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Effects of Different States of Fe on Anaerobic Digestion: A Review

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Abstract: Anaerobic digestion is widely used in the treatment of industrial wastewater, excess activated sludge, municipal waste, crop straw and livestock manure, with the functions of environmental protection and energy recovery. This review summarizes and evaluates the present knowledge of effects of different states of Fe (ZVI, Fe (II), Fe (III)) on hydrogen and methane production in anaerobic digestion process. The potential promotion effects of iron oxides nanoparticles (IONPs), especially magnetite nanoparticles on anaerobic digestion are also mentioned. Fe plays important role in transporting electron, stimulating bacterial growth and increasing hydrogen and methane production rate by promoting enzyme activity. Adding Fe with different morphologies and valence states in anaerobic digestion to increase biogas (hydrogen and methane) production and enhance organic matter degradation simultaneously, which has attracted many scientists' attention in recent years. Rapid progress in this area has been made over the last few years, since Fe is essential to the fermentative hydrogen and methane production, while few is known about how Fe affects the fermentative biogas production. This review is significant to maintain the stable operation of the biogas project.

Keywords: anaerobic digestion; Fe; hydrogen and methane production; iron oxide nanoparticles; magnetite manoparticles

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1 Introduction

Energy crisis and environmental pollution are two serious problems of sustainable development of China, even the world. One of effective approaches to solve the energy problem is developing biomass energy such as biogas, changing energy consumption structure dominated by fossil fuel. In addition, environmental protection technologies require both low energy consumption and high efficiency[1-3]. As a synthesis technique to combine environmental protection, energy recovery and ecological cycle, anaerobic digestion attracts extensive attention worldwide and widely used in the treatment of wastewater, sludge, municipal solid waste and anaerobic fermentation of crop straw, livestock waste[4-10]. Besides degrading of organic waste with low energy consumption and high efficiency, anaerobic digestion can produce large amounts of biogas such as hydrogen and methane, which present greatly economic efficiency.

Anaerobic digestion includes four stages: hydrolysis, acidification, acetic acid production and methane production, which are interdependent and proceed continuously[10]. The complex organic matters can be transformed into carbon dioxide, water, cell products, hydrogen and methane ultimately by the metabolism of microorganism flora, which includes hydrolytic bacterium, acid-producing bacteria, hydrogen-producing acetogens, homo-acetogens, methanodogens. Different microorganisms depend on and restrict each other, creating favorable environment and symbiotic relationship. And efficient anaerobic digestion with high removal rate of organic pollutants and production of hydrogen and methane is the external performance when the symbiotic relationship is adjusted to the optimal condition. Many authors have published literatures on hydrogen and methane production by anaerobic digestion including gas producing kinetic, microflora structure, process optimization, degradation pathway etc[11-17]. Furthermore, a series of anaerobic digestion processes and technologies aimed at hydrogen-generating and methane production have been developed, such as two-phase hydrogen and methane production process which have been used in the treatment of organic wastewater and solid waste[13,18].

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From the obtained conclusions, optimal environmental conditions are very important for the activity of methanogens and hydrogenogens which guarantee methane and hydrogen producing stably and efficiently. Therefore, discovering the environmental conditions affecting the anaerobic microbial metabolic activity, exploring the mechanisms of population structure and metabolic pathways, and creating appropriate environmental conditions for different microorganisms through hierarchical control technology become key point to achieve fully biodegradation of organic matters and high yield of biomass energy-hydrogen and methane.

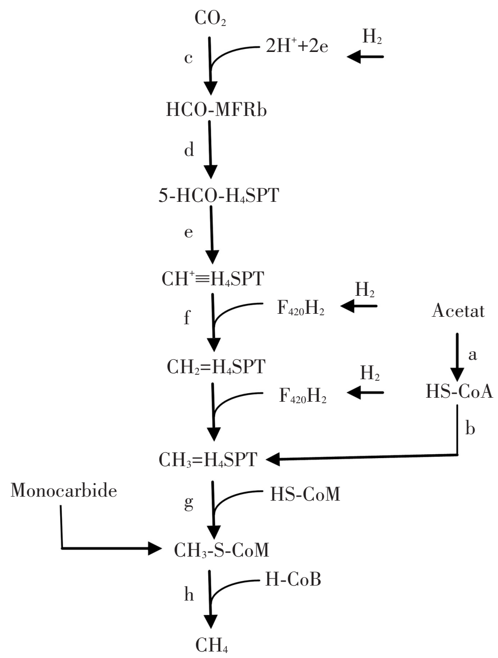
Adding trace metals such as Fe, Co and Ni has been proved as effective methods to stimulate the growth of anaerobic microorganisms[19-20]. Through activating enzyme catalysis in the biochemistry, trace metals can improve bacteria activity, accelerate cell synthesis and then increase the yield of gas[21]. Different chemical forms of Fe are in common used as additives in anaerobic digestion process. The purpose of this review is to critically evaluate the existing knowledge of Fe impacts on anaerobic digestion, taking into consideration the promotion mechanism of hydrogen and methane production, promotion efficiency analysis of Fe with different valence states and potential effects of iron oxides nanoparticles (IONPs) on yield of gas. From the current information, we then identify the current knowledge gaps.

2 Mechanism Analysis of Promotion of Hydrogen and Methane Production by Fe

Fe has an important influence on gas production in anaerobic digestion process. It exists in iron-sulfur clusters and acts as electron carrier in intracellular oxidation-reduction reactions, taking charge of electronic transfer. Fe also involves in the synthesis of cytochrome and oxidase[22].

2.1 Promotion of Fermentative Methane Production by Fe

Methanogenesis create necessary energy to sustain cell proliferation and methane biosynthesis. Up to now, the studies found that methane could be synthesize by three ways (Fig. 1)[23]. Catalysis of a variety of enzymes and coenzymes will be involved in the process of methane production, in addition, most of these enzymes and coenzymes contain metallic element such as Fe and Ni. Therefore, Fe can influence the fermentative methane production by promoting the synthesis of enzymes and activating enzyme catalysis, meanwhile, to maintain a certain concentration of Fe can improve the activity of methanogens by promoting cell synthesis and change microbial community structure of methanogens. Researchers reported that Fe could transform dominant bacteria from methanothrix to methanosarcina barkeri whose specific methanogenic activity is three to five times than that of the former, so it is easy to form high efficient methane-producing populations[24-25]. Sulfide inhibition has been extensively studied for biological methane production[26-27], and Fe is also a very effective heavy metal for sulfide control to reduce toxicity of soluble sulfide to methanogens in anaerobic digestion through precipitation[28-29].



Note: a. Acetyl coenzyme A synthetase; b. Carbon monoxide dehydrogenase (CODH); c. Formylmethanofuran dehydrogenase (Fmd); d. Methyltransferase; e. Methenyl-tetrahydromethanopterin (H4MFT) cyclohydrolase; f. F420-reducing hydrogenase; g. Methenyl-tetrahydromethanopterin (H4MFT): coenzyme M methyltransferase; h. Methyl-coenzyme M reductase.

Fig.1 Biosynthetic pathways of methane

2.2 Promotion of Fermentative Hydrogen Production by Fe

Hydrogen production by pyruvate decarboxylase is dependent on the catalysis of hydrogen-producing enzymes, such as hydrogenases and NADH ferredoxin (Fd) etc in anaerobic digestion process. Fe plays an important role in the electron transport, and can improve hydrogen production by promoting hydrogenase activity. The hydrogen production process of pyruvate decarboxylation contain following two types[30] (Figs. 2 and 3). In both of two types as above, the participation of ferredoxin acting as an electron carrier is needed during the process of fermentative hydrogen production, therefore, hydrogenproduction is closely related with ferredoxin in the hydrogenases.

Fe is a fundamental component making up the ferredoxin additionally, almost all the enzymes in fermentative bacterium contain ferredoxin with four Fe or eight Fe, and ferredoxin whose active center is $Fe_4S_4(S\text{-}Cys)_4$[31] (Fig. 4) is more important. Fe-S atomic clusters is also the active center of hydrogenases which exist in many kinds of bacteria, such as clostridium pasteurianum[31-32]. Researchers noted that the activity of hydrogenases decreases with the consumption of Fe[33], thus the supplementation of Fe is required to improve the ferredoxin in the fermentative hydrogen production process.

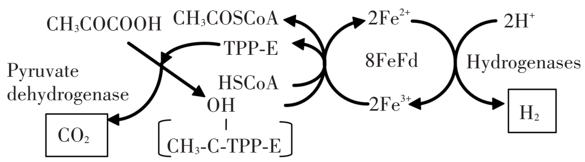


Fig. 2 The hydrogen production process of pyruvate decarboxylation (Clostridium)

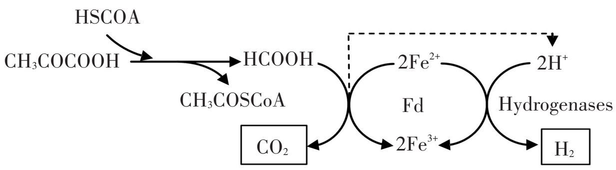


Fig. 3 The hdyrogen production process of formate decomposition (Enterobacteriaceae)

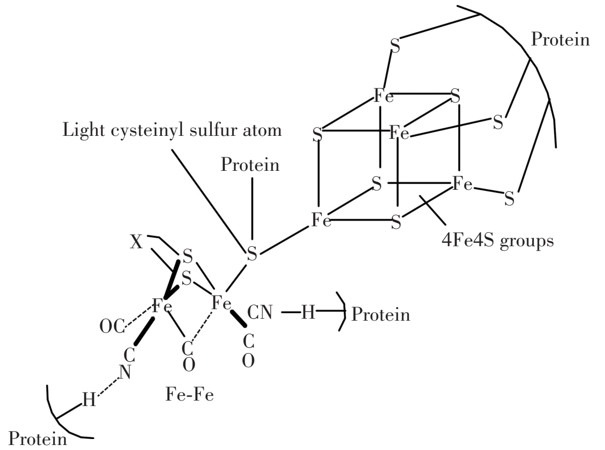


Fig.4 $Fe_4S_4(S\text{-}Cys)_4$-ferredoxin model

2.3 Promotion Efficiency Analysis of Fe with Different Valence States

Fe is one of the essential necessary elements to the growth of methane-producing bacteria and hydrogen-producing bacteria. So far, its effect on anaerobic fermentation has been widely concerned. It is an effective way to improve hydrogen and methaneproduction by adding Fe (II) and zero-valent iron (ZVI) in anaerobic fermentative system. Lin[34] investigated the acceleration of different metal ions including Fe (II) on ability of hydrogen production of high efficient hydrogen-producing bacteria. The hydrogen production promoting order of three kinds of ions for B49 is Fe(II) > Ni (II) > Mg (II), which was also verified in the following studies[35-36]. Wang found that Fe (II) was able to enhance the cumulative hydrogen quantity, and the hydrogen yield by the mixed cultures. The maximum cumulative hydrogen quantity of 302.3 mL and the maximum hydrogen yield of 311.2 mL/g glucose were obtained at the Fe (II) concentration of 300 and 350 mg/L, respectively. When the Fe(II) concentrations were between 100 and 750 mg/L, and there was a high biomass production yield plateau ranging from 259.2 to 334.2 mg/g glucose[35]. Some studies also indicate that only in proper concentration range, Fe (II) will increase the activity of hydrogenases, which can increase fermentative hydrogen production by mixed cultures in turn, while much lower or much higher Fe (II) concentration than the suitable one can decrease the activity of hydrogenases[35,37-38]. Cao explored the effects of Fe with different valence states (ZVI, Fe (II), Fe (III)) on hydrogen production and the results show that Fe (II) is the best. The largest capability of biohydrogen production was 364.8 mL/g sucrose and the concentration of hydrogen was 56.5% which was 1.54 times of the blank sample[39]. Preeti reported when 20 mmol/L Fe (II) was added to the daily-fed cow dung and poultry litter waste digesters, methane production could be increased by 40% and 42%, respectively, and the growth and activity of the prevalent microorganisms were also increased which could promote the turnover rate of total methane[40].

However, most of researches showed that the promoting effects of ZVI are more obvious on the fermentative hydrogen and methane production[27-28]. Ding founded that at the same concentration, the enhancement of Fe is better than Fe (II) when the concentration is higher than 50 mg/L[30], which is similar to the conclusion got by Wang[41]. The reasons may be that ZVI has stronger reducing capacity and it can act as electron donor and active center of ferredoxin and enzymes to participate in bacterial fermentative dehydrogenation process directly or indirectly compared with Fe(II). In addition, ZVI can reduce environmental oxidation-reduction potential (ORP), which is in favor of the growth of fermentative bacteria and the improvement of bacterial metabolic activity, stabilizing pH of the system, increasing the alkalinity through adsorbing CO_2, promoting enzyme activity and cell synthesis of methanogens, and promoting the secretion of extracellular polymers[42-45]. In addition, more appropriate fermentative substrates could be provided for methanogens by promoting acetic acid formation and inhibiting propionic acid production when ZVI was added into single-phase anaerobic reactor[46]. Compared with Fe (II), ZVI can effectively avoid methane-producing inhibition caused by anions such as SO_4^{2-} and Cl^- etc.

About the promotion of microbial metabolic activity, the studies showed that suitable dosage of Fe will improve the production of hydrogen and methane in the process of anaerobic digestion. While problems such as toxicity caused by some complicated compounds formed by high dosage, high consumption rate of iron ion and anion inhibition limit the application of adding iron ions. IONPs (Iron Oxide Nanoparticles) with surface modification present better dispersibility and solubility, they also have unique physichemical properties such as small scale effect, surface effect and magnetic effect. Compared with NZVI (Nanoscale Zero Valentine Iron), unique crystal structure and mixed valence of IONPs can make them easier show direct-releasing and slow-release-effect of Fe (II) which enhances their bioavailability, meanwhile MNPs are much cheaper and chemically stable.

3 Promotion Analysis of IONPs

IONPs mainly include nanoparticles as Fe_3O_4 and Fe_2O_3 etc. Besides physicochemical characteristics which are different from traditional matrix oxides, IONPs have also good superparamagnetism when the size is reduced to critical value. These special properties such as simple preparation, high stability, good bioavailability and easily modification of surface make IONPs be widely used. As one of IONPs, magnetite nanoparticles (MNPs) have attracted more attention especially in the field of environment protection[47]. Based on significant characteristics as above, MNPs have been used in the effective adsorption of heavy metal ions such as Hg (II), Cr (VI) and Cu (II) and phosphate[48-51]. MNPs have also been used in the solid phase extraction (SPE) of polycyclic aromatic hydrocarbons, adsorption and removal of organic dye, microbial fuel cell, promotion of fenton-like system to degrade dyes etc[52-57].

He found that MNPs could promote the growth of actinomycetes in soil, and obviously improve the activity of urease and invertase. The reasons are that due to their tiny size and stabilization, MNPs can be easily transported into soil. Nano-metal oxides have enhanced surface-to-volume ratio, therefore, partial decomposition and release of ions is more likely for nanoparticles compared to the bulk material. Furthermore, nanoparticles have the most active surface sites (mainly Fe-OH site on MNPs) that are able to bind to natural organic compound[58].

However, Fang found that instead of iron ion release, magneto-induced effect may be the main reason for activating amylase, neutral phosphatase, urease and catalase when they investigated the influences of MNPs and Fe_2O_3 nanoparticles on microorganism quantity in red earth and enzyme activity[59]. It is clear that promoting mechanism of MNPs on microbial growth and enzyme activity is still controversial. Little is known regarding the effects of IONPs on anaerobic hydrogen production. Han found that Fe_2O_3Nanoparticles (Hematite Nanoparticles, HNPs) has promoted the effect on anaerobic fermentative hydrogen production due to the slow release of hematite nanoparticles which could keep the proper Fe concentration and inhibit the harm of high Fe concentration for microbe. Hydrogen production could be increased by 66.1% when 200 mg/L HNPs with average particle size of (55±5) nm was added under acidic condition (pH = 6), and the lag phase of hydrogen production could be shortened[60]. Results of Zhao indicated that compared with Fe (II), the effect of MNPs was much more significant, by which the lag phase was shortened dramatically and hydrogen production was increased greatly[61]. Mohanraj found that the enhancement effect of the IONPs on fermentative hydrogen production was higher than that of Fe (II), and the hydrogen production from the glucose and sucrose fed systems using E. cloacae, conformed to the acetate/butyrate fermentation type[62]. Carolina investigated the impact of micrometer-size magnetite (Fe_3O_4) particles supplementation on the methane production rate from propionate by methanogenic sludge, and found that lag phase of propionate degradation in bottles containing magnetite particles was shorter 10 days, and the maximum rate of methane formation 33% higher than in the corresponding unamended controls. The stimulatory effect most probably resulted from the establishment of a direct interspecies electron transfer (Fig.5), based on magnetite particles serving as electron conduits between propionate-oxidizing acetogens and carbon dioxide-reducing methanogens[63]. Therefore, it is meaningful to investigate the promoting mechanisms of MNPs to produce hydrogen and methane in the process of anaerobic digestion. But the promotion mechanism of MNPs on anaerobic fermentative process to produce hydrogen and methane is still unclear.

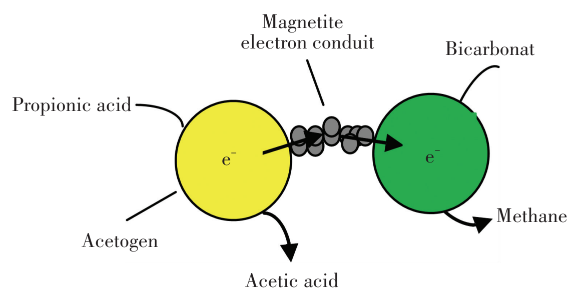


Fig.5 Proposed electron transfer mechanisms between an acetogen and a methanogen in magnetite supplemented cultures

4 Inhibition Risk Analysis of NZVI and IONPs on Anaerobic Fermentative Process

In view of potential ecological toxicity and environmental risks of metal nanoparticles and its oxides, the inhibition risk on anaerobic fermentative process has been always focused on. Some scientists analyzed the impacts of NZVI on anaerobic digestion in sludge. Results showed that due to the lack of dissolved oxygen, nano-toxicity caused by active oxygen did not appear, and NZVI promoted methane production in certain concentration range[64-66]. However, Yang et al. found that although NZVI could increase hydrogen production in the process of anaerobic digestion in sludge, it would cause acid accumulation and then inhibit methane production, which was attributed to high concentration of Fe(II) release caused by quick dissolution of NZVI[67]. What's more, the ecological toxicity of MNPs on bacteria is very limited and will not affect bacterial growth although MNPs could react with the surface of bacteria[68].

5 Conclusions and Prospects

Fe is one of the essential necessary elements to the growth of anaerobeic microorganism and participates in the synthesis of enzymes in the anaerobic fermentative process. However, at present, only preliminary discussion was made about promoting effect of IONPs on anaerobic hydrogen production under conditions of single particle size, different dosage and pH value. Meanwhile, there were few discussions of promotion mechanism of microbial community structure, abundance variation, activation mechanism of key enzymes and metabolic pathways. What´s more, the existing results did not include the environmental behavior, migration mechanism of MNPs-sludge-bacteria and its promotion mechanism on bioavailability under anaerobic condition. In view of the existing deficiency, promotion mechanism about different states of Fe and IONPs on anaerobic fermentative system should be further studied, and potential environmental risk by adding metallic element cannot be ignored.

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