Technical Report

Nitrate Removal of Drinking Water with Chelating Resin TRILITE CLR-N

Samyang Corporation   Ion exchange resin
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Samyang Corporation is the history of Ion Exchange Resin in Korea.

In 1976, Samyang Corporation successfully initiated localized production of IER in South Korea by technical cooperation with Mitsubishi Chemical Corporation, Japan. In 2011, with the successful development of UPW (Ultrapure water grade) resins, we are contributing to enhancing national competitiveness in semiconductor/LCD industries.
In 2016, Asia's largest UPS (Uniform Particle Sized) specialized IER (Ion Exchange Resin) plant; Samyang Fine Technology Corporation was founded. TRILITE is being supplied to the global market and is receiving rave reviews from the users.

Seoul (Head Office)

- **Technical sales force in 3 fields**
  - Demineralization/Ultrapure water /Condensate polishing/Catalyst
  - Food/Amino acids/Pharmaceuticals
  - Wastewater/Chelating resins /Purification
- **One Stop Service**
  - Analysis of IER
  - Equipment diagnosis and design support
  - Technical seminars and trouble shooting guides

Gusan (UPS Resin Plant)

- **Samyang Fine Technology (Joint venture with Mitsubishi Chemicals)**
- **Largest manufacturing capaicty for UPS resins in Asia**
- **Annual production capacity**
  - Cation 13,000kℓ, Anion 7,000kℓ
- **Product lines**
  - Uniform particle sized resins
  - Chromatography resins
  - Ultrapure water grade resins (OLED, LCD application)

Daejeon (R&D Center)

- **Analysis of IER**
- **Recipe improvement of IER**
- **New product development**
  - Tailored/Specialty resins
- **Application process development**
  - Pilot test
  - Engineering data gathering
  - Process proposal

Ulsan (UPW/Tailored/Specialty Resin Plant)

- **Technology licensed by Mitsubishi Chemicals & Self-development**
- **Specialized production of tailored resins**
- **Production capacity**
  - Cation 3,500kℓ, Anion 2,500kℓ
- **Product line**
  - Ultrapure water grade for semiconductor
  - Tailored resins : food, catalyst, pharmaceuticals
  - Specialty resins: chelating resins, synthetic adsorbents, refining of chemicals

No.1 Total Solution Provider

Samyang Corporation presents the full line-up of TRILITE Ion Exchange Resins from water teratement up to specialty applications. Samynag devlops Tailored resins optimized for customer needs and provoides differentiated technical services such as on-site visti for troubleshooting, technical seminars, process and design consulting, etc. Also, Samyang R&D center offers various analysis services for IERs and develops advanced application technologies.

1. Introduction

Nitrates in drinking water are widely known as nontoxic to adult humans however, it may have secondary and tertiary effects to health. When the nitrate concentration exceeds 10ppm (10mg NO_3^--N/ℓ)) the secondary toxicity to infants (especially, less than 6 months newly born babies) can be induced by reduction phenomenon of nitrate (NO_3-N) to nitrate nitrogen (NO_2-N) by microorganism.

Compared to the stomach acid pH of adult human ranging between 2~3, the stomach acid pH range of infant exceed 4 level, which becomes the reason being fatal to infant health due to increasing the rate of nitrate reduction

Reduced nitrite nitrogen (NO_2-N) is adsorbed into the blood flow, and it reacts with hemoglobin causing partial loss of oxygen transport function; generally known as Blue-baby disease. Tertiary toxicity is regarded as a very broad hazard factor as nitrate nitrogen (NO_2-N) reacts with stomach acid and forms Nitrosamines and causes cancer.

Generally, the nitrates are contained less than 5ppm in surface water and do not affect the human health. However, for ground water, it is problematic as more nitrates are contained, derived from the use of fertilizers from agricultural sector.

Oxidation　　Oxidation

Organic matter decomposition → NH_3-N → NO_2-N → NO_3-N → N_2 gas ↑ / NH_3 gas ↑

Continuous increase in the outbreak of hand-foot-and-mouth disease globally accompanies health related problems with Nitrate contained in groundwater. Ions of nitrate and nitrites in drinking water are limited to **10ppm (10mg NO_3^--N/ℓ)**.

Rural areas where small scale water supply system is installed shows high possibility of getting exposed to nitrate nitrogen as the raw water is supplied from the ground water.

The followings are conventionally used method of nitrate removal for drinking water.

- Reverse osmosis
- Electrodialysis
- Biological denitrification
- **Ion exchange resins**

Reverse osmosis and electrodialysis accompany the huge amount energy consumption and concentration waste along with high maintenance cost. Biological denitrification costs large initial cost to set-up. Hence using ion exchange resins is considered to be the most simple and effective way to remove nitrate nitrogen.

In this document, ion exchange method which can selectively remove nitrate nitrogen with TRILITE CLR-N.

2. Selective removal of nitrate from drinking water with TRILITE CLR-N

1) Composition principle of ion exchange resin selective to nitrate.

General Strongly Basic Anion Exchange Resins(SBAERs) has functional group of TMA(Trimethylamine) or DMEA(Dimethylethanolamine) and shows stronger selectivity to Sulfonate(SO_4^{2-}) than the Nitrate nitrogen(NO_3^-).

When the relative concentration of sulfonate ion is relatively lower than that of nitrate there is no issue of removing nitrate. However, if the relative concentration of the ions is reversed, it is problematic such as a decline in operation capacity and the outbreak of the ion leakage exceeding the permitted level. This problem initiated the development of specialized resin, highly selective to nitrate nitrogen.

The assumption was made such that SO_4^{2-} ion has the larger ionic size and introducing the triethylamine as a functional group would make the resin more selective to nitrate nitrogen. The test result is summarized as below;

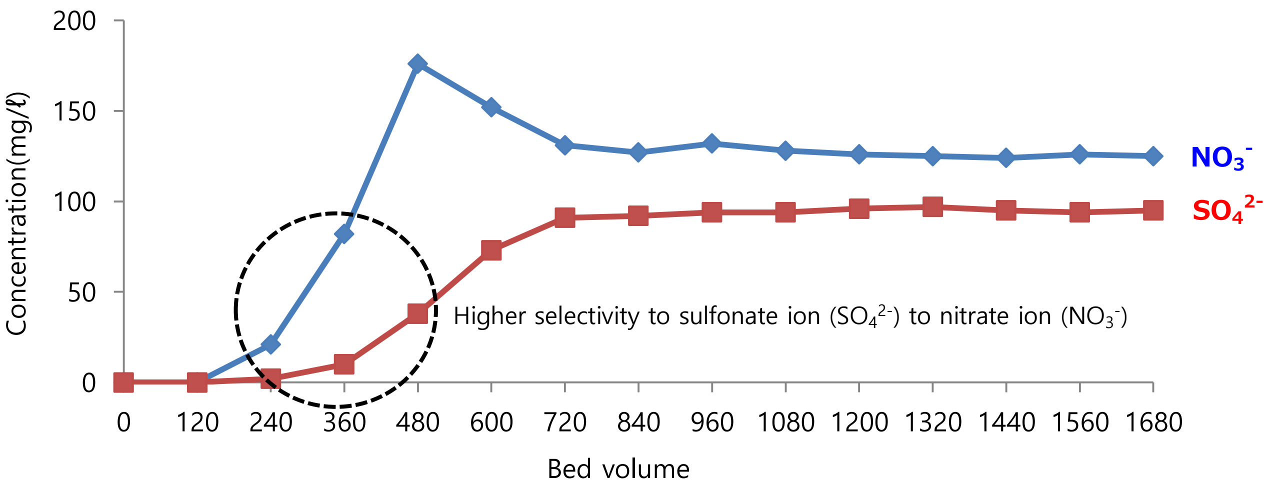
TRILITE CLR-N

Physical and Chemical Properties			
Physical form	Cream spheres	Matrix	Styrene-DVB, Macroporous
Functional group	**Triethylamine**	Ionic form	Cl^-
Total capacity(eq/ℓ)	1.0↑	Shipping density(g/ℓ)	650~750
Moisture retention(%)	48~58	Particle size(mm)	300~1,250

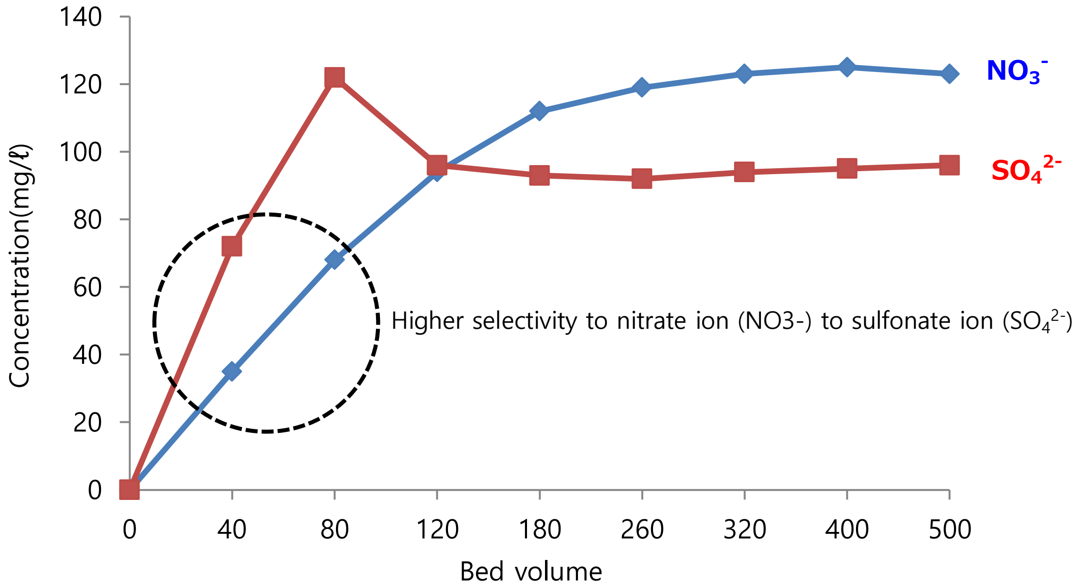
2) Comparison of TRILITE CLR-N and the conventional SBAERs

The following explanation compares the sulfonate (SO_4^{2-}) and nitrate (NO_3^-) removing efficiency between TRILITE SAR10, a Type 1 SBAER, and TILITE CLR-N. The test solution is made (mixed such that nitration(NO_3^-) and sulfonate(SO_4^{2-}) are contained for identical equivalent; NO_3^- = 124mg/ℓ, SO_4^{2-}= 96mg/ℓ) and set the temperature to 25℃. Service the solution through the column filled with 7㎖ of TRILITE SAR10 and TRILITE CLR-N respectively. Measure the ionic concentration of NO3- and SO42- from the treated solution at a given interval.

① Test result: TRILITE SAR10 (SBAER, Type1)



② Test result: TRILITE CLR-N



3) Calculation: Nitrate removal operation capacity of TRILITE CLR-N

When the concentration of NO_3^- is relatively higher than that of SO_4^{2-} (the value of SO_4^{2-}/NO_3^- is less than 1) TRILITE SAR10 is recommended to use.

Classification	Regeneration level (Co-current) (100% NaCl)	Operating Capacity, SAR10	NO_3^- leakage (compared to input concentration)	IER Selection
SO_4^{2-} / NO_3^- < 1	125g/ℓ-R	0.4eq/ℓ-R (20g as $CaCO_3$/ℓ-R)	10~15%	TRILITE SAR10
	250g/ℓ-R	0.5eq/ℓ-R (25g as $CaCO_3$/ℓ-R)	10% ↓	

However, when the concentration of NO_3^- is relatively lower than that of SO_4^{2-} (the value of SO_4^{2-}/NO_3^- is more than 1) TRILITE CLR-N with higher selectivity to nitrate is recommended to use.

Classification	Regeneration level (Co-current) (100% NaCl)	Operating Capacity, CLR-N	IER Selection
SO_4^{2-} / NO_3^- > 1	**125g/ℓ-R**	**0.4eq/ℓ-R (20g as $CaCO_3$/ℓ-R)**	**TRILITE CLR-N**
	250g/ℓ-R	**0.5eq/ℓ-R (25g as $CaCO_3$/ℓ-R)**	

The below table shows the NO_3^- leakage according to the ratio of $NO_3^-/(NO_3^-+SO_4^{2-})$

NO_3^-/ (NO_3^-+SO_4^{2-})	NO_3^- leakage (compared to input concentration)	
	Regeneration level 125g/ℓ-R	Regeneration level 250g/ℓ-R
0%	50%	40%
10%	45%	30%
20%	35%	25%
30%	30%	20%
40%	25%	15%

Considering the above operating capacity, the required resin volume is calculated as below.

Type	Raw water anion quality	
Cl-	10ppm as CaCO3	0.20 meq/ℓ
SO42-	30ppm as CaCO3	0.60 meq/ℓ
NO3-	20ppm as CaCO3	0.40 meq/ℓ
HCO3-	20ppm as CaCO3	0.40 meq/ℓ
SiO2	5ppm as CaCO3	0.10 meq/ℓ
Total anion	85ppm as CaCO3	1.70 meq/ℓ

Assuming that total anions of feed water is as above, the treated volume is 10m^3/hr, 1cycle = 20hr, treated volume per cycle = 200㎥/cycle, and the regeneration level is 125g as 100% NaCl/ℓ-Resin, then the value of SO_4^{2-} / NO_3^- exceed 1, hence the operating capacity can be obtained as 0.4eq/ℓ-R(20g as $CaCO_3$/ℓ-R).

$$\text{Resin Volume} = \frac{NO_3^- \text{ ionic load (per cycle)} \times 1.2 \text{ (Safety factor)}}{\text{Operating capacity}(g\ CaCO_3/\ell\text{-R})}$$

Resin Volume = 20ppm(g/㎥)×200㎥/cycle / 20g as $CaCO_3$/ℓ-R × 1.2 = 240ℓ

However, the flow rate(10㎥/hr/240ℓ×1000 = SV 42) exceed the appropriate standard (SV 10~40). The adjusted resin volume is 250ℓ, setting the flow rate to SV 40.

Leakage of NO_3^-

The ratio of $NO_3^-/(NO_3^-+SO_4^{2-})$ is equal to 40%. Applying NO_3^- leakage to 25% gives approximately, slightly less than 5.0ppm (20ppm(NO_3^- input concentration)×25%=5ppm).

4) Operation Procedure: Nitrate removal with TRILITE CLR-N

Operation	Flow rate	Input	Time	Volume
Service	SV 10～40	Raw water	Cycle time	Same as input volume
Backwash	Bed expansion 50%	Raw water	10～20min	Refer to below diagram
Settling	Until completed	-	5min	-
Regeneration	SV 2～6	10% NaCl	20～40min	Refer to regeneration level
Displacement	SV 2～6	Raw water	20～40min	3～5BV
Rinse	SV 10～40	Raw water	10～20min	1～2BV

Minimum bed depth : 500mm

<Pressure drop and bed expansion of TRILITE CLR-N>