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Energetic valorization of ammonium resulting from nitrate electrochemical reduction—Feasibility of biohydrogen production

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ABSTRACT

The main objective of this work was to examine the feasibility of coupling electrochemical and biological processes to destroy nitrate ions (NO_3^-) while producing biohydrogen. In this integrated process NO_3^- was firstly converted to ammonium using an electrochemical flow cell. After only one pass of concentrated nitrate solutions ($3\,g\,NO_3^-\,L^{-1}$) through the flow cell, ammonium ions selectivity of 98.8%, corresponding to $0.86\,g\,NH_4^+\,L^{-1}$ was recorded. The obtained ammonium solution was then tested as a nitrogen source to produce H_2 in a batch system involving heat-treated aerobic activated sludge.

In the optimal conditions corresponding to pH 5.5 and initial glucose concentration of $15\,g\,L^{-1}$, consumption yields were 97% and 82% for ammonium and glucose, leading to H_2 yield of $0.35\,mol\,H_2\,mol^{-1}$ glucose consumed. The H_2 production was associated with acetic/butyric acids type fermentation. Obtained biogas contains only H_2 and CO_2 and was free of methane, hydrogen sulphide, and nitrous oxide. Therefore, the targeted objectives were achieved since on the one hand selective and quantitative conversion of NO_3^- to NH_4^+ was shown and on the other hand the obtained NH_4^+ was completely assimilated by activated sludge with the production of biohydrogen, a clean energy carrier.

1. Introduction

Nitrate contamination of groundwater, lakes, or rivers has attracted increasing global concern due to several impacts on human health (e.g., gastrointestinal cancer, liver damage) and aquatic ecosystems (e.g., eutrophication) [1]. In this respect, the removal of NO_3^- has been extensively investigated over the last few decades.

Many processes are currently used to eliminate NO_3^- ions from contaminated waters. Nevertheless, there are some disadvantages with these methods that limit their utility for large scale application:

(1) Physicochemical processes such as ion exchange, reverse osmosis, and electrodialysis are costly and not destructive [2]. Hence these methods lead to concentrated effluents of nitrates ($\geq 3\,g\,L^{-1}$) [3] that are very difficult to treat.

(2) Biological denitrification, which mainly involves facultative anaerobes, leading to the need for anoxic conditions in order to reduce nitrate to nitrite (NO_2^-) and subsequently to nitrogen gas (N_2), according to the following sequence [4]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO(g) \rightarrow N_2O(g) \rightarrow N_2(g)$$

However, the knowledge about biological denitrification of industrial wastewaters containing high nitrate concentration still limited. There are two principal problems in the biodenitrification of high NO_3^- wastewater. First, this process is slow and last many days particularly for high strength nitrate waste [5,6]. Secondly, nitrate elimination can be hampered by the accumulation of nitrite during the process, because NO_2^- is an inhibitor of microbial growth [6].

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(3) Electrochemical reduction of NO_3^- which receives, in analytical scale, more and more attention due to its advantages, namely its ease of use, low investment costs, and environmental friendliness particularly if the resulting product is N_2 gas [7]. However, the main problem in this approach is that the transformation of NO_3^- to nitrogen is a difficult reaction since both the rate and the selectivity of the reduction are usually low [8].

One promising and attractive way of treatment which can lead to interesting solutions consists in the coupling of an electrochemical process to a biological treatment [9]. For this purpose, on the one hand, according to the literature, nitrate electroreduction has been widely studied using several electrodes materials such as Pt, Pb, Ni, Zn, Pd, Cu, Ag, and Au. Among these materials, Copper (Cu) is known to exhibit the highest electrocatalytic activity for the nitrate reduction by mainly producing ammonia as final product [10]. On the other hand, many researchers focused on the use of inorganic ammonium (NH_4^+) as a potential nitrogen source for biological hydrogen production [11–15]; and the use of cheap inorganic nitrogen source appears relevant from an economical point of view, contrarily to organic nitrogen sources such as yeast extract [16,17] and polypepton [18,19] which are often more expensive. For these reasons, from an environmental and economical point of view, an electroreduction of nitrate to NH_4^+ over copper cathode can be considered as an attractive way, since it allows not only pollutant treatment, nitrate, but also possible valorization of the treated effluent. Therefore, the combination of nitrate electrochemical reduction and the use of the obtained ammonium solutions as a nitrogen source in a microbial culture is proposed in this study, for the first time to our knowledge.

Hydrogen is considered as an ideal and clean energy carrier owing to its high energy content and non-polluting nature, since its combustion product is water [20]. H_2 may be produced by various processes such as thermocatalytic reformation of hydrogen rich substrates, electrolysis of H_2O, as well as various biological processes [21,22]. Among these methods biohydrogen production by microorganisms is regarded as one of the most promising alternatives for sustainable production due to its potential for low-cost, inexhaustible, and renewable source of clean energy [20].

Biohydrogen production under anaerobic conditions can be classified into two different categories according to the type of microorganisms employed: dark-fermentative hydrogen production and photofermentative hydrogen production [23]. Dark-fermentative has more advantages than photofermentation hydrogen production, including high hydrogen production rate, energy savings, lower maintenance costs, simple process control, and broad spectrum of feedstock [24]. Let's add its applicability to different types of wastewaters and organic wastes from industrial processes [25], reducing furthermore waste disposal problems.

Fermentative hydrogen production processes via mixed cultures are more practical than those using pure cultures, because the former is easier to control and simpler to operate [26]. At present, the microbial consortium present in anaerobic sludge is the most widely used as inoculum for fermentative hydrogen production [27–32]. But according to our knowledge, up to now only few studies in the literature focused on the capacity of aerobic activated sludge for biohydrogen production [33,34]. However, it should be noted that such inoculum has the advantage of containing mostly facultative anaerobic hydrogen-producing bacteria which is very robust and not inhibited by the presence of oxygen trace who accidentally enter in the bioreactor; these facultative anaerobes are then able to install the anaerobic conditions conducive to hydrogen production. Moreover aerobic activated sludge is relatively more available than anaerobic one.

Whilst biological process is considered as a promising approach for hydrogen production, the high production cost is still a key issue for projecting this technology to an industrial-scale. Nitrogen and carbon feedstock represents 30–40% total costs of fermentative hydrogen production [35]. Thus, finding an alternative nitrogen source as substitute for commercial products to reduce the total costs of biohydrogen production would be interesting. For this purpose, the main objective of this report is the energetic valorization of ammonium solution resulting from nitrate electrochemical treatment.

To achieve this goal, a flow electrochemical process was first developed, allowing a selective and quantitative transformation of concentrated nitrate solutions into ammonium. In a second step, the obtained ammonium solution was used as a nitrogen source to evaluate the feasibility of biohydrogen production by dark fermentation.

2. Materials and methods

2.1. Electrochemical nitrates pretreatment

One liter of synthetic nitrate solutions of 3 g NO_3^- L^{-1} was prepared by dissolving potassium nitrate crystals (KNO_3) in phosphoric acid (H_3PO_4 10^{-2} M). The pH of the electrolyte solution was adjusted to pH 1.1 using sulfuric acid 96%. This high nitrate concentration was chosen to be similar to the real effluents obtained after ion exchange treatment process of nitrate-contaminated drinking water [3,36].

Nitrate electrochemical reduction was carried out at room temperature in a single pass through a home-made flow cell presented in Fig. 1.

The working electrode was a copper porous material (5.6 cm diameter and 0.3 cm thickness) prepared as previously described [37]. Graphite felt (RVG 4000) used as metal electrodeposition support was supplied by MERSEN (Paris La Defense, France). Its specific area, measured by the BET method was 0.7 m^2 g^{-1}, its density was 0.088 g cm^{-3} and its carbon yield was 99.9%. The homogeneity of the copper coating obtained after metal electrodeposition was checked by scanning electron microscopy (SEM) (Fig. 2(a) and(b)).

To ensure a good homogeneity of the potential distribution in the three dimensional working electrode, the Cu modified graphite felt was located between two counter-electrodes made of fine platinum grids. The electrical contact with the working electrode was performed with a copper wire. The NO_3^- solutions percolated the

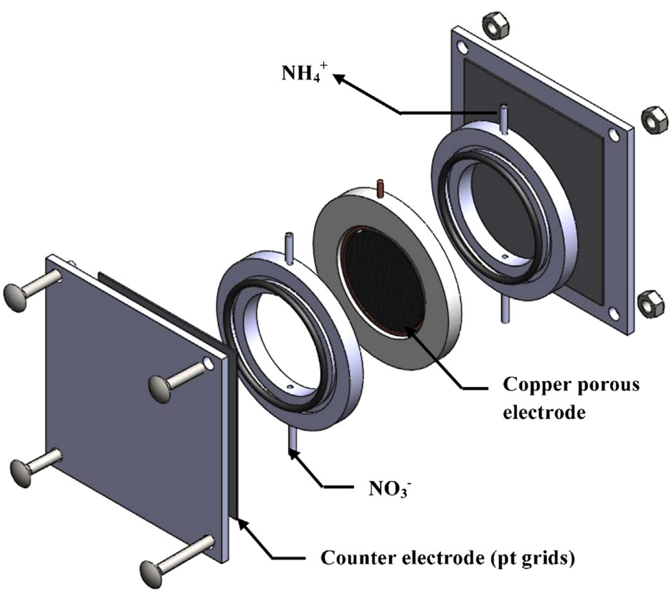

Fig. 1. Flow electrochemical cell used for nitrate electrolysis.