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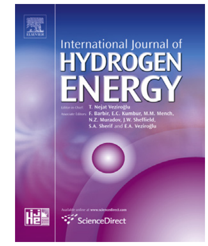

Enhanced bio-hydrogenesis by co-culturing photosynthetic bacteria with acidogenic process: Augmented dark-photo fermentative hybrid system to regulate volatile fatty acid inhibition

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ABSTRACT

To overcome induced fatty acid inhibition during dark-fermentative hydrogen (H_2) production process, a hybrid strategy was designed and evaluated by co-culturing photosynthetic bacteria with acidogenic microflora. Augmented dark-photo fermentation system (ADPFS) illustrated 40% increment in cumulative H_2 production (CHP, 250 ml) compared to dark-fermentation system (DFS) along with 10% enhancement in COD removal efficiency. Co-culturing helped to reduce VFA accumulation by 40% which supports the functional role of photosynthetic organisms in reducing the fatty acid concentration in association to additional H_2 production. Relatively higher reduction in individual fatty acids viz., acetic acid (43%), butyric acid (57%) and propionic acid (65%) was observed with AD-PFS operation. Increment in bacteriochlorophyll (*Bchl*) after augmentation corroborated well with results. At lower pH, pheophytinization was observed which hindered H_2 production. Voltammograms illustrated dominant oxidation behavior during hybrid AD-PFS operation and provides viable option for enhancing performance by regulating system buffering microenvironment.

Introduction

Diversification of energy resources is an essential requirement in the present-day energy scenario [1]. Rapid development of alternative, renewable, carbon-neutral, and eco-friendly fuels is essential to fulfill the burgeoning energy demands. Hydrogen (H_2) gas is an important and promising energy carrier that could play a significant role in the reduction of greenhouse gas emissions. Biologically produced H_2 is a natural and transitory by-product of various microbial-driven biochemical reactions [2–4]. Several strategies have been employed for biological H_2 production which include, direct and indirect biophotolysis of water, photo-fermentation,

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dark-fermentation or hybrid (photo-dark) fermentation. H_2 generation in light dependent (photo-fermentation) and light-independent (dark-fermentation) processes is of practical importance as it can combine both H_2 production and elimination of organic waste materials in a single step [5,6].

The dark-fermentation of H_2 production generates organic acid metabolites which inhibits the H_2 production process. The generation of these organic acids is one of the major problems as they make the H_2 production process unfavorable by limiting the substrate degradation. Various integration strategies were reported for the utilization of acid-rich effluents as the primary substrate for energy recovery e.g., anaerobic dark fermentation for H_2 integrated with the methanogenesis [7], photo fermentation [8–10], bioelectricity through microbial fuel cell [11] and recovery of value added products like bio-plastics [12] at secondary stage. Further utilization of the organic acids towards H_2 production is thermodynamically feasible only if there is an additional energy input. This energy input can be in from of electricity in microbial electrolysis cell (MEC) [13] or in the form of light in 2 stage photofermentation where it allows maximum conversion of the organic carbon to H_2 [14]. Diverse group of photosynthetic bacteria (PSB) are capable of utilizing organic acids as carbon and light as energy sources for H_2 production. Reports are available with two stage process for integrating heterotrophic dark-fermentation with photo-heterotrophic/fermentation processes for additional H_2 production [15,16]. Combination of dark and photo-fermentation could achieve a theoretical maximum yield of 12 mol H_2/mol Hexose [2,3]. A two-stage process i.e., the integration of dark and photo-fermentation has been considered as an effective and efficient system to increase H_2 yield and enhance energy recovery from organic wastewater and lower chemical oxygen demand (COD) in the process effluents [8].

In this communication, we have made an attempt to use hybrid process by integrating dark and photo fermentative processes in a single system for enhancing H_2 production along with wastewater treatment. The hybrid strategy facilitates *in situ* utilization of metabolic intermediates formed during the acidogenic H_2 production simultaneously by co-culturing photosynthetic bacteria. Experiments were designed for evaluating the relative performance of dark-fermentative process and photosynthetic-dark fermentative hybrid process on H_2 production and substrate degradation at two organic loads (OL) i.e., 1 kg COD/m^3-day (OL1) and 1.6 kg COD/m^3-day (OL2).

Materials and methods

Biocatalyst

Anaerobic culture

Anaerobic consortia acquired from a full scale operating anaerobic treatment unit was used as dark fermentative inoculum in the experiments. It was initially enriched in designed synthetic wastewater (DSW) [NH_4Cl – 0.5, KH_2PO_4 – 0.25, K_2HPO_4 – 0.25, $MgCl_2.6H_2O$ – 0.3, $FeCl_3$ – 0.025, $NiCl_4$ – 0.016, $CoCl_2$ – 0.025, $ZnCl_2$ – 0.0115, $CuCl_2$ – 0.0105, $CaCl_2$ – 0.005, $MnCl_2$ – 0.015, $C_6H_{12}O_6$-3.00 (g/l)] for a period of 72 h comprising 3 cycles each with 24 h under anaerobic microenvironment at pH 6.0 (100 rpm; 48 h). After enrichment of the inoculum it was subjected to sequential pretreatment with chemical, heat-shock and acid-shock to enrich H_2 producers (hydrogenic bacteria) as well as to suppress methanogenic bacteria (MB) [8].

Photosynthetic culture

An indigenous mixed photosynthetic consortium was acquired from existing photosynthetic fuel cell (PhFC) reported in our previous experiments [9]. This culture was enriched in a succinate salt broth, consisting of KH_2PO_4 – 0.33 g, $MgSO_4.7H_2O$- 0.33 g, NaCl- 0.33 g, NH_4Cl- 0.5 g, $CaCl_2.2H_2O$- 0.05 g, sodium succinate- 1.0 g, Yeast extract- 0.02 g, Distilled H_2O- 1 L, 1 ml trace metal solution ($ZnSO_4.7H_2O$- 10 mg, $MnCl_2.4H_2O$- 3 mg, H_3BO_3- 30 mg, $CoCl_2.6H_2O$- 20 mg, $CuCl_2.2H_2O$- 1 mg, $NiCl_2.6H_2O$- 2 mg, Na_2MoO_4- 3 mg, Distilled H_2O- 1.0 L, pH 3–4) and 0.02% $FeSO_4.7H_2O$ solution- 0.5 ml. This composition works well for enrichment of

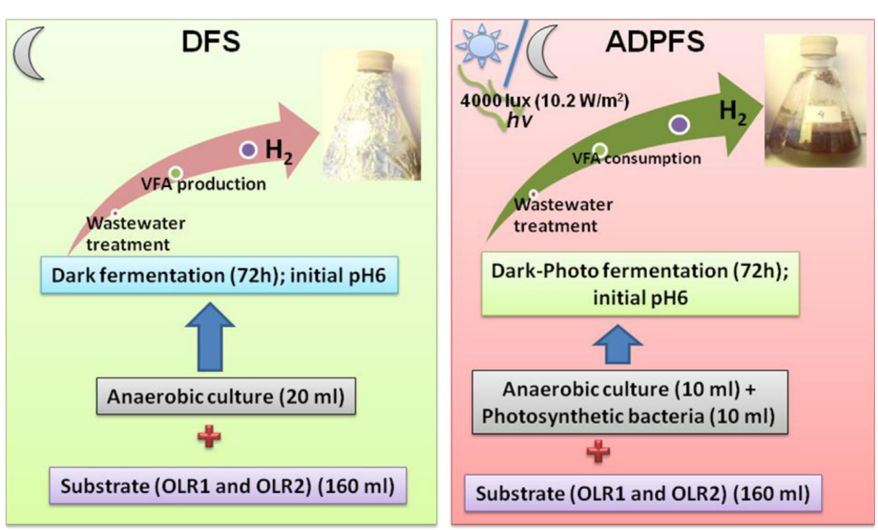

Fig. 1 – Schematic representation of experimental methodology followed during the operation dark-fermentation system (DFS) and augmented dark-photo fermentative system (ADPFS).