Wastewater Electrolysis Cell for Environmental Pollutants Degradation and Molecular Hydrogen Generation

Thesis by

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Dedicated to…

my lovely wife Soojeon

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ABSTRACT

This study proposes a wastewater electrolysis cell (WEC) for on-site treatment of human waste coupled with decentralized molecular H_2 production. The core of the WEC includes mixed metal oxides anodes functionalized with bismuth doped TiO_2 (BiO_x/TiO_2). The BiO_x/TiO_2 anode shows reliable electro-catalytic activity to oxidize Cl^- to reactive chlorine species (RCS), which degrades environmental pollutants including chemical oxygen demand (COD), protein, NH_4^+, urea, and total coliforms. The WEC experiments for treatment of various kinds of synthetic and real wastewater demonstrate sufficient water quality of effluent for reuse for toilet flushing and environmental purposes. Cathodic reduction of water and proton on stainless steel cathodes produced molecular H_2 with moderate levels of current and energy efficiency. This thesis presents a comprehensive environmental analysis together with kinetic models to provide an in-depth understanding of reaction pathways mediated by the RCS and the effects of key operating parameters. The latter part of this thesis is dedicated to bilayer hetero-junction anodes which show enhanced generation efficiency of RCS and long-term stability.

Chapter 2 describes the reaction pathway and kinetics of urea degradation mediated by electrochemically generated RCS. The urea oxidation involves chloramines and chlorinated urea as reaction intermediates, for which the mass/charge balance analysis reveals that N_2 and CO_2 are the primary products. Chapter 3 investigates direct-current and photovoltaic powered WEC for domestic wastewater treatment, while Chapter 4 demonstrates the feasibility of the WEC to treat model septic tank effluents. The results in Chapter 2 and 3 corroborate the active roles of chlorine radicals ($Cl\cdot/Cl_2^-\cdot$) based on *iR*-compensated anodic

potential (thermodynamic basis) and enhanced pseudo-first-order rate constants (kinetic basis). The effects of operating parameters (anodic potential and [Cl^-] in Chapter 3; influent dilution and anaerobic pretreatment in Chapter 4) on the rate and current/energy efficiency of pollutants degradation and H_2 production are thoroughly discussed based on robust kinetic models. Chapter 5 reports the generation of RCS on $Ir_{0.7}Ta_{0.3}O_y/Bi_xTi_{1-x}O_z$ hetero-junction anodes with enhanced rate, current efficiency, and long-term stability compared to the $Ir_{0.7}Ta_{0.3}O_y$ anode. The effects of surficial Bi concentration are interrogated, focusing on relative distributions between surface-bound hydroxyl radical and higher oxide.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES