



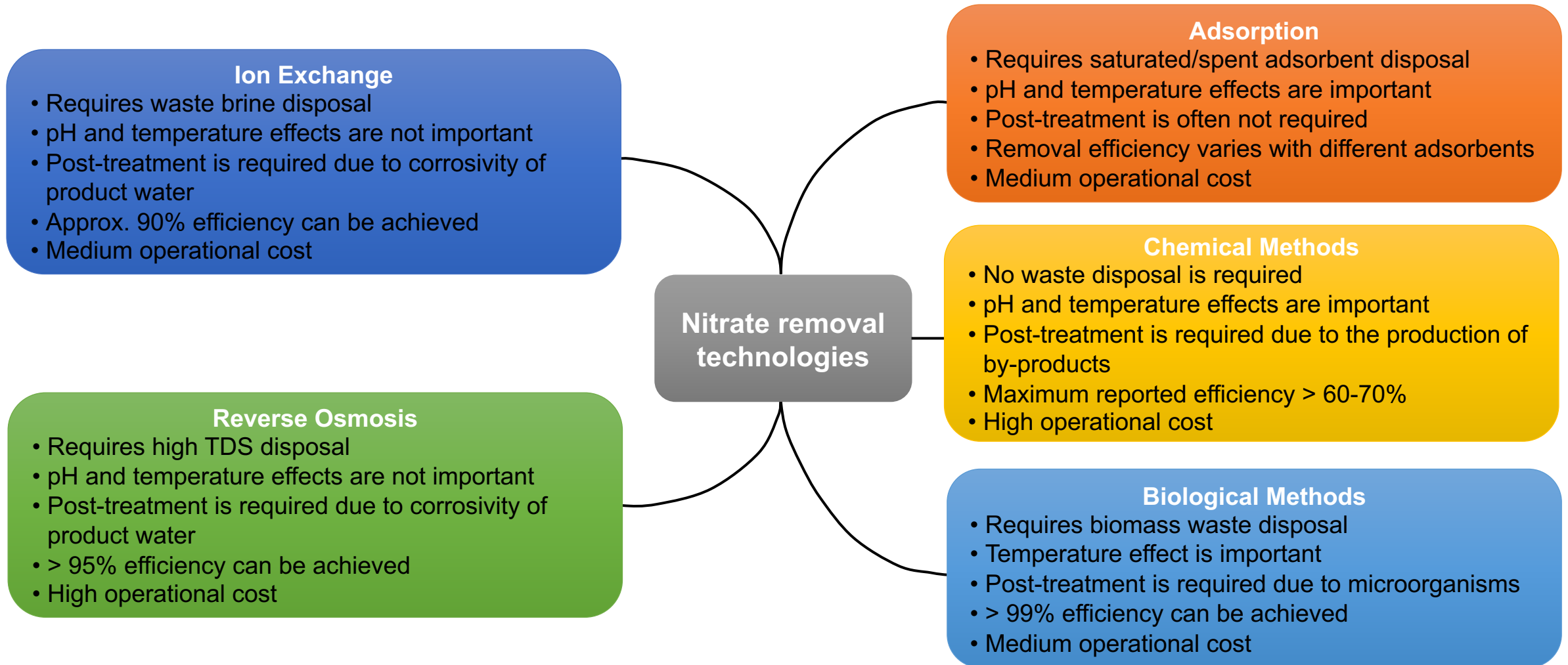
Chemonics Review of Current Knowledge (ROCK)

Nitrogen Pollution in Rivers: In-Plant Technologies

Ahmed Gaber

Cairo, 20 March 2018

Overview: Nitrate removal technologies applied for drinking water purposes



Chemical Treatment (coagulation)

Electrocoagulation

Biochemical Treatment

Adsorption

Reverse Osmosis

Electrodialysis reversal

Biological Treatment Process

Ion Exchange-Catalyst

Membrane bioreactors

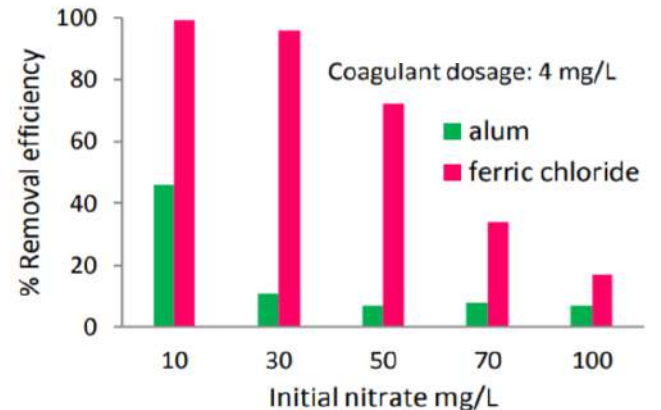
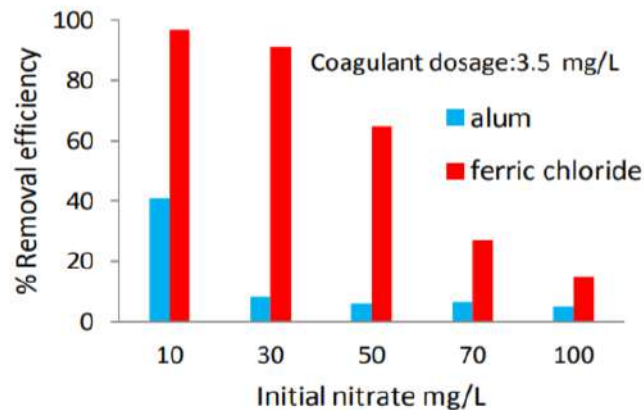
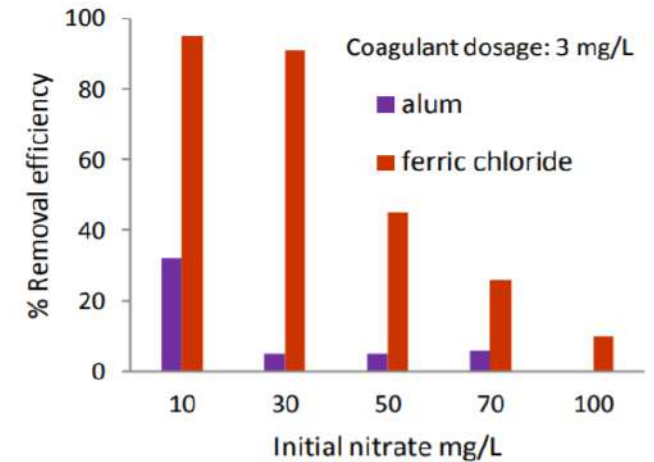
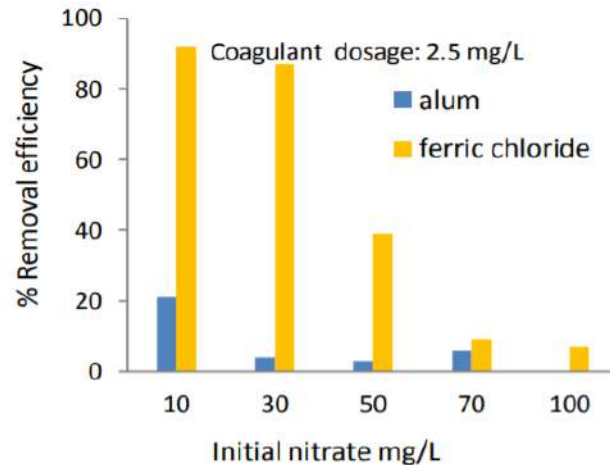
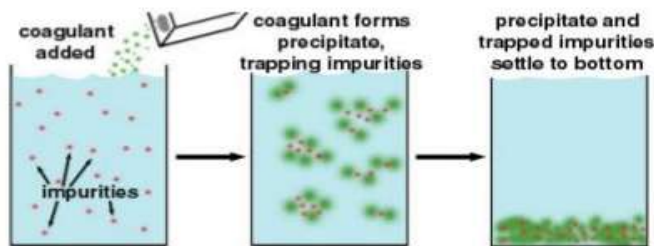
Bio-electrochemical

Other treatment techniques

Using ferric chloride and alum for nitrate (NO_3^-) removal

Coagulation

- pH values should be raised above 9, for pH values less than 9, anions of Cl^- and SO_4^{2-} could compete with nitrate for reduction by coagulants ($\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$).
- the conventional coagulation process using alum and ferric chloride could be effective in removing nitrate at initial concentrations less than 50 mg/l.
- Ferric chloride exhibited a greater removal efficiency than alum.
- The use of ferric chloride for water treatment, even in common dose ranges, can play a basic role in the removal of nitrate from water.



Source: Aghapour et al., (2016) Nitrate removal from water using alum and ferric chloride: A comparative study of alum and ferric chloride efficiency. Environmental Health Engineering and Management Journal, 3(2), 69–73

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Removal of nitrate using electrocoagulation

Electrocoagulation

- A glass chamber of two-liter volume was used for the experiments with DC power supply using two electrode plates of aluminum (Al–Al).
- The maximum removal of nitrate was 63.21% at the optimum operating conditions: current density: 2.65 A/m^2 , EC time: 40 min, inter electrode distance: 0.5 cm, electrode area: 160 cm^2 , initial pH: 7.5 and settling time: 30 min.
- Under optimal operating conditions, the operating cost was found to be $1.01\$/\text{m}^3$ of water in terms of the electrode consumption ($23.71 \times 10^{-5} \text{ kg Al/m}^3$) and energy consumption (101.76 kWh/m^3).

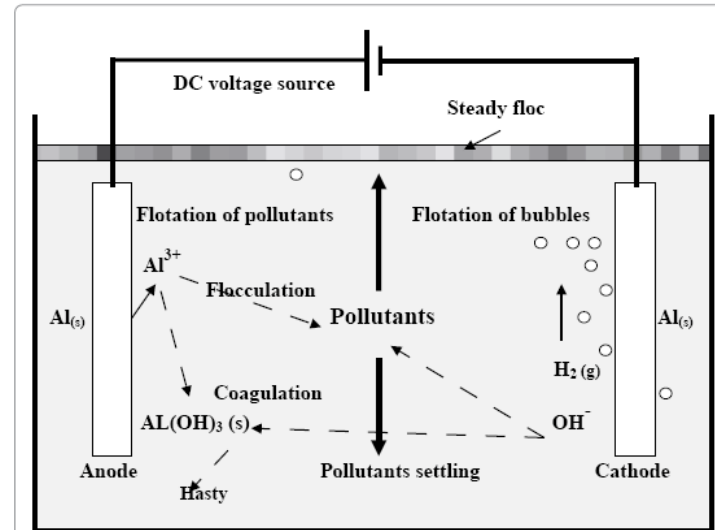
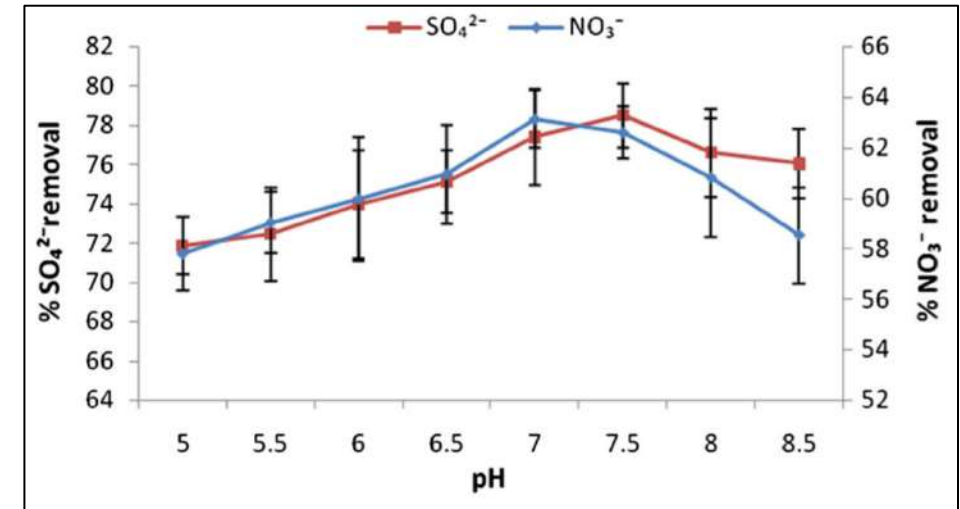


Figure 1: Schematic principle of electro-coagulation.



% Removal of nitrate using Al–Al electrode combination with different pH at constant operating conditions (current density: 2.65 A/m^2 , EC time: 40 min, inter electrode distance: 0.5 cm, electrode area: 160 cm^2 , settling time: 30 min)

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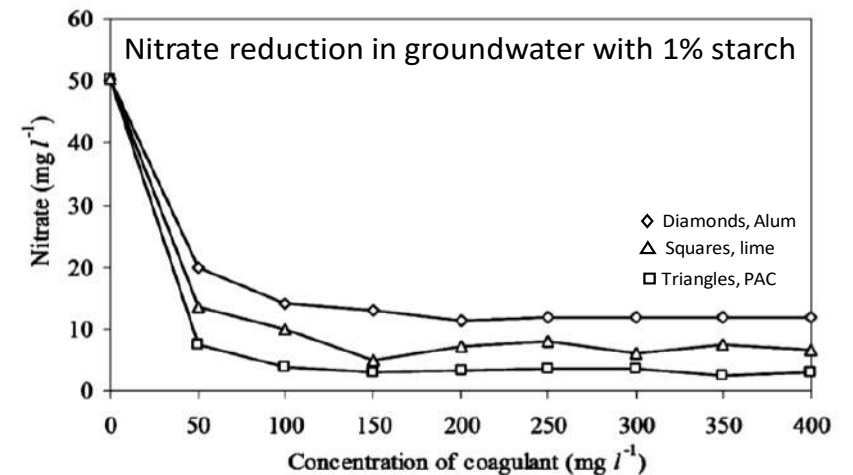
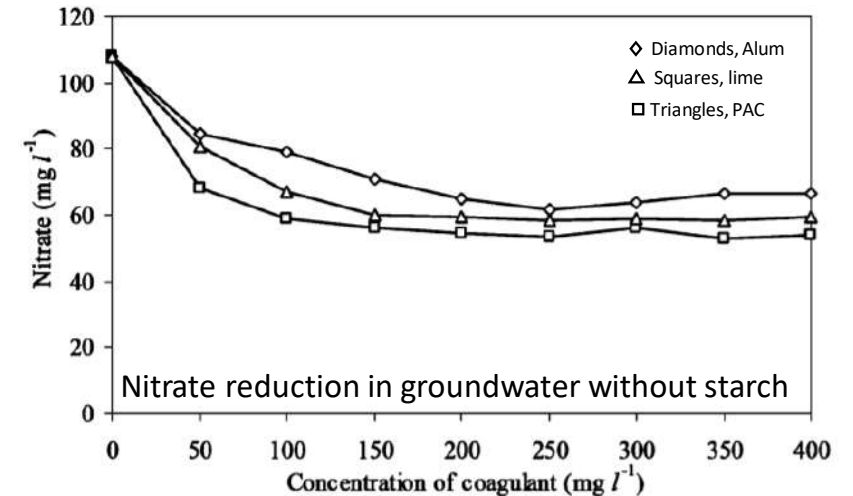
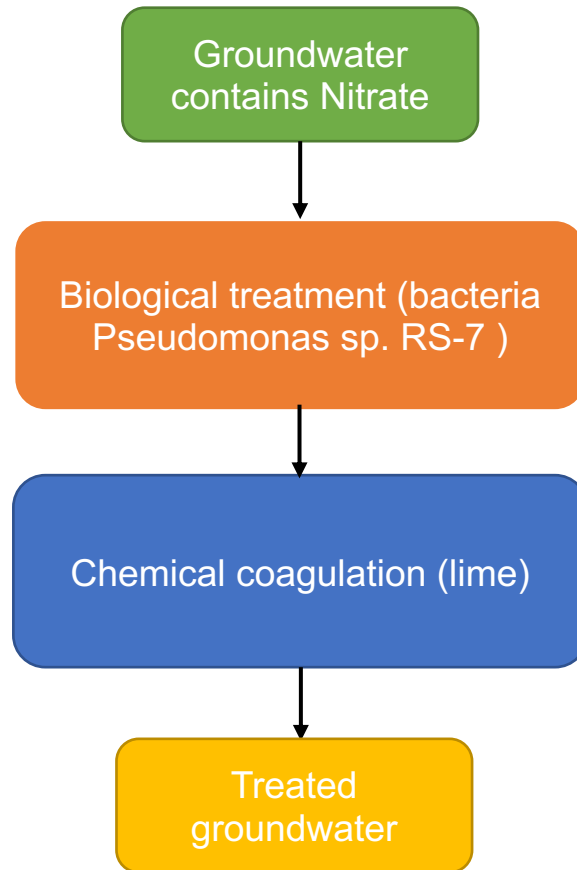
Bio-electrochemical

Other treatment techniques

▪ A combined system of biological and chemical treatments was found to be effective for complete removal of nitrate from groundwater

Biochemical treatment

- In this study, nitrate was removed using a two-stage removal system: one is biological treatment using the nitrate-degrading bacteria *Pseudomonas* sp. RS-7 and the other is chemical treatment using a coagulant.
- The effect of carbon sources on nitrate removal was first investigated, Among three carbon sources, namely, glucose, starch and cellulose, starch at 1% was found to be the most effective.
- About 89% of nitrate was removed.
- Chemical coagulants such as alum, lime and poly aluminium chloride were tested, lime at 150 mg/l exhibited the highest nitrate removal efficiency.



Source: Ayyasamy et al., (2007) Two-Stage Removal of Nitrate from Groundwater Using Biological and Chemical Treatments. JOURNAL OF BIOSCIENCE AND BIOENGINEERING. 104(2),129–134.

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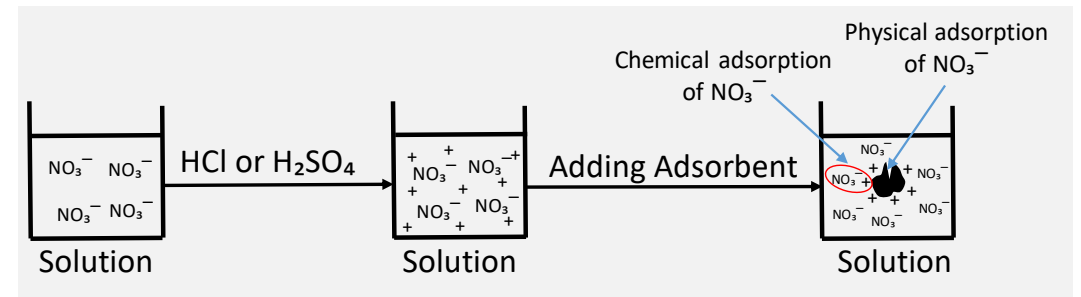
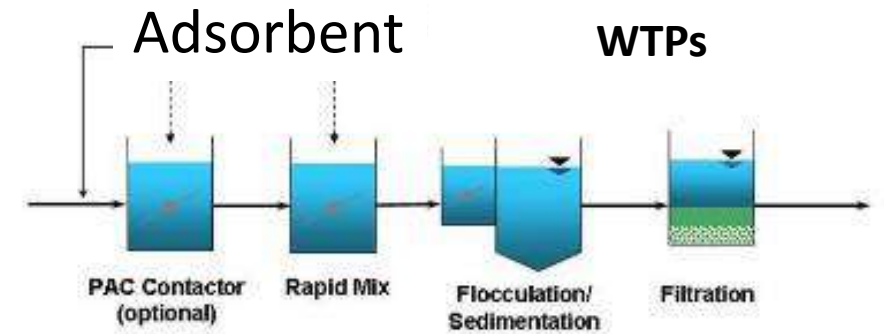
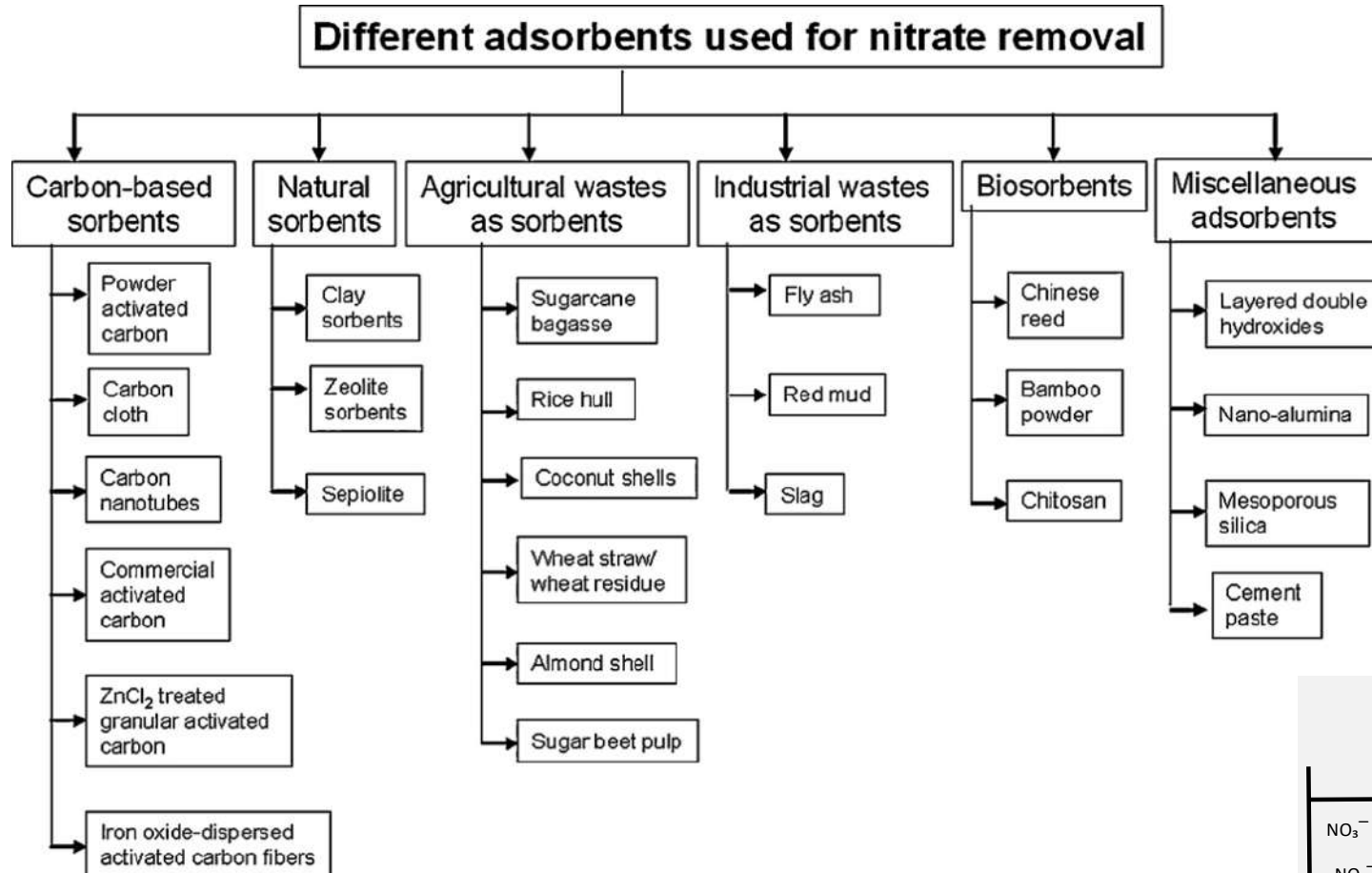
Ion Exchange-Catalyst

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Different adsorbents used for nitrate removal



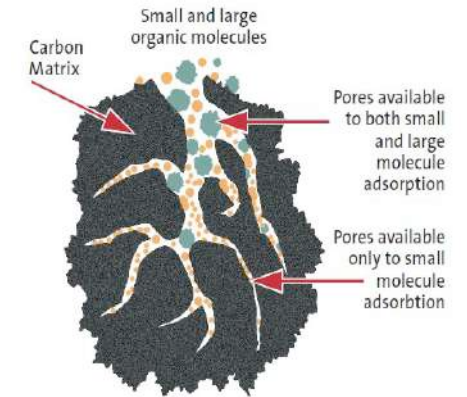
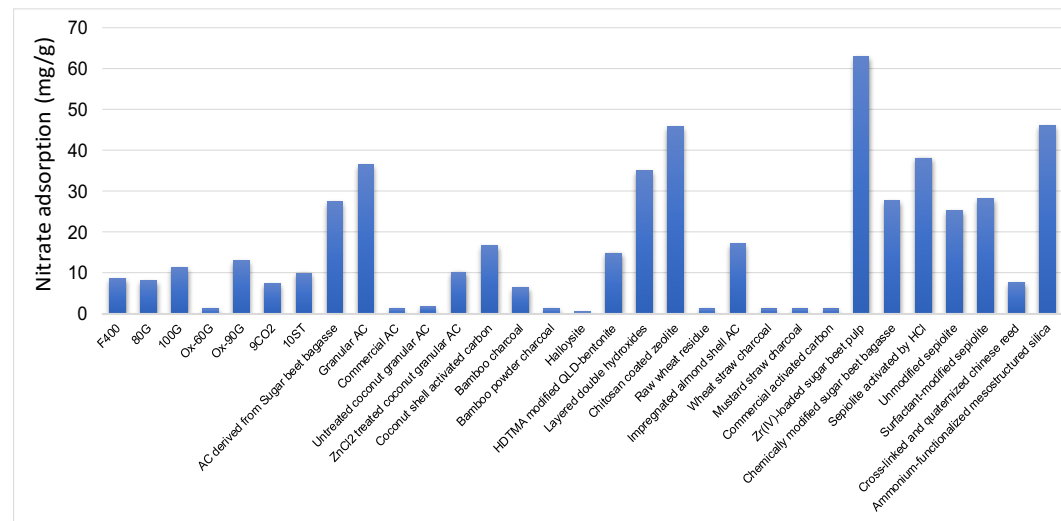
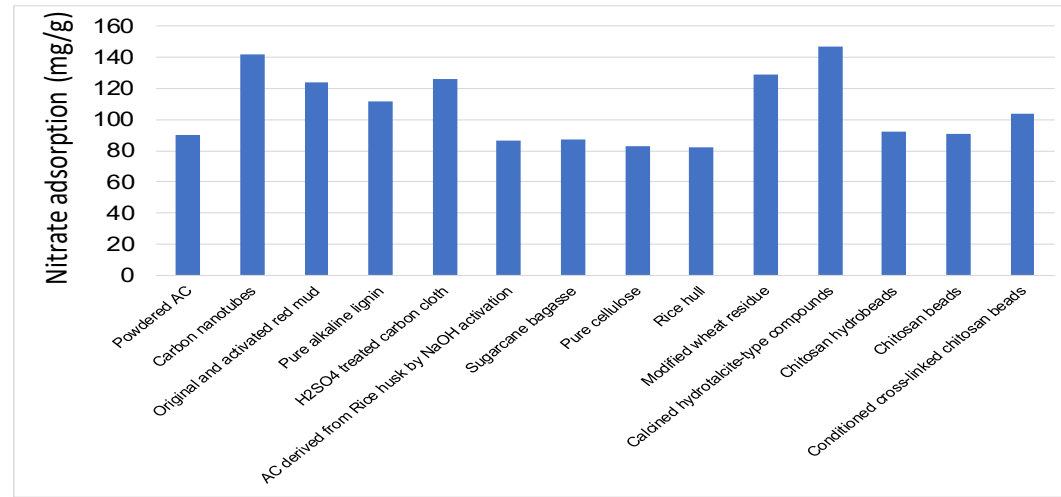
Source: Bhatnagar and Mika (2011) A review of emerging adsorbents for nitrate removal from water. Chemical Engineering Journal.

Calcined hydrotalcite-type compounds and Carbon nanotubes are efficient in nitrate removal

Adsorption

- High NO_3^- adsorption capacity was achieved using Calcined hydrotalcite-type compounds and Carbon nanotubes.
- These two compounds are a good candidate for microporous carbon production.
- And, favorable removal of NO_3^- exhibited that the AC could be considered as the low cost and efficient adsorbent for water treatment.

In another study: the adsorption capacity of NH_4^+ using zeolite reached 9 mg/g with 10 mg-N/L solution.



F400: was sequentially washed with hydrochloric and concentrated fluoric acids, AC was repeatedly boiled with distilled water until pH was no longer changed and dried in oven at 110°C.

80G: F400 was loaded on ceramic boat, placed in quartz tube and heated up to 800°C for outgassing in helium gas flow

100G: F400 was loaded on ceramic boat, placed in quartz tube and heated up to 1000 °C for outgassing in helium gas flow

Ox: F400 was dipped in 8 M HNO_3 solution and heated at 95 °C for 6 h, repeatedly washed with distilled water and calcined in air at 350°C for 4 h

Ox-60G: outgassed Ox was further prepared at 600°C with the similar method described above

Ox-90G: outgassed Ox was further prepared at 900°C with the similar method described above

9CO₂: F400 was extensively activated with CO_2 at 900°C

10ST: F400 was extensively activated with CO_2 at super heat steam at 1000°C

Source: Ota et al., (2013) Removal of nitrate ions from water by activated carbons (ACs)—Influence of surface chemistry of ACs and coexisting chloride and sulfate ions. Applied Surface Science

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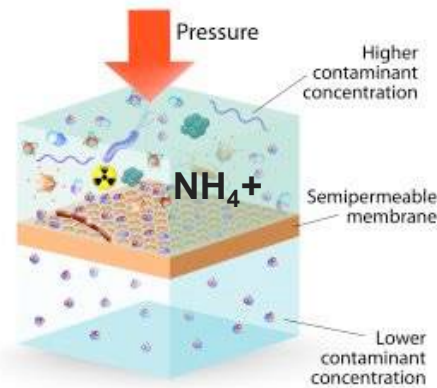
Other treatment techniques

Using brackish water (BW) and saline water (SW) membranes in removal of ammonium

Reverse Osmosis

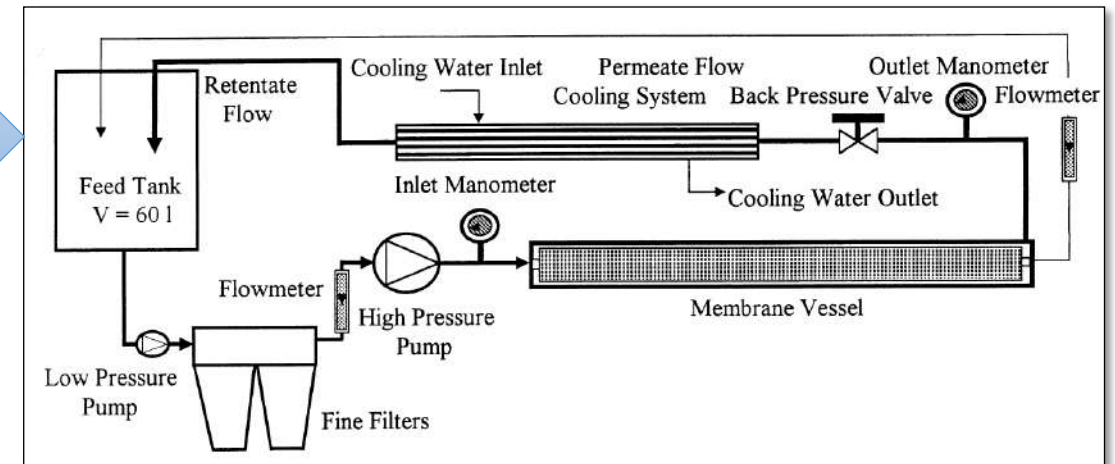
- This study was conducted in Elmali reservoir which is one of the oldest water sources of Istanbul city.
- This reservoir is under the threat of sewage pollution due to discharges of untreated domestic wastewater.
- Therefore, the ammonia levels of the raw water increased to the levels of 3–4 mg/l.
- Ammonia removal was about 95 and 60 per cent by BW and SW membranes, respectively.

REVERSE OSMOSIS



Operating Limits	Reverse Osmosis (SW)	Reverse Osmosis (BW)
Membrane Manufacturer	Filmtech Corp.	Filmtech Corp.
Membrane Type	Thin film Composite	Thin film Composite
Max. Operating Pressure (bar)	70	40
Max. Operating Temperature ($^{\circ}\text{C}$)	45	45
Max. Feed Turbidity (NTU)	1	1
Free Chlorine Tolerance (ppm)	< 0.1	< 0.1
pH Range	2–11	2–11
Max. Feed Flow (l/min.)	23	23
Max. SDI	5	5
Salt Rejection (%)	99.1	98
Single Recovery (%)	10	15

Experiments were conducted using Aquaset 9712 pilot plant membrane filtration equipment. This system contains a spiral wound module which houses membranes with 2 m² total membrane area. A heat exchange permitted all filtration experiments to be controlled at 25–27 $^{\circ}\text{C}$. The applied pressures were 25 bar for BW membrane and 55 bar for the SW membrane.



Source: Koyuncu et al., (2001) Application of the membrane technology to control ammonia in surface water. Water Science and Technology: Water Supply, 1(1): 117–124.

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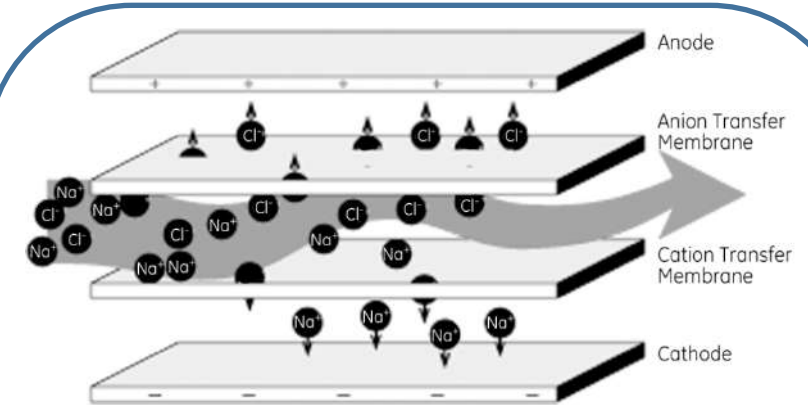
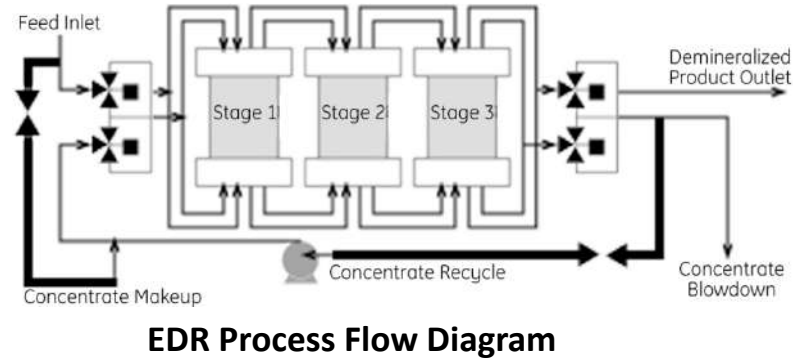
Bio-electrochemical

Other treatment techniques

Applying electrodialysis reversal (EDR) for nitrate and nitrite removal

EDR

- EDR plant typical consists of three-stages.
- A two stage plant removes 50% of the influent minerals and nitrates, a three-stage plant removes about 75%, a four-stage plant removes about 83%, and so on.

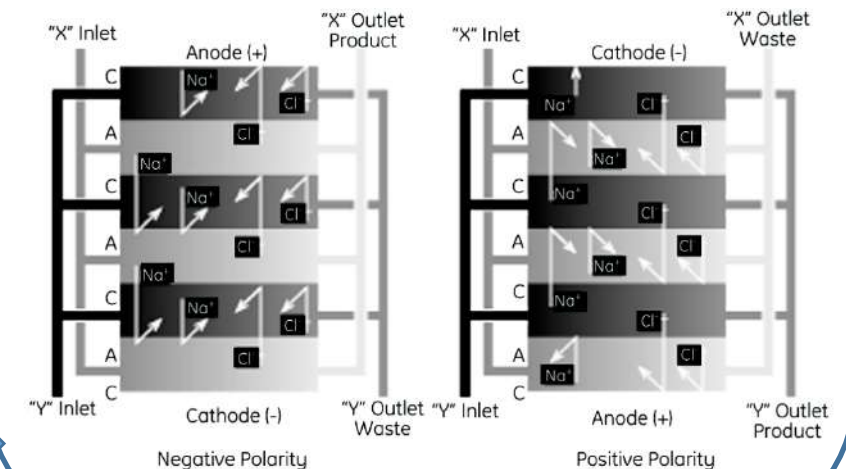


Electrodialysis Diagram

Success stories

- Bermuda: 3 desalting stages, 2,271 m³/day (brackish well): The EDR plants yield 81% demineralization and reduce the nitrate concentration from 66 to 8.8 mg/l.
- Delaware: 3 desalting stages, 1,514 m³/day (agriculturally-contaminated drinking water supply): This three-stage EDR plant yields 88% demineralization and reduces the nitrate concentration from 60 to 4.5 mg/l.
- Industrial: 3 desalting stages, 378 m³/day: 66% demineralization. Nitrate concentration is reduced from 655 to 128 mg/l, and Nitrite concentration is reduced from 64 to 21 mg/l.
- Italy: 2 desalting stages, 1,136 m³/day (municipal wells in agriculture-intensive regions): 53% demineralization with reductions in nitrate from 120 to 37 mg/l.

Water flows in a thin sheet between membranes. Under the influence of the applied DC electric field, ions migrate toward the electrode opposite in charge, passing through membranes which also have fixed oppositely-charged groups bonded to a polymer surface. Membranes with the same charge as the ionic species repel the ions and prevent passage



Electrodialysis Reversal

Source: Prato and Richard (2017). nitrate and nitrite removal from municipal drinking water supplies with electrodialysis reversal. Water Technologies & Solutions: technical paper.

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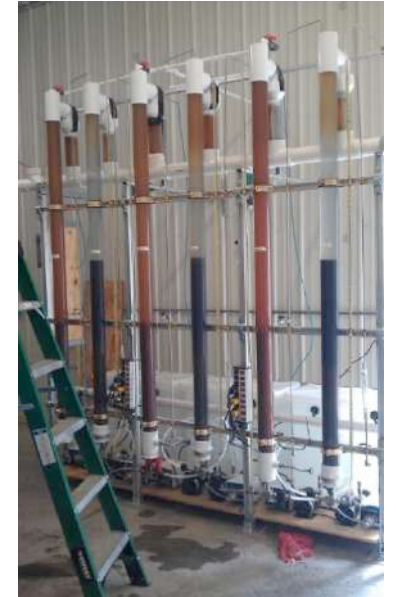
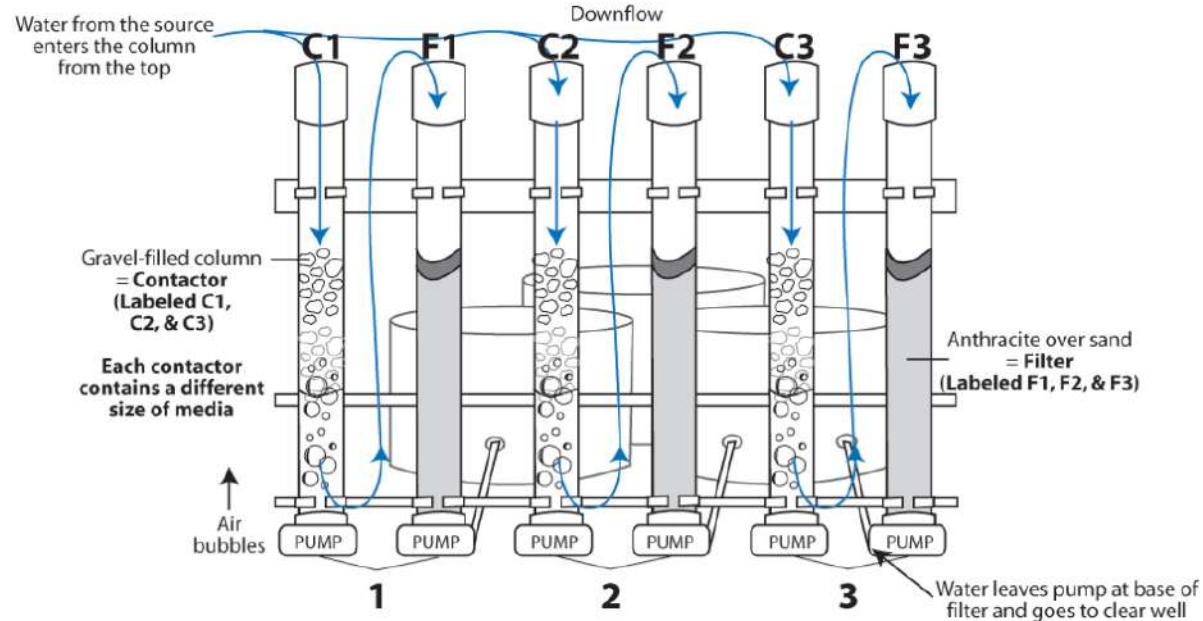
Membrane bioreactors

Bio-electrochemical

Other treatment techniques

Removal of ammonia from a small drinking water system using biological treatment process (EPA-patented)

- The pilot treatment process was based on an EPA-patented approach (Patent No. US 8, 029,674).
- The goal and expectation was that the treatment plant's:
 - ✓ Two contactors would oxidize the bulk of the ammonia through applying bacteria to convert ammonia to nitrate; provided the raw ammonia levels are lower than the nitrate maximum contaminant level (MCL) of 10 mg N/L.
 - ✓ Four dual media filters that followed the contactors was to remove iron particles that developed in the contactors. The filters were also biologically-active and provided additional ability to oxidize ammonia and nitrite that passed through the contactor.
- Water analysis showed a decrease in the Ammonia concentration and an increase in both nitrite and nitrate concentrations which confirm the occurrence of the Nitrification process.

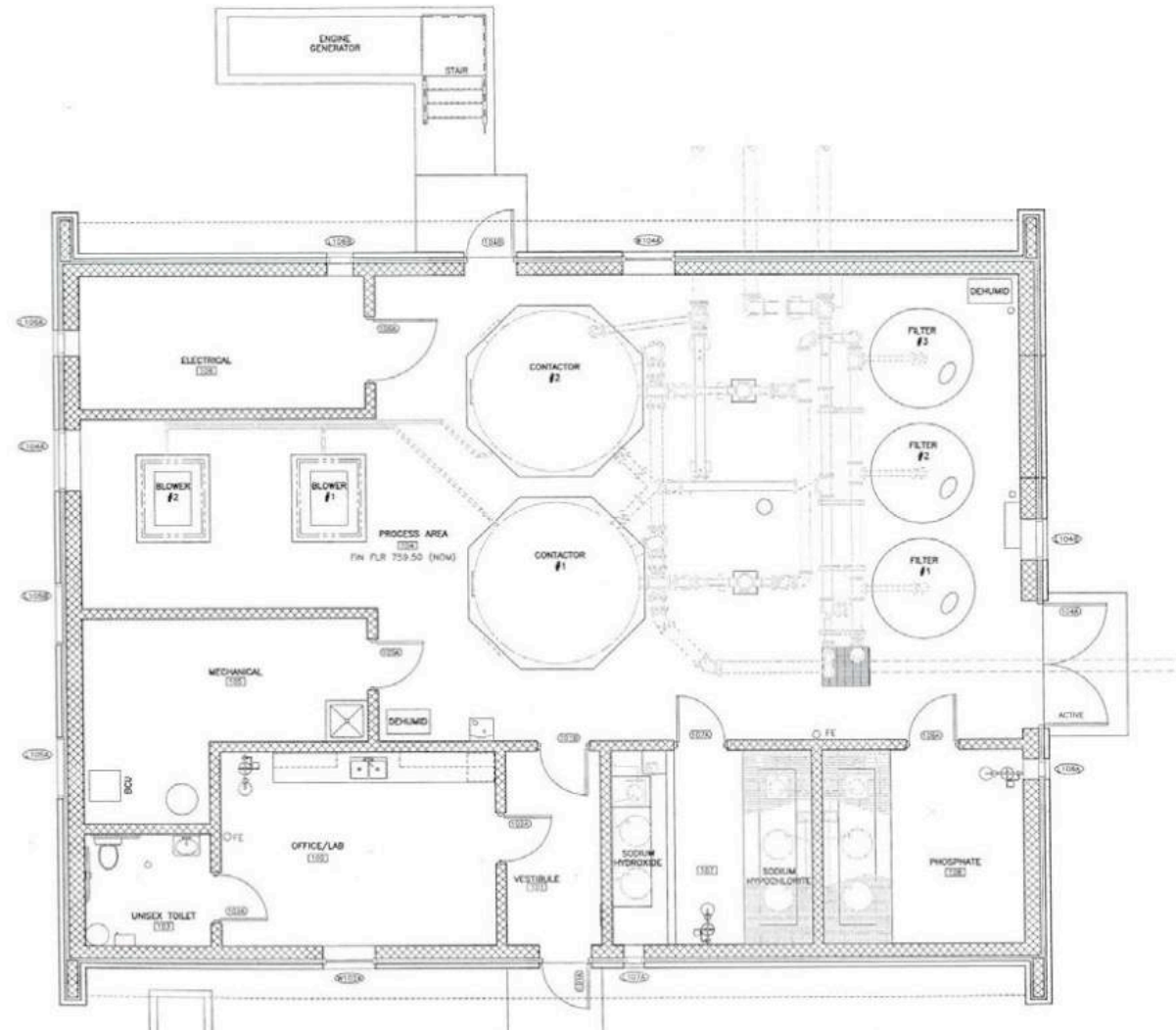


Pilot biological ammonia removal treatment technology system

Analyte	Detection limit (mg/l)	Raw	Raw PO ₄	Contractor 1	Contractor 2	Filter 1	Filter 2	Filter 3	Finished
NH ₃	0.03 (mg-N/L)	3.2±0.1	3.2±0.1	2.6±0.55	0.57±0.27	1.6±1.1	1.5±1.1	1.5±1.0	1.6±1.0
NO ₂	0.01 (mg-N/L)	0.01±0.002	0.01±0.0039	0.11±0.08	0.22±0.04	0.2±0.2	0.18±0.15	0.11±0.09	0.14±0.15
NO ₃	0.02 (mg-N/L)	0.02±0.001	0.024±0.018	0.49±0.41	2.4±0.3	1.4±1.2	1.4±1.2	1.5±1.1	1.3±1.1

Source: EPA (2014) Engineering Design and Operation Report: Biological Treatment Process for the Removal of Ammonia from a Small Drinking Water System in Iowa: Pilot to Full-Scale

EPA full-scale biological water treatment plant



Source: EPA (2014) Engineering Design and Operation Report: Biological Treatment Process for the Removal of Ammonia from a Small Drinking Water System in Iowa: Pilot to Full-Scale

EPA full-scale biological water treatment plant



Contactor Design		
Parameter	Pilot	Full-Scale
Filter Loading Rate	2.2 gpm/ft ² (5.6 m ³ /hr)	2.2 gpm/ft ² (5.6 m ³ /hr)
Air Flow Rate	2.86 cfm/ft ² (0.87 m ³ /min)	1.5 cfm/ft ² (0.46 m ³ /min)
<i>Backwash Conditions:</i>		
Duration	5 minutes	7 minutes
Bed Expansion	0%	0%
Flow Rate	51 gpm/ft ² (2.2 m ³ /min)	15 gpm/ft ² (0.63 m ³ /min)
Contactor Depth	30 inches (76 cm)	45 inches (114 cm)
Contactor Effective Size	1/4 inch (0.65 cm)	1/4 inch (0.65 cm)
Filter Design		
Parameter	Pilot	Full-Scale
Filter Loading Rate	2 gpm/ft ² (5 m ³ /hr)	2.2 gpm/ft ² (5.6 m ³ /hr)
<i>Backwash Conditions:</i>		
Duration	15 minutes	15 minutes
Bed Expansion	50%	50%
Flow Rate	17 gpm/ft ² (0.72 m ³ /min)	17 gpm/ft ² (0.72 m ³ /min)
Filter Anthracite Depth	20 inches (51 cm)	20 inches (51 cm)
Filter Anthracite Size	0.04 inch (0.1 cm)	0.04 inch (0.1 cm)
Filter Sand Depth	10 inches (25 cm)	10 inches (25 cm)
Filter Sand Size	0.018 inch (0.046 cm)	0.018 inch (0.046 cm)
Other Parameter Variables		
Parameter	Pilot	Full-Scale
Hours and Days of Operation	24 hours/day, 7 days/week	January to Late April (2014): ~4 to 5 hours/day, 5 days/week Late April (2014) to Present: ~6 to 7 hours/day, 7 days/week
Phosphate Feed	Orthophosphate: 0.3 mg PO ₄ /L	Blended Phosphate (75% polyphosphate/ 25% orthophosphate): 0.3 mg PO ₄ /L orthophosphate portion
Air/Water Flow Configuration	Counter-Current	Co-Current
Filter Backwash Water	Non-Chlorinated	Chlorinated
Filter Type	Gravity	Pressure

Source: EPA (2014) Engineering Design and Operation Report: Biological Treatment Process for the Removal of Ammonia from a Small Drinking Water System in Iowa: Pilot to Full-Scale

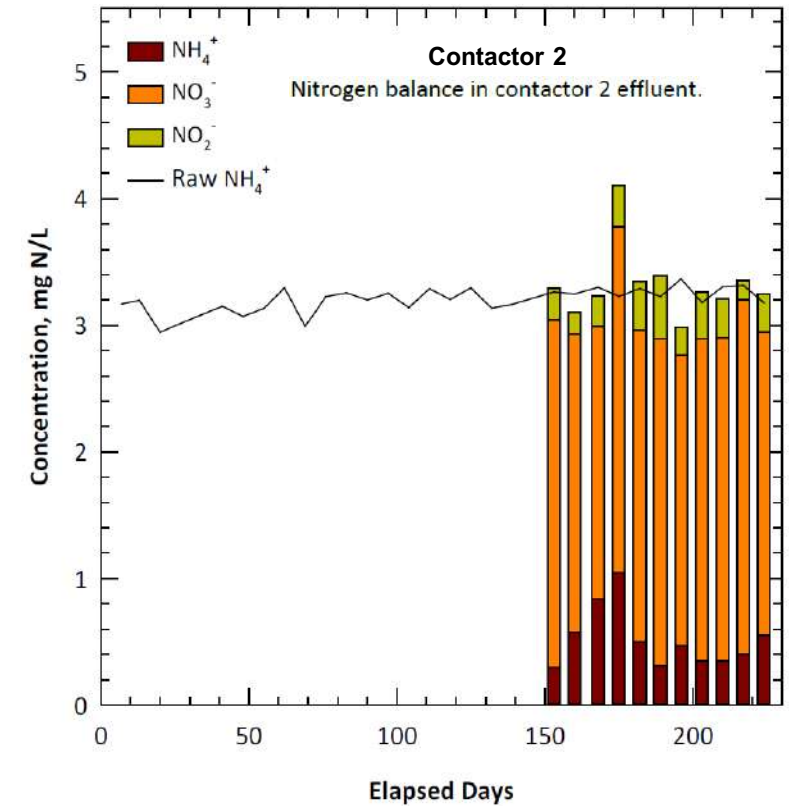
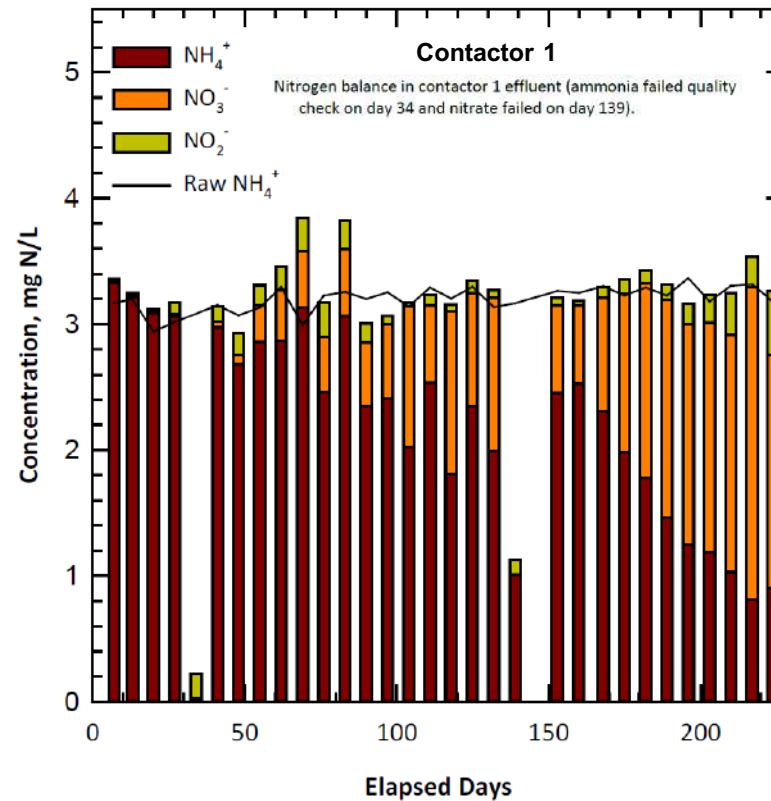
EPA full-scale biological water treatment plant: *Aeration Contactors*

Contactor 1

- The first indication of ammonia oxidation was observed at 28 days when a small amount of nitrite (0.1 mg N/l) and detectable nitrate were observed.
- Over the next five weeks of operation, nitrite levels were no more than approximately 0.2 mg N/l.
- By 35 days into operation, nitrate in the contactor effluent became more evident.
- Nitrate in the contactor effluent gradually increased between 35 days and 130 days to 1 mg N/l.

Contactor 2

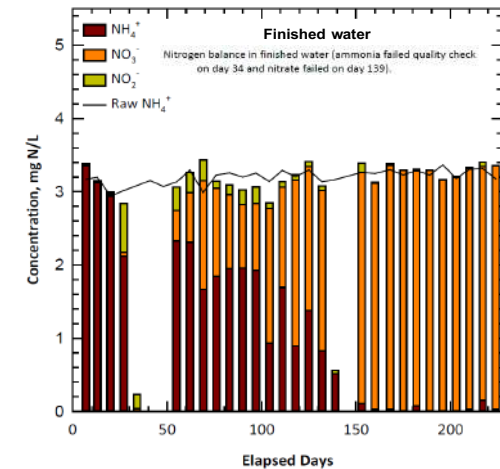
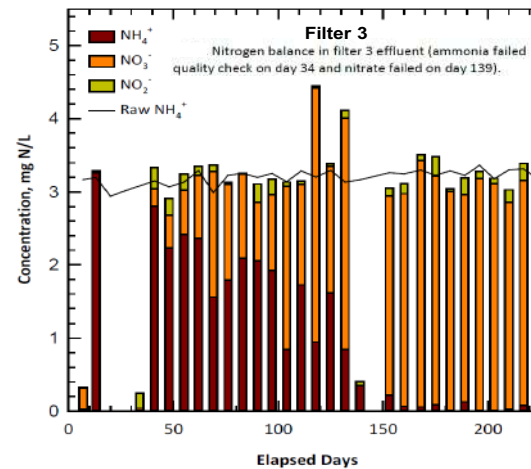
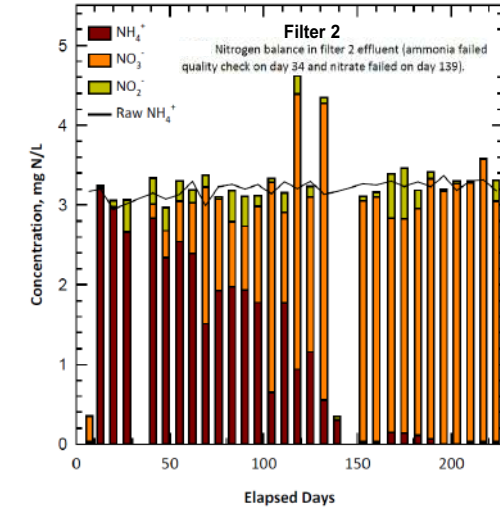
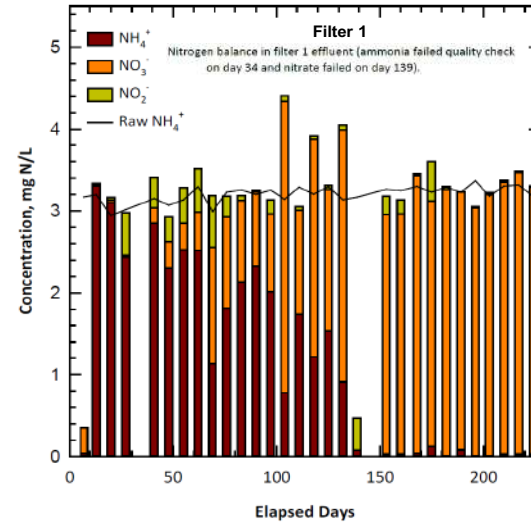
- Over the next 50 days with ammonia levels dropping below 1 mg N/l at the time of reporting.
- During this time, nitrite levels remained very low.
- Measurable levels of nitrite as high as 0.3 mg N/l were observed through the 60-day reporting period



EPA full-scale biological water treatment plant: *Filters*

Filters

- After 138 days, ammonia levels in all filters dropped to very low levels.
- Nitrite on a few rare occasions reached as high as 0.7 mg N/l, but typically were very low.
- The filters improved overall water quality by polishing contactor effluent.
- The finished water ammonia, nitrite and nitrate values paralleled the filters and reflected the combination of all three.
- Nitrite levels in the plant finished water never approached the drinking standard of 1 mg N/l.



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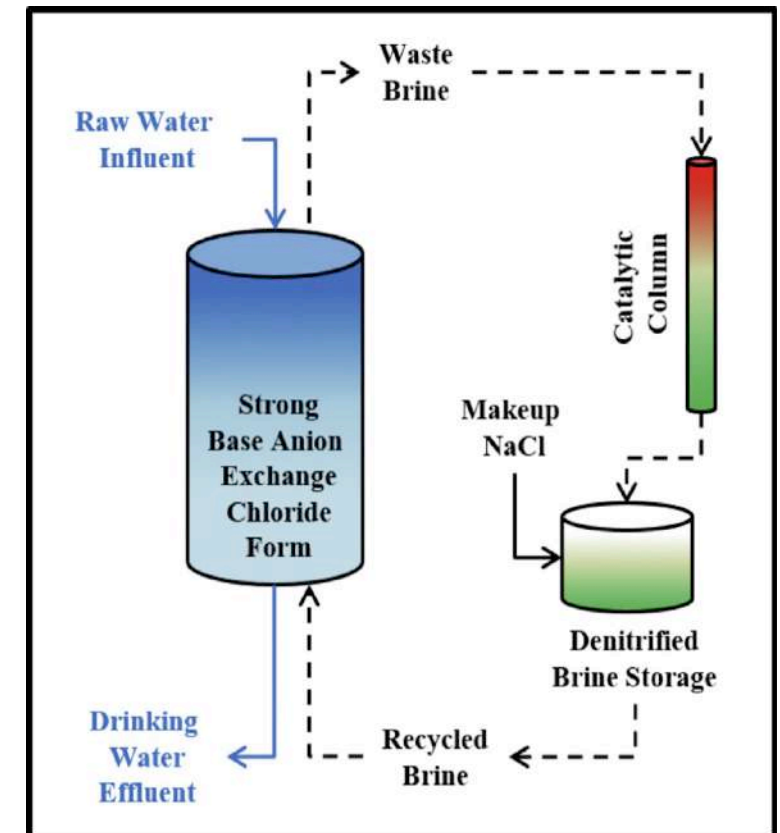
Other treatment techniques

Hybrid ion exchange-catalyst treatment technology for nitrate removal from drinking water

Ion exchange

- Ion exchange (IX) is the most common approach to treating nitrate contaminated drinking water sources, but the cost of salt to make regeneration brine, as well as the cost and environmental burden of waste brine disposal, are major disadvantages.
- A hybrid ion exchange-catalyst treatment system, in which waste brine is catalytically treated for reuse, shows promise for reducing costs and environmental burdens of the conventional IX system.

- The nitrate removal efficiency could reach 80%.
- Model simulations indicate that non-target ions like sulfate and bicarbonate will buildup in waste brines over repeated cycles of reuse, but this buildup will not negatively impact IX performance or lead to permanent deactivation of the Pd metal catalyst.
- Adding makeup salt to treated waste brines is necessary to maintain long treatment cycle run times between regeneration.
- Switching from a conventional IX system with a two bed volume regeneration to a hybrid system with the same regeneration length and sequencing batch catalytic reactor treatment would save 76% in salt cost.



Source: Allison et al., (2016) Evaluation of a hybrid ion exchange-catalyst treatment technology for nitrate removal from drinking water. Water Research, 96: 177-187.

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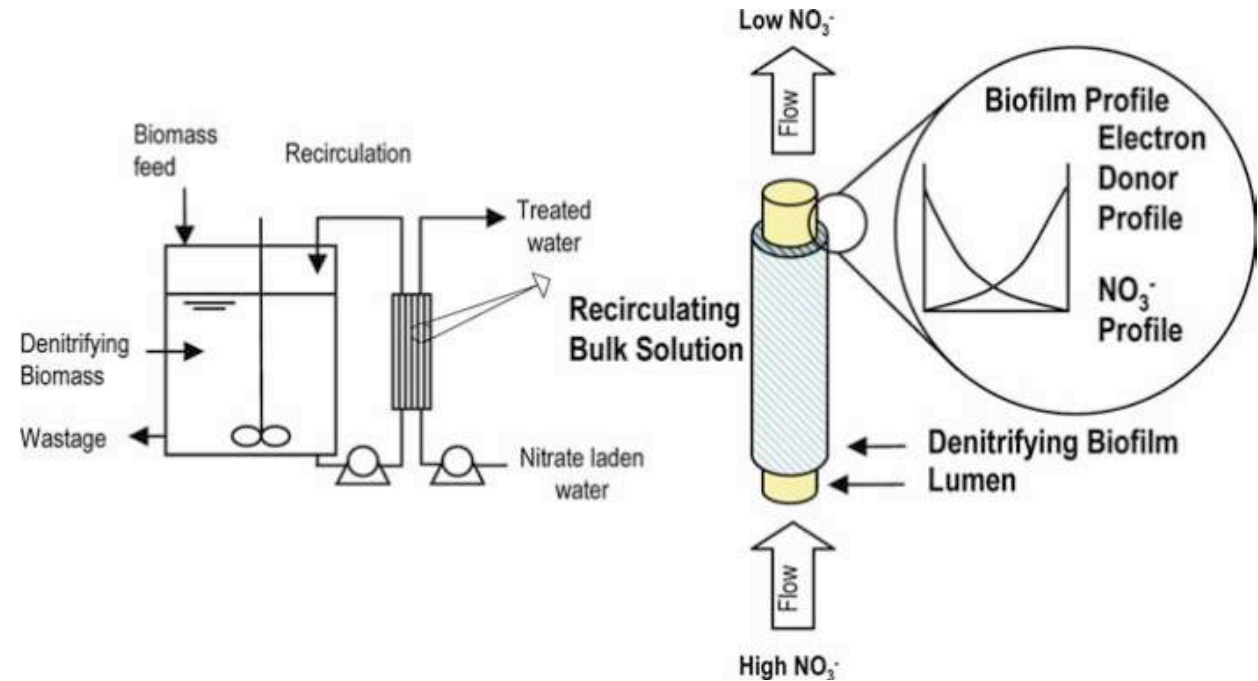
Bio-electrochemical

Other treatment techniques

Extractive membrane bioreactor for Nitrate removal

Extractive membrane bioreactor

- Nitrate is extracted from the pumped raw water by molecular diffusion through a physical barrier to a recirculating solution containing the denitrifying biomass.
- Using a tubular membrane yielding up to 99% removal efficiencies in high loading (200 mg NO_3^- -N-1) environments.

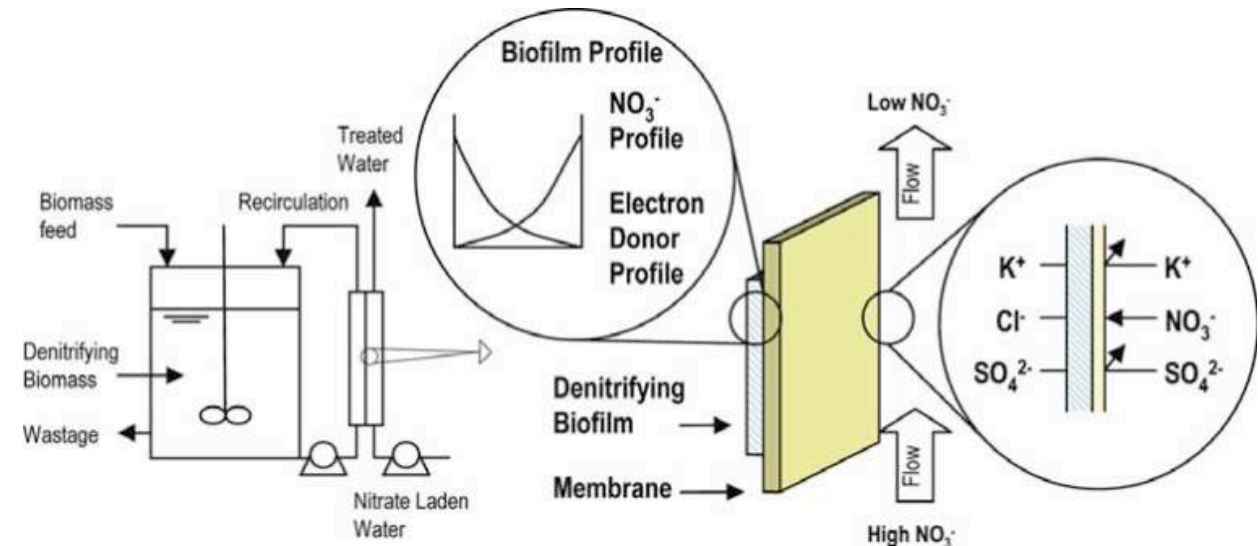


Source: McAdam and Judd (2006) review of membrane bioreactor potential for nitrate removal from drinking water. Desalination, 196: 135–148.

Ion-exchange membrane bioreactor for Nitrate removal

Ion-exchange membrane bioreactor

- Ion-exchange membrane bioreactor is identical to the extractive process except microporous membrane technology is replaced by dense ion-exchange membrane technology.
- The advantage of which is that the nonporous membrane facilitates more specific extraction of nitrate from raw water and in principle hinders the transfer of organic and inorganic pollutants present in the biomedium.
- Nitrate removal efficiency could reach 98%.

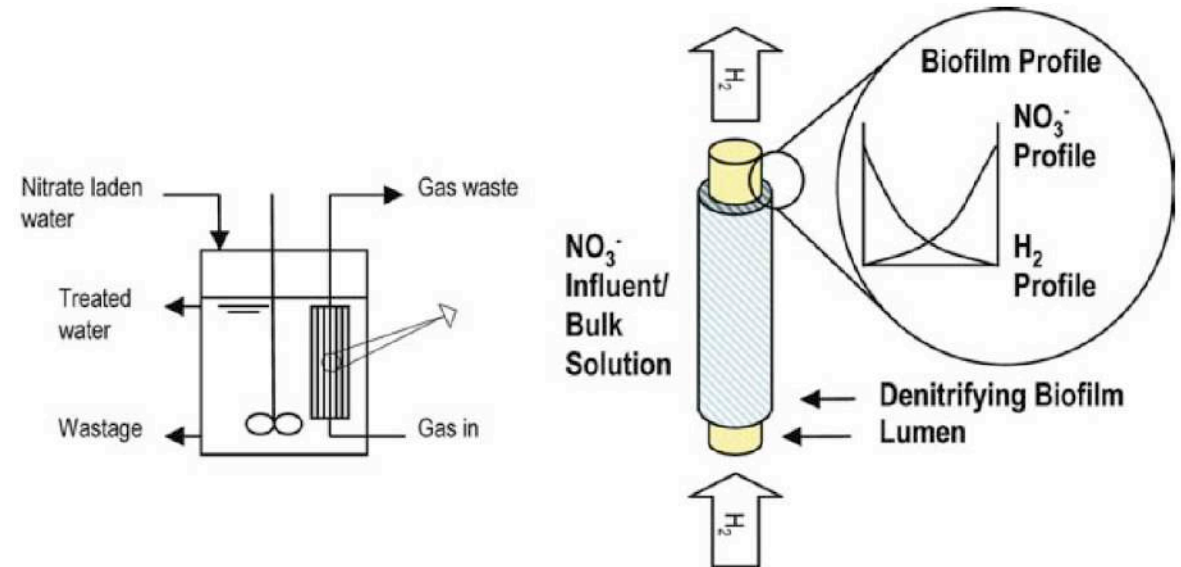


Source: McAdam and Judd (2006) review of membrane bioreactor potential for nitrate removal from drinking water. *Desalination*, 196: 135–148.

Gas transfer membrane bioreactor for Nitrate removal

Gas transfer membrane bioreactor

- To avoid potential secondary contamination associated with utilising an organic substrate, hydrogen (H_2) can be used as the electron donor combined with either carbon dioxide or bicarbonate as the carbon source for autotrophic denitrification.
- Gas transfer membrane bioreactors typically employ gas-permeable hollow fibres (HF).
- High NO_3^- utilization rates was recorded at an influent NO_3^- concentration of $145 \text{ mg } NO_3^- - N/l$.

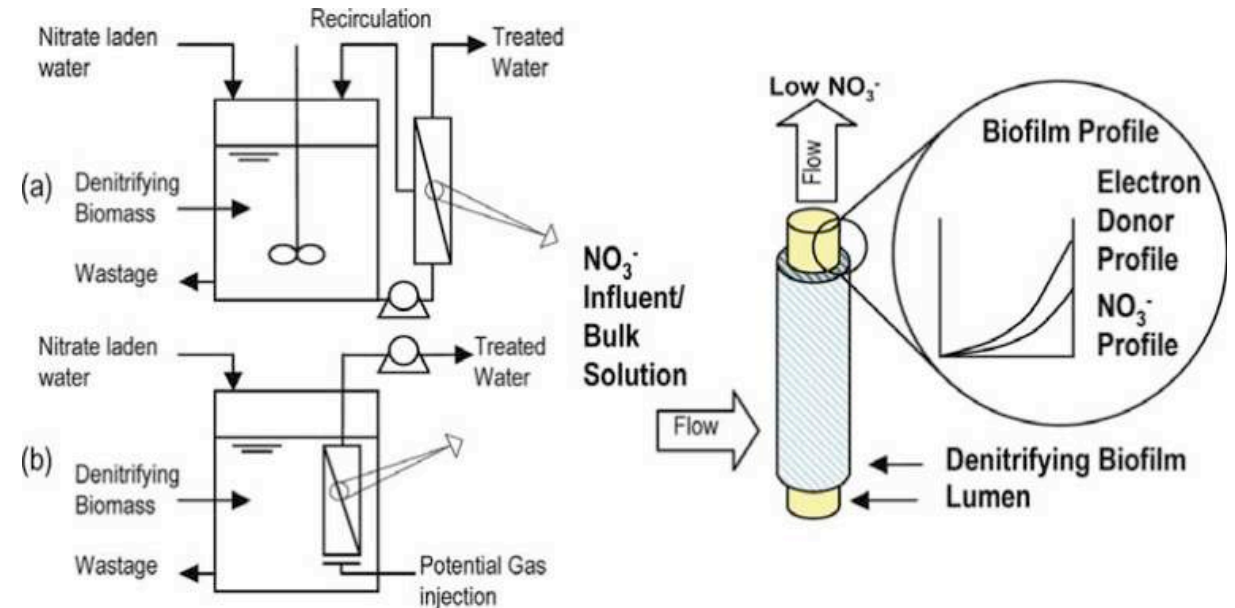


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Pressure driven membrane bioreactor for Nitrate removal

Pressure driven membrane bioreactor

- To avoid potential secondary contamination, this process relies primarily on a suspended denitrifying biomass rather than biofilm development and is thought to have the advantage of extended contact between the denitrifying culture and nitrate in the reactor medium, limited only by mixing rate.
- Rather than supplying the electron donor or acting as a channel for nitrate laden water, the membrane is placed within or external to the bioreactor, physically rejecting the biomass (hence retaining active denitrifiers) and more refined species.
- Nitrate removal efficiencies of up to 98.5% was reported.

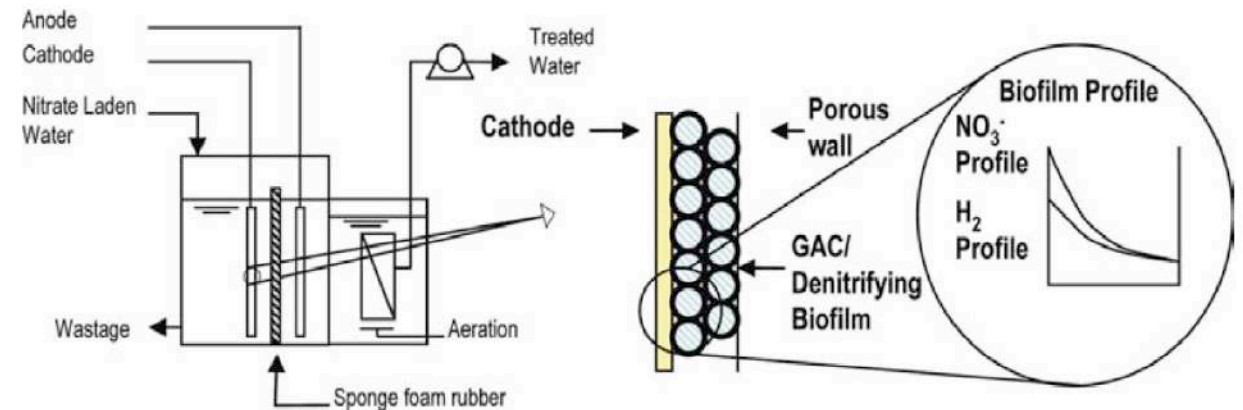


Source: McAdam and Judd (2006) review of membrane bioreactor potential for nitrate removal from drinking water. Desalination, 196: 135–148.

Hybrid systems for Nitrate removal

Hybrid systems

- Prosnansky et al. (2002) produced hydrogen gas electrolytically insitu to supply a biofilm grown at the cathode, the process being termed a biofilm electrode reactor (BER).
- To enhance the surface area for biofilm growth, granular activated carbon (GAC) was packed tightly at the cathode surface and submerged membrane technology was employed in a separate follow-on chamber.
- Following refinement of carbon dioxide flows to compensate for pH shift, improved NO_3^- and NO_2^- removal performance was noted although concentrations of 5–10 mg NO_3^- -N-1 consistently appeared in the effluent throughout testing.
- Nitrate loading rates between 0.024–0.192 kg NO_3^- -N m⁻³ d⁻¹ were trialled with all but the higher loadings resulting in 100% removal performance.



Source: McAdam and Judd (2006) review of membrane bioreactor potential for nitrate removal from drinking water. Desalination, 196: 135–148.

Chemical Treatment (coagulation)

Electrocoagulation

Biochemical Treatment

Adsorption

Reverse Osmosis

Electrodialysis reversal

Biological Treatment Process

Ion Exchange-Catalyst

Membrane bioreactors

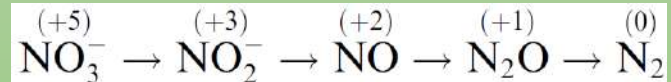
Bio-electrochemical

Other treatment techniques

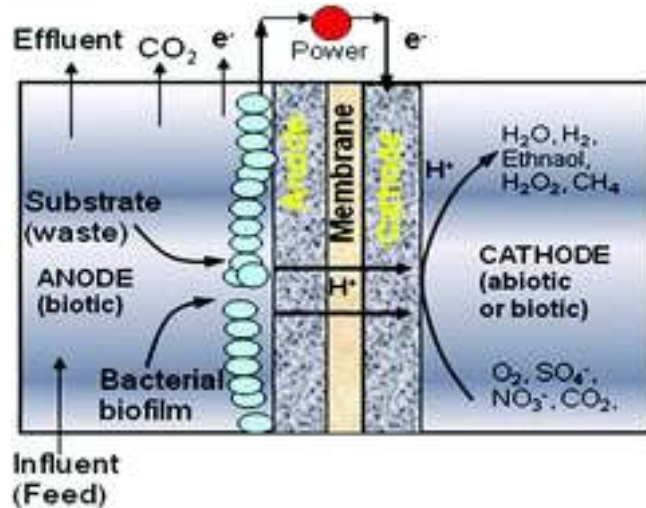
Bio-electrochemical removal of nitrate from water

Bio-electrochemical

- The presumed pathway of complete reduction of nitrate to nitrogen gas which involves four consecutive steps is illustrated below.



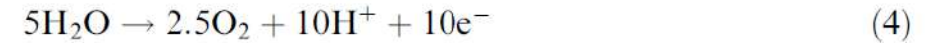
- A stable nitrate removal efficiency of 82–87% was achieved.



Decomposition of nitrate in BERs can be illustrated through seven equations including electrolysis of water which are shown below.

Electrolysis of water:

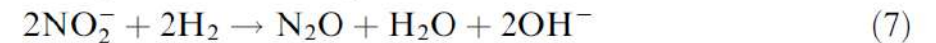
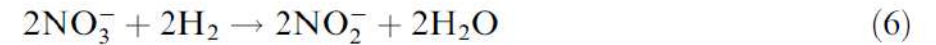
On the anode:



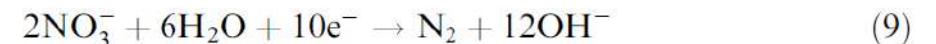
On the cathode:



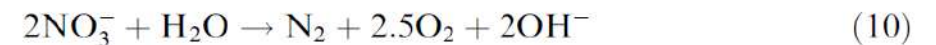
Stepwise autotrophic denitrification of nitrate to nitrogen gas is illustrated below. The main role of hydrogen gas as an electron donor is shown in this decomposition:



Net reaction of denitrification on cathode obtained from Eqs. (5)–(8):



The overall reaction in bio-electrochemical reactor is a combination of Eqs. (4) and (9):



Source: Ghafari et al., (2008) Bio-electrochemical removal of nitrate from water and wastewater—A review. Bioresource Technology, 99: 3965–3974.

Chemical Treatment (coagulation)

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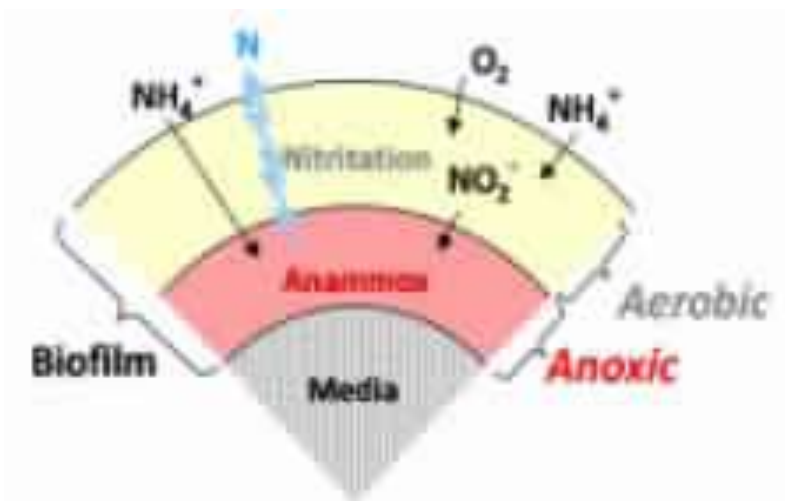
Bio-electrochemical

Other treatment techniques

ANITA™ Mox: Aerobic nitrification and anoxic ammonia oxidation

ANOXKALDNES ANITA™ MOX

- The ANITA™ Mox processes - MBBR (Moving Bed Biofilm Reactor) and Hybas (Integrated Fixed Film Activated Sludge) are single-stage deammonification technologies where greater than 90% of ammonia and 75-85% of total nitrogen can be removed.
- The processes accomplish this removal without the addition of an external carbon source and with considerably less energy in comparison to conventional nitrification-denitrification.
- The ANITA™ Mox process is performed in 2 steps: aerobic nitrification and anoxic ammonia oxidation performed by anammox bacteria.
- The two steps are taking place in a one-stage biofilm process in different layers of the biofilm: nitrification (aerobic) in the outer layer of the biofilm, anammox (anoxic) in the inner layer.



Source: Veolia, SPECIAL IFAT 2016 EDITION HALL A3 BOOTH 151/250

