Full scale experiences with nitrate removal from drinking water

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Abstract Nitrate as a drinking water pollutant became a problem in the last quarter of the 20th century for many water works. Beside sanitation programs and blending strategies, suitable nitrate removal technologies were necessary. Various technologies are applicable, which can be generally divided into different types. Separating processes split the raw water into a drinking water fraction and a small brine fraction. Degrading processes on the other hand destruct the nitrate molecule. Both types of technologies have their particular benefits. Therefore WABAG developed two processes for the nitrate removal from drinking water sources.

The ENR-process is based on electrodialysis technology using particular nitrate selective membranes. The main advantages of the ENR-process are selective nitrate removal, the additional benefit of hardness reduction and the possibility of immediate start-up.

The BIODEN-process is based on the natural process of biological nitrate degradation, which takes place in soil and groundwater. However, in the BIODEN-process the nitrate degradation is enhanced under controlled conditions in a fixed bed biofilter with subsequent aerobic post-treatment. The main advantages of the BIODEN-process are the degradation of the pollutant and the practically complete water recovery.

Both, the ENR-process and the BIODEN-process have proven their reliability and stability in the production of drinking water for nearly one decade.

Keywords Nitrate removal, drinking water, hardness removal, electrodialysis, biological denitrification.

Introduction
Nitrogen is an essential element of life. The simplified nitrogen cycle (see Figure 1) shows, that nitrate as a pre-stage of proteins is important for human alimentation. However, an excessive direct consumption of nitrate can cause negative effects on human health such as methaemoglobinaemia for infants and cancer risks caused by nitrosamines and nitrosamides (Packham 1991). Besides other nutrients, drinking water is a main source of nitrate in human food. With an average nutrition and water consumption of 1.5 lday⁻¹, the nitrate uptake from drinking water amounts to approximately 50%, when the drinking water contains 50 mg NO₃⁻/l (Packer et.al.1995). For this reason, nitrate uptake can be most easily controlled by the regulation of nitrate in the drinking water and nitrate standards for drinking water have been established (WHO 1993).
Nitrate in drinking water sources originates from untreated wastewater and wash out from soil. Normally the nitrate content in ground water is controlled by the natural biological denitrification in the soil and groundwater. However due to uncontrolled wastewater discharge and excessive application of artificial fertilizers and manure, the nitrate concentration exceeded critical levels in many drinking water sources.

![Natural nitrogen cycle](image)

**Figure 1** Natural nitrogen cycle. (Rohmann and Sontheimer 1985)

Sanitation of the affected water sources is difficult and time consuming. Hence water treatment is required at least for the transient period until sanitation effects accomplish respective results.

Whenever blending of different water sources is not possible or cannot achieve drinking water standards, treatment processes for the removal of nitrate are necessary. Nitrate can be removed from the drinking water source either by separation or by degradation. Suitable and approved technologies for the nitrate separation are ion exchange, reverse osmosis and electrodialysis.

There are selective ion exchange resins available. However, the main disadvantage of the ion exchange process is the additional salt load due to the regeneration chemicals. Only by means of the CARIX-process additional salt load can be avoided due to regeneration with carbon dioxide (Hagen 1991). Nevertheless the CARIX-process is not selective to nitrate and can be only applied, when nitrate is the main anion and the sulphate content in the raw water is low.

Also reverse osmosis is an unselective desalination process. Under the force of high pressure water passes the reverse osmosis membrane and the salt ions remain as a brine stream. Due to the high degree of desalination blending with untreated water is possible and necessary in order to accomplish a suitable salt balance in the drinking water.
Electrodialysis is also a membrane based process. Opposed to reverse osmosis not water but the salt ions are passing the membrane. The driving force in case of electrodialysis is an adjustable electric field. Thus selective and partial desalination is possible. Due to the selective desalination, electrodialysis accomplishes the highest brine quality of the separating processes (Rautenbach et al. 1986). Nitrate removal by means of reverse osmosis and electrodialysis have the additional advantage, that besides the nitrate content also the hardness of the drinking water is reduced.

Nitrate degrading processes are mainly based on the natural process of biological denitrification. Biological denitrification occurs in soil and ground water and is technically utilised in wastewater treatment for a long time. For nitrate removal from drinking water biological denitrification is applied under controlled conditions in biofilters with subsequent post-treatment. The established denitrification processes for drinking water application differ in the type of substrate for the cultivation of the denitrifying biomass, the type of biofilters and the details of post-treatment (Gimbel et al. 2004). Besides biological denitrification also chemical nitrate reduction has been investigated. By means of chemical catalysts nitrate is reduced with hydrogen similar to the autotrophic biological denitrification (Tacke and Vorlop 1991). However, the catalytically nitrate reduction had been only tested in pilot scale.

**Electrodialytic Nitrate Removal the ENR-process**

**Description of the ENR-process**

The principle of electrodialysis involves the removal of ionic components from aqueous solutions through ion exchange membranes using the driving force of an electric field. The water to be treated is pumped through a membrane stack, which consists of alternately placed anionic and cationic selective membranes. Separated by gasket frames and spacers, the membranes are fixed between two end plates, which contain the electrodes producing the electric field. In the compartments of the membrane stack, the ion content is diluted or concentrated according to the ion
penetration through the membranes (see Figure 2).

Figure 2    Principle of electrodialysis (A = Anion exchange membrane, K = Cation exchange membrane)

Identical compartments are connected by a distributing and collecting system. Thus the raw water is separated into a diluate and a brine stream. Both streams flow at the same velocity through the membrane stack. As a rule the water to be diluted passes the membrane stack once whereas the brine stream is recycled. Due to the fact that only ions pass the membrane, the brine concentration is adjusted by means of dilution with raw water. Thus the brine stream is operated in a feed and bleed mode. The required dilution rate is determined by the solubility of calcium carbonate and calcium sulphate. In order to transfer the electric current and to remove gases produced by the electrode reactions, the electrode chambers are rinsed with an electrolyte solution (see Figure 3).

Figure 3    Scheme of electrodialysis

The degree of desalination is determined by the strength of the applied electric field and the retention time of the water on the membranes. By the application of monovalent anion exchange membranes nitrate is removed preferably (Mizutani 1990). Thus the total desalination can be decreased and the sulphate transfer into the brine is rather low. As a consequence the brine dilution rate can be kept low – high water recovery – and the brine quality is high, so that agricultural reuse of the brine is possible (Eberhard 1993).

ENR full scale reference Kleylehof

The ENR-plant Kleylehof is designed for a hydraulic capacity of 40 l/s (144 m³/h) with three hydraulic stages and a maximum of 160 mg NO₃/l in the raw water. The guaranteed value for the treated water, in the case of maximum nitrate concentration in the raw water, is less than 50 mg NO₃/l. The special requirement for this plant was
seasonal operation. The plant is remote controlled and works fully automatically. The plant was started up 1997 (Hell and Lahnsteiner 2002).

The raw water is abstracted from a well and pre-filtered with bag filters. According to the water demand, one, two or three hydraulic stages are selected by the remote control. The PLC controls the corresponding flow rate and distributes the raw water to one, two or three electrodialysis stacks.

The stacks are equipped with selective anion exchange membranes. Each stack is allocated to one rectifier. The voltage of the rectifiers is manually adjusted according to the raw water conductivity and the requested nitrate content in the treated water.

The product effluent passes an UV-disinfection unit. The quality of the product is checked by means of conductivity measurement. The treated water is recycled to the well, if a maximum value is exceeded. The product water flows into a buffer tank. From there the water is pumped into the distribution system.

The quality of the brine is controlled by means of conductivity measurement and dilution with raw water. The brine discharge stream is used for rinsing of the electrodes. Finally the brine discharge is pumped into a storage pond. From the brine storage pond the brine is either discharged into the sewer or the brine is charged into the local agricultural irrigation system.

When the plant was started the nitrate content in the raw water was 120 mg NO₃/l. A maximum Nitrate removal of approximately 100 mg NO₃/l was achievable. However, the stack voltage was adjusted to a nitrate removal down to 40 mg NO₃/l. In proportion to the nitrate removal, the hardness of the drinking water was reduced by approximately 23%.

The regular plant service is done after the winter season. The necessary membrane change was always below the guaranteed value of 10% per annum. Also the lifetime of the electrodes is much higher than expected.

Since the plant is in operation the desalination performance has been constant and no decrease in plant performance could be detected. Drinking water and brine quality was always stable.

In the first three years, the plant was only operated from May to October. During winter, the plant was mothballed. Later on this concept was changed. During seasons, where the water demand is low, the treatment plant is only shortly operated from time to time. Thus stagnation of the water is avoided and the plant is available at all times.
The BIODEN process

Description of the BIODEN process

The BIODEN-process is based on the natural process of biological denitrification, which takes place in soil and ground water. However, in the BIODEN-process the denitrification is enhanced under controlled conditions in a fixed bed biofilter with subsequent aerobic post-treatment. The BIODEN-process generally consists of substrate dosing, denitrifying biofilter, aeration, flock-filtration, polishing filter, safety disinfection and backwash system with backwash water recycling (see Figure 4).

As substrate ethanol or acetic acid as carbon source and diluted phosphoric acid as phosphate source are dosed into the raw water. Other nutrients are normally sufficiently present in the raw water. The nitrate degradation takes place in a pressurised fixed bed biofilter. In the following aeration, the denitrified water is saturated with oxygen. Thus aerobic activities in the flock-filters and polishing filters are supported and the final drinking water has sufficient oxygen content. In the flock-filtration the low turbidity, caused by a minor biomass washout is removed by flocculation and dual media filtration. Any accidentally occurring residual substrate is aerobically degraded in the dual media filters and / or subsequent polishing filters. The last stage of the treatment train is safety disinfection. However, long term experiences of full scale plants showed that the treated water already fulfils drinking water standards only after the polishing filters.

Figure 4 Principal scheme of the BIODEN-process
Biofilters, dual media filters and polishing filters are regenerated by means of backwashing with air and water. The used backwash water is collected and clarified in sedimentation basins. The clarified water is recycled to the plant inlet. The settled sludge, containing the excessive biomass and particles from flock-filtration is discharged either as a concentrated liquid or even dewatered sludge.

The main advantages of the BIODEN-process are selective degradation of the pollutant, excellent biomass retention due to the fixed bed biofilter and practically 100 % water recovery. The technology is based on standard filtration processes and does not need any special equipment. Compared to other nitrate removal technologies, the BIODEN-process is very cost effective. The process requires a continuous operation in order to maintain the biological activity. However, performance increase needs only short time as long as the biological activity is maintained at a minimum level.

**BIODEN full scale references**

The BIODEN-process was developed and tested in a two year pilot operation (Lahnsteiner and Hell 1993). The first full scale plant with a capacity of 180 m³/h was started up in Austria in 1997. This plant is now running since then with excellent results. The plant consists of two lines and is operated constantly at full capacity. The nitrate degradation is adjusted to 5 mg/l residual Nitrate. The treated water is mixed with untreated water from the same well field in a drinking water storage tank. In the case of low consumption, the treated water is infiltrated in the caption area of the untreated wells. The sludge from backwash treatment is discharged to the local sewer. The amount of sludge discharge was always lower than the guaranty value of 25 m³/d. So that the water recovery rate is greater than 99.4%. After full ripening of the filters also microbiological drinking water parameters were safely met before disinfection.

Two treatment plants in Italy are also based on the BIODEN-process. One demonstration plant with a capacity of 50 m³/h was started up in 1997 and one 540 m³/h plant was started up in 2004. A 500 m³/h BIODEN-plant was successfully started up in February 2006 in Czestochowa (Poland). This plant consists of 3 lines of biofilters, bubble columns, flock-filtration and polishing filters. The capacity of each line is 50% of the nominal capacity. As there is no sewer connection available, the special requirement of the Czestochowa plant was 100% water recovery. For that reason the plant is also equipped with a sludge dewatering unit. The plant is supplied from several wells with different nitrate concentrations of up to 80 mg/l. 50% of the raw water is treated and then blended with untreated water. Hence the plant had to be designed for varying raw water quality and quantity. For that reason the substrate dosing is controlled according to the nitrate load. The nitrate degradation is adjusted to an effluent concentration in the treated water of 5 mg/l NO₃⁻.
According to the long term experiences the operating costs for chemicals, electric power, sludge discharge, spare parts and service amount to 0.064 €/m³ (based on Austrian prices). Due to the automatic operation of the plant the time expenditure is limited to 20 – 25 hours per week.

Conclusion
Nitrate removal from drinking water is an established technology for drinking water treatment. Both physical and biological processes have proved their reliability and stability in long time operation under waterworks conditions. Operating costs are low. Compared to the biological process the operating costs for physical processes are slightly higher due to membrane replacement costs and costs for brine discharge. However, the additional benefit of hardness removal and the instant availability after operating breaks must be taken into consideration. The strong points of the biological process are the nearly full water recovery and the selective destruction of the pollutant. The choice of the most suitable process depends on the individual circumstances of each single case.

References