

Simultaneous TOC Reduction and Biofouling Prevention in BWP Processed Water

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ABSTRACT

This paper addresses the development of a novel technology to simultaneously reduce total organic carbon (TOC) and microbial count (MC) in biological water processor (BWP) processed water. This approach also creates a biocidal environment in BWP processed water before being fed into the reverse osmosis (RO) and post processing systems. The technology is based on an advanced oxidation process using an on-demand oxidizer generator, which does not require consumable chemicals. The SBIR (Small Business Innovation Research) Phase I feasibility studies successfully demonstrated the process efficacy in the reduction of both TOC and MC of the BWP effluent. Also, the residual disinfectant and reduced TOC in the treated effluent minimized fouling the RO membrane and water lines. In the Phase II project, a prototype is being fabricated and evaluated for its ability to reduce TOC and MC, and extend RO membrane life.

INTRODUCTION

A priority of the regenerative life support systems in extended manned space missions is to recover and process spacecraft wastewater to provide clean water, which is essential for the crew well being and the success of manned space missions.¹ The integrated Advanced Water Recovery Test System (AWRS) at the NASA Johnson Space Center (JSC) is an example of the current water reclamation and recycling strategy, and it may serve as a blueprint for the system to be deployed on extended space missions.^{2,3,4,5} While this system functions adequately, there are still some challenges to be addressed. TOC content after the BWP treatment is sufficient to enable growth and sustenance of bioorganisms in the transfer line surfaces and RO membrane, allowing the formation of biofilms. Also, the high TOC level in this processed water leads to greater load on the secondary processing systems, increasing size and consumable requirements. It may also lead to RO membrane fouling, mold growth on the Air Evaporation System (AES) wicks,⁶ water flux and permeation rate inhibition, and an overall increased equivalent system mass.

The aim of this project is to further develop a novel technology to simultaneously reduce the TOC and microbial count content of BWP processed water, and control biofilm formation on water lines, surfaces and membranes within the water processing units for space applications. This technology is based on Lynntech's innovative on-demand electrochemical hydrogen peroxide generator. Here, H_2O_2 is electrogenerated from water and air fed to the cathode with no consumable chemicals. Air is readily available, and water usage will be mostly recovered and reused. This H_2O_2 is then mixed with the BWP processed water in a small UV reactor situated between the BWP unit and the RO unit (cf., Figure 1). Under UV illumination, $OH^\bullet$ radicals (hydroxyl radicals, one of the most reactive free radicals and strongest oxidants⁷) are generated, and effectively reduce both TOC and MC. Because the water's pH is close to neutral, the TOC oxidation products are bicarbonate ions and water, with no CO_2 production. After the BWP processed water is treated with our system, a residual level of H_2O_2 remains in the water and aids in preventing biofilm formation on water lines, RO membrane, and secondary water processing modules.

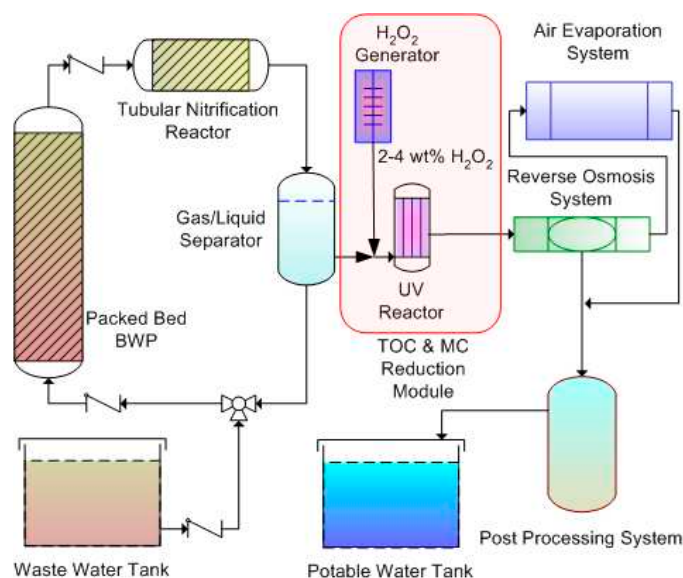


Figure 1. Integration of the TOC and MC reduction module into the integrated Advanced Water Recovery System (AWRS) for use during long term manned space missions.



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The application of this technology in NASA's closed life support systems has two immediate benefits, namely lowered biofilm formation and reduction of MC in the potable water leading to improved crew health and resistance to infection. The long term benefits are equally important, and include increased lifetime of the RO subsystem, AES wicks, associated lines and membranes, and a lowered demand on the polishing system in the secondary processing subsystem. A final potential benefit would be the ability to shunt a portion of the processed water from the TOC reduction module to hydroponic crop systems for improved food self-sufficiency in a future planetary or lunar habitat.

The SBIR Phase I studies successfully demonstrated the process efficacy in the reduction of both TOC and MC of the BWP effluent water. Also, the residual disinfectant and reduced TOC in the treated effluent minimized fouling the RO membrane and water lines. In the Phase II project, a prototype is being fabricated and evaluated for its ability to reduce TOC and MC, and to extend RO membrane life.

ANALYSIS

BWP EFFLUENT SIMULANT

The BWP effluent simulant⁸ was prepared by dissolving the appropriate amounts of commonly present organic and inorganic constituents in deionized water. The BWP ersatz formulation reported by Verostko et al.⁸ is from an integrated water recovery system (IWRS) test conducted at NASA/JSC using an Early Planetary Base (EPB) wastewater stream (urine, humidity condensate, and hygiene water components included). The BWP ersatz formulation contains approx. 60 ppm TOC and 95 ppm TIC (total inorganic carbon). pH adjustment from pH 7 to pH 6 was made using 0.1M HCl.

Table I. Ersatz formulation water chemistry data summary for a BWP effluent (adapted from Ref. 8).

Property or Concentration	Formula	Units	Average Value	Standard Deviation
potential of hydrogen	pH		6.6	± 0.2
conductivity		μS	3,802	± 570
total organic carbon	TOC	mg/L	51	± 5.1
total inorganic carbon	TIC	mg/L	110	± 17
chloride	Cl ⁻	mg/L	608	± 91
nitrite	NO ₂ ⁻	mg-N/L	5.0	± 0.7
nitrate	NO ₃ ⁻	mg-N/L	47	± 7.1
phosphate	PO ₄ ⁻³	mg/L	120	± 18
sulfate	SO ₄ ⁻²	mg/L	117	± 18
sodium	Na ⁺	mg/L	334	± 50
ammonium	NH ₄ ⁺	mg-N/L	154	± 23
potassium	K ⁺	mg/L	240	± 36
calcium	Ca ⁺²	mg/L	-	-
magnesium	Mg ⁺²	mg/L	-	-

TOC

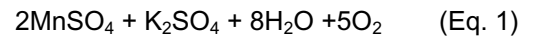
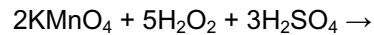
All the TOC analysis has been conducted using a Sievers 800 TOC analyzer (GE Water, Boulder, CO). For each condition, three repeat analyses per sample were run through the TOC analyzer.

In instances when the BWP processed water samples from Texas Tech's AWRS had a very high TIC content, samples were pre-treated for reliable TOC analyses. First, one drop of concentrated HCl was added for every 7.5mL of solution treated. Then the solution was diluted 10X using RO water, and analyzed in the TOC Sievers instrument with the inorganic carbon removal unit attached and an acid rate of 5.0 μL/min.

PEROXIDE CONCENTRATION

H₂O₂ levels lower than 1% were measured using peroxide test strip (Industrial Test Systems, Inc., #440014, Rock Hill, SC).

H₂O₂ levels at 1 wt% and higher were measured using either the titration method with potassium permanganate, as per the following equation:



or a calibrated optical detection method that measures the absorbance at wavelengths between 310 and 325 nm using a UV-Vis-NIR scanning spectrophotometer (Shimadzu UV-3101PC). The average concentration obtained from the optical method is within the experimental error of the titrated value, i.e., approx. ± 4%.

MICROBIOLOGICAL TESTING

Tests were carried out using BWP processed water from Texas Tech's AWRS. After samples were collected, they were serially diluted and plated onto nutrient agar plates. After incubation at 37 °C for 48 hours, colonies were enumerated and colony forming units (cfu) were calculated for each sample. Detection limit is 40 cfu/mL.

FEASIBILITY STUDIES

Figure 2 shows an example of the system capability in the TOC reduction of a BWP effluent simulant. The tests shown in Figure 2 were conducted during the SBIR Phase I project with a UV annular reactor containing a 14 W low intensity UV-C lamp (RPR-253.7 nm lamp, Southern New England Ultraviolet Co., Branford, CT). Figure 2 shows TOC reduction (expressed as C/Co) as a function of the H₂O₂ concentration and retention time. Initial TOC level was close to 60 ppm. It can be observed that within the retention times tested here, no TOC reduction was obtained by UV-C or peroxide alone. On the other hand, in the presence of both UV and peroxide,

over 80% TOC reduction was achieved. It should be emphasized that this TOC reduction was obtained even in the presence of relative high TIC levels (close to 100 ppm). This is relevant, for it is known that carbonate/bicarbonate ions can interfere with TOC oxidation. It can be also observed in Figure 2 that similar TOC reduction is obtained by the two peroxide concentrations if enough time is allowed for the reaction to take place. For example, 45 min retention time with 0.02% peroxide had a 55% TOC reduction. Same TOC reduction could be also obtained with 0.1 % peroxide, 15 min retention time. Thus, by allowing longer retention times, same TOC reduction is achieved with lower peroxide concentration.

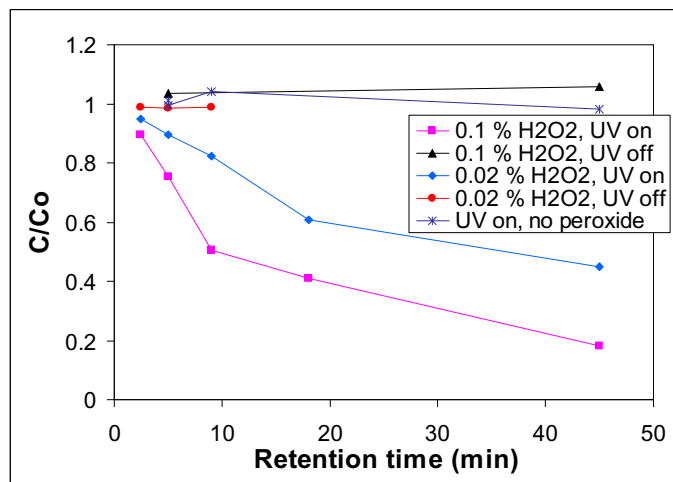


Figure 2. TOC reduction from a BWP effluent simulant as a function of H₂O₂ concentration and retention time.

TESTS ON BWP PROCESSED WATER

Real BWP processed water was generated in a 1/20th scale integrated Advanced Water Recovery System (AWRS) operated in Texas Tech University under the direction of Andrew Jackson and Audra Morse. Pure H₂O₂ were added to the samples to produce 0.1 wt% H₂O₂, and then flown through the UV annular reactor with a low pressure-low intensity UV-C lamp (#99051366, Atlantic Ultraviolet Corp., Hauppauge, NY). Tests were also conducted with no H₂O₂ and/or no UV illumination. The input and output water were analyzed for TOC and microbial count. The UV reactor described in sub-Section “ADVANCED OXIDATION REACTOR” was used in a single pass mode.

MICROORGANISM

Table II and Table III show microbial count with and without H₂O₂. It can be observed that samples collected after the reactor and treated with either H₂O₂, UV-C, or a combination of both H₂O₂ and UV-C show no microorganisms above the detection limit (40 cfu/mL). The project goal is to remove at least 3-log MC in a single pass mode, and this was easily achieved with the system and peroxide levels used here.

Table II. Microorganism test in the presence of 0.1 wt% H₂O₂. Retention time was 10 min. MC level before adding H₂O₂ was 2.5×10^5 cfu/mL.

Sample after Reactor	cfu/mL	Average
No UV, Sample 1	< D.L.	< D.L.
No UV, Sample 2	< D.L.	
No UV, Sample 3	< D.L.	
UV Sample 1	< D.L.	< D.L.
UV Sample 2	< D.L.	
UV Sample 3	< D.L.	

< D.L. = below detection limit (i.e., < 40 cfu/mL)

Table III. Microorganism test in the absence of H₂O₂. Retention time was 10 min. All values after reactor, except the first one level “before reactor”.

Sample	cfu/mL	Average
Before reactor	2.5×10^5	N/A
No UV, Sample 1	3.9×10^4	3.7×10^4
No UV, Sample 2	3.9×10^4	
No UV, Sample 3	3.3×10^4	
UV Sample 1	< D.L.	< D.L.
UV Sample 2	< D.L.	
UV Sample 3	< D.L.	

< D.L. = below detection limit (i.e., < 40 cfu/mL)

TOC

Table IV and Table V show initial results in the TOC removal from the real BWP process water with and without H₂O₂. It can be observed that the combination of H₂O₂ and UV-C is capable of significant TOC removal. This result is outstanding considering that the sample also contained high TIC levels and microorganisms. It can also be observed that the goal of removing 50% TOC was achieved at 20 min. retention time.

Table IV. TOC test in the in the presence of 0.1 wt% H₂O₂. Retention time was 10 min.

Sample		TOC (ppm)	H ₂ O ₂ (ppm)	% Reduction
UV on + H ₂ O ₂	Before reactor	28.8	1000	36.1
	After reactor	18.4	250	
UV on + no H ₂ O ₂	Before reactor	27.6	0	0.0
	After reactor	27.6	0	
UV off + H ₂ O ₂	Before reactor	29.4	1000	1.4
	After reactor	29.0	1000	

Table V. TOC test in the in the presence of 0.1 wt% H₂O₂. Retention time was 20 min.

Sample		TOC (ppm)	H ₂ O ₂ (ppm)	% Reduction
UV on + H ₂ O ₂	Before reactor	30.5	1000	53.1
	After reactor	14.2	250	

Figure 3 shows pictures of the BWP effluent before and after TOC reduction in the Phase I annular reactor. Significant discoloration can be observed.

During the SBIR Phase I project, tests conducted by A. Jackson at Texas Tech compared untreated BWP effluent with Lynntech’s treated BWP effluent. The tests indicated the reduction or suppression of membrane fouling due to the UV/H₂O₂ pretreatment. This in turn will