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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.