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

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Nitroguanidine (NQ)

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 \(\beta\)-D-glucopyranos, its triacetate form, \(\beta\)-N-acetylglucosamine and D-glucosamine, respectively, in the 1 \(\rightarrow\) 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.

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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 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 C1 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 TATB 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:

\[
\Delta E_{\text{BSSE}}(\text{CPCM}) = E_{\text{AB}(\text{CPCM})} - E_{\text{A}(\text{CPCM})} - E_{\text{B}(\text{CPCM})} + \text{BSSE}_{\text{gas}}
\]

where, \(E_{\text{AB}(\text{CPCM})}\) represents the total energy of the complex in the bulk water, \(E_{\text{A}(\text{CPCM})}\) and \(E_{\text{B}(\text{CPCM})}\) represent the total energy of the monomers A and B respectively in the bulk water within the complex geometry optimized in water and \(\text{BSSE}_{\text{gas}}\) 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 Sigma Aldrich with an average molecular weight of...
approximately 30,000 by GPC; this material contained 39.8% acetyl and ≤3.0% water by weight. Chitin (CAS: 1398-61-4) was provided in practical grade, powder form from shrimp shells by Sigma Aldrich. Chitosan (CAS: 9012-76-4) was supplied in practical-grade form from crab shells by Sigma Aldrich.

The DNAN used in this study was purchased from Alpha Aesar (Thermo Fisher Scientific, MA, USA, CAS Number 119-27-7, 98% purity). NQ was supplied by Chem Service, Inc. (PA, USA, CAS number 556-88-7, purity not provided though minimum 20% by weight is composed of water). FOX-7 was synthesized at Los Alamos National Laboratory. TNT was supplied by Eastman Kodak Co. (NY, 25% by weight is composed of water). These materials were each provided in solid form and were dissolved in 18.2 MΩ organic-free reagent water produced onsite using an ELGA PURELAB Classic purifier. Trifluoroacetic acid (TFA; 99.5% purity) was included in this study as a solvent in an eluent stream for HPLC analysis. The scintillation vials were sealed and agitated for 24 hr using an Eberbach shaker at 180 r/min.

1.2.2. Sample preparation
Samples for batch adsorption were prepared such that 500 mg of each adsorbent were collected in 20-mL glass scintillation vials. Then, 2-mg/L solutions of each adsorbate were prepared and added via 1-10 mL pipet to the adsorbent samples. The scintillation vials were sealed and agitated for 24 hr using an Eberbach shaker at 180 r/min.

For distribution coefficient analysis, the following masses of each adsorbent were added to 20-mL glass scintillation vials: 10 mg, 20 mg, 40 mg, 60 mg, 80 mg and 100 mg; samples were measured with ±1 mg precision. For DNAN and TNT, 10 mg/L solutions were prepared using 18.2 MΩ water. Then, 10 mL samples of the adsorbate solutions were individually added via 1-10 mL pipet to the adsorbent samples; three replicates were prepared for each adsorbate-adsorbent mixture. The scintillation vials were sealed and agitated using the procedure described previously.

Supernatant samples were subsequently removed from each adsorbent sample and filtered using 0.45-micron, HPLC-grade PVDF syringe filters. Filtered effluents were analyzed via HPLC for resulting adsorbate concentrations immediately following filtration without subsequent dilution with water or solvent.

1.2.3. Analytical method
Analytes were quantified using a Dionex Ultimate 3000 HPLC system utilizing a TCC-3000SD Thermostatted Column Compartment and a UVD 340 U U/V/Vis Photodiode Array Detector (Thermofisher, MA). Chromeleon 7 software was used for chromatographic analysis. The analytical column used for this study was a Synergi™ 4 micron Polar-RP 80 A, LC column, 250 × 2 mm (Phenomenex, Inc.). This column was chosen based on its enhanced retention of polar and aromatic compounds. A 4 mm ID × 2 mm Polar-RP Security Guard™ column was used to prolong the life of the analytical column.

DNAN and TNT were analyzed using a gradient method. Initially, 100% premixed 18.2 MΩ water +0.1% (V/V) TFA eluent solution was used. After 2 min, the eluent solution was adjusted linearly to provide a solution containing 50% (V/V) 18.2 MΩ water +0.1% TFA and 50% (V/V) ACN 15 min after injection. This final eluent mixture was held constant until the sample run ended 20 min after injection. A 5-min. equilibration period was incorporated between samples to ensure a 100% premixed 18.2 MΩ water +0.1% TFA eluent solution at injection. DNAN and TNT were analyzed at a wavelength of 254 nm. This method was capable of effectively analyzing NQ and FOX-7, as well. However, the analytical method was adjusted to ensure optimum HPLC throughput during analysis.

NQ and FOX-7 were analyzed using an isocratic method with an eluent stream composed of a premixed 18.2 MΩ water +0.1% TFA. NQ and FOX-7 were analyzed at wavelengths of 263 nm and 341 nm, respectively. The runtime for each sample was 5 min; no equilibration stage was used.

For each analytical method used in this study, a flowrate of 0.750 mL/min was maintained. The column temperature was maintained at 30.0°C. The HPLC was calibrated using solutions prepared with TNT, DNAN, NQ and FOX-7 in 18.2 MΩ water. The organic constituents included in these calibration standards were supplied from the solid samples previously discussed. Seven calibration standards containing identical concentrations of each organic material each between 0.05 and 10.0 mg/L were used for calibration.

2. Results and discussion
2.1. Computational approach
Optimized geometries of modeled cellulose, cellulose triacetate, chitin and chitosan, and the structures of munition compounds investigated are shown in Fig. 1. In these models the terminal –OH groups, which are involved in chain progression, are replaced with –OCH3 group to avoid their possible interaction with the adsorbates. In our earlier investigation (Shukla and Poda 2016), we compared the selected dihedral angles of modeled cellulose with the corresponding parameters of crystalline form of cellulose Iα obtained from the cif file (Nishiyama et al., 2002); good agreement was revealed between the experimental and computed data, except for those dihedral angles responsible for the elongation of the chain. Such disagreement is not unexpected since conformational movements are potentially restricted in the crystal environment due to the presence of the inter-chain hydrogen bonds. Similar results are expected for modeled cellulose triacetate, chitin and chitosan. We have also shown that the M062X/6-31G(d,p) level is reliable in predicting structures of DNAN, FOX-7 and TNT compared to the corresponding experimental geometries (Shukla and Poda 2016).

Geometries of the complexes were obtained by the adsorption of adsorbates on modeled cellulose, cellulose triacetate, chitin and chitosan surfaces at the M062X/6-31G(d,p) level in the gas phase and in the bulk water solution; the gas phase optimized geometries were used for geometry optimization in the bulk water solution. Initial geometries of these complexes were generated by putting the adsorbates in orientation which could maximize the number of hydrogen bonds between the adsorbent and the adsorbate. Moreover, adsorbates were adsorbed on both
Fig. 1 – Optimized geometries of modeled cellulose, chitin, cellulose triacetate and chitosan, and munitions compounds 2,4-dinitroanisole (DNAN), 1,1-diamino-2,2-dinitroethene (FOX-7), nitroguanidine (NQ), 2,4,6-trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB).

Table 1 – BSSE corrected interaction energy (kcal/mol) of munitions compounds on cellulose, cellulose triacetate, chitin and chitosan surfaces in the gas phase and in the bulk water.

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th></th>
<th>Cellulose triacetate</th>
<th></th>
<th>Chitin</th>
<th></th>
<th>Chitosan</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Water</td>
<td>Gas</td>
<td>Water</td>
<td>Gas</td>
<td>Water</td>
<td>Gas</td>
<td>Water</td>
</tr>
<tr>
<td>DNAN</td>
<td>−20.0</td>
<td>−11.7</td>
<td>−20.9</td>
<td>−12.9</td>
<td>−21.0</td>
<td>−13.0</td>
<td>−19.9</td>
<td>−11.9</td>
</tr>
<tr>
<td>FOX-7</td>
<td>−29.2</td>
<td>−18.3</td>
<td>−37.2</td>
<td>−18.7</td>
<td>−31.5</td>
<td>−19.7</td>
<td>−22.4</td>
<td>−13.2</td>
</tr>
<tr>
<td>NQ</td>
<td>−26.8</td>
<td>−14.1</td>
<td>−29.5</td>
<td>−6.7</td>
<td>−34.2</td>
<td>−20.7</td>
<td>−25.7</td>
<td>−16.1</td>
</tr>
<tr>
<td>TNT</td>
<td>−26.3</td>
<td>−16.7</td>
<td>−23.7</td>
<td>−15.2</td>
<td>−28.7</td>
<td>−11.1</td>
<td>−22.4</td>
<td>−14.6</td>
</tr>
<tr>
<td>TATB</td>
<td>−30.5</td>
<td>−17.0</td>
<td>−32.9</td>
<td>−23.5</td>
<td>−36.5</td>
<td>−21.4</td>
<td>−22.8</td>
<td>−16.6</td>
</tr>
</tbody>
</table>

*a For DNAN, FOX-7 and TNT data taken from reference 20.*
sides of the surfaces, and a complex with larger binding energy was considered. Computed interaction energies of the complexes in the gas phase and in the bulk water solution are shown in the Table 1. We would like to emphasize that BSSEs obtained in the gas phase calculations were used to correct respective interaction energies in the bulk water using the CPCM approach. Moreover, the gas-phase BSSE energies were found to be in the range of 7–15 kcal/mol. The results displayed in Table 1 show that all energetic compounds considered in the present investigation form stable complexes with cellulose, cellulose triacetate, chitin and chitosan. These complexes are stabilized by the presence of several hydrogen bonds formed between hydrogen bond accepting and donating sites of adsorbates to the complementary sites of the adsorbents. Further, small contributions from stacking interactions for complexes containing ring systems will also help towards the stability of the system. Moreover, such interaction is significantly reduced in the bulk water solution compared to that predicted in the gas phase (Table 1). Generally, TATB is predicted to form relatively stronger complexes with all surfaces. However, FOX-7 with cellulose in bulk water and FOX-7 with cellulose triacetate and NQ with chitosan in the gas phase form stronger complexes relative to TATB under the same conditions. Relative to the other munitions compounds, NQ showed significantly low interaction on cellulose triacetate surface in the bulk water.

2.2. Batch adsorption

The graph containing batch sorption experiments of contaminants on surfaces are shown in Fig. 2. It is clear that cellulose triacetate shows excellent performance in removing DNAN and TNT and moderate removal of FOX-7 from the solution. Chitin, chitosan and cellulose all exhibit poor or moderate performance in removing the contaminants from the solutions used in this study. Experimental data showed no noticeable difference in removal as contact time increased to 48 hr, indicating that equilibrium had been reached.

2.3. Distribution coefficients

Fig. 3 shows isothermal plots of the equilibrium concentration (Cₑ, mg/L) versus unit contaminant concentration adsorbed onto the solid (Cₛ, mg/g) for DNAN and TNT in the presence of cellulose triacetate. Cₑ is a dimensionless quantity defined as the total adsorbate mass adsorbed onto the adsorbent divided by the adsorbent mass. Similar plots are shown for the other adsorbent compounds and these munitions constituents in Fig. 4. Plots depicting the removal of DNAN and TNT at each quantity of adsorbent are included as Fig. 5.

The data show a linear correlation between cellulose triacetate and both DNAN and TNT at the concentrations analyzed for this experiment. Freundlich and Langmuir models were also used to analyze the relationship between cellulose triacetate and these two compounds. These models provided...
fits with similar or reduced accuracy compared to linear analysis. Freundlich models are expected to be more accurate than linear models as the concentration of DNAN or TNT increases in solution, as the amount of available adsorbent sites will diminish per unit mass.

Linear, Freundlich and Langmuir analysis showed no accurate correlation between the other adsorbents and DNAN and TNT. Though, adjustments to the adsorbate concentrations may enhance results in terms of correlation.

The distribution coefficients ($K_D$, mL/g) for adsorption of TNT or DNAN by cellulose triacetate are defined as $C_s/C_e$ for linear isotherms. For this study, the $K_D$ values are the slopes of the isotherms. The $K_D$ values between cellulose triacetate and TNT or DNAN are 461.3 mL/g and 330.3 mL/g, respectively. These results show that cellulose triacetate has a higher affinity for TNT than DNAN.

Thus, we observed that although FOX-7 has been predicted to have strongest binding on cellulose triacetate surface, only about 45% removal was obtained for FOX-7 by the cellulose triacetate while maximum removal (over 90%) was obtained for DNAN and TNT. Further, DNAN has been predicted to have similar interaction energy across all the surfaces considered in the present investigation. However, over 90% removal of DNAN and TNT by cellulose triacetate suggest that respective solubilities of adsorbates, presence of available surface area and the pore size of adsorbents would play dominant role in munitions removal dissolved in water. These aspects influencing contaminant sorption are currently under investigation and will be published elsewhere. Lastly, based upon the structural similarity of TATB with DNAN and TNT, it is expected that cellulose triacetate should also be able to remove TATB from water.

3. Conclusions

Computed interaction energies of investigated complexes have generally suggested that all energetic compounds investigated here form stable complexes on model cellulose, cellulose triacetate, chitin and chitosan surfaces. These complexes are stabilized by the presence of hydrogen bonds formed between adsorbates and adsorbents. We found that cellulose exhibits poor ability to remove the following investigated munitions compounds from water solution: DNAN, TNT, FOX-7 and NQ. The best results were obtained by cellulose triacetate, which is able to remove over 90% of DNAN and TNT and over 45% of FOX 7 from the water solution during the evaluation. Based upon the structural similarity, it is expected that cellulose triacetate could also be used to remove TATB from the water solution. Chitin showed relatively better performance than cellulose in removing contaminants from the water with 40% removal of TNT and
25% removal of DNAN at the evaluated conditions. We speculate that the solubility of the adsorbates, presence of available surface area and pore size of the adsorbents would play dominant roles in munitions removal dissolved in water.

Acknowledgement

The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research conducted under the Environmental Quality Technology Program of the United States Army Corps of Engineers and the Environmental Security Technology Certification Program of the Department of Defense by the USAERDC. Permission was granted by the Chief of Engineers to publish this information. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

REFERENCES


