Biological Ion Exchange for NOM removal – Unforeseen Synergies

H. Wray[*], M. Schulz[*], J. Winter[*], P.R. Bérubé[*], B. Barbeau[**] and W. Bayless[***]

[*] University of British of British Columbia, Vancouver Canada; [**] Ecole Polytechnique de Montréal, Montréal Canada; [***] Opus Dayton & Knight, Vancouver Canada.; corresponding author berube@civil.ubc.ca)

Abstract
The results from the present study indicate that the operation of an ion exchange resin system in which biological activity is promoted can achieve greater NOM removal efficiencies than conventional ion exchange systems, and Biological Activated Carbon (BAC) systems. Frequent regeneration of the resin is not required; periodic regeneration, possibly once every few months, or even less frequently depending on the source water characteristics, is sufficient. As a result, the cost of a biological ion exchange (BIEX) system is expected to be substantially less than that of a traditional ion exchange system. This benefit is of particular importance for small/remote communities that are often challenged by having raw waters containing high NOM concentrations and limited capital to support operation and maintenance expenditures.

Keywords
Biological ion exchange, NOM removal

INTRODUCTION

The design of ion exchange resin systems for Natural Organic Material (NOM) removal has historically been based on column tests (***CTs***). However, multiple loading tests (***MLTs***) are emerging as an alternative to *CTs* because of their simplicity and rapid completion time, and therefore lower cost. The hydrodynamic conditions in MLTs are also more representative of those present in suspended ion exchange systems. Unfortunately, limited information exists regarding the design parameters (e.g. NOM removal efficiency and capacity/time to breakthrough) obtained using *MLTs* and how they compare to those obtained using traditional *CTs*. A side-by-side comparison of *CTs* and *MLTs* was performed. Both tests were performed until exhaustion of the NOM removal capacity of the resin (i.e. breakthrough). Unlike with conventional approaches, the resins used in the column tests were not regenerated for the entire duration of the study (i.e. 3 months-period).

MATERIALS AND METHODS

A strongly basic anion exchange resin (Purolite A860 – Dow Chemicals) designed for NOM removal applications was used. The filtration velocity was set to 0.2 m/h (≈ 2 BV/h). The biological activity was suppressed by dosing sodium azide (0.01% w/v) to the raw water. The BAC used (Picabiol® granular activated carbon - PICA Carbon) was harvested from a BAC column that has been in operation for over 6 years and for which all adsorption capacity is exhausted. Operational conditions, such as filtration velocity and bed volume, were kept consistent with those of the anion exchange resin filters. Two raw waters were considered: a synthetic water including Suwannee River NOM and a natural water (Jericho Pond, Vancouver Canada), both pre-filtered through 1 µm glass fiber filters (Cat # 1827-125, Whatman, UK) and adjusted to a dissolved organic concentration (DOC) concentration of approximately 5 mg/L with tap water. The resulting characteristics of the Jericho pond water were: DOC and TOC of 4.9±0.2 mg/L and 5.3 ±0.5 mg/L, respectively; Light absorbance at 254 nm and 436 nm were 10.7± 0.6 and 0.46±0.06, respectively; and the turbidity was

0.22±0.03 NTU (based on a 90% confidence interval). All experiments were performed at a temperature of 22 °C. Breakthrough was considered to have occurred when less than 30% removal of DOC could be achieved. A summary of the experimental conditions considered is presented in Table 1.

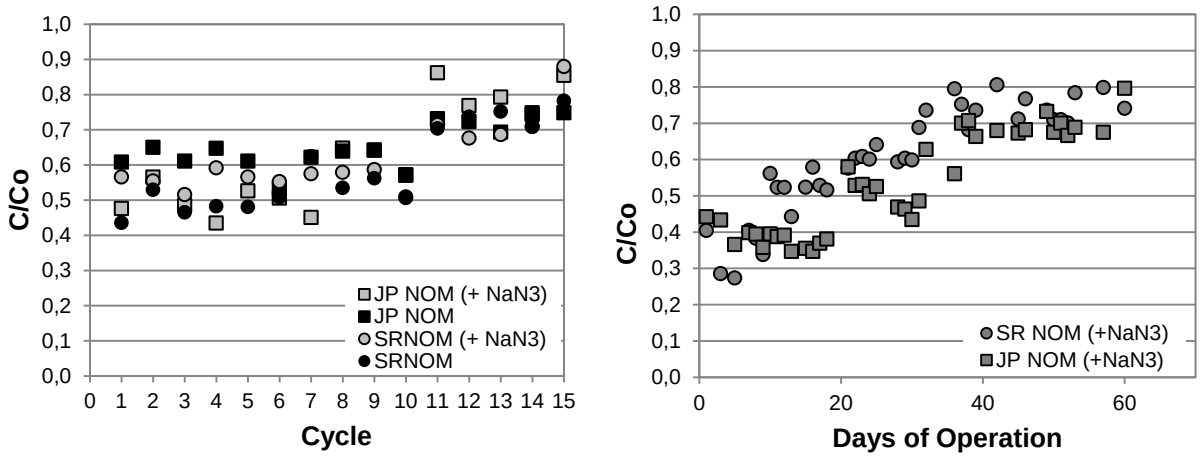
The organic composition of raw water and IEX-filtrate samples was characterized using total organic carbon analysis (Phoenix 8000 TOC analyser, Dohrmann, US) as well as specific light absorption at 254 nm (UVA_{254}) and 436 nm (SAC_{436}) (UV300 UV-vis spectrometer, Spectronic Unicam, US). Adenosine Triphosphate (ATP) was determined in the raw water and effluent of the ion exchange columns as well as in the contained biofilm as an indicator for biological activity using *LuminUltra* Biofilm test kit (LuminUltra, CA, USA). Exchange capacities of the virgin and regenerated resins were determined by replacing the counter ions (Cl^-) of a defined mass of resin by washing it with concentrated sodium nitrate solution (26 g/L). Afterwards the Cl^- concentration in the solution was determined by titration (Mohr Method) and capacity was calculated. DBP formation potential was assessed according to the Uniform Formation Conditions (UFC) technique (Summers et al. 1996) where THM and HAA5 concentrations are measured after a contact time of 24h with a free chlorine residual of 1 mg Cl_2/L at pH 8.0 and T 22°C. Prior to all analyses, samples were pre-filtered using 0.45 µm cellulose nitrate membrane filters (Cat. # 09-719-555, Fisher Scientific, CA). Any samples that could not be analysed immediately were stored at 4 °C. All analyses were carried out at least in duplicate.

Table 1. Experimental Conditions Considered

Parameter	**Column Test**	**Multiple Loading Test**
Ion Exchange resin Activated Carbon (for BAC)	Purolite®A860 Picabiol® PICA Carbon	
Resin volume (mL)	7.55	0.75
Model source waters	Jericho Pond water (with and without 0.01% NaN_3 to inhibit biological growth) Suwannee River NOM water (with and without 0.01% NaN_3)	
Source water DOC	5 mg C/L	
Contact time Bed volumes	30 min EBCT 48/day	30 minute mixing time/cycle 200 equivalent BV/ cycle (15 cycles)

RESULTS AND DISCUSSION

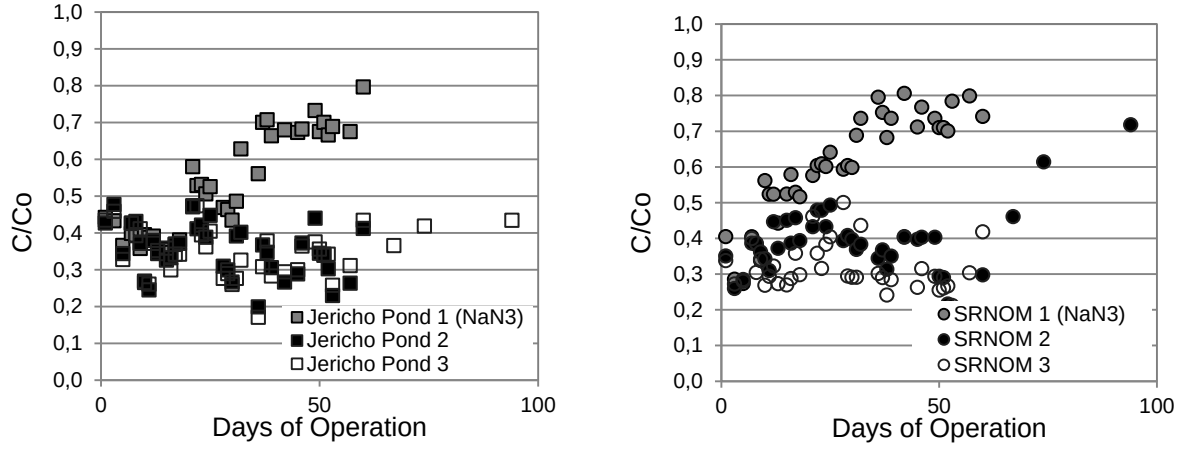
When biological activity was inhibited (achieved by adding sodium azide to the raw feed water), the cumulative mass of NOM (measured as DOC) removed at breakthrough was similar for both the *CTs* and *MLTs*, regardless of the raw water considered (Figure 1). However, greater NOM removal efficiency was observed for the *CTs*, while longer time to breakthrough (i.e. exhaustion of resin NOM removal capacity) was observed for the *MLTs*. The discrepancy between the results was attributed to the different mass transfer conditions (i.e. NOM/resin mass ratio and system hydrodynamics) of each test. The outcomes from the comparison clearly indicate that care must be taken when interpreting results obtained using either approach and that test conditions, especially those that impact mass transfer, must be selected to match the type of full-scale system being considered (i.e. packed bed columns or fluidized bed reactors).



a) Multiple Loading Test b) Column Test

Figure 1. NOM Removal with biological activity suppressed (a: 200 equivalent bed volumes/cycle; b: 48 bed volumes per day)

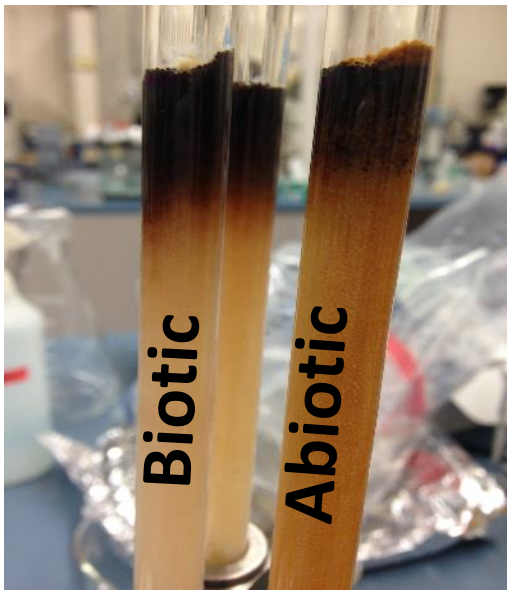
For the *MLTs*, similar results were observed both for conditions when biological activity was and was not inhibited (Figure 1a). This was expected because *MLTs* are completed within 1 to 2 days (i.e. time to achieve a load equivalent to 3000 bed volumes), a period over which biological activity is not expected to become significant. However, significantly different results were observed over a period equivalent to 3000 bed volumes (i.e. 60 days) for the *CTs* when biological activity was and was not inhibited (Figure 2). NOM removal was 65-75% and 35-55% when biological activity was not and was inhibited, respectively. The time to breakthrough was also significantly greater than when biological activity was not inhibited. Depending on the source water, time to breakthrough was either doubled (for raw water containing predominantly humic material – Suwannee River NOM), or breakthrough conditions were not observed (for raw water containing both biopolymers and humic material – Jericho Pond water) over the 60+ day period considered.



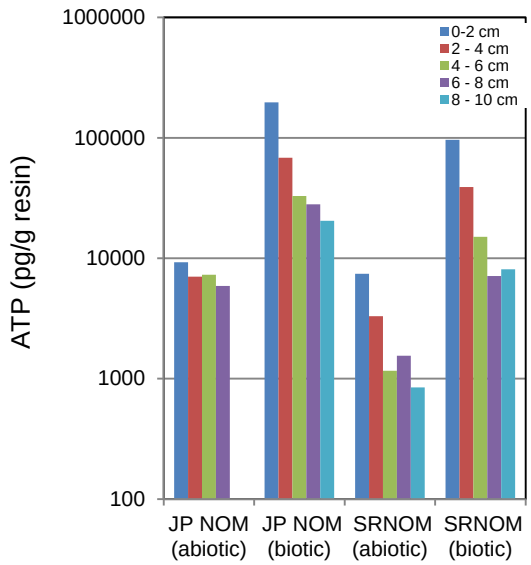
a) Jericho pond water b) Suwannee River water

Figure 2. NOM Removal without biological activity suppressed in column tests (48 bed volumes per day)

Analysis of the column contents for biofilm (using ATP analyses) following the completion of the 3-month column test confirmed that microbial communities had established themselves on the resins (Figure 3). Although the column was populated with a community of microorganisms, if needed, it could be effectively regenerated using solutions of sodium hydroxide (20 g/L) and sodium chloride (100 g/L) as recommended by the resin manufacturer (Schulz et al., 2016). Pre-treatment of the resin prior to regeneration using a disinfectant (i.e. 0.1% peracetic acid) to enhance the release of microorganisms from the resin was not required for effective regeneration.



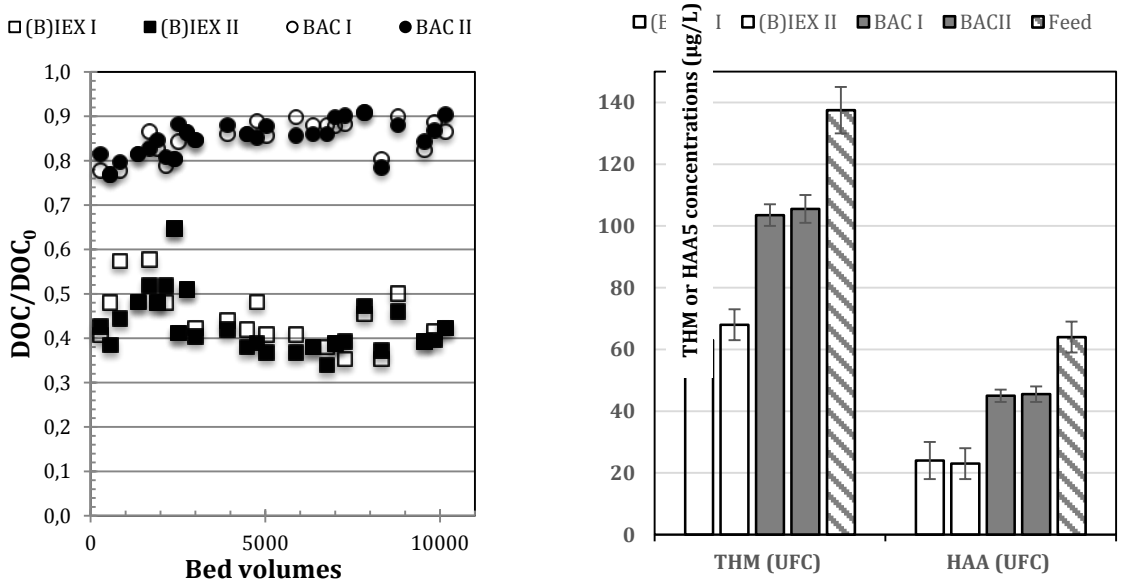
a) Image of Columns



b) ATP measurement

Figure 3. Image of columns (a) from which ATP measurement were taken at different depths (b)

Side-by-side tests comparing NOM removal using an ion exchange column in which microbial activity is not inhibited (Biological Ion Exchange - BIEx) and a Biological Activated Carbon (BAC) column are ongoing. Preliminary results (after operation for 8 months) indicate that approximately 10-20 % NOM removal is being achieved at 22^{o}C with the BAC column at steady state, which is consistent with published literature (Carlson and Amy, 1997); however, NOM removal in excess of 50-60 % is being achieved with the BIEx columns (Figure 4a). As illustrated in Figure 4b, BIEX also provides greater reduction in the formation of disinfection by products (DBPs).



a) DOC removal b) THM Formation Potential

Figure 4. Comparison of BIEX and BAC for NOM and DBP removal (all tests were performed with Jericho Pond water)

CONCLUSIONS

The promotion of biological activity in an ion exchange column (i.e. by applying a low filtration velocity and less frequent regeneration) can significantly enhance the removal of NOM and increase time to breakthrough compared to conventional ion-exchange operation. The microbial community had no negative impact on regeneration. In addition, because of the elimination or reduced frequency of regeneration, the volume of regenerate of which to dispose can be eliminated or substantially be decreased. In addition, the removal of NOM and DBP precursors in a biologically active ion exchange system is greater than the removal that can be achieved in a biological activated carbon system. The results from the present study indicate that biological ion exchange is a promising robust, affordable and easy-to-operate treatment technology to reduce the NOM concentration during drinking water production.

REFERENCES

Orica Watercare. 2007. MIEX® Process Feasibility Testing – Jar Test Evaluation Procedure. Orica Watercare Inc., Watkins, CO, USA.

Calson K., Amy G. 1997. The Formation of Filter-Removable Biodegradable Organic Matter During Ozonation. Ozone Science & Engineering 19, 179-199.

Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., and Wessels, L.P. 2008. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. Water Research 42, 413-423.

Schulz, M., Winter, J., Wray, H., Barbeau, B., and Bérubé, P.R. 2016. Biological-Active Ion Exchange (BIEX) For NOM-Removal and Membrane Fouling Prevention: Synergistic Effects and Impacts on Regeneration, Proceedigns IWA Particle Separation Conference, Oslo, Norway.

Summers, S. R., Hopper, S.M., Shukairy, H.M., Solarik, G., and D. Owen. 1996. Assessing DBP yield: Uniform Formation Conditions. JAWWA, 88(6):80-93.

Acknowledgements: The present research was funded by the Natural Science and Engineering Research Council of Canada RES'EAU-Waternet Strategic Network, which is aimed at developing drinking water treatment processes and technologies for small and remote communities, and Opus Dayton/Knight Consulting Engineers.