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Photocatalytic pretreatment for the redox conversion of waste activated sludge to enhance biohydrogen production

*Chunguang Liu, Wansheng Shi, Mijung Kim, Yingnan Yang, Zhongfang Lei, Zhenya Zhang**

Graduate School of Life and Environmental Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan

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ABSTRACT

Photocatalytic pretreatment of waste activated sludge (WAS) using a flat photocatalytic reactor was undertaken. Photocatalytic pretreatment enhanced the release of soluble substances from WAS, in which the soluble protein and soluble carbohydrate concentration increased by about 50% and 80%, respectively. Significant removal of heavy metal ions from the liquid phase of WAS was also achieved after photocatalytic pretreatment. In addition, the highest hydrogen yield and the highest concentration of volatile fatty acids (VFAs) were achieved from the photocatalysis pretreated WAS by batch anaerobic digestion (55 °C). The cumulative hydrogen yield from photocatalysis pretreated WAS was 211.0 ml/l-sludge, much higher than those from UV pretreated WAS (111.0 ml/l-sludge) and from raw WAS (93.0 ml/l-sludge). The results indicate that photocatalysis is a promising WAS pretreatment method for the enhancement of biohydrogen production, probably due to the photo-oxidation of organics and simultaneous photo-reduction of heavy metal ions in WAS.

1. Introduction

Hydrogen is a promising alternative energy that produces high energy without greenhouse gases during the combustion process [1]. Hydrogen can be produced by both chemical and biological methods. Chemically, hydrogen can be produced by electrolysis and photocatalytic water splitting [2]. The latter is more energy-efficient than the former. Biologically, hydrogen can be generated by both photo-fermentation and dark fermentation [3] with the latter being more effective under present conditions. Some attempts have been tried to test hydrogen production from easily biodegradable organics rich in glucose and sucrose [4,5]. Recently, hydrogen production has also been explored on the wastes containing refractory materials such as cornstalk and waste activated sludge (WAS) [6,7].

As for WAS, however, hydrolysis is the rate-limiting step in anaerobic digestion and its digestion inefficiency resulted from long hydraulic retention time (HRT), which can be overcome under the condition of effective disintegration of microbial cells and hydrolysis of extracellular polymeric substances (EPS) in WAS [8]. Moreover, heavy metal ions (Cr, Pb, Cu, Zn, Ni and Cd) at concentrations above critical values in WAS will be toxic to microorganisms (hydrogenogens and methanogens) in anaerobic digestion process and to the natural ecosystem after being discharged into the environment [9]. Furthermore, the WAS can be easily converted to an

* *Corresponding author*. Tel./fax: +81 29 853 4712.
E-mail address: zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

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agricultural fertilizer, if the heavy metal ions are removed or reduced to a non-toxic state by pretreatment. In order to improve the hydrolysis process as well as increase hydrogen yield, remove heavy metal ions and shorten the retention time, various pretreatment methods have been tested including alkaline pretreatment [10], acidification [11], ultrasonic treatment [12], microwave irradiation [13], enzyme [14], photocatalytic pretreatment [15,16] and thermal hydrolysis [17–19]. However, it should be mentioned that all of the above methods increase the cost of sludge treatment when energy consumption and environmental benefits being taken into consideration. Photocatalysis, as an energy-saving and environment-friendly method, has been tested and used on wastewater treatment. The catalyst (TiO_2) can generate reducing conduction band electrons (e^-_{cb}) and oxidizing valence band holes (h^+_{vb}) in sufficient quantity with UV-light irradiation. However, few reports can be found on the photocatalytic method as a promising pretreatment to improve hydrogen production from WAS via anaerobic digestion [16].

The objective of this research is to evaluate the effect of photocatalytic pretreatment on biohydrogen production from WAS and the photo-reduction capacity for heavy metal ions in WAS. For this purpose, the compositions of WAS and metabolites after anaerobic digestion were determined. In addition, the concentrations of soluble carbohydrate, protein and heavy metal ions (Cu, Zn, Cr, Ni, Pb, Cd) were also analyzed to disclose the changes of photo-oxidation capacity for organics and photo-reduction capacity for heavy metal ions in WAS after pretreatment.

2. Materials and methods

2.1. *WAS, digested sludge and catalyst*

The WAS and digested sludge were collected from a sewage treatment plant in Shimodate, Ibaraki, Japan, then kept at 4 °C. The characteristics of the WAS were shown in Table 1.The ratio (66.90%) of volatile solids (VS)/total solids (TS) indicates that the main components of the sludge were organic substances. The low ratio (9.60%) of soluble chemical oxygen demand (SCOD)/total chemical oxygen demand (TCOD) demonstrates that most COD is insoluble. Digested sludge was used as seeding sludge in the thermophilic anaerobic hydrogen fermentation experiment. The pH, TS, VS, TCOD and SCOD of the digested sludge were 7.1, 10.7 g/l, 7.3 g/l, 19.7 g/l and 0.5 g/l, respectively. Before used as seed inoculums, the digested sludge was heat-treated in a hot air oven at 120 °C for 30 min to inhibit methanogen [16]. The catalyst used in this study was a Degussa P-25 TiO_2 slurry (Degussa AG, Germany).

2.2. *Pretreatment experiments*

Photocatalysis was used as sludge pretreatment method in this study. As reported in our previous study [16], the optimal pretreatment conditions were obtained as TiO_2 dosage of 3 g/l, circulating speed of 350 ml/min, UV-light intensity of 1.5 mW/cm^2, and duration of 6 h respectively in a circulating bed photocatalytic reactor. In this study, 180 ml raw WAS and 3 g/l TiO_2 were mixed completely, and then treated in a circulating bed photocatalytic reactor. In order to test the effect of photocatalysis with TiO_2 addition on WAS, UV-light pretreatment experiment (without TiO_2) was also conducted under the identical conditions.

2.3. *Batch anaerobic digestion for biohydrogen production*

The experiment of biohydrogen production from WAS was conducted in 30 ml serum bottles with a working volume of 25 ml containing 18% (v/v) of inoculum. The batch experiments were performed in duplicate under 55 °C for 5 days, using photocatalysis pretreated WAS, UV-light pretreated WAS and raw WAS (control) as substrate, respectively. The initial pH of the substrate was adjusted to 5.7 with 1 mol/l hydrochloric acid (HCl). The serum bottles were closed with rubber stoppers and caps. After replacement of the headspace with nitrogen to create anaerobic condition, the serum bottles were put into a temperature-controlled water-bath (55 °C). The biogas production was measured every 12 h by water displacement method. The volatile fatty acids (VFAs) concentrations was determined every 12 h by HPLC. The fermentation medium was sampled at the initial and end of the hydrogen fermentation process for the measurement of pH, TS, VS, TCOD, SCOD, ammonia nitrogen, soluble protein, and soluble carbohydrate concentrations.

2.4. *Analytical methods*

COD, TS, and VS were detected in accordance with standard methods [22], and pH was determined by a digital pH meter (Metter-Toledo Group). Liquid sample was centrifuged at 10,000 rpm for 10 min and the supernatant was used to

Table 1 – The characteristics of waste activated sludge (WAS) before and after pretreatment by UV-light and photocatalysis.

Items	Raw WAS	UV-light pretreated WAS	Photocatalysis pretreated WAS
TCOD (total chemical oxygen demand, mg/l)	18,249	17,981	17,210
SCOD (soluble chemical oxygen demand, mg/l)	1752	1893	3620
TS (total solids, mg/l)	7483	7302	6870
VS (volatile solids, mg/l)	5006	5119	5980
Soluble protein (mg/l)	1293	1386	1946
Soluble carbohydrate (mg/l)	486	504	879
NH_4^+–N (mg/l)	106	130	320
pH	6.7	7.3	7.6