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# Effects of anodic oxidation of a substoichiometric titanium dioxide reactive electrochemical membrane on algal cell destabilization and lipid extraction

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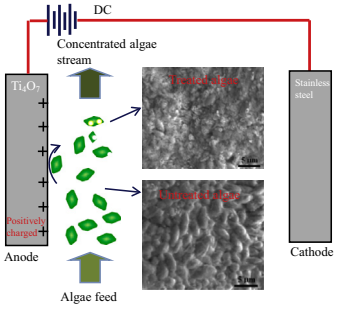
## HIGHLIGHTS

- $Ti_4O_7$ REM could oxidize algal cells under anodic polarization.
- The anodic oxidation led to algal cell destabilization and damage.
- The lipid extraction efficiency was enhanced with the destabilized algal cells.
- REM filtration may potentially incorporate cell pretreatment for enhancing lipid extraction.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Efficient algal harvesting, cell pretreatment and lipid extraction are the major steps challenging the algal biofuel industrialization. To develop sustainable solutions for economically viable algal biofuels, our research aims at devising innovative reactive electrochemical membrane (REM) filtration systems for simultaneous algal harvesting and pretreatment for lipid extraction. The results in this work particularly demonstrated the use of the $Ti_4O_7$-based REM in algal pretreatment and the positive impacts on lipid extraction. After REM treatment, algal cells exhibited significant disruption in morphology and photosynthetic activity due to the anodic oxidation. Cell lysis was evidenced by the changes of fluorescent patterns of dissolved organic matter (DOM) in the treated algal suspension. The lipid extraction efficiency increased from 15.2 ± 0.6 g-lipid g-algae$^{-1}$ for untreated algae to 23.4 ± 0.7 g-lipid g-algae$^{-1}$ for treated algae ($p < 0.05$), which highlights the potential to couple algal harvesting with cell pretreatment in an integrated REM filtration process.



## 1. Introduction

Algal biomass is the third generation feedstock for biodiesel or biofuel production. However, expensive algal harvesting, biomass

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pretreatment, and lipid extraction represent the major hurdles for producing cheap biofuels at industrial scales. Typical structures of algal cell walls contain uronic acids, glucosamine, and polysaccharides that provide cells with formidable defense against environmental conditions (Scholz et al., 2014). Extraction of biolipid that is usually located in globules or bound to cell membranes often involves the use of organic solvents such as n-hexane, chloroform and methanol because of their high selectivity and solubility towards lipids (Cheng et al., 2011; Lee et al., 2010). An efficient extraction requires that the solvent penetrates completely into the biomass and physically contacts the lipid (e.g., triglycerides-esters) located in the photosynthetically active membranes. Therefore, cell disruption is a necessary pretreatment step prior to lipid extraction.

Cell disruption and lipid extraction processes can be energy-intensive, time-consuming and costly. Current cell disruption methods include mechanical and non-mechanical techniques. Mechanical techniques destroy the cell wall using non-specific solid and liquid shear forces or energy transfer through heating and waves (Günerken et al., 2015), which include compression, high-pressure homogenization (HPH) (Park et al., 2015), ultrasonic bath (Greenly and Tester, 2015), autoclave (Lee et al., 2010), bead mill, microwave and magnetic stirring (Cravotto et al., 2008; Virot et al., 2008); while non-mechanical techniques include chemical lysing using enzymes or chemical agents and osmotic shock (Demuez et al., 2015; Harun et al., 2011). Selective interactions between chemical agents (enzymes, antibiotics, chelating agents, chaotropes, detergents, hypochlorite, acids and alkali) and the cell wall or membrane are designed to facilitate biolipid leaching (Günerken et al., 2015). Life-cycle assessment (LCA) of biofuel production from microalgae feedstock determined that cultivation, harvesting and lipid extraction accounted for up to 90% of the total process energy (Brentner et al., 2011). Further decreasing solvent consumption, preventing pollution, and enhancing lipid production (efficiency) are the major challenges in this field.

Reactive electrochemical membranes (REMs) based on electrochemical advanced oxidation processes (EAOPs) are a cutting-edge class of membranes that hold great promise in revolutionizing water/wastewater treatment and bioseparation processes (Zaky and Chaplin, 2013). REMs are porous three-dimensional electrodes that can provide anodic oxidation in addition to physical separation (Liu and Vecitis, 2011; Zaky and Chaplin, 2013). Hydroxyl radicals ($OH^{\cdot}$) form via water oxidation when the REM is anodically polarized (Zaky and Chaplin, 2013). Recent work has shown that porous substoichiometric $TiO_2$ (e.g., $Ti_4O_7$) anodes were operated in a cross-flow filtration mode, leading to a combination of microfiltration and electrochemical oxidation (Zaky and Chaplin, 2014, 2013). By converting $TiO_2$ to $Ti_4O_7$ (usually at temperatures above 900 °C under a $H_2$ atmosphere) (Chen et al., 2002), electrical conductivity can be increased from $10^{-9}\ \Omega^{-1}\ cm^{-1}$ ($TiO_2$) as high as $166\ \Omega^{-1}\ cm^{-1}$ ($Ti_4O_7$). Thus, the REM has shown promising antifouling properties, as adsorbed organic foulants were shown to be removed via the anodic oxidation process (Zaky and Chaplin, 2014). The micrometer-sized pores of the REM produced a high electroactive surface area and advection-enhanced mass transfer rates approximately 10-fold higher than those obtained in traditional flow-by mode. Past research with REMs has focused largely on dissolved compound oxidation, but their ability to separate or pretreat microbial cells such as algae is unexplored. Meanwhile, it is also important to compare the cost effectiveness with traditional membranes or other separation techniques.

Our overall research aim is to explore substoichiometric $TiO_2$ REMs for efficient algal harvesting and pretreatment while maintaining high flux during filtration and excellent stability under anodic and cathodic polarization. In this work we specifically explored the effect of REM anodic potential on algal cell integrity and the effect of algal disruption on lipid extraction efficiency. Our hypothesis is that algal cells, upon exposure to polarized REM surfaces, could be oxidized and destabilized, which may positively increase the downstream lipid extraction efficiency if properly controlled in terms of exposure time and REM polarization. The produced $OH^{\cdot}$ and other oxidative species will likely contribute to the algal cell oxidation. The oxidative disruption of cell integrity was evaluated using various characterization techniques (e.g., optical and electron microscopes, atomic force microscope, measurements of photosynthetic activity and oxygen production), and the influence of cell disruption on the biolipid extraction efficiency is assessed in order to shed new insights into the potential synergistic benefits of the REM in algal harvesting and pretreatment.

## 2. Methods

### 2.1. Substoichiometric $TiO_2$ REM

The REM used in this study is a 10-cm long Ebonex® one-channel tubular electrode with the outer and inner diameters of 10 mm and 6 mm, respectively (Vector Corrosion Technologies, Inc.). Ebonex is a Magneli phase suboxide of $TiO_2$, which consists primarily of $Ti_5O_9$ and $Ti_4O_7$. Synthesis and characterization of the REM was reported previously (Zaky and Chaplin, 2013), which showed an average pore diameter of 1.70 ± 0.02 μm, a porosity of 30.7 ± 2.8% and a specific surface area of $2.8 \pm 0.7\ m^2\ g^{-1}$. As received Ebonex electrodes were subjected to a high temperature reduction treatment (1 atm $H_2$, 1050 °C, 4 h) to produce high purity $Ti_4O_7$. The X-ray Diffraction pattern and scanning electron microscope (SEM) data were acquired to analyze crystallinity and morphology of the prepared REM.

### 2.2. Algal cultivation and preparation

Oleaginous algae (*Scenedesmus dimorphus* or *S. dimorphus*) were cultivated in the modified Bold's Basal Medium (MBBM) with details reported in our previous works (Agbakpe et al., 2014; Ge et al., 2014, 2015). Briefly, *S. dimorphus* was cultivated in 2-L Erlenmeyer flasks and at the room temperature (25 ± 1 °C), with $CO_2$ fed at a rate of $8.5 \times 10^{-4}$ L-$CO_2$ $min^{-1}$·(L-medium)$^{-1}$. The light–dark cycle (12 h/12 h) was maintained at a photon flux of approximately 4200 mW $m^{-2}$ as measured by a spectroradiometer (Spectral Evolution, SR-1100). The algal concentration (g $L^{-1}$) was characterized by the dry cell weight (DCW). The steady-state algal concentration after 14-day incubation was around 1.4 g $L^{-1}$, which was then used for algal harvesting experiments and other tests.

### 2.3. REM exposure experiments

To study the cell damage as a function of the charge passed through the REM, a batch electrochemical reaction cell was used to simulate the algal cell exposure with REM during the cross-flow filtration process. The reaction cell was filled with the algal suspension, and the REM was positioned in the middle of the reactor (anode) and was surrounded by a stainless steel circular mesh (cathode) with a spacing of 2.5 cm. The REM was operated at a constant current (100–500 mA) using a DC power supply (Proteck P6035, Tempe, AZ) corresponding to cell voltages between 10 and 20 V and for different times (30–120 min) to achieve different algal disruption. The effective exposure surface area of the REM was 25.4 $cm^2$. The conductivity of the pure algal medium was 1040 ± 5 μS $cm^{-1}$, whereas the conductivity of the algal medium with growing algal cells ranged from 1580 ± 20 to 2520 ± 10 μS $cm^{-1}$ for newly inoculated algal cultures and cultures after 14 days of incubation, respectively.