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Low-Temperature Electrochemical Wastewater Oxidation

October 2023

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Abstract

In this work, we demonstrated the Clean Sustainable Electrochemical Treatment process that enables the distributed clean-up of biomass-derived wastewater while simultaneously generating hydrogen. The specific goal of this project is to 1) demonstrate the selective removal of chemical oxygen demand, total carbon, and total nitrogen of different wastewaters, 2) optimize the electrode composition to improve electrochemical performance, and 3) perform a high-level techno-economic analysis to obtain levelized costs of disposal.

Summary

In this study, we investigated electrochemical treatment of different wastewaters generated via hydrothermal liquefaction of biomass and waste. We evaluated how the composition of the wastewater and electrochemical reaction conditions (i.e., voltage and current) affect the cost of chemical oxygen demand removal and hydrogen production. We demonstrated that both the voltage and composition of the wastewater affect chemical oxygen demand removal and efficiency. We synthesized and tested different iterations of Ru-based electrodes and observed that they all improved the catalytic activity by up to an order of magnitude. A preliminary techno-economic analysis revealed that the cost of electrochemical treatment is similar to that of the current wastewater tipping fee. Decreasing the cost of the electrolyzer and operating the current density will enable the electrochemical wastewater treatment technology to be a cheaper option than paying for wastewater disposal fees.

Acknowledgments

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Acronyms and Abbreviations

COD	chemical oxygen demand
CleanSET	Clean Sustainable Electrochemical Treatment
HTL	hydrothermal liquefaction

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1.0 Introduction

In this work, we evaluated the performance of the proprietary Clean Sustainable Electrochemical Treatment (CleanSET) technology for electrochemical oxidation of wastewaters (derived via the hydrothermal liquefaction of biomass into fuels) while simultaneously producing hydrogen (H_2). The CleanSET technology was developed at Pacific Northwest National Laboratory to simultaneously oxidize and reduce biomass-derived streams¹ We demonstrated that chemical oxygen demand (COD), total carbon, and total nitrogen can be removed from biomass-derived wastewater feedstocks while simultaneously generating H_2 as byproduct at >100% efficiency (i.e., energy recovered in H_2 byproduct divided by the electrical energy input).

Currently, processing wastewater requires significant infrastructure (e.g., pipes and pumps or trucks) to move the wastewater to centralized locations where the processing occurs. Unlike traditional chemical and biological processes, electrochemical systems can be operated economically at small scales so there is no need for larger, more expensive centralized treatment facilities. Instead, our proposed technology can be co-located at generation sites to treat the wastewater. Additionally, the CleanSET technology relies only on electricity so the small, distributed operations can be powered using electricity from renewable energy sources (e.g., solar photovoltaic panels, wind turbines, etc.) so access to the electrical grid may not be needed.

The proposed feed-agnostic process takes advantage of electrochemical oxidation of organic compounds² and, as we have demonstrated, is more energy efficient for generating H_2 than other competing technologies (i.e., water electrolysis and reforming). It also represents a novel way to electrify the aging wastewater treatment infrastructure. For example, our proprietary RuO_2 -thin film electrode selectively oxidizes the organic compounds present in wastewater while generating H_2 as a side product (e.g., $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$, -0.02 V and 7.7 kWh/kg H_2) at lower energy requirements than water electrolysis ($H_2O \rightarrow 1/2 O_2 + H_2$, -1.18 V and 38.3 kWh/kg H_2).³⁻⁴

2.0 Experimental Approach

We demonstrated the performance of the CleanSET process for the removal of COD and simultaneous H₂ generation as a function of cell voltage (1 to 10 V), composition/pH of the wastewater at room temperature, and atmospheric pressure in batch and continuous flow electrolyzers. The electrochemical performance, such as half-cell potential, full cell potential, and current, were controlled and recorded by an AMETEK VersaSTAT 3.

We synthesized different electrolytes with a constant 0.14 M concentration of additive salts such as sodium hydroxide, sodium carbonate, and sodium phosphate-buffered saline to evaluate the role of pH on electrochemical performance. We synthesized and evaluated different iterations of Ru-based electrodes and their performance were compared against that of the baseline RuO₂ thin film system in terms of current density (i.e., current normalized by the cross-sectional electrode area) and specific area (i.e., current normalized by the total mass of Ru present in the electrode).

The composition of the product waters after CleanSET processing were analyzed via high-performance liquid chromatography, liquid chromatography, inductively coupled plasma spectroscopy, and Hach analysis for COD and ammonia concentration. The gas phase was analyzed via gas chromatography to determine H₂ and carbon dioxide production. We built a preliminary techno-economic analysis model to compare the performance and costs against current direct wastewater discharge costs to identify key areas of optimization.

3.0 Results and Discussion

3.1 Electrode and Condition Screening

Figure 1 summarizes the performance of the different Ru-based electrodes where the number indicates different iterations and modifications. As seen in Figure 1, the modifications affected the electrodes performance (i.e., current density and specific current) at both 1.5 V and 2.0 V versus a reversible H₂ electrode (vs RHE) in the presence and absence of wastewater.

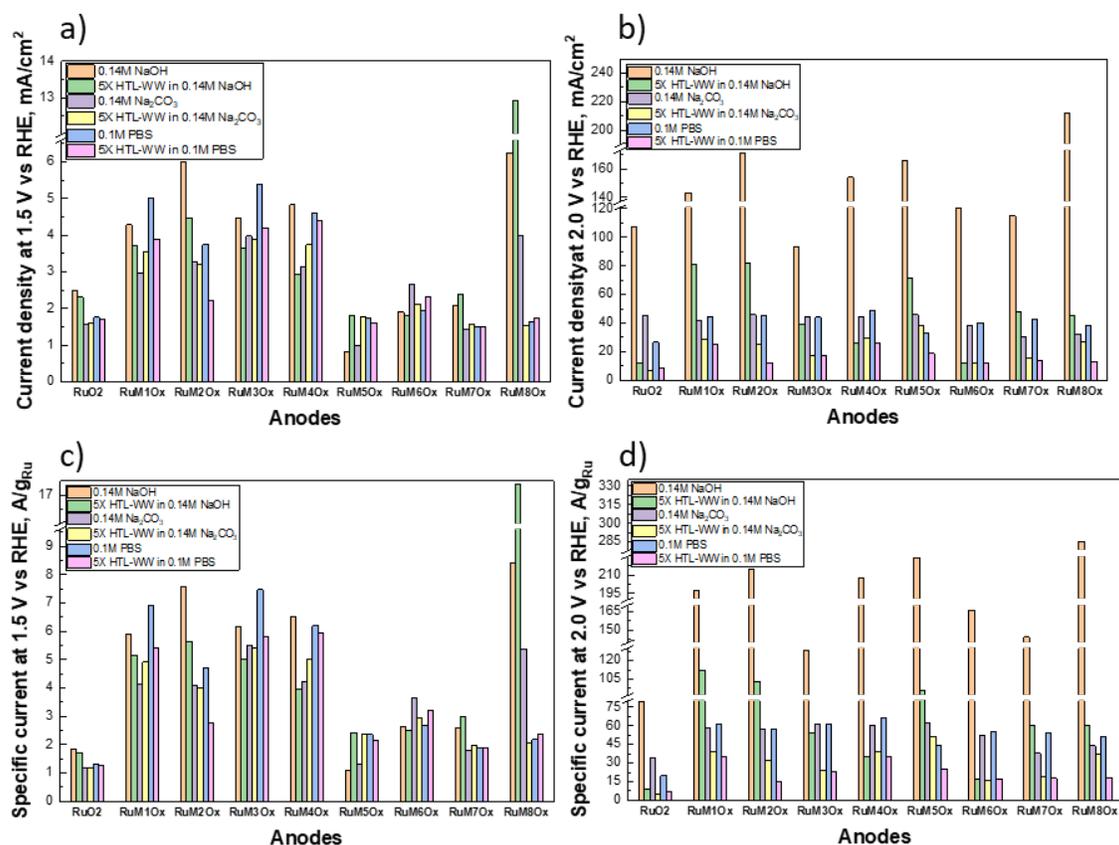


Figure 1. Electrochemical Performance of Ru-based Electrodes in Different Electrolytes with and without Hydrothermal Liquefaction (HTL)-Derived Wastewater at 1.5 and 2.0 V versus RHE. The activity is normalized as (a, b) current density (mA/cm²), and (c, d) specific current (mA/g Ru).

More interestingly, the modifications improved the current density (normalized by cross-sectional area of the electrode) by up to a factor of 4 and the specific current (normalized by the mass of Ru) by up to a factor of 8. The largest increases were observed at 1.5 V vs RHE with the sodium hydroxide system with RuOx8. However, all the electrodes show an increase of activity by factors of 2 and 4 for current density and specific current, respectively. Hence, the modifications resulted in the improvement of the HTL-derived wastewater treatment. Future work will focus on optimizing the modifications for different electrolytes and wastewaters.

3.2 Wastewater Screening

Performance of the baseline RuO₂ system then was tested for low-temperature electrochemical oxidation in a continuous-flow cell at 2.5 V vs RHE using real wastewaters derived from HTL from different sources. Table 1 shows that CleanSET system was able to electrochemically oxidize all the HTL-derived wastewaters treated and simultaneously produce H₂. However, electrochemical performance, such as COD removal, current efficiency (CE), and kilogram of H₂ produced per kilogram of COD removed differ for each wastewater feedstock evaluated. Whereas all the systems were able to generate H₂ at similar production costs, 88.5–108 kWh/kg H₂, the energy required to remove COD decreased by a factor of 3.5 (from 60.8 to 16.6 kWh/kg COD). The changes in COD removal were most likely caused by a change in the CE of the system from 88.6% to 22.3%. The charge-to-failure changed from 11,484 to 23,310 C suggesting that the composition of the wastewater affects the degradation of the RuO₂ baseline electrode.

Future work will focus on processing the wastewaters at different potentials to optimize COD removal, H₂ production, CE, and charge-to-failure with different HTL-derived wastewaters. Once an optimum set of conditions are found, the best electrode iterations identified in the previous section will be tested to evaluate improvements in performance.

Table 1. Performance of the Baseline RuO₂ system for Different Wastewaters Derived from HTL of Different Sources (e.g., spirulina, wood, sludge). The experiments were performed at a constant 2.5 V vs RHE and with equimolar concentrations of buffer. The HTL-derived wastewaters were diluted at constant COD concentration of 12,000 ppm. The experiments were performed in a continuous-flow cell.

PWH	Charge-to-Failure C	COD Removal, kWh/kg COD	CE ^a for COD Removal, %	H ₂ Production, kWh/kg H ₂	Faradaic Efficiency ^b for H ₂ Production %	Kilograms of H ₂ Produced per Kilogram COD Removed
AECOM	13,950	16.6	88.6	94.9	100	0.175
Spirulina	12,834	60.8	22.3	96.1	100	0.633
Sludge AAU	11,484	43.2	45.1	99.8	100	0.433
Sludge PNNL	21,600	60.8	36.6	108	89.5	0.563
Digestate	20,646	37.1	72.5	86.8	100	0.427
Wood AAU	23,310	63.7	21.1	88.5	92.7	0.720

^a Current efficiency towards COD removal instead of other oxidation reactions.

^b Faradaic efficiency towards H₂ production instead of other reduction reactions.

3.3 Tecno-Economic Analysis

Figure 2 shows results from the sensitivity analysis performed on the key performance metrics of the electrochemical systems. This analysis reveals that decreasing the electrolyzer cost (to <\$225/m²) or power consumption (to <10 kWh/kg COD) as well as increasing the current density (to >50 mA/cm²) will make the levelized cost of wastewater electrolysis and simultaneously making H₂ cost competitive with the costs associated with direct discharge of the water. Furthermore, increasing the H₂ production from COD (to >0.25 kg H₂/kg_{COD}) will further decrease the levelized cost and even generate revenue. Co-optimizing all four of the

parameters will result in the cost of wastewater electrolysis being lower than that of direct discharge, while simultaneously generating H₂ as a byproduct that has market value.

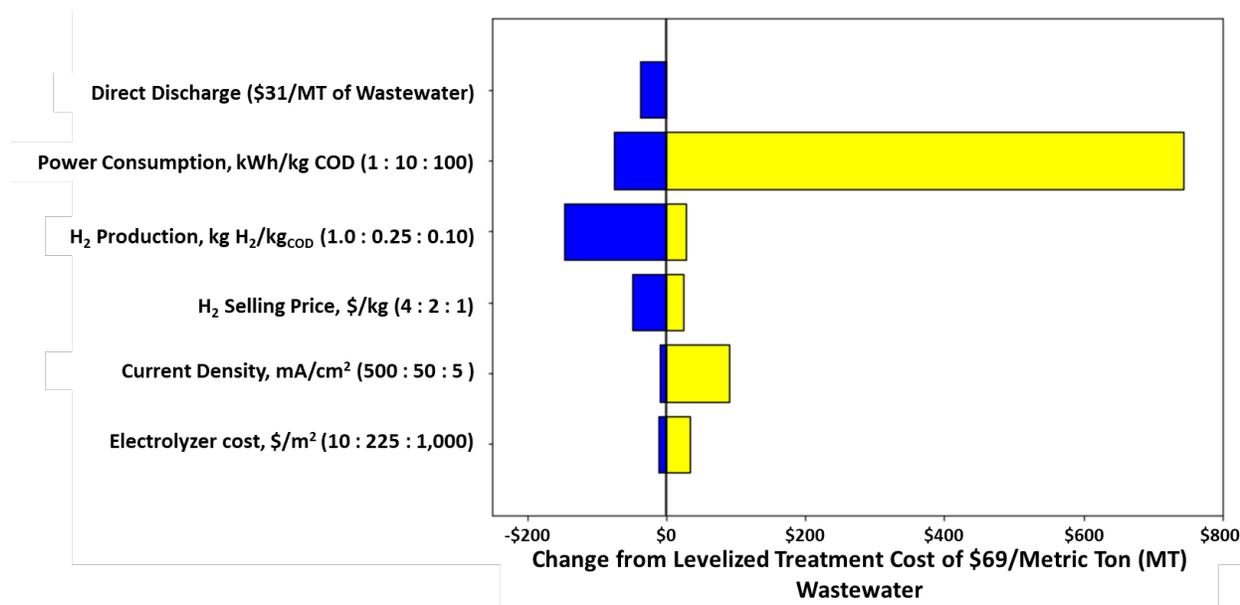


Figure 2. Sensitivity Analysis Performed on the Cost of Wastewater Electrolysis for Simultaneous H₂ Production. The plot represents the changes from the levelized costs in \$/MT for the main performance parameters.

Future work will focus on updating the cost analysis with the performance of the best electrode iteration to assess the key areas of optimization.

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