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14. ABSTRACT Over the past several years the ultimate goal in our laboratories has been to develop new strategies for the transformation of the a variety of lignocellulosic resources into value-added materials and chemicals based on environmentally sustainable and economically viable processing platforms, with ILs playing a central role in these transformations. To this effect we have accumulated a thorough understanding of the way cellulose, lignin and hemicelluloses interact as well as whole wood dissolution occurs in ILs. The present project was conducted to					
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## Report Title

Feasibility study for the use of green, bio-based, efficient reactive sorbent material to neutralize chemical warfare agents

### ABSTRACT

Over the past several years the ultimate goal in our laboratories has been to develop new strategies for the transformation of the a variety of lignocellulosic resources into value-added materials and chemicals based on environmentally sustainable and economically viable processing platforms, with ILs playing a central role in these transformations. To this effect we have accumulated a thorough understanding of the way cellulose, lignin and hemicelluloses interact as well as whole wood dissolution occurs in ILs. The present project was conducted to effect the transformation of cellulose and/or related biopolymers to effect the detoxification of harmful reagents, specifically nerve agents, through a careful and mechanistic study of their interactions and ultimate adsorption and detoxification.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

#### (a) Papers published in peer-reviewed journals (N/A for none)

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**Number of Papers published in non peer-reviewed journals:**

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**(d) Manuscripts**

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**TOTAL:**

**Number of Manuscripts:**

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**Books**

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**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Sanghamitra Sen	1.00
Joseph DeSousa	1.00
<b>FTE Equivalent:</b>	<b>2.00</b>
<b>Total Number:</b>	<b>2</b>

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

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- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00
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**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PHDs**

<u>NAME</u>
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**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

**Technology Transfer**

**ARO Project**  
**“Feasibility study for the use of green, bio-based, efficient reactive sorbent material to neutralize chemical warfare agents”**  
**Final Report**

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*Department of Forest Biomaterials (formerly Wood & Paper Science)*  
*Department of Chemistry*  
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**Statement of Problem Studied:** In this research work, an effort was made to modify a typical polysaccharide to form nerve gas detoxification materials. This final report will focus on the most successful work obtained thus far.

**Experimental:**

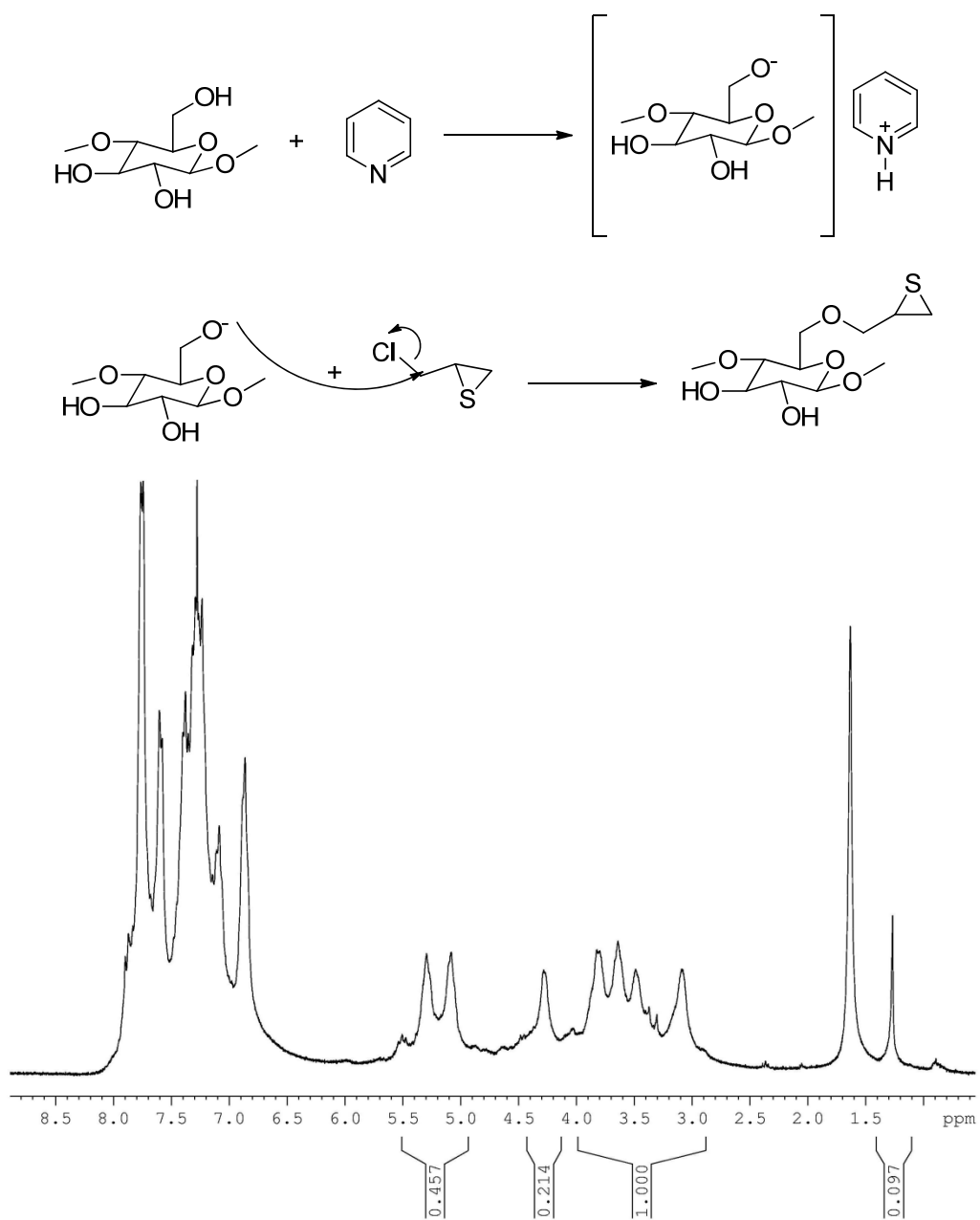
**Materials:** Micro-crystalline cellulose was obtained from Sigma Aldrich and used without further purification. Epichlorothiohydrin, pyridine, benzoyl chloride and dichloromethane were obtained from Sigma Aldrich and used without any further purification.

**Substitution of cellulose:** 0.1 gm of microcrystalline cellulose (0.617 mmol of repeating unit) was dissolved in 1-allyl-3-methylimidazolium chloride (Amim chloride) ionic liquid by heating at 80°C for 3h with occasional vortexing. To this sample 200  $\mu$ L (2.576 mmol) of pyridine and 160  $\mu$ L (1.90 mmol) of epichlorothiohydrin was added and continued stirring at room temperature. After 2h the product was recovered by precipitating from 3:1 mixture of ethanol to water after mixing vigorously for 5 min. The product was washed several times with methanol to remove the remaining amim chloride and dried under vacuum.

**Benzoylation:** The epichlorothiohydrin substituted cellulose is insoluble in any NMR solvent. Therefore, benzoylation of the sample was done. 20 mg of the sample was dissolved in 500 mg of amim chloride in a 15 mL flask by first thoroughly dispersing the sample, followed by heating at 80°C with magnetic stirring until the solution was transparent (about 3 h). Pyridine (200  $\mu$ L, 2.20 mmol) was added, and the mixture was homogenized to form a uniform paste before being allowed to cool to room temperature. Benzoyl chloride (220  $\mu$ L, 1.91 mmol) was then added in one portion, and the sample was subsequently stirred for 3 h at room temperature. The benzoylated product was precipitated by the addition of a 1:3 mixture of deionized water and ethanol with vigorous stirring for 5 min, after which the precipitate was washed several times with methanol and dried under vacuum.

### Summary of Most Important Results:

The NMR spectrum shows two new peaks at 5.1 and 5.4 ppm that verified the substitution of the cellulose molecules with epichlorohydrin. The mechanism of the reaction is given below.



**Figure 1.**  $^1\text{H}$  NMR spectrum of epichlorohydrin substituted cellulose

**Future Plans (with successful support subsequent to this SEED):**

In the next step, the epithiochlorohydrin substituted cellulose will be treated with sodium hydrogen sulfide to synthesis a dithiol and treat the new material with the mimic compounds to examine their efficacy to neutralize the mimic compounds.

