

Project title: Design of a self-cleaning membrane-assisted bioreactor for enhanced removal of nutrients from wastewater

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1. Problem and Research Objectives

Eutrophication is a key driver causing a number of pressing aquatic environmental problems including reductions in light penetration and increases in harmful algal blooms (HABs) [1]. The major factors affecting eutrophication are mineral nutrients such as nitrogen and phosphorus in municipal and industrial wastewater [2]. In Ohio's lakes and rivers, the key symptom of eutrophication is cyanobacterial blooms [3]. The increasing occurrence of HABs in fresh water due to eutrophication of surface water has become an emerging concern threatening human and environmental health because cyanobacteria, more commonly known as blue-green algae, can produce and release potent toxic compounds, which are known as "cyanotoxins" such as microcystins, cylindrospermopsin, saxitoxin, and anatoxin-a [4-7].

The United States has the world's highest water consumption rate per capita (approximately 215 cubic meters per year) [8]. The ever-increasing demand for water leads to need for new sources of longer distance and/or greater depth, however, which would lead to increased environmental costs and economic exploitation. Development of an expanded water portfolio is even more challenging given the high cost of maintenance and upgrade of existing aging and overloaded centralized wastewater conveyance and treatment infrastructures currently serving large metropolitan areas in the U. S. [9]. It is estimated that water infrastructure maintenance and upgrade for the wastewater treatment sector alone would cost more than \$200 billion over the next 20 years in the U. S. [10]. Given the rising burden on centralized water conveyance and treatment systems, wastewater reuse has emerged as a viable approach toward water sustainability.

In nutrient-sensitive estuaries, municipal and industrial water resource recovery facilities are required to implement more advanced treatment methods in order to meet increasingly stringent effluent guidelines for nutrients. According to literature, biological nutrient removal processes that incorporate coupled nitrification/denitrification have the potential to remove total nitrogen (TN) down to about 5 - 12 mg/L, in selected cases, down to 3 mg/L. The TN concentration in effluent is known as less than 10 mg/L at most inland municipal WRRFs. In case of phosphorus, very stringent effluent total phosphorus (TP) limits (0.03 - 0.10 mg P/L) are required in the U.S. but it is challengeable to reach the goal by only biological nutrient removal processes [11, 12].

Achieving these limits demands **very low soluble P and essentially a biomass-free effluent**. In particular, biological nutrient removal systems with a settling tank discharge approximately 10 mg/L of total suspended solids in the effluent. The phosphorus content of the solids contributes approximately 0.3 mg/L to the effluent [13]. Biological nutrient removal systems incorporating membrane technology, which are able to produce solids-free effluent are becoming an attractive technology [14-19].

Membrane bioreactor (MBR) technology can provide complete retention of biomass allowing higher sludge retention time with effective bacterial cultures that can degrade certain types of recalcitrant constituents. However, **membrane fouling** is identified as a major hurdle to the wide

applications of MBRs [20]. Membrane fouling in MBRs takes place mainly due to two reasons: (i) cake layer formation by biomass and (ii) precipitation of inorganics on the membrane surface. In particular, the cake formation that includes sludge particles and biopolymers such as proteins, polysaccharides, and humic substances has been identified as a dominant feature contributing to the deterioration of membrane performance [21-23]. To recover the reduced water permeability through membranes due to fouling, routine membrane cleaning using chemicals is required. However, conventional polymeric membranes that have been widely used for MBRs are sensitive to oxidising disinfectants and the frequent use of chemicals shortens the membrane life-time [24]. Therefore, it is desirable to develop new membranes and approaches for mitigating of membrane fouling.

Due to the continuously increasing occurrence of HABs in Ohio's lakes and rivers and the inefficient or impractical technologies for the elimination of nutrients, there is a critical need to develop an effective solution for a satisfactory removal of nutrients from wastewater sources in order to achieve clean and safe drinking water supplies and protect human health. The main objective of this project is to fabricate a self-cleaning membrane for the efficient removal of nutrients from municipal wastewater. A bench-scale MBR (treatment capacity = 10 L/day) was developed and optimized for simultaneous removal of nitrogen and phosphorus to prevent HABs combined with the self-cleaning carbon nanotube (CNT) membrane.

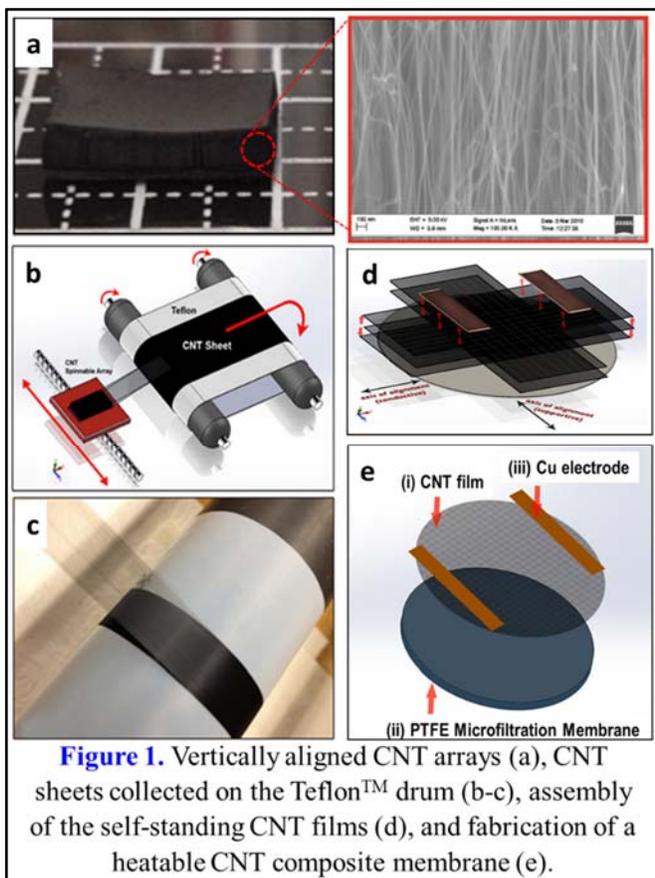
2. Methodology

2.1 Fabrication and surface modification of self-cleaning membranes

We have successfully synthesized prototype **self-standing and electrically heatable CNT composite membranes** (100 cm²). Firstly, **vertically aligned CNT arrays** (**Figure 1a**) ~0.45 mm long with 7~10 nm pore diameter were synthesized through a chemical vapor deposition (CVD) as described in the PI's previous work [51]. CNTs with a production rate of ~ 600 kg/h can be obtained using an industrial-scale catalytic CVD reactor and the average cost of CNTs with these proposed processes lies in the range of **\$25 - \$38/kg** [52].

The synthesis process uses a thin film catalyst of iron and cobalt, sputtered over a 5-nm aluminum oxide buffer layer on a 4-inch silicon wafer. The catalyst-coated silicon wafers are cut into 2-inch pieces of variable width, and loaded into a modified commercial CVD reactor (ET3000, CVD Equipment Corporation) at 740 Torr and 750°C.

Fabrication of **porous CNT sheets** (water contact angle > 140°) (**Figure 1b**)



starts by drawing one edge of the vertically aligned CNT arrays. Approximately each linear millimeter of vertically aligned CNT arrays can be drawn into a linear meter of CNT sheet using a machine at speeds up to 16 m/s by using collecting drums connected to a high-speed motor and collecting the CNT sheets onto the Teflon™ drum (**Figure 1c**).

The CNT sheets were stacked layer-by-layer to form **self-standing CNT films (Figure 1d)** on a 0.20 μm flat-sheet **hydrophilic PTFE membranes** (Sterlitech). The entire hybrid membrane was wetted with ethanol (99.5%, Acros Organics) in order to increase the adsorption of CNTs to the polymeric membrane and improve densification, which occurs after solvent evaporation. Loading of CNTs, surface area, and porosity were controlled by varying number of CNT sheets and orientation on the membrane surface. Finally, a **CNT composite membrane (Figure 1e)** was synthesized by combining 1) the self-standing CNT films on the PTFE membrane and 2) Cu electrodes on the surface of the CNT films.

We modified the surface of the CNT composite membrane using atmospheric pressure plasma facility (**Figure 2**), which allows dry functionalization of CNTs creating hydroxyl (-OH) and amine (-NH) functional groups. Hydroxyl functional groups were created on CNTs by using atmospheric pressure Helium/Oxygen plasma. Also, amine reactive species were created using NH₃ combined with helium flow and generating plasma at atmospheric pressure.

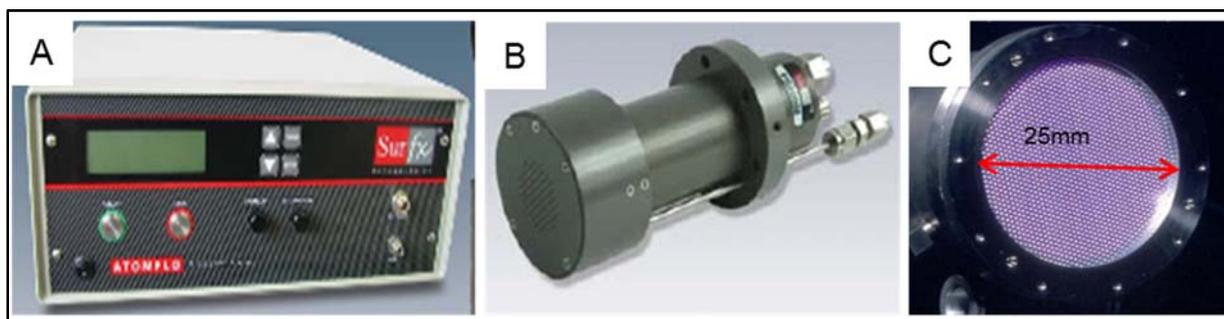


Figure 2. Plasma functionalization of CNTs: The Surfx Atomflo 400D plasma controller (A) with a cylindrical plasma deposition headset (B), and plasma discharge unit (C).

2.2 Electric heating of the CNT composite membrane for mitigation of biofouling

This type of material is easily scalable and electrically conducting to produce heat when connected to electrodes and voltage is applied. For electrical heating of the CNT composite membranes, a bench top direct current (DC) power supply (E3612A, Hewlett Packard) was connected to each sample and electric potentials of 10 V, 15 V, 20 V and 25 V were run for 5 minutes. The surface temperatures were monitored with a FLIR T-640 IR camera. FLIR Tools+ software was used to record, plot, and prepare images and reports from the resulting thermal data.

2.4 A bench-scale MBR system

A bench-scale anoxic and oxic MBR system (treatment capacity = 10 L/day at HRT = 12 hr) (**Figure 3**) was operated at room temperature over 4 months with synthetic wastewater (**Table 1**). The reactor was operated without electrical heating of the CNT composite membranes for about two months (Period I) and then the CNT membrane was electrically heated to remove membrane foulants for about one month (Period II). During these periods, mixed liquor suspended solids (MLSS) concentration in the reactors was maintained at 6.2 ± 0.4 g/L at 30-day SRT. Water permeability through polymeric membrane and the CNT composite membranes was maintained at 10 L/m²/hr (LMH).

Table 1. Characteristic of synthetic wastewater.

Item	Chemical formula	Concentration (mg/L)
Glucose	C ₆ H ₁₂ O ₆	150 (as COD)
Ammonium sulfate	(NH ₄) ₂ SO ₄	30 (as N)
Potassium phosphate	KH ₂ PO ₄	6 (as P)
Sodium bicarbonate	NaHCO ₃	200 (as CaCO ₃)
Calcium chloride	CaCl ₂ ·2H ₂ O	0.50
Cobalt chloride	CoCl ₂ ·6H ₂ O	0.35
Cupric sulfate	Cu SO ₄ ·5H ₂ O	0.15
Ferric chloride anhydrous	FeCl ₃	0.80
Magnesium sulfate	Mg SO ₄ ·7H ₂ O	0.34
Manganese chloride	MnCl ₂ ·4H ₂ O	0.50
Sodium molybdate dihydrate	Na ₂ MoO ₄ ·2H ₂ O	0.20
Yeast extract	-	10
Zinc sulfate	ZnSO ₄ ·5H ₂ O	0.55

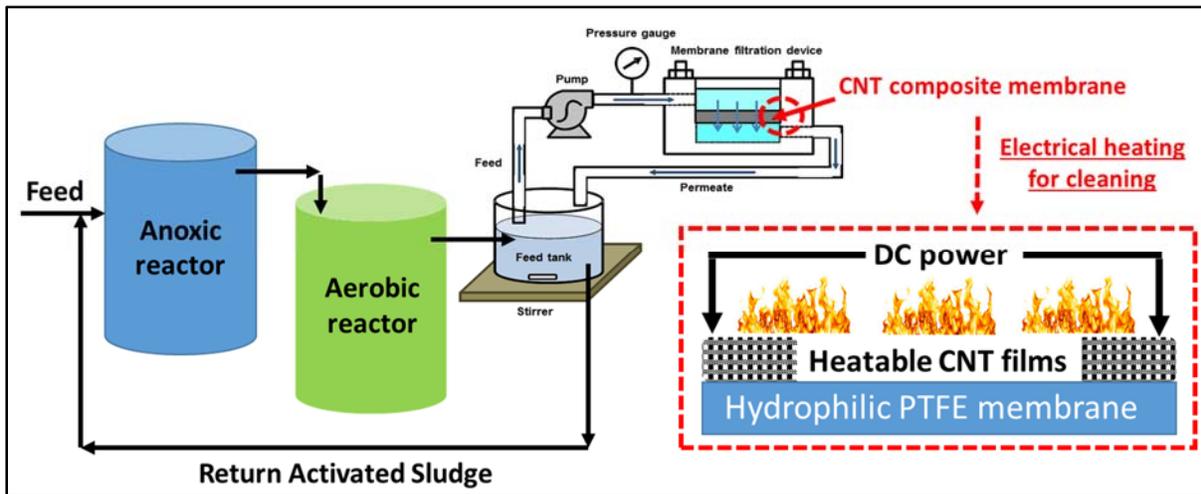


Figure 3. Schematic diagram of a bench-scale MBR system with the electrically heatable CNT composite membrane.

2.5 Analysis of membrane fouling

To determine the effects of the electric heating of the CNT composite membrane in membrane fouling, the resistance-in-series model was used to analyze membrane fouling resistances, which describes the permeate flux - transmembrane pressure (TMP) relationship over the entire domain of pressure as described in the previous study [28]. Based on the model, the permeate flux on the applied TMP can be described by Darcy's law as Eq. (1):

$$J_v = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\mu R_t} \quad (1)$$

where J_v is the permeate flux ($\text{m}^3/\text{m}^2/\text{s}$), V is the total volume of permeate (m^3), A is the membrane area (m^2), ΔP is the TMP (Pa), μ is the dynamic viscosity of permeate ($\text{Pa}\cdot\text{s}$), and R_t is the total membrane resistance (m^{-1}).

2.6 Characterization of the CNT composite membranes

Characterization of the CNT composite membranes were conducted as follows: **Hydrophobicity** or hydrophilicity of the membranes was examined by contact angle measurements using the sessile drop Young–Laplace method (Drop Shape Analyzer, DSA25E, Krüss). **Surface charge** (or streaming potential) of the membranes was determined by measuring streaming potential and streaming current on the material surface (SurPASS, Anton Paar). **Surface area and pore properties** of the composite membranes was investigated using a micropore physisorption analyzer (ASAP 2060, Micromeritics).

2.7 Characterization of wastewater and membrane permeate

Concentrations of various ions such as NO₂-N, NO₃-N, and ortho-P were analyzed using ion chromatography (IC) (Dionex DX-120, U.S.A) after filtering with a 0.45 µm membrane filter (ADVANTEC MFS Inc., Dublin, CA, U.S.A). Temperature and pH were measured using temperature and pH electrodes connected with a pH meter (Orion Model 420A, Orion Research Inc., U.S.A). Concentrations of COD, MLSS, total suspended solid (TSS), TN, and TP of wastewater were measured according to *Standard Methods* [29]. All experiments of this study were performed at least three times. Analysis of variance (ANOVA) was applied for the statistical analysis and differences from controls was considered significant when $p \leq 0.05$.

3. Principal Findings and Results

3.1 Changes in membrane temperature by electric heating

Figure 4 shows the effects of electric potential and power on temperature changes on the surface of the CNT composite membranes. The max temperature is the warmest point recorded by the IR camera and the average temperature is the average values of five different spots on the membrane surface. As electric voltage increased from 10 (0.75 W) to 20 V (3 W), average temperature increased from 53°C to 110°C. However, temperature slightly decreased at 25 V (3.5 W) due to damage of the membrane sustained at the corners where the CNT layers first meets the Cu electrode.

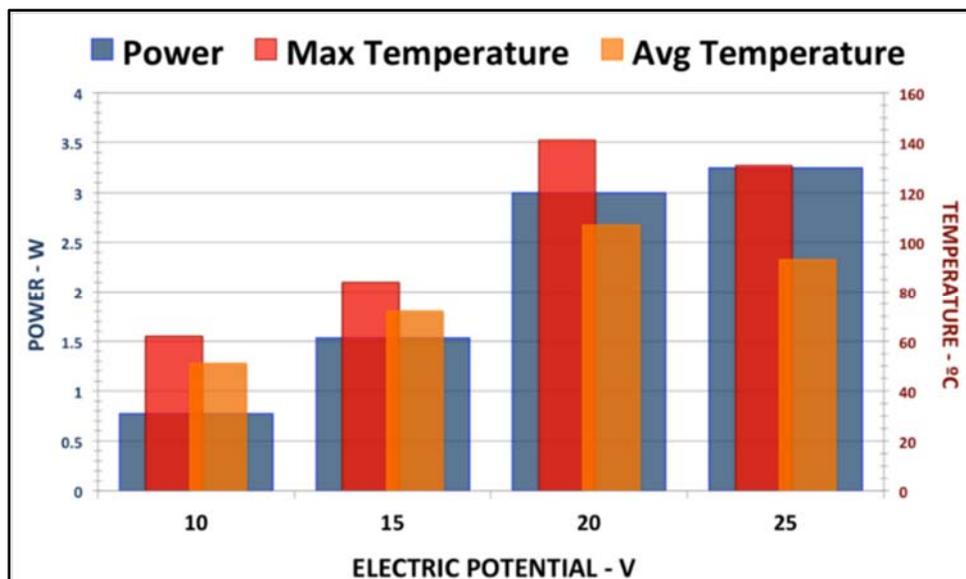


Figure 4. Effects of electric potential on membrane temperature.

In this study, the surface temperature of the CNT membrane increased from 25 to 140°C (Spot 3 in **Figure 5(C-1)**) by electric heating with DC power (20 V). When this membrane was employed, *Escherichia coli* K12 filtered and collected on its surface were successfully annihilated within ten seconds.

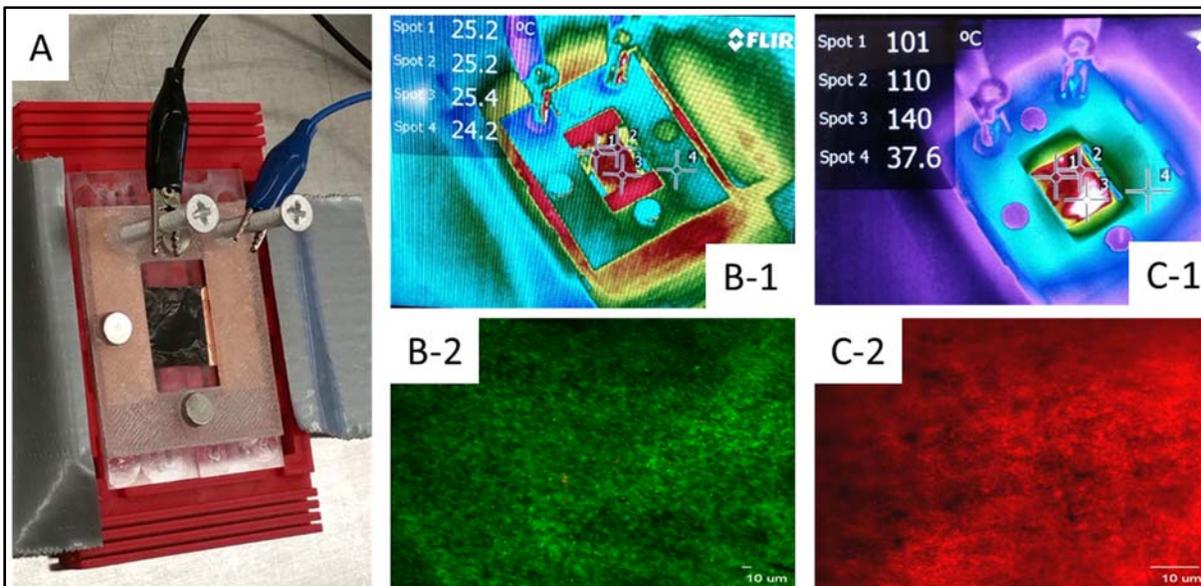


Figure 5. Electric heating device (A) with a DC power supply, IR temperature profile of the CNT arrays (B-1) and *Escherichia coli* (ATCC 25922) stained using the Live/Dead BacLight Bacterial viability kits (B-2) before DC power supply, IR temperature profile of the CNT arrays (C-1) and *Escherichia coli* (ATCC 25922) stained using the Live/Dead BacLight Bacterial viability kits (C-2) after 10-second at 20 V.

3.2 Removal efficiency of organic matter and nutrients by the bench-scale MBR system

As shown in **Table 2**, the bench-scale MBR system showed good performance in removing organic matter and nutrients from synthetic wastewater. Typical removal efficiencies of COD, TN, and TP by the MBR were 95~96%, 83~84%, and 63~65%, respectively. Also, the both polymeric membrane and the CNT composite membrane effectively separate biomass from the final effluent (over 99.9% removal of TSS).

Table 2. Average removal efficiencies of COD, nutrients, and TSS by the bench-scale MBR system.

Removal efficiency	Period I (0 ~ 60 days)	Period II (61 ~ 97 days)
COD	95 ± 3%	96 ± 4%
TN	83 ± 2 %	84 ± 3%
TP	65 ± 5%	63 ± 2%
TSS	Over 99.9 %	Over 99.9 %

3.3 Membrane fouling and recovery from membrane fouling in the MBR system

The bench-scale MBR system was operated at constant flux (*i.e.*, 10 LMH) with the 0.20 μm PTFE membrane for 60 days. **Figure 6** shows variations of TMP during the operation. When the

TMP increased over 50 kPa, there is decreased in water flux so the membrane was replaced with new one. As shown in this figure, the TMP increased over 50 kPa within 6-7 days due to membrane fouling. This was consistent for each experiment during the operation.

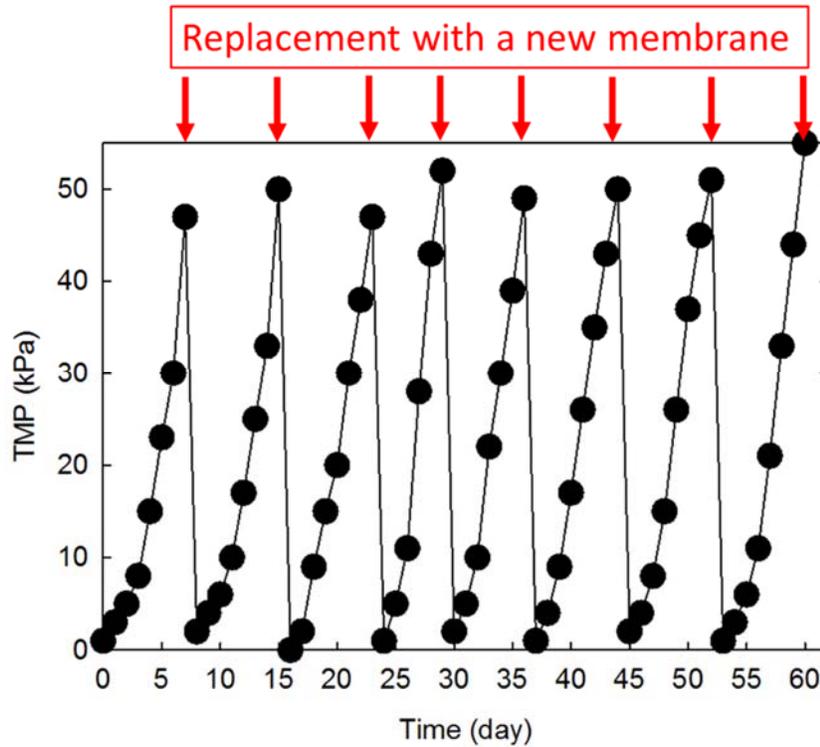


Figure 6. Changes in membrane fouling (*i.e.*, TMP) during the experimental period I.

After 60 days, the PTFE membrane was replaced with the CNT composite membrane (water contact angle $< 20^\circ$) and the MBR system was operated for about one month under the same operating conditions. During this period, the CNT composite membrane was heated over 100°C for 30 seconds using DC power (E3612A, Hewlett Packard) to remove membrane fouling when the TMP increased over 50 kPa. As shown in **Figure 7**, the CNT composite membrane was able to treat wastewater for 9-10 days without cleaning and the membrane was effectively recovered from fouling using electric heating. During this period, any physical damage of the CNT composite membrane was not found by the electric heating.

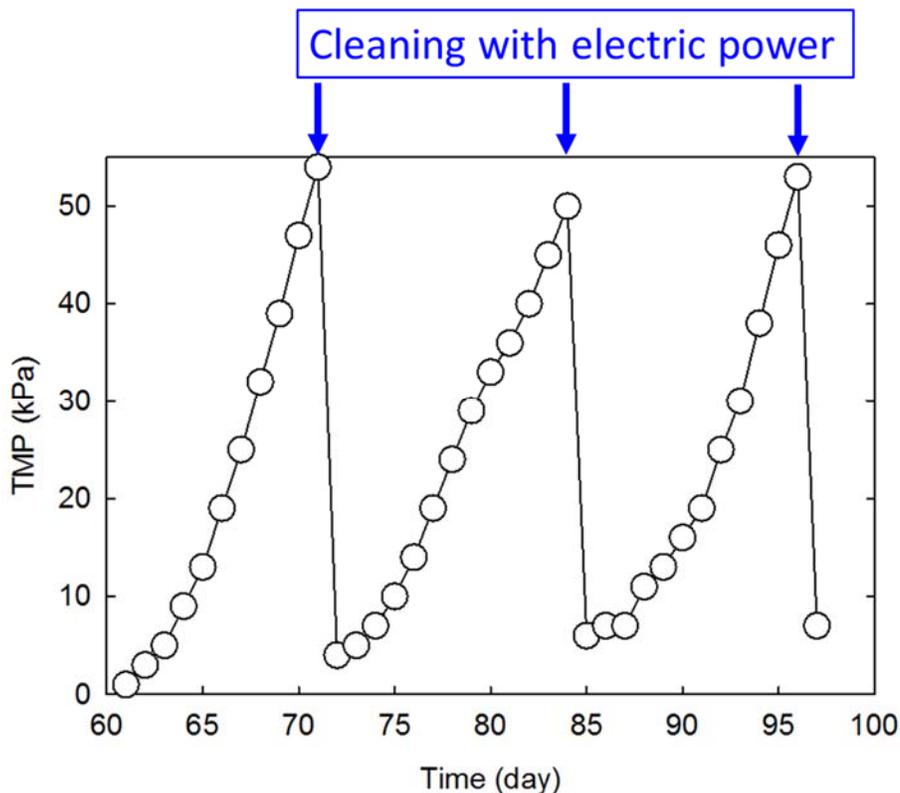


Figure 7. Changes in membrane fouling (*i.e.*, TMP) during the experimental period II.

4. Finding Significance

HABs have a significant impact on drinking water quality, fish and animal habitat as well as ecosystem services. The need to reduce anthropogenic nutrient inputs to aquatic ecosystems in order to protect drinking-water supplies and to reduce eutrophication, including the proliferation of HABs and “dead zones” in coastal marine ecosystems has been widely recognized. MBR is one of the most cost-effective treatment technologies for removal of nutrients from wastewater. However, membrane fouling is identified as a major hurdle to the wide applications of MBRs for wastewater treatment with high MLSS concentration.

From this study, it was found that the CNT composite membrane has an anti-fouling function and electric heating is a sustainable method to clean the CNT membrane after fouling. The results allow for development of novel engineering solutions for the mitigation of membrane fouling and/or recovery from membrane fouling that eventually increase performance of MBR systems and also reduce HABs’ risks to public health and the environment.

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Figure. A graduate student (Brindha Murugesan, M.S. candidate) is optimizing a bench-scale membrane bioreactor system with the carbon nanotube composite membrane for efficient removal of nitrogen and phosphorus from municipal wastewater.