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# An integrated theoretical and experimental investigation of insensitive munition compounds adsorption on cellulose, cellulose triacetate, chitin and chitosan surfaces

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ABSTRACT

This manuscript reports results of combined computational chemistry and batch adsorption investigation of insensitive munition compounds, 2,4-dinitroanisole (DNAN), triaminotrinitrobenzene (TATB), 1,1-diamino-2,2-dinitroethene (FOX-7) and nitroguanidine (NQ), and traditional munition compound 2,4,6-trinitrotoluene (TNT) on the surfaces of cellulose, cellulose triacetate, chitin and chitosan biopolymers. Cellulose, cellulose triacetate, chitin and chitosan were modeled as trimeric form of the linear chain of $^4C_1$ chair conformation of β-D-glucopyranos, its triacetate form, β-N-acetylglucosamine and D-glucosamine, respectively, in the 1 → 4 linkage. Geometries were optimized at the M062X functional level of the density functional theory (DFT) using the 6-31G(d,p) basis set in the gas phase and in the bulk water solution using the conductor-like polarizable continuum model (CPCM) approach. The nature of potential energy surfaces of the optimized geometries were ascertained through the harmonic vibrational frequency analysis. The basis set superposition error (BSSE) corrected interaction energies were obtained using the 6-311G(d,p) basis set at the same theoretical level. The computed BSSE in the gas phase was used to correct interaction energy in the bulk water solution. Computed and experimental results regarding the ability of considered surfaces in adsorbing the insensitive munitions compounds are discussed.



## Introduction

Manufacturing, transportation and storage of traditional munitions compounds are challenging due to their sensitivity towards external stimuli such as temperature, pressure, shock, etc., which can result in an unplanned detonation. In accordance with Department of Defense Instruction (DoDI) 5000.02 and 10 U.S.C. 2389 and to avoid unintentional detonations, a new class of munitions compounds known as insensitive munitions (IMs) is currently being developed (Ampleman, 2010; Walsh et al. 2013; Boddu et al. 2008; Spear et al. 1989). Examples of some of the IM compounds are 2,4-dinitroanisole (DNAN), triaminotrinitrobenzene (TATB), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ) and 1,1-diamino-2,2-dinitroethene (FOX-7). Production, storage, transportation and application of IMs may lead to their leaching in the environment. For example, use of IMs in Army training ranges can contaminate soils and nearby

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aquifers and cause leaching to groundwater; the use of traditional munitions also causes this issue. Detailed environmental fate and effects data of these molecules are currently under intense investigation (Hawari, 2013, 2014). Some studies have suggested the photosensitive nature of these compounds when left exposed to solar radiation or simulated solar radiation (Hawari, 2013, 2014; Rao et al. 2013).

Polysaccharides are ubiquitous in nature and their molecular structures and properties vary over a broad range. Cellulose and chitin are low-cost biodegradable polysaccharides and are the two most abundant biopolymeric materials that are available and environmentally benign in nature. Cellulose is a natural polysaccharide and is a major component of plant cell walls, while chitin is synthesized mainly in lower animals (Kurita 2001). Cellulose is characterized by the linear chain of 1 ➔ 4 linked polymer of β-D-glucopyranose in the $^4C_1$ chair conformation. Chitin, an amino polysaccharide, is structurally similar to cellulose except for the presence of acetamide groups at the C2 position. Commercial production of chitin is obtained from the shells of crustaceans, such as crabs and shrimp, available as wastes from sea food industries. Deacetylation of chitin through the alkaline treatment produces chitosan which has found numerous applications in cosmetics, food processing, fabrics and water treatment (Lee et al. 2013; Kurita 2006). Because of their biodegradable and renewable abilities, both cellulose and chitin are regarded as the greenest available renewable polymeric materials on earth. This class of materials has been studied as potential low cost cellulose-based adsorbents (CBAs) for environmental contaminants such as polycyclic aromatic hydrocarbons (PAHs) and metals (Hokkanen et al. 2016; Perez et al., 2004; Kang et al., 2010; Ritchie et al., 1999). Moreover, cellulose fibers have long served as raw material in the textile and paper industries or in composite material as filler (Bledzki and Gassan 1999). Composting of munitions-contaminated soils, a natural bioremediation process, has been used at laboratory scale as a potential economical bioremediation technique (Doyle et al., 1986; Thorn et al., 2002; Ahmad et al., 2007). Additionally, Jenkins et al. (1987) have investigated the sorption properties of various disposable filter materials against munitions compounds in aqueous and mixed-organic solvent matrices. The cellulose triacetate filter was found to adsorb significant amounts of munitions compounds such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT) (Jenkins et al. 1987). We have recently performed computational and experimental investigation on adsorption of DNAN, FOX-7 and TNT on the cellulose surface (Shukla and Poda 2016). It was revealed that these molecules would show weak adsorption on cellulose surfaces with FOX-7 showing strongest among them and adsorption was characterized by the presence of weak hydrogen bonds. Moreover, cellulose films showed much higher water uptake compared to the adsorbate solutions.

This manuscript reports the results of an integrated computational and experimental investigation of adsorption of some munitions compounds (DNAN, TATB, NQ, FOX-7 and TNT) on cellulose, cellulose triacetate, chitin and chitosan surfaces. The objective of the present investigation is the fundamental understanding of adsorption of these munitions compounds on biopolymer surfaces. Moreover, the possibility of these surfaces as cost-effective and environmentally biodegradable materials for the removal of considered munition compounds in water has also been explored. The novelty of the current research pertains to the possible application of considered biodegradable surfaces for environmental remediation. It was found that cellulose triacetate would be promising material for removal of DNAN and TNT from water bodies. None of the surfaces analyzed removed significant amounts of NQ or FOX-7 from solution. TATB was strictly analyzed computationally due to its extremely poor water solubility.

## 1. Computational and experimental details

### 1.1. Computational approach

In the theoretical calculations, the surfaces were modeled as linear chain of trimer forms of monomers of respective sugar analogs of cellulose, cellulose triacetate, chitin and chitosan in the 1 ➔ 4 linkage. Geometries of the modeled surfaces, adsorbates (DNAN, NQ, FOX-7 and TNT) and modeled surface-adsorbate complexes were optimized in the gas phase and in the bulk water solution using the M06-2X meta-hybrid density functional theory (DFT) functional and the 6-31G(d,p) basis set. Harmonic vibrational frequency analysis was performed to ascertain the nature of potential energy surfaces (PESs) of optimized geometries and all geometries were found to be minima at the respective PES. The conductor-like polarizable continuum model (CPCM) approach was used to model the effect of bulk aqueous solution (Cossi et al. 2003). Interaction energies between the adsorbate and adsorbent in the gas phase were computed at the same theoretical level and using the 6-311G(d,p) basis set and were corrected for basis set superposition error (BSSE) using counterpoise correction scheme (Boys and Bernardi 1970). The interaction energies of complexes in the bulk water solution, hereafter called basis set superposition error (BSSE) corrected interaction energies in bulk water, were obtained using the formula:

$$\Delta E_{Int}(CPCM) = E_{AB}(CPCM) - E_A(CPCM) - E_B(CPCM) + BSSE_{gas}$$

where, $E_{AB}$(CPCM) represents the total energy of the complex in the bulk water, $E_A$(CPCM) and $E_B$(CPCM) represent the total energy of the monomers A and B respectively in the bulk water within the complex geometry optimized in water and $BSSE_{gas}$ represents the BSSE correction obtained from the gas phase calculation using the counterpoise correction scheme. All calculations were performed using Gaussian 09 program (Frisch et al., 2009).

### 1.2. Materials and methods

#### 1.2.1. Materials

The following adsorbents were evaluated in this study: microcrystalline cellulose, cellulose triacetate, chitin and chitosan. Microcrystalline cellulose was provided by J.T. Baker. Cellulose triacetate (CAS: 9004-35-7) was supplied by



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