

Polyamide 66 hybrid TiO₂–pectin flat-sheet membrane applied to wetland water ultrafiltration

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Abstract: This article describes a study in which a hybrid, polyamide 66 flat-sheet membrane is fabricated and then used to eliminate turbidity in wetland water in an area of South Kalimantan, Indonesia. The membrane was prepared by the phase inversion technique, using nylon 66, formic acid solvent, titanium dioxide and pectin as additives. Results show that the pure water flux of the membrane produced is extremely high – reaching 418.04 Lm⁻²h⁻¹ – but decreased to 311.97 Lm⁻²h⁻¹ with the addition of TiO₂–pectin. When applied to wetland water the PA–TiO₂–pectin membrane showed 100% turbidity rejection.

South Kalimantan is an area dominated by wetlands. The water in this area has a high organic content, caused by a range of natural factors such as the decomposition of animals and plants. This means that the turbidity level is high and the water is unfit for use.

Therefore, it is necessary to process wetland water to make it suitable for use. The application of membrane technology has been proven to be an effective way of removing contaminants from water.

Wetland water

In Indonesia wetland water is an important resource. It is used as a source of raw water, in irrigation for agriculture and cultivation, and also plays an important role in transportation and commercial activities in areas such as Kalimantan.^[1]

However, the water does not meet required quality standards. If surface water – such as wetland water – is used directly by people, before it is treated, it could result in a variety of health problems. This raises public concerns about access to decent water sources that can be consumed safely.^[2]

Membrane technology provides an alternative way of producing drinking water. It has the advantage of replacing conventional processes such as coagulation, flocculation and chlorination.^[3]

Membrane technology

Membranes are capable of treating contaminated water, enabling it to meet desired criteria.^[4]

For many years, membrane technology has been applied in separation applications in the industrial world because its use forms the basis of processes that are fast and efficient.^[5]

Membranes are able to remove a variety of pollutants because they contain pores that are smaller in size than the pollutant itself.^[6] Microfiltration (MF) and ultrafiltration (UF) – commonly known as low-pressure membrane processes – have been used in a variety of industries, such as drinking-water treatment and liquid waste treatment, because they are easy to configure.^[7]

Compact configuration – flat sheet

UF membranes are capable of producing high-quality water and removing harmful contaminants such as bacteria, viruses and organic substances.^[8]

The flat-sheet membrane is the commonly used configuration. A flat-sheet membrane can produce high-quality water that is safe to consume because of its ability to remove solid suspensions from wetland water and also reduce its hardness.^[9]

This compact membrane configuration also supports the development and application of useful flat-sheet membranes for long-term use in wetland water treatment applications.^[10]

There are several studies on flat-sheet membranes which show that the membrane can process wetland water and produce clean water. Based on the work of Noguchi, H. *et al.*,^[11] it is possible for the separation of turbidity to reach 95–100%. Other studies also reveal that the separation of turbidity is quite high – up to < 1 NTU.^[12] This indicates that flat-sheet membranes are particularly suitable for use in wetland water management.

Polyamide 66

This study employed a flat-sheet configuration, using polyamide 66 (PA66) as the membrane material.

PA66 has been used lately in membrane technology because of its mechanical strength and hydrophilic properties. It shows stability under heavy physical and chemical conditions, and it also can be used when other membranes are unsuitable or difficult to use.^[13]

PA66 membranes have an average pore size of 0.45 μm , and are commonly used to remove microorganisms and large-scale particles such as organic molecules and nucleases.^[14]

Khan Mohammadi, S. *et al.*^[15] applied a nanofibrous membrane composite – comprising polyamide and polyacrylonitrile (PAN) (PAN/PA/PAN) – to a spunbond–meltblown–spunbond (SMS) polypropylene nonwoven and carbon foam substrate, resulting in a reduction in turbidity of 99.58% and 86.13% in chemical oxygen demand (COD).

In another study, Abd Halim, N.S. *et al.*^[16] developed an electrospun nylon 6,6 nanofibre membrane (NFM), incorporating a zeolitic imidazolate framework-8 (ZIF-8) as the additive, for produced water (PW) filtration. The results showed 98% turbidity rejection.

Additives

PA66 membranes were prepared using the phase inversion method. The membrane was then characterised before it was used in the separation process.

This research aims to determine the effect that adding inorganic titanium dioxide (TiO_2) and organic (pectin) materials to PA66 polymer membranes has on their characteristics and performance in wetland water treatment applications.

Several studies indicate that the addition of TiO_2 to the polymer membrane results in a significant increase in hydrophilic and anti-fouling properties.^[17] Pectin was added to the fabrication of the membranes in order to improve their hydrophilic properties.^[18]

Experimental work

Materials

The following chemicals were used to fabricate the membrane: nylon 66 (PA66), from Asahi Kasei's LEONA™ family of PA66 resins, with a density of 1.14 g/cm^3 ; formic acid 90%, as a solvent, with a density of 1.18 g/ml ; TiO_2 ; apple pectin, which is

commercially available from local chemical distributor PT Tunggal Jaya Kimia, Surabaya, Indonesia; and deionised water as a co-solvent (with coagulation bath).

Preparation of polyamide hybrid membranes

Flat-sheet polyamide membranes were produced using the phase inversion method.

The membrane solution was created by dissolving nylon 66, weighing 17%, in 78% formic acid and 5% water by weight. Hybrid membranes were created by altering the addition of TiO_2 particles (PA- TiO_2), apple pectin (PA-pectin) and TiO_2 -pectin (PA- TiO_2 -pectin). **Table 1** shows the variations in composition.

The membrane dope solution was prepared by dissolving additives (TiO_2 /pectin) with formic acid and water at 350 rpm and applying heat until homogeneous. Polymer (nylon 66) was then added whilst stirring until the solution became homogeneous. The dope solution was allowed to stand for 1 hour to remove air bubbles caused by the stirring.

The solution was then “printed” using a membrane printing machine, with the blade film applicator set to a thickness of 200 μm . It was then poured onto a level glass surface, and a film applicator, with gradual motion, was used to create a thin-film membrane.

The film was allowed to dry for 5 minutes to let the solvent evaporate before being placed in a coagulation bath of purified water.

Following the casting process, the thin-film membrane was immersed in purified water for 24 hours to eliminate any residual solvent and later dried at room temperature before undergoing characterisation. The procedure for creating the membrane is illustrated in **Figure 1**.

Membrane characterisation

The membrane was characterised using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) analysis.

FTIR spectroscopy was used to determine the functional groups of the PA66 membrane, using instrument model Alpha – manufactured by Bruker Corp – with absorption measured in the range 4000–400.

To establish the membrane surface morphology and cross-sectional structure, Hitachi High-Technologies Corp's TM3000 scanning electron microscope was used.

Performance measurement

Flux measurements were made by cutting the membrane into the shape of a disc, with a diameter of 3.5 cm, and inserting this into the test module. It was covered with filter paper on the top and bottom surfaces. Flux testing was done by passing distilled water through the module.

Compaction for an hour was carried out before flux test-data were collected. Flux was measured for 1 hour, with data collected every 5 minutes.

The water flux J ($\text{Lm}^{-2}\text{h}^{-1}$) and rejection R (%) were calculated using **Equations 1 & 2**.^[19 & 20]

where V is the permeate water volume (l); A is the membrane area (m^2), t is the permeation time (h); and C_f is concentration feed and C_p is the concentration permeate. The flux testing process, using the module, can be seen in **Figure 2**.

Contact Angle

The hydrophobic properties of the membrane can be found by measuring the water contact angle.

A certain volume of water (droplets) is deposited on the surface of the membrane being tested using a tight syringe. The contact angle is the angle formed between the film/membrane surface area and the water droplet plane. From this point of view, the wettability of a membrane can be determined using ImageJ (open source software for processing and analysing scientific images).

Swelling measurement

Swelling testing is carried out to determine the water absorption capacity of the membrane.

The test is done by immersing the membrane in pure water for 24 hours. Previously, the membrane was weighed to obtain the initial weight (*W_{dry}*), then after 24 hours the membrane was dried with tissue and weighed again to obtain the final weight (*W_{wet}*). The swelling ratio was calculated using **Equation 3**.^[21]

Results and discussion

Membrane characterisation

The nylon 66 membrane fabricated in this study was characterised by IR spectroscopy in order to analyse the chemical composition changes on its surface. **Figure 3** shows the IR spectrum of four variations of the polyamide 66 membrane.

The IR spectrum of the polyamide 66 membrane with the addition of TiO₂/pectin did not show any significant differences. This is because the addition of pectin and TiO₂ is only in small amounts so that it is not detected qualitatively in the IR spectra graph.

In all variations of the polyamide membrane there are several groups, namely N–H at peak 3299 cm⁻¹, and at 2934 cm⁻¹ and 2859 cm⁻¹ symmetric and asymmetric C–H stretching vibrations occur.

At peaks 1631 cm⁻¹ and 1535 cm⁻¹ two peaks were detected – the strong ones, namely amide I band and amide II band (Figure 3) in the PA and PA–TiO₂–pectin membrane samples, whilst in the PA–TiO₂ and PA–pectin samples, middle bands I and II were detected at peaks of 1631 cm⁻¹ and 1537 cm⁻¹.

This group band shift occurs because the carbonyl group bonds with the amino group to form intramolecular hydrogen bonds, thereby causing a shift in the C=O stretch.^[22–25]

Hydrogen bond interactions can play an important role in the absorption process because hydrogen bonds can form between the phenolic hydroxyl groups of pectin which act as hydrogen bond donors with the carbonyl groups of nylon 66.^[26]

Meanwhile, the amide II band, at the peak of 1535 cm⁻¹, appears because of the C–N attraction and N–H bonds.^[27]

At approximately 1600 cm⁻¹ the OH band of TiO₂ should be detectable.^[28] In addition, at around 1500 cm⁻¹ the Ti–O vibration can be observed.^[29] At peak 1027 cm⁻¹ the C–O stretching group can be found in the PA–TiO₂ sample, near C–C stretching at 935 cm⁻¹.

Morphology

The morphology of the PA66 membrane was investigated using SEM analysis. The choice of polymer, solvent and non-solvent also determines the phase separation characteristics and the membrane structure that is formed.^[30] There are notable differences in the structure of the pure PA membrane and PA–TiO₂–pectin membrane.

Figure 4a and **Figure 4c** show the morphology of the pure polyamide membrane, which appears to be smooth and have a dense surface. The cross-section has a sponge-like, asymmetric structure that has large pores.

However, the PA–TiO₂–pectin membrane appears to have a rough surface and is porous because of the inclusion of pectin. Like the silica–pectin membrane, it also has a rough surface through the addition of pectin.^[5,31]

The membrane with added TiO₂ and pectin has a thickness of 101 μm, and it is thicker than the pure PA membrane. It was determined that the added pectin enhances the viscous solution of the membrane casting, and TiO₂, added to the polymer solution, increases viscosity, thus affecting the phase inversion and aggregation of TiO₂ particles in the dope solution.^[30]

The cross-section of the membrane shown has a sponge-like and non-uniform (asymmetric) porous structure. The upper surface shown is densely porous, and the pores are larger in the lower region. The pore size of the pure polyamide membrane is larger than that of the PA–TiO₂–pectin membrane.

The membrane properties correlate with the morphology and are strongly influenced by the polymer–solvent interaction.^[32] The shape of the membrane surface can also affect performance.^[5]

Contact angle

Contact angle measurements for all variations of the polyamide hybrid membranes show hydrophilic properties because the angle formed is below 90°. ^[33] The overall membrane samples' contact angles are shown in **Figure 5**.

The contact angles of several variations of polyamide membranes in this study varied, but these four variations were still classified as hydrophilic.

The smallest contact angle formed, for pure polyamide (PA) membranes, is 58.4° . This angle is lower than the contact angle of pure polyamide membranes reported by Jusoh, W.Z.A.W. *et al.*^[33] – namely 59.2° . This is because the addition of water in the dope solution reduces the contact angle of the membrane surface formed. Nylon is a natural hydrophilic polymer and has a wide range of compatibility and resistance to organic solvents.^[34]

As shown in Figure 5, the PA membrane with the addition of TiO_2 particles displays an increase in the contact angle (72.0°). This is because TiO_2 is a nanoparticle, which increases hydrophilic properties.

Meanwhile, the addition of pectin also increases the contact angle of the polyamide membrane – namely 67.6° – compared with the variation without the addition of pectin. This is because pectin increases hydrophilic properties so that water absorption in the membrane increases.

The contact angle of the membrane indicates hydrophilic properties and influences the flux of the membrane. A low contact angle can increase flux and otherwise.

Swelling

The swelling capacity (degree of swelling) of the resulting networks is influenced by the amount of cross-links (cross-linking density).^[35, 36]

In porous membranes, macroscopic swelling can lead to an increase in the polymer volume with the closure of porous structures and a subsequent reduction in the flux.^[37-41]

Figure 6 shows that the degree of swelling of the pure PA66 membrane and the PA–pectin hybrid or PA– TiO_2 –pectin hybrid is not markedly different.

However, the PA– TiO_2 hybrid membrane has the lowest swelling degree of 1.53. This happens because the membrane becomes denser and does not expand easily because of the presence of TiO_2 particles, which act as a reinforcing bridge.^[42]

However, when pectin was added, the degree of membrane swelling increased to 2.24. The presence of pectin increases the hydrophilic properties of the membrane – increasing its capacity to absorb water, thereby increasing the degree of swelling.^[43]

The degree of membrane swelling was reduced to 2.19 as a result of the simultaneous addition of pectin and pectin– TiO_2 . This decrease was caused by the increasingly dense membrane through cross-linking between nylon 66, TiO_2 and pectin, so that the degree of expansion decreased.^[44]

Membrane performance

Membrane performance is evaluated through a filtration process using wetland water as a feed for a cross-flow system at a pressure of 1 bar (0.1 MPa) for the flux, and rejection is the membrane's ability to remove contaminants in the water.

The initial characteristics of water samples are shown in **Table 2**. This water sample was taken from Muara Halayung Village, South Kalimantan, Indonesia.

Figure 7 shows the water flux and rejection for variations of the polyamide 66 hybrid membrane. The results show that the pure PA membrane has the highest flux, then the PA– TiO_2 –pectin membrane, whilst the PA– TiO_2 variation shows the lowest flux.

The water flux (highest) of the pure PA membrane is $418 \text{ Lm}^{-2}\text{h}^{-1}$, followed by the PA– TiO_2 –pectin membrane at $312 \text{ Lm}^{-2}\text{h}^{-1}$, with the PA– TiO_2 membrane exhibiting the lowest flux rate of $61 \text{ Lm}^{-2}\text{h}^{-1}$.

Various factors contribute to the membrane flux, including pore size, surface roughness, thickness, hydrophobic properties and operating pressure. It is important to note that membrane pore size and hydrophobicity are amongst the most significant determinants of flux.^[45]

The pore size of the membrane is shown in the morphology images (Figure 4). These reveal that the PA membrane has larger pores, compared with the PA– TiO_2 –pectin membrane. A large pore size increases water flux.^[46]

The surface roughness of the membrane influences the pure water flux – with rough surfaces leading to lower flux.^[47]

This study observed a reduction in flux because of the roughness of the membrane surface caused by the addition of pectin, as illustrated in Figure 4. The PA membrane demonstrates lower contact angles compared with the hybrid variations because of its hydrophobic properties.

A small contact angle indicates hydrophilic properties, resulting in higher flux.^[48] However, this value is contrary to the membrane's rejection capability.

The hybrid polyamide membrane created during this research was successful in reducing turbidity by up to 100% for PA-TiO₂-pectin variations. However, a low degree of conductivity at only approximately 7.89% is likely to be the result of the membrane pores being categorised as micro or meso, which means that they are unable to remove salt ions.

Table 3 provides a summary of the performance of polyamide membranes discussed in this study.

Conclusion

In this study a hybrid membrane was prepared with the addition of TiO₂ and pectin, creating variations, namely PA-TiO₂, PA-pectin and PA-TiO₂-pectin.

Membrane characteristics based on FTIR analysis detected two strong peaks – amide I and amide II, found at bands 1631 cm⁻¹ and 1535 cm⁻¹ (PA and PA-TiO₂-pectin membrane samples), whilst in the PA-TiO₂ and PA-pectin samples amide I and amide II were detected at peaks 1633 cm⁻¹ and 1537 cm⁻¹.

SEM analysis results show that the morphology of the pure polyamide (PA) membrane has a smooth surface, whilst the TiO₂-pectin hybrid polyamide membrane looks rough.

From the cross-sectional appearance, the PA membrane has larger pores than the PA-TiO₂-pectin membrane.

The water flux performance shown for the membrane polyamide (PA), PA-TiO₂-pectin, PA-pectin and PA-TiO₂ was 418.04 Lm⁻²h⁻¹, 311.97 Lm⁻²h⁻¹, 218.38 Lm⁻²h⁻¹ and 61.49 Lm⁻²h⁻¹, respectively.

It was shown that the best turbidity removal from wetland water – namely 100% – was achieved using the PA-TiO₂-pectin and PA-pectin hybrid membranes.

The addition of TiO₂ and pectin increases the contact angle of the polyamide membrane by around 1–2% – that is, 58.4° (PA), 72° (PA-TiO₂), 67.6° (PA-pectin) and 59.1° (PA-TiO₂-pectin). All variations of this membrane are classified as hydrophilic as related by the results of the degree of swelling, namely a low contact angle, which indicates high swelling.

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Figure: Schematic of the apparatus for making flat-sheet polyamide 66 membranes.

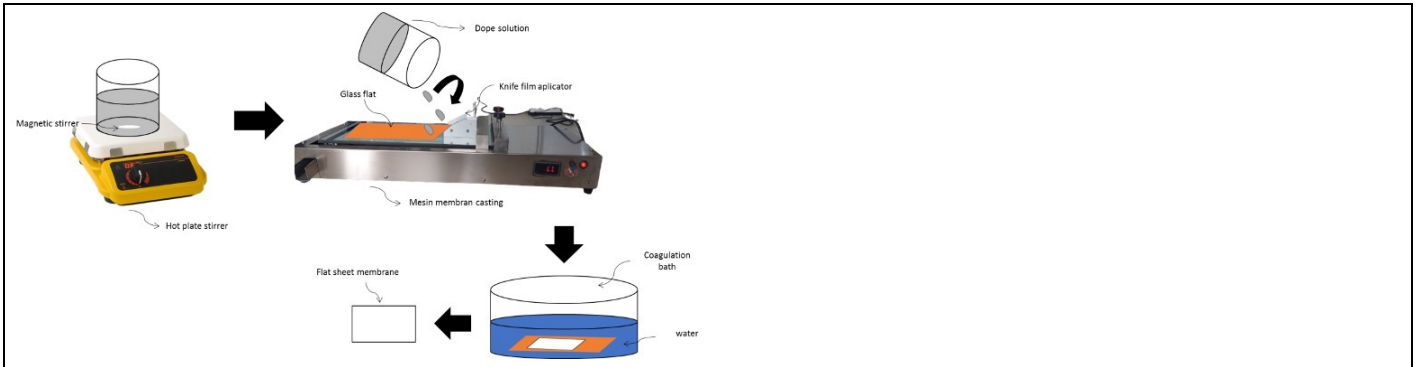


Figure: Schematic of the apparatus, including the cross-flow module for testing the performance of flat-sheet polyamide 66 membranes.

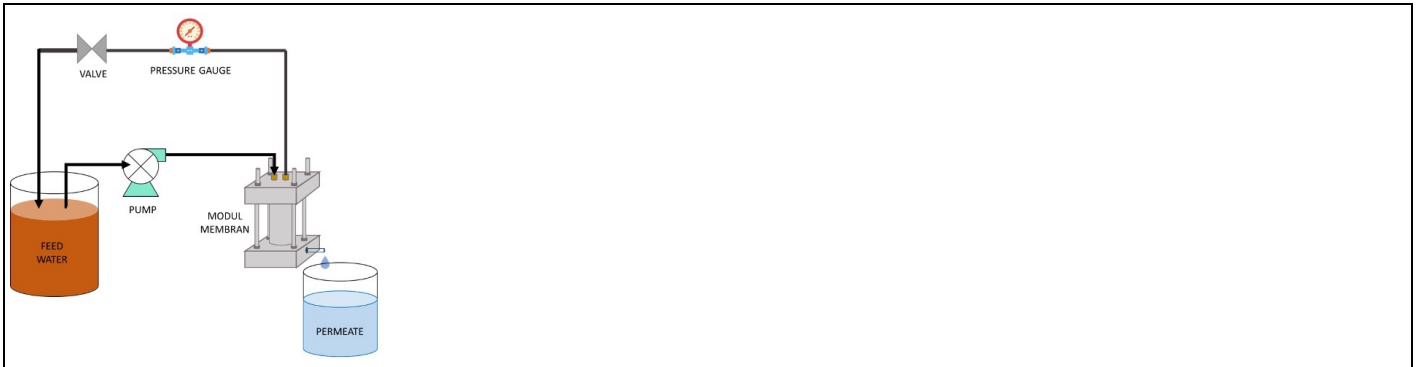


Figure: Infrared spectra of various hybrid polyamide 66 membranes.

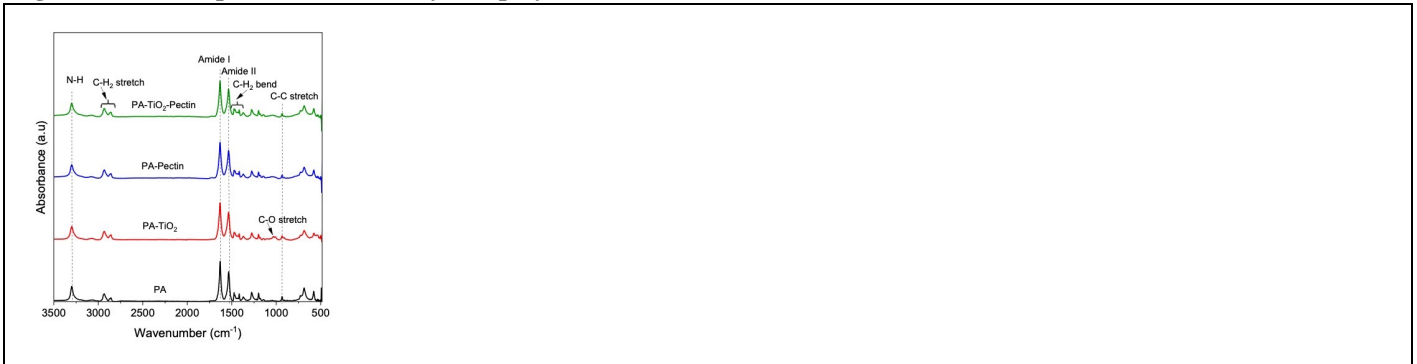


Figure: Cross-section of the pure polyamide (PA) membrane (a); cross-section of the TiO₂-pectin hybrid polyamide membrane (b); surface of the pure polyamide (PA) membrane (c); and surface of the TiO₂-pectin hybrid polyamide membrane.



Figure: Contact angles of various polyamide hybrid membranes.

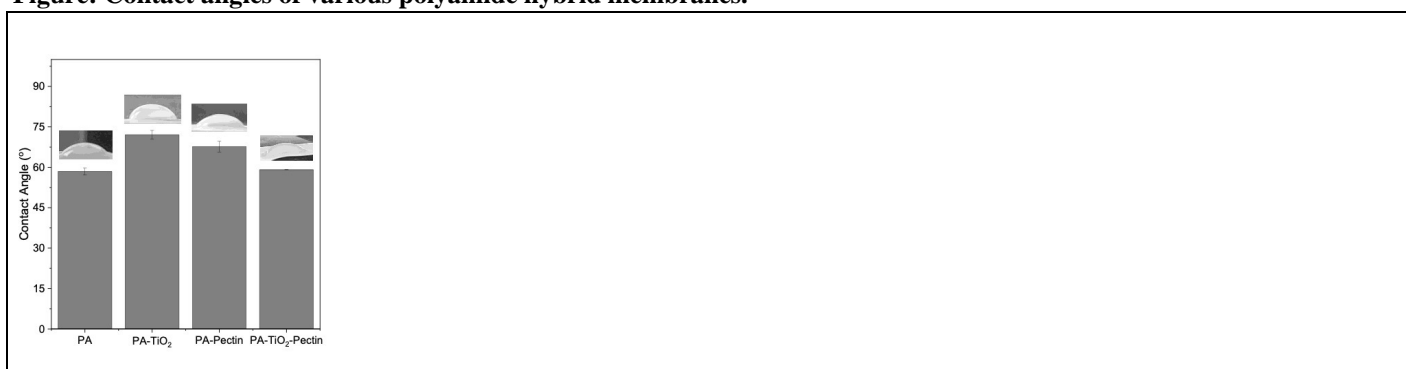


Figure: The swelling ratio measurement of various polyamide membrane variations.

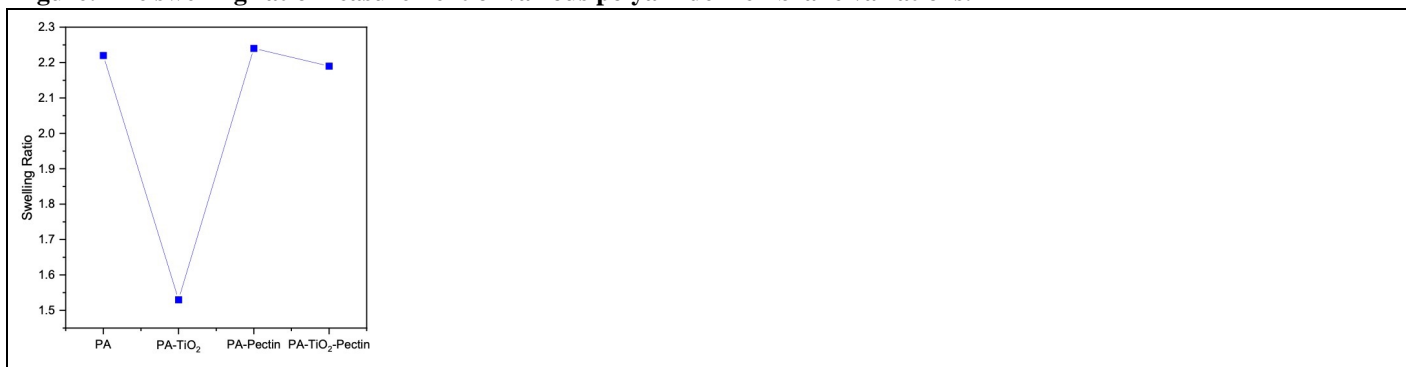


Figure: Performance of various polyamide membranes.



Table 1. Variation in the composition of the membrane dope solution.

Sample name	Composition (% by weight)				
	Nylon 66 (PA66)	Formic acid 90%	Water	TiO ₂	Apple pectin
PA	17	78	5	–	–
PA-TiO ₂	17	73	5	5	–
PA-pectin	17	73	5	–	5
PA-TiO ₂ -pectin	17	73	5	2.5	2.5

Table 2. Characterisation of wetland water – *Indonesian Standard for Hygiene Water (Permenkes No. 2, Year 2023).

Parameter	Unit	Result	Standard*
Turbidity	NTU	31.00	< 3 NTU
Conductivity	µS/cm	1.81	–

Table 3. Summary of the performance of polyamide membranes discussed in this study.

Membrane materials	Fabrication process	Water flux (Lm-2h-1)	Rejection (%)	Reference
CA/PA66/DMSO	Phase inversion	33	89% (oil)	[34]
CA/PA66/FA	Phase inversion	23	95% (oil)	[34]
PC/PA66/FA	Phase inversion	16.3	50% (BSA)	[49]
PA66/FA	Phase inversion	8.5	> 60% (BSA)	[49]
PA66/FA/AC	Electrospinning	533	99.4% (Turbidity), 100% (oil)	[50]
PA66/FA/TiO ₂ /Pectin	Phase inversion	312	100% (Turbidity), 7.89% (Conductivity)	[this work]

References:

- Kido, M. et al., Comparison of general water quality of rivers in Indonesia and Japan, Environmental Monitoring and Assessment, Vol. 156, p. 317–329, 2009.
- Ng, Q.H. et al., Feasibility and practicability of magnetophoretic augmented composite membrane in treating polluted river water: real case application, Environmental Progress & Sustainable Energy, Vol. 38, No. 5, p. 13185, 2019.
- Zularisam, A., Ismail, A. and Salim, R., Behaviours of natural organic matter in membrane filtration for surface water treatment – a review, Desalination, Vol. 194, Nos. 1–3, p. 211–231, 2006.

4. Racar, M., Dolar, D. and Košutiš, K., Chemical cleaning of flat sheet ultrafiltration membranes fouled by effluent organic matter, *Separation and Purification Technology*, Vol. 188, p. 140–146, 2017.
5. Elma, M. et al., Banana peels pectin templated silica ultrafiltration membrane in disk plate configuration applied for wetland water treatment, *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, Vol. 100, No. 1, p. 77–88, 2022.
6. Elsaie, Y. et al., Water desalination in Egypt; literature review and assessment, *Ain Shams Engineering Journal*, 2023, Vol. 14, No. 7, p. 101998, 2003.
7. Tan, Y.Z. et al., Enhancing fouling mitigation of submerged flat-sheet membranes by vibrating 3D-spacers, *Separation and Purification Technology*, Vol. 215, p. 70–80, 2019.
8. Walker, S. and Narbaitz, R.M., Hollow fiber ultrafiltration of Ottawa River water: Floatation versus sedimentation pre-treatment, *Chemical Engineering Journal*, Vol. 288, p. 228–237, 2016.
9. Wei, S. et al., Electro-assisted CNTs/ceramic flat sheet ultrafiltration membrane for enhanced antifouling and separation performance, *Frontiers of Environmental Science & Engineering*, Vol. 15, No. 1, p. 11, 2020.
10. Wenten, I.G. et al., 'Desain Proses Berbasis Membran', 2014.
11. Noguchi, H. et al., Applications of flat sheet ceramic membrane for surface water and seawater treatments –introduction of performance in large-scale drinking water plant and seawater pretreatment pilot system in Singapore, *Water Practice & Technology*, Vol. 14, No. 2, p. 289–296, 2019.
12. Zhao, Y.-X. et al., Direct filtration for the treatment of the coagulated domestic sewage using flat-sheet ceramic membranes, *Chemosphere*, Vol. 223, p. 383–390, 2019.
13. Mahmoudi, E. et al., Enhancing morphology and separation performance of polyamide 6,6 membranes by minimal incorporation of silver decorated graphene oxide nanoparticles, *Scientific Reports*, Vol. 9, No. 1, p. 1216, 2019.
14. Nguyen, D.-B. et al., Surface functionalization of nylon 66 membrane using para-phenylenediamine and carboxylic functionalized multi-walled carbon nanotubes for removal of calcium ions from aqueous solution, *Nanocomposites*, Vol. 7, No. 1, p. 160–171, 2021.
15. Khan Mohammadi, S. et al., High flux nanofibrous membranes for colored effluent treatment, *Water and Environment Journal*, Vol. 34, No. 2, p. 274–283, 2020.
16. Abd Halim, N.S. et al., Electrospun nylon 6,6/ZIF-8 nanofiber membrane for produced water filtration, *Water*, Vol. 11, No. 10, p. 2111, 2019.
17. Pradhana, E.A. et al., The functionalization study of PVDF/TiO₂ hollow fibre membranes under vacuum calcination exposure, *Journal of Physics: Conference Series*, Vol. 1912, p. 012035, 2021 (5th International Conference on Advanced Material for Better Future (ICAMBF 2020), 13–14 October 2020, Surakarta, Indonesia).
18. Elma, M. et al., Hydrogel derived from water hyacinth and pectin from banana peel as a membrane layer, *Materials Today*, Vol. 87, Part 2, 2023.
19. Yu, Y. et al., Preparation of multi-layer nylon-6 nanofibrous membranes by electrospinning and hot pressing methods for dye filtration. *RSC Advances*, Vol. 8, No. 22, p. 12173–12178, 2018.
20. Elma, M. et al., Long-term performance and stability of interlayer-free mesoporous silica membranes for wetland saline water pervaporation, *Polymers*, Vol. 14, No 5, p. 895, 2022.
21. Hsieh, C.-W., Li, B.-X. and Suen, S.-Y., Alicyclic polyimide/SiO₂ mixed matrix membranes for water/n-butanol pervaporation, *Membranes*, Vol. 11, No. 8, p. 564, 2021.
22. Khorriha, N., Mohd Khori, E., Hadibarata, T. and Salmiati, S., A combination of waste biomass activated carbon and nylon nanofiber for removal of triclosan from aqueous solutions, *Journal of Environmental Treatment Techniques*, Vol. 8, No. 3, p. 1036–1045, 2020.
23. Pratiwi, A.E. et al., Deconvolution of pectin carbonised template silica thin-film: synthesis and characterisation, *Membrane*

Technology, Vol. 2019, No. 9, p. 5–8, 2019.

24. Sumardi, A. et al., Designing a mesoporous hybrid organo-silica thin film prepared from an organic catalyst, *Membrane Technology*, Vol. 2021, No. 2, p. 5–8, 2021.

25. Elma, M. et al., Fabrication of interlayer-free P123 carbonised template silica membranes for water desalination: conventional versus rapid thermal processing (CTP vs RTP) techniques, *IOP Conference Series: Materials Science and Engineering*, Vol. 543, 012076, 2019 (The 1st International Symposium of Indonesian Chemical Engineering (ISICChem) 2018 4–6 October 2018, West Sumatera, Indonesia).

26. Xu, J. et al., Sorption of triclosan on electrospun fibrous membranes: effects of pH and dissolved organic matter, *Emerging Contaminants*, Vol. 1, No. 1, p. 25–32, 2015.

27. Peets, P. et al., Reflectance FT-IR spectroscopy as a viable option for textile fiber identification, *Heritage Science*, Vol. 7, No. 1, p. 93, 2019.

28. Li, W. et al., Preparation and characterization of poly (vinylidene fluoride)/TiO₂ hybrid membranes, *Frontiers of Environmental Science & Engineering*, Vol. 7, p. 492–502, 2013.

29. Pradhana, E. et al., The functionalization study of PVDF/TiO₂ hollow fibre membranes under vacuum calcination exposure, *Journal of Physics: Conference Series*, 2021 (5th International Conference on Advanced Material for Better Future (ICAMBF 2020), 13-14 October 2020, Surakarta, Indonesia).

30. Poletto, P. et al., Characterization of polyamide 66 membranes prepared by phase inversion using formic acid and hydrochloric acid such as solvents, *Materials Research*, Vol. 14, p. 547–551, 2011.

31. Elma, M., Pratiwi, A.E. and Rahma, A., The performance of membranes interlayer-free silica-pectin templated for seawater desalination via pervaporation operated at high temperature of feed solution, *Materials Science Forum*, Vol. 981, 2020.

32. Elma, M. et al., PVDF-TiO₂ hollow fibre membrane for water desalination, *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, 2021, Vol. 12, No. 1, p. 1–6, 2021.

33. Jusoh, W.Z.A.W. et al., Fabrication and characterisation of a polyamide thin-film composite membrane on a nylon 6,6 substrate for isopropanol dehydration, *Comptes Rendus Chimie*, Vol. 22, Nos. 11–12, p. 755–760, 2019.

34. Hussain, A. and Al-Yaari, M., Development of polymeric membranes for oil/water separation, *Membranes*, Vol. 11, No. 1, p. 42, 2021.

35. Kuckling, D. et al., Stimuli-Responsive Polymer Systems, ‘*Polymer Science: A Comprehensive Reference*’, Matyjaszewski, K. and Möller, M. (editors), p. 377–413, Elsevier, Amsterdam, The Netherlands, 2012.

36. Lestari, R.A. et al. Organo silica membranes for wetland saline water desalination: effect of membranes calcination temperatures, ‘*E3S Web of Conferences*’, 2020, EDP Sciences.

37. Gugliuzza, A., Membrane Swelling, ‘*Encyclopedia of Membranes*, Drioli, E. and Giorno, L. (editors), p. 1–2, Springer Berlin Heidelberg, Berlin, Heidelberg, Germany, 2015.

38. Elma, M. et al., Development of hybrid and templated silica/P123 membranes for brackish water desalination, *Polymers*, Vol. 12, No. 11, p. 1–13, 2020.

39. Rahma, A. et al., Performance of interlayer-free pectin template silica membranes for brackish water desalination, *Membrane Technology*, Vol. 2020, No. 6, p. 7–11, 2020.

40. Rahma, A. et al., Rapid thermal processing and long term stability of interlayer-free silica-P123 membranes for wetland saline water desalination, *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, Vol. 71, No. 2, p. 1–9, 2020.

41. Elma, M. et al., Coagulation as pretreatment for membrane-based wetland saline water desalination, *Asia–Pacific Journal of Chemical Engineering*, Vol. 15, No. 4, 2020.

42. Sairam, M. et al., Novel dense poly(vinyl alcohol)–TiO₂ mixed matrix membranes for pervaporation separation of water-isopropanol mixture at 30°C, *Journal of Membrane Science*, Vol. 281, p. 95–102, 2006.

- 43.Chen, P.H. et al., Novel chitosan-pectin composite membranes with enhanced strength, hydrophilicity and controllable disintegration, *Carbohydrate Polymers*, Vol. 82, p. 1236–1242, 2010.
- 44.Suleman, M.S., Lau, K.K. and Yeong, Y.F., Plasticization and swelling in polymeric membranes in CO₂ removal from natural gas, *Chemical Engineering & Technology*, Vol. 39, p. 1–14, 2016.
- 45.McCutcheon, J. and Elimelech, M., Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes, *Journal of Membrane Science*, Vol. 318, p. 458–466, 2008.
- 46.Zhu, M. and Mao, Y., Large-pore-size membranes tuned by chemically vapor deposited nanocoatings for rapid and controlled desalination, *RSC Advances*, Vol. 10, No. 66, p. 40562–40568, 2020.
- 47.Woo, S.H., Park, J. and Min, B., Relationship between permeate flux and surface roughness of membranes with similar water contact angle values, *Separation and Purification Technology*, Vol. 146, p. 187–191, 2015.
- 48.Servi, A.T. et al., A systematic study of the impact of hydrophobicity on the wetting of MD membranes, *Journal of Membrane Science*, Vol. 520, p. 850–859, 2016.
- 49.Yan, J. et al., Axial crystal growth evolution and crystallization characteristics of bi-continuous polyamide 66 membranes prepared via the cold non-solvent-induced phase separation technique *Polymers*, Vol. 14, No. 9, p. 1706, 2022.
- 50.Abd Halim, N.S. et al., Improving performance of electrospun nylon 6,6 nanofiber membrane for produced water filtration via solvent vapor treatment, *Polymers*, Vol. 11, No. 12, p. 2117, 2019

Robust membrane makes clean water production more affordable for developing countries

Abstract: Researchers in Singapore have developed membrane technology that has the potential to make large-scale clean water production more affordable for developing nations.

Local water technology start-up Atera Water together with scientists from Nanyang Technological University and the Singapore Institute of Technology have developed an efficient nano-composite membrane.

Referred to as Clarity, it is made using common polymers at a fraction of the cost of the more expensive membranes used by developed nations.

It is produced from special nanoparticles combined with low-cost polymers such as polypropylene (PP). It is easier and more environment-friendly to manufacture than the conventional polyvinylidene fluoride (PVDF) membranes used by developed countries. The researchers say that it is also stronger than other PP membranes that are currently available.

It aims to replace the rudimentary sand filter systems used in many regional countries such as Vietnam and Indonesia, which are currently struggling to clean increasingly polluted groundwater.

As reported in the previous issue of *Membrane Technology*, researchers in the USA, led by a team at University at Buffalo in New York State, say that they have created a new, sturdier membrane that can withstand harsh environments (*Membrane Technology*, Volume 2023, Issue 6, [https://doi.org/10.12968/S0958-2118\(23\)70053-0](https://doi.org/10.12968/S0958-2118(23)70053-0)).

For further information, visit:

www.aterawater.com,

www.ntu.edu.sg &

www.SingaporeTech.edu.sg.

(A technology focus article, which will be published in a forthcoming issue of *Membrane Technology*, will provide further details of the development of this nano-composite membrane, the advantages of using it and also briefly cover the allied water treatment system in which it has been used.)

Mixed-bed resin produces ultra-pure water for fault-free semiconductor manufacturing

Abstract: Lanxess AG has developed a mixed-bed resin for generating ultra-pure water that is required for producing semiconductors. Compared with the firm's established Lewatit UltraPure 1296 MD mixed bed resin, UltraPure 1296 MD PLUS boasts a lower content of metals such as iron, zinc and sodium.

Early installations of the product as a final polishing filter in semiconductor manufacturing have yielded results close to the current analytical limits of detection, according to the German speciality chemicals company.

The manufacturing of semiconductors and displays calls for complex water treatment to ensure that the water used is of the required purity.

The latest generation of wafers and microchips demands a correspondingly high level of quality from the ion exchange resin systems that are employed. Furthermore, new analytical systems are capable of analysing ions in the low parts per trillion (ppt) range. For some types of ion, they can go as low as the parts per quadrillion (ppq) range.

Achieving the performance of semiconductors required by modern industry can necessitate as many as 200 treatment steps. The ultra-pure water needed for this is provided by means of a complex multi-stage process. The most important steps in the operation include conventional primary demineralisation with standard ion exchange resins, reverse osmosis, degasification, ultrafiltration and hydrogen peroxide removal, whilst the last stage is final polishing with an ultra-pure mixed bed.

Lewatit UltraPure 1296 MD PLUS ion exchange resin was developed specifically for this final step, which is absolutely critical to the success of the process as a whole, says Lanxess.

The ultra-pure water treated in this way can be then used in etching and cleaning processes in microchip production.

Hans-Juergen Wedemeyer, Technical Marketing Manager, Liquid Purification Technologies, Lanxess, commented: 'The Lewatit UltraPure 1296 MD PLUS, produced in Germany, is a vital component for cost-effective, sustainable and fault-free manufacturing in the fast-growing international semiconductor industry.'

'The high total capacity and degree of regeneration of the anion and cation exchange resins also result in excellent operating capacity for the removal of boron and silica, as well as metal ions.'

Wedemeyer says that the bead sizes of the monodisperse components are designed to avoid an inadvertent separation of cation and anion exchange resins. The use of a special process to produce Lewatit UltraPure 1296 MD PLUS means that the release of particles and TOC fall within an extremely low range.

As reported recently in the technology focus entitled 'Further functionality targeting the food industry is added to versatile ion-exchange engineering tool', Lanxess has added further functionality to its LewaPlus software – a tool that helps engineers plan and design industrial water treatment facilities that use ion exchange and membrane systems. The latest enhancement targets applications in the food industry (*Membrane Technology*, Volume 2023, Issue 6, [https://doi.org/10.12968/S0958-2118\(23\)70057-8](https://doi.org/10.12968/S0958-2118(23)70057-8)).

This update follows the addition of a module to the software, a year earlier, that covers the industrial treatment of aqueous sugar solutions. The latest addition, covering the calculation of demineralisation systems for aqueous gelatin and collagen solutions, is fully integrated in the software's food module, which is regularly updated and available now.

For further information, visit:

www.lewatit.com

DuPont launches its first ion exchange resin for green hydrogen production

Abstract: To support the production of hydrogen from water, DuPont has launched an ion exchange resin that is designed for the unique chemistry of electrolyser loops.

DuPont says that AmberLite P2X110 ion exchange resin is its first product that is dedicated to the production of green hydrogen.

Designed to endure the thermal and chemical challenges present in an electrolyser, the resin's "recipe" offers durable and reliable water quality that helps prevent contaminant build-up in the electrolyser loop.

These customised features, and improved removal capacity, present a differentiated option for electrolysers with more service time than industry-generic resins.

Commenting on the product, Alan Chan, Global Vice President and General Manager, DuPont Water Solutions, said: 'The pursuit of new sources of clean energy is critical, with green hydrogen well positioned to substantially reduce global carbon emissions.'

According to Chan, AmberLite P2X110 supports trends towards electrification and decarbonisation.

Hydrogen can be produced by several methods from different feed-stocks. Green hydrogen, which is produced from water by electrolysis powered by renewable energy, can play several major roles in the energy transformation – contributing to the decarbonisation of transportation, heat and energy, and as greener feed-stock.

Electrolysis is the process of electrically splitting water molecules into hydrogen and oxygen gas, and whilst there are various types of electrolysers, they all rely on high-purity water as the feedstock to produce hydrogen.

'Our multi-tech portfolio can help create the high-purity water that electrolysers require with our ultrafiltration, ion exchange, biofouling prevention, reverse osmosis and electrodeionisation technologies,' added Verónica Garcia Molina, Global Market Leader, Industrial Water & Energy, DuPont Water Solutions.

'The launch of our AmberLite P2X110 ion exchange resin is an exciting first step into the green hydrogen market.'

For further information, visit:

www.dupont.com/water,

<http://www.dupont.com/brands/amber-series.html> &

<https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/IER-AmberLite-P2X110-Green-Hydrogen-A>

QUA adds three new membrane technologies to its range of water treatment products

Abstract: QUA Group, which specialises in membrane technology for water treatment applications, has diversified its portfolio by introducing three new products spanning electrodeionisation, membrane bioreactors and ultrafiltration.

The first – FEDI GIGA – is described by the company as a next-generation fractional electrodeionisation (FEDI) technology, engineered for high-flow ultrapure water production with minimal space requirements.

Featuring a single inlet and two outlet ports, its unique port design reduces associated piping and instruments. The electrodeionisation stack has just three ports – feed, product and reject.

The company says that FEDI GIGA consistently delivers high-purity product water, effectively removing hardness, silica and boron. This environment-friendly technology is most suitable for larger flow applications in sectors such as the semiconductor, microelectronics, hydrogen, solar-power and refining industries, offering high flows with reduced footprint demands.

QUA has also launched EnviQ RF, a submerged ultrafiltration (UF) membrane designed to enhance membrane bioreactor (MBR) facility operation and maintenance.

This addition to QUA's EnviQ product line features durable polyvinylidene fluoride (PVDF) hollow-fibre membranes with a unique airflow distribution design. Its reinforced PVDF membrane fibres, with high mechanical strength and tolerance to chlorine and chemicals, ensure consistent, high-quality UF, says the firm.

Its compact and adaptable design is also ideal for handling high-feed turbidity across challenging wastewater applications.

The third product to be introduced is the Q-SEP Q-Connect. This compact pre-engineered outside-in high-flow UF rack, is relatively easy to install and can be housed in a container.

Suitable for industrial and municipal water and wastewater treatment applications requiring UF-quality water with a silt density index (SDI) of less than 3, it is a versatile system that is capable of meeting diverse customer requirements.

The company says that Q-Connect also enables closer collaboration with system integrators, reducing the time to engineer and install UF systems – effectively meeting water requirements within a reduced timeframe.

For further information, visit:

www.quagroup.com

(Also see the technology focus article entitled: 'QUA plays vital role in satisfying textile and petrochemical plants' water requirements', *Membrane Technology*, Volume 2019, Issue 6, [https://doi.org/10.1016/S0958-2118\(19\)30116-8](https://doi.org/10.1016/S0958-2118(19)30116-8)).

Pharmaceuticals firm embraces Memsift technology on a commercial scale

Abstract: Impressed by the success of an on-site pilot, a major pharmaceuticals company has decided to embrace, on a commercial scale, technology developed by Memsift Innovations – marking a significant step towards closing its liquid waste loop.

The Fortune 100 pharmaceuticals company has partnered with Memsift Innovations to revolutionise its liquid waste management practices. The commercial implementation of this project is slated to begin in the first quarter of 2024. The commercial contract is worth \$1.62 million.

The global pharmaceuticals company recently conducted successful tests on the Memsift TS-30 Improved Membrane Distillation (IMD) system, signalling a significant leap towards establishing a global standard for sustainable pharmaceuticals manufacturing.

Memsift says that its thermal separation process and patented IMD technology, offer distinct advantages over conventional industrial liquid waste treatment and zero liquid discharge systems. The IMD system employs an innovative thermodynamic principle-based thermal separation process and a proprietary membrane, which significantly reduce the cost of industrial liquid waste treatment.

The pharmaceuticals firm initiated a technical study in collaboration with Memsift in 2019. The study aimed to assess the feasibility of using the TS-30 IMD system to treat liquid waste. The initial results were promising, suggesting the potential to reduce liquid waste volume by over 90%, whilst recovering high-quality nitrogen fertiliser.

Building on the positive outcomes of the study, a full-scale on-site pilot programme was launched in early 2022 and has been in continuous operation for over a year. This demonstrated the system's capability to consistently treat liquid waste and produce exceptionally high-quality water.

Impressed by the success of the pilot, the pharmaceuticals firm decided to embrace this technology on a commercial scale. This bold move will not only enable it to achieve more than 90% cost-savings in waste disposal, but also reduce its carbon footprint by up to 80%, compared with conventional disposal and incineration methods – resulting in an estimated reduction in CO₂ emissions a year of 490 tons.

Dr J. Antony Prince, CEO, Memsift Innovations and the company's founder, expressed his excitement about this collaboration, highlighting the positive partnership with the firm.

He also commended the pharmaceuticals company's support and enthusiasm throughout the project's challenges, emphasising the importance of transforming waste into value.

Dr Prince believes this project serves as an important example of how a global industry leader can collaborate with technology start-ups like Memsift, to address critical global issues such as water conservation (SDG-6) and climate change (SDG-13), whilst preserving resources and a clean environment for future generations.

As reported in 2022, the US Patent Office granted Memsift Innovations patent US11235284, which covers its IMD process, based on the TS-30 system, and various applications in which it is used (*Membrane Technology*, Volume 2022, Issue 2, [https://doi.org/10.12968/S0958-2118\(22\)70025-0](https://doi.org/10.12968/S0958-2118(22)70025-0)).

For further information, visit:

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