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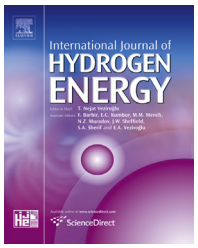

A two-stage process for hydrogen production from cheese whey: Integration of dark fermentation and biocatalyzed electrolysis

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ABSTRACT

This paper explores the potential of a two-stage process (fermentative + biocatalyzed electrolysis) to reduce the organic load of an industrial waste stream (cheese whey) in parallel with hydrogen production. Overall, the combined process helped to significantly reduce the chemical oxygen demand (COD) of the effluent, while producing hydrogen at a maximum yield of 94.2 L H_2 kg_{vs}^{-1}. The low pH of the fermentative effluent fed into the bioelectrochemical reactor helped to control methanogenic and homoacetogenic activity during the second stage of the treatment. However, this acid stream needed to be diluted and amended with salts and acetate to avoid the collapse of hydrogen production rate. Therefore, practical application of a two stage process for the treatment of cheese whey would require the existence of a secondary waste stream for dilution of the acidified effluent, thus balancing its nutrients composition prior to feeding into the bioelectrochemical system.

Introduction

The energy-water nexus has received a growing interest in the past decades as the human population pressure on global resources intensifies. The main idea behind this concept is that water is needed to produce energy, energy is needed to manage water, and both activities are mutually intertwined. As a result, all of the power generation technologies (even solar and wind power) have an associated water footprint. For instance, in 2005 in Spain, water requirements for thermal energy, electricity and transportation fuels amounted to 8.5 km^3, representing 20% of the total water withdraw for human use [1]. Moreover, the water needed for fuels production (hydrocarbons and nuclear fuels) usually becomes polluted with organics, salts, solids, heavy and radioactive metals, microorganisms, etc., thus demanding relatively sophisticated treatments before discharging into the environment.

Likewise, water management systems and technologies have their associated energy footprint. Water must be collected, treated, pumped and disposed, all of these procedures requiring energy. For the particular case of wastewater treatment, this activity demanded in 2009 in Spain about 2476 GWh $year^{-1}$ representing around 1% of the national electricity consumption [2–4].

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To break this mutual dependence and therefore ensure the environmental (and economical) sustainability of water and energy management, new technologies and procedures would need to be developed. For wastewater treatment in particular, this would mean less energy-intensive or even net-energy-production technologies, which could be attained if we could make use of the energy content of the organic matter dissolved into the wastewater [5]. In this paper we will focus on fermentative hydrogen production (FHP) and biocatalyzed electrolysis, two biologically-based technologies devised for wastewater treatment that convert the potential energy stored in the organics into H_2. FHP is a well-known technology easy to scale up, that produces a biogas containing primarily hydrogen and carbon dioxide. However, its practical application is hampered by an important drawback: the maximal H_2 yield is limited to 33% of the theoretical maximum based on stoichiometric conversion of glucose [6]. As a result, investigations have been fostered during the last decades towards finding new methods for maximising the production of H_2. In 2005 biocatalyzed electrolysis emerged as a complementary technology to fermentative processes, allowing to recover up to 90% of the energy content in the substrate [7]. Biocatalyzed electrolysis takes place in a special type of electrochemical reactor known as microbial electrolysis cell (MEC), that make use of electrogenic bacteria to convert a wide range of organic compounds into H_2 under anaerobic conditions and with the aid of a certain electrical input [8–11].

Effluent from cheese factories represents a suitable substrate for hydrogen recovery in a combined FHP-MEC process. Cheese whey (CW), the effluent remaining after the precipitation and removal of milk casein during cheese-making, represents about 85–95% of the milk volume, having an index of biodegradability expressed in terms of biological and chemical oxygen demand (BOD_5:COD ratio) in the range 0.4–0.8 [12], and retaining 55% of milk nutrients such as lactose, soluble proteins, lipids, and mineral salts [13]. In this study we investigated the feasibility of an integrated FHP-MEC process for CW treatment and hydrogen recovery, trying to identify both the optimum rate of CW:inoculum during the FHP treatment and the requirements of the FHP effluent for being fed to the MEC post-treatment.

Material and methods

Inoculum and substrate for the fermentation process

CW was obtained from a cheese facility located in Zamora (Spain) by concentrating a dilute lactose-rich stream via reverse osmosis. The inoculum for the fermentation process consisted of digested sludge obtained from the wastewater treatment plant (WWTP) of the city of León (Spain). The chemical characteristics of the inoculum and substrate are presented in Table 1. FHP tests were performed under batch conditions using different ratios of substrate (CW) and inoculum (I) (referred to as CW:I, and defined as the proportion of volatile solids (VS) between the CW and the I). These ratios were gradually increased from 1.25 to 15.7 to prevent acid build-up that may cause the inhibition of the process.

Table 1 – Chemical characterization of the inoculum and the CW.

Parameters	Inoculum	CW
TS (g L^{-1})	24.0 ± 0.6	126.8 ± 8.6
VS (g L^{-1})	11.2 ± 0.4	116.8 ± 7.8
COD (g O_2 L^{-1})	29.5 ± 1.4	122.1 ± 5.6
Lactose (g L^{-1})	–	103.4 ± 2.1
Organic matter (%)	1.25	–
Organic carbon (%)	0.73	–
Acetate (mg L^{-1})	2 ± 0	246 ± 57
Lactate (mg L^{-1})	252 ± 14	3016 ± 123
Alkalinity (mg $CaCO_3$ L^{-1})	1.1 ± 0.1	1.8 ± 0.2
pH	7.34 ± 0.02	4.68 ± 0.04
$N–NH_4$ (mg L^{-1})	578 ± 12	108 ± 3
N Kjeldahl (mg L^{-1})	1300 ± 28	1200 ± 26
Cl^- (ppm)	38 ± 2	981 ± 9
SO_4^{2-} (ppm)	253 ± 12	430 ± 15
PO_4^{3-} (ppm)	726 ± 74	1455 ± 89
Na^+ (ppm)	131 ± 31	181 ± 19
Ca^{2+} (ppm)	116 ± 15	1260 ± 139
Mg^{2+} (ppm)	399 ± 62	783 ± 68
K^+ (ppm)	20 ± 2	525 ± 18

Batch experiments were performed under mesophilic conditions (35 ± 1 °C) using 250 mL Erlenmeyer flasks equipped with magnetic stirrers. Gas production was recorded by displacement of an acid and saline solution, and data were normalised to standard temperature (0 °C) and pressure (760 mmHg). Biogas and liquid samples were regularly taken and analysed (see below). FHP performance was characterised using the cumulative H_2 production (mL) within the first 24 h of the batch tests, the volumetric H_2 production rate per litre of reactor and hour (m H_2 L_r^{-1} h^{-1}) and the H_2 yield (L H_2 kg_{vs}^{-1}). At the end of the fermentative tests, the effluent obtained from the trial with the highest H_2 production was collected and used as the feeding solution for the MEC. The content of the Erlenmeyer flask was centrifuged (using SIGMA 2-16P centrifuge, 20 min, 7800 rpm) and the supernatant was filtered by means of a vacuum filter (Series 3000/3B, Scherzinger Pump Technology, Furtwangen, Germany) with a polyvinylidene fluoride membrane (RM UV150T 1016, Microdyn-Nadir GmbH, Wiesbaden, Germany).

Microbial electrolysis cell (MEC)

MEC design and operation

A continuous-flow, membrane-less MEC constructed with a series of polycarbonate plates was used in this study (Fig. 1). The cell was equipped with connections for gas exits and liquid entries and exits. Both the anodic compartment and the gas collection chamber had a volume of 50 mL. The anodic compartment contained two layers of 5 mm thick carbon felt of 100 × 50 mm (SIGRATHERM soft felt GFD 2, SGL Carbon Group, Wiesbaden, Germany). The cathode consisted of a gas diffusion electrode (SIGRACET GDL 25 BC, SGL Carbon Group, Wiesbaden, Germany) containing electrodeposited Ni particles (550 μg cm^{-2}). Two 0.6-mm-thick pieces of polyester cloth were sandwiched between the anodic and the H_2 collection compartments to avoid any electrical contact between the two electrodes. The inter-electrode separation was set to 1 mm.