

**DENITRIFICATION OF POTABLE WATER USING BIOLOGICAL AND ELECTROCHEMICAL METHODS****A.K. Benekos<sup>1</sup>, M. Tsigara<sup>1</sup>, S. Zacharakis<sup>1</sup>, S. Lyristi<sup>1</sup>, A.G. Tekerlekopoulou<sup>2</sup>, D.V. Vayenas<sup>1,3,\*</sup>**<sup>1</sup>Department of Chemical Engineering, University of Patras, Rio, 26504 Patras, Greece<sup>2</sup>Department of Environmental and Natural Resources Management, University of Patras, 2 G. Seferi Str., GR-30100 Agrinio, Greece<sup>3</sup>Institute of Chemical Engineering Sciences (ICE-HT), Stadiou Str., Platani, 26504 Patras, Greece(\*[dvaqenas@chemeng.upatras.gr](mailto:dvaqenas@chemeng.upatras.gr))**ABSTRACT**

Elevated concentrations of nitrate (as well as nitrite) in drinking water have always been accused of causing several serious diseases (e.g. various forms of cancer, blue-baby syndrome). In this work both electrochemical and biological processes were examined for nitrate removal from drinking water using various operating conditions. Concerning the biological process, a suspended-growth batch bioreactor was used to examine nitrate removal through hydrogenotrophic denitrification, providing carbon dioxide as carbon source for the microorganism's metabolic procedures. A mixed culture originating from a wastewater treatment plant was used to inoculate the bioreactor with 45 mg L<sup>-1</sup> initial NO<sub>3</sub><sup>-</sup>-N. The performance of electrocoagulation using Aluminum electrodes for the removal of nitrates from water was also studied. Although nitrogen gas was the desirable product of the procedure, significant concentrations of ammonium (NH<sub>4</sub><sup>+</sup>) were detected in the treated water. Therefore, electrochemical oxidation (using Ti/IrO<sub>2</sub> as anodes and Aluminum as cathodes) was also used as post treatment step to further remove such by-products generated from electrocoagulation. Various operating variables such as initial pollutant concentration, applied current density and time were tested for their effects on nitrate removal, in order to conclude whether such a treatment could be feasible and cost efficient.

**INTRODUCTION**

Nitrogen pollution is among the most serious concerns in recent years mainly due to the excessive usage of fertilizers in agricultural regions across the world. Nitrates have been frequently accused of various health problems (carcinogenesis, methemoglobinemia etc.), therefore for drinking water the maximum contaminant limit (MCL) of 10 mg/L of nitrate as nitrogen was set by USEPA, whereas World Health Organization (WHO) and the European Community have set a MCL of 50 mgNO<sub>3</sub><sup>-</sup>·L<sup>-1</sup> which is equal to 11.3 mgNO<sub>3</sub><sup>-</sup>·N·L<sup>-1</sup>.

Numerous methods have been developed to reduce the nitrate concentration in water like reverse osmosis, ion exchange, electrodialysis, biological denitrification, chemical denitrification and adsorption. All the methods have their inherent advantages and disadvantages. Although some of the above-mentioned methods are very effective methods (such as reverse osmosis, biological denitrification and electrodialysis) their major limitation is the disposal concentrated waste stream to environment and risk of nitrite formation (potential incomplete denitrification). Therefore, the full-scale application is currently limited.

In this work both biological and electrochemical processes are examined for nitrate removal from drinking water using various operating conditions

**RESEARCH GOALS AND METHODOLOGY**

Nitrate removal for synthetic water was examined using both biological and electrochemical processes in order to found to their advantages and limitations, in terms of implementation simplicity, efficiency and cost.

Biological denitrification experiments were performed in suspended growth reactors under batch operating condition using a mixed culture originating from a wastewater treatment plant, in order to investigate the kinetics of nitrate consumption from denitrifying bacteria and develop a kinetic model capable of describing the whole bio-denitrification process.

Electrochemical denitrification experiments were also carried out using aluminum electrodes as anode and cathode (Electrocoagulation (EC) process). Various operating variables such as pH (5, 7, 8.5), applied current density ( $10 \text{ mA}\cdot\text{cm}^{-2}$  and  $20 \text{ mA}\cdot\text{cm}^{-2}$ ) and initial concentration of  $\text{NO}_3^- \text{ - N}$  (25, 35, 45, 55  $\text{mg L}^{-1}$ ) were tested for their effects on nitrate removal. Finally, estimation of the treatment cost under various operating conditions were performed. Since ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) was the main by-product of the electrochemical reduction performed throughout EC, a post-treatment method was examined in order to remove such hazardous species from the treated solution. Electrochemical Oxidation using Ti/IrO<sub>2</sub> as anodes and Aluminum as cathodes was used in order to oxidize  $\text{NH}_4^+\text{-N}$ . Furthermore, as electrochemical reduction is still occurring in the cathode metal of such a process, further reduction of nitrate anions to ammonium cations was still possible, in case EC denitrification did not eliminate such species.

## EXPERIMENTAL PART

For the biological denitrification experiments, a continuous stirred bio-reactor of 1 L working volume was used. Temperature was maintained always stable at 25 °C, while gas supplies of carbon dioxide and hydrogen were connected to the reactor (of volumetric flow rates  $24 \text{ mL min}^{-1}$  and  $15 \text{ mL min}^{-1}$ , respectively) to provide a carbon source and an elector donor to the system. For the microbial growth,  $\text{KH}_2\text{PO}_4$  ( $3.39 \text{ g L}^{-1}$ ),  $\text{Na}_2\text{HPO}_4$  ( $3.53 \text{ g L}^{-1}$ ) and  $\text{KNO}_3$  (in order to achieve the desired initial  $\text{NO}_3^- \text{ - N}$  concentration of  $45 \text{ mg L}^{-1}$ ) were inserted to the reactor. As soon as nitrate degradation had completed, 150 mL of liquid was replaced with fresh synthetic water to achieve final concentrations of  $45 \text{ mgNO}_3^- \text{ - N/L}$ . This process comprised one operating cycle.

For the electrocoagulation experiments, an electrolytic cell of 0.15 L working volume under constant stirring (on a rotary shaker) was used. Temperature was maintained between 25 – 30 °C. The overall treatment time was 3 hours and during specific time intervals (30 minutes) 5 mL of samples were drawn from the bulk volume. The samples were left overnight so that aluminum hydroxide complexes could precipitate. Afterwards, the liquid phase of the samples was filtrated and consequently, nitrates and ammonium were measured according to Standard Methods [...anafor;a]. Similar proceeding was followed for the electrochemical oxidation experiments.

## RESULTS AND DISCUSSION

### Biological denitrification

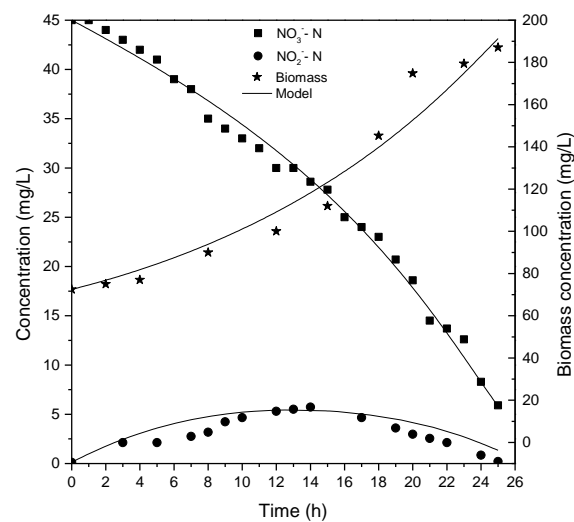
For the hydrogenotrophic denitrification experiment, the respective results are contained in the following graph (Fig. 1). Model of substrate inhibition is used to simulate the biomass growth as well as the substrates consumption. Nitrites and nitrates are the two substrates used for the biomass growth, with nitrites acting as an inhibition factor. The equations used for the evaluation of the model are the following ones:

$$\frac{dX}{dt} = \frac{r_{\max 1} N_1}{K_s + N_1 + k_{d2} N_2 + (N_1^2 / K_i)} X + \frac{r_{\max 2} N_2}{K_n + N_2 + k_{d1} N_1} X - k_d X \quad [1]$$

$$\frac{dN_1}{dt} = -\frac{1}{Y_s} X \frac{r_{\max 1} N_1}{K_s + N_1 + k_{d2} N_2 + (N_1^2 / K_i)} \quad [2]$$

$$\frac{dN_2}{dt} = -\frac{1}{Y_n} X \frac{r_{\max 2} N_2}{K_n + N_2 + k_{d1} N_1} + \frac{1}{Y_s} X \frac{r_{\max 1} N_1}{K_s + N_1 + k_{d2} N_2 + (N_1^2 / K_i)} \quad [3]$$

where  $N_2$  is the nitrite nitrogen concentration ( $\text{mg L}^{-1}$ ),  $r_{\max 2}$  the maximum specific growth rate on nitrite ( $\text{h}^{-1}$ ),  $K_n$  the saturation constant for nitrite ( $\text{mg L}^{-1}$ ),  $Y_s$  the growth yield coefficient on nitrate ( $\text{mg biomass}/(\text{mg NO}_3^- \text{-N})$ ),  $Y_n$  the growth yield coefficient on nitrite ( $\text{mg biomass}/(\text{mg NO}_2^- \text{-N})$ ),  $k_{d1}$  the constant in growth rate expression ( $\text{mg NO}_2^- \text{-N}/(\text{mg NO}_3^- \text{-N})$ ) and  $k_{d2}$  is a constant in growth rate expression ( $\text{mg NO}_3^- \text{-N}/(\text{mg NO}_2^- \text{-N})$ ). The maximum growth rate for the nitrate was  $0.1 \text{ h}^{-1}$  while for the nitrite was  $0.07 \text{ h}^{-1}$

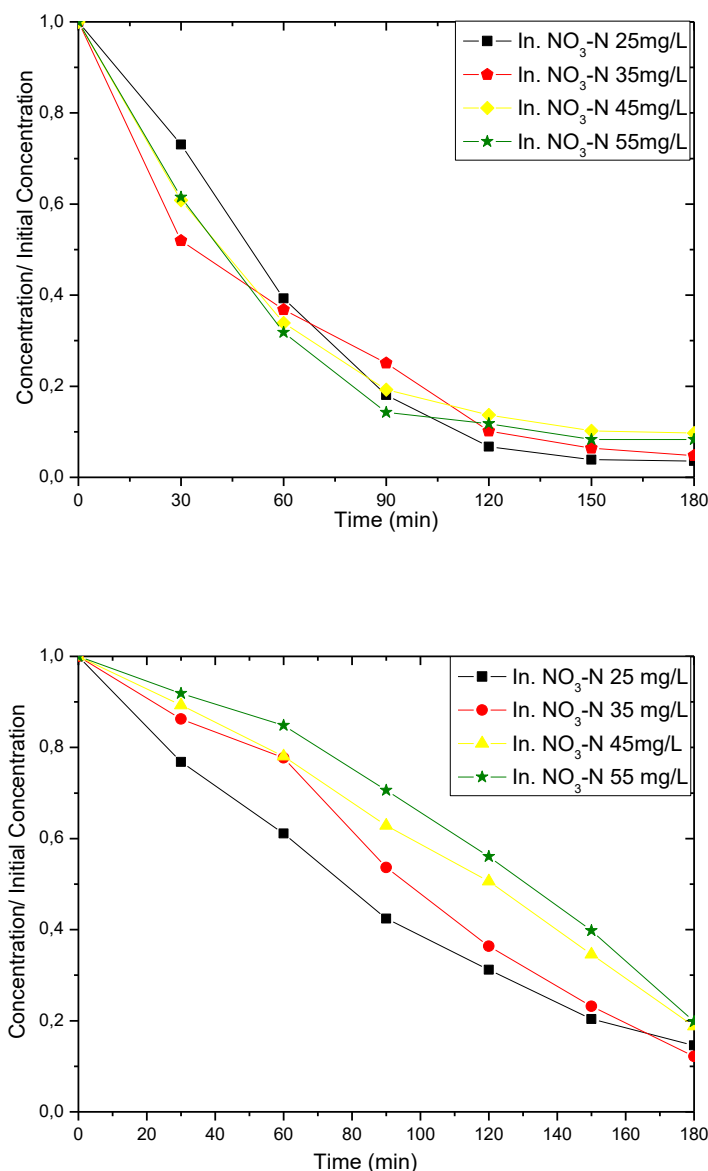


**Figure 1.** Biomass, nitrate and nitrite concentrations as a function of time and the respective model predictions for a denitrification cycle.

### Electrochemical denitrification

Initially electrocoagulation experiments were performed without adjusting pH during the process. Four different initial  $\text{NO}_3^- \text{-N}$  concentrations were examined (25, 35, 45 and  $55 \text{ mg L}^{-1}$ ) under two current densities of  $10$  and  $20 \text{ mA cm}^{-2}$  (Figures 2a and 2b, respectively).

For the applied electric current density of  $10 \text{ mA cm}^{-2}$  the nitrate nitrogen removal can be described as a zeroth order reaction (for 180 minutes treatment time). This means that there is a limit to the quantity of the  $\text{NO}_3^-$  molecules that either reduce to  $\text{NH}_4^+$  or precipitate through adsorption to the aluminum sweep flocs, so that there is dependency of the nitrate concentration throughout the procedure. Apparently, the fact that the applied current density is rather low, implies that both reduction and adsorption processes are highly dependent on the reductive potential and the aluminum oxidation respectively. On the other hand, when  $20 \text{ mA cm}^{-2}$  was applied, the reaction rate could be described by 1<sup>st</sup> order kinetics, as it is obvious from figure 2b (for 180 minutes treatment time). In this case,  $\text{NO}_3^- \text{-N}$  concentration affects the kinetics of the denitrification procedure, since the applied electric current is raised enough to provide sufficiently high reductive potential and coagulant dosing.

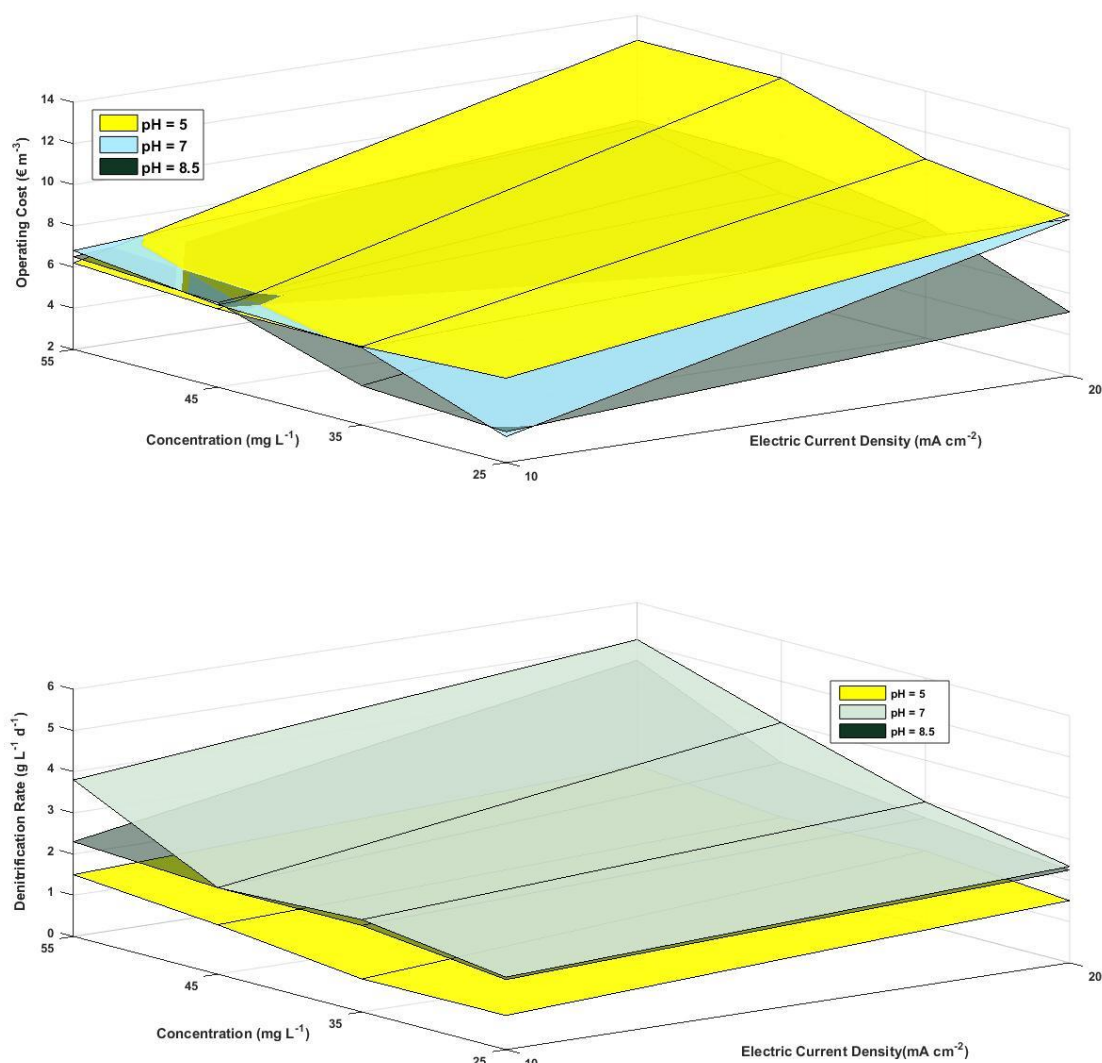


**Figure 2.** 2a) Nitrate removal as a function of time for four different initial nitrate concentrations with no initial pH adjustment and 10 mA cm<sup>-2</sup>, 2b) Nitrate removal as a function of time for four different initial nitrate concentrations with no initial pH adjustment and 20 mA cm<sup>-2</sup>.

Denitrification rates ranged between 0.8 and 5.2 g L<sup>-1</sup> d<sup>-1</sup> as shown in Figure 4a. Influence of initial pH value proved rather unimportant compared to initial NO<sub>3</sub><sup>-</sup>-N concentration and especially current density value, which proved to be the most critical parameter for the enhancement of the denitrification rate.

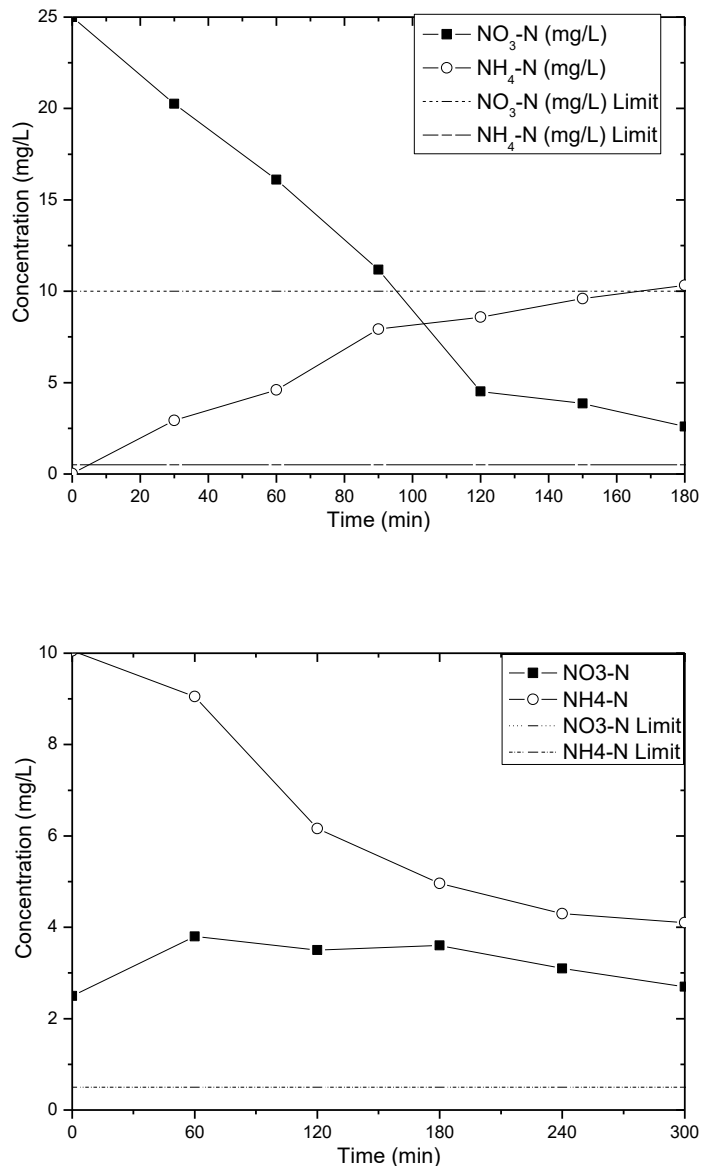
Cost analysis of the EC process showed that it is very essential the estimation of the cost-efficiency of the process. More specifically, applied electric current density is the most influential factor, as operating cost increased proportionally to this factor. Initial pH value is a considerable factor for the treatment cost. For lower initial values, higher treatment times are required and as a consequence this leads to extended operating costs due to the increased aluminum mass that dissolves, as well as the electric energy that is consumed throughout the procedure. Furthermore, concerning the factor of the initial NO<sub>3</sub><sup>-</sup>-N. Figure 3b, depicts the respective operating cost for each experimental run. Although for 10 mA cm<sup>-2</sup> the cost ranges between 2.5 and 6.3 € m<sup>-3</sup>, for higher applied current

density ( $20 \text{ mA cm}^{-2}$ ) this cost increased rapidly ranging between  $4.5$  and  $12.5 \text{ € m}^{-3}$ .



**Figure 4.** 4a) Three-dimensional depiction of operating cost (as a function of current density, initial nitrate concentration and pH). 4b) Three-dimensional depiction of the denitrification rate (as a function of current density, initial nitrate concentration and pH).

Since ammonium nitrogen concentrations that observed throughout the EC experimental runs were significantly high, electrochemical oxidation was applied to remove such by-products. For example, for initial nitrate-nitrogen concentration of  $25 \text{ mg L}^{-1}$  the final ammonium concentration after EC (Fig. 5a) was approximately  $5 \text{ mg L}^{-1}$  (concentration higher than the maximum permitted limit of  $0.5 \text{ mg L}^{-1}$  for drinking water). However, after electrochemical oxidation (Fig. 5b), ammonium percentage removal exceeded the value of 60%. For higher initial ammonium concentrations (up to  $35 \text{ mg L}^{-1}$ ), oxidation process led to higher removal percentages (up to 85%), but in all cases, there was a remaining  $\text{NH}_4^+\text{-N}$  concentration ranging between  $5\text{-}7 \text{ mg L}^{-1}$ . Such results could indicate there are significant mass transport limitations controlling the whole procedure, especially when ammonium concentration is quite low and therefore, its flux towards the anode electrode is decreased. Consequently, this problem should be addressed by developing a reactor-designing model aiming to eliminate such mass transport limitations.



**Figure 5.** 5a) Nitrate removal using electrocoagulation when  $10 \text{ mA cm}^{-2}$  was the applied current density and  $25 \text{ mg L}^{-1}$  was the initial nitrate concentration. 5b) Ammonium oxidation using electrochemical oxidation on the outflow of the experiment presented on figure 5a.

## CONCLUSIONS

In conclusion, concerning the biological denitrification experiment that is presented, the model of double nutrient limitation with inhibition from nitrate proved to adequately predict both the biomass growth as well as the consumption of the two substances. However, it is required to be validated with further experiments under different operating parameters.

Concerning the electrochemical experiments, electrocoagulation results were quite promising, as the process could remove high nitrate concentrations in a quite fast fashion. However, the cost efficiency of the process is a factor to be addressed, as the cost of the aluminum that is dissolved to the bulk volume throughout the process is leading to high treatment costs.



## 1. REFERENCES

- [1] Mary H. Ward, \* Rena R. Jones, Jean D. Brender, Theo M. de Kok, Peter J. Weyer, Bernard T. Nolan, Cristina M. Villanueva, and Simone G. van Breda. Drinking Water Nitrate and Human Health: An Updated Review Int J Environ Res Public Health. 2018 Jul; 15(7): 1557.