Effect of initial pH on biohydrogen production using distillery wastewater by batch process

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ABSTRACT

In this research, the effect of initial pHs 5.0, 5.5, 6.0, 6.5 and 7.0 on biohydrogen production using distillery wastewater by batch process was investigated. From the experimental results, at an initial pH 6.5, the cumulative biohydrogen production, chemical oxygen demand (COD) removal efficiency, oxidation reduction potential (ORP), final pH, volatile fatty acid concentration and volatile suspended solids concentration were found to be 504 mL, 92.73%, -108 mV, 5.5- 5.8, 500-900 mg/L and 4000 mg VSS/L respectively. Thus, the initial pH 6.5 favoured maximum biohydrogen production.

Keywords: Distillery wastewater- Biohydrogen production- Initial pH- Oxidation reduction potential-Volatile fatty acids

INTRODUCTION

Fossil fuel is expected deplete soon due to limited energy resources (Venkatamohan et al., 2007). Hence, there is a need to focus on an alternative energy carrier from a potentially renewable feedstock. Although many alternative sustainable pathways had emerged, the so called hydrogen energy had received special attention and becoming promising energy source because hydrogen is ideal and clean energy resource for the future (Levin et al., 2004). Biological hydrogen production is an attractive alternative providing sustainable green energy. Biohydrogen production using industrial wastewater results in bioenergy recovery and environmental cleanup (Vijayarhagavan et al., 2006; Sridevi et al., 2014). Several industrial wastewaters like, palm oil mill effluent, rice slurry, condensed molasses, distillery wastewater, alcohol industry wastewater are employed in for biohydrogen production by dark fermentation in both batch and continuous process (Kothari et al.,2012). Many process parameters that influence the biohydrogen production are substrate concentration, pH, trace metals, and temperature. The pH is a important key factor in biohydrogen production as it affects hydrogenase activity, metabolic pathways, shifts the volatile acid production and microbial communities in biohydrogen production (Fang et al., 2006; Yu et al., 2002; Guo et al., 2010). Low hydrogen yield at low pH were due to inhibition of microbial growth but the low pH favoured thermodynamics of biohydrogen production (Liu et al., 2011). Moreover, the pH can switch the fermentation to butyric acid type, propionic acid type and ethanol type. Generally, acidogens are less sensitive to pH change than the acetogens and methanogens (Venkatamohan et al., 2007). In this article, the effect of initial pH on biohydrogen production using distillery wastewater was experimented and discussed.

MATERIALS AND METHODS

Wastewater: Distillery wastewater was used as substrate for biohydrogen production. It is one of the high organic content containing agro-industrial wastewater, lacking nutrients. Hence some micronutrients are added in low concentrations for the growth of microorganisms (Rajeshwari et al., 2000). Glucose, the simplest monosaccharide, was used as the sole carbon source along with wastewater (Lee et al., 2008).

Nutrients: All the chemicals used in this study were of analytical grade. The nutrient medium for biomass growth contained the following composition (g/L). NH_4Cl - 0.5, K_2HPO_4 - 0.25, $MgCl_2{\cdot}6H_2O$ - 0.3, $NiSO_4$ - 0.016, $CoCl_2$ - 0.025, $ZnCl_2$ - 0.0115, $CuCl_2$ - 0.0105, $CaCl_2$ - 0.005, $MnCl_2$ -0.015 and $FeCl_3$ - 0.005 (Venkatamohan et al., 2007).

Anaerobic sludge and pre-treatment : The anaerobic sludge was heat pre-treated at 102°C for 1 h to inhibit the methanogens and also to speed up the hydrolysis in anaerobic digestion.

Effect of initial pH by batch experiments: Batch tests were performed in 1 L Erlenmeyer flasks with a working volume of 700 mL. The effect of initial pHs 5.0, 5.5, 6, 6.5 and 7.0 on biohydrogen was conducted at constant initial substrate concentration of 5,000 mg COD /L. The pH was adjusted using 1N HCl or 1N NaOH. The nutrient medium was inoculated with heat pretreated anaerobic sludge of 1000 mg VSS/L under aseptic conditions, and the flasks were incubated at 35ºC for anaerobic fermentation.

Analytical methods: COD, pH, ORP and volatile fatty acids concentration and volatile suspended solids concentration were recorded for every 24h according to standard methods (APHA, 1995). pH and ORP was measured using a pen type pH and ORP meter (Eutech, India). Biogas released from the headspace was recorded by water displacement method.Hydrogen in the biogas was analysed by a gas chromatograph (Shimadzu, 221-70026-34, Japan) equipped with a thermal conductivity detector (TCD) and the column was packed with porapak Q column. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

The effect of initial pH on biohydrogen production was studied by monitoring the COD removal efficiency, final pH, ORP, volatile fatty acid concentration and volatile suspended solids concentration. The studies also revealed that the lag time was 36h and biohydrogen production attained steady state conditions at 120h.

COD removal efficiency: The COD removal efficiencies for different pHs 5.0, 5.5, 6.0, 6.5 and 7.0 were 71, 89, 90.74, 92.73 and 70% respectively (Fig.1). A maximum COD removal efficiency of 92.73 % was obtained at pH 6.5 and the minimum COD removal efficiency of 70% was observed at pH 5.0 and 7.0. It was found that initial pH 5.0 and 7.0 did not favour the biodegradation of high strength wastewaters and resulted in lower biohydrogen production. Sridevi and Mullai (2014) attained a COD removal efficiency of 91.96% at initial pH 6.0 in the biodegradation of distillery wastewater.

Final pH and VFA: The final pH for the various initial pHs 5.0, 5.5, 6.0, 6.5 and 7.0 were 4.2, 5.6, 5.4, 5.3 and 6.2 respectively (Fig.2). Hydrogen production occurs in acidification stage of metabolic process and caused the pH drop to low which is due to acid accumulation in the system. The pH drop resulted in rapid H_2 production with increase in VFA production. The pH drop from 6 to 4.5 was considered to be the ideal pH range for the anaerobic bacteria and for inhibition of methanogenic activity (Venkatamohan et al., 2007). The initial VFA concentration was 100 mg/L at all initial pHs. The final VFA concentrations ranged between 500-900 mg/L (Fig.3). High VFA yield observed at initial pH 6.0 might be attributed to the prevailing acidophilic conditions.

Oxidation reduction potential: The ORP values at 120 h for initial pHs were -54 mV, -60 mV, -70 mV, -108 mV and -49 mV (Fig.4). The recorded ORP values also proved that lower pH 5.0 and 7.0 did not favour the fermentation for biohydrogen production. The recorded ORP value of 108 mV proved that pH 6.5 favoured the anaerobic digestion and that resulted in high biohydrogen production. An ORP value of -150 mV was reported by Venkatamohan et al. (2007).

VSS concentration: The biomass concentration at steady state condition was measured in terms of volatile suspended solids concentration. The VSS concentrations at initial pHs 5.0, 5.5, 6.0, 6.5 and 7.0 were 2000, 2000, 3000, 4000 and 2500 mg VSS/L (Fig.5). The maximum VSS concentration was observed at initial pH 6.5 and helped in maximum biohydrogen production. Thus initial pH affected the concentration of biohydrogen producing organisms.

Cumulative biohydrogen production: The cumulative biohydrogen production for initial pHs 5.0, 5.5, 6.0, 6.5 and 7.0 were 120 mL, 200mL, 310 mL, 500 mL and 100 mL respectively. Decreased fermentation was observed at pH 5.0 and 5.5, which resulted in decreased biohydrogen production of 120 and 200 mL respectively which is also indicated by low ORP values. The maximum cumulative biohydrogen production of 500 mL was obtained at an initial pH of 6.5 (Fig.6). The findings are in agreement with the previous results of Liu et al.(2011). The maximum hydrogen yield by *Clostridium butyricum* CGS2, *Clostridium beijerinckii* L9 and *Clostridium tryobutyricum* FYa102 at pH 6.0, pH 6.4, pH 6.6 were 1.77, 1.72 and 1.83 mmol/mmol glucose respectively (Liu et al., 2011). At initial pH (6.5) and mesophilic condition favored hydrogen production of 0.28 L/L using brewery wastewater (Wongthanate et al., 2014). High hydrogen production rates of 8.3-8.6 L/L/d were obtained at an initial pH of 6.5 using brewery wastewater (Shi et al., 2010). *E. coli* DJT135 in a batch bioreactor gave maximum molar hydrogen yield of 1.51 mol of H_2 /mol of glucose at the optimal conditions of pH 6.5 and 35°C.

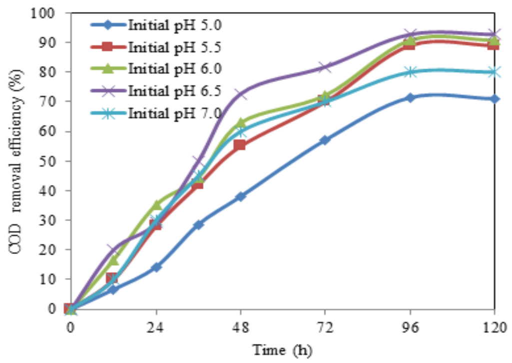

Figure.1.Effect of initial pHs on COD removal efficiency

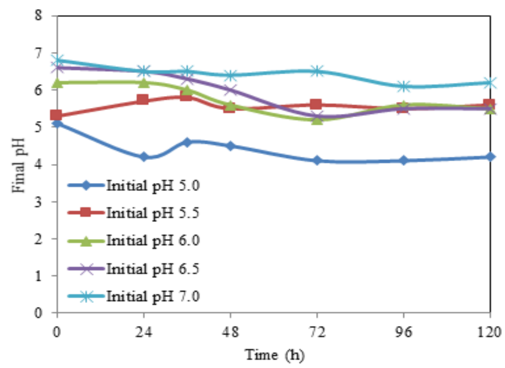

Figure.2.Final pH profile during biohydrogen production

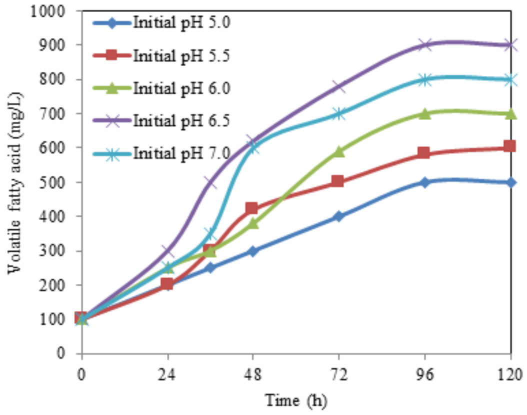

Figure.3.VFA profile at various initial pHs

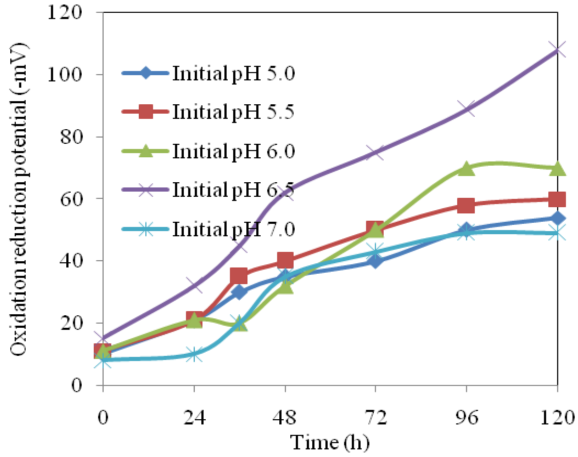

Figure.4.ORP profile at various initial pHs

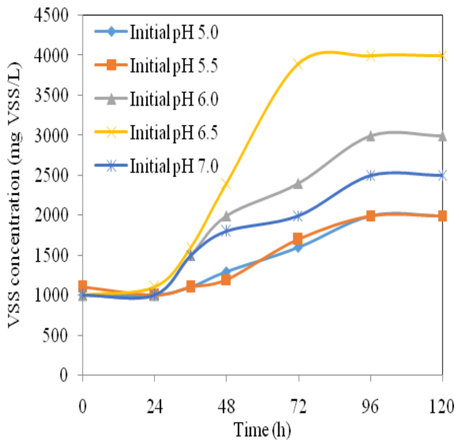

Figure.5.VSS profile at various initial pHs

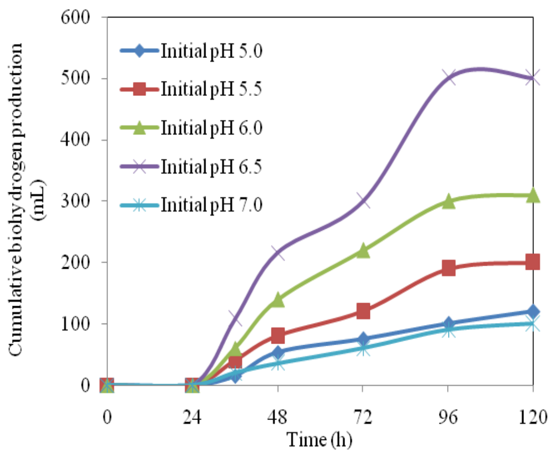

Figure.6. Cumulative biohydrogen production at various initial pHs

CONCLUSION

In the study of effect of initial pH on biohydrogen production revealed that, at initial pH 6.5, maximum COD removal efficiency and maximum cumulative biohydrogen production was attained. Also, favourable initial pH for hydrogen producing anaerobic bacteria was found to be 6.5.

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