning of the need for preventative steps [12–15]. In environmental monitoring, trace detection can make it possible to reduce the costs of remediation through early action. In order to achieve this type of trace detection, it is necessary to provide detection methods of increased sensitivity or methods for enhancing the concentration of targets to within the range detectable by existing techniques. Pre-concentration of targets utilizes large volume samples to provide sufficient analyte mass for obtaining a detectable signal. A recent example of this approach uses an integrated pre-concentrator with an electrochemical detection system applied to the detection of TNT vapor [16]. Solid-phase extraction (SPE) techniques have been successfully applied to the pre-concentration of aromatic explosives from aqueous samples; however, the numerous steps involved in SPE can be lengthy and time-consuming [17–20]. Commercially available resins such as divinylbenzene-vinyl-pyrrolidone (Porapak R) and divinylbenzene-ethylvinylbenzene (LiChrolute EN) have been evaluated for microscale SPE of nitroaromatics and show promise for enhancing LODs [20]. These types of materials offer only low selectivity and a limited number of reuse cycles. As such, new

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materials and techniques [21] for enhancing the performance of electrochemical sensing systems are still desirable [22].

Molecularly imprinted polymers are attractive candidates for the development of pre-concentration materials. Recognition sites for a desired analyte can be created in a polymer through the use of a temple molecule which creates an imprint site complementary in size and electronic structure to the desired analyte [23–28]. Organosilica sorbents synthesized using structure directing surfactants [29–31] have also gained increasing attention as pre-concentration sorbents [32,33] because of their high adsorption capacities [34] as well as their mechanical and thermal stability [35,36]. The ordered pore structures and narrow pore size distributions of benzene-bridged organosilica sorbents are morphologically attractive while similarly prepared diethylbenzene-bridged sorbents traditionally have higher target adsorption capacities and amorphous pore structures with broad pore size distributions [37,38].

Previously, we have demonstrated significant enhancement in detection limits of TNT when molecularly imprinted benzene and diethylbenzene-bridged mesoporous organosilica sorbents were applied as in-line pre-concentration materials. In that study, a glassy carbon electrode was used in an electrochemical flow cell, and an LOD of 5 ppb was obtained [39]. The sorbents applied combined desirable characteristics from molecularly imprinted polymers with those of organosilica sorbents. Molecular imprinting was accomplished through the use of a target analog mixed with the structure directing surfactant during synthesis. Unfortunately, the trinitrobenzene-modified target analog mixed poorly with the Brij®76 surfactant, and the resulting DEB-bridged silica did not display regular mesoporosity. In order to improve the miscibility of the target analog, a new molecule was synthesized through functionalization of Brij®76 with a dinitrobenzene group. Using a mixture of Brij®76 and the modified-Brij®76, a sorbent was synthesized from a mixture of ethane- and DEB-bridging groups [40]. This material offered significantly improved morphological characteristics as well as enhanced selectivity as a result of the imprinting process.

More recently, the synthesis of ethane-DEB and DEB organosilica sorbents with ordered mesopore structures has been accomplished using Pluronic®P123 as the structure directing surfactant [41]. Another development is in the combination of “polymerization-induced phase separation” and surfactant direction in syntheses to create sorbents with hierarchical macropore–mesopore structures [42–45]. Such materials are advantageous for applications in column formats because the macropores of approximately 1 μm can allow more facile flow of solvent and access to mesopores without the prohibitive back-pressures observed in purely mesoporous materials. These types of hierarchical macroporous–mesoporous DEB-containing organosilica sorbents have also been imprinted using the technique described above. They have been applied to the pre-concentration of nitroenergetic targets from a variety of matrices prior to HPLC analysis [22,46]. The binding capacity, binding affinity, and selectivity have been reported previously [47]. In addition, the materials have been reused repeatedly without loss of performance. The study presented here evaluates the effect of differing buffer compositions on pre-concentration and release of TNT from these novel sorbents and presents data on the optimization of protocols for use of the sorbents with electrochemical detection.

2. Experimental

2.1. Materials

Bis(trimethoxysilylethyl)benzene (DEB precursor, a mixture of para and meta isomers) was obtained from Gelest, Inc.; mesitylene (1,3,5-trimethylbenzene or TMB), 3,5-dinitrobenzoyl chloride ≥98%, dichloromethane ≥99.5%, and nitric acid 70% from Sigma–Aldrich; hydrochloric acid 37% from Fisher; and ethanol (200 proof) from the Warner-Graham Company. Pluronic®P123 was a generous donation from BASF. Phosphate buffered saline (PBS) contained 0.01 M phosphate buffered saline (NaCl = 0.138 M; KCl = 0.0027 M) at pH 7.4. All chemicals were used as received. Deionized water was obtained from a Milli-Q water purification system (Millipore). Sea water samples were retrieved from coastal waters near Duck, NC and filtered prior to use.

2.2. Materials syntheses

The target analog was produced by esterification of Pluronic®P123 with 3,5-dinitrobenzoyl chloride [47]. Pluronic®P123 (8 g), 3,5-dinitrobenzoyl chloride (1.27 g), and magnesium turnings were added to dichloromethane (60 mL) and refluxed for 2 h. The solution was shaken with 2% aqueous $NaHCO_3$ (60 mL). The organic phase was collected and evaporated to yield a yellow, derivatized surfactant.

Hierarchical imprinted and non-imprinted DEB-bridged silicas were synthesized as described previously [22,40,47]. A total of 1.9 g surfactant was dissolved with 0.9 g TMB in 0.1 M HNO_3 (7.5 g) with stirring at 60 °C. For the imprinted DEB material (imp-DEB) the surfactant was a mixture of Pluronic®P123 (1.66 g) and target analog (derivatized Pluronic®P123, 0.24 g) while for the non-imprinted DEB material (DEB) it was purely Pluronic®P123. The stirring solution was cooled to room temperature and 2.937 g (0.784 mmol) DEB precursor was added drop-wise. The reaction mixture was stirred until homogeneous and then transferred to a culture tube, which was sealed tightly and heated at 60 °C overnight (approximately 18 h). The tube was unsealed and heated at 60 °C for 2 days, and then 80 °C for 2 days. Product in the form of a white or yellowish monolith was refluxed three times in 1 M HCl/ethanol for at least 12 h to extract the surfactant, transforming the monolith into a powder. Material was collected by vacuum filtration, washed with ethanol and water, and dried at 100 °C.

2.3. Materials characterization

Nitrogen adsorption experiments were performed on a Micromeritics ASAP 2010 porosimeter at 77 K (Micromeritics Instrument Corporation, Norcross, GA). Samples were degassed to 1 μm Hg at 100 °C prior to analysis. Surface area was determined by use of the Brunauer–Emmett–Teller (BET) method, pore size was calculated by the Barrett–Joyner–Halenda (BJM) method from the adsorption branch of the isotherm, and total pore volume was determined 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 nitrogen atmosphere; temperature was ramped 5 °C/min to 800 °C (TA Instruments, Inc., New Castle, DE). Powder X-ray diffraction patterns were collected at room temperature using Cu Kα radiation from a Brüker MICROSTAR-H X-ray generator operated at 40 kV and 30 mA equipped with a 3 m Radian collimator, and a Brüker Platinum-135 CCD area detector. A custom fabricated beam-stop was mounted on the detector to allow data collection to approximately 0.4° 2θ (approximately 210 Å) with a sample to detector distance of 30 cm. After unwarping the images, the XRD^2 plug-in was used to integrate the diffraction patterns from 0.5° to 8.2° 2θ. Scanning electron microscopy (SEM) samples were mounted on SEM stubs using conducting carbon tape. Sputter coating with gold under argon was accomplished using an auto sputter coater (Cressington 108) for a duration of 60 s. SEMs were collected using a LEO 1455 SEM (Carl Zeiss SMT, Inc., Peabody, MA). Instrument settings were as follows: tungsten filament, secondary electron detector,