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# Enhancement of hydrogen production during waste activated sludge anaerobic fermentation by carbohydrate substrate addition and pH control

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#### ABSTRACT

The effects of carbohydrate/protein ratio (CH/Pr) and pH on hydrogen production from waste activated sludge (WAS) were investigated. Firstly, the optimal pH value for hydrogen production was influenced by the CH/Pr ratio, which was pH 10, 9, 8, 8, 8 and 6 at the CH/Pr ratio (COD based) of 0.2 (sole sludge), 1, 2.4, 3.8, 5 and 6.6, respectively. The maximal hydrogen production (100.6 mL/g-COD) was achieved at CH/Pr of 5 and pH 8, which was due to the synergistic effect of carbohydrate addition on hydrogen production, the enhancement of sludge protein degradation and protease and amylase activities, and the suitable fermentation pathway for hydrogen production. As hydrogen consumption was observed at pH 8, in order to further increase hydrogen production a two-step pH control strategy (pH 8 + pH 10) was developed and the hydrogen production was further improved by 17.6%.

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#### 1. Introduction

Hydrogen is a clean source of energy. The anaerobic conversion of biomass has been demonstrated as a technically feasible way for hydrogen production. Waste activated sludge (WAS) from wastewater treatment plant contains high levels of organic matter and thus is a potential substrate for producing hydrogen. Several publications have reported that hydrogen can be biologically produced by anaerobic fermentation of WAS (Cai et al., 2004; Ting and Lee, 2007; Wang et al., 2003), but the hydrogen production per gram dry sludge (g-DS) was very low (i.e., 0.08 mmol-H<sub>2</sub>/g-DS (Huang et al., 2000)).

It is well known that several steps (hydrolysis, acidification and methanogenesis) are involved when complex organic substrate (such as waste activated sludge) is anaerobically fermented. In the literature the main strategy for improving sludge-derived biohydrogen production was to pretreat sludge by ultrasonic, acidic, alkaline, heat-shocking, or freezing-thawing method (Cai et al., 2004; Massanet-Nicolau et al., 2008; Ting and Lee, 2007; Xiao and Liu, 2009). Hydrogen production yield was improved, but it was only 0.7 mmol-H<sub>2</sub>/g-COD (or 15.6 mL/g-COD). It was reported in our previous study that the production of hydrogen from waste activated sludge could be significantly improved by controlling the fermentation pH at alkaline one (Zhao et al., 2010). Nevertheless, there was still large amount of protein in fermentation system at the end of hydrogen production.

One method that might be used to enhance the bioconversion of WAS to hydrogen is to add a carbohydrate substrate to the WAS fermentation system because the COD ratio of carbohydrate to protein (CH/Pr) or carbon to nitrogen mass ratio (C/N) of WAS was only around 0.2/1 or 7/1, whereas the suggested C/N ratio for anaerobic sludge digestion was 20/1 to 30/1 (Parkin and Owen, 1986). It seems that the increase of CH/Pr ratio of sludge anaerobic fermentation system by the addition of carbohydrate would benefit the bioconversion of sludge protein and hydrogen production.

In the literature some researchers studied the anaerobic co-digestion of nitrogen-rich organisms (i.e., sewage sludge and manure) and carbohydrate-rich substrates (i.e., food, fruit and vegetable waste) on hydrogen production under conditions of pH 5-6 (Kim et al., 2004) or uncontrolled pH (Perera and Nirmalakhandan, 2011; Tenca et al., 2011; Zhu et al., 2008). Nevertheless. pH was reported to be an important factor which affected sludge hydrolysis, acidification, fermentation type, and hydrogen generation during sole WAS fermentation (Chen et al., 2007; Yuan et al., 2006), and a maximal biohydrogen production could be achieved by controlling the fermentation pH value at constant pH 10 (Zhao et al., 2010). It was observed in our study that the optimal pH changed with the CH/Pr ratio during sludge fermentation for hydrogen production. Until now, however, the combined influences of CH/Pr ratio and pH on bioconversion of sludge protein and hydrogen production have not been documented.

The purpose of this study was to report the combined effects of CH/Pr ratio and pH on hydrogen production, and to find out the suitable conditions and related mechanisms for maximal hydrogen production. As the produced hydrogen was still consumed under



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