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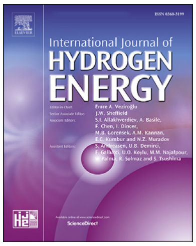
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Synergic effect of various amino acids and ferric oxide on hydrogen production

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ABSTRACT

To overcome nitrogen and iron deficiency in the organic fraction of municipal solid waste, amino acids and ferric oxide were separately added in the feedstock to evaluate their effect on hydrogen production. Furthermore, synergic effect of amino acids and ferric oxide on hydrogen production was evaluated. The co-culture of *E. coli* and *Enterobacter aerogenes* was used in the present study. The amino acids were applied in the concentration range of 1.0, 2.5, 5.0, 7.5 and 10.0 g/L while ferric oxide was used in the concentration range of 10, 20, 30, 40, 50, 100, 150, 200 and 500 mg/L. Modified Gompertz model was used to analyze cumulative hydrogen production (P), maximum hydrogen production rate (Rmax) and lag phases (λ). The results exhibited that the hydrogen production was positively affected by each amino acid at every concentration applied. Application of alanine resulted in the highest cumulative and volumetric hydrogen production of 685.4 ± 10.1 mL and $1.9561 L_{H2}/L_{substrate}$ respectively which increased to 872.5 ± 10.1 mL and $2.492 L_{H2}/L_{substrate}$ for ferric oxide addition along with alanine. COD removal and VFA generation were positively affected by the synergic effect of amino acid and ferric oxide.

Introduction

The wide use of fossil fuels, such as petroleum and coal, has led to the energy crisis and environmental pollution [1]. Currently, hydrogen production is attracting increasing attention due to its environment-friendly characteristics and high calorific value [2]. The conventional methods applied for hydrogen production such as water gas shift reaction, steam methane reforming, water electrolysis and gasification contribute to most of the world-wide hydrogen production [2]. Nevertheless, a large energy input is required for these processes. Utilization of renewable waste biomass for biohydrogen production has attracted increasing attention as it combines energy recovery and waste minimization. Several types of substrate has been utilized for biological hydrogen production through anaerobic digestion such as food waste [3], wheat straw [4], kitchen waste [5], fruits and vegetables waste [6], agriculture waste [7], biodiesel waste [8] and municipal solid waste [9] etc. Currently, organic fraction of municipal solid waste (MSW) has been given attention to be utilized for hydrogen production [10,11]. The generation of MSW amounts to 0.11 kg/capita/day according to central pollution control board [12]. Approx, 60% of municipal solid waste is organic fraction such as waste paper, urban greening waste and kitchen waste [13]. Utilization of OFMSW for hydrogen production alleviates conflict between demand and

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energy supply as well as improves economic feasibility for treatment of municipal solid waste [14].

In the dark fermentation process, the theoretical hydrogen yield depends on the type of microorganisms used [15]. Based on the results of our previous investigations, in the present study, co-culture of *E. coli* and *Enterobacter aerogenes* was used [16]. Both the bacteria are facultative anaerobic and have the capability to grow under strict anaerobic as well as aerobic conditions. *Enterobacter aerogenes* and *E. coli* have been isolated from sewage sludge and applied for production of hydrogen in the previous studies [17–19]. Both the bacterial species can utilize a wide range of substrate with fast growth rate and high tolerance to hydrogen partial pressure and dissolved oxygen [20,21].

Application of co-culture system offers an advantage of improved hydrogen production and yield as compared to mono-culture systems [22]. In the co-culture system, different microbial strains are mixed which improves the individual characteristic that other strain lacks. Thus, the co-culture system eliminates the need for pretreatment steps and use of expensive reducing agents. Thus, the co-culture system is cost-effective as compared to mono-cultures. It offers various advantages such as resistance to environmental fluctuation, reduction in lag phase and provides eight times more stability in hydrogen production rate as compared to mono-culture systems [22].

Several approaches have been applied to increase hydrogen production and yield [23]. To enhance hydrogen production, optimization of fermentation conditions is very important. Microorganisms are sensitive to their culture conditions in the anaerobic digesters. Nutrients in the culture medium are vital to their growth. Among nutritional requirement, nitrogen is an important factor essential for microbial growth. Nitrogen is an important process-limiting factor for fermentation [24]. In anaerobic digestion, nitrogen reaches mainly in the form of urea, protein, and amino acids in order to be further degraded [25]. A variety of microorganisms ferment the amino acids obtained from degradation of proteins via purine and pyrimidine-bases and extracellular proteases. Some amino acids can be used as sole nitrogen or carbon sources, however, often NH_3/NH_4^+ is the end-product of the decomposition process. These by-products are used by the microbes directly as a source of nitrogen which additionally acts as a buffering system for the surrounding media [26]. A lot of previous investigations have shown that proper protein content in the substrate can improve hydrogen production [27–29]. However, the protein-derived amino acids cannot be easily used by hydrogen-producing bacteria due to low C/N ratios and their unique molecular structure [30]. Many investigations have been done to improve the hydrogen production from the protein-rich substrate. Song et al. [31], improved the hydrogen peak rate and yield by adding *Saccharomyces cerevisiae* to defatted milk powder, which produced several proteinases to facilitate degradation of lacto-protein. Xiao et al. [32], produced hydrogen from ultraviolet pretreated protein waste-water and reported 3.8 times greater hydrogen production as compared to control. The increase in the hydrogen production was due to effective disruption of hydrogen bonding networks which unfolds protein and increases their susceptibility to proteases. Amino acids such as alanine can be degraded anaerobically and converted to short-chain volatile fatty acids via coupled oxidation-reduction reaction [33]. The low efficiency of hydrogen production of amino acids derived from proteins in the waste substrate [34,35], is a technical limitation of the industrial application of hydrogen production. In several studies, it has been shown that prior to anaerobic digestion, high molecular weight proteins have to be hydrolyzed to low-molecular-weight amino acids for efficient utilization by fermentative bacteria [36,37]. There is a limitation of investigations on the application of pure amino acids for hydrogen production. Furthermore, in anaerobic fermentation, hydrogen production is dependent on the hydrogen-producing enzymes such as NADH ferredoxin and hydrogenase. It has been proved that trace metals such as iron, cobalt and nickel etc can effectively stimulate the growth of the microorganisms [38]. Trace metals improve the microbial activity by activating enzyme catalysis and accelerate cell synthesis and thus improve the gas yield [39]. Iron plays a crucial role in the process of electron transport and improves hydrogen production. In the pyruvate decarboxylation process of hydrogen production, ferredoxin is needed to act as an electron carrier and therefore hydrogen gas generation is closely related to the ferredoxin in the enzyme hydrogenase [40]. Iron is a fundamental element in the ferredoxin composition. It has been noted that the hydrogenase activity decreases with the iron limitation. Therefore, iron supplementation is required for improvement in the hydrogen production. Iron in the form of nanoparticles has also been used to enhance hydrogen production. Gadhe et al. [40], reported that hematite nanoparticles enhanced the activity of the ferredoxin oxidoreductase by causing an increase in the electron transfer rate enhancing hydrogenase activity. Similarly, Han et al. [41], reported an increase of 32.6% in hydrogen yield from sucrose with the addition of hematite nanoparticles at a concentration of 200 mg/L. The enhancement in the hydrogen production was attributed to the iron release from hematite nanoparticles maintaining proper iron concentration for fermentative microorganisms. Patel et al. [42], examined the effect of the heavy metals on the anaerobic digestion and found that more than 60% increase in the anaerobic digestion was caused by $FeCl_3$. Zhu et al. [43], evaluated the effect of iron on hydrogen production and reported that the hydrogen production yield doubled as compared to control by addition of an optimal dose (8–16 g/L) of iron shavings. Engliman et al. [44], reported that the iron nanoparticles improved the hydrogen production by 53%. Hamilton et al. [45], evaluated the effect of organic or ammonium nitrogen sources on hydrogen production. The aforementioned authors reported that the metabolism of the microbes was favored by the addition of the nitrogen sources. Aly et al. [46], reported that the casamino acid improved the hydrogen production with a hydrogen yield, cumulative hydrogen production and hydrogen production rate of 1.81 mol-H_2/mol glucose, 2505 mL-H_2/L and 160 mL/h respectively. Similarly, Gabrielyan et al. [47], reported positive impact of some amino acids (asparagine, glycine, proline, tyrosin, alanine and glutamate) on hydrogen production.

To the best of author's knowledge, the synergic effect of amino acids and ferric oxide on hydrogen production has not been evaluated so far. Thus, to evaluate the synergic effect of

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