



Enhancing removal of nitrates from highly concentrated synthetic wastewaters using bipolar Si/BDD cell: Optimization and mechanism study



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ARTICLE INFO

Article history:

Received 11 July 2016

Received in revised form 3 October 2016

Accepted 22 October 2016

Available online 25 October 2016

Keywords:

Nitrates

BDD electrode

Response Surface Methodology

Chlorides

Kinetics

ABSTRACT

Electrochemical denitrification of highly concentrated synthetic wastewaters was investigated using bipolar Boron-Doped Diamond on silicone substrate (Si/BDD) electrodes under various experimental conditions. The effects of the key operational parameters on the removal efficiency of nitrates were assessed using the Response Surface Methodology. Results showed that the efficiency of removal of nitrates was mostly sensitive to the applied current density and the duration of treatment, which are optimized, respectively, at 35.7 mA cm⁻² and 120 min. Under these experimental conditions, the removal yield of nitrates was evaluated at 91% with formation of by-products of 0.4% and 3.6% of nitrites and ammonia, respectively. Furthermore, average current efficiency is optimized at 59% with an energy consumption estimated at 0.35 × 10⁻³ kWh(g-N)⁻¹.

To better understand the role of BDD anode/cathode, by-products electrogeneration and disappearance, as well as the effect of chloride ions on pathway electrochemical denitrification, series of experiments were carried out at three concentrations of NaCl. The kinetic constants were calculated using a pseudo first-order kinetic model based on the fitting of the experimental data to established numerical approximations using Matlab software. At first, we noted that the direct reduction to N₂ in the absence of NaCl was very low ($k = 1.7 \times 10^{-9} \text{ s}^{-1}$) compared to NH₃ and NO₂⁻ electrogeneration ($k = 1.7 \times 10^{-5}$ and $5.4 \times 10^{-4} \text{ s}^{-1}$, respectively), where N₂ seemed to be the result of a reduction in by-products. The presence of hypochlorous species had a negligible effect on the kinetic rates of NO₃⁻ reduction.

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1. Introduction

Pollution of water resources caused by nitrogen compounds has been mainly attributed to the intensive use of chemical fertilizers and pesticides in agriculture, uncontrolled wastewater discharges of some industries such as pharmaceutical and agri-food manufacturing, and discharges of leachates from human and animal wastes [1–6]. Nitrates could induce harmful effects to the environment and recreational pursuits, human and aquatic ecosystems [1,2]. Indeed, phosphorus and nitrogen are considered as the main chemical elements responsible for eutrophication of water bodies. This process can seriously disturb the balance of organisms present in water and negatively affect water quality, mainly through the depletion of dissolved oxygen level as the algae increase [7]. On the other hand, high concentrations of nitrates in drinking water could negatively affect animal and human health through methemoglobinemia, liver damage, and sometimes, cancer [8,9]. In this context, the maximum concentration of nitrates in the discharged

wastewaters in the receiving water bodies, which is permissible by Tunisian legislation is fixed at 50 mg L⁻¹ [10], and according to World Health Organization's (WHO) standards for drinking water it is 50 mg L⁻¹ [11].

During the last few decades, various technologies have been tested and applied for the removal of nitrates from wastewaters, such as flocculation, filtration, adsorption, and membrane separation. However, these methods generally require investment of considerable capital, and high costs of maintenance for infrastructure and reagents [12–16].

In recent years, electrochemical reduction of nitrates has been identified as an emerging attractive and promising technology thanks to its effectiveness even at high levels of nitrate pollution [17–27]. Furthermore, it occupied a small area, did not produce sludge, and did not need addition of chemicals either before or after treatment. Therefore, it has been focused upon by a large number of researchers using various cathode materials. Some electrodes such as Cu, Ti, Rh and Cu/Zn [17–21], were found to be efficient promoters for the electro-reduction of nitrates with a considerable removal rate and N₂ selectivity. However, electrochemical nitrates reduction was a complicated mechanism that leads to a relatively broad spectrum of by-products mainly NO₂⁻ and NH₃ as undesirable compounds, and N₂ gas, which is further electrochemically inactive [17–24]. Consequently, before their diffusion to

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the bulk, the electro-generated nitrites and ammonia are oxidized to the initial nitrates and gaseous nitrogen during the anodic cycle. Therefore, the difficulty is to find the optimal condition to perform, simultaneously, both cathodic reduction of nitrates and anodic oxidation of the electro-generated by-products. Lacasa *et al.* [17] studied the effect of cathode materials on reduction of nitrates and electrogeneration of ammonia using Boron-Doped Diamond (BDD) as anode material. Graphite was the most effective cathode for removal of nitrates, while BDD was the least effective with electrogeneration of the highest amount of ammonia [17]. Iron, copper and titanium were selected by Li *et al.* [18] who found that iron was the most effective for the reduction of nitrates, with a removal rate of 87%, and a selectivity to gaseous nitrogen was about 100% in 3 h using a Ti/IrO₂-Pt anode [18]. The effect of anode material was also studied by Lacasa *et al.* [21–24] who compared O₂-Dimensionally Stable Anodes and BDD anodes and found that BDD was more effective for the oxidation of by-products. Compared by using various tested electrode materials, BDD was found to be highly effective for the reduction of nitrates and the oxidation of electro-generated nitrites and ammonia into gaseous nitrogen and nitrates [23–25]. This efficiency is due to the outstanding properties of BDD, such as low and stable voltammetric background current, a wide working potential window, and high overpotential for oxygen and hydrogen evolution in aqueous electrolytes. These properties made BDD electrode effective for a large number of pollutants [23–34]. On the other hand, adding chloride ions to the solution leads to the generation of chlorine at the BDD anode, which immediately reacts with water to form hypochlorite [23,24]. Thereafter, electro-generated hypochlorite can react with ammonia and enhance its oxidation [22–24]. The effect of active chlorine species on the kinetics of nitrates removal and by-products oxidation [22–24] was also reported. In fact, Diaz *et al.* [9], Pérez *et al.* [23] and Lacasa *et al.* [24] have mentioned the positive effect of these species on the oxidation of ammonia contrary to the kinetic of nitrates removal that decreased with the addition of chloride ions.

Furthermore, the activity and the efficacy of the electrochemical process is already controlled by both the nature of the electrode material and several operational parameters such as pH, temperature, electrolyte composition, applied current or potential and cell configuration [17–25]. Therefore, there is need for studying the effect and the optimization of such parameters, which influence the electrochemical efficiency of the removal rate of nitrates by bipolar BDD electrode. For assessing the effect of various parameters on removal rate, the Response Surface Methodology (RSM) approach is widely used as the experimentation design [35–40]. However, the application of this approach was not widely used in the electrochemical reduction of nitrates. It was used by Li *et al.* [39] in order to study the effect and the interaction between three parameters (NaCl contents, applied current density, and electrolysis time) on removal of nitrates by using a palladium-copper alloy as cathode and Ti/IrO₂-Pt as anode [39]. Another study was performed by Talhi *et al.* [40] using stainless steel as anode/cathode material and studying the effect of four parameters (anode-cathode distance, applied voltage, initial pH, and electrolysis time) on removal of nitrates [40]. Nonetheless, the application of this approach on nitrates removal using bipolar BDD cell still remains to be studied.

Therefore, the main objectives of this study were (i) to study the influence of some key parameters, such as initial concentration of nitrates, concentrations of chlorides and sulfates, applied current density, and electrolysis time on the removal efficiency of nitrates by using a bipolar BDD cell, (ii) to assess the best conditions permitting both cathodic reduction of nitrates ions and a simultaneous oxidation/reduction of the resultant by-products, such as ammonia and nitrites, thanks to the central composite design (CCD) approach, (iii) to determine the impact of the presence of chloride ions on the removal of nitrates, and (iv) to better understand the mechanisms involved and the related kinetics according to a mathematically fitting approach.

2. Materials and methods

2.1. Electrochemical experiments

During this work, electrolysis of the synthetic solutions with high concentrations of nitrate was performed under galvanostatic mode by using an electrolytic cell (Adamant Technologies, Switzerland). This is composed of three compartments with two bipolar BDDs between two monopolar BDD electrodes. BDD is considered as cathode and anode material with an active surface was 70 cm² (for each one), and an electrode gap of 1 mm. For all the experiments presented below, a total volume of 1 L was recirculated with the use of a peristaltic pump (Invertek Drives Optidrive, Tunisia) (Fig. 1) with a fixed flow rate of 194.4 L h⁻¹ at an ambient temperature of 25 ± 3 °C.

Synthetic solutions were prepared by dissolving commercial sodium nitrate (NaNO₃, Sigma-Aldrich; purity ≥99.0%) in the presence of sodium chloride (NaCl, Panreac; purity ≥99.0%) or/and sodium sulfate (Na₂SO₄, Sigma-Aldrich; purity ≥99.0%) as supporting electrolyte in ultrapure water. For all the experiments, the initial pH was fixed at 5.5 ± 0.2.

2.2. Analyses and measurements

Concentrations of nitrates and nitrites were analyzed by using ion chromatography (IC-861, Metrohm) provided with an AS4A-SC column 150 mm × 4 mm. The eluents composed of solutions of Na₂CO₃ (3.2 mM) and NaHCO₃ (1 mM) were pumped inside the column at an average flow rate of 0.7 mL min⁻¹ and a pressure of around 2000 psi. Concentrations of ammonium and ammonia were analyzed by using the Nessler method and UV-visible spectroscopy (Thermo Spectronic model) at a wavelength of 420 nm [41,42]. Finally, the concentrations of gaseous nitrogen (N₂) were determined through the application of the mass balance. The monitoring of the pH of the solutions versus electrolysis time was performed by a calibrated pH meter (Metrohm). It is worth mentioning that the hydrazine and hydroxyl amine contents were not followed because of the alkaline pH of the electrolyzed solutions [43].

2.3. Calculations

The Average Current Efficiency (ACE) is an important index in the evaluation of the efficiency of the electricity utilized. It was calculated by using Faraday's law of electrolysis as follows:

$$ACE = 100 \times \frac{(C_{in} - C_{out})nFV_s}{It} \quad (1)$$

where C_{in} and C_{out} are the influent and effluent concentrations of nitrates (mol L⁻¹), respectively, n is the stoichiometric coefficient ($n = 5$ if N₂ is the final product, 2 if NO₂ is the final product, and 8 if NH₃ is the final product), F is the Faraday constant (= 96,485 C mol⁻¹), V_s is the volume of reactor (L), t is the total electrolysis time (s), and I is the applied current (A).

The Energy Consumption (EC (kWh (g-N)⁻¹)) was calculated according to the following equation:

$$EC = \frac{IEt}{\Delta C_N V_s} \quad (2)$$

where I is the applied current (A), E is the average cell voltage (V), V_s is the solution volume (L), ΔC_N is the decay in concentration of nitrogen (g L⁻¹), and t is the total electrolysis time (h).

The limiting current density (j_{lim}) was calculated from the expression given below:

$$j_{lim} = nFk_m C_{NO_3^-} \quad (3)$$

where k_m is the mass transfer coefficient calculated from a standard Fe(CN)₆³⁺/Fe(CN)₆²⁺ limit current test (= 1.2 × 10⁻⁵ ms⁻¹, [17]), $C_{NO_3^-}$ is the initial concentration of nitrates (mol L⁻¹), and n is the valence number.

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