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Dark fermentative hydrogen production by anaerobic sludge growing on glucose and ammonium resulting from nitrate electroreduction

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ABSTRACT

The main objective of this work was to study the feasibility of biohydrogen production by heat-treated anaerobic sludge with glucose as carbon substrate and ammonium as nitrogen source, obtained from the electrochemical reduction of concentrated nitrate solutions (3 g L^{-1} NO_3^-), namely model solutions simulating those obtained after physicochemical denitrification of industrial wastewaters. Experiments were realized in bacth systems involving 125 mL (without pH control) and 3 L (with pH control) reactor, respectively.

In order to find the optimal conditions for H_2 production, the first set of experiments were conducted without pH control at various initial pH (pH 5.5, 6.5 and 7.5) and glucose concentrations (5–30 g L^{-1}); and the highest H_2 yield (1.1 mol H_2 $mol^{-1}_{glucose\ consumed}$) was reached for a glucose concentration of 25 g L^{-1} and at pH 6.5. These optimal conditions were then considered to examine the effect of pH control on biohydrogen production, in a 3 L bioreactor. The pH control allowed a considerable improvement of the hydrogen gas conversion efficiency, which reached 2.02 mol H_2 $mol^{-1}_{glucose\ consumed}$.

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Introduction

Hydrogen is considered as an attractive future clean and renewable energy carrier due to its environmental-friendly conversion. Indeed, its combustion product is water and it has a high energy content [1], since the energy yield of hydrogen is 122 kJg^{-1}, namely 2.75 times that of fossil fuel [2].

During the last decades, several processes have been used for hydrogen production [3], including electrolysis of H_2O, thermocatalytic reformation of hydrogen rich substrates and various biological processes [4,5]. Among these methods, microbiological hydrogen production has attracted considerable attention because it has the potential to convert low cost residues or organic waste/wastewater to hydrogen [1–3]. According to the type of employed microorganisms, biological H_2 production under anaerobic conditions can be classified into two different categories: dark and photo fermentation processes [6]. The most promising and widely investigated process is dark fermentation. It has more advantages than photofermentative H_2 production, including lower costs since energy provided by sunlight is not required, high hydrogen production rate and simple process control with a wide range of temperature and pressure conditions which can be implemented [7,8].

Theoretically, a maximum of 4 mol of hydr*ogen per mole glucose converted via the acetate pathway can be generated via dark hydrogen fermentation; however, the reported yields are typically below this value, due to the generation of by-products [9]. In addition to acetate, small organic compounds such as butyrate and ethanol are also produced, and are termed ''dead-end'' or ''fermentation barrier,'' and limit the hydrogen yield to a maximum of 2–3 mol H_2 [7]. Usually, no more than one third of the total potential electrons in complex biomass can be transferred to hydrogen, while the remaining, namely two thirds, end up in the form of these fermentation by-products, enhancing therefore the total costs of biohydrogen production process. High hydrogen yields are however required to make the process economically feasible [10].

The most noteworthy study is that lately reported by Rivera et al. [11] in which they proved that the bio-electrochemical systems fed with dark fermentation effluents is a way forward to get higher H_2 production efficiency.

Many factors must be taken into consideration for enhancing hydrogen production in fermentation systems, such as pH, substrate concentration, inoculum, temperature and nitrogen sparging [12,13]. Abiotic factors such as the type of bioreactor is also of key interest, since it was demonstrated by Kumar et al. [14] that advanced fermenter configuration incorporating upstream, such as H_2 production and subsequent downstream including biohydrogen recovery and purification may lead to novel and promising biohydrogen systems.

A broad spectrum of carbohydrate rich substrates have been considered to producebiohydrogen, such as starch [15], xylose, agricultural wastes [16], lignocellulose [14] and glucose [17–22]. However, the use of glucose or the conversion of raw material to glucose is favored because it is easily biodegradable by most of bacteria [12]. Nevertheless, the chosen glucose concentrations must be low enough in order to minimize pH changes resulting from acids produced during fermentation [23]. Indeed, it was shown that pH is among the major environmental factors which affects biohydrogen production due to its effect on the hydrogenase activity, the enzyme involved in the metabolism of hydrogen in most bacteria [24]; optimal initial pH value for biological hydrogen production is generally found to be between 5.0 and 6.5 [25]. However, optimum pH value can vary according to the carbon substrate used, from pH 9 for sucrose [26] to pH 5.5 for glucose [27].

Consequently, lowering production cost is still a key issue to project this technology to an industrial-scale. Nitrogen and carbon feedstock represents 30–40% total costs of fermentative hydrogen production [28]. Nitrogen is one of the most essential nutrients needed for the growth of hydrogen-producing bacteria. It is a very important component for nucleic acids, proteins and enzymes that are of great significance to the growth of hydrogen-producing bacteria. Thus, an appropriate level of nitrogen addition is beneficial to the growth of hydrogen-producing bacteria and to dark fermentative hydrogen production accordingly [29].

One way to make biological hydrogen production providing simultaneously economic and environmental benefits consist of the coupling the biohydrogen production to another physicochemical depollution process, such as that of nitrate ions (NO_3^-).

NO_3^-contamination of water sources has become a serious problem around the world [30]. Nitrate causes methemoglobinemia in infants and eutrophication of water bodies [31].

The transformation of NO_3^- to the non-toxic nitrogen gas (N_2) is the most widely used electrochemical method for nitrate removal from contaminated water [32–35], however the rate and the selectivity of the reaction are usually low, limiting therefore their utility for large scale application [36]. In this context the use of coupling process can allow to overcome these limitations.

Electrochemical and biological processes were coupled for the removal of heavy metals [37] and biorecalcitrants compounds [38,39]. However and to the authors' knowledge, their previous work was the sole study dealing with the feasibility of such coupled process to produce biohydrogen while treating nitrate ions from water [36]. On the one hand, according to the literature copper cathode (Cu) is known to be the most efficient electrocatalyst for the electro-reduction of nitrate by mainly producing ammonium as final product [30,40]. On the other hand, inorganic ammonium (NH_4^+) was the most widely investigated nitrogen source for fermentative hydrogen production [18,22,23,41,42], owing to its lower cost if compared to organic nitrogen sources, such as for instance yeast extract [43,44] and polypepton [45,46].

For these reasons, from an environmental and economical point of view, an electrochemical reduction of nitrate to NH_4^+ over Cu cathode can be considered as a promising and an attractive way, since it allows not only the treatment of nitrate, but also energetic valorization of the nitrate treated effluent.

Therefore, the interest of this work does not reside only in the biological hydrogen production, but also in the finding of an alternative nitrogen source, ammonium solution resulting from nitrate electrochemical treatment, as substitute for