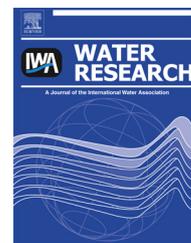


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)

# Urban net-zero water treatment and mineralization: Experiments, modeling and design

James D. Englehardt<sup>a,\*</sup>, Tingting Wu<sup>a</sup>, George Tchobanoglous<sup>b</sup>

<sup>a</sup> Civil, Architectural, and Environmental Engineering, PO Box 248294, Coral Gables, FL 33124-0630, USA

<sup>b</sup> Department of Civil and Environmental Engineering, University of California Davis, One Shields Avenue, Davis, CA 95616, USA

## ARTICLE INFO

### Article history:

Received 15 November 2012

Received in revised form

12 May 2013

Accepted 16 May 2013

Available online 28 May 2013

### Keywords:

Distributed

Direct potable reuse

Iron-mediated aeration

Ambient

Mineralize

Net-zero water

## ABSTRACT

Water and wastewater treatment and conveyance account for approximately 4% of US electric consumption, with 80% used for conveyance. Net zero water (NZW) buildings would alleviate demands for a portion of this energy, for water, and for the treatment of drinking water for pesticides and toxic chemical releases in source water. However, domestic wastewater contains nitrogen loads much greater than urban/suburban ecosystems can typically absorb. The purpose of this work was to identify a first design of a denitrifying urban NZW treatment process, operating at ambient temperature and pressure and circum-neutral pH, and providing mineralization of pharmaceuticals (not easily regulated in terms of environmental half-life), based on laboratory tests and mass balance and kinetic modeling. The proposed treatment process is comprised of membrane bioreactor, iron-mediated aeration (IMA, reported previously), vacuum ultrafiltration, and peroxone advanced oxidation, with minor rainwater make-up and H<sub>2</sub>O<sub>2</sub> disinfection residual. Similar to biological systems, minerals accumulate subject to precipitative removal by IMA, salt-free treatment, and minor dilution. Based on laboratory and modeling results, the system can produce potable water with moderate mineral content from commingled domestic wastewater and 10–20% rainwater make-up, under ambient conditions at individual buildings, while denitrifying and reducing chemical oxygen demand to below detection (<3 mg/L). While economics appear competitive, further development and study of steady-state concentrations and sludge management options are needed.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

The treatment of water to high purity at low energy is a challenge, if energy demands increase exponentially with treatment level, and energy demand is higher still for saline source water. A portion of this energy can be recovered from the wastewater, for example through the use of microbial fuel cells to generate electricity from the microbial oxidation of wastewater (Logan and Rabaey, 2012), or anaerobic treatment

to recover methane (Tchobanoglous et al., 2003). In fact it has been estimated that chemical energy recovered from municipal wastewater might supply enough energy for treatment (McCarty et al., 2012). However, of the 4% of US electric power used for municipal water and wastewater management, the energy required for conveyance averages approximately four times that required for treatment (Cohen et al., 2004; ICF Consulting, 2002), much more than the available chemical energy. Also, while segregation of “grey water” from “black

\* Corresponding author. Tel.: +1 305 284 5557; fax: +1 305 284 3492.

E-mail addresses: [jenglehardt@miami.edu](mailto:jenglehardt@miami.edu) (J.D. Englehardt), [tingtingwu@miami.edu](mailto:tingtingwu@miami.edu) (T. Wu).  
0043-1354/\$ – see front matter © 2013 Elsevier Ltd. All rights reserved.  
<http://dx.doi.org/10.1016/j.watres.2013.05.026>

water” can allow treatment of this stream at lower energy in some applications, in centralized systems, the associated dual distribution system multiplies the cost of conveyance further.

Of note, treated municipal wastewater today represents a stable, non-seasonal, freshwater source meeting, for example, 87 of the 93 numerical drinking water standards on average across South Florida without further treatment (Bloetscher et al., 2005). Reuse of this water source could avoid the need for high-energy desalination, and water restrictions. As a result, the National Research Council has recently recommended general consideration of potable water reuse (NRC, 2012). Further, the report recommended consideration of potable water reuse without environmental buffer (PRWEB), also termed “direct potable reuse,” due to lack of evidence that discharge to, and recovery from, an environmental water body enhances the quality of the treated water relative to other engineered reuse systems.

The concept of net-zero water (NZW) buildings, a term defined here to refer to building systems neither withdrawing nor releasing water off-site, offers several advantages. In addition to alleviating water rationing, the approach would address (a) the demand for conveyance energy, (b) current *de facto* reuse of wastewater-derived surface water, and (c) the need to treat for toxic chemical releases and pesticides, representing roughly 1 mg/L loading on U.S. surface and groundwater runoff. The latter approximation can be found by adding the total 2010 toxic chemical releases of 1.78 billion kg (U.S. Environmental Protection Agency, 2011) to the annual U.S. pesticide usage of 0.514 billion kg (Grube et al., 2011) and dividing by total U.S. surface and groundwater runoff of 6.8 billion m<sup>3</sup>/d (van der Leeden et al., 1990). Moreover, with the principal toxic chemical load eliminated, treatment could focus instead on mineralizing pharmaceuticals and personal care products, which are not regulated in terms of environmental half-life as are other chemicals, thereby alleviating their associated endocrine-disrupting effects in the environment. Finally, a NZW system could efficiently retain thermal energy in the wastewater.

Net-zero water treatment was implemented successfully by the Pure Cycle Corp. from 1976 to 1982. These systems were installed in remote mountain locations without central water and wastewater services, monitored electronically, and maintained centrally by the company. Though Pure Cycle eventually exited the business due to the expense of maintaining systems across sparsely-populated mountainous regions, central systems across the same region would presumably have been more expensive. In testament to the success of the approach, many homeowners subsequently petitioned the state and obtained permits to continue operation independently (Harding, 2009).

Aside from psychological challenges to NZW living, several technological challenges need to be addressed. A potential challenge is management of the urban and suburban nitrogen balance. While many natural water and nutrient reuse options are viable in rural areas where most food is grown, most food is transported to urban/suburban areas, imparting a nitrogen load to wastewater far above drinking water standards and typically much more than can be absorbed by local vegetation. For example, three residents on a quarter-acre suburban lot produce ~13 lb N/1000 ft<sup>2</sup>, roughly five times the amount of nitrogen that would be required for turfgrass fertilization

across the property and roof. Hence, to avoid nitrate contamination of the groundwater, nitrogen must be returned either to rural areas or to the atmosphere.

Several approaches to the design of urban NZW systems can be considered. First, greywater and blackwater can be segregated, and this approach has advantage for residents interested e.g. in operating “dry” toilets to produce compost for onsite use. However, in general this approach requires homeowner operation of two multi-process treatment systems. Alternatively, infant drinking water could be segregated for additional treatment, potentially allowing the general nitrate drinking water standard (which guards against methemoglobinemia in infants) to be relaxed. However, such an approach would not address accumulation of nitrate in local groundwater. Similarly, drinking water could be segregated for additional treatment, though the concept further implies bathing and washing in non-potable water.

In contrast with segregation schemes, the seminal Pure Cycle system design of Howard Selby III relied on automated aerobic biological treatment, cloth filtration, ultrafiltration, deionization, and ultraviolet disinfection technology to treat commingled household wastewater (Selby, 1979). However, the system discharged nitrogen to the environment in concentrated brine, which today might also contain endocrine disrupting compounds (EDCs) including pharmaceuticals and personal care products. Also, the cost of acid and caustic regenerant may have been on the order of \$1.32/m<sup>3</sup> (\$5/1000 gal) treated water. In addition, the ultrafiltration membranes employed likely operated at pressures more than three times higher than ambient. Hence costs and energy may have been high as compared with natural biological systems that operate at nearly ambient temperature and pressure, and circum-neutral pH.

The purpose of the work reported in this paper is to identify a first design for an urban/suburban ambient net-zero water (UANZW) treatment process including mineralization of waterborne organics, and demonstrate the design versus laboratory and modeling results. Specifically, requirements were potable treatment, denitrification, and effluent mineralization of commingled domestic wastewater in individual buildings, at ambient temperature and pressure, and circum-neutral pH so as to minimize life-cycle energy. Recent membrane bioreactor, iron-mediated aeration (IMA, to be described), vacuum ultrafiltration, and peroxide advanced oxidation processes were tested and modeled, along with cistern make-up water and H<sub>2</sub>O<sub>2</sub> disinfection residual. Because field data on steady state concentrations in such a closed-loop system were not found and cannot reasonably be simulated in a laboratory, the proposed system is under construction at a university residence hall for future demonstration. Modeling of the MBR biological treatment process, including nitrification/denitrification, is described elsewhere (Perera and Englehardt, 2012). Analysis of sludge management options and associated chemical/biochemical transformations is beyond the scope of the current project.

---

## 2. Materials and methods

The design of the proposed treatment system was based on preliminary laboratory screening of electrochemical, cloth

filtration, and steel wool-based IMA processes, and literature review. The design was refined further based on hydraulic, mass balance, and peroxone kinetic models developed by spreadsheet, equilibrium modeling performed with the Visual Minteq v. 3.0 equilibrium model (KTH Royal Institute of Technology, Stockholm), and physico-kinetic models of the MBR. Laboratory tests of the IMA and peroxone advanced oxidation processes were conducted to refine and verify the design parameters. All laboratory reagents were analytical grade, and were used as received. Error bars represent  $\pm 1\sigma$  (standard deviation) across triplicate samples, except as noted.

### 2.1. IMA and peroxone laboratory tests

The term IMA is a general title applied to water treatment processes comprising aeration of water containing metallic iron. The process has been shown to: (1) precipitate nutrients, metals, arsenic, and bicarbonate; (2) oxidize organics through production of  $H_2O_2$  and other reactive oxygen species; and (3) coagulate organic and inorganic constituents (Deng et al., 2013; Englehardt et al., 2007). IMA processes employing steel wool (Englehardt et al., 2007) and 325 mesh iron powder (Narayanan et al., 2009) have proven effective for treatment of secondary effluent. However, to reduce relatively high iron costs, the IMA process was adapted in this work to use iron rod electrodes. Tests thus comprised aerated electrocoagulation (AEC), flocculation, and vacuum ultrafiltration. Aeration of both the AEC and floc vessels was tested for its effect on phosphorus and nitrate removal.

The AEC unit consisted either of a nominal 1 L polyethylene or 400 mL Plexiglass<sup>®</sup> vessel fitted with inflow and outflow tubing and Teflon<sup>®</sup> aeration stone. A rubber stopper suspended two parallel rows of five iron rod electrodes each, spaced 1 cm apart in each direction. The electrodes measured 3.2 mm in diameter by 50.8 mm effective length. A 60–80 mA current was supplied by Tektronix CPS250 DC power supply (Tektronix, Beaverton, OR), providing  $\sim 61$  mg/L Fe. The floc vessel consisted of a nominal 1 L Plexiglass<sup>®</sup> vessel fitted with inflow and outflow tubing and paddle stirrer on a jar test apparatus (Phipps and Bird, Richmond, VA). Synthetic reuse water having the composition shown in Table 1 was prepared with Milli-Q water (18.2 M $\Omega$ -cm). Soy flour was chosen to represent the mix of low and high molecular weight organics. The solution was mixed fully for 1 h and then aerated at a rate of 3 L/min for 16 h, to equilibrate with atmospheric  $CO_2$ . This synthetic potable reuse water was run through the EC vessel

to the floc vessel at a continuous flow of 19–23 mL/min via peristaltic pump. Aeration, when supplied, was at 0.5 L/min. After five residence times, a 300 mL effluent sample was collected from the outflow of the floc vessel and vacuum-filtered through 0.45  $\mu$ m membrane. Influent and filtrate were analyzed for pH, electrical conductivity, alkalinity, nitrate, and phosphate. Dissolved oxygen (DO) in the EC and floc vessels was also measured at the end of some runs.

Peroxone experiments were performed using a Microzone 300 laboratory ozonator (ClearWater Tech, San Luis Obispo, CA) and diffuser stone with nominal pore size  $\sim 25$   $\mu$ m, fitted at the bottom of a 61 cm (24 inch) tall, 5.1 cm (2 inch) diameter PVC column reactor in a hood. The  $H_2O_2$  solution was prepared by adding 0.6 mL 30%  $H_2O_2$  to 200 mL Milli-Q water and supplied at a flow rate of 5 mL/h via peristaltic pump. Secondary effluent was sampled on 05/07/2012 from the Miami-Dade County South District Wastewater Treatment Plant, Miami, Florida, stored in a refrigerator, and brought to room temperature for testing. Prior to peroxone experiments, the secondary effluent was pretreated by the IMA process as described above with EC reactor aerated. Residence times in EC and floc vessels were 12 and 27 min, respectively. Effluent of the floc vessel was vacuum-filtered through 0.1  $\mu$ m membrane. Aliquots were withdrawn from the peroxone reactor for analysis after 1, 2, 4, and 8 h.

### 2.2. Analytical methods

Conductivity, pH, and dissolved oxygen were measured with Orion Star A3295 multimeter (Thermo Scientific, USA). Alkalinity measurements were performed using Standard Method 2320 (APHA et al., 2005). Phosphate, nitrate, and chemical oxygen demand (COD) were measured colorimetrically with a spectrophotometer (UV-Vis model DU720, Beckman Coulter, Brea, CA) using Hach phosphorus method 8048, 0.02–2.5 mg/L  $PO_4^{3-}$ , Hach nitrate method 8039, 0.3–10 mg/L  $NO_3^- - N$ , and Hach COD method 8000, 0.7–40 mg/L (Hach Co., Loveland, CO). Samples were diluted as necessary to fall within the appropriate measurement range. Hydrogen peroxide was measured by iodometric titration (Gordon et al., 1992) and ozonator output was calibrated by potassium iodide wet-chemistry test (Rakness, 1996).

## 3. Pilot system conceptual design

A mineralizing UANZW treatment system was designed to accept all wastewater from sinks, toilets, showers, dishwasher, and laundry for a 4-bed university residence hall unit. Design was substantially over-sized, as estimated from experimental, modeling, and literature results, to ensure resident safety while allowing research optimization. However, in a closed-loop system, constituents such as soluble salts, not removed in treatment to the extent that they are added in residential use, will accumulate. To control salt accumulation at ambient temperature and pressure and circum-neutral pH, a combination of (a) salt-free treatment, (b) 10–20% rainwater make-up and concomitant discharge of treated water, and (c) IMA was specified.

**Table 1 – Composition of synthetic reuse water.**

Chemical	Concentration (mg/L)
KCl	44 mg/L $K^+$
$MgCl_2 \cdot 6H_2O$	28 mg/L $Mg^+$
$Na_2SO_4 \cdot 10H_2O$	90 mg/L $SO_4^{2-}$
$Na_2HPO_4$	40 mg/L $PO_4^{3-}$
$NaHCO_3$	90.7 mg/L $Na^+$
Soy flour	11.3 mg/L
$CaCl_2$	5.7 mg/L $Ca^{2+}$
$NaNO_3$	18.8 mg/L $NO_3^-$

A process flow diagram for the proposed system is shown in Fig. 1. Wastewater flows to a below-grade 4.15 m<sup>3</sup> (1094 gal) septic tank. Supernatant passes to a membrane bioreactor (MBR) (Membrane BioBarrier<sup>®</sup>, BioMicrobics Inc., Shawnee, KS), with calcium carbonate and ethanol feeders for nitrification and denitrification respectively, if needed. Effluent is then aerated in a 4.15 m<sup>3</sup> (1094 gal) dosing tank to precipitate any excess calcium carbonate, followed by computer-controlled blending with rainwater from a 17.1 m<sup>3</sup> (4500 gal) cistern. The blended water is pumped to an IMA system, to be described, designed and fabricated in-house except for the floc tank (114 L, FKC Co., Ltd., Port Angeles, WA). From the IMA process the water is pumped to parallel-redundant (for research purposes) vacuum ultrafiltration units, also fabricated in-house, each incorporating 16 ZW-10 membranes (Zenon Environmental Corp., Oakville, Ontario), aeration cleaning, and automated backwash. Effluent is pumped from a 625 L (165 gal) clearwell to either of two peroxone treatment tanks, 3790 L (1000 gal) nominal, 2840 L (750 gal) working volume, each of which can be recirculated through either or both of two peroxone/UV advanced oxidation treatment systems (Spartox A60 UV, 60 g/h ozone, 30 mJ/cm<sup>2</sup> 185&254 nm UV, Spartan Environmental Technologies, LLC, Beachwood, OH). At any time, the tank not being treated is filling (~38 h) prior to treatment (~38 h). Effluent is then pumped at 45.5 L/min (12 gpm) through dual granular activated carbon (GAC) filters (CQE-CO-02051, Crystal Quest<sup>®</sup>, Marietta, GA) mounted in series, provided for redundancy and removal of any possible halogenated oxidative byproducts, to a 5.12 m<sup>3</sup> (1350 gal) treated water tank. A 2 mg/L hydrogen peroxide residual was designed to be maintained by chemical feed pump, for biofilm prevention. This residual value is based on

the Recommended Exposure Limit for H<sub>2</sub>O<sub>2</sub> (National Institute for Occupational Safety and Health, 1992), and adult consumption of 2.3 L/d drinking water (U.S. Environmental Protection Agency, 1997). For the demonstration project, all water for drinking and cooking is supplied by Miami-Dade County Water and Sewer Authority, via water dispensers, separate from the recycle loop. To streamline permitting, excess treated potable water is discharged to sewer, as agreed with regulatory agencies. However, sewer would not be available in most NZW buildings, and therefore the water is disposed after final treatment to provide mineralization of pharmaceuticals and allow future reuse for irrigation. Routine backwash waters return to the septic tank. Excess septic, aerobic, and iron sludge, including sludge from semiannual MBR cleaning, are disposed to sewer for purposes of the current project.

### 3.1. Description of commercial MBR pilot process

Details of the design of the 1895 L/d (500 gpd) BioMicrobics<sup>®</sup> BioBarrier MBR system, which includes aerated and anoxic zones for nitrification/denitrification, can be found elsewhere (BioMicrobics Inc., 2010). Effluent concentrations were projected based on literature values and the experience of the manufacturer. These systems reportedly produce COD from 10 to 20 mg/L assuming normal residential wastewater influent, <5 mg/L biochemical oxygen demand (BOD), <2 mg/L total Kjeldahl nitrogen (TKN), and 5–10 mg/L NO<sub>3</sub><sup>-</sup> - N (Shams, 2011). As expected, these values are lower than the 10–50 mg/L total nitrogen (TN) reported for MBRs without anoxic zone (Di Bella et al., 2008; Mannina et al., 2011). The MBR vacuum membrane is designed to be operated at

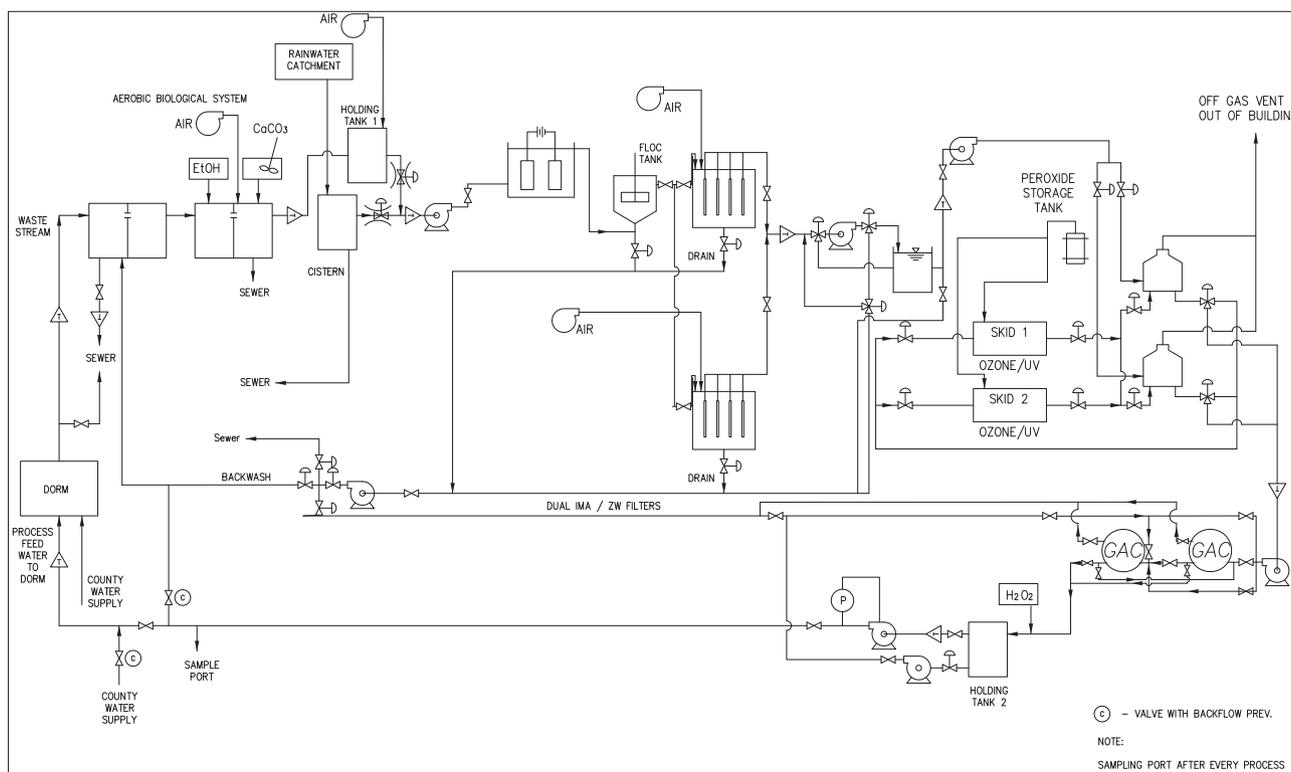


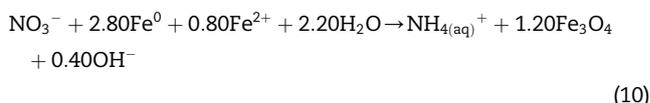
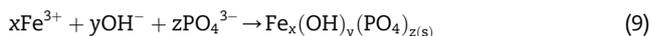
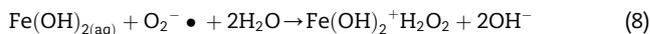
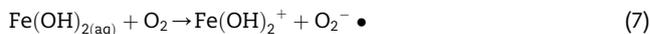
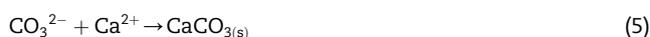
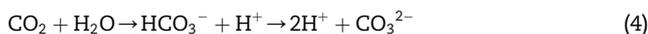
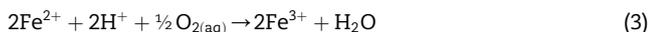
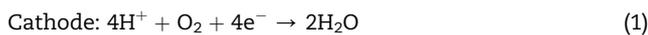
Fig. 1 – Net-zero water treatment system process flow diagram.

<0.34 atm gauge pressure (5 psig) even when dirty. The nominal membrane pore size of 0.04–0.06  $\mu\text{m}$  will exclude bacteria, protozoa, and many viruses. *Giardia*, though having nominal diameter at least two orders of magnitude larger than membrane pores, can occasionally pass MBR membranes, but are inactivated relatively easily during disinfection (LeChevalier, 2012).

### 3.2. Description of fabricated IMA/vacuum ultrafiltration pilot process

The IMA process selected for the pilot system comprised aeration of the dosing tank (MBR effluent holding tank) for precipitation of calcite (Chao and Westerhoff, 2002); aerated electrocoagulation; and flocculation, followed by vacuum ultrafiltration. The process is diagrammed in Fig. 2. The AEC unit was constructed from a 56.9 L (15 gal) tank fitted with twelve 2.54 cm (1 in) diameter, 43.18 cm (17 in) effective length iron rod anodes and cathodes, across which a constant 0.3–2 A DC current is to be applied by external power source (1–10V DC). Two blowers were mounted with tubing and aeration stones to supply a maximum total 76 L/min to the tank bottom. At a 400 GPD design flow with 20% rainwater makeup and 28 mg/L Fe dosage, the twelve electrodes would reach replacement diameter of 1.27 cm after 278 days.

The principal process reactions are:



Equation (1) is thermodynamically favored over hydrogen evolution in the presence of dissolved oxygen. Also, according to Equations (4) and (5), the IMA process precipitates  $\text{CaCO}_3$  from many ground-waters and other waters that are super-saturated with  $\text{CaCO}_3$  upon equilibration of  $\text{CO}_2(\text{aq})$  with atmospheric  $\text{CO}_2$ . This equilibration may produce water having ca. 50 mg/L  $\text{Ca}^{2+}$  as  $\text{CaCO}_3$ , and pH from 7 to 8.5, depending on the matrix. Equations (7) and (8) were proposed previously to explain, in general, the oxidation of organics via the IMA process (Englehardt et al., 2007). Equation (10) was proposed recently by Suzuki and co-workers (Suzuki et al., 2012) to describe the stoichiometry of aqueous denitration in the presence of iron and DO. Their work indicates that  $\text{Fe}^{2+}$  supports the reduction of nitrate by Fe(0) through maintenance of a conductive  $\text{Fe}_3\text{O}_4$  layer on the iron. The IMA process can further strip ammonia as it continuously equilibrates with ammonium (Equation (11)). Remaining COD and inorganics, including calcium carbonate, arsenic, and metals, are removed by co-precipitation, coagulation, flocculation, and vacuum ultrafiltration, the latter having nominal pore size 0.04  $\mu\text{m}$  and operating at <0.34 atm (5 psig) at all times.

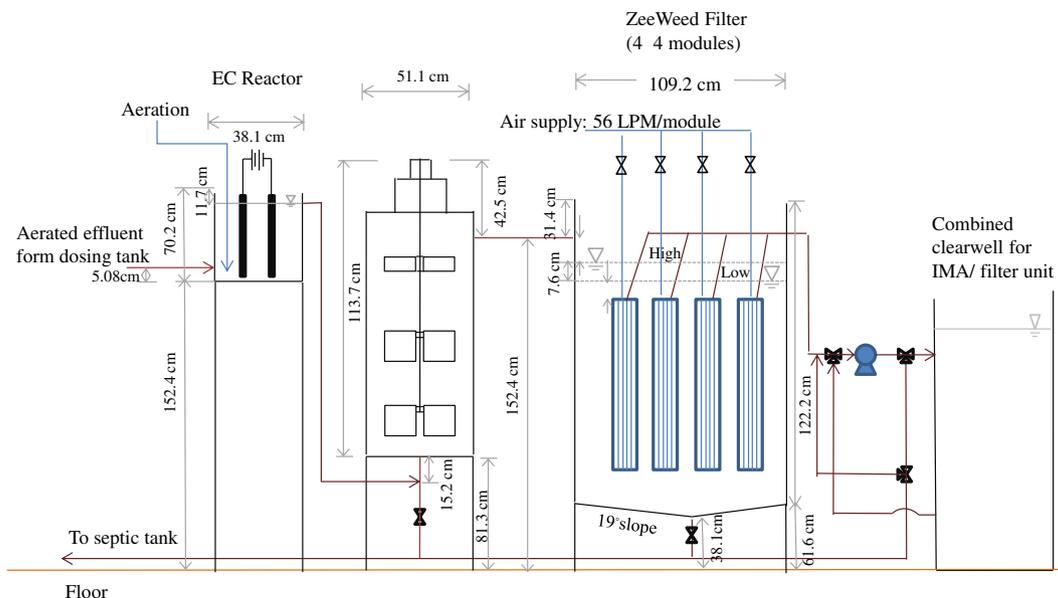


Fig. 2 – Diagram of the iron-mediated aeration/vacuum ultrafiltration system.

### 3.3. Description of commercial peroxone/UV pilot process

Peroxone advanced oxidation involves simultaneous addition of  $O_3$  and  $H_2O_2$  for generation of the strongly oxidative, non-selective  $OH\cdot$  radical. The process was chosen for its ability to mineralize total organic contamination as measured by COD to below the 3 mg/L detection limit, without the addition of acid, chlorine, or salt, and without high effluent  $H_2O_2$  concentrations which may have health effects and are not removed easily. Water recirculates through the treatment tank to a UV reactor, for oxidation of UV-photolyzed organics including NDMA and other nitrosamines, followed by injection of ozone and hydrogen peroxide. At any time, one of the two peroxone/UV systems, each capable of supplying 60 g/h ozone, is projected to serve as a redundant emergency backup, based on limited available field data on peroxone oxidation of COD in secondary effluent (Ried et al., 2006). However, if needed for mineralization of COD to below the 3 mg/L detection limit and to meet all primary drinking water standards, the two may be operated in parallel.

## 4. Results

### 4.1. Hydraulic modeling of pilot system

Flow equalization is a challenge in small, multi-process net-zero water systems, and ultimately storage capacities and placement will require careful optimization to minimize space requirements and installation cost. For the present research study, a hydraulic model including all treatment units and their mode of operation was developed by spreadsheet, as a basis for tank sizing. Hydraulic head along the treatment train was simulated as a function of time over 5 days with a model resolution of 1 min. Typical influent flow variation with time (Tchobanoglous et al., 2003) was assumed, with exaggerated peak- and low-flows, peaking factor 40, as expected for an average design flow of 1516 L/d (400 gpd). A conservative cistern make-up water rate of 25% was assumed for purposes of tank sizing. Variation in hydraulic head in the tanks with time is illustrated in Fig. 3.

### 4.2. IMA laboratory tests

IMA/vacuum ultrafiltration laboratory experiments were conducted to determine whether aeration should be provided to the AEC and/or flocculation vessels, for control of phosphate, nitrate, and bicarbonate salinity; iron solubility; and hydroxyl radical scavenging by bicarbonate and carbonate during peroxone treatment. Experimental results for the synthetic reuse water are shown in Table 2.

As shown, nitrate removal averaged 80.3% when the EC vessel was aerated. Further, nitrate removal was constant at  $\sim 2.5$  mg/L in all aerated tests. Given that  $Fe^{2+}$  was produced electrochemically for a relatively uniform period in these tests, results are consistent with current-limited, zero-order reduction of nitrate by  $Fe(0)$ . In the absence of aeration nitrate was not removed, though effluent DO and therefore presumably ferric hydroxide remained high. This result can be

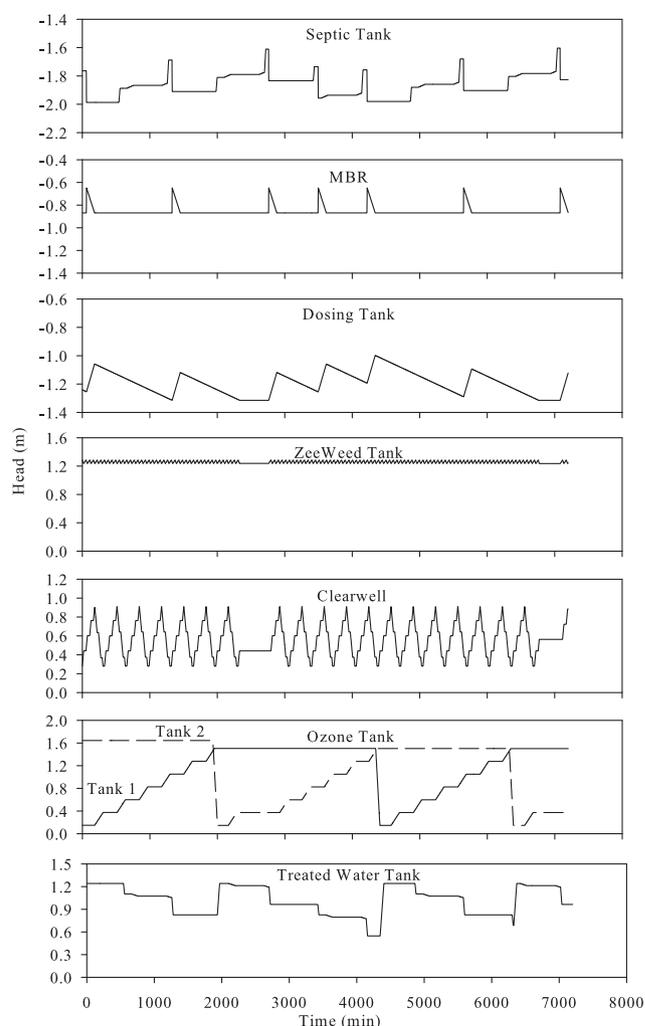


Fig. 3 – Hydraulic head through the proposed net-zero water treatment process as a function of time.

explained by the significantly higher pH, which disfavors Equation (10), and perhaps by the absence of ammonia stripping which, by eliminating ammonium removal, disfavors Equation (10) as well. Higher pH was attributed to lack of re-equilibration with atmospheric  $CO_2$ . In contrast with nitrate, 80–90% of phosphate was removed in the filtered sample irrespective of aeration. These results are consistent with results reported previously for the process, which showed, in addition, the oxidation and removal of endocrine-disrupting organics, COD, metals, arsenic, total coliform, and *Escherichia coli* (Deng et al., 2013; Englehardt et al., 2007). No significant change in alkalinity was observed in the present tests. The lack of a significant change was attributed to pre-equilibration of the synthetic water with atmospheric  $CO_2$ , and to the  $Ca^{2+}$  and  $NO_3^-$  concentrations in the synthetic reuse water of Table 1 which were unintentionally low relative to the steady state concentrations ultimately projected in the recycled water (to be described). Based on these results, IMA was selected over simple electro-coagulation, with aeration of the AEC vessel, to remove nitrogen; precipitate phosphorus and  $CaCO_3$ ; oxidize organics; and maintain iron as insoluble  $Fe^{3+}$  floc agglomerates to be removed by vacuum ultrafiltration.

**Table 2 – Results of laboratory IMA/Filtration of synthetic reuse water.<sup>a</sup>**

Aeration conditions		pH	Conductivity ( $\mu\text{S}/\text{cm}$ )	Alkalinity ( $\text{mg}/\text{L}$ as $\text{CaCO}_3$ )	$\text{PO}_4^{3-}$ (mg/L)	$\text{NO}_3^- - \text{N}$ (mg/L)	Final DO (mg/L)	
							EC	Floc
AEC and floc	Influent	8.14	807	56.5	39.2	3.17	–	–
	Effluent	8.01	773	60	3.6	0.72	–	–
AEC only	Influent	8.09	847	57	38.2	3.11	–	–
	Effluent	8.45	798	54	3.4	0.52	9.42	6.36
Floc only	Influent	7.87	934	56.5	35.2	6.71	–	–
	Effluent	8.58	910	52.5	5.6	4.38	–	–
Neither	Influent	8.05	842	57.5	38.8	2.61	–	–
	Effluent	9.39	814	57	7.6	2.67	8.78	7.02

<sup>a</sup> Residence time: 45 min EC, 41 min flocculation vessel, except "Floc only" run: 38 min EC, 35 min flocculation vessel.

#### 4.3. Peroxone laboratory tests

Laboratory tests were conducted to size the pilot system, in light of the lack of literature on peroxone mineralization of organics in secondary effluent. As a strong oxidant,  $\text{O}_3$  can react directly with a compound (direct reaction) or produce the stronger, non-selective  $\text{OH}^\bullet$  through reaction with  $\text{OH}^-$ , which can then react with a constituent organic (indirect reaction). However,  $\text{H}_2\text{O}_2$ , as well as carbonate and bicarbonate, are known  $\text{OH}^\bullet$  scavengers. Thus, the ratio of  $\text{H}_2\text{O}_2$  to  $\text{O}_3$  dosage is critical to peroxone treatment efficiency. Theoretically, two moles of  $\text{O}_3$  react with one mole of  $\text{H}_2\text{O}_2$  according to the overall equation (Glaze and Kang, 1989; Gottschalk et al., 2010):



However, an adjustment of the applied ratio from stoichiometric is required, because  $\text{O}_3$  is generally more reactive with organic and inorganic matter in wastewater than  $\text{H}_2\text{O}_2$ , and the efficiency of  $\text{O}_{3(\text{g})}$  transfer to the aqueous phase varies depending on injection method and reactor geometry. In particular, typical  $\text{O}_3$  mass transfer efficiency of bubble diffusers is reportedly 10–15%, in contrast with current field systems employing venturi injectors that may achieve 90% transfer (Ozone Solutions September 1, 2012). Accordingly, the molar ratio of applied  $\text{O}_3$  to applied  $\text{H}_2\text{O}_2$  was 17.3:1 in these experiments. Assuming an actual molar ratio  $\text{O}_{3(\text{aq})}:\text{H}_2\text{O}_{2(\text{aq})} \geq 2$ , the actual transfer efficiency in the laboratory studies was  $\geq 11.5\%$ . The removal of COD in the secondary effluent as a function of time is shown in Fig. 4.

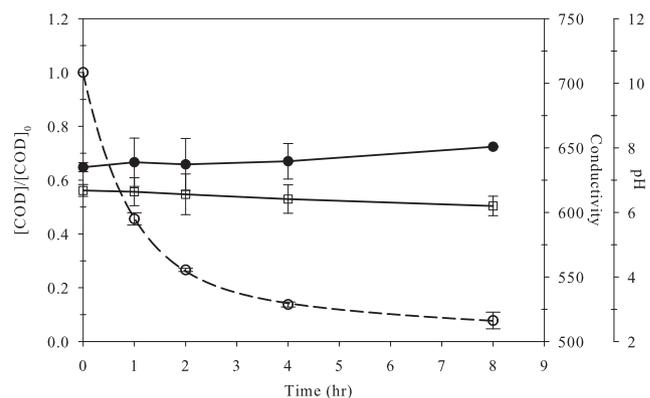
Bicarbonate was present in the secondary effluent at higher concentration than residual organics, and so was expected to consume hydroxyl radical. Specifically, bicarbonate reacts with  $\text{OH}^\bullet$  to form carbonate radical, which can react further to oxidize residual organics. In Fig. 5, the progression of alkalinity and pH through the IMA-peroxone treatment train is shown. As reported in Fig. 5, a 32.8% reduction of 119 mg/L alkalinity and 92.2% removal of 28.3 mg/L COD occurred over 8 h of peroxone treatment. The effect of the water matrix composition on alkalinity reduction by the IMA/vacuum ultrafiltration process is also illustrated: 33% alkalinity reduction in secondary effluent compared with no noticeable change in synthetic water (Table 2). This difference is due to the difference between the two waters in terms of

calcium carbonate super-saturation following aeration/equilibration of  $\text{CO}_{2(\text{aq})}$  with atmospheric  $\text{CO}_2$  (Equations (4) and (5)).

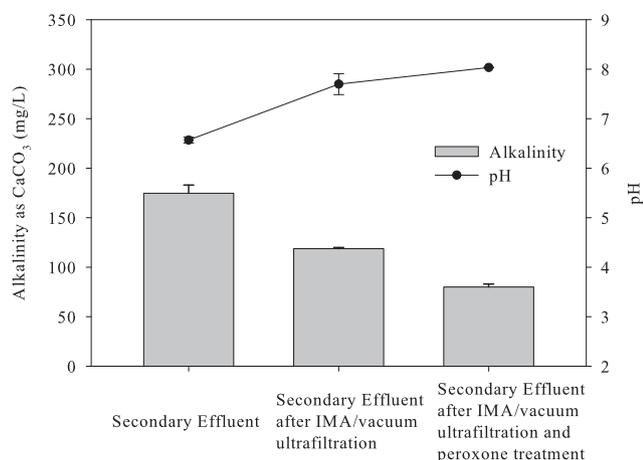
#### 4.4. Peroxone kinetic modeling

In the peroxone process, generation of  $\text{OH}^\bullet$  via chain reaction occurs preferentially because the rate constant for the initial reaction of  $\text{O}_3$  with  $\text{HO}_2^-$  ( $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) is much higher than that of  $\text{O}_3$  with  $\text{OH}^-$  ( $70 \text{ M}^{-1} \text{ s}^{-1}$ ) (Gottschalk et al., 2010). Direct oxidation of organics by  $\text{O}_3$  is a selective reaction with a relatively low rate constant. Generally, such direct oxidation predominates only at  $\text{pH} < 4$ , while at  $\text{pH} > 10$  indirect reaction prevails (Gottschalk et al., 2010). At the circum-neutral pH of the secondary effluent used in this study, direct ozone oxidation cannot be neglected. In that case, and assuming a molar ratio  $\text{O}_{3(\text{aq})}:\text{H}_2\text{O}_{2(\text{aq})} \geq 2$ , the process can be modeled by representing the variety of organics present in secondary effluent, typically ranging widely in molecular weight, by two fractions in terms of rate of oxidation, as follows:

$$\frac{d[\text{COD}]}{dt} = k_{\text{or}}[\text{COD}]_r[\text{O}_{3(\text{aq})}] + k_{\text{os}}[\text{COD}]_s[\text{O}_{3(\text{aq})}] + k_{\text{hr}}[\text{COD}]_r[\text{OH}^\bullet] + k_{\text{hs}}[\text{COD}]_s[\text{OH}^\bullet] \quad (13)$$



**Fig. 4 – Measured COD (○), pH (●), and electrical conductivity (□), and predicted COD (---) in secondary effluent versus time of peroxone treatment. [Conditions: 1 L sample water; 28.3 mg/L initial COD concentration; 120 mg/h  $\text{O}_3$  supply; 4.9 mg/h  $\text{H}_2\text{O}_2$  dosage. Error bars represent  $\pm 1$  standard deviation of triplicate runs.]**



**Fig. 5 – Progression of pH and alkalinity from secondary treatment through the IMA/vacuum ultrafiltration and peroxone processes.**

in which subscripts o and h stand for ozone and hydroxyl radical, respectively, and subscripts r and s stand for rapidly- and slowly-oxidized, respectively. In addition, ozone and hydrogen peroxide were supplied at a constant rate, and assuming excess  $[HCO_3^-]$  is reasonably constant then  $[O_{3(aq)}]$  and  $[OH^*]$  may be assumed approximately constant. Then, letting  $k_1 = k_{or}[O_{3(aq)}] + k_{hr}[OH^*]$  and  $k_2 = k_{os}[O_{3(aq)}] + k_{hs}[OH^*]$ :

$$\frac{d[COD]}{dt} = -k_1[COD]_r - k_2[COD]_s \quad (14)$$

$$\frac{d[COD]_r}{dt} = -k_1[COD]_r, \frac{[COD]_r}{[COD]_{r0}} = e^{-k_1 t}, \text{ and } \frac{d[COD]_s}{dt} = -k_2[COD]_s, \frac{[COD]_s}{[COD]_{s0}} = e^{-k_2 t} \quad (15)$$

Letting  $[COD]_r/[COD]_0 = f_1$  and  $[COD]_s/[COD]_0 = f_2$  (so that  $f_1 + f_2 = 1$ ), results in:

$$\frac{[COD]_r + [COD]_s}{[COD]_0} = \frac{[COD]}{[COD]_0} = f_1 e^{-k_1 t} + f_2 e^{-k_2 t} \quad (16)$$

The proposed model (Equation (16) and Table 3) fits the experimental data well, as shown in Fig. 4 ( $R^2 = 0.99$ ). However, individual dissolved constituents are ostensibly converted to and from the rapidly and slowly oxidized fractions present over the course of their mineralization. Therefore the close fit may be due to the facts that (a) the IMA-pretreated sample water, having presumably undergone preferential removal of larger molecular weight moieties, contained predominantly rapidly oxidizable organics, and (b) the apparent total molar fractions,  $f_1$  and  $f_2$ , of each group, and their associated rate constants, remained relatively constant. A presumptive pseudo-first order rate constant for  $HCO_3^-$  oxidation would thus be  $0.0496 \text{ h}^{-1}$ , small relative to  $k_1$  and  $k_2$ .

#### 4.5. Design of the pilot scale peroxone process

Based on Equation (16) and laboratory results of Table 3, and assuming 11.5%  $O_3$  transfer efficiency in the laboratory, 0.459 g/L h would be necessary to achieve 90% removal of COD in 6.0 h. Also by the assumptions of Equation (16), required treatment time varies in direct proportion to ozone dosage.

**Table 3 – Empirical peroxone oxidation reactions and kinetic constants.**

Organic oxidation reactions in terms of COD <sup>a</sup>	Kinetic constants <sup>b</sup>
$COD_r + O_3 \xrightarrow{k_{or}} CO_2 + H_2O$ $COD_r + OH^* \xrightarrow{k_{hr}} CO_2 + H_2O$	$k_1 = k_{or}[O_{3(aq)}] + k_{hr}[OH^*] = 1.09 \text{ h}^{-1}$ $f_1 = \frac{[COD]_{r0}}{[COD]_0} = 0.77$
$COD_s + O_3 \xrightarrow{k_{os}} CO_2 + H_2O$ $COD_s + OH^* \xrightarrow{k_{hs}} CO_2 + H_2O$	$k_2 = k_{os}[O_{3(aq)}] + k_{hs}[OH^*] = 0.14 \text{ h}^{-1}$ $f_2 = \frac{[COD]_{s0}}{[COD]_0} = 0.23$

a The composition of components  $COD_r$  (rapidly-oxidized COD) and  $COD_s$  (slowly-oxidized COD) varies dynamically due to serial reactions of individual organic constituents leading to mineralization and refractories production.  
 b  $[O_{3(aq)}]$  and  $[OH^*]$  assumed approximately constant.

Because peroxone process capital costs currently dominate operating costs, ozone systems are generally operated continuously for 24 h/d. Hence, transfer of 20.6 g  $O_3$ /h to the 2.84 m<sup>3</sup> pilot treatment tank over a 38 h average residence time is estimated to be required. Based on manufacturer’s experience, 90% mass transfer efficiency to the liquid phase by the pilot venturi injectors can be assumed. Therefore, required ozone supply is estimated at 23 g/h. Assuming an apparent  $O_3:H_2O_2$  molar ratio of 2.4 (Metropolitan Water District of Southern California et al., 1991),  $H_2O_2$  dosage would be 6.7 g/h. Projected  $O_3$  dosage is low relative to the previously reported 1260 g  $O_3$ /m<sup>3</sup> (injector type not specified) for 90% oxidation of COD in secondary effluent (Ried et al., 2006), equivalent to 79.6 g/h for a 1516 L/d (400 gpd) design flow.

#### 4.6. Water quality modeling: pilot system

To estimate the rate of make-up water addition required for salinity control, steady-state concentrations in the recycled water were computed by mass balance and equilibrium modeling, as follows. Loadings of  $Cl^-$ ,  $SO_4^{2-}$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were based on loadings reported to be typical for municipal water use (Tchobanoglous et al., 2003). These values may be conservative, in that some of the reported increase may derive from geological input. Loading of  $Na^+$  was assumed equal to that of chloride, typical for human-derived wastewater not impacted by water softener brine. Removal of these ions in treatment was assumed negligible, except for  $Ca^{2+}$  which was assumed subject to aerated precipitation of calcite as described below. Loading of  $PO_4^{3-}$  was estimated based on typical human elimination rates in urine (Everyday Health, 2011; U.S. National Library of Medicine, National Institutes of Health) and fecal matter (Mayo Clinic, Mayo Medical Laboratories, 2012), and on reported input from municipal water use (Tchobanoglous and Burton, 1991). Precipitation of 90% of  $PO_4^{3-}$  as the ferric salt by IMA was assumed (Table 2). Because manufacturer’s experience suggests 80% removal of TN by the MBR with anoxic zone, and because IMA field data were not available, 80% TN removal was assumed conservatively for MBR and IMA combined, from

an average TN load of 40 mg/L (Tchobanoglous et al., 2003). It was assumed for the current analysis that precipitated total phosphorus (TP) remains in the sludge phase for disposal/energy recovery, and that TN is volatilized by denitrification to N<sub>2</sub> (MBR) and NH<sub>3</sub> (Equations 10 and 11), though field study of these aspects is needed.

Steady state concentrations were calculated by mass balance as a function of time for all constituents, assuming (a) the loadings shown in Table 4, (b) continuous 20% discharge of treated water to sewer, and (c) continuous 20% make-up with rainwater containing negligible salt concentrations. Computed steady state concentrations were finally input to the Visual MINTEQ equilibrium model to estimate equilibrium steady state concentrations of all ions including CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, following equilibration with atmospheric CO<sub>2</sub> and precipitation of calcite. Resulting water hardness is projected to be moderate at 152 mg/L as CaCO<sub>3</sub>, allowing moderate soap and detergent usage/input.

Projected water quantity and quality through the treatment train are shown in Table 5. In this assessment, the design flow of 1516 L/d is assumed conservatively to be increased by 20% rainwater make-up following MBR treatment, and similarly reduced following disposal of 20% finished water. The pH through the system was estimated based on results presented in previous sections. Grab samples of raw wastewater from a different residence hall not having kitchens were measured to have 346 mg/L COD (12/3/2010) and TKN 102, BOD 468 (12/10/2010). However, due to grab sample variability, average raw wastewater COD, TN, and TP were estimated at 500, 40, and 8 mg/L, respectively, and average fecal coliforms (FC) were estimated at 10<sup>8</sup> counts/100 mL (Tchobanoglous et al., 2003). Projected COD removal in the MBR was based on manufacturer's experience, as described in Section 3.1. The IMA process was shown previously to remove 44% of COD from secondary effluent in 60 min (Deng et al., 2013). However, removal from the secondary effluent sampled on 5/7/2012 and tested in this work was reduced only from 29.6 mg/L following 16 h aeration (to simulate the field process), to 28.3 mg/L following IMA. Therefore, COD reduction between MBR and IMA processes was assumed

conservatively due only to dilution, whereas 90% removal was projected for peroxone treatment (Fig. 4). Bicarbonate was assumed reduced by 33% following peroxone oxidation (Fig. 4), reducing TDS by 33 mg/L. TN was estimated as described for Table 4.

As indicated in Table 5, synthetic estrogen, 17 $\alpha$ -ethinylestradiol (EE2), was selected to represent pharmaceutical removal, due to its widespread usage, endocrine-disrupting effect, and oxidative recalcitrance relative to natural estrogen. Conservatively and hypothetically assuming a loading of 18  $\mu$ g EE2/d and 400 GPD design flow, the initial concentration is 28 ng/L, high relative to reported values at centralized treatment plants (Zuehlke et al., 2004). Also conservatively assuming 70% EE2 removal by MBR (Baronti et al., 2000; Zuehlke et al., 2004) and 20% makeup water, the EE2 concentration influent to the peroxone process is 7 ng/L.

Peroxone oxidation of an individual organic, B, in natural water/wastewater can be represented:

$$-\frac{d[B]}{dt} = r_B = k_{\text{HOB}}[\text{OH}^*]_{\text{ss}}[B] \quad (17)$$

in which the second order rate constant  $k_{\text{HOB}}$  is reported as  $1.08 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for EE2 (Rosenfeldt and Linden, 2004). Based on previous modeling studies (Beltrán, 2004; Glaze and Kang, 1989), assuming neutral pH and reaction of EE2 exclusively with OH<sup>\*</sup>, representing ozone and H<sub>2</sub>O<sub>2</sub> dosage rates in M s<sup>-1</sup> by D and F, respectively, and operating the reactor to maintain  $D \geq 2F$  such that H<sub>2</sub>O<sub>2</sub> is consumed as fast as it is introduced, the following expression for the steady state concentration of OH<sup>\*</sup> can be found (Wu, 2013):

$$[\text{OH}^*]_{\text{ss}} = \frac{2F}{k_{\text{HOB}}[B] + (1+w)k_c[\text{HCO}_3]_T + k_{\text{NOM}}[\text{NOM}]} \quad (18)$$

The numerator of Equation (18) represents the overall rate of OH<sup>\*</sup> formation (Equation (12)); the denominator represents principal OH<sup>\*</sup>-scavenging reactions;  $w$  is the fraction of carbonate ion radicals that reacts with H<sub>2</sub>O<sub>2</sub> as opposed to other reactants;  $[\text{HCO}_3]_T$  represents total carbonate species; NOM is natural organic matter;  $k_c[\text{HCO}_3]_T = k_{\text{HCO}_3}[\text{HCO}_3^{1-}] +$

**Table 4 – Projected steady state treated water salinity.**

Total dissolved ionic species	Reference for loading	Loading (g/d)	Steady state, 20% rainwater make-up (mg/L)	Steady state, 20% rainwater, equilibrated with atmos. CO <sub>2</sub> and calcite (mg/L)	Steady state, 10% rainwater, equilibrated with atmos. CO <sub>2</sub> and calcite (mg/L)
Cl <sup>-</sup>	(Tchobanoglous et al., 2003)	53	140	140	316
SO <sub>4</sub> <sup>2-</sup>	(Tchobanoglous et al., 2003)	34.1	90	90	203
PO <sub>4</sub> <sup>3-</sup>	(Tchobanoglous and Burton, 1991) and conc. in urine, feces	15.2	0.9	0.9	1.0
HCO <sub>3</sub> <sup>-</sup>	–	–	–	99	184
NO <sub>3</sub> <sup>-</sup> (as NO <sub>3</sub> <sup>-</sup> )	(Tchobanoglous et al., 2003)	269	34	34	39
Na <sup>+</sup>	Cl <sup>-</sup> molarity	34.4	91	91	204
K <sup>+</sup>	(Tchobanoglous et al., 2003)	16.7	44	44	99
Mg <sup>2+</sup>	(Tchobanoglous et al., 2003)	10.6	28	28	63
Ca <sup>2+</sup>	(Tchobanoglous et al., 2003)	16.7	44	14	6
pH	–	–	–	8.4	8.6
TDS	–	–	–	541	1114

**Table 5 – Projected process water quality.<sup>a</sup>**

Parameter	Raw wastewater	MBR effluent	IMA influent <sup>b</sup>	ZW effluent	Peroxozone effluent	Res. Hall feed <sup>c</sup>
Flow (Lpd/gpd)	1516/400	1516/400	1819/480	1819/480	1819/480	1516/400
pH	6–7	6.5–7.5	8–8.5	7.7	8	8
TDS (mg/L)	726	726	581 <sup>d</sup>	543 <sup>e</sup>	510	510
COD (mg/L)	500	20	17	17	1.7	1.7
TN (mg/L)	40	–	–	8 <sup>e</sup>	8	8
TP (mg/L)	11	11	9	1 <sup>e</sup>	1	1
HCO <sub>3</sub> <sup>-</sup> (mg/L)	141 <sup>f</sup>	>80 <sup>g</sup>	>67	99 <sup>e</sup>	66	66
FC (100 mL) <sup>-1</sup>	10 <sup>8</sup>	0	0	0	0	0
EE2 (ng/L)	28	8.4	7	7	0	0

a Based on reported mineral increase from domestic use (Tchobanoglous et al., 2003) and Table 4.

b Includes 20% rainfall make-up water.

c Up to 20% treated water disposed.

d ZW effluent plus 8 mg/L TP plus 30 mg/L Ca<sup>2+</sup>.

e From Table 4.

f Feed to residence hall plus reported mineral increase from domestic use (Tchobanoglous et al., 2003).

g Estimated alkalinity required to maintain pH >7 for denitrifier growth (Henze et al., 2011).

$k_{\text{CO}_3}[\text{CO}_3^{2-}] = (k_{\text{HCO}_3} + k_{\text{CO}_3} 10^{\text{pH}-\text{pK}_2})(10^{\text{pH}-\text{pK}_1}/1 + 10^{\text{pH}-\text{pK}_1} + 10^{2\text{pH}-\text{pK}_1-\text{pK}_2})[\text{HCO}_3^-]_T$ ;  $\text{pK}_1 = 6.3$  and  $\text{pK}_2 = 10.3$ ;  $k_{\text{HCO}_3} = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{CO}_3} = 4.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $k = 2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (Beltrán, 2004); and  $k_{\text{NOM}} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (Crittenden et al., 2012). At the dosage proposed in this paper (6.7 g/h H<sub>2</sub>O<sub>2</sub> and 22 g/h O<sub>3</sub>); the projected 1.62 mM HCO<sub>3</sub><sup>-</sup> and 0.0841 mM CO<sub>3</sub><sup>2-</sup> concentrations; and NOM estimated at  $5 \times 10^{-4} \text{ M}$  based on projected 17 mg/L COD, EE2 removal is estimated to be virtually complete in 38 h (239-log removal at  $w = 1$ ).

Based on the data presented in Tables 4 and 5, treated water is expected to meet U.S. primary and secondary drinking water standards, with total dissolved solids (TDS) determined by the fraction of rainwater make-up provided. In view of the projected TDS in Table 5, it appears that the mineral water produced will meet U.S. standards for low- (250–500 mg/L) to moderate- (500–1500 mg/L) mineral content.

## 5. Discussion

A preliminary assessment of the operation and maintenance (O&M) costs of the proposed design for a typical home system treating 1137 L/d (300 gpd) is shown in Table 6, as one approximate indicator of system life-cycle energy. O&M costs and overall hydraulic head differential across the system (~7.6 m of water) are competitive with existing requirements for water and wastewater services. Capital costs for a system might be dominated by ozonator purchase, and installation of the buried aerobic system and cisterns. Based on equipment prices realized in this project capital costs may be on the order of \$50,000 currently. Thus, at this early stage of development and for a system that mineralizes waterborne pharmaceuticals, projected cost is on the same order as the ca. \$20,000 per housing structure projected for upcoming renovation of centralized water and wastewater infrastructure in Miami-Dade County, FL (Rabin, 2012). In contrast with the Pure Cycle system design, the proposed system returns nitrogen to the atmosphere, in addition to mineralizing organics. The addition of alkalinity and external carbon for nitrification/

denitrification may not be required, through the use of IMA for denitrification and organic nitrogen removal. Rainwater requirements depend upon temporal rainfall distribution in the area and maximum TDS level desired in the finished water. Many questions remain as to, for example, steady-state effluent concentrations, trace perozone byproducts, the need for GAC or other polishing process e.g. for a small drinking water stream, and sludge management options.

Though many off-grid water systems, including cistern, well, septic, and biological systems may be considered NZW, such systems generally are not designed to address the nitrogen balance when employed widely across an urban area. Such systems have used or use moderate and/or high-pressure membrane separation, high-temperature catalysis,

**Table 6 – Preliminary projected O&M costs for a 1137 L/d (300 gpd) net-zero water treatment system.**

Item	Basis <sup>a</sup>	Cost (\$/3790 L, \$/1000 gal)
Ozonation electric power	0.18 kW continuous	\$1.45
UV electric power	43 W continuous	\$0.34
UV lamp replacement	\$100/y	\$0.91
H <sub>2</sub> O <sub>2</sub> chemical cost	5.9 g O <sub>3</sub> /h, 1 mol H <sub>2</sub> O <sub>2</sub> : 2 mol O <sub>3</sub> , 35% H <sub>2</sub> O <sub>2</sub> @ \$0.55/kg (\$0.25/lb)	\$0.74
Iron electrode cost	30 mg Fe <sup>3+</sup> /L @ \$1.21/kg (\$0.55/lb)	\$0.15
Electrocoagulation electric power	30 mg Fe <sup>3+</sup> /L @ 4 V	\$0.03
Aeration electric power	Aeration of 2 tanks, 3 ft. depth @ 120 V, 0.3 A each	\$0.29
Pump electric power	5 pumps @ 0.13 W h/L (0.5 W h/gal)	\$0.25
Labor	4 h/y including membrane cleaning @ \$40/h	\$1.46
Administration	20% of total O&M	\$1.12
Total		\$6.74

a Assumptions: \$0.10/kWh; negligible cost if any for added alkalinity and carbon sources.

or low-temperature condensation (Carter, 2009; Dempster, 1999; du Pisani, 2006; Harding, 2009; Tchobanoglous et al., 2011), and generally require nitrogen transport and disposal, particularly if employed widely across an urban area. Only the Pure Cycle and International Space Station systems have accepted wastewater as the principal source water. Therefore if successful, the proposed process will be the first UANZW system, to our knowledge, designed to address this nitrogen balance in urban areas where most people live today. The proposed system would also be the first to substantially mineralize organics in process effluent.

## 6. Conclusions

Use of UANZW may minimize water rationing, address current *de facto* potable reuse of source waters in urbanized areas, and remove water demand on the natural freshwater system. Further, implementation of mineralizing UANZW technology may address ecological endocrine disruption. Eventually, wider use of distributed systems may also allow more rapid evolution of municipal water and wastewater technology, based on smaller-scale trials tailored to local conditions. Specific conclusions of this study include:

1. Based on laboratory and modeling it appears that a treatment process comprised of a MBR, IMA, vacuum ultrafiltration, peroxone, and UV may be capable of producing moderate mineral-content potable water from commingled domestic wastewater at individual buildings, and mineralizing waterborne COD to below detection, at ambient temperature and pressure, and circum-neutral pH;
2. Peroxone oxidation of COD in secondary effluent was well-described as a simultaneous pseudo-first order decomposition of rapidly (77%) and slowly (23%) oxidizable fractions, proceeding in parallel with kinetically-disfavored conversion of bicarbonate alkalinity;
3. Further study is needed of steady-state concentrations, of the ability of MBR and IMA to control nitrogen without substrate addition, of peroxone byproducts, and of the need for GAC or other polishing treatment e.g. for drinking water; and
4. With further process development and identification of options for sludge management, urban ambient mineralizing NZW treatment may prove cost-competitive for rehabilitation of water and wastewater infrastructure.

## Acknowledgments

The authors would like to thank Reza Shams, Anthony Sacco, and Lloyd Johnson for their guidance in process design, and Alessandra Marie Leon and Sabina Rakhimbekova for help with laboratory experiments. Academic, industrial, and government partners and student volunteers and interns too numerous to mention are also sincerely thanked for help on the project. Finally, the support of the US National Science Foundation (EFRI-SEED Award 1038257), the U.S. Environmental Protection Agency, the University of Miami, Engineered Control Systems,

Inc., BioMicrobics, Inc., BK Precision Corp., Hazen and Sawyer, P.C., and RTI Supply for this work is gratefully acknowledged.

## REFERENCES

- APHA, AWWA, WEF, 2005. Standard Methods for the Examination of Water and Wastewater, twenty-first ed. American Public Health Association, American Water Works Association, and Water Environment, Washington DC.
- Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A., Gentili, A., Samperi, R., 2000. Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water. *Environmental Science and Technology* 34 (24), 5059–5066.
- Beltrán, F.J., 2004. Ozone Reaction Kinetics for Water and Wastewater Systems. Lewis Publishers, Boca Raton, FL.
- BioMicrobics Inc., 2010. BioBarrier(TM) Membrane Bioreactor. <http://www.biomicrobics.com/?p=124> (08/2012, 2012).
- Bloetscher, F., Englehardt, J., Chin, D., Rose, J., Tchobanoglous, G., Amy, V., Gokgoz, S., 2005. Comparative assessment of municipal wastewater disposal methods in southeast Florida. *Water Environment Research* 77 (5), 480–490.
- Carter, D.L., 2009. Status of the regenerative ECLSS water recovery system. NASA technical paper 2009-01-2352. In: Proc., 39th International Conference on Environmental Systems, Jul 12–16. SAE International, Savannah, GA.
- Chao, P., Westerhoff, P., 2002. Assessment and optimization of chemical and physicochemical softening processes. *Journal American Water Works Association* 94 (3), 109–119.
- Cohen, R., Nelson, B., Wolff, G., 2004. Energy Down the Drain: the Hidden Costs of California's Water Supply. Natural Resources Defense Council, Pacific Institute, Oakland, CA.
- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012. *MWH's Water Treatment: Principles and Design*, third ed. John Wiley & Sons, Inc, New York.
- Dempster, W.F., 1999. Biosphere 2 engineering design. *Ecological Engineering* 13, 31–42.
- Deng, Y., Englehardt, J., Abdul-Aziz, S., Bataille, T., Cueto, J., De Leon, O., Wright, M., Gardinali, P., Narayanan, A., Polar, J., Tomoyuki, S., 2013. Ambient iron-mediated aeration (IMA) for water reuse. *Water Research* 47, 850–858.
- Di Bella, G., Mannina, G., Viviani, G., 2008. An integrated model for physical-biological wastewater organic removal in a submerged membrane bioreactor: model development and parameter estimation. *Journal of Membrane Science* 322, 1–12.
- du Pisani, P., 2006. Direct reclamation of potable water at Windhoek's Goreangob reclamation plant. *Desalination* 188, 79–88.
- Englehardt, J.D., Meeroff, D.E., Echegoyen, L., Deng, Y., Raymo, F.M., Shibata, T., 2007. Oxidation of aqueous EDTA and associated organics and coprecipitation of inorganics by ambient iron-mediated aeration RID B-4570-2011. *Environmental Science and Technology* 41 (1), 270–276.
- Everyday Health, 2011. Phosphate in Urine – Results. <http://www.everydayhealth.com/health-center/phosphate-in-urine-results.aspx> (September 30, 2012).
- Glaze, W.H., Kang, J., 1989. Advanced oxidation process: description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semibatch reactor. *Industrial & Engineering Chemistry Research* 8, 1573–1580.
- Gordon, G., Cooper, W.J., Rice, R.G., Pacey, G.E., 1992. *Disinfectant Residual Measurement Methods*, second ed. AWWARF and AWWA, Denver, CO.
- Gottschalk, C., Libra, J.A., Saupe, A., 2010. *Ozonation of Water and Waste Water: a Practical Guide to Understanding Ozone and Its Applications*, second ed. Wiley-VCH, New York.

- Grube, A., Donaldson, D., Kiely, T., Wu, L., 2011. Pesticide Industry Sales and Usage: 2008 and 2007 Market Estimates. U. S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, pp. 1–33. EPA 733-R-11-001.
- Harding, M., 2009. Personal Communication. President, Pure Cycle Corp., Denver, CO. October 29.
- Henze, M., van Loosdrecht, M., Ekama, G., Brdjanovic, D., 2011. Biological Wastewater Treatment: Principles, Modelling and Design. IWA Publishing, London.
- ICF Consulting, 2002. Water and Sustainability: U.S. Electricity Consumption for Water Supply & Treatment – the Next Half Century. EPRI, Palo Alto, CA.
- LeChevalier, M., 2012. Impact of wastewater disinfection on reuse applications. In: Presentation, WateReuse Symposium, Hollywood, FL. WateReuse Association, Alexandria, VA. September 12.
- Logan, B.E., Rabaey, K., 2012. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. *Science* 337 (6095), 686–690.
- Mannina, G., Di Bella, G., Viviani, G., 2011. An integrated model for biological and physical process simulation in membrane bioreactors (MBRs). *Journal of Membrane Science* 376, 56–69.
- Mayo Clinic, Mayo Medical Laboratories, 2012. Test ID: CLF8467 Chloride, Random, Feces. [http://www.mayomedicallaboratories.com/test-catalog/print.php?unit\\_code=8467](http://www.mayomedicallaboratories.com/test-catalog/print.php?unit_code=8467) (September 7, 2012).
- McCarty, P., Bae, J., Kim, J., 2012. Domestic wastewater treatment as a net energy producer: can this be achieved? *Environmental Science and Technology* 45, 7100–7106.
- Metropolitan Water District of Southern California, James M. Montgomery, Consulting Engineers, AWWA Research Foundation, 1991. Pilot-scale Evaluation of Ozone and Peroxone. AWWA Research Foundation and Amer. Water Works Assoc., Denver, CO.
- Narayanan, A., Gadzinski, E., Kelly, P., Silverman, A., 2009. Iron-Mediated Aeration with Polymer Addition for the Treatment of Phosphorous and Nitrogen: Reuse of Wastewater for Coastal Wetland Rehydration. *Civil, Arch., and Environ. Engrg.*, University of Miami, Coral Gables, FL.
- National Institute for Occupational Safety and Health, 1992. Recommendations for Occupational Safety and Health: Compendium of Policy Documents and Statements. Publication no. 92–100. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH), Cincinnati, OH.
- NRC, 2012. Water Reuse: Potential for Expanding the Nation's Water Supply through Reuse of Municipal Wastewater. Committee on the Assessment of Water Reuse as an Approach to Meeting Future Water Supply Needs, National Research Council, Washington, DC.
- Ozone Solutions, September 1, 2012. Venturi vs Diffusers. <http://www.ozonesolutions.com/info/venturi-vs-diffusers> (September 30, 2012).
- Perera, K., Englehardt, J., 2012. A Mathematical Model of a Nitrifying/Denitrifying Membrane Bioreactor with Alkalinity and Carbon Addition. Unpublished Notes.
- Rabin, C., 2012. Upgrades for water, sewer could exceed \$12B. *The Miami Herald*, A, 1A–2A. (September 18).
- Rakness, K., 1996. Guideline for measurement of ozone concentration in the process gas from an ozone generator. *Ozone: Science and Engineering* 18 (3), 209–229.
- Ried, A., Mielcke, J., Kampmann, M., 2006. The right treatment step ozone and ozone/H<sub>2</sub>O<sub>2</sub> for the degradation of non-biodegradable COD. In: Proc., Wasser Berlin 2006: International Conference Ozone and UV, April 3rd, pp. 25–33.
- Rosenfeldt, E., Linden, K., 2004. Degradation of endocrine disrupting chemicals bisphenol a, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environmental Science and Technology* 38 (20), 5476–5483.
- Selby III, H.W., 1979. Water recycling system. Pure Cycle Corp., Boulder, CO, U. S. Patent no. 4,145,279.
- Shams, R., 2011. "Vice President, Advanced Process Technology, BioMicrobics, Inc., Shawnee, KS." Personal communication, Feb. 22 and July 20.
- Suzuki, T., Moribe, M., Oyama, Y., Niinae, M., 2012. Mechanism of nitrate reduction by zero-valent iron: equilibrium and kinetics studies. *Chemical Engineering Journal* 183, 271–277.
- Tchobanoglous, G., Leverenz, H., Nellor, M., Crook, J., 2011. Direct Potable Reuse: a Path Forward. WateReuse Research Foundation, Alexandria, VA.
- Tchobanoglous, G., Burton, F., Stensel, H.D., 2003. Wastewater Engineering: Treatment and Reuse, fourth ed. McGraw-Hill, Inc., New York.
- Tchobanoglous, G., Burton, F., 1991. Wastewater Engineering: Treatment, Disposal, and Reuse, third ed. McGraw-Hill Publishing Co., Inc., New York.
- U.S. Environmental Protection Agency, 2011. 2010 Toxics Release Inventory National Analysis Overview. <http://www.epa.gov/tri/tridata/tri10/nationalanalysis/overview/2010TRINAOOverview.pdf> (02/08, 2011).
- U.S. Environmental Protection Agency, 1997. Exposure Factors Handbook. US Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Cincinnati. <http://www.epa.gov/ncea/pdfs/efh/front.pdf>.
- U.S. National Library of Medicine, National Institutes of Health. "MedlinePlus." <<http://www.nlm.nih.gov/medlineplus/ency/article/003601.htm>> (September 7, 2011).
- van der Leeden, F., Troise, F., Todd, D., 1990. The Water Encyclopedia, second ed. Lewis publishers, Boca Raton, Florida.
- Wu, T., 2013. Excess Ozone Single Organic Peroxone Advanced Oxidation Model. Unpublished Notes, Mar. 11, pp. 1–2.
- Zuehlke, S., Duennbier, U., Heberer, T., Fritz, B., 2004. Analysis of endocrine disrupting steroids: investigation of their release into the environment and their behavior during bank filtration. *Ground Water Monitoring and Remediation* 24 (2), 78–85.