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Enhanced biological nitrate removal by alternating electric current bioelectrical reactor: Selectivity and mechanism

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ABSTRACT

This work was aimed at investigating the performance of the biofilm inducing by applying an alternating current (AC) as an innovative bioelectrical reactor (BER) for simultaneous removal of hard biodegradable organic carbon (i.e., ibuprofen) as a model of pharmaceuticals and nitrate in a single chamber reactor. The performance of this system improved with the increase in the applied AC voltage until peak-to-peak voltage (Vp-p) reaches 8 Vp-p. The results showed that the highest removal of (ibuprofen) Ibu and ~96% of nitrate reduction as high as 99% of N_2 selectivity was achieved at a contact time of 6.5 h, while for control reactor N_2 selectivity as high as 78% obtained at 24 h. The reactor effluent concentrations of nitrite and nitrate at a contact time of 6.5 h were below the drinking water standards. FTIR spectra showed only a peak at 695.39 cm^{-1} that corresponded to Ibu in the effluent. Therefore, this system provides an efficient process in which both Ibu and nitrate removals occur efficiently. This system can be considered a simple and powerful method to remove nitrate in the presence of hard biodegradable and toxic organic carbon sources, and thus can be valuable for industrial applications.

1. Introduction

There are many industries or specific process with side streams containing a high level of nitrate and organic compounds. Denitrification using the heterotrophic process to nitrate removal is technically and economically advantageous because of the simultaneous removal of nitrate and organic compounds [1,2]. Hence, using this method obviates the need for the multi-step treatment process. However, the toxic and inhibitory nature of the organic compound for the denitrifying microorganism is controversial [2–4]. For example, the wastewater produced from the equipment washing and the one from the formulation process in a pharmaceutical factory has a high level of toxic, complex, and hard biodegradable compounds along with nitrogen [5]. Biological removal of nitrate from recalcitrant pharmaceutical wastewater is very problematic due to its strong biotoxicity. Therefore, high-concentration and cost effectiveness of biotechnologies are looming obligatory for nitrogen removal from nitrate-rich pharmaceutical wastewater [5]. These pharmaceuticals as emerging pollution sources are receiving more attention due to their impact on public and environmental health. Ibuprofen is one of the most widely used classes of pharmaceuticals, which are non-steroidal anti-inflammatory drugs, also known as NAIDs [2]. Also, the antimicrobial activity of ibuprofen, both direct and indirect, has been reported by some authors [6]. Generally, three pathways of biodegradation, sorption, and air stripping might occur for removing Ibu throughout sole biological wastewater [2,7]. Based on Ibuk_H, 1.39×10^{-4}, it has no tendency to volatilization; therefore, air stripping is not its major removal pathway [2]. Consequently, it is believed that sorption of Ibu on sludge mass and consequent of biological degradation processes can result in its elimination. The removal Ibu by adsorption on anaerobic sludge is reported from 30 to 60% [8]. The suggested biodegradation pathways of ibuprofen in the literature can be presented in few classes. The Ibu and Ibu metabolites biotransformation in the biological process can be classified (Table 1) as follows [2]:

Organic carbon demand for heterotrophic denitrification is a critical parameter in nitrate reduction. Also, organic matter concentration is effective in nitrate removal [9]. Enhancing heterotrophic denitrification using a combination of electricity and biological system to wastewater treatment is a favorable system [10]. In this system, the biological denitrification and organic matter oxidation can be stimulated by supplying electric current [11–13]. Furthermore, as a result of the simultaneous and supportive role of microbial biofilm, electrolytic decomposition and electrochemical oxidation/reduction of the carbon content and nitrate can be performed using single step and plant effectively. By

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applying the electric current to induce biofilm activity, both biological and electrochemical process might be combined. Thus, various mechanisms can take place and the system can treat complex compounds. Biofilm formed on bio-electrodes in BERs serves as a buffer and increase the biodegradability of complex compounds. Although there are limited studies concerning denitrification by using toxic and hard biodegradable organic compounds, they are increasing regarding the cost effectiveness of concurrent removal of nitrate and an organic compound. Nitrate removal pathways occurring in BER are described through Eqs. (5) to (8) [14]:

Biological denitrification:

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \tag{5}$$

Electrochemical nitrate reduction:

$$\begin{aligned} NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \rightarrow NO + NH_2 \rightarrow N_2 + H_2O \\ \rightarrow N_2O + 2e^- + 2H^+ \rightarrow N_2 + H_2O \end{aligned} \tag{6}$$

$$\begin{aligned} &NO_2^- + 8e^- + 6H_2O \rightarrow NH_3 + 9\,OH^-\ (\text{cathode}) \\ &2NH_3 + 6OH^- \rightarrow N_2 + 6e^- + 6H_2O\ (\text{anode}) \end{aligned} \tag{7}$$

Bio-electrochemical nitrate reduction:

$$\begin{cases} 5H_2O \rightarrow 2.5O_2 + 10H^+ + 10e^-\ (\text{at bio anode}) \\ 10H_2O + 10e^- \rightarrow 5H_2(g) + 10OH^-\ (\text{at bio-cathode}) \\ 2NO_3^- + 6H_2O + 10e^- \rightarrow N_2(g) + 12OH^-\ (\text{cathode nitrate reaction}) \\ 2NO_3^- + H_2O \rightarrow N_2(g) + 2OH^-\ (\text{Bio-electrochemical nitrate reduction}) \end{cases} \tag{8}$$

Eq. (5) is a general relation according which hydrogen acts as the electron donor during denitrification and nitrate is reduced to gaseous nitrogen [15]. In addition, NO_3^- reduction to N_2 by consuming the acid equivalent (H^+) leads to pH rising after the denitrification. Cathodic reduction of nitrate (Eq. (6)) is a reductive pathway for removal of oxidized compounds in a bioelectrochemical system (BES) [16]. Through this reaction, two denitrification intermediates (i.e., NO and N_2O) are produced. These two intermediates are unwanted products due to the harmful and green house potential. Paired electrolysis (Eq. (7)) by combination of the anodic and cathodic reactions is the selective oxidation of NH_3 to N_2 for cathodic NH_3 production in an alkaline environment [16]. This pathway occurs during electrochemical denitrification. Eq. (8) represents brief reaction sequence of bioelectrochemical nitrate reduction using hydrogen gas [17]. In case of hydrogentrophic denitrification that need hydrogen [18] the denitrification reactions can be described through Eqs. (9) to (11) [19,20]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{9}$$

$$NO_3^- + H_2 \rightarrow NO_2^- + H2O \tag{10}$$

$$2NO_2^- + 3H_2 + 2H^+ \rightarrow N_2 + 4H_2O \tag{11}$$

The overall reaction can be written as Eq. (12):

$$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O \tag{12}$$

The prerequisites for removing nitrate and Ibu are reduction and oxidation process, respectively; therefore, their simultaneous removal in a single process is an efficient, cost effective, and affordable, but complex process. To the best of our knowledge, there are no available studies conducted on the denitrification with BER supplied with low-voltage AC at low-frequency mode that not decomposes water [21,22]. The one chamber cell, unlike the typical 2-chamber BES, can remove organics and nitrate simultaneously and without using an exchange membrane. Having both oxidation and reduction reactions simultaneously in an undivided AC biofilm reactor is possible. Furthermore, a previous

Table 1
Some reported biodegradation pathways for Ibu.