ELECTROCHEMICAL NITRIFICATION OF AMMONIUM IN SIMULATED GROUNDWATER USING BORON-DOPED DIAMOND ELECTRODES

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Abstract
In this work, the electrochemical oxidation of ammonium from simulated groundwater on boron-doped diamond (BDD) electrodes was assessed in order to be integrated within the drinking water treatment technology. All nitrogen species, *i.e.*, nitrate, nitrite and total nitrogen, were monitored to assess the electrochemical nitrification of ammonium until gaseous nitrogen. For the simulated groundwater containing ammonium concentration of about 1 mgL^{-1}, the application of electrochemical oxidation at lab scale using BDD electrodes at the current density of 50 Am^{-2} assured an efficient oxidation of ammonium resulting nitrate at the concentration below maximum allowance concentration, as main intermediate of the electrochemical nitrification.

Introduction
It is well-known that the presence of ammonium in groundwater used as source for the drinking water represents a public health issue in developing and developed countries [1]. The Romanian legislation imposes the maximum allowance concentration (MAC) for ammonium in drinking water of 0.5 mg/L and higher concentrations require its removal. The ammonium presence in groundwater influences the selection of drinking water treatment process [2-4], the conventional method consisting in the „break-point"chlorination [2]. The drawbacks of the conventional method demand to find new technological solution for the ammonium removal from drinking water.

The electrochemical oxidation represents an advanced oxidation process studied for the removal of organic and inorganic compounds especial from wastewater [5, 6] and less from drinking water, except in disinfection stage. In general, the electrochemical oxidation actS to destroy the pollutants by direct oxidation on the electrode surface or by indirect oxidation through various powerful oxidants generated within the electrolyte depending on the electrolyte composition, *e.g.*, hydroxyl radical, Cl_2, etc.

The process performance key is given by the electrode material that besides the water composition dictates the type of direct or indirect oxidation. Boron-doped diamond (BDD) anodes have been successfully applied for advanced treatment of wastewater and also, disinfection due to its great mechanical and electrochemical properties, such as: resistance, inertness to the corrosion media, stability etc. The promising results have been reported for the application of BDD electrode for ammonium oxidation from waterwaters [7-9]. However, there are a few reports related to ammonium removal from drinking water. The results of the test applied for removal of ammonium form groundwater using an electrooxidation module integrated within the groundwater treatment pilot plant was reported by our group [10].

The aim of this paper is to study the performance of electrooxidation process using BDD electrodes at the laboratory scale to assure the electrochemical nitrification in order to remove the ammonium fROm simulated chloride containing groundwater.

Experimental

For bulk electrolysis a rectangular cell made of stiplex, with intercalated vertical anodes and cathodes, was used. The cell arrangement consisted of boron-doped diamond (BDD) anodes with the active surface area of 0.021 m^2 intercalated with the stainless steel cathodes at the distance between anodes and cathodes of 1 cm. The electrolysis was carried out at room temperature (22-25 °C) in batch mode under galvanostatic working regime for 1 mgL^{-1} ammonium in 250 mgL^{-1} NaCl supporting electrolyte. The BDD/Nb electrodes (100 mm x 50 mm x 1 mm) by CONDIAS, Germany were used as anodes, and stainless steel plates (100 mm x 50 mm x 1 mm) were employed as cathodes. A regulated DC power supply (HY3003, MASTECH) was used to assure galvanostatic regime at current densities of 50 mA cm^{-2} and 100 mA cm^{-2}.

At given time intervals, samples were drawn from the cell to monitor the performance of the electrochemical process in terms of nitrogen species concentrations. Determination of the nitrate, nitrite and ammonium concentrations was performed according to the standardized methods. For the determination of ammonium concentration, SR ISO 7150-1 / 2001 was used by the spectrophotometric method, the determination of nitrite content was carried out using the molecular absorption spectrometry method SR ISO 6777/1996 and the determination of nitrate content was performed using the method SR ISO 7890-1 / 1998 by spectrophotometric method with 2,6 dimethylphenol. Total nitrogen was determined using the total organic carbon analyzer, TOC-L CPH SHIMADZU.An Inolab WTW pH meter was used to measure the solution pH.

The specific energy consumption, W_{sp}, was calculated with the relation (1):

$$W_{sp} = \frac{\left(Q * V^{-1}\right)U}{1000} \quad \text{(kWh dm}^{-3}\text{)} \tag{1}$$

where Q represents the specific charge consumption, U is the cell voltage (V), V is the solution volume (dm^3).
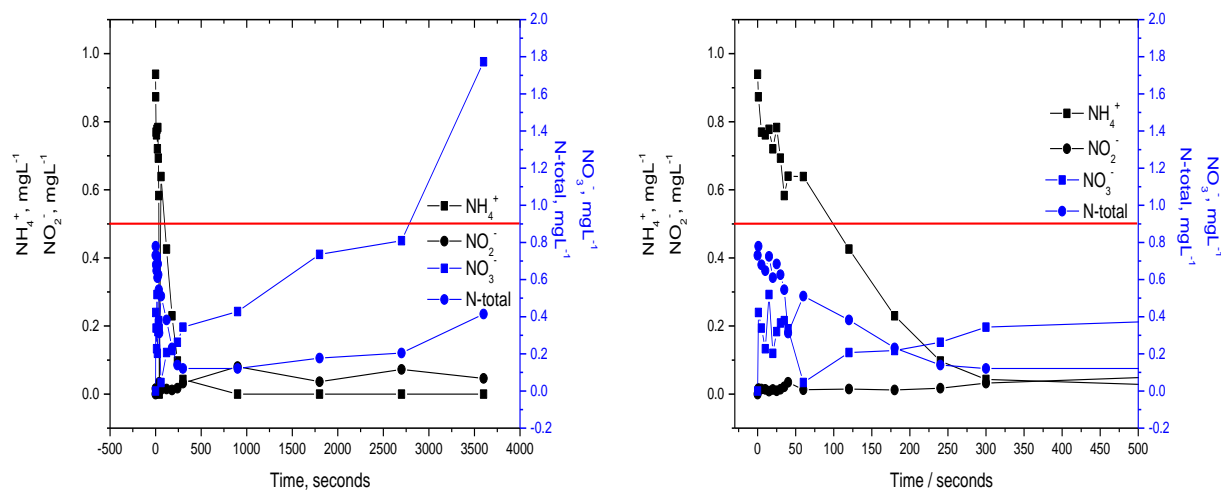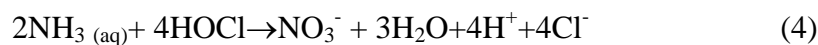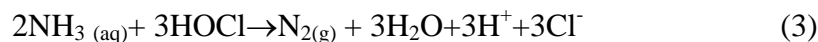
Results and discussion

Even if the ammonium conversion into nitrogen represents the main reaction characteristics to the electrochemical nitrification (eqs. 2, 3), some intermediates of nitrogen species (nitrite and nitrate) should be generated (eq. 4), which are undesired and affecting the water quality. The electrolysis process was conducted to maintain all nitrogen species below the maximum allowance concentrations (MAC) regulated by the legislation with minimum energy consumption. The evolution of the nitrogen species during the electrolysis process under conditions of applying a current density of 50 Am^{-2} for a synthetic water containing 0.906 mgL^{-1} NH$_4^+$ is presented Figure 1a. It can be seen a fast decrease of ammonium concentration and after 150 seconds the ammonium concentration reached below the MAC of 0.5 mgL^{-1} (Figure 1b). Also, during the first stage of the electrolysis the nitrate concentration increased followed by the sharp decreasing and then, a further slight increasing occurred. Total nitrogen as sum of the all nitrogen species followed the nitrate tendency characterized by the lower value, which means that the major intermediate is nitrate besides the gaseous nitrogen.

The main reactions that govern the electrochemical process are [7, 10]:

$$2NH_{3 \text{ (aq)}} + 6\ OH^- \rightarrow N_{2\text{(g)}} + 6H_2O + 6\ e^- \tag{2}$$
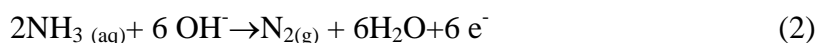
In the presence of chlorine generated electrochemically from chloride present into the water, the ammonium oxidation should occurred in according with equations (3) and (4).

$$2NH_{3\,(aq)} + 3HOCl \rightarrow N_{2(g)} + 3H_2O + 3H^+ + 3Cl^- \qquad (3)$$

$$2NH_{3\,(aq)} + 4HOCl \rightarrow NO_3^- + 3H_2O + 4H^+ + 4Cl^- \qquad (4)$$

a)   b)

Fig. 1. a) Concentration profile for ammonium, nitrite and nitrate species during electrolysis on BDD operated at 50 Am^{-2} for simulated water containing 0.9 mgL^{-1} ammonium and 250 mgL^{-1} NaCl at pH=7.7; b) Detail of Figure 1a

A very important working parameter for the electrolysis operation is considered current density that dictates the process kinetics. Two current densities of 50 and 100 Am^{-2} were applied and the evolution of the nitrogen species are presented in Figures 2 a and b. A slight enhancement of the process performace is noticed for 100 Am^{-2} but the question that arises is given by the economic aspect.
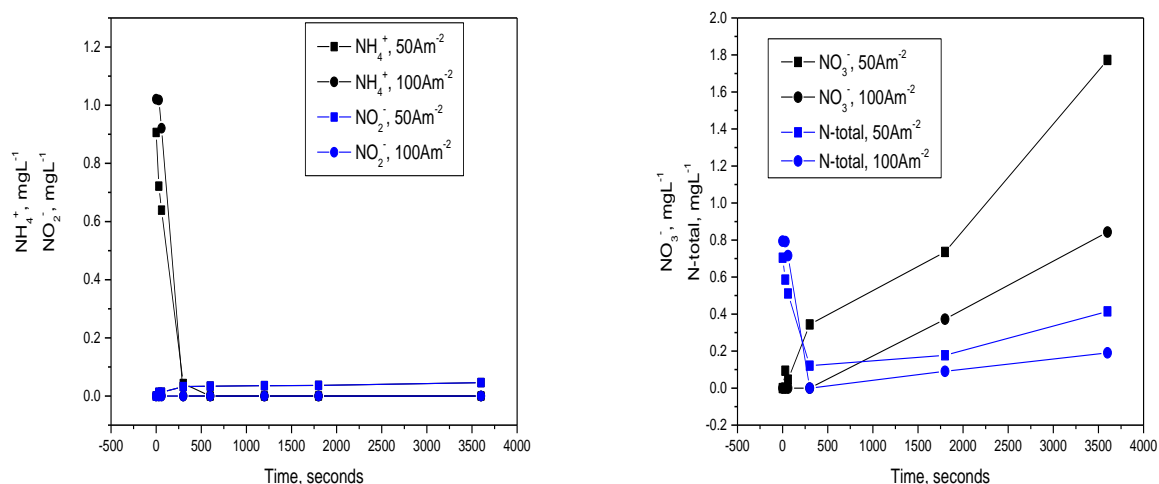
a)   b)

Fig. 2. Comparative concentration profiles for nitrogen species during electrolysis on BDD operated at 50 and 100 Am^{-2} for simulated water containing 0.9 mgL^{-1} ammonium and 250 mgL^{-1} NaCl at pH=7.7: a) ammonium and nitrite; b) nitrate and total nitrogen

The specific energy consumption is considered the main component of the economic aspect and its evolution is presented comparatively for both current densities in Figure 3. It is obviously that the longer electrolysis time the higher specific energy consumption and also, higher current density higher the energy consumption, thus, the electrolysis time and the current density should be selected in according with the concrete application.
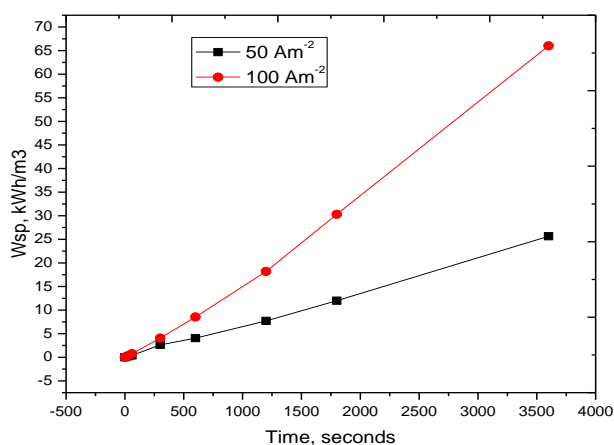

Fig.3. Specific energy consumption during electrolysis process

Conclusion
The electrochemical oxidation of ammonium from simulated groundwater on boron-doped diamond (BDD) electrodes assured the electrochemical nitrification of ammonium for both applied current densities of 50 and 100 Am^{-2}. Besides the desired conversion of ammonium into gaseous nitrogen, nitrate, nitrite and total nitrogen were identified as intermediates, nitrate being the main intermediate but under the maximum allowance concentration of 50 mgL^{-1}. Higher current density allowed the ammonium conversion of ammonium to gaseous

nitrogen more effectively in comparison with lower current density but the application of high current density is limited by the economic aspect. Thus, for the simulated groundwater containing ammonium concentration of about 1 mgL^{-1}, the application of the current density of 50 Am^{-2} assured an efficient oxidation of ammonium at short electrolysis time of 250 seconds, when the all nitrogen species intermediates were generated at the concentrations below the maximum allowance concentrations avoiding water pollution. However, the presence of nitrate within the real groundwater matrix at the concentration higher than maximum allowance concentration limited the application of this cell arrangement and operating conditions of the electrochemical process within the drinking water treatment technology.

Acknowledgements

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