A Novel Electrochemical Filtration Treatment of Antibiotics Contaminated Wastewater

Overview

A laboratory study will be conducted in this project to explore a novel reactive electrochemical membrane (REM) system to treat mixed antimicrobial contaminants that are commonly present in wastewater, including tetracycline (TC), sulfadimethoxine (SDT), and ciprofloxacin (CIP), which enriches the population of resistant microorganisms and affect the functional diversity of natural microbial communities. The REM system involves a Ti₄O₇ ceramic membrane that serves as both an electrode and a membrane. REM systems can be operated in different electrolytes, pH, voltages and flow rates to achieve efficient and cost-effective removal and degradation of mixed antibiotic contaminants.

Background

Electrochemical treatment is one approach that is nearly universally applicable, and thus may treat mixed contaminants all together without being interfered by the presence of multiple chemicals. Various mechanisms take effect in electrochemical treatment processes, dependent on applied voltage and conditions, including redox reactions by direct electron transfer or indirect free radical reactions and sorption/retention by electric filed. Electrooxidation is one most common electrochemical treatment process that oxidizes contaminants by either direct electron transfer or by hydroxyl radicals generated on anode, and has been proven effective for most organic contaminants.

Ti₄O₇ is one of the Magnéli phase titanium sub-oxides that have recently been explored as promising candidates for electrochemical applications because of their high conductivity, chemical inertness, and low cost of production. These materials comprise a series of distinct compounds having the generic formula TiₙO₂ₙ₋₁ (3< n <10), while Ti₄O₇ has the greatest electric conductivity, comparable to graphite. Ti₄O₇ is robust in aggressive solution media, such as highly acidic and basic solutions, and has been widely used in cathodic protection, fuel cell, and as supporting materials for coating various materials including noble metals and carbon. Ti₄O₇ can serve as an ideal electrode in electrochemical wastewater treatment, being stable with respect to water decomposition under anodic (> 2.0 V vs SCE) and cathodic (~ -1.4 V vs SCE) polarizations. Studies have shown that Ti₄O₇ behaves as typical “non-active” electrodes and thus produces physisorbed ·OH via water oxidation, and is also active for direct electron transfer reactions.

Figure 1. (Left) The photos and SEM images of porous Ti₄O₇; (Right) Results of Hg intrusion porosimetry analysis of pore size distribution.
Traditional electrooxidation reactors usually utilize parallel plates as electrodes operated in a batch mode. Our preliminary study already demonstrated success removal of tetracycline in a traditional batch experiment with porous TiO$_2$ served as anode (Figure 2). However, such a hydrodynamic configuration promotes a thick boundary layer (~100 μm) on the electrode surface that limits mass transfer$^6$. Recent studies on overcoming such mass transfer limits have focused on porous electrodes, such as membranes, operated in a filtration mode$^5$-$^7$. The filtration mode significantly improves mass transfer via convection-enhanced dispersion. In addition, the porous structure in the 3-D electrode provides abundant electrochemically active surfaces for reactions. Furthermore, if the 3-D electrode material can strongly adsorb the contaminants, the electrooxidation efficiency can be further improved with the contaminants concentrated at higher concentrations on the electrode surfaces. Therefore, the adsorptive 3-D electrode system involves filtration, sorption and electrooxidation in a synergistic manner, which offers a transformative technology that may potentially address a wide range of challenges in wastewater treatment and recycling.

![Figure 2](image)

Figure 2. (Left) Setup of electroxidation operated in batch mode; (Right) Removal of tetracycline using TiO$_2$ electrode as anode in bath study.

**Work plan and intended results**

**Task 1. Antibiotic Electro-filtration and oxidation pathway**

A laboratory scale REM system with more than 5 L/hr treatment capacity will be assembled as illustrated in Figure 3. Porous TiO$_2$ ceramic membrane will work as both anode and cathode physically isolated by silicon rings. Antibiotic mixed solution will be delivered through the system via a peristaltic pump. This REM system will be operated as a 3-D anode to remove and degrade antibiotics in water. To this end, a solution containing 10 μM TC, 10 μM SDT, 10 μM CIP and 100 mM Na$_2$SO$_4$ as supporting electrolytes is passed through the REM that is operated as anode at a potential ranging in 1.0~3.0 V vs. SHE with a flow rate varies from 5 ml/min to 100 ml/min. The concentration of each antibiotic and their degradation intermediates will be analyzed by UPLC-MS/MS. Changes of total organic carbon (TOC) content will be monitored during operation and used to calculate current efficiency and energy consumption under each anode potential-flow rate combination.

**Task 2. Electrochemical removal of antibiotics in spiked WWTP effluent**

To explore the efficiency of REM system in treating real wastewater samples, 10 μM TC, SDT, and CIP will be spiked into water collected from wastewater treatment plant (WWTP). REM system will be operated under the most cost-efficient anode potential and flow rate combination screened in task 1. The
concentrations of antibiotics and TOC will be recorded as discussed above to assess how organic matter and saline ions contained in wastewater can affect the filtration and oxidation efficiency. Therefore, in task 2, we are going to determine the practicality of REM system for removal of antibiotics from wastewater matrix.

Figure 3. The dead-end filtration REM unit consisting of (1) Titanium caps, (2) Ti$_4$O$_7$ membrane anode/cathode, and (3) silicone rubber ring separator.

**Task 3. Toxicity Assessment**

The major consequence of antibiotics release in natural environment is the selection of resistant bacteria and the evolution of resistance genes. To evaluate the antimicrobial activity of influent and effluent samples, the disk agar-diffusion biocidal susceptibility method will be performed by dropping samples to *Escherichia coli* (*E. coli*) cells inoculated on Lysogeny broth (LB) plate. Toxicity of filtration products will be compared with the influent antibiotic sample by measuring the diameters of their inhibition zone. Complete detoxified sample will not show visible inhibited area yet it is supposed to be seen around influent sample treated area.

**References**