



Electro-oxidation of tetracycline by a Magnéli phase Ti_4O_7 porous anode: Kinetics, products, and toxicity



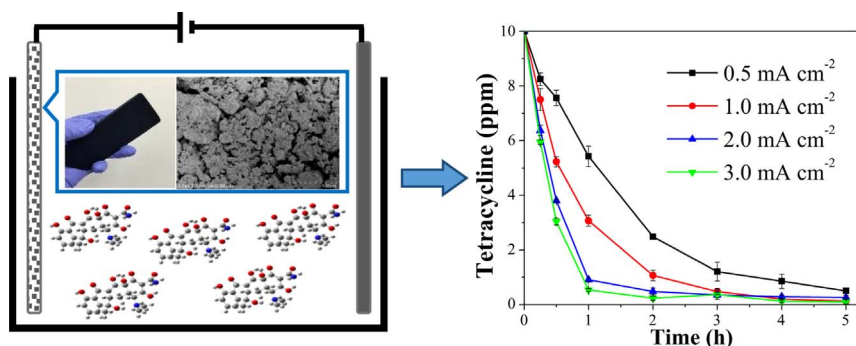
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GRAPHICAL ABSTRACT



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ABSTRACT

The goal of this study is to evaluate Magnéli phase titanium oxide (Ti_4O_7) as an anode material for potential application in electrochemical oxidation of organic pollutants in water. The removal of tetracycline (TC) was systematically investigated in terms of kinetics, reaction mechanisms and pathways, and multi-species toxicity. Application of 0.5–3 mA cm⁻² current densities resulted in > 90% total removal of TC over a wide range of initial concentrations from 1 ppm to 50 ppm with half-lives between 28 mins and 75 mins. The oxidation mechanisms were further elucidated using salicylic acid (SA) as a hydroxyl free radical trap. At least 40% of total TC removal was attributable to reactions mediated by hydroxyl radicals, which were generated on Magnéli phase Ti_4O_7 at a rate of 2×10^{-9} mol cm⁻² min⁻¹ under 0.5 mA cm⁻² applied current density. Tests on *Escherichia coli* culture indicated that electro-oxidation of TC by Magnéli phase Ti_4O_7 anode successfully reduced the original antimicrobial activity to a level below detection limit. However, for freshwater micro algae *Scenedesmus obliquus*, inhibitory effects persisted in the first couple of hours and then dramatically reduced during the last stage of treatment, likely due to intermediate products that later mineralized and detoxified. Reaction pathways were proposed based on the data of high-resolution mass spectrometry, and oxidation products with antibiotic potency similar to or greater than TC were identified in 1 h treatment sample, but not detectable in the end-of-treatment solution.

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1. Introduction

Electrochemical processes are considered as the next-generation technologies for treating contaminated water owing to its ability to degrade a wide spectrum of pollutants [1]. Unlike traditional advanced oxidation processes, electrochemical oxidation requires no addition of chemicals, and can be operated under ambient conditions. Electrochemical treatments are versatile, and therefore adaptive to various decentralized wastewater treatments, such as ballast water and wastewater from mobile facilities and rural homes and farms [2,3]. However, its application has been hindered due to the relatively high cost, limited lifetime of electrodes, and possibility of releasing toxic metals during the treatment [4]. After continuous operation, passivation may occur on electrode surface, where certain chemical species gradually accumulate and eventually cover the surface, blocking it from further reaction [5]. Boron-doped diamond (BDD) electrode shows exceptional resistance to electrode passivation, and has been demonstrated to degrade refractory compounds efficiently, yet their costs are relatively high [6,7]. SnO₂- or PbO₂- based electrodes are economically feasible, but are at the risk of releasing toxic metals [8]. Therefore, the environmental application of electrochemical treatment processes is hinged on the availability of appropriate electrode materials that is cost-effective, durable, and environmentally benign.

Magnéli phase titanium suboxides are substoichiometric titanium oxides with the general formula of Ti_nO_{2n-1}, where n is an integer between 4 and 10 (i.e., 4, 5, 6, and 8) [9]. Magnéli phase titanium suboxides are typically manufactured by first heating titanium dioxide, a cheap, abundant and non-toxic metal oxide, to over 900 °C and then allowed to cool down using reducing agents [10,11]. Among various compositions produced, Ti₄O₇ exhibits the highest conductivity (1500 S cm⁻¹), comparable to that of graphite [12], as well as resistance to aggressive chemical conditions and corrosion [13]. High conductivity, chemical stability and relatively low production cost make Magnéli phase titanium suboxide attractive as a promising electrode material. Therefore, the application of Magnéli phase titanium oxides has been intensively studied in the fields of chlorine generation, battery, fuel cell and cathodic protection.

The study on the use of Magnéli phase Ti₄O₇ in electrochemical oxidation for potential environmental applications is rather limited, despite its outstanding electrochemical properties. In addition to the many merits mentioned above, Magnéli phase Ti₄O₇ has high overpotential for hydrogen (~ -0.8 V vs. RHE) and oxygen (~ 2.5 V vs. RHE) evolution [14], which allows for direct electrochemical treatment of pollutants in water over a wide range of redox potentials. Trichloroethylene (TCE) was removed from aqueous solution by oxidation with Magnéli phase Ti₄O₇ as the anode [15]. Removal of p-substituted phenol was achieved on Ti₄O₇ porous ceramic anode operated in either batch or cross-flow filtration mode [16,17].

There is thus a great need to evaluate the use of Magnéli phase titanium oxides in anodic oxidation of various pollutants, and explore associated reaction behaviors and mechanisms to support its potential applications in water/wastewater treatment. This study systematically investigated the removal and transformation of tetracycline, a model antibiotic widely present in aqueous environments, on a Magnéli phase Ti₄O₇ anode. The electrode was synthesized by high-temperature reduction of TiO₂ and sintering, and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Hg porosimetry. Electrochemical oxidation of tetracycline on Ti₄O₇ anode was investigated under various operation conditions. The rate behavior was examined and modeled, and the products were identified, with reaction mechanisms explored via free radical probing approach. The toxicity of the tetracycline solution, without and with electro-oxidation treatment for different durations, was assessed using *Escherichia coli* and green algae *Scenedesmus obliquus* as receptors.

2. Materials and methods

2.1. Preparation of Magnéli phase Ti₄O₇ electrode

Magnéli phase Ti₄O₇ was produced through high temperature sintering. Magnéli phase Ti₄O₇ powder was produced by heating titanium oxide nano powder at 950 °C and subsequently reduced under a hydrogen flow. The resulted Magnéli phase Ti₄O₇ powder was mixed (0.5%, m/m) with polyacrylamide/polyvinyl alcohol (95/5, m/m) and 5% of water. The spray drying process was performed by a PZL-15 spray drying granulation apparatus (YCdry, Inc., China) with a heating power at 54 kW to form granules (40~80 mesh). Then the granulates were pressed at 30 MPa for 5 min in a mold to form ceramic material before sintering in vacuum at 1350 °C for 11 h.

2.2. Material characterization

Scanning electron microscopy (SEM) of Magnéli phase Ti₄O₇ material was taken on a Hitachi's S-4800 FE-SEM system (Hitachi, Japan). The crystal structures of the samples were characterized by a PANalytical X'Pert PRO MRD X-ray diffractometer (XRD) (PANalytical, Netherlands) at an incidence angle of 2.5°. The XRD scans were recorded with a CuKα1 radiation (λ = 1.541 Å) in the 2θ range from 20° to 80° with a step size of 0.020° and a step time of 1 s. The pore structure and porosity of the Magnéli phase Ti₄O₇ ceramic material was characterized using Micromeritics AutoPore IV 9500 mercury porosimetry (Norcross, GA).

Linear scan voltammetry (LSV) was conducted with a Ti₄O₇ ceramic plate (1 cm × 1 cm) as the anode, a platinum foil (2 cm × 2 cm) as the counter electrode, and a silver chloride electrode (SCE) in an electrolysis cell containing 0.5 M H₂SO₄ background electrolyte, at a linear scan rate of 100 mV s⁻¹ driven by a CHI 660E electrochemical workstation (Austin, TX)

2.3. Chemicals

Chemicals used in this study were reagent or higher grade. Tetracycline (TC), salicylic acid (SA), 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA), sodium sulfate (Na₂SO₄), HPLC grade acetonitrile, and formic acid were obtained from Sigma-Aldrich (St. Louis, MO). All solutions were prepared in Barnstead Nanopure water (≥ 18 MΩ cm⁻¹ at 20 °C).

2.4. Electro-oxidation procedure

Electrochemical oxidation experiments were conducted in an electrolytic cell (10 cm × 5 cm × 2.5 cm) with a Ti₄O₇ ceramic plate or a Ce-PbO₂ plate (8 cm × 5 cm) as the anode and a 304 stainless steel plate of the same size as the cathode. The thickness of the anode is 3 mm. The electrical connection was made directly from DC power source to electrodes using copper wire and alligator clamps. The Ce-PbO₂ electrode was prepared as previously described [8]. In each treatment, 100 mL of a solution containing 1, 10, or 50 ppm tetracycline and 100 mM Na₂SO₄ as background electrolyte was placed in the electrolytic cell with continuous stirring. A direct current was supplied at different current density (0.5, 1.0, 2.0 or 3.0 mA cm⁻²) by a controllable DC power source (Electro Industries Inc., Monticello, MN), while the anode potential was monitored using a CHI 660E (CH Instruments, Inc., Austin, TX) electrochemical workstation with silver chloride electrode placed in the cell. Triplicate samples were withdrawn from each reactor at pre-selected time intervals and stored at 4 °C for subsequent analysis. The energy consumption for degrading one mole of TC molecules was calculated according to Eq. (1) [18]:

$$E = 10^{-3} \times (V \times I \times t) / M \quad (1)$$

where:

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