

# Magnetically Aligned Nanotubes in Nanocomposite Membranes for High-Performance Filtration Applications

P.A. Ignacio-de Leon\*, X. Chen\*\*, E.J. Rabe, M. Urgun-Demirtas\*\*\*, M. Puga, Z. Zhou and R.W. Brotzman

\*Argonne National Laboratory, Energy Systems

9700 S. Cass Ave. Argonne, IL USA 60439, patriciadl@anl.gov

\*\*Argonne National Laboratory, Argonne, IL, USA, xchen@anl.gov

\*\*\*Argonne National Laboratory, Argonne, IL, USA, demirtasmu@anl.gov

## ABSTRACT

Nanocomposite membranes, with magnetic nanotubes embedded in polyethersulfone (PES) membrane to form a permselective layer on microporous supports, are reported for potential applications in wastewater treatment. Iron cobalt oxide ( $\text{Fe}_2\text{CoO}_4$ ) nanotubes, with 20-25 nm diameter and aspect ratio *ca.* 10,000, function as nanochannels spanning the permselective layer. We obtained pure water flux values of 9.4 and 4.8  $\text{L/m}^2\text{-h}$  through membranes with vertically-aligned and randomly-oriented nanotubes, respectively, at 40 psi. We used these membranes to filter lignin, a contaminant in effluent wastewater from paper and mill industries and lignocellulosic biofuels production. The lignin % rejection from a 10,000 ppm feed at 40 psi through a PES support increases from 7.3% to 39.1% (5.3 $\times$  higher) and 62.8% (8.6 $\times$  higher) through membranes prepared with and without a magnetic field, respectively.

**Keywords:** magnetic nanotube, vertically-aligned nanotube, iron cobalt oxide nanotube, nanocomposite membrane, lignin filtration

## 1 INTRODUCTION

The need for new, energy-efficient water treatment and purification methods has been increasing with the rising demand for clean drinking water and process water.<sup>1</sup> Ultrafiltration (UF) is a promising technique for water treatment, producing high quality water without exceedingly high pressures.<sup>2</sup> The energy-efficiency of current commercial UF membranes can be improved by increasing water flux through the membrane and can be achieved through the development of novel materials with higher permeability.<sup>3</sup> Carbon nanotubes (CNT) composite membranes have received a great deal of attention in this area for their controllable pore size and high-flux potential.<sup>4</sup> However there is a trade-off between achieving maximum flux and ease of membrane fabrication. For maximum flux, the nanotubes must be aligned to obtain a high pore density. This requires the tubes to be grown vertically from nanoparticle catalysts, which then must be removed from the system by secondary treatment.<sup>5</sup> Alternatively, CNT

alignment can be achieved by inducing a direct current electric field.<sup>4</sup> Without employing these methods, CNTs are dispersed randomly throughout the composite, lacking a consistent vertical orientation.<sup>6</sup> Recently, other groups have also reported the use of halloysite nanotubes (HNTs) composed of alumina-silicates with tubular structure similar to CNTs as alternative materials due to its lower production cost.<sup>7</sup>

While much work has been done using CNTs, there are limited studies on iron cobalt oxide ( $\text{Fe}_2\text{CoO}_4$ ) nanotubes, which offer two key advantages: (1) The metal oxide surface is already hydrophilic, eliminating a functionalization step needed to treat the hydrophobic surfaces of CNTs.<sup>3, 6</sup> The inherent hydrophilic surface also provides improved antifouling properties, as increased hydrophilicity has been correlated with a decrease in fouling.<sup>8</sup> (2) The magnetic properties of this material coupled with the high aspect ratio of the structure allow for tube alignment via a magnetic field. The ability to take nanotubes synthesized at gram scale and efficiently align them in minutes, and maintain orientation in a polymer matrix demonstrates the potential scalability of this process.<sup>9</sup> To maintain vertical alignment and ensure that nanotubes remain in the permselective layer, we used interfacial polymerization to provide a polyamide encapsulant.<sup>10</sup> Interfacial polymerization is a facile method for generating thin polymeric layers as monomers dissolved in immiscible solvents react in the boundary between the two phases.<sup>6</sup> In this study, we demonstrate that MNTs can be vertically aligned in the presence of an external magnetic field onto a polymer support to create a permselective layer in a nanocomposite membrane.

## 2 EXPERIMENTAL

### 2.1 Nanotube Production

$\text{Fe}_2\text{CoO}_4$  nanotubes were prepared using an in-house instrument with integrated electrospinning, heating and pneumatic collection of engineered nanomaterials (U.S. patent pending, serial number 14/665,932), following the nanotube formation principles by electrospinning and heat treatment first introduced by Chen et al.<sup>11</sup> The precursor solution consisted of 5 weight % PVP, 5 weight % total

salts (2:1 atomic ratio Fe:Co salts) in 1:1 DMF:IPA. A general description of this integrated system is given elsewhere.<sup>12</sup>

## 2.2 Composite Membrane Preparation

PES supports pre-soaked in water were first immersed in an aqueous solution of *m*-phenylenediamine. In a separate container, MNTs were dispersed in water via sonication. To prepare vertically-aligned MNT composites, the amine-saturated PES support was transferred onto a weighing boat which is placed atop a magnet. The nanotube suspension was added dropwise onto the PES support, followed by slow addition of a 1,3,5-benzenetricarbonyl trichloride in hexane solution to minimize perturbation of the nanotubes. A polyamide film immediately forms,<sup>8</sup> and the nanocomposite membrane is allowed to dry overnight atop the magnet. Control nanocomposite membranes prepared without an applied magnetic field and without nanotubes (i.e. polyamide alone) were fabricated following this general procedure.

## 2.3 Control of Polyamide Thickness

Post-synthesis treatment of dried nanocomposite membranes were performed by immersing samples in a dilute solution of Protease E at pH 7.5, following protocol as recommended by manufacturer.<sup>13</sup> Membranes were shaken at 165 rpm at 37 °C and the etching reaction quenched by addition of an aqueous EDTA solution. Etched membranes were washed repeatedly with deionized water to ensure complete removal of proteins and salts, followed by air-drying.

## 2.4 Membrane Performance Testing

All membranes tested for filtration performance were initially soaked in deionized water. All membrane filtration tests were performed at ambient temperature at an operating pressure of 40 psi from a N<sub>2</sub> cylinder. Flux measurements were conducted by automatically recording the mass of the filtrate using a balance interfaced to a computer. Feed solutions tested include pure water, 1000 and 10,000 ppm lignin solutions. Lignin % rejection values were calculated from measurements of lignin concentration in the filtrate via UV-Vis spectroscopy from a calibration curve at a local  $\lambda_{\max}$  280 nm. Flux and lignin % rejection values were averaged from repeated (at least in triplicate) trials and evaluated for at least three different samples for each membrane type (bare support, polyamide only, and with nanotubes added with or without the presence of a magnetic field).

# 3 RESULTS AND DISCUSSION

The transport properties of our nanocomposite membranes are defined by the MNTs incorporated as

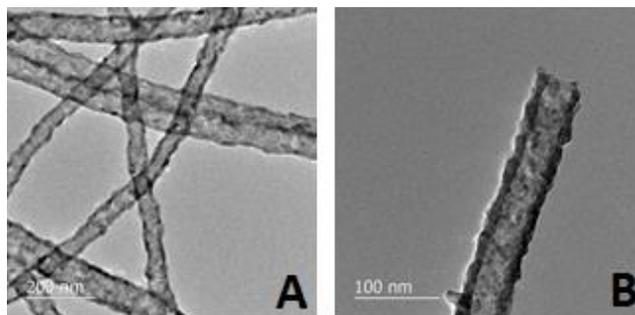


Figure 1: TEM images showing (A) individual MNTs with high aspect ratios and (B) bearing open ends.

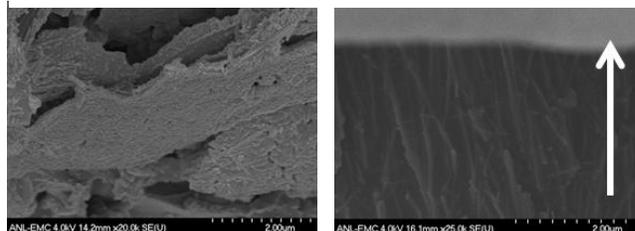


Figure 2: SEM images of cross-sections of nanocomposites show (Left) randomly-oriented polymer-encapsulated MNTs without an external magnetic field; (Right) vertically-aligned MNTs with long axes parallel to applied magnetic field lines.

nanopores within a permselective layer supported by a polymeric support. To obtain high flux through the membrane, the nanotube should not be too long to maintain low operating pressures (longer MNTs result in thicker membranes, which present additional resistance to mass transfer). MNTs (Figure 1) as produced from our in-house electrospinning apparatus integrated with IR heating are typically characterized by aspect ratios as high as 10,000 and outer and inner diameters of 50 and 25 nm, respectively. We found an optimal sonication time of 1.5-2 min that result in majority of the MNTs having *ca.* 7 μm length while preserving the desired nanostructure.

Vertical alignment was achieved *in situ* during the process of incorporating MNTs onto a commercial porous PES support by applying a magnetic field as low as 1 T. SEM images of cross-sections of nanocomposites distinctly show the difference in MNT orientation on the support (Figure 2). Without an external magnetic field, MNTs cover the support in a random distribution with majority of MNTs oriented with long axes parallel to the surface. However, in the presence of an applied magnetic field, the long axes of the MNTs align parallel to the field lines and perpendicular to the surface of the support.

To maintain alignment and retain MNTs within the permselective layer, a polyamide encapsulant was applied via interfacial polymerization between amine and acyl chloride monomers at the immiscible water/hexane interface. To ensure nanotube ends remain unblocked to enable flow of feed solution through the nanotubes,

Feed solution		PES Support	MNTs in magnetic field	MNTs without magnetic field	Polyamide (no MNTs)
Pure Water	Flux (L/m <sup>2</sup> •h)	50.9 ± 2.4	9.4 ± 1.7	4.8 ± 1.3	2.8 ± 1.4
	Ratio relative to slowest	18.4	3.4	1.7	1.0
Lignin 1000 ppm	Flux (L/m <sup>2</sup> •h)	19.1 ± 1.2	4.0 ± 0.9	3.0 ± 0.5	2.9 ± 1.2
	Ratio relative to slowest	6.7	1.4	1.0	1.0
	% Rejection	2.1 ± 1.3	21.5 ± 0.2	31.2 ± 7.2	11.7 ± 4.9
	Ratio to support	1.0	10.2	14.8	5.6
Lignin 10,000 ppm	Flux (L/m <sup>2</sup> •h)	7.6 ± 0.4	2.7 ± 0.6	1.7 ± 0.2	1.2 ± 0.1
	Ratio relative to slowest	6.5	2.3	1.5	1.0
	% Rejection	7.3 ± 4.0	39.1 ± 13.7	62.8 ± 27.5	60.1 ± 5.4
	Ratio to support	1.0	5.3	8.6	8.2

Table 1: Summary of comparison of membrane filtration performance at operating pressure of 40 psi.

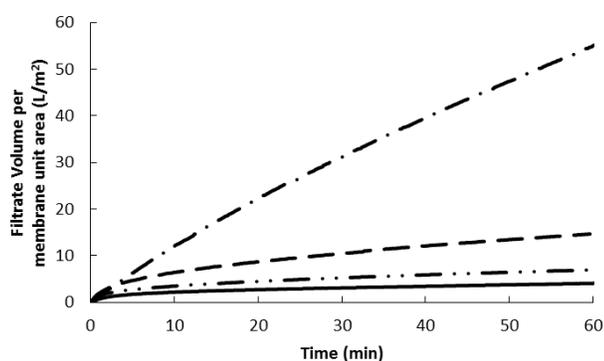


Figure 3: Representative pure water flux through various membranes (—●— PES support, --- MNTs in magnetic field, -●- MNTs without magnetic field, — polyamide only).

nanocomposite membranes were treated post-synthesis with a dilute solution of Protease E, an enzyme that specifically cleaves amide bonds via catalyzed hydrolysis.<sup>13</sup> Remaining polymer thickness was estimated from SEM images of nanocomposite cross-sections.

To determine the efficacy of MNT addition and its orientation on membrane performance, pure water flux was measured through various membrane samples containing MNTs prepared in the presence and absence of an external magnetic field as well as membranes without MNTs (bare support and with the polyamide alone). Figure 3 and Table 1 show a trend in pure water flux according to expectations that an extra layer will act as an additional barrier to mass transfer. Compared to the unmodified PES support, flux was reduced almost by a factor of 20 from 50.9 to 2.8 L/m<sup>2</sup>-h upon incorporation of a ca. 6 μm-thick polyamide layer. The presence of randomly oriented MNTs in the permselective layer allows some flux recovery to 4.8 L/m<sup>2</sup>-h (1.7× faster compared to polyamide only), which can be attributed to the morphology of the hollow nanotubes that offers paths of less resistance within the permselective layer. Nanocomposite membranes prepared in the presence

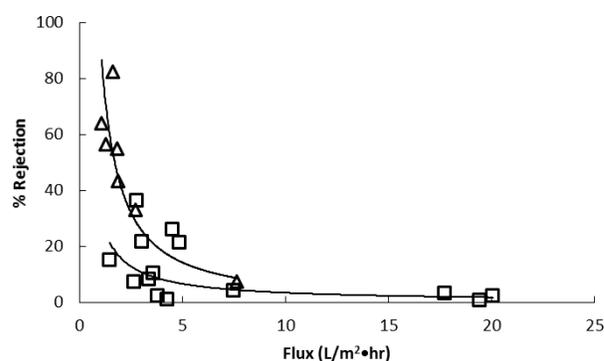


Figure 4: Interdependence of flux and % rejection with feed concentration (□ 1000 ppm; Δ 10,000 ppm).

of an external magnetic field doubled the recovery of flux to 9.4 L/m<sup>2</sup>-h (3.4× faster compared to polyamide only), which is in agreement with observations from SEM that the MNTs were indeed vertically aligned to decrease mass transfer resistance. Similar patterns in flux were observed for feed solutions containing 1000 and 10,000 ppm lignin. Per expectations, flux values decrease significantly with increasing feed solution concentrations; for example, average flux for pure water, 1000 ppm and 10,000 ppm lignin feed solutions through nanocomposite membranes with vertically-aligned MNTs were measured to be 9.4, 4.0 and 2.7 L/m<sup>2</sup>-h, respectively (Table 1).

To measure the extent to which our membrane samples can retain contaminants in feed solutions, we prepared lignin solutions at 1000 and 10,000 ppm. Lignin with average molecular weight 10 kDa was chosen as a model compound suitable for our demonstration. Lignin is a polyphenol and represents a main class of structural materials found in plants and some algae and is therefore a typical contaminant in process water produced from lignocellulosic biofuel production processes and wastewaters produced from paper and mill industries. Percent rejection (% R) values were calculated by comparing the concentrations of filtrate samples from the

different membranes investigated in this study against the initial concentrations of the feed solutions using the formula given in Equation 1, where  $C_0$  and  $C_f$  are initial feed and filtrate concentrations, respectively:

$$\% R = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

Lignin concentrations were quantified via UV-Vis spectroscopy from absorbance values at 280 nm. Comparison of percent rejection for the different membranes in this study show a trend opposite to that for flux, i.e. in general, lignin retention in the feed solution is highest for membranes in which flux values were lowest). Membranes with permselective layers consisting of polyamide only and with randomly-oriented MNTs exhibited on average 60% rejection of lignin from a 10,000 ppm feed solution (Table 1). In contrast, a modest 40% rejection was measured for vertically-aligned MNTs nanocomposite membranes; nevertheless, this is still higher by a factor of 5.3 compared to native PES membranes (unmodified support). This apparent trade-off between membrane permeability and filtration efficiency was also observed from filtration tests for a feed solution with lower lignin concentration (1000 ppm). Membranes with randomly-oriented MNTs appear to have the best retention at 31% rejection (15× improvement over bare support) while vertically-aligned MNT composite membranes performed only slightly worse (22% rejection, an order of magnitude increase over unmodified PES). Figure 4 illustrates the interdependence of the two key figures of merit for membrane performance, flux and % solute rejection, as affected by concentrations of the feed solution. This implies that, for membranes investigated in this study, solute retention seems to be primarily dependent on the ability of the membrane to act as barrier to mass transfer at 40 psi. While it may be expected to obtain improved solute retention by lowering the operating pressure (economically favorable as well), the flux will mostly likely be impacted negatively as to reduce the practicality of our nanocomposite membranes. Nevertheless, continuous effort in the improvement of the structure of MNT nanocomposite membrane (increased density and/or surface coverage with more MNTs nanochannels, fine-tuning the inner diameter of the MNTs), potential for scalable production of MNTs, as well as the ease with which nanotube vertical alignment can be achieved are factors that make our novel MNT membrane and fabrication process promising.

## 4 SUMMARY AND CONCLUSIONS

Novel magnetic iron cobalt oxide nanotube composite membranes were prepared and their potential applicability demonstrated for wastewater treatment. While % rejection values for test solute lignin remain modest, there is a large window of opportunity for performance improvement via

the optimization of membrane structure. In particular, the ability to prepare densely packed arrays of MNTs parallel to each other and perpendicular to the membrane support can maximize flux and allow for even lower operating pressures which, in turn, can lead to improved energy savings and % solute rejection values. The novel membrane fabrication procedures detailed above have the potential to eliminate the substantial performance gap between laboratory-scale versus commercial membranes by developing processes that employ controllable forces (e.g., magnetic fields) to manipulate responsive material phases or components to affect and direct nanostructure assembly.

## 5 ACKNOWLEDGMENTS

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