USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: *Quality and Membrane Treatability of the Lake Houston Water Supply*

Focus Categories:

Keywords: Microfiltration, Ultrafiltration, Nanofiltration, Disinfection by-products, Colloids, Water Quality, Fouling

Duration: 3/1/00 – 2/28/01

Federal Funds Requested: $25,000

Non-Federal (matching) Funds Pledged: $50,007

Principal Investigator: Shankar Chellam, University of Houston

Congressional District: 18th (current representative: Sheila Jackson Lee)

Statement of Critical Water Problems

Currently, sections of Harris and Montgomery counties located North and Northeast of Houston use groundwater almost exclusively. These areas have witnessed substantial population growth and associated increases in water demand. In 1999 approximately 60% of potable water in Houston and its adjoining communities was produced from surface water. The remaining approximately 40% was derived from groundwater. However, the "Subsidence District" which is the authority responsible for granting groundwater permits has mandated that groundwater use needs to be decreased to 20% within the next few years so as to limit subsidence.

Pipelines are not available to distribute purified water from the existing surface water treatment plants located in the South and East of Houston to the Northern areas that actually require additional water. Because Lake Houston is located in the geographical area of interest and is a surface water source, the City of Houston is interested in developing it for its future water needs. Additionally, a favorable hydraulic gradient exists from the Lake to the proposed service areas in Harris and Montgomery counties.

Federal regulations such as the Stage II of the Disinfectant/Disinfection By-Products Rule (Federal Register, 1998a) and the Enhanced Surface Water Treatment Rule (Federal Register, 1998b) are expected to be promulgated in the near future. These rules are anticipated to introduce more stringent maximum contaminant levels (MCLs) for total trihalomethanes (THMs) and haloacetic acids (HAAs), possibly introduce new MCLs for individual species of THMs and HAAs, reduce turbidity levels, and enhance inactivation/removal requirements for *Cryptosporidium*. (*Cryptosporidium* was the causative protozoan for the more than 400,000 cases of acute gastrointestinal disease in

Milwaukee, WI in March 1993.) The treatment processes in the City of Houston's existing water purification plants are not expected to be sufficient in meeting these anticipated regulations.

Therefore, both regulatory pressures and engineering considerations point towards Lake Houston as an attractive surface water source for the next water purification plant to supply potable water to the City and its adjoining communities. However, water quality in Lake Houston can be characterized as being poor with high concentrations of turbidity, color, total organic carbon (TOC), nutrients such as phosphorus and nitrogen, etc. Acute or chronic toxicity levels for various metals have also been exceeded at various points in the Lake's watershed (HGAC, 1994). Therefore, changes in water quality between background, and storm flow conditions will be established in order to develop an understanding of the dynamic aspects of water quality in Lake Houston. Both actual concentrations and speciation of contaminants can change during a storm event. Hence, particle size distributions and apparent molecular weight distribution of organic carbon will also be measured. Such information is valuable in determining their fate in the water column as well as in water treatment processes.

Pressure-driven membrane processes can be employed as effective barriers against a wide range of contaminants including particles, turbidity, protozoan cysts and oocysts, bacteria, viruses, color, organic carbon, disinfection by-product (DBP) precursors, and dissolved metals. Additionally, microfiltration (MF) and ultrafiltration (UF) pretreatment may be necessary to reduce fouling rates and increase chemical cleaning intervals during surface water nanofiltration (NF) (Chellam et al. 1997). Therefore, an integrated membrane system employing MF or UF pretreatment to NF is expected to be an important treatment candidate for Lake Houston water.

Very little is known about proper scale-up of membrane systems employed for water treatment both in terms of fouling and water quality necessitating long pilot-studies in support of design. One of the primary objectives of the proposed work is to investigate fundamental approaches in determining scale-up procedures for MF and UF fouling and NF water quality.

Statement of Results of Benefits

The proposed research is both fundamental and applied in nature. The applied research will focus on developing site-specific information to assist the City of Houston in its future piloting efforts especially for process selection and implementation at the proposed new water purification plant. Another tangible benefit of this work will be the increase in familiarity and comfort level with membranes for the City of Houston staff. The proposed research may also be employed in reducing the duration of future pilot-studies, and in the better design of membrane systems on Lake Houston water resulting in substantial cost savings to the City.

The fundamental components of the proposed research have both engineering and policy implications. Methods to scale-up low-pressure membrane processes, understanding molecular mass transfer processes in NF systems employed for color and disinfection by-product (DBP) precursor removal, and the impacts of pretreatment on fouling of nanofilters are proposed. Quantifying changes in water quality during storm events is especially important in formulating options for source management and evaluating storm-water treatment strategies.

More specifically, a model of cake filtration for flat sheet, inside-outside, and outside-inside hollow fiber geometries will be formulated. This will be linked to measurements of permeability and compressibility of deposits from dead-end experiments. Such an approach is expected to allow better scale-up of MF and UF processes incorporating fundamental fouling mechanisms. Thus, pilot-scale studies that will be conducted by the City of Houston in the near future can be more thoroughly interpreted in support of plant design and construction.

Because of the low alkalinity of Lake Houston water, NF membranes need to be carefully chosen so that they selectively reject color and DBP precursors and not further reduce buffering capacity. This is important to keep post-treatment costs at a minimum. Bench-scale crossflow NF experiments will be used in part to screen membranes prior to pilot testing. Again, an approach where results from well-controlled bench-scale experiments will be used in support of larger scale testing is expected to substantially reduce costs for the City of Houston.

Nature, Scope and Objectives

The specific objectives of the proposed research on Lake Houston water are:

1. To characterize the size distributions of particles and the molecular weight distribution of natural organic matter under background conditions and periods of elevated flow during storm events,

2. To develop a meso-scale fouling model to assist in the scale-up of MF and UF processes,

3. To determine the effects of MF and UF pretreatment on NF fouling under various permeate fluxes and feed water recoveries, and

4. To quantify the effects of permeate flux and feed water recovery on NF permeate water quality especially in terms of organic carbon and disinfection by-product precursors.

This project will attempt to relate changes in water quality in terms of colloidal and organic compositions due to storm events to differences in the performance of membrane systems. Simple mathematical tools are proposed to better understand the factors controlling the performance of MF, UF, and NF systems. If found to be successful, these tools can be extremely valuable in the better scale-up of bench-, and pilot-scale testing results and in the better design of pilot-scale experiments ultimately resulting in substantial cost savings. Specifically, a model based on cake filtration will be evaluated for MF and UF. Another model based on solution-diffusion theory will be developed and evaluated for the removal of organics and disinfection by-products by NF membranes. Finally, site-specific experiments that will assist the City of Houston in their future membrane pilot-testing efforts are also proposed.

Methods, Procedures and Facilities

All of the equipment necessary to conduct experimental and analytical measurements are either already available in the Environmental Engineering laboratories at the University of Houston or will be established as part of my start-up package. The proposed work comprises of the following four tasks:

Task 1. Establish variations in concentrations and size distributions of particles, as well as concentrations and apparent molecular weight distribution of organic carbon between background and storm flow conditions. One of the points at which the City of Houston has been monitoring Lake Houston's water quality is designated as "intake tower". This location is not only close to the shore (< 20 feet) but also shallow (~ 1 foot) in order to facilitate frequent sampling. Water samples for the proposed research are not expected to be collected at this point because a new intake facility has been recently installed. This new intake is approximately 700 feet from the shore, and 24.5 feet deep and will be employed to supply water to the proposed new water purification plant.

Important Lake Houston's water quality parameters for 1998 (obtained at the intake tower point) are summarized in Table 1. Thus, Lake Houston water can be designated as being highly colored, and turbid, with low buffering capacity. It is slightly alkaline, with both turbidity and TOC values showing large fluctuations with time (Figure 1). Absorbance at 254 nm and one cm path length (UV_{254}) is often monitored as a surrogate for aromatic organics that have been shown to form DBPs upon chlorination (Singer, 1999). This is a much simpler analysis to conduct compared to measuring total organic carbon especially because portable spectrophotometers are available. Hence, further analysis of the collected data was attempted and a strong correlation (R=0.87) between UV_{254} values and TOC concentrations was observed (Figure 2). (The outer dashed lines in Figure 2 depict the 95% confidence intervals of the mean of the observations.) Some of the proposed work will investigate developing simple relationships between DBPs and appropriate surrogate parameters. Such expressions may allow control measures to be implemented prior to obtaining actual laboratory results for DBPs that often takes more than one week to obtain.

At least two background samples will be collected during the course of this project. Further, a minimum of five samples will be collected during one storm event to track dynamic changes in water quality with flow. Storm flow data will be gathered from existing U.S. Geological Survey gages to facilitate the computation of time-variant mass loadings.

Table 1. Summary of important physical-chemical water quality parameters measured during the period 1/1/98 – 12/31/98 in Lake Houston.

Parameter	Units	Average	Minimum	Maximum
Turbidity	NTU	43.2	8.72	212
TOC concentration	mg/L	10.3	6.3	15.5
UV_{254}	cm^{-1}	0.47	0.18	0.84
pH	-	7.68	7.12	8.89
Color	Co-Pt units	37	10	76
Total phosphorus	mg/L as P	0.35	0.06	1.05
Nitrate	mg/L as N	0.19	< 0.05	0.48
Total alkalinity concentration	mg/L as $CaCO_3$	42	22	64
Total hardness concentration	mg/L as $CaCO_3$	53	32	70
Total iron	mg/L	1.56	0.13	2.60
Total manganese	mg/L	0.04	< 0.01	0.14

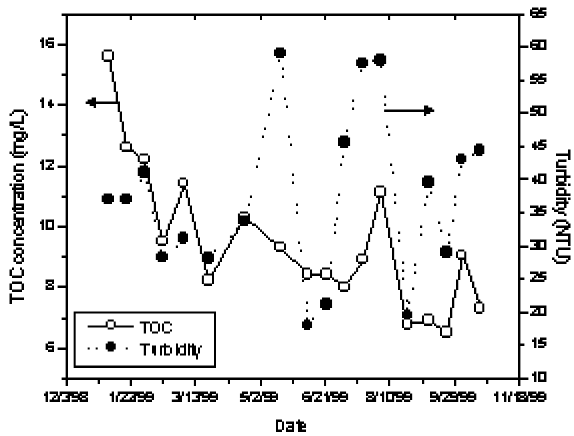

Figure 1. Temporal profiles of total organic carbon concentration and turbidity in Lake Houston measured in 1999.

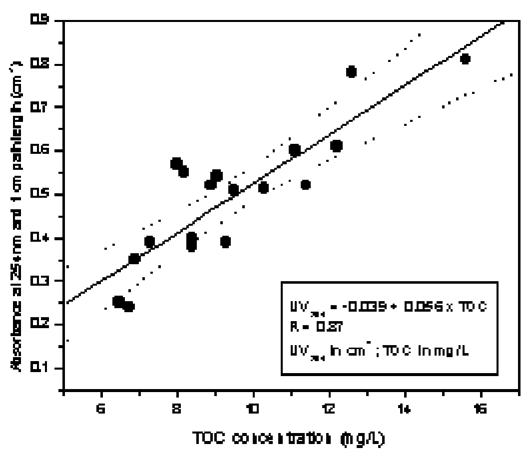

Figure 2. Correlation between total organic carbon concentration and UV_{254} in Lake Houston measured in 1999.

Grab samples will be collected using a detergent cleaned, acid rinsed, polyethylene bucket at the newly installed intake. The intake has been designed to draw from two depths: 11.5 feet and 20.5 feet by operating different sets of pumps for each depth. The sampling depth for the proposed research will be finalized during our first technical meeting with the City staff (see Section 14 "Information Transfer"). The sampling bucket will be rinsed with three volumes of sample water that will be discarded prior to obtaining the actual sample. The sample handling and container cleaning procedures of Laxen and Harrison (1981) and Perret et al. (1994) will be followed to reduce contamination and changes in composition during storage and handling. All samples will be analyzed within 48 h of sampling and will be refrigerated at 4 ºC prior to analysis.

In order to better compare results from this study to previously published data for the Houston area (Characklis and Wiesner, 1997), cellulosic membranes of various nominal pore size or molecular weight cutoffs will be employed to fractionate samples. Particle size distributions will be measured using laser light scattering (Malvern Zetasizer 5000, Worcestershire, U.K.). Size distributions will be depicted on the basis of particle number, surface area and volume. If high concentrations of particles larger than ~ 5 um are observed, a Malvern Mastersizer (Worcestershire, U.K.) will be employed for sizing.

Organic carbon measurements will be made on samples acidified to a pH < 2 (Shimadzu, TOC5050A, Tokyo, Japan). Apparent molecular weight of NOM will be measured by filtration by employing membranes with successively lower molecular weight cut-offs (MWCOs). Based on the data reported by Kim and Symons (1991) on molecular weight fractionation of treated Lake Houston water, it is anticipated that MWCOs of 10,000, 5,000, and 1,000 Da will be employed. An additional lower MWCO membrane of 500 Da may be employed if necessary.

Task 2. Derive and validate a mechanistic model for scale-up of MF and UF processes. For highly turbid waters such as in Lake Houston, cake formation is expected to be the dominant fouling mechanism in MF and UF systems. A simple model of dead-end, cake filtration for hollow fiber and flat-sheet geometries will be developed for both constant pressure and constant flux operation. Unstirred, dead-end, constant pressure experiments using 0.1-mm disc membranes (Durapore, Millipore Corporation, Marlborough, MA) will be conducted in the pressure range ~ 30 – 200 kPa to determine the specific resistance (or permeability) and compressibility of deposits (Fane 1986). A minimum of 200 mL of the test suspension will be filtered during these experiments that will be conducted using a stainless steel cell (Osmonics, Livermore, CA). By monitoring the cumulative volume filtered (V) as a function of time (t), the specific resistance (a) can be calculated using (Mallevialle et al., 1997):

$$\frac{t}{V} = \frac{\mu R_m}{A \Delta P} + \frac{\mu \alpha \rho \phi_o V}{2 A^2 \Delta P} \qquad (1)$$

where m is the absolute viscosity, R_m is the clean membrane resistance, A is the membrane area, DP is the applied pressure, r is the fluid density, and f_o is the bulk volume fraction. Therefore, as suggested in Eq. 1, the slope of linear fits for data from constant pressure experiments plotted as t/V versus V give the specific cake resistance if other physical parameters are known.

Because both the concentration and size (molecular weight) distribution of particles and organics are expected to change with rainfall, bench-scale filtration experiments will be performed during both background and storm flow conditions.

Task 3. Determine differences in NF fouling rates with MF and UF pretreatment. This task is primarily intended to support the City of Houston's future piloting efforts in terms of NF membrane screening. Currently no quantitative model of NF fouling is available. Additionally, developing such a model is beyond the scope of the proposed work. Hence, an empirical approach will be employed where Lake Houston water will be first treated with MF and UF membranes. These MF and UF filtered waters will be further treated using at least two NF membranes that selectively reject organics and color but are highly permeable to calcium, magnesium, and bicarbonate ions. Linear regression will be employed to calculate fouling rates based on both time and volume filtered as independent variables. Fouling rates under different experimental conditions (Table 2) will be employed in part to suggest appropriate parameters for longer term pilot-scale testing.

Table 2. Summary of proposed NF experiments [a]

Parameter	Number of test conditions	Comments
Membrane composition	2	Polyamide, polypiperazine
Permeate flux	4	12 – 60 $L/m^2/h$
Feed water recovery	3	70 – 90 %
Operational mode	1	Constant pressure
Crossflow velocity	1	~ 1 m/s
Lake Houston water level	2	High flow and background

[a] All NF experiments will be conducted using thin-film composite membranes

Short-term NF fouling rates depend on operating conditions (flux and recovery), colloidal and organics concentrations and characteristics as well as membrane properties. To date, very little is known about quantitative modeling of the interactions between organics, colloids and membrane surfaces in order to be able to *apriori* calculate the kinetics of specific flux decline during nanofiltration of natural and treated waters. Hence, experiments will be conducted using feed waters obtained under conditions of high flow as well as under background conditions at Lake Houston in order to capture possible changes in both concentrations and characteristics of NF foulants.

Task 4. Model NF permeate water quality. A model based on solution-diffusion in the membrane polymer will be developed for the NF system under consideration (Matsuura 1993; Taylor et al. 1994). To my knowledge, this will be one of the first applications of a fundamental approach to describing the permeation behavior of natural organic matter in multi-component systems. It is expected that the mass transfer coefficients derived from this method will be site-specific. However, if the modeling approach is found to be successful, it will be valuable in scaling up these results for the City's future piloting efforts. More work will be necessary to universalize the mechanistic basis of calculating mass transfer coefficients as well as to develop more fundamental descriptions of NF separation processes during drinking water treatment.

Related Research

Lake Houston is a constructed reservoir with a volume of approximately 180 x 10^6 m^3. It is also relatively shallow, with a mean depth of ~ 3.6 m and a maximum depth of ~ 15.2 m. Although some gross water quality parameters have been measured (Bedient et al., 1980; Lee and Rast, 1997), detailed particle size distributions and molecular weight distributions of natural organics are not yet available. Some aspects of its hydrodynamics and mixing have been studied (Kilson, 1992) even though the impacts of elevated flow events on its water quality are not yet well understood.

MF and UF membranes offer the potential to be virtually complete barriers to *Cryptosporidium* and *Giardia* cysts (Jacangelo et al. 1995) in addition to being very effective barriers against particles, turbidity, and bacteria. MF and UF pretreatment can also effectively protect NF membranes against premature fouling especially during surface water treatment (Chellam et al. 1997). However, the underlying mechanisms of membrane fouling during water treatment have not yet been well understood thereby necessitating long duration pilot-studies in support of plant design. Much research has investigated the fundamental causes of fouling under well controlled situations especially for crossflow operation (Belfort et al., 1994). However, these approaches are not directly applicable to water and wastewater membrane filtration partially because of the complexity of the feed suspension. Hence, the proposed approach aims at taking a meso-scale approach to modeling micro-, and ultra-filtration of natural colloidal matter. Thus, cake properties will be included in a time-dependent, one parameter model of permeate flux decline (during constant pressure filtration) or pressure increase (during constant flux operation). Such an approach is expected to allow the better scale-up and improved design of pilot-scale filtration experiments.

An empirical approach is proposed for selected NF experiments and associated data analysis procedures. Given the state-of-the-art knowledge in NF, such an approach is necessary to develop site-specific information that will be valuable for the City of Houston in supporting some of its future piloting efforts. However, the water quality aspects of NF are being proposed to be modeled using fundamental concepts of solution and diffusion in polymers (Matsuura, 1993; Taylor et al., 1997).

Information Transfer

Because the City is planning to initiate membrane pilot-studies next year there is much interest from them on the results to be generated from this research. The City staff will review all reports to be written for this grant. Additionally, my student and I are planning to make at least three presentations to the City staff to solicit input to the sampling plan, experimental variables, and data analysis procedures as well as in interpreting research results. Further, one of the City's employees William Reavis who is responsible for much of the pilot-testing efforts for the City of Houston will actually perform some of the bench-scale tests proposed in this research at the University of Houston. We will train him on various aspects of membrane related measurements once we perfect them in our laboratories. My student or I will present the results of this work at a national American Water Works Association conference. One of the City employees will present the more applied aspects of the proposed research at the Texas Section Water Utilities Association conference. We will also pursue independent peer-review of the research for publication in a scientific journal. We will make available the study's findings to the consultant responsible for design and/or the pilot-study of the proposed water purification plant at Lake Houston.

Training Potential

This proposal is written with the intent to support one graduate student (at the M.S. level) working under my supervision in Environmental Engineering and one undergraduate student in any field of experimental study including both science and engineering departments. Further, technical staff from the City of Houston will be trained on specialized membrane monitoring tools that will be developed in our laboratories.

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