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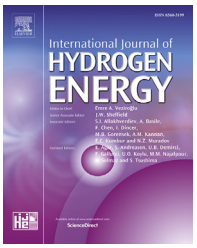

Ferric oxide/carbon nanoparticles enhanced bio-hydrogen production from glucose

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ABSTRACT

Hydrogen (H_2) gas represents renewable resource candidate to traditional energy resource. Methods to promote the H_2 evolution rate attract increasing attentions. In the present research, ferric oxide/carbon nanoparticles (FOCNPs) were synthesized and evaluated the feasibility to enhance the production rate of H_2 gas from glucose through anaerobic fermentation by mixed bacteria. The results demonstrated that appropriate dose of FOCNPs promoted, while excessive concentration of FOCNPs suppressed the production of H_2. Addition of 200 mg/L FOCNPs resulted in the highest yield of 218.63 ml H_2/g glucose, 33.7% higher than 163 ml H_2/g glucose of the control test without addition of FOCNPs. However, 400 mg/L of FOCNPs inhibited the H_2 evolution to 154 ml/g glucose, 5.5% lower than the control. It was revealed that the H_2 evolution followed the acetic pathways. The FOCNPs had a specific surface area of 27.63 m^2/g, and thus addition of FOCNPs could provide more attachment sites for the growth of anaerobes. Moreover, FOCNPs could promote the activity of hydrogenase and electron transfer efficiency, beneficial for the bio-H_2 evolution. However, excessive addition of FOCNPs could be toxic to microbes, and further suppressing the H_2 production. The present research provided an effective method to promote the evolution rate of H_2 gas.

Introduction

The rapid depletion of non-renewable fossil fuels such as coal, petroleum and natural gas, has caused severe environmental pollution and energy crisis [1]. Development of alternative resources is significant issue facing human beings. Hydrogen (H_2) has been widely regarded as an available alternative energy carrier due to its high-energy content, carbon-free property, and absence of greenhouse gas emissions after oxidation/combustion [2–4]. H_2 could be generated through bio-techniques including light-drive process and dark fermentation. Theoretically, light-drive process is more feasible because that solar light is the energy source to drive the H_2 evolution by photosynthetic bacteria. However, it is hard to apply in practice due to the difficulties in designing light reactor and low utilization efficiency of light. Dark fermentation is conducted by the dark-anaerobic hydrogenogens, possessing many advantages such as the favorable

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Nomenclature

BC	bio-char
BET	Brunauer-Emmett-Teller
CHY	cumulative H_2 yield
FOCNPs	ferric oxide/carbon nanoparticles
FONPs	ferric oxide nanoparticles
FT-IR	Fourier transform-infrared spectroscopy
HCB	hydrogen-consuming bacteria
HPB	hydrogen-producing bacteria
MPHY	maximum potential H_2 yield (ml)
NADH	nicotinamide adenine dinucleotide
NPs	nanoparticles
SCOD	soluble chemical oxygen demand, mg/L
SMPs	soluble metabolic products
SS	sewage sludge
SSA	specific surface area (m^2/g)
TFESEM	thermal field emission scanning electron microscope
TS	total solid (wt.%)
VFA	volatile fatty acid (mg/L)
XRD	X-ray diffraction

carbon balance and long-term sustainability [5]. Moreover, it requires less energy compared to other H_2 production processes [6]. However, the main drawback of dark-fermentation is the low conversion efficiency of substrate to H_2; and hence, optimizations of process design and operational parameters are required to maximize H_2 yield [7].

Many methods were evaluated to enhance the H_2 production ability of microorganisms [8]. Due to complex composition and polymeric structure, complex carbon must be converted or released to simple sugars. Thus, glucose and sucrose are readily degradable and thus are often used as model substrates for H_2 evolution. Moreover, H_2 yield is computed based on sugar equivalents consumed and H_2 generation [9]. Theoretically, the complete conversion of glucose into H_2 is 1493 ml H_2/g glucose, but the practical H_2 yield appears to be limited to 498 ml H_2/g glucose because there are unknown existing anaerobic microbes and their metabolic pathways [10]. To enhance the H_2 yield and production rate of anaerobic bacteria or hydrogen-producing bacteria (HPB), previous reports have focused on metabolic bioengineering including hydrogenase over-expression and parameter optimization (e.g., substrate concentration, pH and temperature) [11,12], as well as microbial immobilization [13].

Recently, some inorganic materials especially inorganic nanoparticles (NPs) have attracted great interests, because of their unique physicochemical characteristics, to enhance the production of bio-H_2 through promoting the activity of HPB [1]. The porous structure of the immobilized beads could be attributed to improving the mass transfer of the gaseous products, and lowering the lag phase time [13]. Ferric oxide nanoparticles (FONPs) were confirmed to promote the electron transfer rate of *ferredoxin oxidoreductase*, and thus increased the activity of hydrogenase [1]. With addition of 200 mg/L FONPs, the H_2 yield from glucose was enhanced from 164.5 to 192.4 ml/g, with *Enterobacter aerogenes* as inoculum [1]. A similar phenomenon was observed by Engliman et al. [14]. Their results demonstrated that H_2 production from glucose was increased by 53.0% with addition of 50 mg/L FONPs. Moreover, addition to Fe NPs, other materials such as nickel oxide NPs could as promote the production of H_2 [14–16]. Gadhe et al. observed that H_2 yield from dairy wastewater increased 27% by co-adding hematite and nickel oxide NPs and inoculation of mixed HPB [15]. Han et al. found that the H_2 yield from sucrose increased by 32.6% at the Fe_2O_3 NPs concentration of 200 mg/L, due to the iron released by the NPs [16]. Other studies have reported that the suitable concentrations of Fe^{2+}, Fe_2O_3 and Fe_3O_4 NPs can improve the activity of Fe-hydrogenase and H_2 yield [17–19]. In addition, cell immobilization techniques, like affinity immobilization, adsorption and entrapment, can increase the cell density and improve the cell wall permeability [20], which can lower the lag phase and raise H_2 yield of bio-H_2 process. Besides, bio-char (BC) could be served as an additive to promote biogas production by anaerobic digestion because of its ability to enhance biofilm formation and mitigate acid [21,22]. It was reported that the maximum methane (CH_4) production rate increased by 86.6% and the corresponding lag phase time decreased by 30.3% at BC concentration of 10 g/L [23]. Sunyoto et al. found that the BC addition could reduce the lag time by 21.4%–35.7%, and improved the H_2 potential by 14.2%–31.0% [24]. The addition of zero-valent iron (Fe^0) was revealed to produce 38.2% H_2, and the coupled system of activated carbon and Fe^0 could further enhance the H_2 yield by 50.2% [25]. The related reports exhibited that the application of inorganic or conductive materials was a promising approach to promote H_2 evolution from various substrates [14–16,26,27], because of their high surface area or uniquely physical and chemical characteristics [28,29].

Although the aforementioned materials, i.e. activated carbon, bio-char, hematite and magnetite particles, are reported to be capable of improving electron transfer, enriching anaerobic bacteria, and accelerating the bio-H_2 or bio-CH_4 process, to the best of our knowledge, the behaviors and mechanisms of ferric oxide/carbon NPs (FOCNPs) of bio-H_2 fermentation have not been reported to date. This work was carried out to (1) study the effects of FOCNPs on H_2 production from glucose in terms of metabolites distribution, hydrogen yield and production rate, (2) evaluate the kinetics of H_2 evolution using the modified Gompertz model, (3) clarify the possible mechanisms of H_2 yield improvement, and (4) investigate the inhibitory effects of excessive FOCNPs on H_2 fermentation.

Materials and methods

FOCNPs preparation

The FOCNPs were prepared by a heat treatment of Fe_3O_4/starch mixture as previously reported [30]. Firstly, 44.72 g of $FeCl_2 \cdot 4H_2O$ was dissolved in 300 ml of H_2O, and then 50 g of starch was added into the blue solution with vigorous magnetic stirring at 80 °C. Finally, 35 ml H_2O_2 (1.0 mol/L) was poured followed by 100 ml NaOH (5.0 mol/L), resulting in black

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