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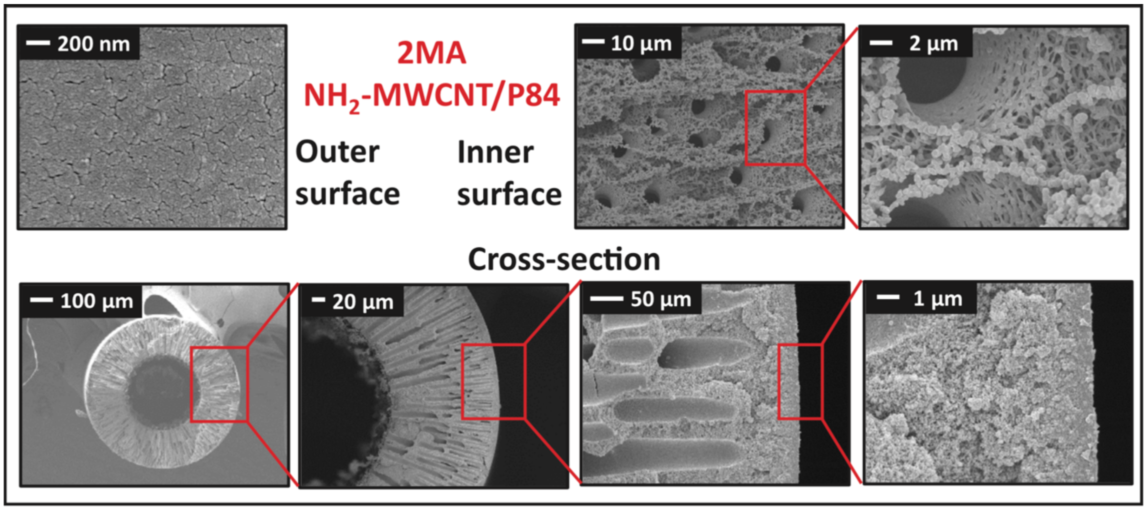
# Developments in Next-Generation Organic Solvent Nanofiltration and its Potential Application to Industry Processes




*Scanning Electron Microscope (SEM) images of a single fiber from the hollow fiber membrane.*
Credit: M.H. Davood Abadi Farahani, T.-S. Chung, and The University of Singapore

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*Recently, researchers in the Department of Chemical & Biomolecular Engineering at the National University of Singapore have had promising results in designing tougher hollow fiber membranes (HFMs) through polymer mixtures without sacrificing and instead improving performance. These membranes promise scalability and production, show greater mechanical and thermal stability, exhibit remarkable, high rejections, and demonstrate application in industries such as food, pharmaceutical, and petrochemical. (See Figure 1 below) In this article, the goal is to give a background and conceptual explanation on this topic.*

| **Rejections (% solute blocked)** | 3MA: P84 | 2MA: $NH_2$-MWCNT/P84 |
|---|---|---|
| Dye, Remazol Brilliant Blue (RBB) | 98.6 | 99.9 |
| Dye, Methylene Blue (MB) | 97.2 | 99.8 |
| Food Additive, L-α-lecithin | 96.3 | 99.3 |
| Antibiotic, Tetracycline (TC) | 89.3 | 97.4 |
| Petrochemical Reaction Catalysis, BINAP-Ru(II) | 95.5 | 98.2 |

*Figure 1:* Impermeability of Molecules used in various industries for currently common industry filter vs. Hollow Fiber Membrane Filter

# In Brief: Background and Conceptualization

Organic solvent nanofiltration (OSN) is a simple yet effective method in which dope (polymer solute) is separated from bore fluid (solvent). OSN and other methods enjoy the benefits of being a continuous process[1], while also being far more energy efficient while operating in mild temperatures. These properties allow OSN to have been successful in many industries where products are thermally unstable[2] and large quantities of organic solvents are used. Primarily, OSN is used for the separation of solutes from organic solvents but also for the recycle of the organic solvents as they tend to be very costly. A solvent resistant nanofiltration membrane is key to the OSN process. However, despite the advantages of OSN, the number of OSN membranes on the market is limited; not to mention their drawbacks which range from insufficient permeability[3] of the solvent to leaching of metals into the solvent[4]. OSN hollow fiber membranes have remained rare because most studies are devoted to the synthesis of flat sheet membranes. However, when comparing the two, hollow fiber membranes have more surface area per unit volume and a self-supporting structure. Flat sheet membranes also require a porous base to support their own weight, but stronger organic solvents will delaminate[5] the two layers. In which case, the filter: 1) is not doing its job, 2) stops the process (losing money), and 3) requires frequent replacement (costing more money). This motivated research into a single-layer OSN method without the mentioned disadvantages.

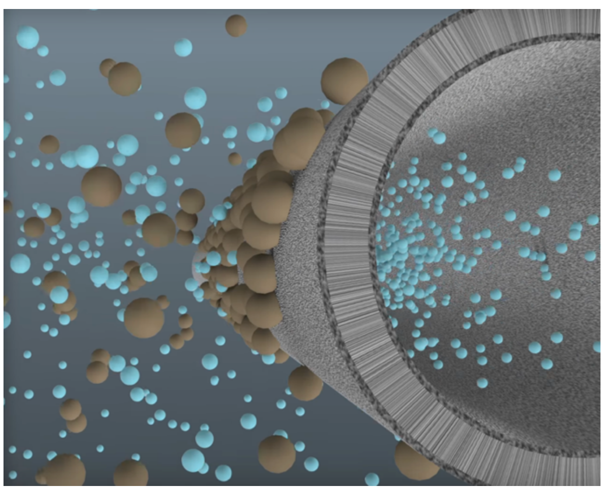

*Figure 2:* An illustration of a single HFM fiber filtering dope molecules (darker) from solvent molecules (lighter).

Hollow fiber membranes (HFM) are made up of hundreds to thousands of individual hollow fibers, illustrated in *Figure 2* to the left. Like all membranes, HFMs are selectively permeable in that they will only allow certain molecules to pass through while keeping others out. However, unlike the usual planar[6] membrane which functions like a coffee filter, HFMs do not have planar geometry. Imagine drinking soda through a straw; lowering the pressure on one end of the straw creates an overall negative pressure difference. Since pressure is defined as a force applied over an area, the force applied by the weight of the atmosphere is greater than the pressure on the other end. Thus, the atmosphere pushes the soda up the straw. Now, imagine that the straw's far opening was closed and instead has hundreds of pores along its length. These pores are small enough so that the water in the soda can pass through, while the many additives dissolved in the soda (flavoring, $CO_2$, preservatives, etc.) cannot do so and are left outside of the straw. In such case, one would be drinking water from soda. This is essentially what is happening with HFMs, many straw-like fibers acting like pipes with pores big enough for the solvent to pass through but not the dope. An example of HMFs being used in the way described above is the LifeStraw® product, which was proven to filter virtually all bacteria, parasites, and microplastics from contaminated water ("LifeStraw Evidence Dossier", 2015).

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1 continuous flow of the input and outputs
2 becomes altered or destroyed, essentially unrecoverable, if not kept at the correct temperature
3 ability to pass through the membrane, think of sieving beach sand to find seashell fragments
4 metals dissolving into the solvent, think of the romans being poisoned by their lead plumbing
5 to separate from one another
6 a flat sheet

## Diving Deeper: Amine-Functionalized Multi-walled Carbon Nanotubes/P84 Matrix

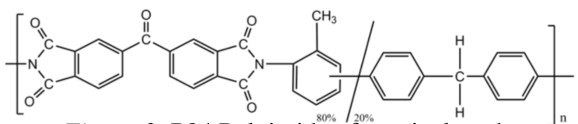

*Figure 3:* P84 Polyimide of *n* units length

P84 polyimide is commonly used for OSN purposes. Polyimides are a class of polymer[7] known for being chemically stable[8] yet limited in chemical resiliency. Many of the harsher organic solvents such as N-methyl pyrrolidone (NMP) and N,N-dimethylformamide (DMF) will eat away at the polyimide polymers until they break apart. To improve its resistance to harsh solvents, various *pairs* of amine bonds were formed, laterally connecting the fibers together. The bonds are formed by soaking the polyimide polymer in 1,6-hexanediamine (HDA). This modification, referred to as diamine crosslinking, has been proven to improve the resistance of P84 membranes to the harsher organic solvents. However, by fixing one problem, another is created. According to Chung and Farahani, "diamine crosslinking modifications cause a severe flux[9] decline." This was likely seen as the limit of progress to previous researchers and thus improvement research for P84 polyimide ceased. Enter Chung and Farahani, who theorized that filler compounds may be added to the polymer to decrease the amount of these diamine crosslinks per unit volume. They hoped that doing so would result in permeance/flux similar to before the addition of diamine crosslinks. Indeed, they were successful with one such filler, carbon nanotubes.

Carbon nanotubes[10] (CNTs) have been an obsession of the science community for the past few years. CNTs are a sort of jack-of-all-trades, possessing properties such as high electric conductivity, able to be conductors and insulators, 4x the tensile strength of steel, and being able to stretch by 20%. Mixed matrix membranes are a common term used to describe a polymer matrix, 3D structure, in which a filler molecule has been added. According to Chung and Farahani, "several studies have confirmed the advantages of using CNTs as nanofillers in [other] MMMs." Advantages have included high flexibility, low mass density, a large ratio of length to diameter, among others. The previous explains the researchers' interest in adding such a filler in the P84 membranes. Furthermore, they found that bonding amine functional groups to CNTs resulted in even greater resistance to solvents. This was because the tubes were actually bonded to the polyimide polymer rather than interspersed throughout the fiber.

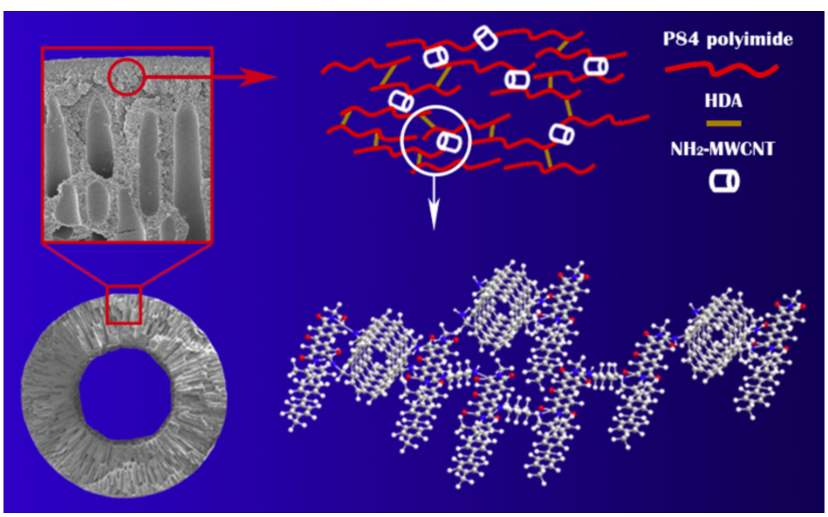


*Figure 4:* SEM images of the result of all the above, a simplified illustration of the membrane's structure, as well as a complex but more accurate molecular model below. Note: $NH_2$-MWCNT stands for the amine functionalized (*$NH_2$-*) carbon nanotubes (*CNTs*), which are actually multi-walled (*MW*) meaning concentric, multiple layers of tubes inside of each other.

[7] a long molecule chain composed of repeated units
[8] tendency of a material to resist change or decomposition in its natural environment
[9] flow rate represented as a vector quantity
[10] quite literally, a tube made solely of carbon atoms bonded together.

## Conclusion

More testing will be needed before $NH_2$-MWCNTs/P84 HFMs enter industries, particularly rigorous testing by the federal regulatory divisions. It is likely that these industries can expect to see the new technology within a decade or sooner depending if companies who would benefit from this technology decide to invest to further its development. Hopefully, with the knowledge presented here, chemical engineers can be prepared for their arrival with a strong sense of understanding on the topic.

For further readings and insights of the properties of $NH_2$-MWCNTs/P84 HFMs, see the research paper below.

"Solvent resistant hollow fiber membranes comprising P84 polyimide and amine-functionalized carbon nanotubes with potential applications in pharmaceutical, food, and petrochemical industries" by M.H. Davood Abadi Farahani, T.-S. Chung, and The University of Singapore

(https://www.sciencedirect.com/science/article/pii/S1385894718305114)

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Analysis

The goal was to translate the scholarly research paper, *Solvent resistant hollow fiber membranes comprising P84 polyimide and amine-functionalized carbon nanotubes with potential applications in pharmaceutical, food, and petrochemical industries,* into a chemical engineering trade publication. A trade publication was chosen as the popular genre of writing rather than a magazine because the topic is not relevant to those who do not or do not plan to work in the industry. Therefore, the audience targeted was chemical engineers who work or plan to work in industries such as food, pharmaceutical, petrochemical, as well as any other industry that would need to filter their organic solvents from their products. This audience will typically understand most chemistry terminology such as solvent, solute, and IUPAC molecule identifiers ($NH_2$, 1,6-hexanediamine, etc.). However, to allow this article to apply to those in the industry who aren't or aren't yet chemical engineers, the more abstract jargon was defined such as dope vs. bore fluid, continuous process, etc.). Note that while some terms are defined in the body of the article, the majority were defined in footnotes. This allows those who understand the jargon to continue reading uninterrupted while also allowing those who aren't as familiar with the jargon to educate themselves. The audience is also more likely to favor raw data. Therefore, part of the abstract page was a chart displaying improvements in 3 different fields; this is an appeal to logos. While the article contains SEM images of $NH_2$-MWCNTs/P84 HFMs, simplified illustrations are utilized throughout the article to assist in the conception of the complex topic. 3-dimensional polymer matrices containing carbon nanotubes, polymer chains, as well as diamine crosslinking is much harder to grasp through words and dense, black and white SEM images than with the illustration in the top right of *Figure 4*. While a trade publication will have semi-formal qualities to target a niche audience of those who work in or are interested in a particular field, a trade publication will also have relaxed qualities associated with a magazine. Since a trade publication, like a magazine, is concerned with selling copies and gaining more profit, the cover of the publication will aim to be eye-catching. Hence, the cover page image was chosen to be striking, bright, and overall blue which captures the attention of a passerby. While many small design elements were implicated throughout the article, such as the 'no profile picture' icon to the left of the author's name, the right half of the header, or the drop cap, another major element in the design was the overall structure. By organizing the article into three sections, being a summary and conceptualization, an in-depth analysis of the mechanisms, and a short conclusion, the article telescopes into the topic, explaining the intricacies more as the article continues. This targets an audience with varying knowledge backgrounds and allows the audience to read to a depth that they prefer to go to while providing satisfying conclusions at each point. To conclude, the translation was made to allow those of varying knowledge who are chemical engineers or are interested in the field to understand a very complex research paper about filtration.

Works Cited

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