ELONITA

LAYMAN'S REPORT

LABORELEC

Electrabel

Life

UCL
Université catholique de Louvain

Many industries are faced with the need to reduce the nitrogen content of their wastewater. In particular, nitrate and ammonium ions are harmful and toxic components (figure 1) and need to be kept to the lowest level as possible.

The presence of nitrates, nitrites and ammonium in the wastewater of a power plant for example has two main sources:

1. The *water demineralisation process* is necessary for a good operation of the plant: the demineralisation process consists of a sequence of resins that absorb selectively ions initially present in the water. In order to regenerate these resins, a water stream, called the regeneration effluent, flows through the resins removing all the absorbed ions. This regeneration effluent contains many ions and can contain many nitrates ions.

2. Effluent of the *vacuum pump circuit* of the power plant: generally ammonia is used to limit corrosion problems in the installation.

This project contributes to the sustainable use of Europe's waters, human health and aquatic life. Very well defined regulations have been put in place by the authorities. The threshold values are 15 mgN/l en 0.5 mg/l for N-nitrate and ammonia, respectively, whereas in effluents from power plant we find a complex wastewater containing:

- Nitrate/Nitrite ions (200 to 1000 mg/l)
- Ammonium ions (500 mg/l to 10 g/l)
- High ionic content

ELONITA® (**El**ectro-destruction **o**f toxic **nit**rate and **a**mmonia ions) is a project that aims at getting rid of these impurities, based on the principle of electrolyse. ELONITA® overcomes many disadvantages of the existing methods.
There are several existing techniques for eliminating these ions: Biologic treatment (based on nitrification-denitrification), catalytic process, reverse osmosis, ion exchange and stripping. The last three methods don't give satisfactory results because they only transfer pollution to another effluent, which still has to be treated thereafter. The catalytic process has a good performance but have many disdavantages like the use of hydrogen and the high investment cost.
Therefore, two feasible techniques are now available: bio-techniques and ELONITA®. Figure 2 shows the technical differences for both ELONITA and biology.

The solution conductivity appears to be of primary importance. Indeed, a high conductivity guarantees the use of the entire electrode surface. On the other hand, when it is insufficient, only a small part of the available surface will be used for the electrochemical reactions. This results of course in a lower reaction rate and yield.
Moreover, a high conductivity is most crucial when the nitrate concentration is low because this is when the whole available surface is required to compensate the diffusion limitations.
Laborelec and the "Université Catholique de Louvain-la-Neuve" have been cooperating in developing this technique since 2002.

Nitrite/Nitrate (NO_2^-/NO_3^-)	***Ammonia (NH_3)***
Eutrophication	*Toxic for aquatic life*
Reaction with the hemoglobine, causing a decrease in the oxygen transport's ability	

Figure 1: possible effects of nitrate/nitrite and ammonia ions

ELONITA	***BIOLOGICAL TREATMENT***
Stable process	*Needs a long time for bacteria's maturation*
No sludge production	*Sludge production*
Operates for a large range of concentrations	*Highly sensible to a variation of concentration and flow*
Needs Cl- ions	*Inhibition of bacteria's by some product initially present in the effluent, necessary for a good operation of the power station (copper, hydrazine, chloride ions and salts)*
Needs conductivity: the conductivity allows spreading of the electrons along the whole electrode, thus increasing the efficiency.	*Needs organic matter*
By-products formation	
Gaseous ammonia release	
Inhibition by organic matter present in the solution	
Suited to treat high concentrations (~ g/l)	

Figure 2: Technical comparison of the two technologies

Description of the ELONITA technology

ELONITA® is an innovative technique based on electro-degradation that removes ammonium and nitrate ions from industrial discharge water. This technique allows a coupled electro-destruction of both pollutants. Therefore, the energy consumption is less and the operating costs are reduced.
The electrochemical cell consists of two compartments, respectively the cathode compartment and the anode compartment. Between them lies a cationic membrane that allows the passage of ions in order to close the electrical circuit (figures 3 & 4).

The cathode consists of reticulated vitreous carbon doped with Cu to increase the performance.
The anode is a plane electrode in titanium, with a RuO_2 coating. We use tri-dimensional electrodes because they exhibit a high surface of reaction and thanks to their structure, they increase the turbulence and thus the mass transfer is improved.
The electric current is provided by a continuous source and the current density is 500 A/m^2.

The degradation is performed in two steps:

1. Reduction of nitrates in the cathode and production of ammonium ions:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^-$$

2. Oxidation of these ammonium ions by means of hypochlorite (HClO) and production of nitrogen:

$$2NH_4^+ + 6Cl^- \rightarrow N_2 + 6HCl + 6e^- + 2H^+$$

The right pH conditions are regulated by means of HCl and NaOH.

Organic compounds initially present in surface water may interact with the cathode causing a reduction of efficiency. Therefore a first pre-oxidation to eliminate them is necessary.
Since the rate of reduction of nitrates is much slower than the rate of oxidation of ammonia, the cell can be implemented so that both reactions can take place in the same time (coupling of the reactions). That characteristic makes ELONITA® an attractive technique. Indeed, the oxidation of ammonia provides electrons for the reduction of nitrates and therefore energy consumption is lowered.

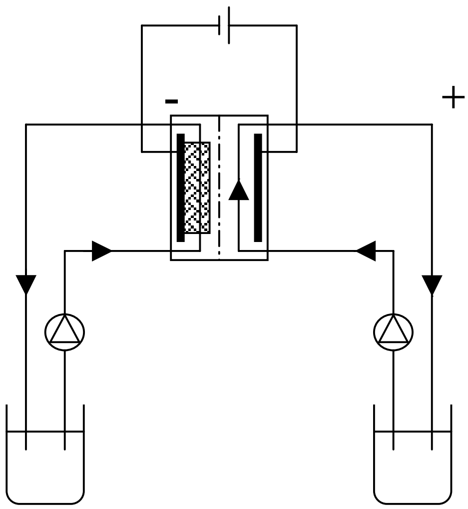


Figure 3: Scheme of the process

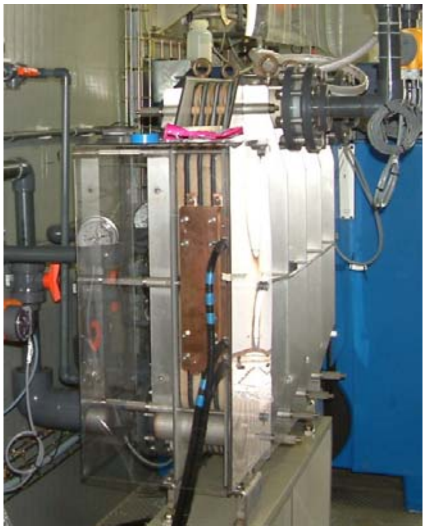


Figure 4: Electrochemical cell

- < 5 mg/l of ammonium ions

Methodologies and description of the pilot plant

The LIFE ELONITA® project started in 2002. Before, successful laboratory and small pilot tests proved electro-degradation to be an effective, flexible and environmentally friendly treatment. Laborelec has then built a full-scale pilot plant situated in Gent (Belgium) in order to evaluate the effectiveness and the reliability of the technique on industrial scale. In particular, the goal was to test the large-scale feasibility and to calculate the economical viability of the process.

During this assessment period some parameters were carefully considered. In term of performances assessments, Laborelec looked at:

- The impact of the organics oxidation on the nitrate reduction
- The nitrate reduction yield
- The ammonia oxidation yield

Laborelec studied also the chemicals (HCl and NaOH were used to adjust the pH) and the energy consumption.
The influence of many parameters on the efficiency of the process was also assessed. These parameters are: influence of copper in the electrode, pH, presence of cations Ca/Mg, initial concentration in nitrates, current density, anions content and organic matter.
Finally, some additional tests were performed in order to determine the content of by-products formed during the reaction. These are:

- AOX (Adsorbable organo-halogenated compounds)
- NOx (Nitrogen oxides: NO, NO_2, N_2O)
- Chlorine derivatives
- Gaseous ammonia (NH_3)

The pilot plant consists of two tanks with a capacity of 10 m^3 each. The total volume treated doesn't exceed 7.5 m^3 though.
The electrochemical cell has an electrode surface of 1.2 m^2 and can approximately treat 100 l/h.

Laborelec treated on site regenerated effluent from the resins of the demineralised water process. This wastewater contains high nitrate and nitrite contents as pollutants.

Environmental impact

ELONITA® has several environmental benefits.
In contrast to other biologic treatments, Elonita doesn't produce sludge, thus further treatment is avoided.
This process can also contribute significantly to the decrease of nitrates and ammonia pollution for power plants.

This technique gives interesting results in term of reduction of nitrogen content. We can reach a value that lies under the threshold defined by the authorities in several hours, depending on the operating conditions (size of the cell, type of effluent, initial concentration etc).
The regeneration effluent from the power plant where we performed the trials is roughly 40 m^3 every two days. Assuming a concentration of nitrate of about 750 mg/l and knowing the rate of removal, the surface of electrodes can be computed. To treat every day 20 m^3 of effluent, we would need a total surface of electrode of roughly 17 m^2.

We get the following nitrogen content in the final regeneration effluent:

- < 20 mg/l of nitrates
- < 0,2 mg/l of nitrites

A pre-treatment for organic matter lasting roughly 20 hours has to be taken into account. For a regeneration effluent, the reduction rate of nitrate ions is maximum **37g NO_3^-/h/m²**.

The oxidation rate of ammonium ions varies **between 41 and 96 g NH_3/h/m²** for this type of effluent. Other tests performed in laboratory attested that a much higher oxidation rate of ammonium ions could be obtained for different effluents, depending on several criteria. Rates up to 150 g NH_3/h/m^2 were reached for effluents containing only ammonia.

The technique also rejects some by-products: AOX, NOx, chlorine derivatives and gaseous ammonia. Depending on their final concentration, further treatment in order to remove them would be investigated. Ion exchange system, adsorption and membrane reactor are common means to remove chlorates ions. Oxidation and adsorption processes can remove AOX.

Moreover, since ELONITA® allows the coupled electro-destruction of both components, electrons produced by the oxidation are used to perform the reduction and energy consumption is reduced as a result. The total energy consumption was computed and a value of 56 kWh/m^3 was found.

ELONITA® is an easy operation, which is not sensitive to high salt content in contrast to biological methods and allows reaching the low desired level in both toxic components.

Economical impact

In order to assess the economical viability of the process, we have to calculate and analyse both investments costs and operation costs.

Investment costs

Investments costs consist of:

- Electrochemical cell
- Rectifier
- Necessary other equipments (pumps, pipes, instrumentation)
- External assistance costs (assembling and programmation)

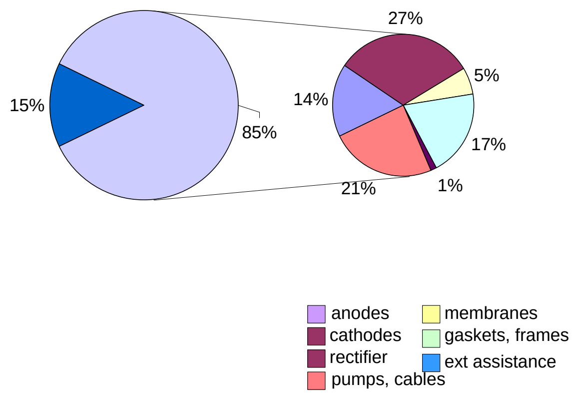
The electrochemical cell consists of a two compartments module and has a maximum projected electrode area of 16 m^2. Since the cell is a sequence Anode-Membrane-Cathode, each sequence measuring 0.4 m^2, we can place a sequence of 20 anodes, 30 membranes and 20 cathodes.
Since the total surface of electrodes is known, the rate of reduction of nitrates, and assuming roughly the concentration of nitrates in the solution (750mg/l), we can estimate the maximum flow rate for one cell.

For a rate of 37g NO_3^-/h/m^2, a maximum flow rate of 19 m^3/day (in case of regeneration effluent containing a low content in organic matter) can be treated. This corresponds to a treatment capacity of 15 kg NO_3^-/day.

For treatment of effluents containing only ammonia, the configuration of the electrochemical cell is similar but instead of a cationic membrane, we place an anionic membrane. It cost much less (450 euros/each) than the cationic membrane.
In order to have a good estimation of such a cell, we need to extrapolate somehow the estimations made during the pilot

plant tests. For the number of gaskets, sets, frames sets, we just multiplied by ten the initial quantity.
Concerning the other equipments and the external assistance costs, they are quite similar since only the flow rate is different.

A total price of **724.000 euros** was calculated for one cell treating about **15 kg NO_3^-/day**. Following pie shows the costs repartition between material and man-hour for such an installation.



Cost calculation for the treatment of an **ammonia-containing effluent** of a power plant (vacuum pump circuit effluent) shows that the investment for an ELONITA plant is similar to a biological nitrification-denitrification.
For a vacuum pump effluent of a 50 m^3/d flowrate and a NH_3 concentration of about 2 g/l, investments cost is the following one (based on an oxidation rate of 100 g NH_3/h/m^2 obtained at lab scale) : **735.800 euros** (treatment capacity: 100 kg NH_3/day).

Operating costs

Operating costs concern the chemicals consumption, the energy consumption and the specific membranes and electrodes replacement costs.
- The chemical consumption is the consumption of HCl and NaOH to adjust the pH during the process. We get a chemicals cost of about 2.9 €/m^3 of treated effluent.
- Energy consumption, as already mentioned, is about 56 kWh/m^3 of treated effluent.

These two points are the results from deep studies in the pilot plant but we assume that the consumption for an industrial scale is the same or lower.

Final conclusions

This technique gives interesting results in term of reduction of nitrogen content. The lab-test results provided rates up to 70 g NO_3^-/h/m^2 for regeneration effluent containing a high nitrate content without organic matter content.

The rate of 37 g NO_3^-/h/m^2 was found on laboratory for a regeneration effluent containing a higher amount of organic matter. In this case, an anodic pre-treatment can be used to increase the performances but can lead to by-products formation. At pilot scale, a maximum rate of 37 g NO_3^-/h/m^2 was obtained. The total energy consumption was computed and a value of 56 kWh/m^3 was found.

The nitrate reduction current yield is 20 to 40% (percentage of electrons that serve effectively for nitrate reduction), which is the same what was achieved during the lab-scale test.

The oxidation rate that could be achieved varied between **41 to 96 g NH_3/h/m^2**, for the oxidation of ammonium ions coming from the reduction of nitrate (regeneration effluent of anionic resins).

By-products (chlorine derivatives, AOX) can be formed during the oxidation step of ammonia.

The following nitrogen content in the final effluent is obtained:
- 20 mg/l of nitrates
- < 0,2 mg/l of nitrites
- < 5 mg/l of ammonium ions

ELONITA® is suited to treat effluent with a high salinity but is however sensitive to scaling.
Organic matter can influence the yields of nitrate and ammonia removals. The start-up is very easy and short.
A typical effluent that could be directly treated with ELONITA® is an effluent:

- With at least a conductivity of 3 mS/Cm (> 10 mS/cm is better)
- With a high nitrate or ammonia concentration (at least 1 g/l)
- With a high chloride content (at least 3 g/l)
- With a low organic content
- Without any suspended solids (but a solid-liquid separation will be sufficient as pre-treatment)
- Without or with low Ca/Mg concentrations

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