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Simultaneous hydrogen gas formation and COD removal from cheese whey wastewater by electrohydrolysis

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ABSTRACT

Cheese whey (CW) was subjected to DC voltages between 0.5 and 5 V for hydrogen gas production with simultaneous COD removal by electrohydrolysis of CW organics. Hydrogen gas formation and COD removal were investigated at different DC voltages using aluminum electrodes. The highest cumulative hydrogen production (5551 mL), hydrogen yield (1709 mL H_2 g^{-1} COD), hydrogen gas formation rate (913 ml d^{-1}), and percent hydrogen (99%) in the gas phase were obtained with 5 V DC voltage within 158 h. Energy conversion efficiency reached the highest level (80.7%) at 3 V DC voltage with cumulative hydrogen production of 4808 mL and hydrogen yield of 1366 mL H_2 g^{-1} COD. Hydrogen gas was mainly produced by electrohydrolysis of CW organics due to low H_2 gas production in water and CW control experiments. The highest COD removal (22%) was also obtained with 3 V DC voltage. Major COD removal mechanism was anaerobic degradation of carbohydrates producing volatile fatty acids (VFA) and CO_2. Hydrogen gas was produced by reaction of protons released from VFAs and electrons provided by DC current. Hydrogen gas production by electrohydrolysis of CW solution was proven to be an effective method with simultaneous COD removal.

1. Introduction

There has been considerable interest in developing clean fuels to replace fossil fuels over the last fifty years. Coal and petroleum-based fuels are responsible for emission of CO_x, NO_x, SO_x and volatile organic compounds (VOC) to atmosphere causing air pollution problems. It is widely believed that hydrogen gas is an attractive energy carrier of the future with high energy content of 122 kJ g^{-1} and reduced green house gas emissions as compared to fossil fuels. Hydrogen gas can also be used in fuel cells to generate electricity [1,2]. However, hydrogen gas is not readily available in nature and is produced by costly processes such as steam reforming of natural gas or electrolysis of water requiring high energy inputs [1,2].

Hydrogen gas production by fermentation of renewable resources such as biomass has been considered as a viable approach due to operation under mild conditions. Due to low rates and yields of hydrogen gas production fermentative processes are not feasible for large scale operations [3,4].

Electrolysis of water for hydrogen gas production has been studied extensively despite the negative energy balance [5–8]. Energy requirement for electrolysis of water is 4 kW h m^{-3} H_2 while the energy content of hydrogen gas is 3.55 kW h m^{-3} H_2. Three major electrolysis processes used for H_2 gas production are alkaline electrolysis, proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC). Photoelectrochemical (PEC) water splitting is a newly developed technology for H_2 gas production. Catalytic or high temperature steam

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Table 1 – Characteristics of raw cheese whey wastewater.

Total chemical oxygen demand (TCOD, mg L^{-1})	86,830
Total sugar (TSG, mg L^{-1})	62,320
Total volatile fatty acids (TVFA, mg L^{-1})	5450
Suspended solids (SS, g L^{-1})	4.95
Total solids (TS, g L^{-1})	54.1
Total N (mg L^{-1})	812
Total P (mg L^{-1})	230
NH_4–N (mg L^{-1})	150.8
pH	4.6
ORP (mV)	154.5
Conductivity (mS cm^{-1})	6.52

electrolysis was also developed to improve H_2 gas production by electrolysis. Proton exchange membrane (PEM) containing electrolysis cells were used for H_2 gas production from water with net energy input [8].

Hydrogen gas production by electrohydrolysis of organics present in waste materials is a newly developed approach. A few recent patents on hydrogen gas production by DC current application to organic wastes and fermentation effluents have been reported [9–11]. Hydrogen gas production from wastewater using microbial electrolysis cells (MEC) has also been investigated [12–14]. In our previous studies on H_2 gas production from electrohydrolysis of organic wastes, anaerobic sludge, olive mill wastewater (OMW) and landfill leachate were used as raw materials [15–20].

Cheese whey (CW) is a high strength wastewater (COD = 50–60 g L^{-1}) of cheese manufacturing processes and is considered as a nutritionally rich medium for production of fuels (ethanol, methane) and chemicals (organic acids) by fermentation due to high carbohydrate (5–6% w v^{-1} lactose), protein (0.8–1%), and fat (0.06%) contents [21–24]. Cheese whey has also been used for bio-hydrogen production by dark fermentation [25–28]. Hydrogen gas production by electrohydrolysis of cheese whey has not been reported in literature. Therefore, this study constitutes the first report on hydrogen gas production by electrohydrolysis of cheese whey solution. DC voltages between 0.5 and 5.0 V were applied to diluted CW solution for hydrogen gas production using aluminum electrodes. CW control experiments with no voltage application and water control experiments with DC voltage application were also carried out to determine the extent of hydrogen gas production by bacterial fermentation and by electrolysis of water, respectively.

2. Materials and methods

2.1. *Experimental setup and procedure*

Batch electrohydrolysis experiments were performed using 1 L serum bottles with 500 mL working volume. The bottles contained two aluminum electrodes (L = 24.5 cm, $D_{cathode}$ = 8 mm, D_{anode} = 6 mm) immersed in cheese whey solution and connected to DC power suppliers (TT-T-ECHNI-C MCH-305T and MCH-305D-II, China). The bottles were closed tightly by silicone rubber stoppers and screw caps and were sealed carefully using silicone to avoid any gas leakage. Duplicate bottles were placed on magnetic stirrers (aprox. 100 rpm) at room temperature (T = 25 ± 2 °C). Applied DC voltages were varied between 0.5 and 5 V voltage. Cheese whey was obtained from Pinar Sut Company, Pinarbasi, Izmir. Composition of the raw CW is summarized in Table 1. The initial COD, pH, ORP and conductivity of the diluted CW are presented in Table 2.

Two control experiments were performed for every applied DC voltage. In water control, the same voltages were applied to water to determine H_2 production by electrolysis of water. CW control was used to determine H_2 production by anaerobic fermentation of CW with no DC power application. Al(III) ions and electrons were released to the solution upon application of DC power according to the following reaction.

$$\text{Anode: } Al^{\circ} \rightarrow Al(III) + 3e^{-} \quad (1)$$

The released electrons combined with the protons released from dissociation and decomposition of organic compounds (mainly VFAs) present in the CW.

$$nH^{+} + ne^{-} \rightarrow n/2H_2(g) \quad (2)$$

Organic compounds in CW are carbohydrates (mainly lactose), volatile fatty acids (VFAs) produced by anaerobic fermentation of carbohydrates, proteins and NH_4^+–N.

Anaerobic conditions were maintained by passing argon gas from the head space of the bottles for 15 min at the beginning of the experiments. Liquid samples were removed from the bottles everyday for COD, pH and oxidation-reduction potential (ORP) measurements after gas analysis. Total sugar (TSG), total volatile fatty acids (TVFA), suspended solids (SS), total solids (TS) were also measured at the beginning and the end of the experiments. The initial and final weight of the electrodes were also measured to determine Al(III) loss to the solution.

Table 2 – Initial characteristics of diluted CW wastewater.

DC voltage (V)	Total COD (g L^{-1})	Total sugar (mg L^{-1})	TVFA (mg L^{-1})	pH	ORP (mV)	Conductivity (mS/cm)	SS (g L^{-1})	TS (g L^{-1})
0.5	32,062	23,457	2020	4.7	135.4	4.31	2.6	19.5
1	32,062	23,457	2020	4.7	135.4	4.31	2.6	19.5
2	32,062	23,457	2020	4.7	135.4	4.31	2.6	19.5
3	31,838	23,449	1948	4.8	133.7	4.29	1.79	19.5
4	31,838	23,449	1948	4.8	133.7	4.29	1.79	19.5
5	32,098	25,601	1960	4.7	137.2	4.17	1.96	22.1