REPORT

Title Effects of Salinity on Dissolved Organic Carbon (DOC) Removal in Combined Biological Activated Carbon/Reverse Osmosis Systems.

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Abstract

Reverse osmosis (RO) is one of the most practiced technologies used for salinity removal and is necessary for areas such as West Texas where surface waters are rich in salts. Membrane fouling is a major drawback of RO and results in increased operating costs. This can be mitigated in wastewater systems by pretreating water with biological activated carbon (1), but it is unknown whether biological activated carbon (BAC) is an appropriate pretreatment strategy for partially saline surface waters intended for RO and potable use. We propose a combined BAC-RO system to study: i) the effects of varying salinity concentrations on DOC removal in BAC and ii) how BAC permeate influences membrane flux and organic fouling in downstream RO systems. This work evaluates BAC using small-scale glass columns packed with activated carbon and measures influent/effluent organic carbon concentration and size distribution. Both synthetic and actual West Texas surface water were used for these preliminary studies, allowing for a better understanding of how salinity influences BAC system performance. Future work will evaluate BAC permeate filtration through RO membranes.

Problem and Research Objectives

Critical State Water Problem. Surface water is a significant water resource within the State of Texas. Use of surface water is expected to increase as groundwater resources are depleted, and the Texas Water Development Board (TWDB) estimates that surface water will comprise ~45 % of total water supplies in the state by year 2070 (2). Waters in West Texas can be partially saline, with sulfate (SO_4^{2-}) present as the dominant anion (3). The extent of salinity in water determines its application (*e.g.* drinking water, livestock, industrial usage, irrigation, etc.). As surface water usage in West Texas increases, so will issues associated with salinity. Additionally, surface waters are likely to contain high levels of dissolved organic carbon (DOC).

Salinity is roughly equivalent to total dissolved solids (TDS). The Texas Commission on Environmental Quality (TCEQ) has established a secondary drinking water standard for TDS of 1,000 mg/L, which is higher than EPA's (500 mg/L). This reflects the higher saline waters typical of Texas. Several rivers in Texas exceed these limits, including the upper portions of the Red, Wichita, Colorado, Brazos, and Rio Grande, located in the western part of the state (TDS = 5,000 mg /L or more). These regions have recommended water management strategies to address salinity issues (4).

Reverse osmosis (RO) is a high-pressure filtration process that removes minerals, monovalent and divalent salts, pathogens, and organic contaminants. It is the most common technique for salt removal, but organic fouling of the membranes is still a major issue, limiting its efficiency. Fouling is usually due to accumulation or adsorption of organic matter in the membrane micropores and surfaces, which results in declining flux, increasing operating pressures, and increasing energy costs. Fouling is problematic for RO systems treating West Texas surface water, because these waters are high in both TDS (requiring RO treatment) and DOC (responsible for RO fouling). A current research priority of the TWDB is to minimize fouling by implementing pretreatment strategies before RO. One proposed treatment, biological activated carbon (BAC), is a low energy pretreatment strategy applied upstream of RO units that removes DOC via microbial oxidation. BAC has excellent removal efficiency in wastewater treatment systems, mitigating membrane fouling (1), but it is unknown how salinity may affect DOC oxidation in waters intended for potable use. **This study is the first step in evaluating the impact of salinity upon DOC removal in BAC systems upstream of RO units treating West Texas surface water.**

The objectives of this research are to:

Evaluate the effects of salinity on carbon removal in small-scale BAC column experiments. Water of varying salinity levels was passed through biological activated carbon filters operated in parallel. Artificial and natural water sources were evaluated. Influent and BAC permeate waters were collected and analyzed for DOC.

Evaluate the effects of salinity on DOC size distribution in small-scale BAC column experiments. Water of varying salinity levels was passed through biological activated carbon filters operated in parallel. Artificial and natural water sources were evaluated. Influent and BAC permeate waters were collected and analyzed size distribution of natural organic matter (NOM).

Materials/Methodology

Bench top experiments were conducted in Dr. Millerick's environmental microbiology laboratory using glass columns. Methods and procedures are described below.

Biological Activated Carbon (BAC) Columns: Eight glass columns (25 mm inner diameter, 150 mm height) operated in parallel served as upflow columns. A glass fiber filter separated the influent line from the column. The first 25 mm of column height was packed with Teflon pieces (~5 mm in diameter). Activated carbon (Calgon 400) comprised a height of approximately 100

Figure 1: BAC columns for TWRI project.

mm. The last 25 mm of column height was again packed with Teflon pieces, and a second glass fiber filter was added to the end of the column prior to the effluent line. Completed BAC columns (prior to covering with black felt) can be seen in Figure 1.

To equilibrate columns, Water 1 (see below) was diluted 1:1 with deionized (DI) water and pumped through each of the columns via Peristaltic pump at a flow rate of 0.8 mL/min. This flow rate resulted in an empty bed contact time (EBCT) of ~ 27 minutes per column. To prevent photosynthetic growth, columns, feed lines, and reservoirs were covered in black felt. Columns were allowed to equilibrate for 57 days prior to experimentation.

Source Water: Column experiments were conducted using the following two different waters.

Water 1: Surface water collected downstream of Ransom Canyon in Slaton, TX, as shown in Figure 2. The collection point is where water flowing from Buffalo Springs Lake intersects Hwy 400; pH ≈ 8.5. 20 L of this surface water was collected weekly and stored at 4 °C prior to use. The TOC of this water was 8.1 mg/L carbon.

Water 2: Distilled, deionized water containing 30 mM $NaHCO_3$ buffer; pH ≈ 8.1. This water was prepared daily.

Feed Water Preparation:

Water 1 (natural water) was filtered via vacuum extraction using a glass fiber disk filter to remove large particles. This water was then diluted 1:1 with DI water, producing a finished water of ~ 4 mg/L carbon.


Figure 2: Hwy 400 Sampling Location

Water 2 (buffered DI water) was amended with 4 mg/L carbon. Carbon was ameded as wheat grass extract. Briefly, wheat grass extract was prepared by packing wheat into a 2 L bottle, filling void spaces with boiling water, and sealing. Sealed bottles were placed on a platform shaker at 150 rpm and allowed to equilibrate overnight. After equilibration, samples were filtered via vacuum extraction using a .45 μm disk filter and stored at 4 °C. The TOC of this extract was approximately ~ 427 mg/L carbon. This was spiked into buffered DI water for a final concentration of ~4 mg/L carbon.

Biological Activated Carbon (BAC) Experiments:

The eight columns received feed water (described in Table 1) at a flow rate of 1 mL/min.

Table 1: BAC Column Descriptions

Column	Name	Feed Water	Amendments
Column 1	Natural – Control	Water 1	25 mg/L HOCl (disinfectant)
Column 2	Natural – No Salt	Water 1	None
Column 3	Natural – Low Salt	Water 1	1 g/L K_2SO_4; 1 g/L KCl
Column 4	Natural – High Salt	Water 1	4 g/L K_2SO_4; 4 g/L KCl
Column 5	Artificial – Control	Water 2	25 mg/L HOCl (disinfectant)
Column 6	Artificial – No Salt	Water 2	None
Column 7	Artificial – Low Salt	Water 2	1 g/L K_2SO_4; 1 g/L KCl
Column 8	Artificial – High Salt	Water 2	4 g/L K_2SO_4; 4 g/L KCl

Feed water was stored in 2.5L bottles (reservoirs). Reservoirs were exchanged daily with fresh, feed water prepared in cleaned bottles. Feed water was stored 4 °C until 4 hours prior to use, when it was brought to room temperature.

Columns were backwashed approximately every 2 weeks. Columns were backwashed for 30 minutes at 5 mL/minute using column-specific amended waters, as described in Table 1.

Sample Collection and Analysis:

Samples were collected twice a week at the reservoirs, at the column inlet, and at the column effluent. The following analyses were performed:

Dissolved Organic Carbon (DOC): Water samples were filtered through PTFE filters, acidified to remove inorganic carbon, and analyzed on a Vario TOC Select (Elementar).

Natural Organic Matter (NOM): Changes in natural organic matter size and composition were quantified with high performance size exclusion chromatography using an HPLC (Agilent 1200) equipped with a UV-Diode array detector and a size exclusion column (SEC). Polystyrene sulfonate sodium salt standards were used for quantification.

Salinity: Salinity in surface water samples prior to amendment with salts was measured as conductivity using a probe (HACH). Surface water samples had a conductivity of approximately 1544 μS/cm at 21 °C.

Anions: Concentrations of common anions (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, Br^-, F^-) were measured using ion chromatography (IC; Dionex) equipped with AS14A column for separation.

Principal Findings

Overall, the work summarized below describes a study in progress – biological growth occurred much more rapidly than anticipated and was prolific throughout the columns and feed lines. While data show that organic matter changed in speciation, discrepancies between DOC speciation in reservoirs and column influents suggest that much of the biodegradation occurred within the feed lines and not within the activated carbon portion of the filtration columns. This could also be observed visually – despite black felt, discoloration due to biofilm formation in the feed lines could be observed for all eight columns (including columns receiving chlorinated water). For this reason, this project had to be taken off-line early so that feed lines could be cleaned. Initial attempts at cleaning feed lines by pumping chlorine through them were unsuccessful, so instead lines and columns were cleaned with a concentrated solution of percarbonate to remove residual biofilms (this was successful). Now sterile, this project is in the beginning stages of restart, and we anticipate finishing this project later this year.

Most of our useful data was obtained through size exclusion chromatography (SEC) chromatograms, which provide a relative size distribution of DOC. Instead of including each of these chromatograms, below is a summary of our data and observations we made prior to taking the columns off-line:

Water Quality: Anionic concentrations in undiluted Water 1 at the time column equilibration began were as follows (all units in mg/L): Cl^- = 4.0, F^- = 2.6, NO_2^- = 2.5, NO_3^- = 3.05, PO_4^{3-} = 4.9, and SO_4^{2-} = 13.72. This sulfate concentration was significantly lower than we had expected and is lower than other values reported for this region, but was consistent with other sulfate concentrations in Water 1 during the equilibration period (Fall 2017). The sampling location of Water 1 is downstream of the effluent discharge location of the Lubbock South Wastewater Treatment Plant and is adjacent to several agricultural fields, which may partially explain elevated concentrations in phosphate and fluoride. Elevated phosphate may have increased the likelihood of the line fouling that was observed.

Use of Wheat Extract as a DOC Source: Wheat extract was selected as a DOC source over Suwannee River Natural Organic Matter because of the quantities required (columns each required 1,440 mL of feed water per day, at a carbon concentration of 4 mg/L). We prepared our wheat extract as described in another column study, which described a mother solution of ~ 80 mg/L carbon. Our solution, at 427 mg/L carbon, was five times as concentrated. SEC results suggest that most of this was readily biodegradable, as concentrations and size distributions decreased rapidly when these samples were bought to room temperature. We originally selected wheat extract as a DOC source believing that it would mimic DOC from a natural water source; however, this substrate was considerably more biodegradable than the naturally occurring DOC obtained in Water 1. More tests need to be conducted on wheat extract to identify the assimilable organic carbon (AOC) portion and to better understand its makeup, as all low molecular weight compounds in this matrix became undetectable via SEC when passed through feed lines and columns. These preliminary SEC results suggest that waters containing wheat extract may better mimic carbon in wastewater (rather than water), may lead to over-ripening over long-term experiments, and may not well-mimic carbon in natural surface water bodies.

Decreased Flow during Experimental Phase: Flow was maintained using peristaltic pumping, which assumes no pressure buildup. Flow fluctuation was observed in several of the columns, likely due to the biofilm buildup in the flow lines. This was particularly pronounced right before the columns were taken off-line in Columns 6, 7, and 8, which contained wheat extract but no chlorine. This suggests that i) backwashing should be conducted more frequently, ii) lines may need to be replaced, not simply backwashed, in this system and iii) the concentrations of wheat extract may be inappropriate for this system.

Disinfectant Dosage: SEC results for influent and effluent water samples in Columns 1 and 5 (intended as sterile controls) suggest DOC transformation despite chlorination. This suggests that the biofilm created in these columns over the 57-day equilibration period was partially resistant to chlorinated flow-through waters and that DOC may be consuming free chlorine, reducing its potency. A more aggressive treatment for the sterile control columns is needed between equilibration and the start of experiments, and free chlorine will need to be consistently confirmed to better maintain sterility.

Significance

This is a very attractive project, given its probable applications. It is also versatile in a sense that in the future, it will test two uniquely significant systems (BAC and RO) and their combined

effect. This project originally intended to study both the BAC and RO systems (and we have a miniature RO system for future work), but the work described here suggests that the BAC system must be better understood prior to investigating the RO system.

Our preliminary results show significant changes in DOC speciation as a result of the biofilms we grew, and future work will build upon this to better understand how this may affect BAC-RO system. The materials purchased under the TWRI/USGS fund were used to construct a reusable flow-through system that we will keep using as we complete this study.

We will begin re-equilibration of the columns shortly. The following are amendments we intend to make with this second trial:

- Provide a longer equilibration time (closer to 6 months) for columns, as this would increase biofilm stability, and quantify ATP as a relative measurement of biofilm maturity (fluctuations in carbon concentration indicated that our biofilm may have still been in growth phase).
- Focus solely on natural waters, as wheat extract may be too artificial for this system, and may encourage wastewater-like fouling.
- Investigate more aggressive sterilization treatments for columns intended as abiotic controls.

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