Electrochemical treatment of wastewater polluted by nitrate: selective reduction to N\textsubscript{2} on Boron-Doped Diamond cathode

V. Georgeaud, A. Diamand, D. Borrut, D. Grange and M. Coste

ABSTRACT

Electrochemical tests of nitrate reduction on Boron-Doped Diamond cathode are investigated through a Design of Experiments (DOE) method. The results show good reduction of nitrate into almost exclusively N\textsubscript{2}. In the studied domain, the best experimental conditions are high initial nitrate content, low acidic pH values and low working current densities. The application of DOE conclusions on an agro-industrial wastewater gives really satisfying results: final nitrate contents lower than 50 mg/L without nitrite or ammonium formation, and with low energy consumption (under 25 kWh/kgNO\textsubscript{3}).

Key words | Boron-Doped Diamond (BDD), design of experiments, electro-reduction, nitrates

INTRODUCTION

An excessive use of nitrogenous fertilizer in agriculture and of nitrogen salts in industries leads to major pollution issues in water fields (aqueous ecosystem eutrophication, human health diseases through nitrite formation in drinking water) as well as high level of nitrogen concentration in industrial wastewaters. Therefore legislators have introduced maximum admissible concentrations for nitrates in drinking water (50 mg/L in the European Community). Concerning discharge limits in wastewaters, they depend on the location of discharge (limitation in global N in protected area for example, can be of 15 mg-N/l). When it is possible, industries treat their wastewaters \textit{in-situ} biologically before discharge or are connected with municipal WWTP. But biological treatments are very sensitive to high nitrate load, load variations and pH variations. Otherwise, nitrates have to be disposed \textit{ex-situ}, generating financial and environmental costs due to the transport.

REVIEW OF NITRATE TREATMENT PROCESSES

Conventional processes and recent studies

The most common technology used to treat non hazardous and nontoxic wastewaters consists in a biological denitrification, like in the natural nitrogen cycle. In the biological treatment plants, extensive regulations of parameters like pH, temperature, carbon supply are needed to maintain their life conditions and to avoid tracks of hazardous components in water. In fact, methanol or acetate is added (\textit{Wastewater Engineering: Treatment and Reuse 4th Edition}). On the other hand, denitrification step is producing biological sludges which have to be disposed and/or treated. Industrial wastewater volumes and nitrate contents (above several g/L) are not compatible with the load capacity of WWTP.

In order to treat nitrates in high concentrations (until 100 g/L) or contained in toxic or corrosive wastewaters, destruction in incinerator for industrial hazardous waste
has been used for long. This method is expensive as it requires much energy to reach the high temperatures needed. Moreover, the smoke gases containing NO₃ have to be treated to form N₂, via a metallic catalyst and ammonia or urea injection for instance, inducing additional costs. The financial and environmental cost of the transport has also to be taken into account, because of the limited number of adapted incinerators.

Other techniques have been studied recently where nitrates are treated chemically. Photo-catalysis of nitrates on Ag/TiO₂ particles could seem efficient when chemical reagents (4.2 g of methanoic acid/g of NO₃) are added (Zhang et al. 2005). Nitrates could also be reduced thanks to zero valent metallic components (Shrimali & Singh 2001) such as Fe, Al, Cu or Zn, leading to the formation of NH₃/NH₄⁺ and a successive treatment to eliminate these species based on their oxidation by Cl₂, O₃ or HClO. Process instabilities and high costs prevent these chemical treatments from being scaled up.

Electrochemical processes

Chemicals reactions

The most promising treatment for problematic wastewater may be electro-reduction. This method fits with industrial nitrate concentrations while limiting the addition of chemical reagents. However, there are many possible products and the selectivity is difficult to obtain (Table 1).

<table>
<thead>
<tr>
<th>Oxidation number</th>
<th>Product</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>-III</td>
<td>NH₄⁺/NH₃</td>
<td>Ammonium/Ammonia</td>
</tr>
<tr>
<td>-II</td>
<td>N₂H₄</td>
<td>Hydrazine</td>
</tr>
<tr>
<td>-I</td>
<td>NH₂OH</td>
<td>Hydroxylamine</td>
</tr>
<tr>
<td>0</td>
<td>N₂</td>
<td>Dinitrogen</td>
</tr>
<tr>
<td>I</td>
<td>H₂N₂O₂/N₂O</td>
<td>Hyponitrous acid/Dinitrogen monoxide</td>
</tr>
<tr>
<td>II</td>
<td>NO</td>
<td>Nitrogen monoxide</td>
</tr>
<tr>
<td>III</td>
<td>NO₂⁻</td>
<td>Nitrite</td>
</tr>
<tr>
<td>IV</td>
<td>NO₂</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>V</td>
<td>NO₃⁻</td>
<td>Nitrate</td>
</tr>
</tbody>
</table>

In a neutral media, nitrates are mainly reduced in N₂, NH₃, or NO₂⁻ as described by the following half-equations:

\[
\begin{align*}
\text{NO}_3^- + H_2O + 2e^- &= NO^- + 2OH^- \\
\text{NO}_3^- + 3H_2O + 5e^- &= \frac{5}{2}N_2 + 6OH^- \\
\text{NO}_3^- + 6H_2O + 8e^- &= NH_3 + 9OH^- 
\end{align*}
\]

Nitrites and ammonia formations, usually predominant, are to be avoided to the benefit of N₂ which can be directly rejected to the atmosphere (N₂ represents 78% of the troposphere).

Metallic electrodes

Studies showed that nitrates could be reduced electrochemically on several metallic cathodes like Rh (Brylev et al. 2007), Pt (De Groot & Koper 2004; Dima et al. 2005), Cu (Kerkeni et al. 2002), Ni (Armijo et al. 2004) or Au (El-Deab 2004). The addition of a second metal on the electrode surface often promotes their activity (Paidar et al. 1999; Kerkeni et al. 2002). That is why binary and ternary metallic catalysts have been developed, in particular palladium based catalysts (Pd-Ge, Pd-Cu, Pd-Sn, Pd-In, Pd-Zn...) (Prüss et al. 2000; Gauthard 2003). However selectivity is still hard to reach: N₂ but also NO₂, N₂H₄, N₂O, NO and NH₂ can be produced during nitrate reduction. A possibility consists in reducing nitrates into ammonia thanks to a Reticulated Vitreous Carbon (RVC) before oxidizing ammonia into N₂ (Vanlangedonck et al. 2004), leading to an energy consumption of 47 kWh/kg treated NO₃ on industrial wastewaters.

Selectivity towards N₂ can be obtained on Sn cathode, but corrosion limits its application (Katsounaros et al. 2006). Even if studies proved the efficiency of metallic electrodes, their major drawback is their low stability in concentrated acidic or alkaline media, which are typical conditions for industrial wastewaters.

BDD electrodes

Boron-doped diamond electrodes have remarkable chemical and electrochemical properties (Cerisoli & Panizza 2005; Kraft 2007). Unlike metallic electrodes, they are resistant to corrosion even in very acidic media. Moreover, their potential window is very wide before hydrogen evolution, making them particularly attracting for nitrate reduction. According to the early works (Levy-Clément et al. 2003), nitrate electro-reduction on a BDD cathode would lead to gaseous products only, but when H₂ is formed a chemical reduction of nitrate would occur simultaneously.
and provoke nitrite and ammonium formation. A complementary gas analysis during the electrolysis of a solution of HNO₃ 1 M showed that the products were H₂, N₂ and N₂O. Only small amounts of NO₂ were detected (Georgeaud et al. 2008). In Veolia Water Research Center, we highlighted electrochemical specific reactions of nitrate at acidic and neutral pH on BDD electrodes thanks to cyclic voltammetry at a laboratory scale (Figure 1).

MATERIALS AND METHODS

Pilot unit

The electrolyser has two compartments separated by a cationic membrane. BDD electrodes (disk of 68 cm² active surface) distant of 10 mm are used as anode and cathode. Two pumps recycle the anolyte and the catholyte between the dedicated tanks and the cell (Figure 2). The cathodic tank is stirred and its pH is regulated with sulphuric acid injection for this application. Parameters such as temperature, pH, redox potential, conductivity, current, voltage are continuously recorded and/or regulated in each tank.

Experimental Method

Synthetic effluent

The nitrate reduction is investigated using a two levels fractional factorial design of experiments (DOE) 2⁷⁻³ and 3 centered points (19 experiments). Instead of optimization or robustness designing, this screening investigation with seven factors is characterized by the studied parameters which are aliased to the 4 main factors and to the 3 three-factor interactions. It enables to qualify and quantify the most important factors with high certainty, but not the two-factor interactions due to mutual confoundings. Some additional experiments are run in or out the experimental domain to validate the results and to reduce statistical approximations. The studied factors and the setting variations are reported in Table 2.

Table 2  Definition of controlled parameters and component level ranges

<table>
<thead>
<tr>
<th>factors</th>
<th>unit</th>
<th>low</th>
<th>center</th>
<th>high</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial nitrate content</td>
<td>g/L</td>
<td>3</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>pH in cathodic tank</td>
<td>–</td>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>pH in anodic tank</td>
<td>–</td>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>current for polarity</td>
<td>A/m²</td>
<td>450</td>
<td>1475</td>
<td>2500</td>
</tr>
<tr>
<td>inversion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>current for reduction</td>
<td>A/m²</td>
<td>1475</td>
<td>2213</td>
<td>2950</td>
</tr>
<tr>
<td>temperature of tanks</td>
<td>°C</td>
<td>20</td>
<td>27</td>
<td>34</td>
</tr>
<tr>
<td>recycling flow for each</td>
<td>m³/h</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>half-cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1  Cyclic voltammograms on BDD cathode in 0.1 M solution of NaNO₃ and NaCl at pH 7 (on the left) and pH 1 (on the right).

Figure 2  Simplified process diagram of the electrolysis unit: E1, C1 cathodic tank, C2 anodic tank, P1-2 recycling pumps, C3 acid tank for pH regulation.
The method used to fit the mathematical and statistical model to the data is PLS (“Partial Least Squares” or “Projection to Latent Structures”) through MODDE 8.0 software for design of experiments and optimization, using PLS2 NIPALS algorithm. PLS method enables to fit simultaneously the variation of all the responses to the variation of the factors, taking the responses covariances into account.

Cathodic and anodic solutions are prepared with NaNO₃ Normapur and K₂SO₄ Normapur respectively, and distilled water. The pH value is regulated with H₂SO₄ 98% Rectapur.

During the experiments, samples are periodically collected for ions analysis. Nitrate and nitrite concentrations are determined by UV-spectroscopy (302 nm and 354 nm respectively) on a DR 5000 (Hach Lange) and with Lange kits (LCK 340 and LCK 342). Ammoniums are quantified thanks to an ion-selective electrode DC218-NH₄ (Mettler Toledo).

The responses of DOE shown in this paper are nitrate removal (%), nitrite and ammonium formation (g/L) and current efficiency CE, defined as the ratio between the nitrates experimentally reduced into N₂ and the nitrates theoretically reduced into N₂ if all electrons were participating exclusively in the nitrate reduction. The experimental value is calculated considering that the nitrates transformed in N₂ are those which have been removed during the experiments without forming nitrite or ammonium, as shown in the current efficiency definition:

\[ CE = \frac{5n_{NO_3\text{removed}} - 2n_{NO_2\text{formed}} - 8n_{NH_4\text{formed}}}{I/F} \]

where \( I \) is the current intensity (A), \( t \) the time (s), \( F \) the Faraday constant (96485 C/mol), and \( nX \) the quantity of \( X \) (mol).

All responses are measured all along the reaction, but only those at a given moment \( T_0 \) are presented in the first subpart of results and discussion part: \( T_0 \) is the theoretical time necessary to reduce the totality of the initial nitrates considering CE equal to 1

\[ T_0 = \frac{5n_{NO_3\text{initial}}}{I/F} \]

**RESULTS AND DISCUSSION**

**Nitrate synthetic solutions**

The choice is made for the investigation of data through PLS method, to consider only the principal factors and to remove from the model the higher order terms (interactions) to increase the degree of freedom of the system. In this case, the data analysis of centered and/or replicated experiments indicates first, that the experimental reproducibility is far better than the variability caused by the factor variations, and secondly, that the relationship between the factors and the responses (except for nitrite formation) is most likely linear as the centered experiments are located close to the center of the response variations.

Figure 3 indicates mean values (constant term) of each considered response in the studied experimental model, and quantifies the positive or negative effect of each factor high level value on each response compared to their constant.

The initial nitrate content of the effluent has a large positive effect on each response (except nitrite formation), while the values of cathode pH has a large positive effect on each response (except ammonium formation). The temperature of reaction could present only a small positive effect exclusively on nitrate removal. Due to high confidence intervals, the other factors can be considered as insignificant for all responses.

Table 3 points out some numerical results in function of nitrate concentration and working current. These data illustrate clearly the previous remarks given by the DOE investigation. It is also demonstrated the possibility of an exclusive electro-reduction of nitrate in N₂ without by-production (or in very small amount) of ammonium or nitrite.

In the experimental domain, the optimal conditions are regulated pH value, initial nitrate concentration and temperature at the highest level, namely 2.5, 27 g/L and 34°C respectively. The explanation is mainly based on the competition between hydronium and nitrate ions in solution: for low pH values (higher hydronium ion concentrations) and low nitrate concentrations, the main product on the cathode would be H₂ instead of N₂.

Concerning the electric energy consumption, the calculation underlines less consumption for low level of working current. That could be explained by the mass transport limitation of nitrate ions toward the constant working current fixed for each experiment. However, the energetic values shown in Table 3 depend largely on the pilot unit conformation. The energy consumption could be largely decreased by using low overpotential metallic anode instead BDD anode, using small resistivity membrane and/or reducing the inter-electrode gap.
Agro-industrial wastewater

A part of previous conclusions are used for the configuration of the pilot unit and to fix the working parameters to treat a real agro-industrial wastewater. For example, BDD anode is replaced with platinum coated titanium electrode to reduce the needed voltage to produce oxygen gas in anodic circuit. The working currents are fixed at low values in or out the domain studied through DOE investigation.

Table 4a/ points out the results at $T_0$ to compare with the results obtained on synthetic effluent shown in Table 3. A good nitrate removal is obtained in spite of the low nitrate initial content of the effluent. No nitrite and low levels of ammonium formation are noted. The lower current efficiency is observed for the higher working current, showing the effect of mass transport limitation of nitrate ions during the electrochemical process.

The experiments are carried out until the end of the reactions to remove the totality of nitrate ions (Figure 4). Tables 4b/ and 4c/ present the results obtained at different steps, with treatment objectives respectively of 100 and 50 mg/L residual nitrate contents. In addition to a great nitrate removal, these tables show the absence of nitrite formation and low ammonium formation in the fixed experimental conditions.

Concerning the energy consumption, the values vary between 24 and 120 kWh/kg treated nitrate for working current respectively of 300 and 750 A/m$^2$ (Table 4). The

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Table 3 | Some experimental conditions and results at $T_0$ obtained on synthetic solutions

<table>
<thead>
<tr>
<th>[NO$_3$] Initial (g/L)</th>
<th>Working current (A/m$^2$)</th>
<th>NO$_3$ removal (%)</th>
<th>Current efficiency (%)</th>
<th>NO$_3$ formation (mg/L)</th>
<th>NH$_4$ formation (mg/L)</th>
<th>Energy (kWh/kg NO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>2500</td>
<td>89</td>
<td>86</td>
<td>24</td>
<td>200</td>
<td>34.7</td>
</tr>
<tr>
<td>27</td>
<td>450</td>
<td>80</td>
<td>73</td>
<td>74</td>
<td>760</td>
<td>20.0</td>
</tr>
<tr>
<td>3</td>
<td>2500</td>
<td>51</td>
<td>44</td>
<td>95</td>
<td>66</td>
<td>108.5</td>
</tr>
<tr>
<td>3</td>
<td>450</td>
<td>37</td>
<td>13</td>
<td>30</td>
<td>80</td>
<td>51.4</td>
</tr>
</tbody>
</table>
current efficiency results and energy consumption values reinforce the hypothesis on the effect of mass transport limitation on the global reaction, and emphasize clearly the necessity to adjust the working current to the nitrate content in the effluent to treat in viable economical conditions.

CONCLUSION

Electro-reduction of nitrate into N\textsubscript{2} is successfully carried out at pilot scale on a BDD cathode. A DOE methodology first pointed out the significant process parameters and their optimum values in the studied domain: high nitrate content, low acidic pH, and high temperature. The tests then run on an agro-industrial wastewater confirmed that a remaining nitrate content below 50 mg/L could be reached while no nitrite and few ammonium were produced. With an energy consumption inferior to 25 kWh/kg NO\textsubscript{3}, the process appears as fully competitive for the treatment of industrial wastewaters containing toxic compounds or high content of nitrates.

REFERENCES


