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A REVIEW ON INFLUENCE OF PRETREATMENT AND SYSTEM OPERATING CONDITION FOR HYDROGEN PRODUCTION FROM WASTEWATER

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Abstract*: *H_2 is a sustainable and viable form of green/alternative energy source. This study reviews the work on H_2 production from wastewater treatment relating to inoculum pretreatment and system working conditions. Process was assessed and examined taking into account pretreatment methodology procedures applied on mixed parent anaerobic culture to selectively enrich acidogenic culture, operating pH and retention time in concurrence with wastewater type as substrate.

Keywords: **Biohydrogen, pH, Chemical Oxygen Demand, Wastewater treatment.**

I. INTRODUCTION

Capturing of energy as molecular biohydrogen (H_2) especially from wastewater treatment process is gaining prominence. Various biological routes of H_2 production include biophotolysis, photo-fermentation and dark-fermentation processes or by a combination of these processes[1-4]. Fermentative conversion of substrate to H_2 is complex biochemical process manifested by diverse group of bacteria by a series of biochemical reactions similar to anaerobic conversion[5].

Anaerobic conversion requires four major steps and five physiologically distinct groups of microorganisms where hydrocarbons are converted from complex to simple molecules through H_2 and acid intermediates (Fig. 1). Hydrocarbons are ultimately converted to carbon dioxide (CO_2) and methane (CH_4). Fermentative/ hydrolytic microorganisms hydrolyze complex organic polymers to monomers, and then ferment monomers to a mixture of low-molecular-weight organic acids and alcohols.

Obligatory H_2 producing acetogenic bacteria (AB) oxidize fermentation products to acid intermediates and H_2, which also include acetate production from H_2 and CO_2 by acetogens and homoacetogens and finally acetoclastic methanogens convert organic acids to CH_4 and CO_2[5-7]. Many thermophilic systems use syntrophic oxidation of acetate to CO_2 and H_2 by acetogenic or homoacetogenic bacteria coupled to H_2 consumption by hydrogenotrophic methanogens[5]. H_2-producing AB grow in syntrophic associations with hydrogenotrophic methanogens (H_2 consuming), which keep H_2 partial pressure low enough to allow acetogenesis to become thermodynamically favorable by interspecies H_2 transfer[5]. Using mixed consortia as biocatalyst for H_2 production can be a practical and

promising option for scaling up of technology especially when wastewater is used as substrate.

This review summarizes the work carried out on H_2 production pertaining to inoculum pretreatment and system operating conditions during wastewater treatment. Process was evaluated and discussed based on pretreatment procedures applied on mixed anaerobic culture to selectively enrich acidogenic H_2 producing culture, operating pH, hydraulic retention time (HRT) and substrate loading rate in concurrence with wastewater used as fermentable substrate.

II. PRETREATMENT METHOD

Pretreatment of parent inoculum/culture used in fermentative H_2 production process permits selective nrichment of specific group of bacteria. H_2 production with dark fermentation process shows many common features with methanogenic anaerobic digestion[5].Typical anaerobic mixed cultures cannot produce H_2 as it is rapidly consumed by methane-producing bacteria[8]. Most effective way to enhance H_2 production from anaerobic culture is to restrict or terminate methanogenesis process by allowing H_2 to become an end product in metabolic flow. Induction of H_2 accumulation in fermentative consortia is related with inhibition of H_2 consumers (especially methanogens), which is essential for its further scale-up and industrial application[9].

It is important for acidogenic H_2 producing process and also inhibits bacteria that are not required especially when mixed cultures are used as parent inoculum. Physiological differences between H_2 producing bacteria and H_2 uptake bacteria form fundamental basis for methods used for preparation of H_2 producing seeds[10].

H_2 producing inoculum. Seed preparation affects both start up and overall efficiency of H_2 production[3].

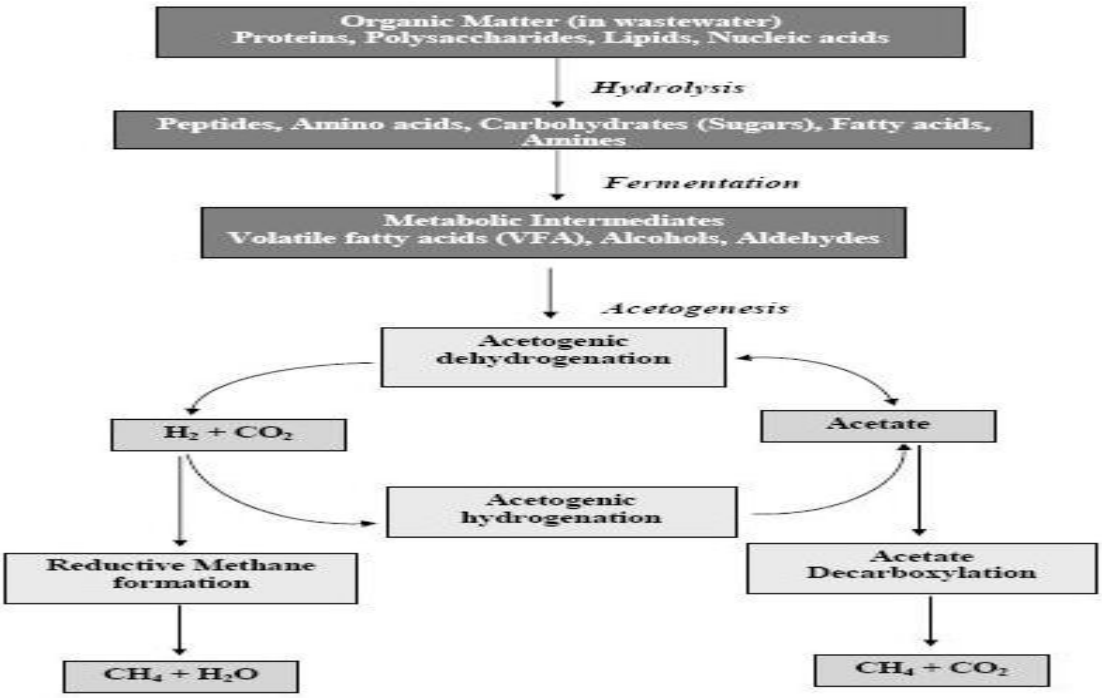

Figure 1: Anaerobic process of wastewater treatment depicting both acetogenesis/acidogenic and methanogenic process during conversion of complex organic material to methane and carbon dioxid[4].

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Heat-shock Treatment (HST)

HST facilitates suppression of non-spore forming bacteria and allows growth of spore forming bacteria, which are important for H_2 production. HST relies on thermal suppression of methanogenic *Archaea* and non-sporulating bacteria, thereby enriching culture with sporulating H_2 producing bacteria. . It also facilitates suppression of methanogenic activity, which leads to H_2 production associated with concomitant volatile fatty acid (VFA) generation. HST parameters[10] vary with temperatures (80-104°C) and exposure times (15-120 min)[1,2,4].

It is efficient to remove H_2 consuming bacteria while protecting spore forming bacteria and reported[34] to repress methanogenic activity completely. HST kills vegetative cells of non spore-forming microorganisms, some of which consume H_2 such as methanogens but in this process it could also kill H_2-producing microorganisms (*Enterobacter* sp), which are unable to sporulate[4, 5]. On the contrary, HST may activate dormant spores of strains able to germinate and produce H_2 when conditions become optimal, for example, spores of *Clostridial* species.

Acid Treatment

Most methanogens are limited to a relatively narrow pH range (6.8-7.2), while most H_2 producing bacteria can grow over a broader pH range Methanogens are repressed by controlling cultivation conditions at low pH (5.5)[1, 4, 5]. Acid treatment is efficient in removing H_2 consumer bacteria and also protects spore-forming bacteria by repressing methanogenic activity. Acidic pH (5.0-5.5) was considered to be ideal for effective H_2 production due to its influence on repression of methanogenic activity thus indirectly promoting H_2 producers within the system[4, 5, 6].

Load-shock Treatment (LST)

LST is reported more effective than HST due to the presence of higher diversity of microbes, as no physical or chemical treatment was applied. On the other hand, overloading or shock-load treated sludge led to accumulation of organic acids, resulting in decrease of pH from 5.5 to 4.6; hence, not suitable for growth of methanogens[4]. LST facilitates preparation of H_2 producing by physical pretreatment by means of direct cultivation of digested sludge without any chemical pretreatment LST is reported to be effective compared to base, acid, chemical (BESA) and HST methods for enriching thermophilic H_2 producing seeds, as it completely repressed methanogenic activity along with good H_2 production[4, 6,7].

Chemical Treatment

H_2 consuming methanogens in mixed culture could be eliminated by applying inhibiting chemicals [iodopropane, acetylene and 2-bromoethanesulfonic acid (BESA)]. BESA is a structural analog of co-enzyme-M specifically found in methanogens only. Chemical treatment by BESA facilitates selective inhibition of methanogenic activity without disturbing H_2 production where co-enzyme M reductase complex, a chief component for methanogenesis, inhibits In addition, BESA could inhibit acetate producing process and long-term operation with BESA addition were not found sustainable and likely to have side effects on H_2 producing bacteria as well as occurrence of BESA-resistant mutants in anaerobic fermentation[4, 7]. Chemical pretreatment method has an advantage of being readily applied as and when required.

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III. FACTORS INFLUENCING BIOHYDROGEN PRODUCTION

System operating conditions significantly influence overall performance of H2 production process in association with wastewater treatment. Data enveloping analysis (DEA) performed on H2 production process illustrated the importance of pH microenvironment, nature of mixed consortia, composition, nature and complexity of fermentative substrate used7.

pH

Bacteria respond to changes in internal and external pH by adjusting their activity and synthesis of proteins associated with many different processes, including proton translocation, amino acid degradation, adaptation to acidic or basic conditions and virulence. Depending on organism and growth conditions, changes in external pH can bring about subsequent alterations in several primary physiological parameters, including internal pH, concentration of other ions, membrane potential and proton-motive force[8, 9, 11]. This is especially important for fermentative H_2 production where activity of acidogenic group of bacteria is considered to be crucial and rate limiting. pH plays a critical role in governing metabolic pathways of organism where activity of AB is considered to be crucial[4, 10].

pH are integral expressions of acid-base conditions of any anaerobic process and also an intrinsic index of balance between two of the most important microbial groups[4, 13]. Production of acids gradually reduces buffering capacity of system, which, in turn, resulted in a concomitant decline in the system pH in all experimental variations studied, due to accumulation of organic acids leading to process inhibition, If pH is not maintained in optimum range, cessation of H_2 production will result along with marked shift in microbial population[29]. Higher concentration of soluble metabolite production (VFA) is observed under acidophilic experiments over the corresponding neutral microenvironment and corroborates well with H_2 production observed. During acidophilic operation, soluble metabolites distribution showed acid-forming (formation of acetic acid) metabolic flow, which is considered optimum for effective H_2 production[13].

Hydraulic Retention Time (HRT)

HRT also influences H_2 generation process. Fermentation time is considered as an important operational parameter to restrict the process of methanogenesis during acidogenic H_2 production. It facilitates metabolic shift in concurrence with extended fermentation time, nature of inoculum, nature of substrate, applied loading rate and fermentation pH[13]. A number of workers have used short HRT and acidophilic pH. Optimum HRT between 8.0 and 14 h has been reported to yield maximum H_2 with inhibition of methanogenesis. Continuous H_2 production from a mixed culture was observed at long HRT of 3 days (pH 6.4) without encountering problems with methanogenesis[13, 14]. Provision of short HRT's during reactor operation may wash out slow growing methanogens and can reduce reactor size and capital cost.

Substrate Loading Rate

Apart from wastewater characteristics, substrate/ organic loading rate (OLR) of wastewater had marked influence on H_2 production. H_2 yields were inversely related to glucose feeding rate, while highest H_2 yields were observed at lowest glucose loading rate Glucose concentration exceeding 2 g/l (as co-substrate) showed suppression in H_2 production[4,13, 15]. Feed consisting of only glucose as substrate showed low H_2 yield, while feed with chemical wastewater admixed either with glucose or with sewage wastewater as co-substrates demonstrated relatively high H_2 yield Adding glucose and sewage wastewater as co-substrates along with chemical wastewater showed positive influence on H_2 generation rate. H_2 production was studied using chemical wastewater as substrate in which a marked reduction in H_2 production rate was observed with increase in OLR [specific hydrogen yield - 13.44 mol H_2/kg COD-day (6.3 kg COD/m^3-day), 8.23 mol H_2/kg COD-day (7.1 kg COD/m^3-day) and 6.064 mol H_2/kg COD-day (7.9 kg COD/m^3-day)][4, 10, 17]. Increase in H_2 yield may be due to end product inhibition by over-accumulated (supersaturated) H_2 in liquid at high COD. H_2 production rate increased with increase in initial glucose concentration from 0.5-2.0% but dropped at 2.5% indicating substrate inhibition[17].

However, for effective H_2 yield and substrate degradation, significantly diverse system operational conditions are required individually under anaerobic microenvironment[17]. Balancing conditions for combined effective performance and process optimization in this direction are especially important to sustain economic viability[17, 18]. In this direction, a study was performed to evaluate the system performance by combining both output parameters using two diverse mathematical approaches [data enveloping analysis (DEA) and Taguchi design of experimental (DOE) methodology][4, 19]. Feed composition showed stronger influence followed by pH and pretreatment with respect to H_2 production. Acidophilic pH responded favorably to H_2 generation. Feed composition showed significant influence on H_2 production and substrate degradation[19].

Concluding Remarks

Pretreatment applied to parent inoculum, operation conditions such as feeding and operating pH, HRT, etc. significantly contribute to H_2 production and substrate degradation apart from nature and characteristics of wastewater. Amount of substrate degradation is important when process efficiency is considered when dealing with wastewater as fermentative substrate for H_2 production. Balancing the conditions for combined effective performance are especially important for up-scaling the process and to sustain its economic viability. One of the vital aspects to be paid significant attention is non-utilized organic fraction, which remains as a soluble fermentation product from acidogenic H_2 production process.

REFERENCES

[01] Das D & Veziroglu T N, Hydrogen production by biological process: a survey of literature, *Int J Hydrogen Energy*, **26**

[02] (2001) 13-28.

[03] Logan B E, Biologically extracting energy from wastewater: biohydrogen production and microbial fuel cells, *Environ Sci Technol* , **38** (2004) 160A-167A

[04] Hawkes F R, Dinsdale R, Hawkes D L & Hussy I, Sustainable fermentative hydrogen production: challenges for process optimization, Int J Hydrogen Energy, 27 (2002) 1339.

[05] Venkata Mohan S, Fermentative hydrogen production with simultaneous wastewater treatment:

[06] influence of pretreatment and system operating conditions Journal of Scientific & Industrial Research, Vol. 67(2008) 950-961.

[07] Angenent L T, Karim K, Al-Dahhan M H, Wrenn B A & Domíguez-Espinosa R, Production of bioenergy and

[08] biochemicals from industrial and agricultural wastewater, Trends in Biotechnol, **22** (2004) 477-85.

[09] Dinopoulou G, Sterritt R M & Lester J N, Anaerobic acidogenesis of a complex wastewater kinetics of growth inhibition, and product formation, *Biotechnol Bioeng* 31 (1988) 969-978.

[10] Venkata Mohan S, Chandrasekhar Rao N, Prasad K K, Muralikrishna P, Rao R S & Sarma P N, Anaerobic treatment of complex chemical wastewater in a sequencing batch biofilm reactor: process optimization and evaluation of factors, interaction using the Taguchi dynamic DOE methodology, *Biotech Bioengng* 90 (2005) 732-745.

[11] Sparling R, Risbey D & Poggi-Varaldo H M, Hydrogen production from inhibited anaerobic composters *Int J Hydrogen Energy*, 22 (1997) 563-566.

[12] Valdez-Vazquez I, R1os-Leal E, Munoz-Paez K M, Carmona-Mart1nez A & Poggi-Varaldo H M, Effect of inhibition treatment, type of Inocula, and incubation temperature on batch H2 production from organic solid waste, Biotechnol Bioeng 95 (2006) 342-349.

[13] Zhu H, & Beland M, Evaluation of alternative methods of preparing hydrogen producing seeds from digested wastewater sludge, *Int J Hydrogen Energy*, **31** (2006) 1980-1988.

[14] Kim J, Park C, Kim T-H, Lee M, Kim S, Kim S. Seung-Wook & Lee J, Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, *J Biosci. Bioeng*, 95 (2003) 271-275.

[15] Lin C Y, Chen C C & Lin M C, Hydrogen production in anaerobic acidogenesis process-influences of thermal isolation and acclimation environment, *J Chin Inst Environ Eng.*

[16] Lay J J, Biohydrogen generation by mesophilic anaerobic fermentation of microcrystalline cellulose, *Biotechnol Bioeng*, 74 (2001) 280-287.

[17] van Ginkel S, Sung S W, Li L & Lay J J, Role of initial sucrose and pH levels on natural, hydrogen producing, anaerobe germination, in *Proc 2001 DOE Hydrogen Program Review, NREL/ CP-570-30535* , 2001.

[18] Valdez-Vazquez I, Sparling R, Rinderknecht-Seijas N, Risbey D & Poggi-Varaldo H M, Hydrogen from the anaerobic fermentation of industrial solid waste, *Biores Technol*, 96 (2005) 1907-1913.

[19] van Ginkel S, Sung S W & Lay J J, Biohydrogen production as a function of pH and substrate concentration, *Environ Sci Technol, 35* (2001) 4726-4730.

[20] Yu H, Zhu Z, Hu W & Zhang H Hydrogen production from rice winery wastewater in an upflow anaerobic reactor by using mixed anaerobic cultures, *Int J Hydrogen Energy,27* (2002) 1359-1365.

[21] Watanabe H, Kitamura T, Ochi S & Ozaki M, Inactivation of pathogenic bacteria under mesophilic and thermophilic conditions, *Wat Sci Technol*

[22] Venkata Mohan S, Harnessing of biohydrogen from wastewater treatment using mixed fermentative consortia: process evaluation towards optimization, *in Proc Int Workshop on Biohydrogen Technology (IWBT 2008)* (IIT, Khargapur) 7-9 February 2008.

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