

Simultaneous H₂ Production and Treatment of Starch Wastewater in a Combined Up-Flow Anaerobic Staged Reactor Followed by Down-Flow Hanging Sponge System

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Abstract. This study was carried out to investigate the efficiency of up-flow anaerobic staged reactor (UASR) for hydrogen production from starch wastewater industry. The reactor was continuously operated at pH value of 6.86 ± 0.5 , temperature of 32 °C and organic loading rate (OLR) of 4.6 gCOD/l.d. Results revealed that, the reactor achieved an average hydrogen production of 6.0 lH₂/d, corresponding to 0.35 mol H₂/mol glucose. Furthermore, the drop of influent pH values from 6.86 ± 0.5 to 5.65 ± 0.76 during the UASR was associated by increase in VFAs from 46 ± 27 to 160 ± 58 mg/l respectively. The effluent quality of UASR is not complying for discharge into sewerage network. Therefore, post- treatment is needed. Down flow hanging sponge (DHS) system for treatment of UASR effluent was operated at an HRT of 1.5 h and OLR of 10 gCOD/l.d. The reactor in combination with UASR as a pretreatment achieved an overall removal efficiency of 83%. Moreover, pH value was adapted in DHS from 5.65 ± 0.76 to a value of 6.54 ± 0.48 . Also, the results obtained for the UASR profile showed that 50 % of TVFAs and 87% of MLSS were accumulated at the reactor bottom at a level of 10%.

Keywords: Starch Wastewater; Up-flow Anaerobic Staged Reactor; Hydrogen Yield; Down-flow Hanging Sponge; Carbohydrate; COD

1. Introduction

Starch manufacturing factories discharge huge amount of wastewater which is rich in biodegradable organic matter. This wastewater has to be treated prior discharging into sewer network. Generally, the chemical oxygen demand (COD) levels of starch wastewater range from 6 to 10 g/l and it can impose heavy loads on the environment or be expensive in terms of sewer disposal [1]. Previous studies have proved the feasibility of converting starch wastewater into hydrogen gas by dark fermentation process [2]. Anaerobic digestion of wastewater for hydrogen production has been extensively investigated for its advantages of low operational cost and effectiveness. Hydrogen production from renewable substrates is rapidly emerging as an alternative to fossil fuels, since it has triple the energy yield of hydrocarbon fuels [3] and produces only water with no CO, CO₂, hydrocarbons, or fine particles when combusted [4]. Hydrogen does not contribute to the greenhouse effect and has a high energy yield of 142 kJ/g, which is 2.75 times more than that of other hydrocarbon [5]. However, most of reports were conducted in batch cultivation pure H₂ producing bacteria [6; 7; 8]. Reports on continuous H₂ production from starch wastewater via dark fermentation process were relatively scarce, although the simultaneous COD degradation and H₂ production from starch wastewater in

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pilot-scale operation were promising, i.e. Lay et al. [9] obtained H₂ yield of 1.29 l/g-starch using a chemostat reactor at a hydraulic retention time (HRT) of 17 h. Lower H₂ yield of 0.031 l/g-wheat was found by Hawkes et al. [10] who used hydrolysate wheat feed as a sole substrate in a continuously completely stirred anaerobic reactor (CSTR). Lin et al. [11] conducted batch and continuous experiments to evaluate fermentative hydrogen production from starch and found that the optimal initial cultivation pH was 5.5 with peak values of H₂ yield of 1.1 molH₂/mol hexose. In another study, Chen et al. [12] achieved a H₂ yield of 0.24 l/g-starch using glass vessel for continuous operation at HRT of 12 h. Zhang et al. [13] found that the maximum H₂ yield of 92 ml/g starch added at pH 6.0 under thermophilic condition.

Therefore, the aim of this study is to investigate the efficiency of an Up-flow Anaerobic Staged Reactor (UASR) followed by Down-flow Hanging Sponge (DHS) for treatment of starch wastewater industry, with the emphasis on COD removal and carbohydrate conversion. Moreover, the UASR was operated mainly for H₂ production efficiency, while the DHS was used for removal of the remaining portions of COD and VFA for complying to discharge into sewerage network.

2. Materials and Methods

2.1. Starch Wastewater Characteristics

The starch wastewater was used as the sole substrate throughout the present study. The substrate was diluted with tapped water to attain the COD concentration of 1.8 ±0.69 g/l, without additions of nutrient or trace metal. Carbon to nitrogen ratio (COD:TKj-N) was estimated as 2000:10 which indicates insufficient nitrogen nutrients in the feed [14]. Starch wastewater had the following characteristics (Table 1).

Table 1. characteristics of the starch wastewater used in the experiments

COD (g/l)		Carbohydrates (g/l)		Nitrogen (mg/l)		Proteins (mg/l)	VFAs (mg/l)	pH
Total	Soluble	Total	Soluble	NH ₄ -N	TKj-N	60	46	6.86
1.8	1.2	1.6	1.2	1.68	9.6			

COD: Chemical Oxygen Demand; TSS: Total Suspended Solids; VFAs: Volatile Fatty Acids; Proteins = 6.26*TKj-N

2.2. Experimental Setup of the Pilot Scale

Fig. 1 shows a novel schematic diagram of the up-flow anaerobic staged reactor (UASR) fed with starch wastewater followed by a down flow hanging sponge (DHS). The working volume of the UASR reactor is 28 l. The reactor dimensions are 19.5 cm in length, 19.5 cm in width, and 75 cm in height. The reactor is provided by inclined baffles to increase the contact time between the H₂ producing bacteria and the substrate. Moreover, gas solid separator was situated at the top of the reactor in order to collect gases resulted from the anaerobic conversion processes [15].

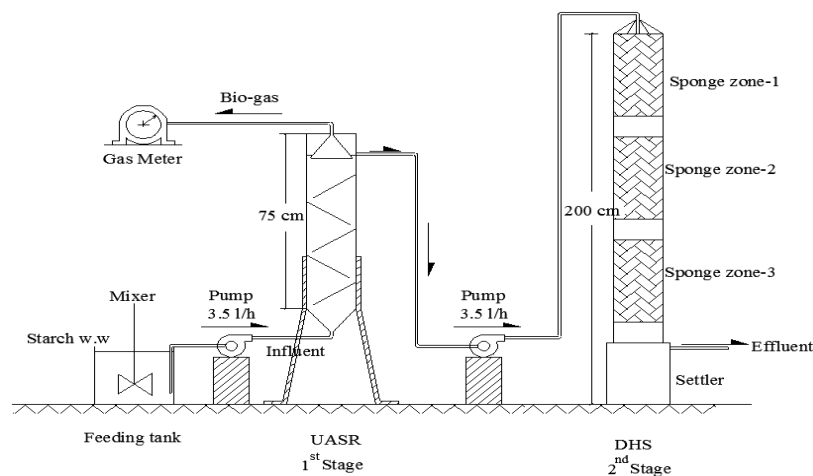


Fig. 1: Schematic diagram of the UASR treating starch wastewater industry

The DHS system with a capacity of 33 l was designed and fabricated from polyvinyl chloride (PVC). It consists of three similar segments connected and supported vertically. Each segment is filled with 1.77 l of

sponge distributed randomly. Thus, the total volume of the sponge was amounted to 5.3 l. The dimensions of the used sponge (cylindrical shape) are 50 mm height×20 mm diameter. The DHS system had an internal diameter of 15 cm. The height of the reactor is 200 cm. The DHS is filled with 16% sponge with the following criteria: surface area = 256 m²/m³, density= 30 kg/m³, voids ratio = 0.9, and pores size = 0.63 mm.

2.3. Operational Conditions and Inoculum Sludge

The wastewater flows from the feeding tank to the UASR (first stage) using prestatlitic pump at a flow rate of 3.5 l/h. The organic loading rate OLR is adjusted to a value of 4.6 gCOD/l.d. The experimental conditions of UASR are summarized in Table.2

Table.2 Operational conditions of UASR treating starch wastewater industry

Temperature °C	Flow rate l/h	HRT (h)	SRT (d)	OLR gCOD/l.d	pH	MLVSS g/l	F/M gCOD/gMLVSS.d
32	3.5	8	8.3	4.6	6.5 - 7	18	0.3

HRT: Hydraulic Retention Time; SRT: Solids Residence Time; OLR: Organic Loading Rate; MLVSS: Mixed Liquor Volatile Suspended Solids; F/M: Food to Micro-organisms ratio

Prior starting the experiment, the UASR was inoculated with 10 l sludge harvested from El-Agamy domestic wastewater treatment plant (WWTP). The harvested sludge was pre-heated at 90 °C for 20 minutes to inactivate methanogenic bacteria. After the first stage, the treated wastewater is pumped to the distributor which is located on the top of the DHS system (second stage). The DHS reactor has advanced accessibility that it supports large amounts of biomass as well as wide range of microbial diversity (both within and on the surface of the sponge medium).

2.4. Analysis and Methods

The parameters studied included Chemical Oxygen Demand COD (soluble and particulate), Carbohydrates (soluble and particulate), Volatile Fatty Acids VFAs, Ammonium Nitrogen NH₃-N, Total Kjehldahl Nitrogen TKj-N, the nature of the microorganisms, Mixed Liquor Suspended Solids MLSS, Mixed Liquor Volatile Suspended Solids MLVSS. Samples were withdrawn for analyses at regular intervals from the inflow and outflow at each stage and were determined according to Standard Methods [16]. Protein was calculated as (6.26 × TKj-N) [17]. The carbohydrate was measured according to the phenol - sulfuric acid method, using glucose as the standard.

3. Results and Discussions

3.1. COD Removal Efficiency

In this study with a raw solution COD of 1800 ±690 mg/L, the COD removal efficiency of the UASR reached 71%. On the other hand, COD removal efficiency at the DHS stage recorded 12%, so that the overall COD removal efficiency reached up to 83%. Fig.2 presents the COD sequence during the operating period of the experimental work.

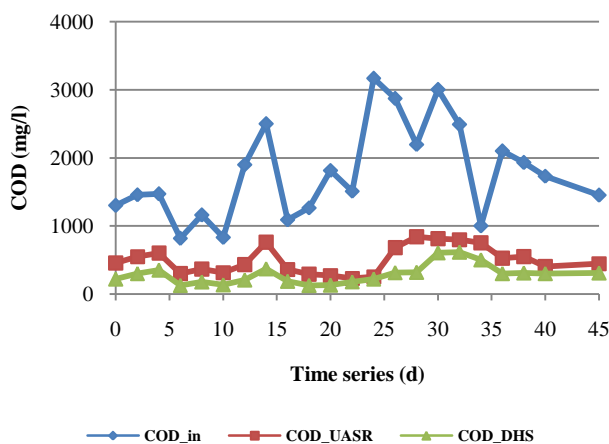


Fig.2: COD sequence of an Up-flow Anaerobic Staged Reactor followed by a Down-flow Hanging Sponge

The COD mass balance for the UASR was computed considering the measured influent and effluent CODs, and the equivalent CODs for both gas and biomass are shown in Table 3.

Table 3 – Summary of products and COD mass balance of UASR

Measured parameters	UASR
VSS reactor (g/L)	18
VSS out (g/L)	0.72
VSS out (gCOD/d) ^a	85.8
sCOD _{out} (g/L)	0.48
Hydrogen Gas (L/d)	6
Hydrogen Gas (gCOD/d) ^b	4.32
Yield (mol H ₂ /mol glucose)	0.35
COD balance (%) ^c	86

^a Based on 1.42 gCOD/gVSS; ^b Based on 8 gCOD/g H₂; ^c COD balance (%) = (VSS_{out} + H₂ + sCOD_{out})/TCOD_{in}

3.2. Volatile Fatty Acids Generation VFAs and pH Drop of the UASR

Results showed that, the drop of influent pH values from 6.86 ±0.5 to 5.65 ±0.76 during the UASR was associated by increase in VFAs from 46 ±27 to 160 ±58 mg/l respectively. pH range of 5.5–6.0 was considered as an optimum pH range for effective H₂ generation [15]. However, the optimum pH values of H₂ production in the comparable processes differ significantly among studies (pH 4–7). However, pH was increased slightly at the DHS stage from 5.65 ±0.76 to a value of 6.54 ±0.48. Fig.3 presents the VFAs and pH sequence during the operating period of the experimental work.

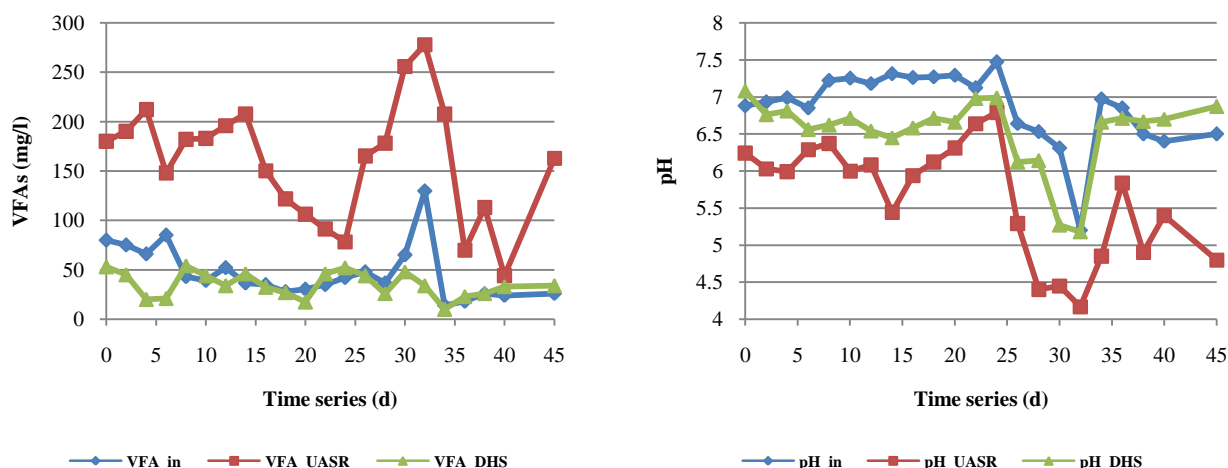


Fig.3 VFAs and pH sequence of an Up-flow Anaerobic Staged Reactor followed by a Down-flow Hanging Sponge

3.3. Hydrogen Yield and Hydrogen Production

Although steady-state was observed after 10 days of startup, the system was kept in operation at steady-state for 65 – 70 days. Portion of COD was converted to VFAs to increase the H₂ production. The average hydrogen production yield obtained at the UASR in this study was observed as 6 lH₂/d, corresponds to 0.35 mol H₂/mol glucose. This value is equivalent to 15% compared to the maximum theoretical value of 2.5 mol H₂/mol glucose. However, interestingly, the operational conditions to maximize the hydrogen yields differ drastically in other reports.

4. Conclusion

The results obtained here revealed that the integrated system consisting of UASR and DHS is a promising technology for simultaneous hydrogen production and treatment of starch wastewater.

- The combined system achieved an overall removal efficiency of 83% for COD at a total HRT of 9.5 h which is complying for discharge into sewerage network.
- Drop of influent pH values from 6.86 ±0.5 to 5.65 ±0.76 during the UASR was associated by increase in VFAs from 46 ±27 to 160 ±58 mg/l respectively.

- At the DHS stage, pH was adapted from 5.65 ± 0.76 to a value of 6.54 ± 0.48 prior discharging to public sewer system.
- The UASR observed an average hydrogen production yield of 6 l/d, corresponds to 0.35 mol H₂/mol glucose (15% of the maximum theoretical value of 2.5 mol H₂/mol glucose.
- 50% of VFAs and 87% of MLSS are accumulated at 10% of the reactor's height.

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6. References

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