Continued Development of the Electro Oxidation and Membrane Evaporator for Urine Processing and Water Recovery

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This paper describes the continued development of wastewater processing and water reclamation applications using the Electro Oxidation and Membrane Evaporator (EOME). The EOME purifies wastewater (augmented urine, flush water, and pretreat) by breaking down organic compounds with powerful oxidants such as reactive oxygen species (ROS) and chlorine containing species (CCS) created from oxygen, water, and chloride salts in the wastewater on Boron-Doped-Diamond (BDD) coated electrodes. Waste heat generated from the electro-oxidation process is used to facilitate water evaporation through a gas-liquid contactor (GLC), allowing water evaporated from the wastewater to be recovered elsewhere. The purpose of developing and testing the EOME is to explore its potential for reducing the size, mass, power, and complexity of an Exploration wastewater treatment system, to increase the recovery of useful gases from waste products, and reduce waste volume. A full scale bench top EOME was developed based on previous work, including upgraded GLCs for evaporating water and a trace contaminant control system (TCCS) to capture previously identified off-gassed contaminants in the humid air. Tests with human urine were performed and gas and wastewater were sampled to help understand the EOME performance.

Nomenclature

BDD = Boron-Doped Diamond
°C = Degrees Celsius
CCS = Chlorine Containing Species
Cl^- = Chloride
Cl_2 = Chlorine
ClO = Hypochlorite
ClO_2 = Chlorine Dioxide
CO_2 = Carbon Dioxide
$CO(NH_2)_2$ = Urea
DO = Dissolved Oxygen
EOME = Electro Oxidation and Membrane Evaporator
GLC = Gas-Liquid Contactor
H^+ = Proton
H_2 = Hydrogen
H_2O = Water, Water Vapor
H_2S = Hydrogen Sulfide
HClO = Hypochlorous Acid
mg/L = milligrams/liter
N_2 = Nitrogen
NASA = National Aeronautics and Space Administration
NH_3 = Ammonia
NO = Nitric Oxide
NO_2 = Nitrogen Dioxide

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OSS = Oceaneering Space Systems
O_2 = Oxygen
O_3 = Ozone
ppm = Parts Per Million
Redox = Reduction and Oxidation
ROS = Reactive Oxygen Species
slpm = Standard Liters per Minute
SO_2 = Sulfur Dioxide
TCCS = Trace Contaminant Control System
TN = Total Nitrogen
TOC = Total Organic Carbon

I. Introduction

THIS paper reports on the development progress of the Electro Oxidation and Membrane Evaporator (EOME), a partial gravity compatible urine processor. EOME oxidizes urine, evaporates water and acid gases, scrubs acid gases, and outputs water vapor and other trace gases (e.g., carbon dioxide) to be recovered elsewhere such as in a cabin condensing heat exchanger for water and a Sabatier reactor for carbon dioxide. The resulting wastewater effluent is offloaded to a brine water recovery system to recover the remaining water in the effluent. A functional block diagram of the EOME concept is shown in Figure 1. In previous EOME development phases, the water evaporation rate, trace gas generation rates, and changes in the wastewater and acid gas constituents were obtained [1, 2]. The present work investigated (1) how evolved gas constituents and generation rates changed at different reduction oxidation (redox) cell voltages and current, (2) stability of the resulting wastewater effluent, and (3) use of more efficient GLCs for faster water evaporation and a Nafion dryer to prevent condensation in a trace contaminant control system (TCCS) that removes evolved trace contaminant gases.

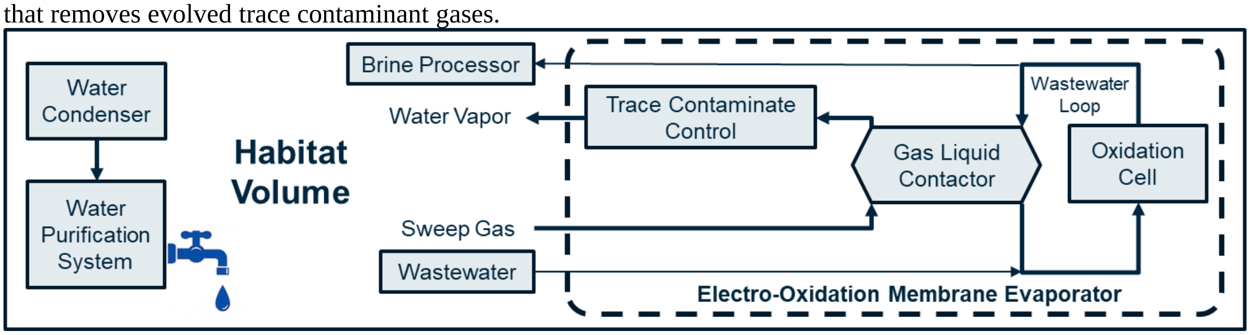


Figure 1: Functional block diagram of EOME concept

II. EOME Overview

Figure 2 shows the updated EOME test schematic consisting of the wastewater loop (thick grey line in Figure 2), the GLC sweep gas flowpath (thick black line in Figure 2), and the Nafion sweep gas flowpath (medium black line in Figure 2). In the wastewater loop, a pump circulates wastewater (urine, flush water, and pretreat/stabilizer if any) through a heat exchanger (optional), the tank, and the redox cell. The redox cell (Diamonox Model 200, John Crane, Chicago, IL) decreases Total Organic Carbon (TOC), Total Nitrogen (TN), ammonia-nitrogen, chloride, and total solids by breaking down organic compounds with powerful oxidants such as reactive oxygen species (ROS) and chlorine containing species (CCS) created from oxygen (O_2) and chloride salts in the wastewater on an anode coated with Boron-Doped-Diamond.

The reactions to generate free chlorine [3–6] and oxidation of urea [5, 6], the major organics in raw urine, are known as:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^- \leftrightarrow ClO^- + 2H^+ + Cl^-$$

$$CO(NH_2)_2 + 3HClO \rightarrow CO_2 + N_2 + 3HCl + 2H_2O$$

Urea hydrolysis is known to generate ammonia-nitrogen [7]. The EOME redox process also generates ammonia-nitrogen (cathodic reaction) at the beginning of the process, but at the end of the process, ammonia-nitrogen is converted to nitrate. Refer to [2] for a summary of known reactions involving nitrogen and chlorine species. In brief, the majority of chlorine ends up as chloride, free chlorine, and combined chlorine.

The generated gases and water vapor leave the wastewater from the tank, GLCs, and Nafion module. Two hydrophobic Sumitomo POREFLON modules (Sumitomo Electric Industries, Ltd., Japan) were used as GLCs due to their chemically inert construction. The GLC sweep gas flowpath consists of fans to introduce room air as sweep gas to the shell side of the GLCs, then to the lumen side of Nafion module FC400C5-2500-10HP (Permapure, Toms River, NJ), and then to a gas scrubber bed that contains activated carbon pellets. The sweep gas runs through the GLC shell side and evaporates water and acid gases from the wastewater in the lumen sides. A small amount of sweep gas also runs through the head space of the tank to avoid accumulation of generated gases. The Nafion module transfers water vapor from the nearly saturated GLC sweep gas to the Nafion sweep gas flowing through the shell side of the Nafion module for recovery by a cabin condensing heat exchanger. The less humid GLC sweep gas then exits the Nafion lumens and enters the gas scrubber bed that absorbs acid gas species and passes air, water vapor, hydrogen (H_2), and CO_2. The scrubber bed is approximately 29 cm in diameter and 150 cm long, and was designed to scrub a total of ~1.4 kg of evolved trace contaminant gases using 22 kg of various activated carbons. This sizing was designed to support EOME operations suitable for processing the urine from four crew for one year.

The electro-oxidation process brings the wastewater pH down without acidic pretreatment. The on-site generation of acidic, oxidant-rich wastewater via electro-oxidation provides a number of benefits including acidifying urine without consumables, decreasing TOC and making the plumbing less habitable for bacteria and fungi, and converting wastewater components that would otherwise be stored as waste into recyclable gases such as CO_2. Use of a vacuum pump (vacuum distillation) would also work to evaporate water in the GLC, although it would require additional components and power related to producing the vacuum.

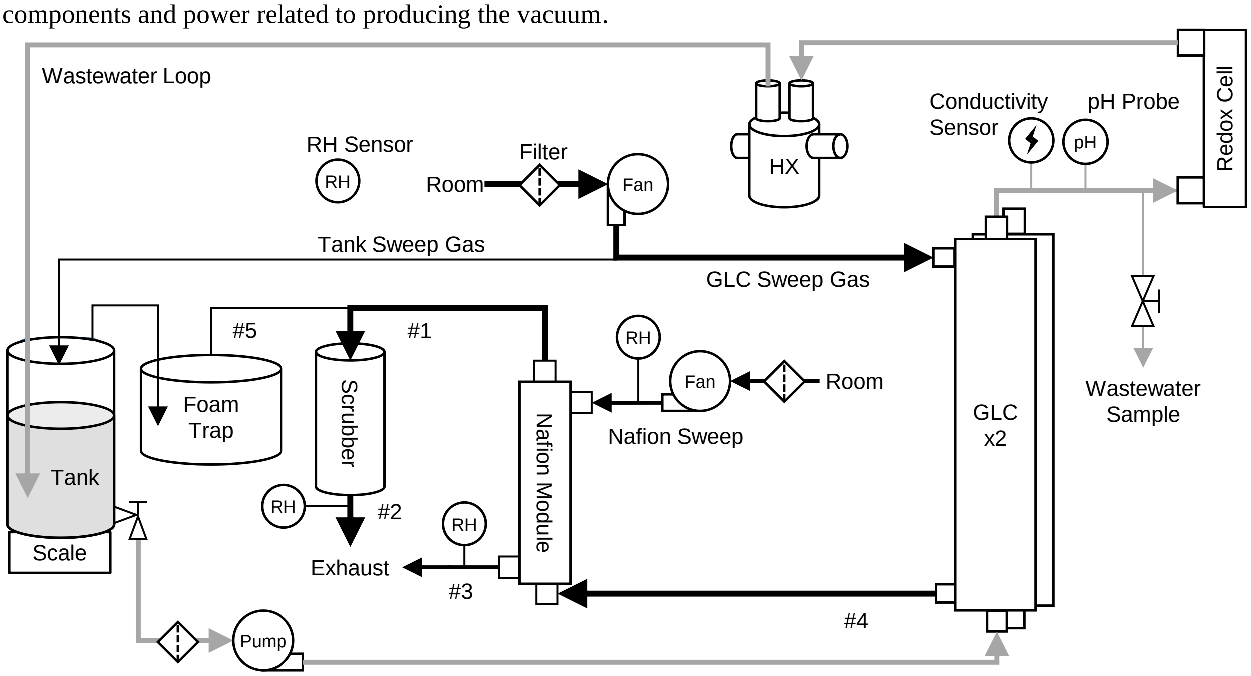


Figure 2: EOME Test Schematic

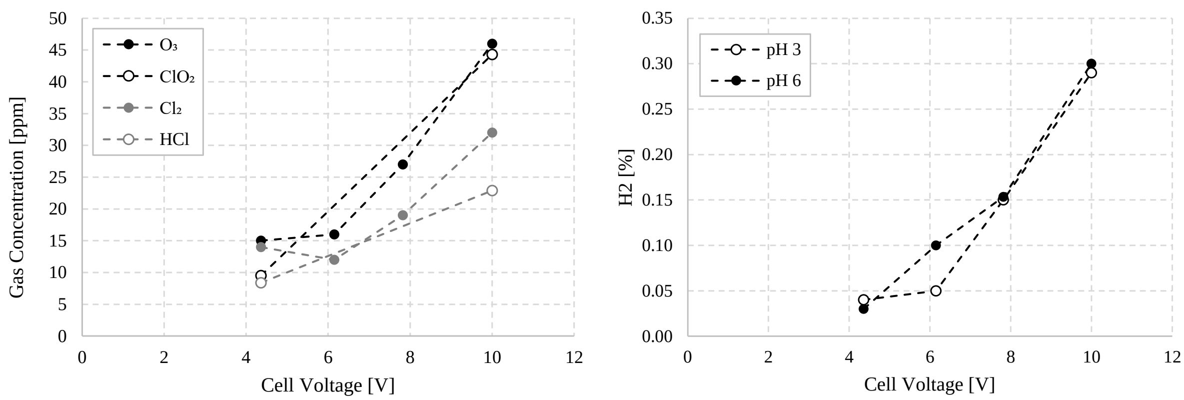
III. Evolved Gas Constituents and Generation Rates as a Function of Redox Cell Voltages and Current

In the previous tests, the redox cell current was set to 30 Amps throughout the duration of the tests [1, 2], and the cell voltage ranged between 10-15 V. Those tests demonstrated generation of gas species such as chorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), ammonia (NH_3), hydrogen (H_2), and carbon dioxide (CO_2). In the present exploratory work, different cell voltages (4.4, 6.2, and 7.8 V) were used to see if different gas species were generated such as nitric oxide (NO), nitrogen dioxide (NO_2), and 1,2-dichloroethane, a possibility indicated in related literature

[8, 9]. Because Hydrogen cyanide (H_2S) and sulfur dioxide (SO_2) cause interference with the Cl_2 and O_3 sensors, H_2S and SO_2 sensors were used to detect the concentrations of those gases and enable determination of the true levels of Cl_2 and O_3 through published interference tables. Similarly, because chloroform causes interference with the 1,2-dichloroethane detector tube, chloroform detector tubes were used to determine if the interfering gas was present which would negate the 1,2-dichloroethane reading.

8.4 L of raw urine was processed by EOME. To maximize the effluent quantity, the GLCs were removed to limit the gas-liquid contacting surface and minimize water evaporation. The only water-evaporating surface was inside the tank which had a room air sweep gas flow rate of ~93 standard liters per minute (slpm). The scrubber bed was not used. The test was stopped when the lowest pH value (~3) was achieved. In order to expedite the process, the redox current was set to 30 Amps for the majority of the test. When the highest pH (~6) and lowest pH (~3) were achieved, the cell voltage was temporarily reduced for a few minutes to 7.8 V (15 Amps), 6.2 V (9 Amps), and 4.4 V (3 Amps), and the sweep gas was sampled for gas species and gas generation rates were obtained.

The gas generation rates generally had a linear relationship to the cell voltages at the lowest pH ~3 (Figure 3a). At the highest pH (~6), acid gas species were not generated or were below the detection limits. The generation rate trend of H_2 gas at pH 3 and 6 were similar (Figure 3b). Throughout the test at different voltages H_2S, NO, NO_2 SO_2, chloroform, and 1,2-dichloroethane were below the detection limits except 2-ppm nitrogen dioxide (NO_2) at 4.4 V (3 Amps) was observed. From this study, it was found not advantageous to reduce redox voltage (current) to the range of 4.4 – 7.8V (3 – 15 Amps) in terms of gas generation rates and species.



(a) Acid Gases (Wastewater pH = ~3) (b) H_2

Figure 3: Generation rates of different gas species at varying redox voltage

IV. Stability of Wastewater Effluent

EOME produces acid liquid effluent. The purpose of this study was to investigate the stability of the effluent. The effluent from the low voltage and current test (Section III, 4.4 – 7.8 and 10 V, 3 – 15 and 30 Amps) was used because the test was conducted mostly at the nominal cell current (30 Amps) and closely represented a nominal testing condition. The effluent samples were contained in HDPE sealed cups at room temperature that were opened only to draw off liquid for analysis. TN, TOC, dissolved oxygen (DO), pH, and turbidity were measured. As shown in Figure 4, the effluent remained stable over approximately one month. TN and TOC were around 600 mg/L. DO remained saturated (100%) in the effluent, indicating minimal or zero biological activities. The pH and Turbidities ranged between 3.4 – 3.49 and 0.54 – 0.7, respectively.

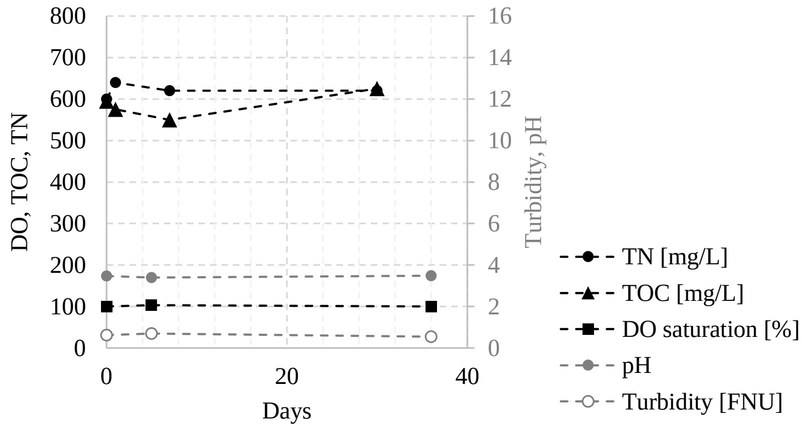


Figure 4: Changes in the wastewater properties of the effluent

V. Evaporation Performance of GLC and Nafion Modules

The goal of the test was to obtain evaporation performance data on the GLCs and Nafion module. 7.3 L of raw urine was introduced into the tank and circulated by the wastewater pump. The redox cell current was set to 30 Amps. The flow rates of the GLC sweep gas and Nafion sweep gas were each set to ~190 slpm. Figure 5 shows the water vapor balance in the EOME system. The sweep gas entering the GLCs from the room contained 1.65 g/min of water vapor, and 3.65 g/min of water vapor was evaporated into the sweep gas in the GLCs. 3.8 g/min is the theoretical maximum amount that can be evaporated into the flow at that temperature, providing an indication of the good GLC performance. The total of 5.3 g/min water vapor entered the Nafion lumen side, where 3.3 g/min of water vapor was removed from it into the room air sweep gas in the Nafion shell side (originally containing 1.7 g/min water vapor). The dehumidified GLC sweep gas left the Nafion module and entered the scrubber bed, and the scrubber outlet had 2 g/min water vapor, which completes the mass balance for water. As a whole, 3.35 g/min of water vapor entered the EOME system in the two sweep gas flows, the GLCs evaporated 3.65 g/min, and 7 g/min left the system to complete the water balance. 90% of the water vapor evaporated into the sweep gas by the GLCs was removed by the Nafion module (3.3/3.65=0.9). The test demonstrated that the GLCs were able to evaporate water vapor from the wastewater at near theoretical maximum performance, and the Nafion module was able to dry the nearly saturated GLC sweep gas to minimize water condensation in the downstream gas scrubber bed. Because Nafion is poisoned by ammonia that is evolved from EOME during operation, further investigation is necessary to estimate the service life of the Nafion module as part of the EOME system. Alternatively, a condensing heat exchanger could be used in place of the Nafion module if ammonia poisoning is an issue.

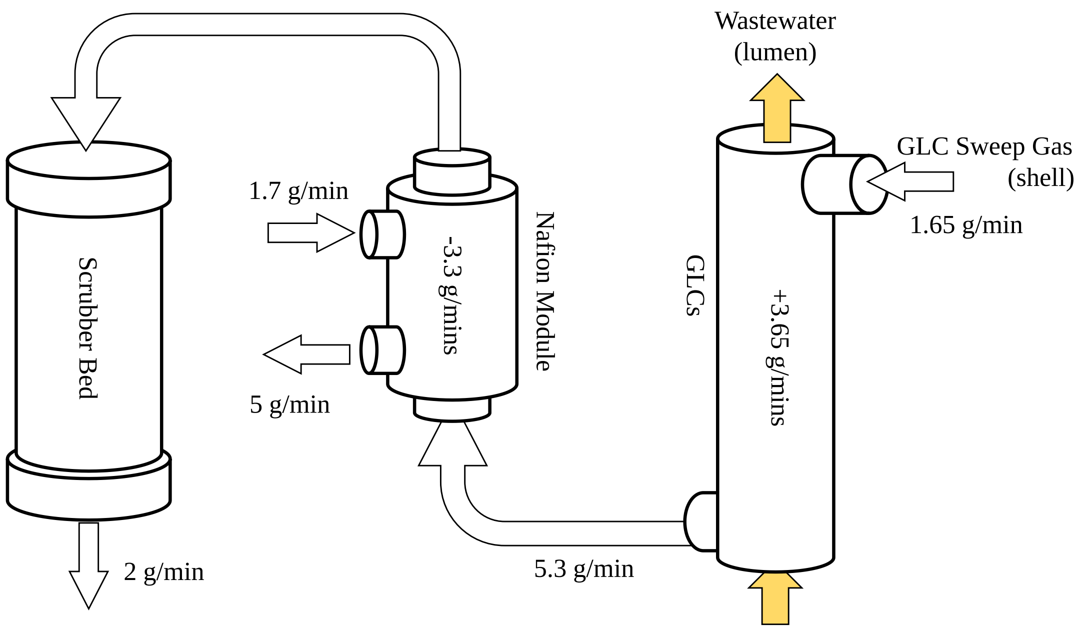


Figure 5: Water vapor balance around GLCs and Nafion module

VI. Conclusion

The present study demonstrated that

1. The generation rates of the evolved gas species are linearly correlated with the redox cell voltage. No significant difference in evolved gas species was seen when the redox cell was run at different voltages.
2. The resulting effluent in the wastewater loop from the EOME process was stable over at least a 5-week period with little change in TN, TOC, dissolved oxygen, pH, and turbidity.
3. The new GLCs were able to nearly saturate the sweep gas with water vapor. The Nafion module removed 90% of the water vapor evaporated into the sweep gas by the GLCs, which will minimize water condensation in the downstream gas scrubber bed.

Future work includes

1. Processing consecutive human urine batches until maximum urine concentration is reached which may expose unknowns related to repeated daily use.
2. Developing dormancy start up and shut down scenarios and operationally testing 1st day start up after dormancy and 30th (last) day shut down for dormancy to drive out dormancy related procedures and requirements.
3. Performing greywater processing with EOME to assess EOME capability to recover water from greywater and to stabilize greywater.

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