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Improvement of hydrogen production from glucose by ferrous iron and biochar

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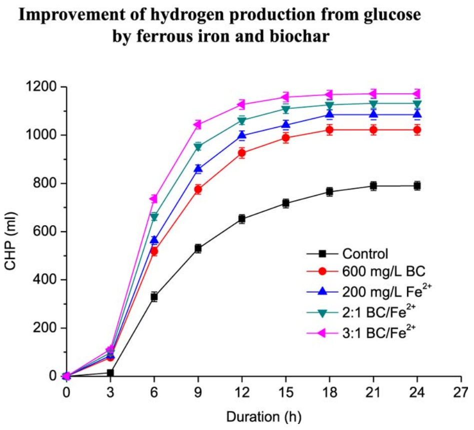
GRAPHICAL ABSTRACT

Effects of biochar (BC) and ferrous iron (Fe^{2+}) additions on hydrogen (H_2) production from glucose were investigated. Results showed that suitable Fe^{2+} concentration could enhance [Fe-Fe]-hydrogenase activity, while BC addition could facilitate hydrogen-producing bacteria growth. Both of them could synergistically improve H_2 production, indicating a simple, cost effective and practical process.



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ABSTRACT

Effects of biochar (BC) and ferrous iron (Fe^{2+}) additions on hydrogen (H_2) production from glucose were investigated using batch experiment. The glucose with both BC and Fe^{2+} additions were incubated at 37 °C for H_2 production. As compared with the control group (without BC and Fe^{2+} additions), the synergic effects of BC and Fe^{2+} make the lag phase time decease from 4.25 to 2.12 h, and H_2 yield increase from 158.0 to 234.4 ml/g glucose. Moreover, suitable concentrations of BC and Fe^{2+} serve to enhance volatile fatty acid generation during H_2 evolution. These results indicate that H_2 production is improved by BC and Fe^{2+} regulations, where synergic mechanisms are described as follows: BC acts as support carriers of anaerobes and system pH buffers, which promotes the biofilm formation and maintains suitable pH environment; Appropriate Fe^{2+} concentration can improve hydrogenase activity in H_2 production.

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1. Introduction

The combustion of fossil fuel has been predominated approximately 80% of the global energy consumption since the industrialized era (Chen et al., 2008). Besides, in the last decade the huge increase in world energy consumption has taken place, which will continue to occur in the next fifty years (Lucas et al., 2015), due to modernization and population increase (Lucas et al., 2015). Hydrogen (H_2) has been widely considered as an available alternative energy carrier due to its effectiveness and cleanness. However, over 96% of world H_2 production relies on fossil fuels, resulting in environmental pollution and energy crisis (Zhang et al., 2015a). Thus, it is urgent to develop other techniques for H_2 production in a sustainable, cost effective and eco-friendly way. Among various H_2 production methods, biological processes like photosynthesis microbial electrolysis cells and fermentation can provide H_2 from abundant and cheap sources like organic wastes from biorefinery industries (Zhang et al., 2015a). Moreover, dark fermentation for H_2 production requires less energy compared to other H_2 processes. Bio-H_2 techniques mainly include dark fermentation process and photosynthetic H_2 production. Compared to photosynthetic H_2 production, dark fermentation process has evolved to the cutting-edge technology due to its economic efficiency, operation simplicity, and its independence on the availability of solar irradiation. Bio-H_2 production via dark fermentation also reveals the advantages of sustainable energy and carbon balance. Nonetheless, the major drawbacks of this technique are lower microbial conversion efficiency of substrate into H_2 and large amounts of CO_2 emissions.

Dark fermentation for H_2 has been established for several decades, but it still needs to be optimized in the case of process stability, inhibition problems and higher H_2 yields (Bundhoo and Mohee, 2016). Theoretically, the complete bioconversion of glucose into H_2 could give 1493 ml H_2/g glucose (12-mol H_2/mol glucose). However, during the practical conversion there are no known existing anaerobes and metabolic pathways that may be capable of doing that and practical H_2 yields appear to be limited to 4-mol (498 ml) H_2/mol glucose (Hallenbeck, 2009). A well-known issue concerning H_2 fermentation from carbon-rich organic materials such as food waste, cane molasses, starch wastewater, fruit and vegetable wastes, is inhibition due to the vulnerability of fermentation micro-ecology. Many efforts have aimed to enhance the enrichment and activity of anaerobic microbes, and the additions of carrier and some trace elements are regarded as necessary measures (Mumme et al., 2014; Luo et al., 2015; Zhang et al., 2013). In addition, to improve H_2 yield by dark fermentation, previous reports have focused on metabolic bioengineering (e.g., over-expression of hydrogenase) and key parameter optimization such as microbial selection and pH regulation (Zhang et al., 2011).

Recently, considerable attention has been paid to the potential application of carbon-rich material as carbon sequestration, soil amendment and pollutant remediation (Ahmad et al., 2014). The material is produced by thermal decomposition and recognized as biochar (BC) that is expected to improve crop productivity and reduce greenhouse gas emission. However, the broad application of BC is impeded due to relatively high costs (Roberts et al., 2010). It is necessary to overcome this major drawback in order to obtain economic benefits via expanding the BC value chain. For example, BC was served as an additive that increased biogas production in anaerobic digestion due to its ability to promote bio-film formation and mitigate acid and ammonia inhibition (Gong et al., 2011; Mumme et al., 2014). 10 g/L of BC addition to mesophilic anaerobic bioreactor inoculated with anaerobic granules and fed with 4 g/L glucose significantly increased maximum methane (CH_4) production rate by 86.6% and decreased methanogenic lag phase time by 30.3% than the control test without BC (Luo et al., 2015). Another similar report about the improvement of H_2 production from organic fraction of municipal solid waste by BC addition showed that BC addition shortened lag phase time from 12.5 ± 0.6 h at control without BC to 8.1 ± 0.5 h with 12.5 g/L BC and harvested maximum H_2 yield of 96.63 ± 2.8 ml H_2/g carbohydrates (Sharma and Melkania, 2017). There was a slight difference in optimal concentrations of BC, which was likely due to the main differences in substrate, inoculum and their metabolic pathways. Sunyoto et al. (2016) also found that BC addition could reduce the lag phase time of bio-CH_4 by 21.4–35.7%, and it further increased the subsequent H_2 production potential by 14.2–31.0%. These reports indicated that porous BC would provide a relatively big surface area for the adhesion and growth of anaerobes and reduce the inhibition behavior by absorbing inhibitors (Wang and Han, 2012). However, there have been limited investigations on the application of BC for the fermentative production of organic acids or H_2.

Besides, some elements such as sodium (Na), magnesium (Mg), zinc (Zn) and iron (Fe) are essential micronutrients for bacterial metabolism, affecting hydrogen production. Among them Fe is a vital micronutrient, which acts as the co-factor for Fe-S protein and hydrogenase (Junelles et al., 1998). Wide varieties of prokaryotes contain hydrogenase that functions in the treatment of excess electrons by H_2 formations. The Fe-S protein in ferredoxin serves as an electron carrier during pyruvate oxidation into CO_2 and acetyl CoA (Schonheit et al., 1979). The addition of zero-valent iron (Fe^0) was shown to obtain 38.2% more H_2, and the coupled system of activated carbon and Fe^0 could further improve H_2 yield (50.2%) (Zhang et al., 2015a). The maximum H_2 yields of 140.6 ml and 145 ml/g glucose were observed at 50 mg/L of Fe^{2+} by Karadag and Puhakka (2010) and Wu et al. (2017), respectively, while the maximum H_2 yield of 131.9 ml/g glucose was obtained at 352 mg/L of Fe^{2+} in another previous study (Lee et al., 2001). Although the optimal Fe^{2+} concentrations for different bio-H_2 production processes were not the same, these studies showed that shortage of iron could limit the activities of hydrogen-producing bacteria (HPB). Moreover, a suitable concentration of iron in batch process can help to raise H_2 yield at various temperatures (Zhang and Shen, 2006). Li et al. (2009) compared the H_2 yield from glucose by supplementing Fe^0 and Fe^{2+}, respectively. They found that Fe^0 played a better role in promoting bio-H_2 production than Fe^{2+}, and the inhibition of high concentration of Fe^0 to HPB was lower than that of Fe^{2+} (Li et al., 2009). The maximum H_2 conversion efficiency of 353.5 ml H_2/g COD was harvested under the optimized conditions of 7000 mg COD/L, 150 mg Fe^0/L and pH of 5.5 (Yogeswari et al., 2016). Fe^0 is essential for enriching the dominant HPB (Yogeswari et al., 2016). However, the corrosion of Fe^0 strongly depends on solution pH, and ferrous oxides formed on Fe^0 surface may lower the activity of iron (Zhang et al., 2015a). Furthermore, it is difficult to treat the fermentation residue containing Fe^0. Multiple lines of evidences indicate that the application of BC or Fe in anaerobic fermentation might be beneficial. Nonetheless, related studies are largely unavailable, and some essential mechanisms are unclarified, especially the synergic effects of Fe^{2+} and BC.

To the best of our knowledge, there has been no report on the synergic behaviors of BC and Fe^{2+} in H_2 fermentation until date. Hence, this study was conducted to assess the performances of BC/Fe^{2+} system in bio-H_2 process and to investigate the mechanism of improving H_2 production in such eco-system. To achieve this aim, the effects of Fe^{2+} and BC concentrations on H_2 fermentation from glucose medium were firstly investigated. Then the improvement of H_2 production by BC/Fe^{2+} system was evaluated, which was compared with adding BC and Fe^{2+}, respectively. Finally, the possible mechanisms of increase in H_2 yield and process stability were clarified.

2. Materials and methods

2.1. Anaerobic sludge and materials

Corn-bran residue (CBR) was obtained from a cornstarch plant in Shandong, China. The CBR was dried and crushed in order to keep its sizes ranging from 60 to 120 mesh (Zhang and Zheng, 2015). After that, it was used to produce BC at 600 °C with heating rate of 5 °C/min. Both