Recent Advances and Future Perspective on Nanocellulose-based Materials in Diverse Water Treatment Applications

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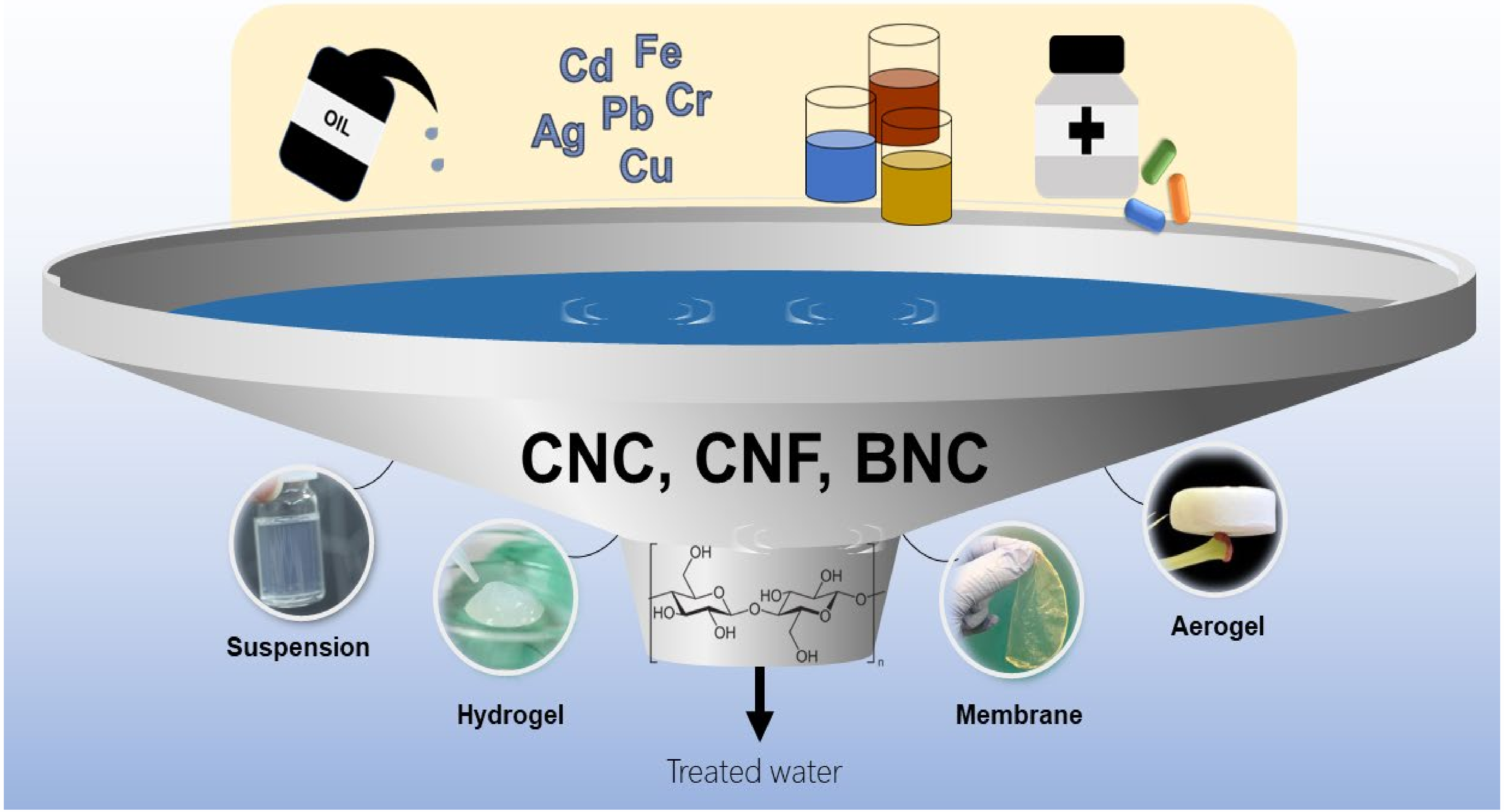
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CNC, CNF, BNC
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Suspension
Hydrogel
Membrane
Aerogel
Treated water

Introduction

- Cellulose is the most abundant polymer on earth; it is found in plants (wood, oil palm biomass, bamboo, hemp, flax, kenaf and coconut husk), bacteria, algae, and tunicates.
- It hydrophilic, biodegradable and nontoxic making it a suitable material for numerous applications.
- Nanocellulose exhibits the merits of cellulose but with larger surface area (100 to 200 m^2/g), higher tensile strength, excellent stiffness, and chemical inertness.
- Nanocellulose is rich in reactive hydroxyl groups that form strong H-bonding, permitting a broad range of application and ease of surface functionalization

Extraction of nanocellulose

The preparation of nanocellulose from cellulose involves two stages

1. Elimination of non-cellulosic constituents including hemicellulose and lignin by acid chlorite or alkaline pre-treatments
2. Isolation of nanocellulose from cellulose fibrils using various physical, chemical, or enzymatic extraction methods

The resulting materials have at least one or more nanoscale dimensions and are called nanocellulose

Nanocellulose structure and extraction

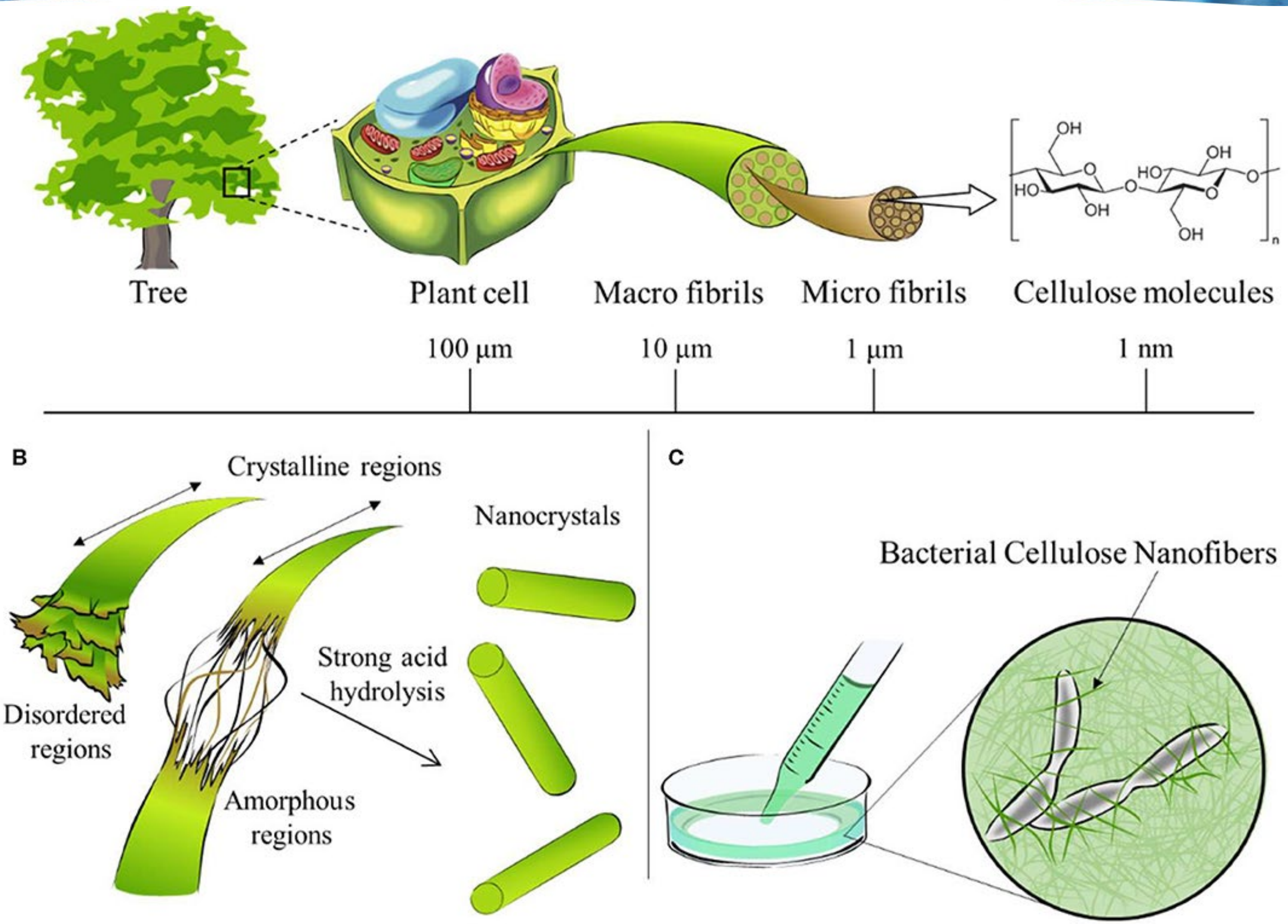

Figure from: Trache, D., Tarchoun, A. F., Derradji, M., Hamidon, T. S., Masruchin, N., Brosse, N., & Hussin, M. H. (2020). Nanocellulose: from fundamentals to advanced applications. Frontiers in Chemistry, 8, 392.

Types of nanocellulose

- **Cellulose nanofibers (CNF):** long, thin fibers (5-60 nm in diameter and a few micrometres in length) that have crystalline & amorphous domains. Their production involves breakdown of plant cell walls using intensive mechanical disintegration.
- **Cellulose nanocrystals:** rodlike structures with lengths between 100-250 nm and diameters between 4-10 nm. Extracted from cellulose fibrils by acid hydrolysis which selectively dissolves the amorphous domains
- **Bacterial nanocellulose:** ribbon-like obtained from bacterial cells, using a bottom-up approach
- **Electrostatically stabilized nanocrystalline cellulose:** Extracted via chemical treatments using NaIO4 followed by $NaClO_2$ as oxidants to solubilize the amorphous regions while leaving some "hairs" projecting at the ends of the crystalline structure.

Application forms of nanocellulose as an adsorbent

- **Suspended matter**
  - Simple application, easy storage
  - Difficult to recover loss of material

- **Hydrogel**
  - Easy recovery, flexible, water retention ability
  - Poor mechanical properties, sensitive to temperature

- **Aerogels**
  - Light weight, high porosity, superabsorption ability, excellent for oil absorption
  - Long processing times, require energy intensive instruments such as freeze-dryer

- **Membranes**
  - Easy to operate, reusable and recyclable
  - Short life span

Types of nanocellulose and their application forms

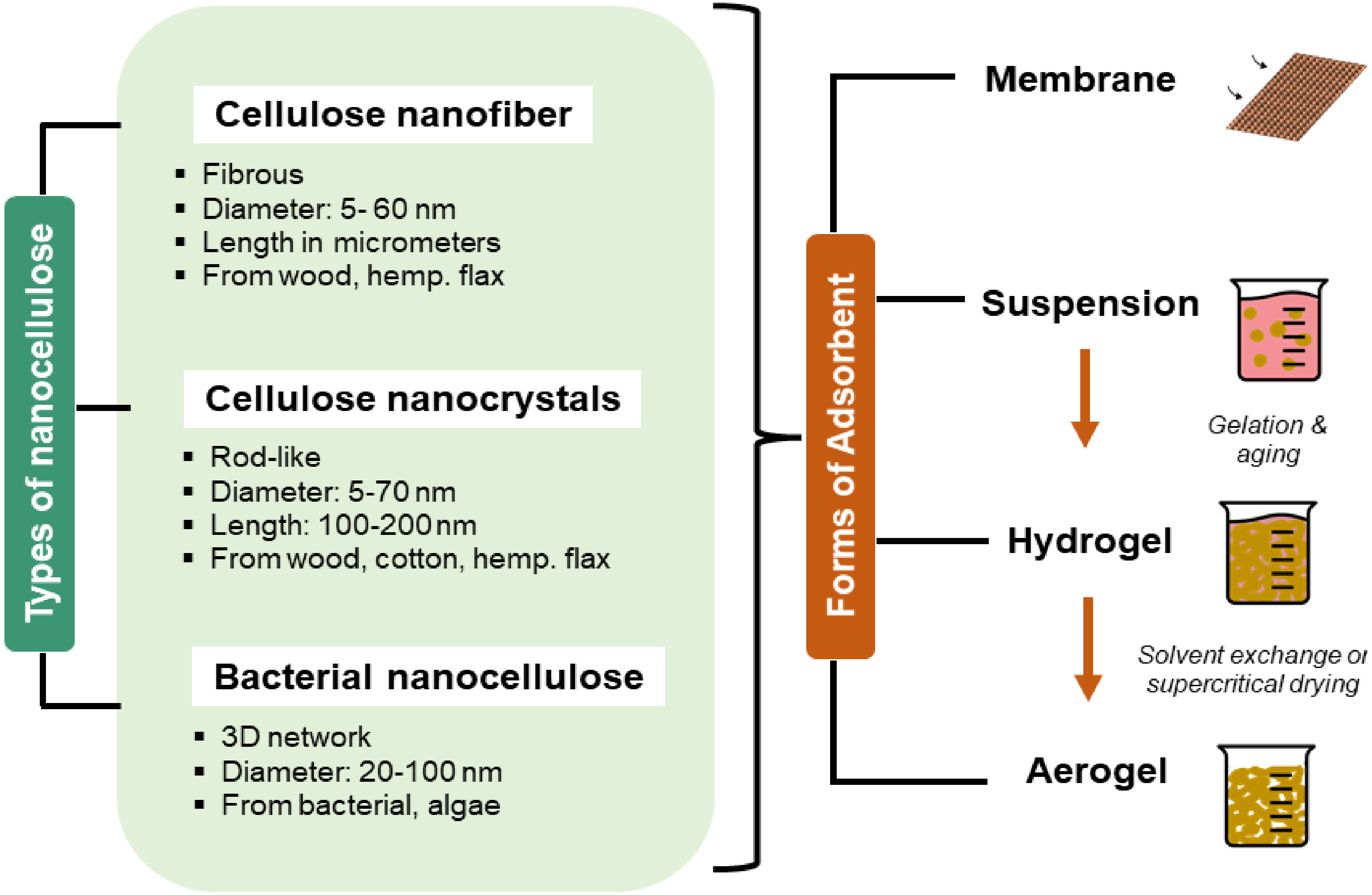

Figure from: Aoudi, B., Boluk, Y., & El-Din, M. G. (2022). Recent advances and future perspective on nanocellulose-based materials in diverse water treatment applications. Science of The Total Environment, 156903.

Modifications of nanocelluloses for enhanced adsorption

- CNC, CNF or BNC, have hydroxyl groups which facilitate a wide range of surface modifications for targeted applications.
- However, the broad applicability is constricted by its poor dispersibility in nonpolar solvents and inadequate interfacial adhesion with hydrophobic matrixes.
- Nanocellulose materials are susceptible to aggregation which diminishes the surface area available for adsorption processes.
- Surface modifications may be necessary to change the hydrophilicity and improve the compatibility and dispersity of nanocellulose in diverse solvents.

Modifications of nanocelluloses for enhanced adsorption

- *Oxidation* (TEMPO, maleic anhydride, NaIO4/$NaClO_2$,…)
  - Adsorption of cations e.g methylene blue
- *Silylation* (chlorosilanes ,alkoxy silanes)
  - Suitable for oil adsorption
- *Amination* (APTES, acrylamide, ethylenediamine)
  - Adsorption for anions e.g Congo red
- *Polymer grafting* (polyvinyl alcohol, poly lactic acid, polyvinyl chloride….)
  - Improves the tensile strength and decreases the elasticity

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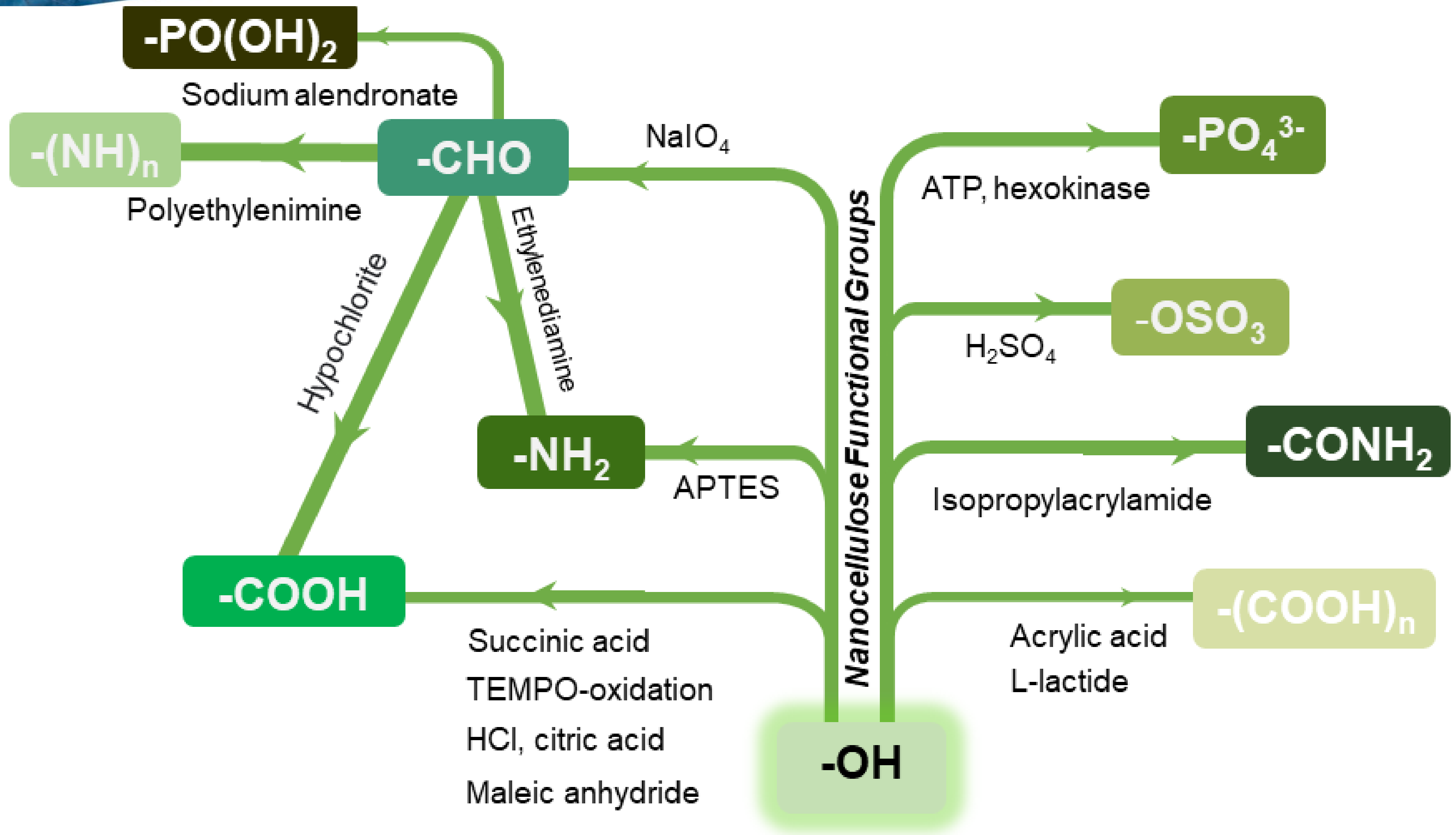

Surface modifications of nanocellulose

Figure from: Aoudi, B., Boluk, Y., & El-Din, M. G. (2022). Recent advances and future perspective on nanocellulose-based materials in diverse water treatment applications. Science of The Total Environment, 156903.

Nanocellulose nanocomposite materials

- Nanomaterials can be integrated into the substrate by direct incorporation of nanoparticles into the matrix, in situ generation of nanoparticles via reduction in a polymer matrix, polymerization of monomers, or via layer-by-layer assembly.
- Nanocellulose is an attractive continuous phase material that can host diverse nanoparticles to form nanocomposites and **prevent aggregation.**
- AgNPs/nanocellulose composites in different forms e.g., suspensions, paper, films, and hydrogel have displayed an incredible ability to eradicate microbes.

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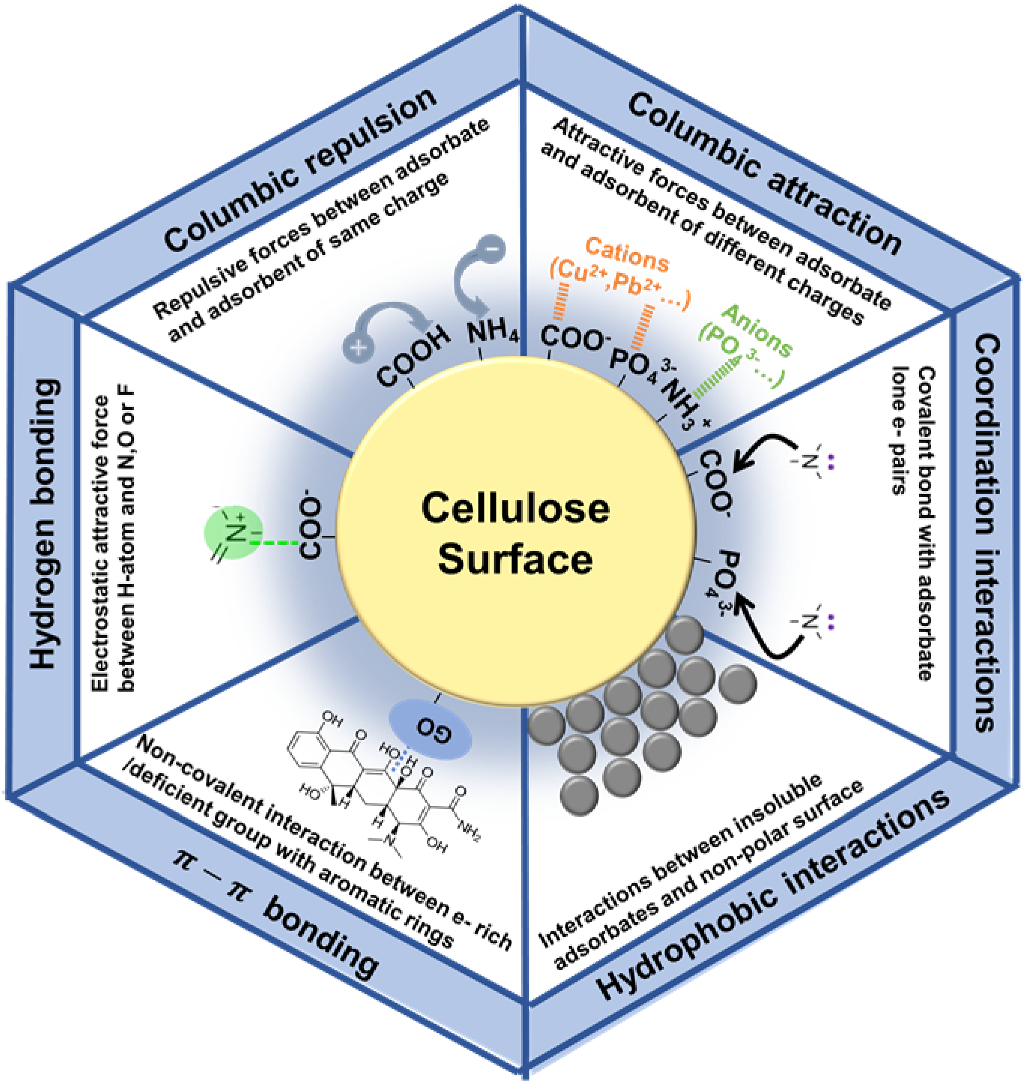
Application of nanocellulose in adsorption of contaminants

- Numerous studies have reported the removal of heavy metals, dyes, pharmaceuticals and pesticides, lipids, and oils from aqueous solutions using nanocellulose adsorbents.
- Contaminants are adsorbed onto nanocellulose by chelation, complexation, ion exchange, precipitation which are governed by hydrogen bonds, van der Waals, and dipole- dipole interaction.
- The desorption of adsorbed contaminants onto nanocellulose surface can easily be achieved by acidic treatments /alkaline treatments.

Adsorption mechanisms of contaminants onto cellulose surface



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Challenges and Future of nanocellulose

Challenges	Possible solutions
Handling &storage	Surface modification Redispersibility
Scaling up	Life cycle assessments More pilot scale studies
Adsorbent recovery	Hydrogel beads Magnetic nanocomposites
Unclear toxicity	More toxicity studies require Pilot scale experiments
High production cost	Enzymatic/ chemical pretreatment Nonwoody cellulose feedstock

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References

Aoudi, B., Boluk, Y., & El-Din, M. G. (2022). Recent advances and future perspective on nanocellulose-based materials in diverse water treatment applications. Science of The Total Environment, 156903.

Boluk, Y. and Danumah, C., 2014. Analysis of cellulose nanocrystal rod lengths by dynamic light scattering and electron microscopy. Journal of nanoparticle research, 16(1), 1-7.

Klemm, D., Heublein, B., Fink, H.P. and Bohn, A., 2005. Cellulose: fascinating biopolymer and sustainable raw material. Angewandte chemie international edition, 44(22), 3358-3393.

Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D. and Dorris, A., 2011. Nanocelluloses: a new family of nature-based materials. Angewandte Chemie International Edition, 50(24), 5438-5466.

Köse, K., Mavlan, M. and Youngblood, J.P., 2020. Applications and impact of nanocellulose based adsorbents. Cellulose, 27(6), 2967-2990.

Mahfoudhi, N. and Boufi, S., 2017. Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review. Cellulose, 24(3), 1171-1197.

Norrrahim, M.N.F., Kasim, N.A.M., Knight, V.F., Misenan, M.S.M., Janudin, N., Shah, N.A.A., Kasim, N., Yusoff, W.Y.W., Noor, S.A.M., Jamal, S.H. and Ong, K.K., 2021. Nanocellulose: A bioadsorbent for chemical contaminant remediation. RSC Advances, 11(13), 7347-7368.

Rajinipriya, M., Nagalakshmaiah, M., Robert, M. and Elkoun, S., 2018. Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: a review. ACS Sustainable Chemistry & Engineering, 6(3), 2807-2828.

Reshmy, R., Philip, E., Madhavan, A., Pugazhendhi, A., Sindhu, R., Sirohi, R., Awasthi, M.K., Pandey, A. and Binod, P., 2022. Nanocellulose as green material for remediation of hazardous heavy metal contaminants. Journal of Hazardous Materials, 424, 127516.

Trache, D., Tarchoun, A. F., Derradji, M., Hamidon, T. S., Masruchin, N., Brosse, N., & Hussin, M. H. (2020). Nanocellulose: from fundamentals to advanced applications. Frontiers in Chemistry, 8, 392.

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