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Enhanced biohydrogen and subsequent biomethane production from sugarcane bagasse using nano-titanium dioxide pretreatment

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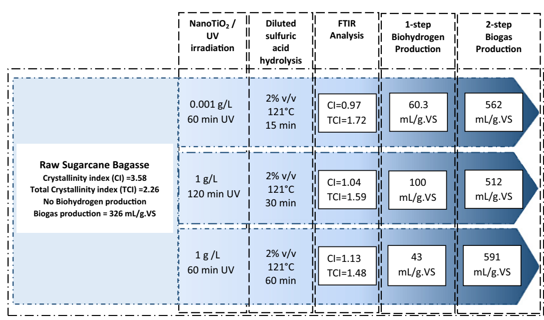
HIGHLIGHTS

- NanoTiO_2–dilute H_2SO_4 hydrolysis was used to enhance the fermentation of bagasse.
- Using nanoTiO_2 pretreatment, the acid hydrolysis time duration was reduced.
- Dark H_2 fermentation was enhanced up to 127% using nanoTiO_2 pretreatment.
- Biogas production was enhanced up to 74% compare to the raw bagasse.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano-titanium dioxide (nanoTiO_2) under ultraviolet irradiation (UV) followed by dilute sulfuric acid hydrolysis of sugarcane bagasse was used to enhance the production of biohydrogen and biomethane in a consecutive dark fermentation and anaerobic digestion. Different concentrations of 0.001, 0.01, 0.1 and 1 g nanoTiO_2/L under different UV times of 30, 60, 90 and 120 min were used. Sulfuric acid (2% v/v) at 121 °C was used for 15, 30 and 60 min to hydrolyze the pretreated bagasse. For acidic hydrolysis times of 15, 30 and 60 min, the highest total free sugar values were enhanced by 260%, 107%, and 189%, respectively, compared to samples without nanoTiO_2 pretreatment. The highest hydrogen production samples for the same acidic hydrolysis times showed 88%, 127%, and 25% enhancement. The maximum hydrogen production of 101.5 ml/g VS (volatile solids) was obtained at 1 g nanoTiO_2/L and 120 min UV irradiation followed by 30 min acid hydrolysis.

1. Introduction

Fossil fuels have been the main energy source for societies and industries during the last decades. Nowadays, due to over-consumption, depletion of reserves, and the rise of the prices, together with the huge environmental hazards and greenhouse gas emission caused by transportation and combustion of fossil fuels, renewable and clean alternatives have received considerable attention by researchers, governments, and industries. Biofuels have been shown to have an excellent potential to be used as a kind of renewable energy due to its main environmental advantages, including no sulfur content and harmful gas emissions, abundance and renewability, clean energy, and landfills reduction, thereby making it possible to create different products (Ghimire et al., 2015; Sharma and Ghoshal, 2015).

Biological hydrogen and methane are alternative biofuels with promising approaches to meet the growing demand for energy. Hydrogen has high energy content of 142 MJ/kg and the only product of its combustion is water (Poo and Reungsang, 2013). Biohydrogen is produced via dark fermentation and photofermentation. Dark fermentation has the ability to use various types of substrate

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with no light requirement. Biohydrogen production from agricultural residues, wastewaters, and manure as feed stocks has been shown to be economical and environmentally friendly. Hydrogen production is associated with the accumulation of volatile fatty acids (VFAs) whose excessive accumulation causes the inhibition of fermentation (Jiang et al., 2013). Volatile fatty acids are intermediate components of anaerobic digestion for biomethane production. Anaerobic digestion consisting of acetogenesis and methanogenesis converts the VFA to methane as a final product (Jiang et al., 2013). Therefore, VFAs accumulated from dark hydrogen fermentation together with the residual carbohydrates and other organic residues of feedstock are efficiently consumed and transformed under anaerobic digestion. Bacterial community of anaerobic digestion is expected to be more diverse and adaptable to the consumption of more complicated organic compounds, while, because of microbial pretreatment in dark fermentation, hydrolyzing bacteria and usually the bacterial community can be affected, leading to the decline of its diversity (Jiang et al., 2013). Therefore, anaerobic digestion may consume more complicated organic compounds not used under dark fermentation.

Yang et al. (2015) investigated methane production from the effluent of the hydrogen production stage in a two-stage process. The maximum methane production rate was 0.2–1.7 times higher for the effluents. Buitrón et al. (2014) evaluated the feasibility of hydrogen and methane potential from tequila vinasses in sequencing batch reactors using the preheated sludge as the inoculum. Compared to the one-stage process, the two-stage one resulted in reasonable organic removal (73–75%) and a high amount of biofuel production. Jariyaboon et al. (2015) used skim latex serum as the feed for the two-stage hydrogen and methane digester. The maximal amounts of 1.57 L H_2/L and 12.2 L CH_4/L were achieved with 60% (v/v) skim latex serum. Kvesitadze et al. (2012) investigated the two-stage hydrogen and biogas combined production from municipal solid wastes. Hydrogen and methane production in the two-stage process were increased to 23% and 26%, as compared to the one-stage process, respectively.

Sugarcane bagasse (SCB) is produced in huge amounts from various agricultural crop residues in the tropical countries. Its world annual production is about 140 million tons (dry weight), with about 2.4 million tons of it being in Iran. Each metric ton of sugarcane generates 280 kg of bagasse. There is a great opportunity for the biological production of fuels (biohydrogen, biogas and ethanol) with economic and strategic gains (Adsul et al., 2004; Peng et al., 2009). Sugarcane bagasse is composed of cellulose (40–45%), hemicellulose (30–35%), and lignin (20–30%). Lignin has a nonporous complex structure covering cellulose and hemicellulose, leading to a rigid structure protecting them against the hydrolyzing enzymatic attack. Removal or destruction of crystalline and the rigid structure of lignin and hemicellulose can make it more accessible and enhance microbial hydrolysis and the fermentation of cellulose (Cheng and Zhu, 2013).

In order to facilitate the hydrolytic reaction, different types of pretreatment including chemical (e.g. alkaline or acidic), physical (e.g. steam explosion, liquid hot water process, and wet oxidation), physicochemical (ammonia fiber explosion), and biological methods have been developed (Ramadoss and Muthukumar, 2015). Diluted acid pretreatment can dissolve lignin and enhance the porosity of lignocellulose. There are several studies related to the acid pretreatment of SCB. Diluted H_2SO_4 for the hydrolysis of SCB was used which 1% (v/v) H_2SO_4 at 120 °C for 60 min was reported as the optimum pretreatment for hydrogen production, using preheated elephant dung as the inoculum (Fangkum and Reungsang, 2011). Aguilar et al. (2002) studied the acid hydrolysis of SCB in the range of 2–6% (g/g liquor) H_2SO_4 solution and reported 2% H_2SO_4 at 122 °C for 24 min as the optimum conditions for xylose production (21.6 g xylose/L). In another study, 2% (v/v) sulfuric acid at 121 °C was obtained as the best condition for the hydrolysis of SCB for dark fermentative H_2 production (Rai et al., 2014). Based on these studies, it was found that increasing H_2SO_4 concentrations to more than 2% might lead to the continuous rise of acetic acid and furfural during the hydrolysis, thereby resulting in the inhibition of bacterial fermentation.

All pretreatment methods consume high energy to create harsh operational conditions (high temperature and pressure, high concentrations of acid, alkali, or ionic liquids). Application of TiO_2 can help to pretreat under a bit milder operational conditions, to reduce consumption of energy, and moreover to reduce the production of inhibitors. The semiconductor TiO_2 is long-term stable and strong oxidizing agent which has been investigated and used for the destruction and degradation of complex organic compounds in wastewater treatment (Puskelova et al., 2014). The photocatalyst TiO_2 generates reducing conduction band electrons (e_{cb}^-) and oxidizing valence band holes (h_{vb}^+) in sufficient quantity under ultraviolet (UV) light irradiation. The following equations summarize the formation and fate of $TiO_2(h^+)$ and $TiO_2(e^-)$ under photocatalytic condition for model substrate S representing the electron-deficient and electron-rich parts in the structure of TiO_2, respectively (Machado et al., 2000):

$$TiO_2 \xrightarrow{h\upsilon} TiO_2(e^- + h^+)$$

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + HO^{\cdot} + H^+$$

$$TiO_2(h^+) + S \rightarrow TiO_2 + S^{+\cdot}$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + HO^{\cdot}$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{-\cdot}$$

$$OH^- + O_2 \rightarrow HO^{\cdot} + O_2^{-\cdot}$$

$$OH^{\cdot} + O_2^{-\cdot} \rightarrow HO^- + O_2^-$$

Puskelova et al. (2014) used TiO_2–Pt aerogel for photodegradation of organic pollutant. Zheng et al. (2009) used Pt/TiO_2 for the conversion of acid acetic to hydrogen. Kuznetsov et al. (2009) investigated the addition of TiO_2 within a mixture of acetic acid and hydrogen peroxide for the catalytic delignification of fir wood in the absence of ultraviolet irradiation. A high yield of fibrous products (48.8 wt%) was provided with the cellulose content of 89.5% and the residual lignin of 0.8 wt%, using 0.5 wt% TiO_2 at 130 °C in the presence of 6.4 wt% H_2O_2 and 23 wt% acetic acid for the time duration of 2–3 h. Potential of TiO_2/UV irradiation system as a pretreatment of rice straw to enhance its saccharification for ethanol production was reported (Kang and Kim, 2012). The maximum yield of saccharification was obtained under 0.1 w/v% of TiO_2 subjected to UV irradiation. However, it is important to note that this process has been performed at room temperature and atmospheric pressure and the requirement of little energy is its main advantage. Specific shape nanoparticles showing high active interface with the reaction medium have the ability to improve the interface efficiency and therefore, the reaction rate (Puskelova et al., 2014). To the best of authors' knowledge, no study has reported the effect of nano-titanium dioxide on the pretreatment of bagasse for two-stage dark fermentation–anaerobic digestion.

This study was aimed to enhance the dark fermentative biohydrogen and the subsequent anaerobic digestive biomethane production from sugarcane bagasse under mesophilic conditions. Nano-titanium dioxide (nanoTiO_2) powder was used as a photocatalyst under UV irradiation to improve the acidic post-hydrolysis.