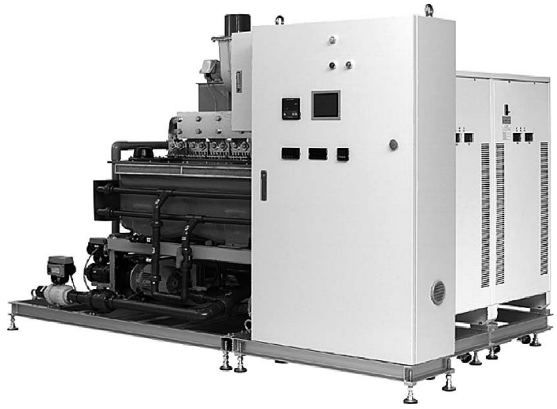

Decomposition System of Nitrogen Compounds in Waste Water with Electrolysis

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With waste water contained nitrogen compounds becoming a growing problem, legal controls are being promoted to treat nitrogen compounds. Conventional biotreatment for removing nitrogen requires much space for installing conventional large-scale facilities. Electrolytic denitrification completely unlike conventional biotreatment and using electrolysis has been developed and commercialized to solve this problem, as detailed below.

1. Introduction

Conventional biotreatment for removing nitrogen is widely applied to different types of wastewater, turning nitrogen into harmless nitrogen gas. Biotreatment, which is easily affected by load variation, requires complex control depending on the load status to keep appropriate activity of microorganism and addition of methanol to accelerate denitrification from wastewater with a low carbon/nitrogen (C/N) ratio. The resulting sludge treatment is also required. Cost reduction and easy operation are becoming big problem in waste water treatment. To improve the facility of nitrogen removal, large-scale construction such as installing new equipment is required, and makes it difficult to implement measures for preventing nitrogen emission via biotreatment.

Given this background, Mitsubishi Heavy Industries, Ltd., (MHI) has developed denitrification technology differing from conventional biotreatment and using electrolysis, commercializing electrolytic denitrification applicable to wastewater containing a wide range of nitrogen concentrations and to organic wastewater containing organic substances in hybrid use with the conventional biotreatment.

Table 1 Denitrification technologies

Denitrification technologies	Advantages	Problems
Biotreatment (Nitrification and denitrification)	Harmless conversion to nitrogen gas, wide application range	Requires large installation space and long treatment time.
Chlorine injection at discontinuous points	Low construction cost and easy application	High treatment cost and probable byproducts
Ammonia stripping	Effective for high-concentration wastewater	Removal of ammonia alone possible, high treatment cost
Ion exchange	Effective for low-concentration wastewater	High construction and treatment cost, requiring waste solution reprocessing

2. Comparison of nitrogen removal technologies

Table 1 shows nitrogen removal technologies developed to date. Different nitrogen removal technologies have been put to practical use, but compared to biotreatment, few have been actually applied.

3. Electrolytic denitrification features

Electrolytic denitrification features the following:

(1) Stable treatment

Stable denitrification is ensured because electrolytic denitrification is stable in removal using electrolysis, and responds immediately to load variations by adjusting the electrolytic current and chloride ion concentration.

(2) Easy operation

Compared to conventional biotreatment, electrolytic denitrification handles load variations, temperature changes, etc., of treatment solution flexibly, ensuring stable nitrogen removal and reducing power and labor for operation. Because equipment is easy to operate, it enables continuous, automatic operation.

(3) Space-saving

Being compact, equipment requires minimal space and no large-scale remodeling at installation, dramatically reducing construction time.

Electrolytic denitrification are used independently and automatically adjust treatment capacity, facilitating their application to existing treatment facilities.

(4) Reduction of secondary waste

Unlike biotreatment, electrolytic denitrification removes nitrogen from wastewater with a low C/N ratio or containing little organic matter without adding carbon sources such as methanol, etc. This produces less sludge than biotreatment, dramatically reducing secondary waste.

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4. Electrolytic denitrification reaction mechanism

The denitrification mechanism in an electrolytic denitrification, shown below, implements excellent removal, especially of ammonium-nitrogen (**Fig. 1**).

(1) The electrode reaction at the anode generates chlorine (Cl_2) from chloride ions (Cl^-) (equation 1), hydrolyzing chlorine and generating hypochlorous acid and hydrochloric acid (equation 2).

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \longrightarrow HClO + HCl \quad (2)$$

(2) Ammonia in wastewater reacts with hypochlorous acid generated in equation 2 to produce monochloroamine and dichloroamine (equations 3 and 4).

$$NH_3 + HClO \longrightarrow NH_2Cl + H_2O \quad (3)$$

$$NH_2Cl + HClO \longrightarrow NHCl_2 + H_2O \quad (4)$$

(3) Monochloroamine and dichloroamine react, becoming harmless nitrogen gas.

$$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3HCl \quad (5)$$

5. Application to night soil treatment

MHI's new system is applicable to inorganic and organic wastewater containing ammonia at widely concentrations. Application to night soil treatment involves the following:

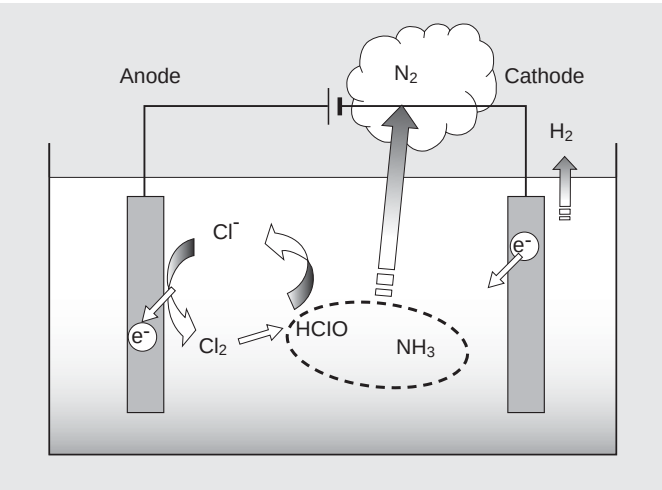

Fig. 1 Principle of electrolytic denitrification

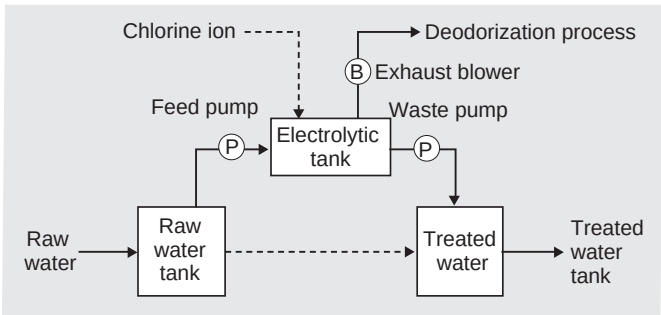

Fig. 2 Overview of electrolytic denitrification

(1) Problems with night soil treatment equipment

Recent nationwide trends in diluting night soil to promote flush systems and the spread of combination septic tank have generated large amounts of septic tank sludge and substantial variations in waste properties, making it difficult to maintain stable denitrification by basic biotreatment equipment, which cannot be managed only by operation control efforts. Intensive stable denitrification is thus needed.

Electrolytic denitrification require that treated solutions have a suspended substance (SS) content of 1 000 mg/L or less. Electrolytic denitrification are applicable in night soil treatment to solutions for dehydration and separation before the generation of septic tank sludge with low SS content and ammonia-nitrogen or to solutions for solid-liquid separation after biotreatment. Hybrid treatment combining conventional biotreatment with the electrolytic denitrification using electrolysis for denitrification have been developed and commercialized.

(2) Features of hybrid electrolytic denitrification

Table 2 compares conventional biotreatment technology. Compared to conventional biotreatment denitrification, hybrid treatment entails shorter construction time and ensures more effective denitrification at lower remodeling cost.

(3) Basic electrolytic denitrification configuration

Electrolytic denitrification consist of a power supply including a control panel and DC power supply, an electrolytic tank, pumps, and exhaust fans.

The unit is operated basically using batch treatment involving feeding water from raw water tanks and water treatment tanks preceding and following the electrolytic tank , electrolysis and discharge transferring treated solutions to the next process, and repetition of these processes (**Fig. 2**).

Table 2 Comparison of biotreatment

	Conventional denitrification (biotreatment)	Hybrid electrolytic denitrification
1. Treatment overview	Biological denitrification	Electrolytic denitrification + biotreatment
2. Treatment time	Long time	Short time
3. Installation space	Large	Small
4. Operability	Complex control, long treatment time, and poor flexibility	Correspondence to concentration variation through automatic control, showing capacity immediately after operation
5. Maintenance performance	–	Easy maintenance because of simple equipment
6. Construction time	Long, requiring construction work	Short
7. Operating cost	Almost equivalent (Depending on treatment conditions)	

(4) Control under optimized conditions

(a) Denitrification features

An example of results confirming denitrification performance using electrolysis is shown in **Fig. 3**. Denitrification speed was confirmed to be almost constant (zero reaction), regardless of the ammonia concentration in the solution.

In actual system operation where nitrogen (ammonia-nitrogen) is removed rapidly, real-time data on treatment progress through ammonia concentration is difficult to obtain. Hence, the behavior of the concentration turning to upward trend from downward trend when the entire ammonia is treated was used as an index to determine treatment progress, and electrolysis conditions were based on concentration (pH) behavior.

This enables electrolysis conditions (time and electrolytic current) to be set without being too high or too low.

(b) Automatic control based on inlet concentration

Using control based on pH behavior, automatic control was implemented based on variations in nitrogen (ammonia-nitrogen) content in the treatment solution.

Planned electrolysis time t_A per batch is fixed from the planned volume of treatment per day and effective electrolysis time t_S obtained by subtracting time t_I for solution supply and time t_O required for discharge from planned electrolysis time t_O: $t_S = t_A - t_I - t_O$.

If denitrification ends within effective electrolysis time t_S (case A in **Fig. 4**), current in the next batch is decreased. If denitrification does not end within t_S (case B in Fig. 4), current in the next batch is increased. Optimized control thus realizes automatic optimization of current, ensuring treatment using only required electrolysis time without excess electrolysis.

(5) Delivery record

(a) Background

The first electrolytic denitrification for removing nitrogen from night soil started in October 2004. The system continues to run smoothly, stabilizing denitrification.

(b) Applicable flow

The applicable flow and example of electrolytic denitrification at the human-waste treatment facility are shown in **Figs. 5** and **6**. The flow is applied to a membrane filtrated solution after biotreatment.

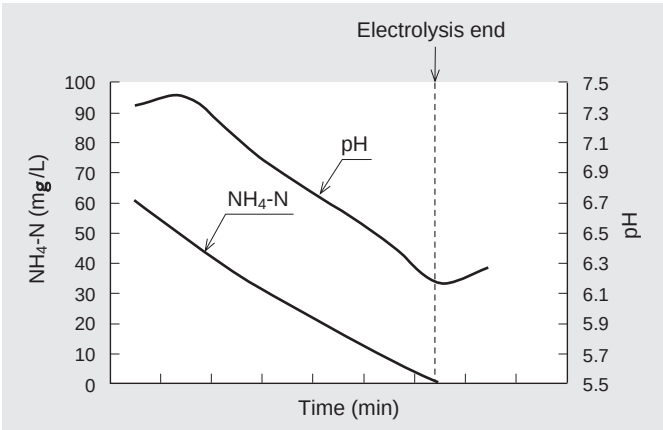

Fig. 3 Correlation between nitrogen (ammonia-nitrogen) concentration and pH in electrolytic treatment

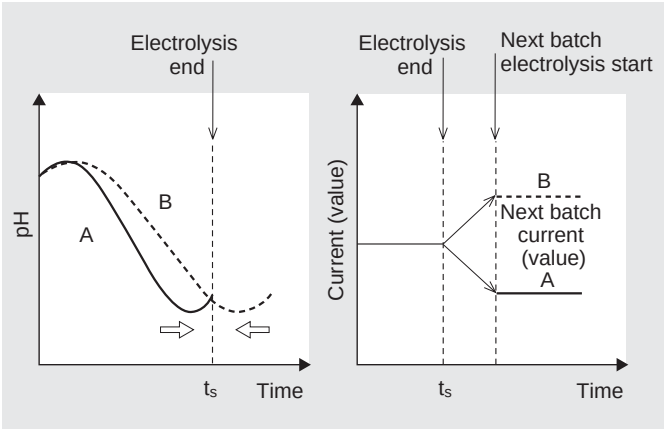

Fig. 4 Setting pH variation with time and batch current

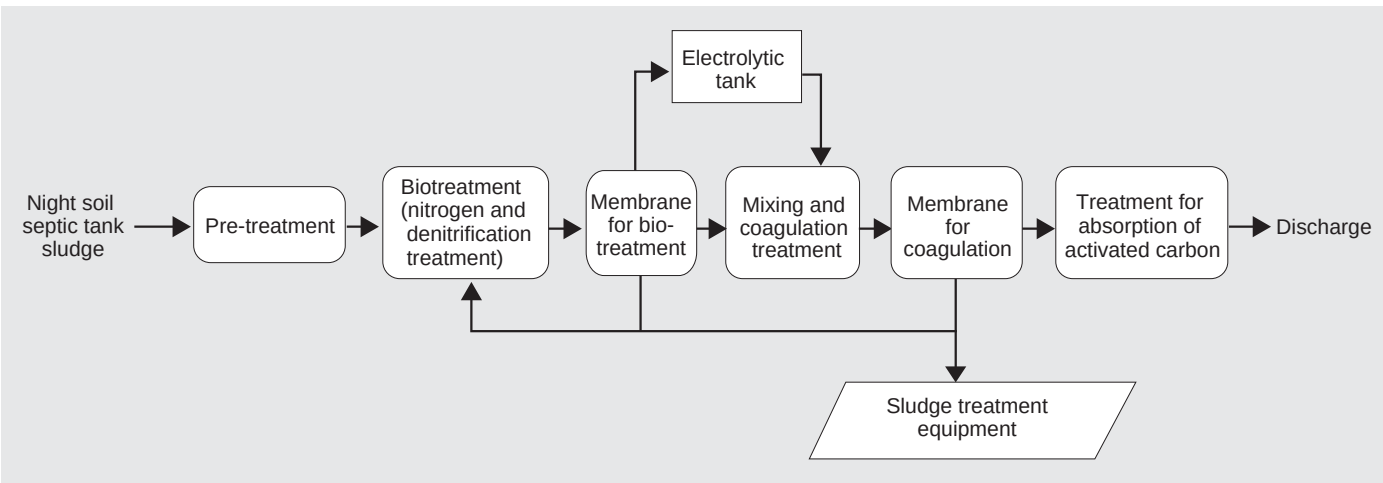

Fig. 5 Application flow

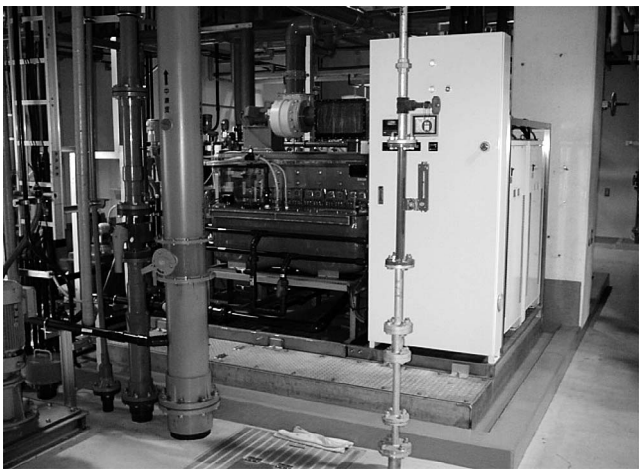

Fig. 6 Example of electrolytic denitrification delivery

Table 3 Example of operation data (Unit: mg/L)

Item	Unit inlet	Unit outlet
NH_4-N	84.0	<0.5
NO_2-N	0.9	<0.1
NO_3-N	1.9	5.9
COD_{Mn}	129	93

(c) Operation record

Table 3 is an example of operation data. Salt water is added and the chlorine ion concentration in the treatment solution is adjusted to 2 000 mg/L to ensure rapid denitrification.

Results show linear reduction of ammonia NH_4-N concentration due to electrolysis treatment, with gradual reduction seen also in the COD_{Mn} concentration, while nitrous acid NO_2-N and nitric acid NO_3-N concentrations remaining almost unchanged.

Color components are decomposed with brown treatment solution becoming nearly colorless after treatment, suggesting a dramatically reduced load of activated carbon in subsequent stages (**Fig. 7**).

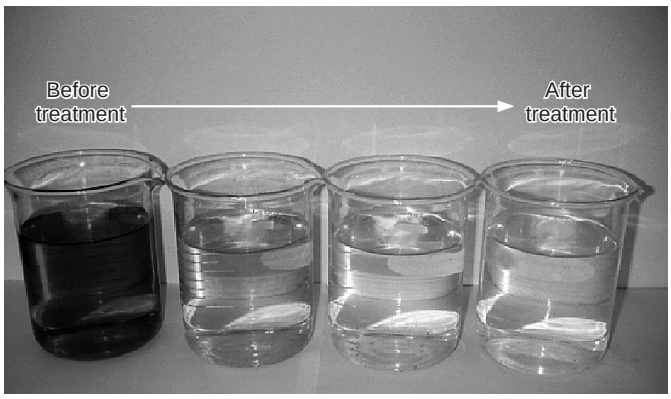

Fig. 7 Color change in treated solution after electrolytic treatment

5. Conclusions

MHI's new electrolytic denitrification has excellent performance. Through hybrid operation with biotreatment, it is widely applicable to wastewater containing organic substances. Its application to inorganic wastewater such as plant wastewater, etc., despite differences in operation control, is expected to be widespread.

Since denitrification performance largely depends on symbiotic substances and chlorine ion concentration in the treatment solution, the new electrolytic denitrification system is considered optimum treatment based on the properties of the treatment solution. In addition to package contracts including installation, lease contracts including maintenance and supply of spare parts are also available at system introduction. MHI offers a wide variety of treatment systems as a solution to environmental problems.

With legal regulations against nitrogen emission increasing for water quality conservation, we view electrolytic denitrification as a key technology for enhanced, stable denitrification. These systems also provide sterilization and decoloration and are expected to be applied to other substances as the optimum total solution to meet diversified needs.


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