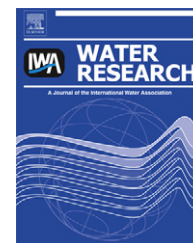


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Energy recovery during advanced wastewater treatment: Simultaneous estrogenic activity removal and hydrogen production through solar photocatalysis

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ABSTRACT

Simultaneous estrogenic activity removal and hydrogen production from secondary effluent were successfully achieved using TiO₂ microspheres modified with both platinum nanoparticles and phosphates (P–TiO₂/Pt) for the first time. The coexistence of platinum and phosphate on the surface of TiO₂ microspheres was confirmed by transmission electron microscope, energy-dispersive X-ray and X-ray photoelectron spectroscopy analyses. P–TiO₂/Pt microspheres showed a significantly higher photocatalytic activity than TiO₂ microspheres and TiO₂ powders (P25) for the removal of estrogenic activity from secondary effluent with the removal ratio of 100%, 58.2% and 48.5% in 200 min, respectively. Moreover, the marked production of hydrogen (photonic efficiency: 3.23×10^{-3}) was accompanied by the removal of estrogenic activity only with P–TiO₂/Pt as photocatalysts. The hydrogen production rate was increasing with decreased DO concentration in secondary effluent. Results of reactive oxygen species (ROS) evaluation during P–TiO₂/Pt photocatalytic process showed that O₂ and OH were dominant ROS in aerobic phase, while OH was the most abundant ROS in anoxic phase. Changes of effluent organic matter (EfOM) during photocatalysis revealed that aromatic, hydrophobic, and high molecular weight fractions of EfOM were preferentially transformed into non-humic, hydrophilic, and low MW fractions (e.g. aldehydes and carboxylic acids), which were continuously utilized as electron donors in hydrogen production process.

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1. Introduction

In recent years, development of clean energy and reuse of renewable resources have drawn great attention due to increasing global concerns on energy shortage and environment deterioration (Lloyd and Subbarao, 2009; Canterino et al., 2009). Hydrogen has been identified as one of the major clean energy sources of the future due to its high energy content

(122 kJ g⁻¹) and reduced greenhouse gas emissions as compared to fossil fuels. Ever since the electrochemical photolysis of water on a TiO₂ electrode was first discovered by Fujishima and Honda, great progress has been achieved in understanding the microscopic process involved in the photocatalytic systems, and in the modulation of photocatalyst structures for visible light harvesting (Fujishima and Honda, 1972; Walter et al., 2010; Chen and Mao, 2007).

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Photocatalytic reaction is initiated by excitation of a semiconductor photocatalyst, which results in the promotion of an electron (e^-) from the valence band (VB) to the conduction band (CB) of the semiconductor and creation of a hole (h^+) in the VB. The photogenerated electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor (Chen and Mao, 2007). For the process of photocatalytic hydrogen production, the CB electrons are important as their role is to reduce protons to hydrogen molecules. The CB level should be more negative than the hydrogen evolution level to initiate hydrogen production (Ni et al., 2007). Among the semiconductor materials which fulfill the requirement, TiO_2 has attracted the most attention because of its chemical and photochemical stability, biological inertness, and low cost (Chong et al., 2010; Zhang et al., 2012a; Gupta et al., 2007).

For high-rate hydrogen production in a photocatalytic system, an excess amount of electron donors (e.g. organic acids, alcohols, sulfide/sulfite) is normally required to speed up h^+ consumption and slow down e^-h^+ recombination, which can dramatically enhance hydrogen evolution by several orders of magnitude (Ni et al., 2007; Kim and Choi, 2010). Recently, a series of studies have been achieved in using organic pollution instead as electron donors for H_2 production, such as phenolic compounds, dyes, organic acids, urea/urine and so on (Ni et al., 2007; Kim and Choi, 2010; Kim et al., 2012; Daskalaki et al., 2010).

Nevertheless, simultaneous hydrogen production and organic pollution removal during wastewater treatment still faces many challenges for practical application, such as (1) the photocatalytic hydrogen production requires anoxic condition which was usually achieved by purging inert gases (e.g. Ar and N_2) in photocatalytic reactors prior to irradiation (Kim and Choi, 2010; Kim et al., 2012; Daskalaki et al., 2010). Such an approach is uneconomical in wastewater treatment; and (2) the organic pollutants in wastewater usually cannot be directly utilized as electron donors in photocatalytic hydrogen production process (Pirkanniemi and Sillanpää, 2002). It is hardly to achieve simultaneous hydrogen production and wastewater purification only through photocatalysis.

Wastewater reclamation from municipal wastewater treatment plants (MWWTPs) has been considered as one of the most important approach for resources reuse (Zhang et al., 2010). It has been extensively employed for various purposes around the world (Zhang et al., 2010). However, reusable wastewater should be free of any toxic pollutants which escape from conventional wastewater treatment. Unfortunately, in most countries, including China, the only standard for determining organic pollution in reclaimed wastewater is the chemical oxygen demand (COD). Micropollutants are ignored, potentially threatening water utility customers during wastewater reuse. Today, what are known as "emerging contaminants" (ECs), found in treated wastewater, are causing particular concern, due to their potential adverse effects on aquatic organisms and humans health (Joss et al., 2004; Kim et al., 2007; Klammer et al., 2010). One of the best known detrimental effects of these compounds in environment is the disruption of endocrine systems in wild species, affecting their growth, physiology and reproduction (Seeland

et al., 2012). The effects could be measured as a result of estrogenic activity (EA), as has been used in many studies (Wu et al., 2009; Zhao et al., 2008; Zhang et al., 2012b). Therefore, effective advanced treatments are required to remove these pollutants and ensure the quality of the reused water.

Among the advanced treatments capable of degrading ECs, TiO_2 photocatalytic oxidation has been one of the most promising technologies (Coleman et al., 2000; Zhang et al., 2012b; Gupta and Ali, 2008). Photocatalytic degradation of organic pollutant largely depends on the oxidative power of VB holes and hydroxyl radicals (Zhang et al., 2012a). In this case, the generated CB electrons are usually scavenged by oxygen molecules. It has been reported in our previous studies that TiO_2 photocatalytic treatment of secondary effluent would preferentially degrade large molecular weight (MW) effluent organic compounds (e.g. humic/fulvic acid-like compounds and soluble microbial byproduct-like compounds) into small MW organic compounds, and then mineralize them into CO_2 and H_2O (Zhang et al., 2012c). The process was accompanied with the removal of emerging contaminants from secondary effluent, especially for the estrogenic chemicals (Zhang et al., 2012c). The generated small MW organic compounds, such as organic acids, alcohols, and aromatic compounds, seem easier to be used as electron donors than their parent compounds. They are self-sustaining energy of wastewater. Moreover, the photocatalytic degradation of large MW organic compounds into small MW organic compounds was a dissolved oxygen (DO) consuming process. If the small MW organic compounds generated from aerobic photocatalytic oxidation could be used as electron donors in the following anoxic photocatalytic hydrogen production process, it could be possible to achieve simultaneous advanced wastewater treatment and energy recovery.

In order to verify this hypothesis, a dissolved oxygen-controlled solar photocatalytic reactor was developed for simultaneously EA removal and hydrogen production. Surface phosphate and platinumized TiO_2 (P- TiO_2 /Pt) microspheres were prepared as photocatalysts because the hybrid modified TiO_2 powders (P25) were proven to exhibit excellent photocatalytic activities for simultaneous degradation of organic compounds and hydrogen production, wide working pH range (from 3 to 11), and good stability by Choi and co-workers (Kim and Choi, 2010, 2011; Kim et al., 2012). In order to better understand the photocatalytic process, changes of reactive oxygen species (ROS) and effluent organic matter (EfOM) were evaluated. This new idea may offer a promising idea to realize simultaneous water resource reclamation and clean energy production from natural energy.

2. Material and methods

2.1. Reagents

Titanium dioxide powder P25 (greater than 99.5% purity, average primary particle size of 21 nm, BET surface area of 50 ± 15 m²/g) used in this study was purchased from Degussa (Germany). Methanol, alcohol, nonanoic, tetra-n-butyl titanate, chloroplatinic acid, 1,5-diphenylcarbohydrazide (DPCI),

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