Cellulose Membrane Technology for Water Purification

A Breakthrough Innovation

Benjamin S. Hsiao
Distinguished Professor
Chemistry Department
Classification of Membrane Filtration

- **Nanofiltration (NF)**
- **Reverse Osmosis (RO)**
- **Ultrafiltration (UF)**
- **Microfiltration (MF)**
- **Conventional Filtration**

**Inorganic Ions**
- H₂O
- Sugars & Multivalent Ions

**Natural Organic Matters**
- Colloidal Silica
- Viruses
- Bacteria
- Yeast Cell

**Membrane Pore Size**
- 0.1 nm
- 1 nm
- 0.1 µm
- 10 µm

**Driven Force**
- Can be gravity-driven

Conventional Water Filtration Membranes (since 70’s)

**Size exclusion range**
- RO (Reverse Osmosis): < 1 nm
- NF (Nano-Filtration): 1 – 10 nm
- UF (Ultra-Filtration): 10 – 100 nm
- MF (Micro-Filtration): 0.1 – 50 μm
  - Aqueous salts: 0.3 – 1.2 nm
  - Pesticides, herbicides: 0.7 – 1.2 nm
  - Virus: 10 – 100 nm
  - Bacterial: 200 nm – 30 μm
Fiber Diameter and Pore Size in Non-woven Membranes

Fiber diameter ratio: 1 : 3 : 10; Porosity: 80%

Smaller fiber diameter, smaller effective pore size

Hierarchical Structure of Plant Cellulose

Cellulose fiber
Width 20-30 μm
Length 1-3 mm

Cellulose nanofiber/microfibril aggregate
Width 10-20 nm

Cellulose microfibril/nascent crystal
Width 3-4 nm
Length > 2 μm

Cellulose molecular chain (side view)

Plant cell wall

Plant cell

Plant

Cellulose molecular chains (cross section view)

Delamination

Cellulose nanostrand
New Concept: Nanofibrous Membranes with Hierarchical Fiber Diameters
Preparation of Cellulose Nanofibers

Cellulose wood pulp
Fiber diameter ~ 40 µm

100 µm

→

TEMPO/NaBr/NaClO
Mechanical treatment

Oxidized cellulose fibers

Cellulose nanofibers
Fiber diameter ~ 5 nm

0.50 µm

Carboxylate groups (negatively charged and chelation): 0.70 mmol/(g cellulose)

Aldehyde groups (chemical reactivity): 0.25 mmol/(g cellulose)

Hydroxyl groups (chemical reactivity): 2.0 mmol/(g cellulose)
Waterborne Diseases Caused by Bacteria, Viruses and Heavy Metals

E. Coli
- 0.5 µm in diameter
- 2 µm long

Leptospirosis
- 0.2 µm in diameter
- 10~20 µm long

SARS
- 100 nm
- pI = 4.5

Hepatitis A
- 20-30 nm
- pI = 3~4

Most bacteria have sizes over 0.2 µm
- Filtered by Size Exclusion

Most viruses have pI < 7, with negative charges at pH = 7
- Adsorbed by Charge Interactions

As (III), (V)
- in pesticide and burning coal

Cr (VI)
- in dye and paint

Most heavy metal ions have charges and can be interacted via chelating agents
- Adsorbed by Charge Interactions & Chelating Agents

http://www.hyfluxmembranes.com/
http://en.wikipedia.org/wiki/
Cellulose Nanofibers MF Membrane for Removal of E. Coli by Size Exclusion

The surface of the membrane was covered by E. Coli particles, whereas the retention ratio was 99.9999%.

Top view after filtration

Cross-sectional view after filtration

Cellulose Nanofibers MF Membrane for Removal of Virus and Toxic Metal by Adsorption

The adsorption capacity of UCN for $\text{UO}_2^{2+}$ was 167 mg/g;

The adsorption capacity of commercially available activated carbon for $\text{UO}_2^{2+}$ was 57 mg/g.

The adsorption capacity of CN based MF membrane for MS$_2$ was 99%, i.e., ~10X better than the adsorption capacity of commercially available GS9035 for MS$_2$ which was 90%.

Preliminary Data
Property of NYS Center for Clean Water Technology at Stony Brook University
Nanofibrous UF Membranes

- Permeation flux of nanofibrous UF membrane can be 10 X higher than conventional UF membranes (at the same rejection ratio) - due to higher porosity (80%) of non-wovens
- Cellulose nanofibers barrier layer is anti-fouling and more chemical resistant

Nanofibrous NF/RO Membranes

The nanocomposite barrier layer (cellulose nanofibers + polyamide matrix)
- is stronger than the conventional barrier layer
- introduces “directed water channels” to increase the flux by 2-5 X for RO desalination

Sources of Cellulose in Nature

• Higher plants (fibers, parenchyma etc.)
• Seaweeds (Valonia, etc.)
• Animals (Tunicates, Salpae etc.)
• Bacteria (Acetobacter, etc.)
• Fungi (Saprolegnia, etc.)
• Amoebae (Dictyostelium, etc.)
Our Goal

Sustainable membrane fabrication (MF, UF, NF RO, and MBR) using nanocelluloses from diverse biomass sources to treat a wide range of water problems.