

2-2018

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## Recommended Citation

Todde, G., Jha, S. K., Subramanian, G., Shula, M. K. (2018). Adsorption of TNT, DNAN, NTO, FOX7, and NQ Onto Cellulose, Chitin, and Cellulose Triacetate. Insights From Density Functional Theory Calculations. *Surface Science*, 668, 54-60.  
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# Adsorption of TNT, DNAN, NTO, FOX7, and NQ onto Cellulose, Chitin, and Cellulose Triacetate. Insights from Density Functional Theory Calculations

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## Abstract

Insensitive munitions (IM) compounds such as DNAN (2,4-dinitroanisole), NTO (3-nitro-1,2,4-triazol-5-one), NQ (nitroguanidine), and FOX7 (1,1-diamino-2,2-dinitroethene) reduce the risk of accidental explosions due to shock and high temperature exposure. These compounds are being used as replacements for sensitive munition compounds such as TNT (2,4,6-trinitromethylbenzene) and RDX (1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine). NTO and NQ in IM compounds are more soluble than TNT or RDX, hence they can easily spread in the environment and get dissolved if exposed to precipitation. DNAN solubility is comparable to TNT solubility. Cellulosic biomass, due to its abundance in the environment and its chemical structure, has a high probability of adsorbing these IM compounds, and thus, it is important to investigate the interactions between cellulose and cellulose like biopolymers (*e.g.* cellulose triacetate and chitin) with IM compounds. Using Density Functional Theory methods, we have studied the adsorption of TNT, DNAN, NTO, NQ, and FOX7 onto cellulose I $\alpha$  and I $\beta$ , chitin, and cellulose triacetate I (CTA I). Solvent effects on the adsorption were also investigated. Our results show that all contaminants are more strongly adsorbed onto chitin and cellulose I $\alpha$  than onto CTA I and cellulose I $\beta$ . Dispersion forces were found to be the predominant contribution to

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the adsorption energies of all contaminants.

*Keywords:* DFT, cellulose, TNT, DNAN, FOX7, insensitive munitions, adsorption

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## 1. Introduction

Armed forces around the world are developing and adopting insensitive munitions (IMs), that are designed to reduce the risk of unintentional detonation due to shock and high temperature exposure[1, 2]. Examples of IM compounds include DNAN (2,4-dinitroanisole), NTO (3-nitro-1,2,4-triazol-5-one), NQ (nitroguanidine), and FOX7 (1,1-diamino-2,2-dinitroethene). These IM compounds have a lower risk of accidental detonation than TNT (2,4,6-trinitromethylbenzene) or RDX (1,3,5-hexahydro-1,3,5-trinitro-1,3,5-triazine). IMs are produced with different formulations where either IM compounds or both the IM compounds and traditional compounds might be present in different ratio. The four IM compounds mentioned, *viz.* DNAN, NQ, NTO and FOX7, have a relatively higher solubility in water than TNT or RDX[3, 4, 5, 6, 7]. The production, storage, and usage of IMs may result in their dispersion in the environment. Moreover, due to their higher solubility, if IMs are exposed to precipitation they might be dissolved and the contamination can spread to groundwater and move off from its original location. Nevertheless, munitions containing compounds like TNT, RDX, and HMX are known to cause the same problem. **The toxicity and impact on soil, water, and plants of explosives such as TNT and RDX has been studied in details[8, 9, 10, 11, 12, 13, 14].** IM compounds can be regarded as emerging new contaminants. Cellulosic biomass (like cellulose and chitin), due to its vast abundance in the environment, and its chemical structure, is very likely to interact with IM compounds. And thus, it is crucial to investigate the adsorption of IM compounds onto cellulose and cellulose derivatives. This investigation can help to understand the forces and interactions involved in the adsorption mechanisms of these compounds, and also serve as a starting point for the development of new materials intended

for remediation and detection technologies. Furthermore, due to the abundance of cellulose in the environment, the study of IM compounds adsorption onto cellulose will also help understanding the impact of these materials on the environment. Soil is also very likely to adsorb IM compounds, but IMs adsorption on soil is not within the scope of this study.

Cellulose is the most abundant biomaterial on earth as it is the main constituent of plants, and also found in bacteria, algae, and fungi[15]. Cellulose is a natural polymer formed by chains of  $\beta$ -D-glucanopyranose units linked by 1 $\rightarrow$ 4 glycosidic bonds[16, 17]. In its natural crystalline structure, cellulose can be found in two forms:  $I\alpha$  and  $I\beta$ [18]. The two allomorphs are not only found within the same cellulose sample[19], but also in the same microfibril[20]. The relative amounts of the two forms depend on the source.  $I\alpha$  is the most abundant form in the cell walls of algae and bacteria, while  $I\beta$  is the most abundant form in wood, cotton, and ramie fibers[21, 22]. Cellulose can also crystallize in other forms, named cellulose II, III and IV. In cellulose II, which is obtained by regeneration or mercerization[23], glucan molecules run antiparallel. Cellulose III is obtained when either cellulose I or II is treated with liquid ammonia, the resulting allomorphs are called cellulose  $III_I$  or cellulose  $III_{II}$  respectively[24]. Heating of cellulose  $III_I$  or  $III_{II}$  produces cellulose  $IV_I$  and  $IV_{II}$  respectively[25]. X-ray and neutron diffraction measurements[26, 27] have shown that cellulose  $I\alpha$  crystallizes in a triclinic P1 unit cell containing one cellobiose molecule, while cellulose  $I\beta$  has a monoclinic P2<sub>1</sub> unit cell containing two nonequivalent cellobiose molecules. In both allomorphs the chains of glucan molecules run in parallel forming sheets packed in a "parallel-up" fashion[26, 27]. Within the same sheet, the glucan molecules are held together by inter-chain hydrogen bonds formed between the hydroxylic groups. Adjacent sheets are held together by van der Waals dispersion forces[28].

Cellulose triacetate (CTA) is one of the most common derivatives of cellulose obtained by acetylation of cellulose fibers. CTA has many applications in the textile industry and is also used in the production of membranes and films. Depending on the acetylation procedure, two different polymorphs of

CTA can be obtained. They are named CTA I and CTA II similarly to cellulose polymorphs, where in cellulose I chains run in a parallel fashion, while in cellulose II chains run antiparallel. CTA I is obtained by heterogeneous acetylation of cellulose I fibers[29]. Instead, CTA II can be obtained from either heterogeneous acetylation of cellulose II[30] or from homogeneous acetylation of cellulose I[31]. In CTA all cellulose hydroxyl groups are replaced by acetyl groups. The acetylation of hydroxyl groups increases the contact surface per glucose unit of CTA, which may results in the adsorption of larger quantity of contaminants. In its crystal structure, a monoclinic unit cell of CTA I is formed by a single polymer chain in a  $2_1$  helix conformation[31].

The second most abundant biopolymer on earth[32] is chitin, which is found in the exoskeleton of arthropods, and also in mollusks, algae, and fungi. Chitin is formed by  $\beta$ 1,4-linked units of acetyl-D-glucosamine. Chitin, like cellulose, is found in two forms:  $\alpha$  and  $\beta$ . The  $\alpha$ -form is the most common and in its crystal structure, the orthorhombic unit cell is formed by antiparallel chains in a  $2_1$  helix conformation[33, 34].

The adsorption of small molecules onto cellulose surfaces has been recently investigated by both experimental and theoretical groups. Several studies were focused on the adsorption of carbohydrates[35, 36, 37, 38], while other research groups studied the adsorption of aromatic compounds[39, 40, 41, 42], small proteins[43], and nanoparticles[44]. While Density Functional Theory (DFT) studies have shown that dispersion forces play a key role in the adsorption process and that they must be taken into account in order to correctly describe that the geometry and the energy of the complexes[37], a relatively small number of recent studies have included dispersion effects on the absorption of small molecules onto cellulosic surfaces[45, 46, 47].

In this article, we use DFT to compute the interaction energies of DNAN, NTO, NQ, FOX7, and TNT (see Figure 1) adsorbed onto cellulose ( $I\alpha$  and  $I\beta$ ), chitin, and cellulose triacetate I (100) surfaces. The interaction energies were calculated both in gas-phase and in water, and dispersion forces have been included.

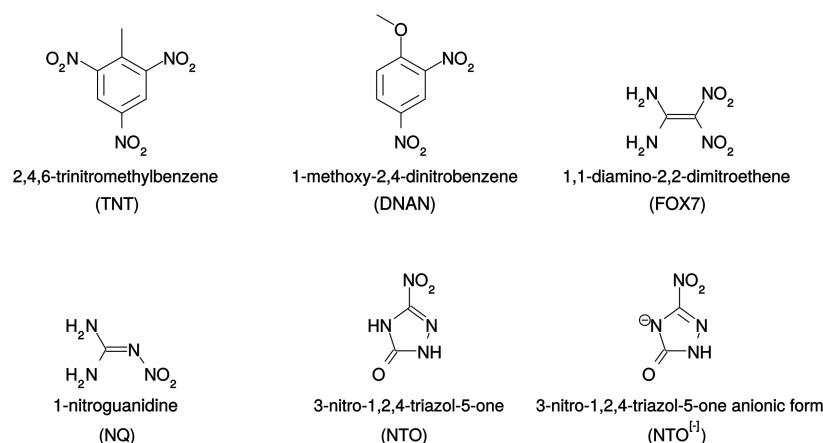


Figure 1: Schematic of the IM compounds along with their chemical names and abbreviations.

## 2. Computational Methods

90 The model for both cellulose surfaces,  $I\alpha$  (100) and  $I\beta$  (100), are formed by two parallel strands of glucose tetraose (see Figure 2 and 3). Both cellulose models were built using the coordinates obtained from the crystallographic data of Nishiyama *et al.*[26, 27]. The model for the chitin surface is formed by two antiparallel chains containing four glucosamine units each, and was

95 built using the coordinates obtained from the crystallographic data of Sikorski *et al.*[34]. The model for CTA I is formed by two parallel chains of glucose tetraose, where hydroxy groups on C2, C3, and C6 are acetylated (see Figure 2). The cellulose triacetate model was built using the coordinates obtained from the crystallographic data of Sikorski *et al.*[31]. In all models, the chains

100 are terminated by attaching methoxy groups to atoms C1 and C4 (see Figure 2). The geometries of the surface models were optimized at the DFT[48, 49, 50, 51] level of theory using both B97D[52, 53, 54] functional with 6-31g basis set, and M06-2X[55] functional with 6-31g(d,p)[56, 57, 58, 59, 60, 61, 62, 63, 64, 65] basis set. **The B97D and M06-2X functionals were chosen because they both include dispersion energy contributions, which are crucial interactions in the physisorption process. The 6-31g basis set was used to allow us to calculate the**

105

zero point vibrational energies, since these calculations request large amount of memory. The surface models were built large enough to take into account all possible long range interactions with the adsorbates molecules. The models  
110 for the surface/contaminant complexes were built placing the contaminants at different locations (see Figure 3) on the optimized surfaces at a distance of approximately 4-5 Å. The complex structures were then optimized using the same functionals and basis set mentioned above. Single point calculations using the 6-31g(d,p) basis set were performed on all B97D/6-31g optimized geometries.  
115 The effect of bulk water solvation was modeled performing single point calculations on the optimized geometries using the CPCM approach[66, 67] with dielectric constant value equal to 80.0. The interaction energies of all complexes were corrected for basis set superposition error (BSSE) using the counterpoise correction scheme[68, 69].

120 The optimized geometries obtained at the B97D/6-31g level of theory were used to perform frequency calculations in order to estimate ZPVEs. The obtained ZPVE corrections (B97D/6-31g) were thereafter included in the interaction energies calculated with M06-2X/6-31g(d,p) and with B97D/6-31g(d,p). We have assumed that the ZPVE corrections do not vary significantly with the  
125 different functionals. The dispersion energy contribution to the electronic energy was calculated from the optimized geometries (with the B97D functional) through the D2 function developed by Grimme[53, 54] using the XYZ-Viewer software[70]. The number of atoms of the adsorbates and the surfaces are available in the Supporting Material (see Table S1). In order to avoid severe distortion of the surface models, the position of C2 and C5 atoms of all sugar rings  
130 were kept fixed during the optimization. All calculations were performed using the Gaussian09[71] software package.

The interaction energies ( $E_{int}$ ) between the contaminants and the different surfaces in gas phase and in water solution are obtained using the following

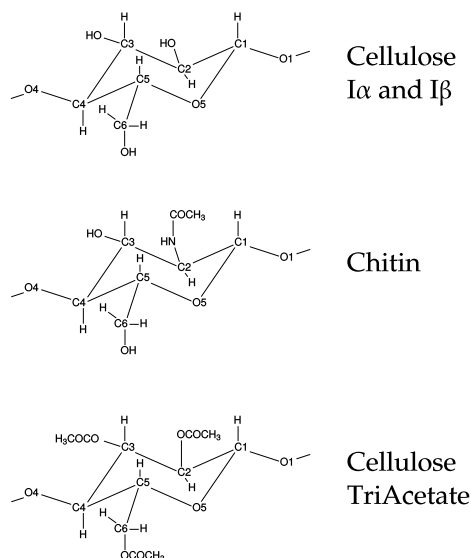


Figure 2: Schematic of the monomeric units of the surfaces, along with numbering of the atoms used in this paper.

135 formulae respectively:

$$E_{int(gas)} = E_{AB(gas)} - E_{A(gas)} - E_{B(gas)} + BSSE_{(gas)} + ZPVE_{(gas)} \quad (1)$$

$$E_{int(water)} = E_{AB(gas)} - E_{A(gas)} - E_{B(gas)} + BSSE_{(gas)} + ZPVE_{(gas)} + CPCM_{(water)} \quad (2)$$

where  $E_{AB(gas)}$ ,  $E_{A(gas)}$ , and  $E_{B(gas)}$  represent gas phase calculations of the electronic energy ( $E_{elec}$ ) of the complex (AB), the surface (A), and the contaminant (B) respectively.  $BSSE_{(gas)}$  is the basis set superposition error correction,  $ZPVE_{(gas)}$  is the zero-point vibrational energy correction, and  $CPCM_{(water)}$  is the bulk water solvation contribution.

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### 3. Results and discussion

Of the different complex configurations used to start the geometry optimizations of each contaminant (see Figure 3), only the geometries with the



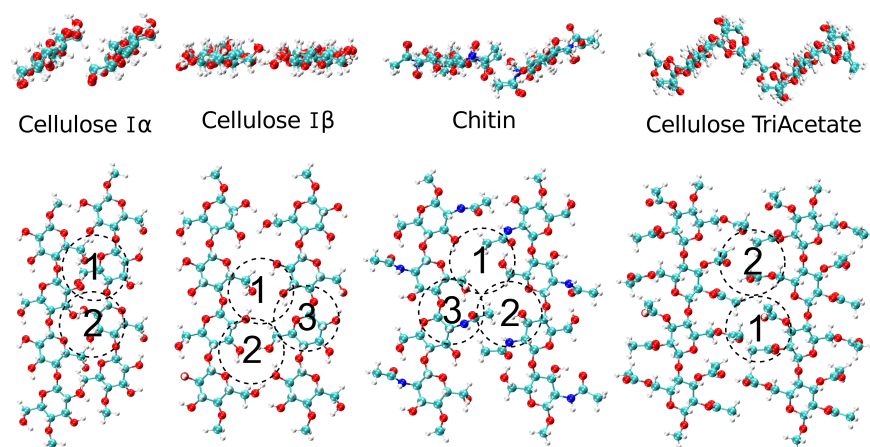


Figure 3: Surface models for cellulose I $\alpha$ , I $\beta$ , chitin, and cellulose triacetate I. The top part of the figure shows the side view of the (100) surfaces, while the bottom part shows the top view. Circled numbers represent the starting position for all contaminants in the geometry optimization of the complexes. Atom colors scheme: C in cyan, O in red, N in blue, and H in white.

largest interaction energies will be discussed. In all optimized complexes, the  
 145 contaminant was found adsorbed onto the same location over the biopolymer  
 surfaces as revealed by both functionals, and the adsorption locations of the  
 individual contaminants obtained with both functionals are reported in the  
 Supporting Information (see Table S2). Since NTO is an acid with a  $pK_a$  value  
 of 3.70-3.76[72, 73], its two forms, neutral and anionic, were investigated.

### 150 3.1. Cellulose I $\alpha$ and I $\beta$

The calculated interaction energies of all contaminants with cellulose I $\alpha$   
 (100) and I $\beta$  (100) surfaces are presented in Table 1 for both gas phase and  
 water solution. In both cases, gas phase and water solution, cellulose I $\alpha$  shows  
 stronger  $E_{int}$  than I $\beta$  for all contaminants. The same trend was found with  
 155 both functionals. The only exception is represented by NTO<sup>[-]</sup>, which shows  
 a slightly larger  $E_{int}$  with cellulose I $\beta$  in aqueous solution (3-5 kcal/mol, de-  
 pending on the functional). The anionic form of NTO is very unlikely to be  
 found in the gas phase (where the neutral form is predominant), while in wa-

Table 1: Interaction Energies of TNT, DNAN, FOX7, NTO (in gas phase), NTO<sup>[-]</sup> (in water solution), and NQ adsorbed onto Cellulose I $\alpha$ , I $\beta$ , Chitin, and CTA I. All Energies Are Expressed in kcal/mol.

	Cell. I $\alpha$		Cell. I $\beta$		Chitin		CTA I	
	gas	water	gas	water	gas	water	gas	water
B97D								
TNT	-21.9	-13.5	-16.7	-10.1	-24.7	-11.6	-11.4	-5.1
DNAN	-22.4	-11.3	-14.5	-10.2	-22.1	-7.2	-15.7	-7.4
FOX7	-20.7	-9.2	-9.3	-2.6	-35.3	-12.7	-17.3	-7.2
NTO	-19.4	...	-16.9	...	-23.7	...	-20.5	...
NTO <sup>[-]</sup>	...	-8.9	...	-13.5	...	-20.2	...	-4.1
NQ	-25.0	-15.8	-16.9	-8.6	-31.7	-12.8	-17.4	-7.7
M06-2X								
TNT	-23.4	-13.2	-15.5	-8.4	-25.5	-11.6	-14.9	-9.3
DNAN	-23.2	-10.8	-12.8	-8.2	-20.6	-6.5	-13.5	-7.2
FOX7	-20.6	-8.5	-8.8	-2.2	-39.5	-16.9	-18.6	-8.5
NTO	-21.6	...	-18.1	...	-24.7	...	-22.5	...
NTO <sup>[-]</sup>	...	-11.9	...	-11.3	...	-21.8	...	-3.3
NQ	-24.9	-12.7	-18.2	-9.4	-28.8	-12.4	-17.5	-8.1

Table 2: Dispersion Energy as a Percentage of Electronic Interaction Energies ( $E_{elec}$ ) of TNT, DNAN, FOX7, NTO,  $\text{NTO}^{[-]}$ , and NQ adsorbed onto Cellulose  $I\alpha$ ,  $I\beta$ , Chitin and CTA I.

	Cell. $I\alpha$	Cell. $I\beta$	Chitin	CTA I
	B97D			
TNT	71.8	98.1	79.0	84.0
DNAN	70.9	93.6	73.5	90.0
FOX7	52.2	87.9	49.3	72.0
NTO	64.5	68.3	52.3	65.2
$\text{NTO}^{[-]}$	35.1	30.1	26.0	53.6
NQ	52.8	71.0	51.1	68.0

ter,  $\text{NTO}^{[-]}$  is the predominant form. Keeping this in mind, we can summarize  
 160 that cellulose  $I\alpha$  shows the strongest binding for all contaminants in gas phase.  
 The same results are also found in water where  $\text{NTO}^{[-]}$  represents the only  
 exception as mentioned above.

While the two cellulose allomorphs,  $I\alpha$  and  $I\beta$ , are formed by the same glu-  
 can molecules, surfaces have different properties due to the mutual orientation  
 165 of the glucan molecules. On the (100) surface of cellulose  $I\alpha$ , the sheets are not  
 parallel to the surface. The glucan molecules are tilted exposing the free hy-  
 droxyl groups, therefore the surface is hydrophilic[37]. On the flat (100) surface  
 of cellulose  $I\beta$ , the glucan molecules are arranged in a parallel fashion having  
 the OH groups side by side forming interchain hydrogen bonds (see Figure 3).  
 170 Hence, none of the hydroxyl groups are exposed and the resulting sheets are  
 mainly hydrophobic[74].

When adsorption is driven by noncovalent interactions, there are four dif-  
 ferent components contribute to the total interaction energy[75]: electrostatics  
 (between permanent multipoles), induction (between permanent and induced  
 175 multipoles), dispersion (between instantaneous and induced multipoles) and  
 Pauli repulsion (short-range interaction between electrons with same spin). Ta-  
 ble 2 summarizes the dispersion energy as a percentage of the electronic in-

teraction energy ( $E_{elec}$ ) calculated with the B97D functional. Comparing the amount of dispersion energy with the  $E_{elec}$  of the complexes (see Table 2), we  
180 have found that in case of the hydrophobic surface of cellulose I $\beta$ , dispersion energy plays a predominant role. In fact, the amount of dispersion energy of cellulose I $\beta$  complexes is always at least 20% larger than that of the cellulose I $\alpha$  complexes. On the other hand, for the hydrophilic surface of cellulose I $\alpha$ , even though dispersion is still the predominant contribution to the interaction  
185 energy (>50%), the other three types of interaction become more significant.

In both the gas phase and in water, all contaminants have comparable interaction energies with cellulose I $\alpha$ . The same is also found for cellulose I $\beta$ , except for FOX7. The different interaction energies of FOX7 with the two cellulose surfaces depend mainly on the nature of the interaction. Hoja *et al.* have  
190 shown that the dispersion contribution increases with the contact area between the surface and the adsorbate[37]. The molecular size of NQ and NTO is similar to FOX7 as is their dispersion energy when interacting with cellulose I $\beta$ . Nevertheless, the dispersion energy accounts for just the 70% of  $E_{elec}$  in case of NQ and NTO, while for FOX7 dispersion represents 90% of  $E_{elec}$ . Hence  
195 NQ and NTO form stronger interactions than FOX7 with cellulose I $\beta$  because for the former, interactions other than dispersion are more significant. On the other hand, TNT and DNAN exhibit stronger interactions with cellulose I $\beta$  than FOX7, even though they also have about 90% of their  $E_{elec}$  coming from dispersion. We believe that it is because of the larger molecular size of TNT  
200 and DNAN when compared with FOX7.

### 3.2. Cellulose Triacetate I

The  $E_{int}$  of all contaminants with CTA I are generally weaker than their complexes with cellulose I $\alpha$  both in gas phase and in water (see Table 2). NTO shows slightly stronger interactions with CTA I than cellulose I $\alpha$  in gas phase  
205 with both functionals. On the other hand, NTO<sup>[-]</sup> in water shows weaker interactions with CTA I than cellulose I $\alpha$ , moreover NTO<sup>[-]</sup> has the weakest interactions among all the contaminants with CTA I.

Comparison between CTA I and cellulose  $I\beta$ , however, shows the opposite trend. Generally all contaminants forms stronger interactions with CTA I than  
210 cellulose  $I\beta$  in gas phase, except TNT. TNT is found to have weaker or similar  $E_{int}$  with CTA I than cellulose  $I\beta$  depending on the functional. In water the difference between the two surfaces become smaller. The only significant difference is found for  $\text{NTO}^{[-]}$ , which binds more strongly to cellulose  $I\beta$  than CTA I.

215 The structural difference between cellulose (both  $I\alpha$  and  $I\beta$ ) and CTA I is due to the acetylation of all hydroxyl groups in CTA I. When all OH groups of cellulose are replaced by acetyl groups to form CTA I, the resulting surface is found to be more hydrophobic. Moreover, the hydrophobicity of cellulose acetate increases with increasing acetylation[76]. The different hydrophobicity  
220 of cellulose  $I\alpha$  and CTA I is at least partially due to the different possibility of the materials to form hydrogen bonds. Cellulose  $I\alpha$  can form hydrogen bonds both as a donor (through the exposed OH groups) and as an acceptor (through O1, O4 and O5, see Figure 1). On the other hand, CTA I can only form hydrogen bonds as an acceptor, since all OH groups are replaced with acetyl groups. The  
225 different hydrophobicity of cellulose  $I\alpha$  and CTA I is also manifested in the dispersion contribution to the  $E_{elec}$  (see Table 2). The amount of dispersion energy (as a percentage of the  $E_{elec}$ ) for the complexes with CTA I is closer to that of the complexes with cellulose  $I\beta$ , rather than that of the complexes with cellulose  $I\alpha$ . As mentioned above,  $\text{NTO}^{[-]}$  is found to bind more strongly to  
230 cellulose  $I\beta$  than to CTA I. In this case, the negative charge imparts to  $\text{NTO}^{[-]}$  the ability to form strong hydrogen bonds with the OH groups of cellulose  $I\beta$  (see Supporting Information Figure S22). On the other hand, such strong hydrogen bonds can not be formed with CTA I due to the absence of hydroxyl groups. This is supported by the fact that for the  $\text{NTO}^{[-]}/I\beta$  complex, only  
235 30% of the  $E_{elec}$  comes from dispersion while dispersion counts for about 54% of  $E_{elec}$  for the  $\text{NTO}^{[-]}/\text{CTA I}$  complex.

### 3.3. Chitin

All contaminants adsorbed onto chitin show  $E_{int}$  (within 2-3 kcal/mol) similar to their complexes with cellulose  $I\alpha$  in gas phase (see Table 2). Only FOX7 shows much stronger  $E_{int}$  (15-19 kcal/mol greater, depending on the functional) with chitin than with cellulose  $I\alpha$ . We have found that all contaminants show generally higher or much higher affinity for chitin than for cellulose  $I\beta$  or CTA I. The presence of exposed OH groups and acetylamino groups (bound on C2, see Figure 2) imparts to chitin the ability to form more hydrogen bonds than cellulose  $I\beta$  or CTA I. Hence, the interactions between chitin and the contaminants are only partially due to dispersion. This is in contrast with the fact that dispersion forces are the main contribution to  $E_{elec}$  for cellulose  $I\beta$  and CTA I. Furthermore, the complexes with chitin and cellulose  $I\alpha$  show very similar dispersion contributions to the  $E_{elec}$ .

The  $E_{int}$  of chitin in water shows a different trend. The inclusion of solvent effects in the calculations decreases the difference in  $E_{int}$  between chitin and cellulose  $I\alpha$ . TNT and NQ become more strongly bound to cellulose  $I\alpha$  than to chitin. FOX7 and NTO<sup>[-]</sup> are still more strongly bound to chitin than to cellulose  $I\alpha$ , but the difference in interaction energies between the two surfaces decreases significantly. DNAN, which showed stronger interactions with cellulose  $I\alpha$  than chitin in gas phase, is still found to bind more strongly to cellulose  $I\alpha$ . The same trend is found when comparing the  $E_{int}$  of IMs with chitin with that of cellulose  $I\beta$  and CTA I. All contaminants still show higher affinity for chitin than the two other surfaces, but the difference in energy between chitin and cellulose  $I\beta$  or CTA I decreases. In case of DNAN, the presence of water modifies the  $E_{int}$  in such a way that DNAN becomes more strongly bound to CTA I and cellulose  $I\beta$  than to chitin.

The results obtained presented in this work are slightly different from one of our previous studies[77] on IMs adsorbed onto cellulose, as well as from a more comprehensive investigation on IMs adsorbed onto cellulose, CTA, chitin, and chitosan[78]. The differences in our findings are in part due to the different models used for the surfaces. In the present study, we have adopted

a larger surface model which should account for the wider contact area between adsorbent and adsorbate, but lesser interactions with side groups due to their involvement in interchain interactions stabilizing the bigger models considered in the present investigation. Jenkins *et al.*[79] have found that the cellulose triacetate filter adsorbs significant amounts of munition compounds such as HMX, RDX, TNT, and 2,4-DNT from water. In our recent investigation also[77] the CTA was found to remove significant amount of TNT and DNAN from the solution. Based upon the results of the present investigation, it appears that in those investigations the physical adsorption dominate where pore size and available surface play dominant role.

### 3.4. Electron Density Maps

A qualitative and visual description of the interactions between the contaminants and the surfaces can be obtained calculating an Electron Density Map Difference (EDMD). EDMDs are calculated by subtracting both the electron density of the adsorbate and the surface from the electron density of the complex. The resulting image (shown in Figure 4 for the complexes of chitin and CTA I with DNAN. For the EDMDs of all other complexes see Supporting Information) shows the differences in electron density generated by the interaction between the adsorbate and the surfaces. These differences are shown as regions where the electron density increases (yellow clouds in Figure 4) and regions where the electron density decreases (purple clouds in Figure 4). The solvent effect on the different surfaces can also be qualitatively evaluated from the EDMDs. Comparing the images in the second column (calculated in gas phase) with the images in the third column (calculated in water) of Figure 4, it is possible to see that the solvent weakens the interactions of DNAN with chitin more than it does with CTA I. As a general rule, looking at the EDMDs for all complexes, we see that the more hydrophilic a surface is the more its interactions with the contaminant are weakened.

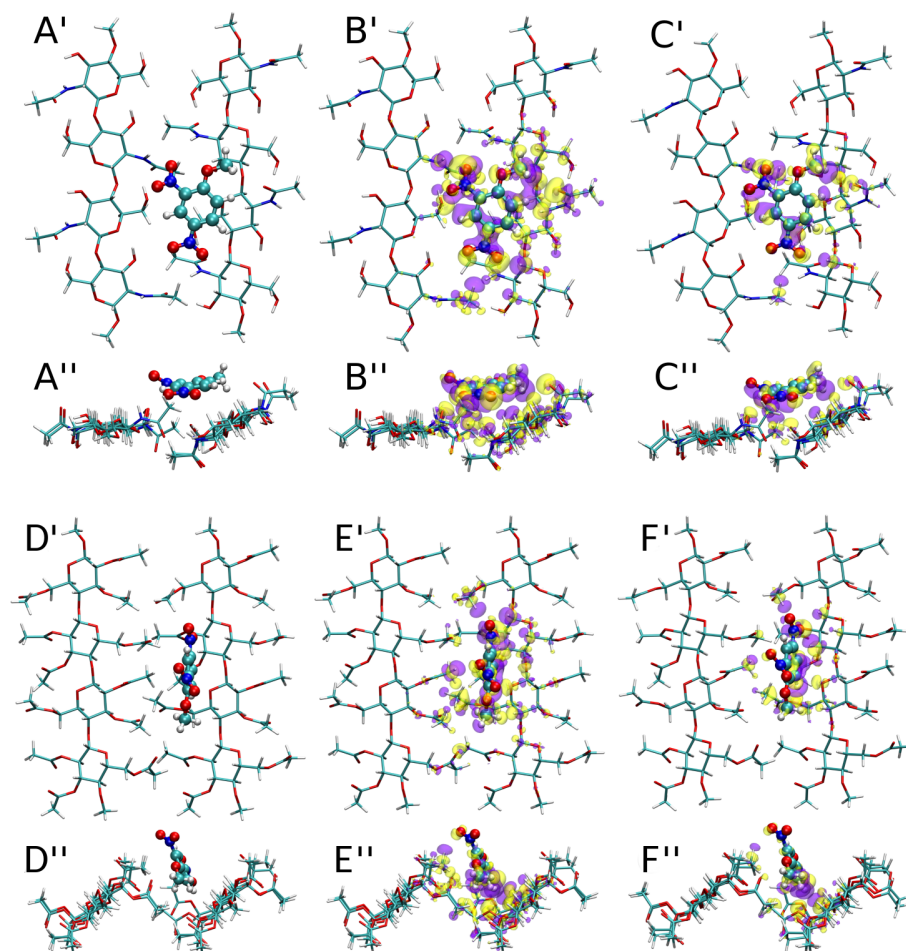


Figure 4: Electron Density Map Difference (EDMD) calculated for the adsorption of DNAN onto Chitin. EDMD isosurface value corresponds to  $0.0005 \text{ e}/\text{au}^3$ . Yellow regions represent electron density gain, and purple regions represent electron density loss. A) and D) show the structure of the complexes of chitin and CTA I (shown in "licorice" representation) respectively, with DNAN (shown in "ball and stick"); B) and E) show the EDMD calculated in gas phase for chitin and CTA I respectively; C) and F) show the EDMD calculated in water for chitin and CTA I respectively. The symbols ' and '' refer to top and side view of the surface plane respectively. Atom colors scheme: C in cyan, O in red, N in blue and H in white.



#### 4. Conclusions

We have studied the adsorption of different insensitive munition compounds, *viz.* DNAN, FOX7, NTO, NQ, and TNT onto two cellulose allomorphs ( $I\alpha$  and  $I\beta$ ), chitin, and CTA I. The investigation was carried out applying DFT methods and using two different functionals: B97D and M06-2X. Solvent effects were also included in our calculations. Dispersion energies are found to be the predominant contribution to the electronic interaction energy of all complexes. Moreover, the more hydrophobic the surface the more predominant the dispersion energies. CTA I and cellulose  $I\beta$  complexes are found to have 15-30% higher contribution to their  $E_{elec}$  coming from dispersion energy than chitin or cellulose  $I\alpha$ .

Of the different surfaces, cellulose  $I\alpha$  and chitin show the strongest interactions with all contaminants both in gas phase and in water. In gas phase, chitin is found to be the strongest adsorption surface for almost all contaminants. The exception is DNAN, which has the largest  $E_{int}$  with cellulose  $I\beta$  (2-3 kcal/mol more than chitin). In water, chitin was found to have similar  $E_{int}$  to cellulose  $I\alpha$  for TNT and NQ, slightly weaker interactions for DNAN than all other surfaces and significantly stronger interactions for FOX7 and NTO<sup>[-]</sup> than all other surfaces. Chitin can be considered the strongest adsorbent for all contaminants considered in our study, with the exception of DNAN. Cellulose  $I\alpha$  is found to be the strongest adsorbent for DNAN. Considering our results and the natural abundance of the different biopolymers, perhaps chitin has to be considered the best adsorbent overall. This is because chitin is the second most abundant biopolymer after cellulose, but as mentioned in the introduction, the  $I\alpha$  allomorph is the most abundant in the wall cell of algae and bacteria while the  $I\beta$  is the most abundant in wood, cotton, and ramie fibers.

#### Acknowledgements

G.T, S.K.J and G.S. acknowledge startup funds from the University of Southern Mississippi, and support from the U.S. Department of Defence via BAA-

325 16-0062. The use of trade, product, or firm name in this report is for descrip-  
tive 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 Qual-  
ity Technology Program of the United States Army Corps of Engineers and  
330 the Environmental Security Technology Certification Program of the Depart-  
ment 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.

### 335 **Supplementary Material**

The Supplementary Material contain the interaction energies of all com-  
plexes calculated in both the gas phase and water solution, the adsorption loca-  
tion of all contaminants onto the different surfaces, and the EDMDs calculated  
for all complexes.

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