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Photoelectrochemical degradation of acetaminophen and valacyclovir using nanoporous titanium dioxide

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ABSTRACT

Electrochemically treated nanoporous TiO_2 was employed as a novel electrode to assist in the photoelectrochemical degradation of acetaminophen and valacyclovir. The prepared electrode was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Cyclic voltammetry (CV), Mott-Schottky plots, ultraviolet-visible light (UV-vis) absorbance spectroscopy, and a total organic carbon (TOC) analyzer were employed to investigate the photoelectrochemical degradation of acetaminophen and valacyclovir. The results indicated no obvious removal of acetaminophen and valacyclovir over 3 h when separate photochemical degradation and electrochemical oxidation were employed. In contrast, acetaminophen and valacyclovir were rapidly eliminated via photoelectrochemical degradation. In addition, electrochemically treated nanoporous TiO_2 electrodes significantly enhanced the efficacy of the photoelectrochemical degradation of acetaminophen and valacyclovir, by 86.96% and 53.12%, respectively, when compared with untreated nanoporous TiO_2 electrodes. This enhanced performance may have been attributed to the formation of Ti^{3+}, Ti^{2+}, and oxygen vacancies, as well as an improvement in conductivity during the electrochemical reduction process. The effect of temperature was further investigated, where the activation energy of the photoelectrochemical degradation of acetaminophen and valacyclovir was determined to be 9.62 and 18.42 kJ/mol, respectively.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have been considered as emerging pollutants over the last few decades, which have a low concentration in the environment and typically do not exhibit acute toxicity; however, they may impart potential damage to human and ecological health due to long-term exposure [1–5]. Acetaminophen, also referred to as paracetamol, is one of the most frequently used over-the-counter analgesic pain relievers and antipyretic fever reducers worldwide [6,7]. It is generally safe for use at recommended doses, but may be toxic when overdosed [8]. In recently years, acetaminophen has garnered much attention due to its propensity for inducing liver and kidney damage [9,10]. There have been many reports of acetaminophen being detected in rivers, ambient waterways, the influents of wastewater treatment plants, and the effluents of sewage treatment plants [11–13]. Valacyclovir is an oral antiviral drug, which is active against the herpes viruses. It is used to treat infections of shingles (herpes zoster), genital herpes (herpes simplex genitalis), and cold

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sores (herpes labialis) [14]. Because acetaminophen and valacyclovir are of growing concern, a viable approach is urgently required for their effective removal from wastewater.

A number of biological, physical, and chemical methods have been introduced to eliminate organic pollutants from wastewater [15–22]. Among them, advanced oxidation processes (AOPs), particularly photochemically, electrochemically and photoelectrochemically related, are very promising [23–27]. A wide range of electrocatalysts and photocatalysts (e.g., Pt, IrO_2, SnO_2, TiO_2, WO_3, C, PbO_2, and ZnO) have been explored for the efficient removal of organic toxic compounds [28–35]. Undoubtedly, TiO_2 is one of the most intensively researched semiconductors due to its unique combination of eminent characteristics, such as high efficiency, non-toxicity, biological and chemical inertness, high stability, environmentally compatibility, and comparative cost effectiveness [31,36–38]. However, TiO_2 does not have the capacity to utilize solar energy effectively, as it is limited by its large band gap (~3.0 eV for rutile and ~3.2 eV for anatase) [39–41]. In addition, due to the large band gap, unmodified TiO_2 has low conductivity and is considered as an inefficient electrocatalyst. Therefore, it is desirable to reduce the band gap in TiO_2 to expand its scope of applications in photochemistry and photoelectrochemistry. Doping with metal and non-metal elements, such as Au, Ag, Pt, Zn, Fe, Ni, Cu, Co, C, N, F, and S, has shown to enhance visible light absorption in TiO_2 [42–50]. However, complex synthesis processes may limit its practical application and suitability.

Reduced TiO_2 has gained increasing interest recently, and various strategies have been implemented for the reduction of TiO_2 [46,51–54]. In this study, we have successfully synthesized and electrochemically treated nanoporous TiO_2 electrodes for the effective photoelectrochemical degradation of acetaminophen and valacyclovir. Both the kinetics and effect of temperature on the photoelectrochemical oxidation of acetaminophen and valacyclovir have been systemically investigated.

2. Experimental

2.1. Reagents

Acetaminophen (99%) and HPLC-grade valacyclovir hydrochloride (≥ 98%) were purchased from Sigma-Aldrich and Sigma, respectively. Generic tablets of acetaminophen (500 mg) and valacyclovir (500 mg) were obtained from the Thunder Bay Regional Health Sciences Center Pharmacy. Titanium plates were purchased from Alfa Aesar. All other reagents were of analytical grade and were used without further purification. All solutions were prepared with pure water (18.2 MΩ cm), which was generated by a Nanopure Diamond water system. All acetaminophen and valacyclovir solutions were freshly prepared and used within 24 h.

2.2. Fabrication and treatment of nanoporous TiO_2

Highly ordered nanoporous TiO_2 was grown directly onto titanium plates utilizing anodic oxidation. Prior to modification, the titanium plates (1.25 cm × 0.8 cm × 0.5 mm) were sonicated in acetone for 15 min. After being rinsed with pure water, the Ti plates were etched in 18% HCl at 85 °C for 15 min; and subsequently immersed in a solution containing ethylene glycol + 0.3 wt% NH_4F + 2 wt% H_2O in two-electrode cell, to serve as the anode, with a Pt coil as the cathode. The Ti plate was initially anodized at 50 V for 5 h; the rough as-grown nanoporous TiO_2 layer was thereafter peeled off through the application of masking tape. For the second-step, anodization was applied at 50 V for 2 h, whereafter the newly formed nanoporous layer on the Ti plate was again removed using the masking tape technique. A third-step included anodization at 50 V for 15 min, whereupon highly organized nanoporous TiO_2 was eventually generated on the Ti plate. In order to obtain an anatase crystal structure, the Ti plate was annealed at 450 °C for 3 h. An electrochemical reduction treatment was then conducted on the obtained nanoporous TiO_2 in 0.1 mol/L H_2SO_4 at a cathodic current of −5 mA/cm² for 10 min using a three-electrode system, where a Pt coil with a 10-cm² surface area was utilized as the auxiliary electrode, an Ag/AgCl electrode was employed as the reference electrode, and the prepared nanoporous TiO_2 served as the working electrode. The current density was calculated based on the geometric surface area.

2.3. Characterization of fabricated nanoporous TiO_2

The fabricated nanoporous TiO_2 was characterized via field-emission scanning electron microscopy (FE-SEM, Hitachi SU 70). The electrochemical measurements were carried out using a Voltalab 40 Potentiostat (PGZ301). The experimental temperature was maintained using a water bath (20, 40, and 60 °C) or a water/ice mixture (0 °C). Unless specifically mentioned, all experiments were conducted at 20 °C. Cyclic voltammograms (CVs), and Mott-Schottky plots were employed to characterize the electrochemical activity of nanoporous TiO_2. CVs were recorded in a 0.1 mol/L Na_2SO_4 solution at a sweep rate of 20 mV/s; Mott-Schottky plots were measured at a fixed frequency of 500 Hz in a Na_2SO_4 solution (0.1 mol/L).

2.4. Photoelectrochemical degradation of acetaminophen and valacyclovir in 0.1 mol/L Na_2SO_4

All experiments were carried out in a three-electrode cell system. The acetaminophen, valacyclovir and mixed acetaminophen and valacyclovir solutions were deaerated with ultrapure argon gas for 10 min prior to and during the experiments. The UV-visible light was supplied using an ADAC Systems™ Cure Spot™ 50 UV spot lamp with three peaks of emission, at ca. 365, 405 and 435 nm, and two small peaks of emission, at ca. 315 and 330 nm. Light with an intensity of ca. 130 mW/cm² was introduced into the cell through a fiber optic cable, which was affixed 2 cm above the electrode. For the photoelectrochemical degradation of acetaminophen and valacyclovir, the applied electrode potential was 1.0 V vs Ag/AgCl. Samples were extracted at regular intervals, and variations in the concentrations of acetaminophen or valacyclovir, and the TOC of the solution were analyzed. The UV-vis spectra