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## Point-of-Use Drinking Water Purification: Electrochemical Cross-Flow Filtration Device Scale-up and Evaluation --Manuscript Draft--

<b>Manuscript Number:</b>	IWA-10841
<b>Full Title:</b>	Point-of-Use Drinking Water Purification: Electrochemical Cross-Flow Filtration Device Scale-up and Evaluation
<b>Article Type:</b>	Full Paper
<b>Keywords:</b>	electrochemistry; point-of-use; carbon nanotubes; Ultrafiltration; scale-up; cross-flow
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<b>Manuscript Region of Origin:</b>	UNITED STATES
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<b>Manuscript Classifications:</b>	60.1: Ultrafiltration and nanofiltration membranes in water treatment

# Point-of-Use Drinking Water Purification: Electrochemical Cross-Flow Filtration Device Scale-up and Evaluation

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Keywords: electrochemistry; point-of-use; carbon nanotubes; ultrafiltration; scale-up; cross-flow

## Abstract

As the world population continues to increase, the gravity of the drinking water crisis will also intensify, especially in the developing world. In this study, an electrochemical cross-flow device was designed and evaluated for application in decentralized water treatment, termed point-of-use (POU) water treatment. The sustainability of current POU technologies is limited by the fouling of the filtration media. The hybridization of electrochemistry and filtration may provide a solution. An electrochemical cross-flow filtration device utilizing carbon nanotube filters was scaled-up and evaluated with regard to drinking water treatment. The electrochemical cross-flow filter (ECF) was evaluated with respect to permeate flux, effluent composition, and fouling potential. To assess the impact of the electrochemistry, the evaluations were completed with the CNT-polymer-CNT hybrid membrane under applied voltages of 0, 1, 2, and 3 V and compared to the polymer membrane alone as a control. The successful performance of the scaled-up electrochemical cross-flow filter by drinking water treatment standards, with a flow rate of 1-2 L per hour, demonstrates the viability of the technology for point-of-use applications. Furthermore, it was found that in all cases with the CNT-polymer-CNT membrane, the natural water flux was greater than the ultrapure water flux whereas with the polymer membrane alone, the natural water flux was less than the ultrapure water flux. This suggests that not only could the CNT-polymer-CNT hybrid be more resistant to fouling than a polymer membrane, but also that it could result in 'negative' fouling and thus provide point-of-use drinking water treatment with significantly longer lifetimes than current point-of-use membrane technologies.

## Introduction

The lack of infrastructure for centralized drinking water treatment in the developing world has led to the increased importance of and demand for POU water filtration devices. One of the main factors reducing the sustainability of the current point-of-use membrane technologies is fouling. Fouling is the blocking of the membrane pores by particles and molecules, precipitation of multivalent dissolved solids, and biofilm formation. In centralized systems, the rapid particle fouling can be eliminated by backwashing, i.e., reversing the flow to remobilize and remove the foulants. However, backwashing is not possible in current point-of-use systems, and when there is significant fouling of these POU membranes, the used membrane is discarded as waste and replaced. For example, cartridges must be replaced for the Seldon Waterbox after filtration of 4,500 liters of water.<sup>1</sup> The cost of a replacement cartridge is \$399 and, in turn, the cost to produce a cubic meter of drinking water is \$89.<sup>2</sup> Similarly, the LifeSaver cartridges require replacement after filtration of roughly 3,800 liters of water;<sup>3</sup> the cost of a replacement cartridge is \$119, and thus the cost to produce a cubic meter of drinking water with the LifeSaver bottle is \$31.<sup>4</sup> In contrast, the cost of conventional, centralized drinking water in Cambridge, MA in 2010 was \$1.05 per cubic meter.<sup>5</sup> Though the WaterBox and LifeSaver bottle have the potential to be

used for POU drinking water treatment, the high cost (30-85x greater than conventional treatment) severely limits the application of these technologies in the developing world. Thus, as Huang et al. point out, “easy and cost-effective fouling control” is the key to advancing membrane technologies for point-of-use applications.<sup>6</sup> If a point-of-use filter design were able to control fouling *in situ*, the lifetime of the filter could be extended, allowing the system to operate for a longer period of time prior to replacement. This in turn would reduce POU treatment cost, and make membrane and filtration technologies more viable for POU drinking water in developing countries.

Electrochemistry may provide a solution to fouling in granular media or membrane filters by *in situ* and real-time production of chemical oxidants. It is also important to note that electrochemistry is a viable POU option, as it can be powered remotely by photovoltaics.<sup>7</sup> The electrooxidation process also inactivates bacteria and viruses, reducing the possibility of biofilm fouling and eliminating pathogenic activity. However, conductive granular media, such as a packed-bed of activated carbon or carbon nanotube granules, requires a high voltage, >10 V, to produce oxidants and effectively degrade contaminants.<sup>8</sup> Recently, an electrochemical carbon nanotube filter was shown to be effective for removal and inactivation of bacteria and virus at an applied voltage of 2 to 3 volts.<sup>7</sup> Therefore, the electrochemical carbon nanotube filter provides a superior water treatment device as compared to granular carbon-based devices as it requires less voltage to drive the electrochemistry and less material to produce the filter. However, the current lab-scale device can only produce a few liters per day. There is potential for scale-up as thin (40-50 micron) carbon nanotube networks are available commercially in large sheets, up to 1 m<sup>2</sup> for a reasonable cost from NanoTechLabs, Inc (Yadkinville, NC). Thus, a scaled-up electrochemical carbon nanotube filter has the potential to treat water at the point of consumption in regions lacking centralized filtration infrastructure, as the pressure can be driven by gravity and the electrochemistry can be powered by photovoltaics.

In this study, a scaled-up electrochemical cross-flow water filtration device was developed and evaluated with respect to the permeate flux, effluent composition, and fouling potential. Turbidity, UV-VIS, and coliform analyses were completed on the effluent and indicated drinking water standards were met. The increased flux of the hybrid membrane when challenged with natural water compared to ultrapure water suggests that the device has the potential for POU drinking water treatment due to its superior fouling control.

## **Materials and Methods**

### **CNT-Polymer-CNT Hybrid Membrane Preparation**

Carbon nanotube networks and a PVDF membrane were used to produce the CNT-Polymer-CNT hybrid membrane. The carbon nanotubes used in this study had a specific surface area of around 100 m<sup>2</sup>/g, which provides a large number of active adsorption and deposition sites for molecular and particulate/microorganism removal, respectively. The network of carbon nanotubes (CNT film), acquired from NanoTechLabs, Inc (Yadkinville, NC), had a depth of ~40-50 microns and was cut into rectangles of 187 cm<sup>2</sup>. Polyvinylidene fluoride (PVDF), acquired from Sterlitech Co. (Kent, WA), was selected as the material for the polymeric membrane to separate the two CNT film electrodes due to its mechanical strength and chemical resistivity. The PVDF membrane had a molecular weight cut-off of 120,000 Daltons.

The CNT-Polymer-CNT hybrid membrane was prepared by pressing a stack of membranes arranged in the order – CNT film, PVDF membrane, CNT film. An 11 x 17 cm rectangle of CNT film was attached to either side of a 12 x 18 cm rectangle of PVDF membrane. The CNT-polymer-CNT hybrid membrane was assembled with a laboratory press to ensure that the CNT film was firmly attached to both sides of the PVDF membrane. The hybrid membrane

was pressed with 0.25 metric tons at room temperature for 5 minutes. Before the CNT-polymer-CNT hybrid membrane was evaluated in the ECF device, it was pre-wetted with ethanol.

### **Cross-flow filtration permeate flux and fouling evaluations**

This study utilized a standard cross-flow filtration pumping and monitoring system to evaluate the performance of the ECF device. The main components of the system were the water reservoir, water pump, influent tube, concentrate tube, cross-flow device, permeate tube, permeate flow meter, differential pressure sensor, pressure sensor/valve, and feed flow sensor. The system operated by pumping the feed, which ranged from 17-19 L/h, from the reservoir to the cross-flow device and recycling the concentrate that did not permeate through the membrane back into the reservoir. Permeate flow was determined with the permeate flow meter.

A standard DC power supply was used to apply a voltage to the electrodes of the ECF device. The positive lead was clipped to the anodic Ti connector to the CNT film on the feed side of the membrane and the negative lead was clipped to the cathodic Ti connector to the CNT film contacting the permeate side of the membrane.

The electrochemical cross-flow water filtration device was evaluated with respect to the permeate flux, natural surface water treatment for drinking water production, and the fouling potential. To assess the impact of the electrochemistry, the cross-flow device was operated with the CNT-polymer-CNT hybrid membrane under applied voltages of 0, 1, 2, and 3 V. The device was evaluated with both ultrapure and natural water. The realized flux was determined using permeate flow evaluations in the cross-flow device. The control of fouling was evaluated through a determination of the ratio of natural water to ultrapure water fluxes. For comparison, the flux, the treatment of natural water, and the level of fouling was evaluated for the PVDF membrane (with no CNT film attached) as well.

### **Effluent composition measurements**

The natural water that was used to challenge the device was obtained from Fresh Pond Reservoir in Cambridge, MA. Measured average parameters for this water source, as of 2010, are 18 CFU/100 mL *E.Coli* bacteria, 3.07 mg/L TOC, 0.083 A/cm UV 254, and 0.42 NTU turbidity.<sup>9</sup> The efficacy of the water treatment process was assessed with a turbidity measurement to determine particle content, a total coliform measurement to determine microorganism content, and a UV-VIS analysis to determine organic content. Turbidity is a measure of the amount of light scattered by a fluid sample, which reflects the amount of suspended particulate impurities. It is also a surrogate measurement for suspended microorganisms such as bacteria and viruses, which can also be considered 'particles'. A coliform measurement is a surrogate measure for the amount of pathogens in a sample of water and is significant because preventing the transmission of waterborne pathogens is an important objective in water engineering. The UV 254 measurement is a measure of the amount of natural organic matter (NOM) in a water sample. This measurement is obtained by determining the amount of UV light absorbed by a water sample. The three most important species of NOM revealed in this study are fulvic acids, humic acids, and humins. The UV 254 measurement is given as an absorbance value  $A$ , which relates to concentration of NOM and tube width by Beer's Law,  $A = \epsilon cl$ , where  $\epsilon$  is the extinction coefficient,  $c$  is the concentration, and  $l$  is the width of the sample.

## **Results and Discussion**

## Efficacy of Scaled-Up Cross-Flow ECF for Drinking Water Treatment

Permeate samples were collected during cross-flow operation with the CNT-polymer-CNT hybrid membranes at 0, 1, 2, and 3 V where the anode contacting the feed solution and the cathode contacting the permeate solution. Permeate samples were also collected after filtration through the PVDF membrane. Turbidity, UV-VIS, and coliform evaluations were performed on all permeate samples, as well as a sample of natural water feed solution, for comparison. All experiments were completed in at least duplicate.

### (a) Turbidity

The turbidity was measured for the samples of natural water treated with the CNT-polymer-CNT hybrid membrane and the PVDF membrane, as well as a sample of untreated natural water, for comparison. The results of the turbidity analysis are recorded in Table 1.

Table 1. Turbidity Analysis Results

Sample	Turbidity (NTU)	UV 254 Measurement
Feed Fresh Pond (natural water)	0.809 ± 0.281	0.142 ± 0.001
Permeate CNT-polymer-CNT at 0 V	<b>0.125</b> ± 0.025	0.065 ± 0.011
Treated w/ CNT-polymer-CNT hybrid w/ 1 V	<b>0.095</b> ± 0.003	0.078 ± 0.021
Treated w/ CNT-polymer-CNT hybrid w/ 2 V	<b>0.107</b> ± 0.033	0.062 ± 0.003
Treated w/ CNT-polymer-CNT hybrid w/ 3 V	<b>0.295</b> ± 0.083	0.115 ± 0.005
Treated w/ PVDF w/ 0 V	<b>0.132</b> ± 0.002	0.128 ± 0.012

\*Values in bold indicate turbidity measurement is below EPA drinking water regulations.

The turbidity of the influent (Fresh Pond water) was measured to be 0.809 NTU. Cross-flow filtration through the CNT-polymer-CNT hybrid membrane produced permeate of 0.125 NTU when 0 V was applied, 0.095 NTU when 1 V was applied, 0.107 NTU when 2 V was applied, and 0.295 NTU with 3 V was applied. With the PVDF membrane alone, an effluent of 0.132 NTU was produced. In all cases, the cross-flow filtration produced effluents that met Environmental Protection Agency (EPA) drinking water standards i.e., the turbidity must be less than or equal to 0.3 NTU 95% of the time and must never exceed 1 NTU.<sup>10</sup> Comparing the results of the hybrid membrane at 1V and 2 V (0.095 and 0.107 NTU, respectively) to the results of the PVDF membrane and the hybrid membrane at 0 V (0.132 and 0.125 NTU, respectively) indicates that the CNT-polymer-CNT improves turbidity reduction at 1 V and 2 V likely due to charging of the CNT electrodes resulting in increased electrostatic removal of charged particles.<sup>7</sup>

### (b) Coliform

A total coliform and *E. coli* measurement was completed for the samples of natural water treated with the CNT-polymer-CNT hybrid membrane and the PVDF membrane alone, as well

as a sample of untreated natural water, for comparison. The influent (Fresh Pond natural water) was determined to have a coliform count of  $213 \text{ L}^{-1}$  and an *E. coli* count of  $63 \text{ L}^{-1}$ , but after filtration through the CNT-polymer-CNT membrane and the PVDF membrane, coliform and *E. coli* were not detected in the permeate.

### (c) UV 254

The UV 254 measurement is a measure of the amount of natural organic matter (NOM) in a water sample. In similar fashion to the turbidity and coliform measurements, the UV 254 measurements were obtained for the samples of natural water treated with the CNT-polymer-CNT hybrid membrane and the PVDF membrane, as well as a sample of untreated natural water, for comparison. The results of the UV 254 analysis are recorded in Table 1. Even without the NOM extinction coefficient, the UV 254 measurement can be used to monitor trends in overall NOM removal. The UV 254 measurements of the effluents produced by the hybrid membrane (ranging 0.062 – 0.115) were all lower than that of the effluent produced by the PVDF membrane (0.128). The results demonstrate that the CNT-polymer-CNT hybrid membrane (at all applied voltages) outperformed the PVDF membrane in NOM removal likely due to the strong sorptive interactions between the NOM and the CNTs.

### Permeate Flux and Fouling Evaluation

Permeate flux evaluations were completed on the cross-flow device, operating the system for 15 minutes at each voltage (0, 1, 2, and 3V) and applying ~0.5 bar of pressure to the membrane. Two CNT-polymer-CNT hybrid membranes were evaluated and although the absolute fluxes varied between the membranes, the same relative flux vs. applied voltage trend was observed. The variability in the fluxes of the different membranes is believed to be a function of the amount of ethanol used to pre-wet the CNT-polymer-CNT hybrid membrane, i.e., a lower flux indicates insufficient pre-wetting. While the application of increasing voltage did not significantly alter the flux, an increase in the natural water flux as compared to the ultrapure water flux was observed.

For the first membrane evaluated, the flux was  $239.0 \pm 14.3 \text{ LMH-bar}$  for natural water at 0V, while  $108.2 \pm 5.0 \text{ LMH-bar}$  for the ultrapure water at 0V. For the second membrane evaluated, the flux was  $563.4 \pm 38.5 \text{ LMH-bar}$  for natural water at 0V while  $389.1 \pm 22.1 \text{ LMH-bar}$  for the ultrapure water at 0V. The remaining observed fluxes, with the application of the different voltages, can be found in Table 2.

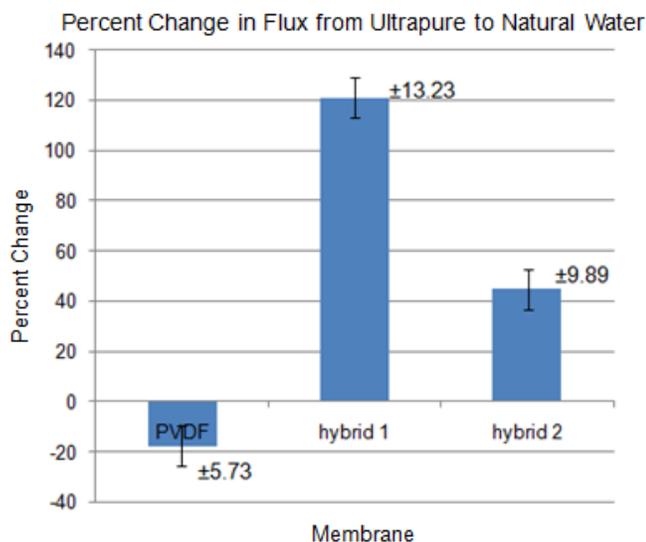
Table 2. Permeate Flux Results

Applied Voltage	Hybrid Membrane 1 Flux (LMH-bar)		Hybrid Membrane 2 Flux (LMH-bar)	
	Ultrapure water	Natural water	Ultrapure water	Natural water
0 V	$108.2 \pm 5.0$	$239.0 \pm 14.3$	$389.1 \pm 22.1$	$563.4 \pm 38.5$
1 V	$116.1 \pm 6.2$	$255.2 \pm 12.3$	$423.6 \pm 38.4$	$598.1 \pm 10.4$
2 V	$104.5 \pm 13.0$	$251.7 \pm 18.8$	$391.1 \pm 44.1$	$606.2 \pm 0$
3 V	$62.0 \pm 9.8$	$118.8 \pm 6.3$	$109.2 \pm 62.0$	$261.8 \pm 0$

The fluxes observed at 3V were outliers and this is likely due to production of bubbles. When a high enough voltage is applied to the electrodes, the anode potential increases past the thermodynamic limit for water oxidation and oxygen production yielding bubbles ( $2 \text{ H}_2\text{O} + 4 \text{ h}^+ \rightarrow 4 \text{ H}^+ + \text{O}_2$ ;  $E^\circ = 1.23 \text{ V}$ ). When narrowing in on the results of a membrane with a specific influent, the permeate flux does not vary significantly between 0, 1, and 2 V, and yet the increase in flux between the ultrapure and natural water is significant. The combined flux results indicated that the flux of the natural water through the CNT-polymer-CNT membrane was 140-240% of that of the ultrapure water through the membrane.

The observation of the increased natural water flux is novel given that the flow rate of natural water through a membrane is typically less than or equal to the flow rate of ultrapure water since natural water has more suspended particles, organic matter, and microorganisms than ultrapure water. The majority of suspended particles present in natural water carry a negative charge<sup>11</sup> and consequently, the increased flux maybe a result of the CNT film interacting on a molecular level with these negatively-charged particles present in the natural water, reducing their fouling potential, and effectively drawing more water into the membrane. This gives reason to believe that there is a component in the natural water that is adsorbed onto the carbon nanotubes and leads to increased hydrophilicity of the hybrid filters. When the pure PVDF was evaluated, the typical natural water to ultrapure water relationship was observed i.e., the ratio of the LMH-bar of natural water to the LMH-bar of ultrapure water was determined to be 0.82. This percent change in flux can be seen compared to the percent changes in flux observed (from ultrapure to natural water) with the CNT-polymer-CNT hybrid membranes in Figure 1.

Figure 1. Visual of observed flux increase in hybrid membrane with natural water- While, as expected, a decrease in flux was observed between ultrapure and natural water with the simple PVDF membrane, an increase in flux was observed between the ultrapure and natural water with the hybrid membrane. This observation of 'negative fouling' suggests potential for dramatically increased membrane lifetime.



## Conclusion

The scale-up of the electrochemical carbon nanotube filter ( $L's\ hr^{-1}$ ) and conversion to the cross-flow device configuration was successfully demonstrated in this study. The increased flow rate of natural water through the device and its effectiveness in producing water of low turbidity and free of coliform indicate that the electrochemical cross-flow filter may have potential for decentralized drinking water treatment. The negative natural water fouling data suggests that the electrochemical carbon nanotube filter does reduce fouling, which is critical for the sustainability of the device. The reduction in fouling also suggests a more cost-effective device than the technologies that currently exist, but in order to prove this hypothesis, the lifetime of the CNT-polymer-CNT hybrid membrane in terms of water volume produced before replacement must be determined.

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