Next Generation Ultrafiltration for Wastewater Treatment: Characterization and Performance of Fouling-Resistant Polymeric and Lyocell Cellulose Nanofiber Membranes

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June 20, 2019

A. Rationale

Four billion people in developing nations are expected to face water shortages by 2050 and providing sustainable and affordable clean is an imperative goal [1-5]. Imminent global water scarcities are increasing demand for alternative water sources, such as reclaimed wastewater [6-12]. Membrane technology, specifically ultrafiltration, is a key component of wastewater reclamation due to its separation efficiency, minimal energy consumption, and economic feasibility [13-16]. However, electrospun polymer ultrafiltration membrane applications are deterred by two major obstacles: electrospun membrane are 1) susceptible to fouling caused by surface hydrophobicity and electrostatic adhesion to foulants [23, 24] and 2) environmentally and economically unsustainable due to non-biodegradability and resource-intensive manufacturing [25, 26]. Addressing the first limitation, membrane fouling results in inefficient membrane performance, decreased membrane lifetime, increased operating costs and physical or chemical maintenance requirements [27-30] but can be mitigated through facile modifications with hydrophilic additives. Fibrous and sustainable cellulose nanofiber (CNF) coatings improve the antifouling dynamics of polymeric membranes due to inherent hydrophilicity [31-37]. However, currently, it is unclear how CNF layer thickness and surface charge play a role in the antifouling behavior of CNF coated electrospun membranes [38-45]. To address the second limitation– environmental and economic unsustainability– of current electrospun polymeric membranes, lyocell has been introduced as a regenerated cellulose fiber extracted from wood pulp currently applied in the textile industry. However, it has exhibited promise as an alternative ultrafiltration scaffold due to its biodegradability, simplistic synthesis, superior hydrophilicity, remarkable mechanical fiber properties, and benign economic and environmental impact [46, 47]. Improvements to current electrospun polymer membranes, such as electrospun polyacrylonitrile (ePAN), through investigation of CNF layer thickness and surface charge and the introduction of lyocell as a sustainable alternative scaffold are imperative steps for the enhancement of wastewater reclamation.

B.

Research Questions

- What are the antifouling properties of the CNF coated ePAN membrane and how can they be characterized pre- and post- fouling?
  - What are the optimal CNF layer thicknesses and surface charge for fouling resistance?
- How does the novel CNF coated lyocell membrane compare to the CNF coated ePAN membrane, and commercially available polyvinylidene difluoride (PVDF) and how can it be characterized post fouling?
- How can the pore blocking and cake formation values of the CNF coated lyocell, CNF coated ePAN, and PVDF membranes be obtained computationally?
- How can the permeate quality of the CNF coated lyocell, CNF coated ePAN, and PVDF membranes be quantified and classified under government regulations?
- What are the antifouling properties of an all-cellulose homogenous lyocell-CNF mixture membrane?

Engineering Goals

- Improve the antifouling characteristics of the CNF coated ePAN membrane in regard to thickness and surface charge.
- Develop and compare the CNF coated lyocell membrane to the ePAN membrane and commercial membranes in regard to fouling, flux and permeate quality.

Hypotheses

- CNF-coated membranes will have greater fouling resistance due to improved hydrophilicity, enhanced permeate quality due to hierarchical membrane structure, and superior environmental sustainability.
- High CNF layer thickness and surface charge will increase fouling resistance because greater exposure of negatively charged hydroxyl and carboxyl groups.

- CNF coated lyocell membrane will have enhanced flux recovery because lyocell provides another hydrophilic layer for improved fouling resistance.
- Pore blocking and cake formation will be most apparent in commercial membrane, PVDF, due to its inherent hydrophobic nature.
- Permeate quality of both CNF coated membranes (ePAN and lyocell) will be greater than PVDF because of its hierarchical nature.

Expected Outcomes

- High CNF-layer thickness and surface charge will yield high flux recoveries on the ePAN membrane due to improved hydrophilicity.
    - Minimal fouling peaks and high water contact angles post-fouling are expected for fouling-resistant membranes.
- CNF coated lyocell as a fouling-resistant, efficient and sustainable alternative to current polymer membranes.
    - Lyocell is expected to have improved antifouling properties as well as long term sustainability because of inherent hydrophilicity, distinctive mechanical properties, and benign economic and environmental impact.
    - Minimal fouling peaks and high water contact angles post-fouling are expected for fouling-resistant membranes.

C.

Procedure

-- *Materials*--

- TEMPO-oxidized CNF fibers originating from wood pulp (0.15 weight % (wt%) suspension)
- 12 wt% homogenous PAN solution electrospun on polyethylene terephthalate
- EFTec Nanofibrillated Lyocell Fiber, Engineered Fibers Technology (0.5 wt% suspension)
- Polyvinylidene difluoride A6 Membrane, Sterlitech Corporation
- Scanning Electron Microscope Crossbeam 340, Carl Zeiss Microscopy, LLC
- Electrokinetic Analyzer for Solid Surface Analysis: SurPASS™ 3 by Anton Paar

- Sterlitech Co. HP4750 Stirred Dead End Cell
- Fourier transform Infrared Spectrometer, Nicolet™ iS™ 10
- Water Contact Angle Goniometer, OCA 15 EC, DataPhysics
- Jupyter Notebook, v. 5.5.0, on Anaconda Navigator, v.1.8.7
- Dead-end Hermia's fouling models repository on GitHub [48]
- Purified municipal wastewater preliminary treated through an aeration bioreactor, Riverhead Sewage Treatment Plant
- 6 x 8" glass plates
- 250 mL beaker
- 250 mL Erlenmeyer flask
- Compressed nitrogen gas tank, pressure gauges and knobs setup
- 0.5 wt% polyacrylate emulsions (PAE)
- 0.1 wt% Sodium hypochlorite bleach solution
- Ohaus AX1502 Digital Scale
- IKA Magnetic Stirring Plate
- Stopwatch
- Microsoft Excel (Version 16.30)
- 1 mM KCl
- 15 mL Falcon tubes

--Methodology--

Membrane Preparation

ePAN Membranes

- Immerse the previously prepared ePAN scaffold in 0.5 wt% PAE for 10 minutes.
- Once removed, scotch tape the crosslinked scaffold onto a glass plate.
- Place in the oven at 120°C for 20 minutes.
- Measure out the previously prepared 0.15 wt% CNF suspension (of varying degrees of oxidation (DO) and area densities (AD)).
- Carefully pour the CNF suspension onto the scaffold and remove all impurities.
- Place the glass plate in the oven at 70°C for 20 minutes.

- Cut the membrane from the glass plate using an exacto knife and store in a plastic bag.

Lyocell Membranes

- Pour 0.5 wt% lyocell suspension into a large ceramic funnel with a polyethylene terephthalate supporting substrate.
- Allow for overnight filtration.
- Dry the ceramic funnel at 50°C for 3 hours.
- Remove the membrane from the funnel.
- Repeat previous procedure for ePAN membranes.

Dead-End Fouling Tests

- Place the membrane (circular - 2 inch diameter) in the cell.
- Assemble the bottom half of the cell.
- Measure 250 mL of distilled water and slowly pour into the cell.
- Add the magnetic stirrer.
- Assemble the top half of the cell.
- Place on magnetic stirring plate at 800 rotations per minute.
- Screw on pressure tube to the top of the cell.
- Adjust operating pressure.
- Start the stopwatch as the first drop of permeate falls into a 250 mL Erlenmeyer flask on the digital scale.
- Record permeate mass and operating pressure in one minute intervals for the first 20 minutes and in five minute intervals for the next 40 minutes.
- After an hour, detach the pressure tube.
- Transfer collected permeate into labelled 15 mL Falcon tubes.
- Disassemble the cell.
- Wash the membrane with distilled water for 10 seconds.
- Reassemble the cell.
- Add 250 mL of purified municipal wastewater.
- Repeat fouling cycle for another hour.
- Repeat for 4 cycles.

- Treat remaining sludge with 0.10 wt % sodium hypochlorite for 24 hour then discard.
- Store fouled membrane in a labelled plastic bag.
- Clean dead end cell, beakers, flasks and tools with distilled water and 0.10 wt % sodium hypochlorite and then dry.

Membrane Characterization

Scanning Electron Microscopy

- Prepare the membrane.
- Place inside the plasma chamber and slowly close.
- Run the test.
- Repeat for all membranes.

Zeta Potential

- Use a pH of 7 and 1 mM KCl as the electrolyte solution.
- Place the membrane on a 20×10 mm gap cell with a gap distance of approximately 115 μm.
- Run the zeta potential.
- Repeat for all membranes.

Fourier Transform Infrared Spectroscopy (FTIR)

- Set up the instrument for attenuated total reflectance mode 4000 and 400 cm-1 at 64 scans per spectrum with a resolution of 4 cm-1.
- Place the ePAN membranes under the probe.
- Run the spectra.
- Repeat for all membranes.

Water Contact Angle

- Fill the glass syringe (0.52 mm diameter) with distilled water.
- Set up parameters: 2.5 μL droplet of distilled water at a dosing rate of 0.2 μL/s.
- Record movie for 30 seconds.
- Repeat for ePAN membranes.

In Silico Hermia's Fouling Models

- Download the GitHub repository on Jupyter Notebook.

- Insert time and flux values for membranes as a .csv file.
- Run the code.

Risk and Safety

TEMPO- oxidized CNF, ePAN, lyocell, purified municipal wastewater (Riverhead Sewage Treatment Plant), polyacrylate emulsions (PAE), and sodium hypochlorite bleach must be handled wearing personal protective equipment (gloves, goggles, disposable face masks, and lab coat) at all times in the lab. Long pants, closed toed shoes and long hair tied back is required. When using purified municipal wastewater, work solely under the fume hood while wearing personal protective equipment. Do not eat or drink while using chemicals listed above. Seek medical attention for any changes in health while exposed to these chemicals. The purified municipal wastewater must be treated with sodium hypochlorite for 24 hours prior to disposal. Chemicals ready for disposal are placed in labelled containers and email HazWaste@stonybrook.edu for hazardous waste disposal pick up. No significant risks are associated with these chemicals if all safety precautions are complied with.

Data Analysis

All experiments were performed in triplicate and results were averaged. Microsoft Excel was used to calculate standard deviation and render graphs.

1. **Human Participants Research: N/A**
2. **Vertebrate Animal Research: N/A**
3. **Potentially Hazardous Biological Agents: N/A**
4. **Hazardous Chemicals, Activities & Devices Risk Assessment:**

    A. **Risk Assessment Process**

    TEMPO- oxidized CNF (0.5 wt%) [49]

    - Toxicity: 0
        - Eye: N/A
        - Skin: N/A
        - Inhalation: N/A
        - Ingestion: N/A
    - Reactivity: 0

- Flammability: 0
- Corrosiveness: 0

ePAN [50]

- Toxicity: 0
  - Eye: May cause eye irritation.
  - Skin: May be harmful if absorbed through skin. May cause skin irritation.
  - Inhalation: May be harmful if inhaled. May cause respiratory tract irritation.
  - Ingestion: May be harmful if swallowed.
- Reactivity: 0
- Flammability: 0
- Corrosiveness: 0

Lyocell (0.15 wt%) [51]

- Toxicity: 0
  - Eye: May cause eye irritation.
  - Skin: May cause skin irritation.
  - Inhalation: May cause respiratory tract irritation.
  - Ingestion: N/A
- Reactivity: 0
- Flammability: 0
- Corrosiveness: 0

Purified municipal wastewater [52-53]

- Toxicity: 2
  - Eye: May cause severe eye irritation.
  - Skin: May cause severe skin irritation.
  - Inhalation: May be harmful if inhaled. May cause respiratory tract irritation.
  - Ingestion: May be harmful if swallowed.

- Reactivity: 1
- Flammability: 0
- Corrosiveness: 1

Polyacrylate Emulsions (PAE; 0.5 wt%) [54]

- Toxicity: 2
    - Eye: May cause eye irritation.
    - Skin: N/A
    - Inhalation: N/A
    - Ingestion: N/A
- Reactivity: 0
- Flammability: 0
- Corrosiveness: 0

Sodium hypochlorite bleach (5 wt%) [55]

- Toxicity: 2
    - Eye: May cause eye irritation.
    - Skin: May cause skin irritation.
    - Inhalation: May cause respiratory irritation
    - Ingestion: Moderately toxic if ingested
- Reactivity: 0
- Flammability: 0
- Corrosiveness: 1

B. Supervision

Adult supervision, by designated supervisor, will be provided at all times in the lab during experimentation.

C. Safety Precautions

Purified municipal wastewater requires careful handling to minimize any contamination and harm to the student and surrounding scientists. To ensure this, all handling of purified municipal wastewater will be conducted under a ventilated fume hood. Personal protective equipment (gloves, goggles, disposable face masks, and lab coat) will be worn at all times in the lab.

D. Methods of Disposal

Wastewater and fouled membranes were sterilized with bleach overnight then disposed of. All other chemicals were disposed of in properly labelled and managed waste containers and picked up for disposal by Stony Brook University’s Environmental Health and Safety Department.

Addendum:

- Completed FTIR and Water Contact Angle of the Lyocell Membrane as per procedures listed above to determine cross-linking and hydrophilicity of the lyocell membranes
- Completed Turbidity Analysis for the wastewater sample, PVDF permeate, ePAN permeate and lyocell permeate to determine water quality of the permeate.
    - Placed sample of the permeate in the automatic turbidity meter (Oakton T100 T-100 Turbidity Meter)
- Completed Dead End Fouling Test for the All-Cellulose Membrane according to the procedure above.

D. **Bibliography**

[1] “Why Water? The Water Crisis in Africa,” *The Water Project*. [Online]. Available: https://thewaterproject.org/why-water/water-crisis. [Accessed: 16-Sep-2019].

[2] UNICEF, *Progress on drinking water and sanitation: 2014 update*. Geneva: World Health Organization, UNICEF, 2014.

[3] X. Zheng, Z. Zhang, D. Yu, X. Chen, R. Cheng, S. Min, J. Wang, Q. Xiao, and J. Wang, “Overview of membrane technology applications for industrial wastewater treatment in China to increase water supply,” *Resources, Conservation and Recycling*, vol. 105, pp. 1–10, 2015.

[4] S. Nair, B. George, H. M. Malano, M. Arora, and B. Nawarathna, “Water–energy–greenhouse gas nexus of urban water systems: Review of concepts, state-of-art and methods,” *Resources, Conservation and Recycling*, vol. 89, pp. 1–10, 2014.

[5] C. Y. Tang, Z. Yang, H. Guo, J. J. Wen, L. D. Nghiem, and E. Cornelissen, “Potable Water Reuse through Advanced Membrane Technology,” *Environmental Science & Technology*, vol. 52, no. 18, pp. 10215–10223, 2018.

[6] Z. Zhang and J. W. Balay, “How Much is Too Much?: Challenges to Water Withdrawal and Consumptive Use Management,” *Journal of Water Resources Planning and Management*, vol. 140, no. 6, p. 01814001, 2014.

[7] K. Xiao, Y. Xu, S. Liang, T. Lei, J. Sun, X. Wen, H. Zhang, C. Chen, and X. Huang, “Engineering application of membrane bioreactor for wastewater treatment in China: Current state and future prospect,” *Frontiers of Environmental Science & Engineering*, vol. 8, no. 6, pp. 805–819, Aug. 2014.

[8] K. Xiao, Y. Xu, S. Liang, T. Lei, J. Sun, X. Wen, H. Zhang, C. Chen, and X. Huang, “Engineering application of membrane bioreactor for wastewater treatment in China: Current state and future prospect,” *Frontiers of Environmental Science & Engineering*, vol. 8, no. 6, pp. 805–819, Aug. 2014.

[9] R. Nazari, S. Eslamian, and R. Khanbilvardi, “Water Reuse and Sustainability,” *Ecological Water Quality - Water Treatment and Reuse*, 2012.

[10] P. Roccaro, “Treatment processes for municipal wastewater reclamation: The challenges of emerging contaminants and direct potable reuse,” *Current Opinion in Environmental Science & Health*, vol. 2, pp. 46–54, 2018.

[11] M. Gündoğdu, Y. A. Jarma, N. Kabay, T. Ö. Pek, and M. Yüksel, “Integration of MBR with NF/RO processes for industrial wastewater reclamation and water reuse-effect of membrane type on product water quality,” *Journal of Water Process Engineering*, vol. 29, p. 100574, 2019.

[12] D. Dolar, M. Racar, and K. Košutić, “Municipal Wastewater Reclamation and Water Reuse for Irrigation by Membrane Processes,” *Chemical and Biochemical Engineering Quarterly*, no. 3, Apr. 2019.

[13] S. M. Sadr and D. P. Saroj, “Membrane technologies for municipal wastewater treatment,” *Advances in Membrane Technologies for Water Treatment*, pp. 443–463, 2015.

[14] B. A. Getachew, S.-R. Kim, and J.-H. Kim, “Self-Healing Hydrogel Pore-Filled Water Filtration Membranes,” *Environmental Science & Technology*, vol. 51, no. 2, pp. 905–913, Jun. 2017.

[15] X. Li, L. Jiang, and H. Li, “Application of Ultrafiltration Technology in Water Treatment,” *IOP Conference Series: Earth and Environmental Science*, vol. 186, p. 012009, Nov. 2018.

[16] M. Aslam, A. Charfi, G. Lesage, M. Heran, and J. Kim, “Membrane bioreactors for wastewater treatment: A review of mechanical cleaning by scouring agents to control membrane fouling,” *Chemical Engineering Journal*, vol. 307, pp. 897–913, 2017.

[17] X. Li, L. Jiang, and H. Li, “Application of Ultrafiltration Technology in Water Treatment,” *IOP Conference Series: Earth and Environmental Science*, vol. 186, p. 012009, Nov. 2018.

[18] G. Fan, Z. Su, R. Lin, X. Lin, R. Xu, and W. Chen, “Influence of Membrane Materials and Operational Modes on the Performance of Ultrafiltration Modules for Drinking Water Treatment,” *International Journal of Polymer Science*, vol. 2016, pp. 1–8, 2016.

[19] D. S. Lakshmi, S. Jaiswar, M. Saxena, F. Tasselli, and H. D. Raval, “Preparation and performance of biofouling resistant PAN/chitosan hollow fiber membranes,” *3 Biotech*, vol. 7, no. 3, 2017.

[20] P. Bahmani, A. Maleki, H. Daraei, M. Khamforoush, R. Rezaee, F. Gharibi, A. G. Tkachev, A. E. Burakov, S. Agarwal, and V. K. Gupta, “High-flux ultrafiltration membrane based on electrospun polyacrylonitrile nanofibrous scaffolds for arsenate removal from aqueous solutions,” *Journal of Colloid and Interface Science*, vol. 506, pp. 564–571, 2017.

[21] S. Talebian, A. M. Afifi, and H. M. Khanlou, “Fabrication and characterization of chitosan/polyvinyl alcohol nanofibres via electrospinning,” *Materials Research Innovations*, vol. 18, no. sup6, May 2014.

[22] Y. Liu, R. Wang, H. Ma, B. S. Hsiao, and B. Chu, “High-flux microfiltration filters based on electrospun polyvinylalcohol nanofibrous membranes,” *Polymer*, vol. 54, no. 2, pp. 548–556, 2013.

[23] D. Hou, Z. Wang, K. Wang, J. Wang, and S. Lin, “Composite membrane with electrospun multiscale-textured surface for robust oil-fouling resistance in membrane distillation,” *Journal of Membrane Science*, vol. 546, pp. 179–187, 2018.

[24] M. Faccini, G. Borja, M. Boerrigter, D. M. Martín, S. M. Crespiera, S. Vázquez-Campos, L. Aubouy, and D. Amantia, “Electrospun Carbon Nanofiber Membranes for Filtration of Nanoparticles from Water,” *Journal of Nanomaterials*, vol. 2015, pp. 1–9, 2015.

[25] X. Zhang, S. Yang, B. Yu, Q. Tan, X. Zhang, and H. Cong, “Advanced Modified Polyacrylonitrile Membrane with Enhanced Adsorption Property for Heavy Metal Ions,” *Scientific Reports*, vol. 8, no. 1, 2018.

[26] G. M. Tolba, A. Bastaweesy, E. Ashour, W. Abdelmoez, K. A. Khalil, and N. A. Barakat, “Effective and highly recyclable ceramic membrane based on amorphous nanosilica for dye

removal from the aqueous solutions," *Arabian Journal of Chemistry*, vol. 9, no. 2, pp. 287–296, 2016.

[30] X. Bao, Q. Wu, W. Shi, W. Wang, Z. Zhu, Z. Zhang, R. Zhang, X. Zhang, B. Zhang, Y. Guo, and F. Cui, "Insights into simultaneous ammonia-selective and anti-fouling mechanism over forward osmosis membrane for resource recovery from domestic wastewater," *Journal of Membrane Science*, vol. 573, pp. 135–144, 2019.

[31] J. Ochando-Pulido, V. Verardo, A. Segura-Carretero, and A. Martinez-Ferez, "Technical optimization of an integrated UF/NF pilot plant for conjoint batch treatment of two-phase olives and olive oil washing wastewaters," *Desalination*, vol. 364, pp. 82–89, 2015.[30] D. Lu, T. Zhang, L. Gutierrez, J.

[32] Jepsen, Kasper, et al. "Membrane Fouling for Produced Water Treatment: A Review Study From a Process Control Perspective." *Water*, vol. 10, no. 7, 2018, p. 847., doi:10.3390/w10070847.

[33] W. Zhang and B. Dong, "Effects of physical and chemical aspects on membrane fouling and cleaning using interfacial free energy analysis in forward osmosis," *Environmental Science and Pollution Research*, vol. 25, no. 22, pp. 21555–21567, 2018.

[34] V. Freger, J. Gilron, and S. Belfer, "TFC polyamide membranes modified by grafting of hydrophilic polymers: an FT-IR/AFM/TEM study," *Journal of Membrane Science*, vol. 209, no. 1, pp. 283–292, 2002.

[35] A. Isogai, T. Saito, and H. Fukuzumi, "TEMPO-oxidized cellulose nanofibers," *Nanoscale*, vol. 3, no. 1, pp. 71–85, 2011.

[36] L. Kong, D. Zhang, Z. Shao, B. Han, Y. Lv, K. Gao, and X. Peng, "Superior effect of TEMPO-oxidized cellulose nanofibrils (TOCNs) on the performance of cellulose triacetate (CTA) ultrafiltration membrane," *Desalination*, vol. 332, no. 1, pp. 117–125, 2014.

[37] S.-S. Shen, H. Chen, R.-H. Wang, W. Ji, Y. Zhang, and R. Bai, "Preparation of antifouling cellulose acetate membranes with good hydrophilic and oleophobic surface properties," *Materials Letters*, vol. 252, pp. 1–4, 2019.

[38] C. Ao, W. Yuan, J. Zhao, X. He, X. Zhang, Q. Li, T. Xia, W. Zhang, and C. Lu, "Superhydrophilic graphene oxide@electrospun cellulose nanofiber hybrid membrane for high-efficiency oil/water separation," *Carbohydrate Polymers*, vol. 175, pp. 216–222, 2017.

[39] F. Yalcinkaya, A. Siekierka, and M. Bryjak, "Surface modification of electrospun nanofibrous membranes for oily wastewater separation," *RSC Advances*, vol. 7, no. 89, pp. 56704–56712, 2017.

[40] Z. Xu, X. Li, K. Teng, B. Zhou, M. Ma, M. Shan, K. Jiao, X. Qian, and J. Fan, "High flux and rejection of hierarchical composite membranes based on carbon nanotube network and ultrathin electrospun nanofibrous layer for dye removal," *Journal of Membrane Science*, vol. 535, pp. 94–102, 2017.

[41] J. Saththasivam, W. Yiming, K. Wang, J. Jin, and Z. Liu, “A Novel Architecture for Carbon Nanotube Membranes towards Fast and Efficient Oil/water Separation,” *Scientific Reports*, vol. 8, no. 1, Sep. 2018.
[42] Y.-F. Guan, B.-C. Huang, Y.-J. Wang, B. Gong, X. Lu, and H.-Q. Yu, “Modification of forward osmosis membrane with naturally-available humic acid: Towards simultaneously improved filtration performance and antifouling properties,” *Environment International*, vol. 131, p. 105045, 2019.
[43] S. Murad and L. C. Nitsche, “The effect of thickness, pore size and structure of a nanomembrane on the flux and selectivity in reverse osmosis separations: a molecular dynamics study,” *Chemical Physics Letters*, vol. 397, no. 1-3, pp. 211–215, 2004.
[44] Y. Zhao, M. Zhang, and Z. Wang, “Underwater Superoleophobic Membrane with Enhanced Oil-Water Separation, Antimicrobial, and Antifouling Activities,” *Advanced Materials Interfaces*, vol. 3, no. 13, p. 1500664, 2016.
[45] Z. Anari, A. Sengupta, K. Sardari, and S. R. Wickramasinghe, “Surface modification of PVDF membranes for treating produced waters by direct contact membrane distillation,” *Separation and Purification Technology*, vol. 224, pp. 388–396, 2019.
[46] E. Borbély, “Lyocell, The New Generation of Regenerated Cellulose ,” *Acta Polytechnica Hungarica* , vol. 5, no. 3, 2008.
[47]K. E. Perepelkin, “Lyocell fibres based on direct dissolution of cellulose in N-methylmorpholine N-oxide: Development and prospects,” *Fibre Chemistry*, vol. 39, no. 2, pp. 163–172, 2007.
[48]Y. Zhao, M. Zhang, and Z. Wang, “Underwater Superoleophobic Membrane with Enhanced Oil-Water Separation, Antimicrobial, and Antifouling Activities,” *Advanced Materials Interfaces*, vol. 3, no. 13, p. 1500664, 2016.
[49]“Nanocellulose Data Sheets - The Process Development Center - University of Maine.” *The Process Development Center*, https://umaine.edu/pdc/nanocellulose/nanocellulose-spec-sheets-and-safety-data-sheets/.
[50] “American Polymer Standards Corporation.” *Polyacrylonitrile Safety Data Sheet*, http://www.ampolymer.com/SDS/PolyacrylonitrileSDS.html.
[51] “Tencel® Lyocell Short-Cut Fiber.” *EFT*, http://www.eftfibers.com/prod_lyocell.php.
[52] “Safety Data Sheets.” *LSB*, https://www.lsbindustries.com/content/safety-data-sheets.
[53] “Buy Liquid Nitrogen or Purchase Compressed Nitrogen Gas (N2).” *Praxair*, https://www.praxair.com/gases/buy-liquid-nitrogen-or-compressed-nitrogen-gas.
[54] “Products.” *Palmer Holland - Products*, https://www.palmerholland.com/products.
[55] “Bleach (Sodium Hypochlorite) Safety Tips: Bleach Safety Instruction.” *MSDSonline*, 15 Sept. 2017, https://www.msdsonline.com/2014/02/12/bleach-sodium-hypochlorite-safety-tips-bleach-safety-instruction/