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Simultaneously photocatalytic treatment of hexavalent chromium (Cr(VI)) and endocrine disrupting compounds (EDCs) using rotating reactor under solar irradiation

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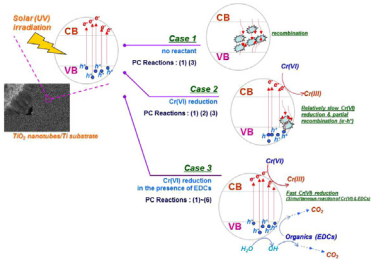
HIGHLIGHTS

- Self-rotating reactor including TiO_2 NTs is applied under solar irradiation.
- Simultaneously photocatalysis of Cr(VI) and EDCs is observed to be up to 95%.
- Photocatalytic reactions of Cr(VI) and EDCs are favorable under acidic pH.
- Charge interaction and hole scavenge between TiO_2 and pollutants are synergy factors.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, simultaneous treatments, reduction of hexavalent chromium (Cr(VI)) and oxidation of endocrine disrupting compounds (EDCs), such as bisphenol A (BPA), 17α-ethinyl estradiol (EE2) and 17β-estradiol (E2), were investigated with a rotating photocatalytic reactor including TiO_2 nanotubes formed on titanium mesh substrates under solar UV irradiation. In the laboratory tests with a rotating type I reactor, synergy effects of the simultaneous photocatalytic reduction and oxidation of inorganic (Cr(VI)) and organic (BPA) pollutants were achieved. Particularly, the concurrent photocatalytic reduction of Cr(VI) and oxidation of BPA was higher under acidic conditions. The enhanced reaction efficiency of both pollutants was attributed to a stronger charge interaction between TiO_2 nanotubes (positive charge) and the anionic form of Cr(VI) (negative charge), which are prevented recombination (electron–hole pair) by the hole scavenging effect of BPA. In the extended outdoor tests with a rotating type II reactor under solar irradiation, the experiment was extended to examine the simultaneous reduction of Cr(VI) in the presence of additional EDCs, such as EE2 and E2 as well as BPA. The findings showed that synergic effect of both photocatalytic reduction and oxidation was confirmed with single-component (Cr(VI) only), two-components (Cr(VI)/BPA, Cr(VI)/EE2, and Cr(VI)/E2), and four-components (Cr(VI)/BPA/EE2/E2) under various solar irradiation conditions.

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1. Introduction

Photocatalysis is one of attractive processes for water splitting hydrogen evolution and water purification. In recent years, a lot of research has been done to synthesize TiO_2 catalysts with different methods, characterized their physical properties, and determined their photocatalytic performances. However, the photocatalysis has been simultaneously criticized as being relatively low efficiency and expensive compared to other processes [1].

Conventional photocatalysts are particles applied in the slurry form. This process is related to the number of active spots in the TiO_2 suspensions. On the other hand, immobilization of particulate photocatalysts on the substrates (e.g., glass and metals) decreases active spots and mass transfer, which bring about operating limitations. Although various types of photocatalyst slurries show many aspects of advantages in terms of their properties, the problem of catalyst recovery remains after reaction [2,3]. For these reasons, the separation (sedimentation and membrane filtration) and fixation (immobilization) are considered to avoid the loss of photocatalyst [4–7]. Among those strategies, the fabrication of self-grown nanotubular TiO_2 on the titanium substrates is the one of immobilization techniques through the anodization [8–11].

The band-gap energy of TiO_2 is well-known (3.2–3.4 eV), which are equivalent to the ranges of UV wavelength (~400 nm); therefore, TiO_2 is excited by UV irradiation. The generation of holes on TiO_2 is strongly oxidizing during the oxidative destruction of dissolved organic pollutants by hydroxyl radicals ($OH^{\bullet}$). TiO_2/UV is famous for the one of advanced oxidation processes (AOPs) based on the generation of strongly reactive hydroxyl radicals to eliminate trace organic pollutants, pathogens, and disinfection by-products in water [12,13]. In addition, various inorganic species with reduction potentials consume electrons and complete reaction at the conduction band of photocatalyst. For these merits, photocatalytic reduction has been highlighted and reported to be effective for removing toxic ions and metals [14–21].

Recently, endocrine disrupting compounds (EDCs) have been found in water supplies and wastewater effluent originated from synthetic sources. Among the EDCs, some of important and commonly detected compounds are including bisphenol A (BPA), 17α-ethinyl estradiol (EE2), and 17β-estradiol (E2). These compounds, used as organic target pollutants in this study, are utilized in industrial processes (i.e., BPA is used as a plasticizer), produced artificially as a pharmaceuticals (i.e., EE2 is used as an ovulation inhibitor), or created naturally in the body (i.e., E2 is a reproductive hormone) [22,23]. In addition, hexavalent chromium (Cr(VI)), utilized as an inorganic target pollutant in this study, is known for carcinogen to humans. It is highly water-soluble and makes the different anionic forms, chromate ($HCrO_4^-$/CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), according to its concentration and pH. Cr(VI) species are more hazardous than trivalent chromium (Cr(III)) owing to solubility and mobility which is 100 times more toxic than that of Cr(III) [24,25]. Therefore, reducing Cr(VI)–Cr(III) is desirable to decrease toxicity and suppress the mobility in water [26,27].

In our previous studies, various TiO_2 nanotubes were fabricated on Ti substrates with anodizing method for use as photoeletrode for hydrogen production [28–31] and photocatalyst for water purification [32,33]. In particular, in a previously performed Cr(VI) reduction with TiO_2 nanotubes [34], we focused on establishing a rotating TiO_2/Ti reactor to enhance reaction performance and investigated the effects of rotating speed and number of TiO_2/Ti mesh on the Cr(VI) reduction.

Hence, the present study focused on establishing a scale-up rotating TiO_2/Ti reactor based on our previous results to investigate the effect of pH on Cr(VI) reduction with an organic compound (BPA), and reaction mechanisms. In addition, several photocatalytic experiments were performed to remove the target pollutants with the rotating TiO_2: the reduction of single component (Cr(VI) only); the simultaneous reduction/oxidation of two-component (Cr(VI)/BPA, Cr(VI)/EE2, Cr(VI)/E2); and the simultaneous reduction/oxidation of all components (Cr(VI)/EDCs mixture); under solar irradiation conditions.

2. Materials and methods

2.1. Preparation of TiO_2 nanotubes/Ti mesh

Prior to the potentiostatic anodization, the Ti mesh was chopped into pieces (100 cm^2, 1.67 mm thickness, 99% purity, TTM, Korea). The anodization was executed in an electrochemical cell connected to a power supply (DC) and controlled by a computer program (CIMON-SCADA, KDT Systems, Korea). Fe foil was employed as the counter-electrode (100 cm^2, 0.25 mm thickness, 99.5% purity, Goodfellow, England), with magnetic stirring in the mixed electrolytes made up of NH_4F-H_2O-$C_2H_6O_2$. The nanotubular TiO_2/Ti was then annealed in the furnace under ambient oxygen. Details of the chemical compositions of the electrolytes and preparing conditions are summarized in Table 1. The prepared samples were chopped into pieces (10 cm^2, 2 cm × 5 cm) and were put into the rotating axis depending on whether they were used for reactor type I or II.

2.2. Chemicals

Ethylene glycol ($C_2H_6O_2$, 99.8%), ammonium fluoride (NH_4F, ≥99.99%), and 1.5-diphenylcarbazide ($C_{13}H_{14}N_{40}$, ACS reagent), bisphenol A ($C_{15}H_{16}O_2$, BPA, >99%), 17α-ethinylestradiol ($C_{20}H_{24}O_2$, EE2, >99%) and 17β-estradiol ($C_{18}H_{24}O2$, E2, >99%) were purchased from Sigma–Aldrich (USA). Hydrofluoric acid (HF, Duksan, Korea) and potassium dichromate ($K_2Cr_2O_7$, Oriental Chemical Industry, Korea) were of extra pure grade. The solvent, acetonitrile (CH_3CN), was HPLC grade (DAEJUNG Chemicals & Metals Co., Korea).

2.3. Experimental set-up

A representational diagram of the photocatalytic reaction system is displayed in Fig. 1(a). The system was composed of 3 parts: a reactor vessel (tubular shape), a rotating body including TiO_2 nanotubes/Ti meshes, and a light source. This system also contained a digital flow-meter, pump, tachometer to observe revolution speed, radiometer to measure UV intensity from the light sources (the lamp and the sun), a reservoir connected with the chiller to maintain temperature constant, and chemical to adjust pH.

As shown in Fig. 1(b), the two types of tubular shaped reactor vessels consisted of quartz, with an inner diameter of 7 cm, thickness of 3 mm, length of 12 cm, and volume of 325 mL (total volume, 1000 mL) for the type I; and an inner diameter of 7 cm, thickness

Table 1
Fabrication condition for nanotubular TiO_2/Ti mesh (10 cm × 10 cm).

Metal substrate	Anodization condition				Annealing condition		
	Chemical composition	Voltage (V)	Temp. (°C)	Time(min)	Temp. (°C)	Time (hr)	Ambient (mL/min)
Titanium (Ti) mesh	0.3M NH_4F + 2 vol.% H_2O + $C_2H_6O_2$	50	25	30	450	2	400 (O_2)