Student Checklist (1A)
This form is required for ALL projects.

1. a. Student/Team Leader: Isha Brahmbhatt Grade: 12
   Email: ishabrahmbhatt02@gmail.com Phone: (914) 263-4097
   b. Team Member: ______ c. Team Member: ______
2. Title of Project:
   Removal of Rare Earth Metal Ions from Contaminated Water by Sustainable Carboxycellulose Nanofibers Derived from Agave through Nitro Oxidation Process
3. School: Ardsley High School School Phone: (914) 295-5800
   School Address: 300 Farm Road
   Ardsley, NY, 10502
4. Adult Sponsor: Diana Evangelista Phone/Email: devangelista@ardsleyschools.org
5. Does this project need SRC/IRB/IACUC or other pre-approval? ☐ Yes ☑ No Tentative start date: ______
6. Is this a continuation/progression from a previous year? ☐ Yes ☑ No
   If Yes:
   a. Attach the previous year's ☑ Abstract **and** ☑ Research Plan/Project Summary
   b. Explain how this project is new and different from previous years on
   ☐☐ Continuation/Research Progression Form (7)
7. This year's laboratory experiment/data collection:

   06/27/19 — Actual Start Date: (mm/dd/yy)
   08/07/19 — End Date: (mm/dd/yy)

8. Where will you conduct your experimentation? (check all that apply)
   ☑ Research Institution ☐ School ☐ Field ☐ Home ☐ Other: ______

9. List name and address of all non-home and non-school work site(s):
   Name: Stony Brook University
   Address: John S. Toll Road
   Stony Brook, NY, 11794
   Phone/email: ______

10. **Complete a Research Plan/Project Summary following the Research Plan/Project Summary instructions and attach to this form.**

11. **An abstract is required for all projects after experimentation.**

Research Plan/Project Summary Instructions

A complete Research Plan/Project Summary is required for ALL projects and must accompany Student Checklist (1A).

1. All projects must have a Research Plan/Project Summary
   a. Written prior to experimentation following the instructions below to detail the rationale, research question(s), methodology, and risk assessment of the proposed research.
   b. If changes are made during the research, such changes can be added to the original research plan as an addendum, recognizing that some changes may require returning to the IRB or SRC for appropriate review and approvals. If no additional approvals are required, this addendum serves as a project summary to explain research that was conducted.
   c. If no changes are made from the original research plan, no project summary is required.

2. Some studies, such as an engineering design or mathematics projects, will be less detailed in the initial project plan and will change through the course of research. If such changes occur, a project summary that explains what was done is required and can be appended to the original research plan.

3. The Research Plan/Project Summary should include the following:
   a. **RATIONALE:** Include a brief synopsis of the background that supports your research problem and explain why this research is important and if applicable, explain any societal impact of your research.
   b. **RESEARCH QUESTION(S), HYPOTHESIS(ES), ENGINEERING GOAL(S), EXPECTED OUTCOMES:** How is this based on the rationale described above?
   c. Describe the following in detail:
      - **Procedures:** Detail all procedures and experimental design including methods for data collection. Describe only your project. Do not include work done by mentor or others.
      - **Risk and Safety:** Identify any potential risks and safety precautions needed.
      - **Data Analysis:** Describe the procedures you will use to analyze the data/results.
   d. **BIBLIOGRAPHY:** List major references (e.g. science journal articles, books, internet sites) from your literature review. If you plan to use vertebrate animals, one of these references must be an animal care reference.

Items 1–4 below are subject-specific guidelines for additional items to be included in your research plan/project summary as applicable.

1. **Human participants research:**
   a. **Participants:** Describe age range, gender, racial/ethnic composition of participants. Identify vulnerable populations (minors, pregnant women, prisoners, mentally disabled or economically disadvantaged).
   b. **Recruitment:** Where will you find your participants? How will they be invited to participate?
   c. **Methods:** What will participants be asked to do? Will you use any surveys, questionnaires or tests? If yes and not your own, how did you obtain? Did it require permissions? If so, explain. What is the frequency and length of time involved for each subject?
   d. **Risk Assessment:** What are the risks or potential discomforts (physical, psychological, time involved, social, legal, etc.) to participants? How will you minimize risks? List any benefits to society or participants.
   e. **Protection of Privacy:** Will identifiable information (e.g., names, telephone numbers, birth dates, email addresses) be collected? Will data be confidential/anonymous? If anonymous, describe how the data will be collected. If not anonymous, what procedures are in place for safeguarding confidentiality? Where will data be stored? Who will have access to the data? What will you do with the data after the study?
   f. **Informed Consent Process:** Describe how you will inform participants about the purpose of the study, what they will be asked to do, that their participation is voluntary and they have the right to stop at any time.

2. **Vertebrate animal research:**
   a. Discuss potential ALTERNATIVES to vertebrate animal use and present justification for use of vertebrates.
   b. Explain potential impact or contribution of this research.
   c. Detail all procedures to be used, including methods used to minimize potential discomfort, distress, pain and ~~injury~~ to the animals and detailed chemical concentrations and drug dosages.
   d. Detail animal numbers, species, strain, sex, age, source, etc., include justification of the numbers planned.
   e. Describe housing and oversight of daily care
   f. Discuss disposition of the animals at the termination of the study.

3. **Potentially hazardous biological agents research:**
   a. Give source of the organism and describe BSL assessment process and BSL determination.
   b. Detail safety precautions and discuss methods of disposal.

4. **Hazardous chemicals, activities & devices:**
   - Describe Risk Assessment process, supervision, safety precautions and methods of disposal.
   - Material Safety Data Sheets are not necessary to submit with paperwork.

Isha Brahmbhatt
Environmental Engineering

Removal of Rare Earth Metal Ions from Contaminated Water by Sustainable Carboxycellulose Nanofibers Derived from Agave through the Nitro Oxidation Process

Rationale:

The long-standing water contamination problem has left 785 million people globally without access to clean drinking water[8]. The increased production of lanthanides due to their good electrical, optical, and metallurgical properties is rapidly contributing to this problem[1]. As lanthanides compose less than 1% of Earth's crust, current methods of producing lanthanides, primarily mining, are highly intensive and damaging to the environment[2]. When released in nature, lanthanide ores can cause water pollution, loss of arable land, and increase mortality rates of aquatic and terrestrial organisms[2]. There will be increased mining ventures to keep up with the rising demand for lanthanides in technologies, and consequently increased public exposure to the lanthanides. Many current mechanisms of removing lanthanides from water sources involve expensive, advanced technologies that are difficult to implement in the primarily rural communities that mine for lanthanides[3]. Developing sustainable materials and procedures for the new, long-term water problems caused by the lanthanide production is an important gap in literature to address in response to rising environmental challenges today.

An alternate method of removing lanthanides may be through carboxycellulose nanofibers (CNF), which are negatively charged chelation agents extracted from biomass, or plant waste[4]. As lanthanides are typically found in water as M^{3+} ions, the use of negatively charged materials can be an effective method to remove these ions from solution. CNF overcomes the limitations posed by expensive and environmentally harmful water purification mechanisms by utilizing a sustainable plant source and upcycling waste materials. Agave is an invasive species with large growth in areas that are the main producers of lanthanides, so CNF derived from agave will represent a more sustainable and cost-effective solution for lanthanide contamination in water[5]. Current methods of generating CNF are often costly and require high chemical and water consumption. The nitro oxidation upcycles biomass sources by employing only two low-cost chemicals, nitric acid and sodium nitrite, in a one-step process that reduces chemical and water consumption as compared to the existing multi-step methods[6,7].

This study will explore agave CNF extracted from raw agave biomass through the nitro oxidation process as an effective lanthanide ions removal agent. Specifically, this study will evaluate the adsorption capacity and efficiency of agave CNF for La^{3+} ions due to toxicity and radioactivity constraints for other lanthanide ions.

Research Question:

How effective are CNF derived from agave biomass through the nitro oxidation process for removing and recovering La^{3+} ions from contaminated water?

Hypotheses:

1. Agave CNF will possess a high adsorption efficiency for La^{3+} ions while also being an accessible and sustainable material.

2. The flocculation of La^{3+} ions and agave CNF may be able to be treated to recover La^{3+} ions as an added benefit of this method.

Engineering Goals:

1. To synthesize CNF that possesses high carboxyl content and a negative surface from raw agave biomass using the one-step nitro oxidation process as a viable material to remove La^{3+} ions from contaminated water.
2. To characterize the agave CNF in terms of its fiber morphology and chemical bonding properties.
3. To evaluate the efficiency of agave CNF at removing La^{3+} ions from solution.
4. To evaluate the potential of recovering La^{3+} ions from the floc formed by the ions and the agave CNF.

Expected Outcomes:

1. Performing the nitro oxidation process on agave biomass will yield agave CNF with high carboxylate content and a highly negative surface.
2. Agave CNF will have a lanthanide ion adsorption capacity that is similar to or higher than that of currently existing removal mechanisms.

Procedure:

1. Synthesis of Agave Carboxycellulose Nanofibers using the Nitro Oxidation Process
   a. The nitro oxidation process will be performed on raw agave biomass samples imported from India, Africa, and the Philippines. In this process, nitric acid and sodium nitrite will simultaneously form salts with the lignin and hemicellulose in raw biomass, and oxidize the CH_2OH functional group into a COOH functional group at the C6 position on the cellulose to form nitro oxidized CNF. Then, dialysis, bicarbonate treatment, secondary dialysis, and homogenization steps will be performed to refine the agave CNF.
2. Characterization of Agave Carboxycellulose Nanofibers
   a. Conductometric titration will be performed to measure the carboxyl content of CNF.
   b. Zeta potential analysis will be performed to measure the degree of negativity of the CNF surface. Conductometric titration and zeta potential analysis will help determine the CNF's ability to chelate La^{3+} ions from contaminated water
   c. FTIR will be performed to evaluate the change in bond lengths between the raw agave biomass and agave CNF and confirm functional groups that are typical to CNF.
   d. Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) will be performed on the CNF to observe the changes in elemental composition between the raw agave biomass and agave CNF, confirm the removal of impurities, and observe the surface morphology of agave CNF.
   e. To observe the morphology of agave CNF, transmission electron microscopy (TEM) will be performed to measure fiber length and width, and atomic force microscopy will be performed (AFM) to measure fiber depth.
   f. Carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance spectroscopy (^{13}C CPMAS NMR) will be performed to confirm the isolation of cellulose in the agave CNF from the raw agave biomass and the conversion of agave fibers to agave nanofibers.

3. Evaluation of Lanthanide Ion Removal by Agave Carboxycellulose Nanofibers
    a. La^{3+} ion solutions of varying concentrations will be mixed with agave CNF. The flocculated portion will be separated using a 0.1 microL syringe filter. The extracted portion of the flocculation will be characterized using FTIR and SEM/EDX. FTIR will be performed to measure any interactions between the La^{3+} ions and the COO^- ions in the agave CNF. SEM/EDX will be performed to confirm the lanthanum elemental peak in the flocculation and to observe changes on the fibrous structures of the agave CNF.
    b. The supernatant portion will be diluted down to 100 ppb with 2 wt % nitric acid to prepare samples for further testing. The extracted and diluted supernatant will be characterized using the standard inductively coupled plasma mass spectrometry (ICP-MS) technique while maintaining the pH of the sample.
    c. The difference between the adsorption of the La^{3+} ions before and after mixing with the CNF suspension will be calculated to determine the adsorption efficiency. The adsorption capacity will be determined by calculating both ideal capacity, based on the available La^{3+} ions and the available mass in grams of CNF in suspension, and the experimental adsorption capacity, the product of the adsorption efficiency and ideal adsorption capacity.
    d. The adsorption capacity and efficiency of the agave CNF will be calculated by fitting the ICP-MS data to Langmuir isotherm, based on a monolayer model, and Freundlich isotherm, based on a multilayer model. The Langmuir isotherm will yield Q_{max} values that represent adsorption capacity in mg/g.
    e. The adsorption capacity and efficiency of agave CNF will be compared to existing methods for removing La^{3+} ions from solutions in literature.
4. Recovery of Lanthanide Ions from Flocculation
    a. The extracted flocculation will be treated with dilute hydrofluoric acid treatment, which will dissolve the agave CNF from the flocculation, and leave behind the La^{3+} ions that do not dissolve in hydrofluoric acid. The recovery of the La^{3+} ions will be confirmed by diluting the remaining contents of the solution down to 100ppb and tested with ICP-MS studies.

Risk and Safety:

There is a risk in the use of lanthanide ions, but safety precautions will include the use of personal protective equipment including nitrile gloves, lab coats, and eye goggles.

Containers used to contain the nitro oxidation reaction will be cleaned with bleach, and disposed of as hazardous material.

Data Analysis:

Origin will be used to analyze and plot the data from FTIR, 13C CPMAS NMR, adsorption studies, and recovery studies.

ImageJ will be used to analyze the data from TEM and AFM measurements.

The element compositions from the SEM will be used as a graph.

Bibliography:

1. Negrea, A., Gabor, A., Davidescu, C. M., Ciopec, M., Negrea, P., Duteanu, N., & Barbulescu, A. (2018). Rare Earth Elements Removal from Water Using Natural Polymers. *Scientific Reports,8*(1). doi:10.1038/s41598-017-18623-0
2. Rim, K. T., Koo, K. H., & Park, J. S. (2013). Toxicological Evaluations of Rare Earths and Their Health Impacts to Workers: A Literature Review. *Safety and Health at Work, 4*(1), 12-26. doi:10.5491/shaw.2013.4.1.12
3. Pereao, O., Bode-Aluko, C., Fatoba, O., Laatikaine, K., & Petrik, L. (2018). Rare earth elements removal techniques from water/wastewater: a review. *Desalination And Water Treatment*, *130*, 71–86. doi: 10.5004/dwt.2018.22844
4. Wang, D. (2018). A critical review of cellulose-based nanomaterials for water purification in industrial processes. *Cellulose,26*(2), 687-701. doi:10.1007/s10570-018-2143-2
5. Mielenz, J. R., Rodriguez, M., Thompson, O. A., Yang, X., & Yin, H. (2015). Development of Agave as a dedicated biomass source: production of biofuels from whole plants. *Biotechnology for Biofuels*, *8*(1). doi: 10.1186/s13068-015-0261-8
6. Zhan, C., Sharma, P. R., Geng, L., Sharma, S. K., Wang, R., Joshi, R., & Hsiao, B. S. (2019). Structural characterization of carboxyl cellulose nanofibers extracted from underutilized sources. *Science China Technological Sciences*, *62*(6), 971–981. doi: 10.1007/s11431-018-9441-1
7. Sharma, P. R., Joshi, R., Sharma, S. K., & Hsiao, B. S. (2017). A Simple Approach to Prepare Carboxycellulose Nanofibers from Untreated Biomass. *Biomacromolecules,18*(8), 2333-2342. doi:10.1021/acs.biomac.7b00544
8. Drinking Water. (2019, June 14). Retrieved from https://www.who.int/news-room/fact-sheets/detail/drinking-water.