Improvement of wastewater treatment performance of the Fukashiba treatment plant

K. Hirose*, T. Igarashi*, E. Ochiai*, H. Seya* and S. Matsui**

*Kashima Prefectural Sewerage Office, Kitahama 9 Kamisumachi, Kashimagun, Ibarakiken, Japan, 314-0101 (E-mail: *kage@pref.ibaraki.lg.jp*)

**Graduate School of Global Environmental Studies, Kyoto University, Yoshida-honmachi Sakyo-ku, Kyoto City, Japan, 606-8501 (E-mail: *gozzira@Kyoto-u.ac.jp*)

Water Science & Technology **Vol 53 No 11 pp 127–133**

Abstract The Fukashiba Treatment Plant Kashima Rinkai Specified Sewage Works has received wastewater from the petrochemical complex (90%) and public sewage of Kamisu and Hasaki town (10%). For this reason, the plant is facing many difficulties in producing good quality effluent.

In order to solve these difficulties, we are reviewing the treatment performance and making efforts for its improvement with nitrification inhibition, control of bio-persistent substances and the PRTR approach.

Keywords Discharge of bio-persistent substances; nitrification inhibition; pollutant release and transfer register

Operation for limiting nitrification

When the operation of nitrification is applied to the plant process, as applied to other public sewage treatment plants, nitrification does not run to completion but stops at building of nitrite.

Nitrite of the effluent can be measured in terms of COD_{Mn}. The plant faces the difficulty of meeting the effluent standard of COD_{Mn}, which is a daily average of 40 mg/L and a daily maximum of 50 mg/L. According to the sewage test of Japan, the nitrite concentration can be corrected in terms of COD_{Mn} with the following equation:

$$\text{Corrected } COD_{Mn} = COD_{Mn} - (NO_2\text{-N} \times 1.14),\ NO_2\text{-N} > 1.0\,\text{mg/L} \qquad (1)$$

However, the plant took the position of nitrification without the advantage of using the corrected COD_{Mn}. The main reasons for incomplete nitrification are high ammonia, inhibiting substances and high waste water temperatures of 38 °C during summer in inflow. In order to better control nitrification, the influent ammonia concentration was reduced from 130 to 30 mg/L. However, it still needs to operate the level of DO below 2 mg/L to suppress nitrification to meet the effluent standard of COD_{Mn}.

Nitrification inhibition by industrial wastewater

Nitrification-type activated sludge was produced from the activated sludge (nitrification-inhibition-type) obtained at the treatment plant by using a sludge incubator (see Figure 1) and nitrification inhibition tests were conducted.

Test method

Nitrification sludge developed by the plant activated sludge was used as a test for finding inhibition of nitrification. The experiment was conducted on test equipment as shown in Figure 2.

doi: 10.2166/wst.2006.345

Figure 1 Activated sludge incubator

Of the industrial wastewaters highly loaded to this plant (approximately 500 kg/day or more of COD loads) 5, 10 and 30% was taken in 1 L graduated cylinders, respectively. Then, two-fold diluting water from the primary effluent of the treatment plant was added to these cylinders to prepare 1 L solutions. The dilution water was also used for the control wastewater.

For this test, a chloride ion concentration was regulated from 5,000 to 8,000 mg/L in accordance with operating conditions of the plant, while ammonia nitrogen and MLSS concentrations were controlled to approximately 30 and 2,000 mg/L, respectively.

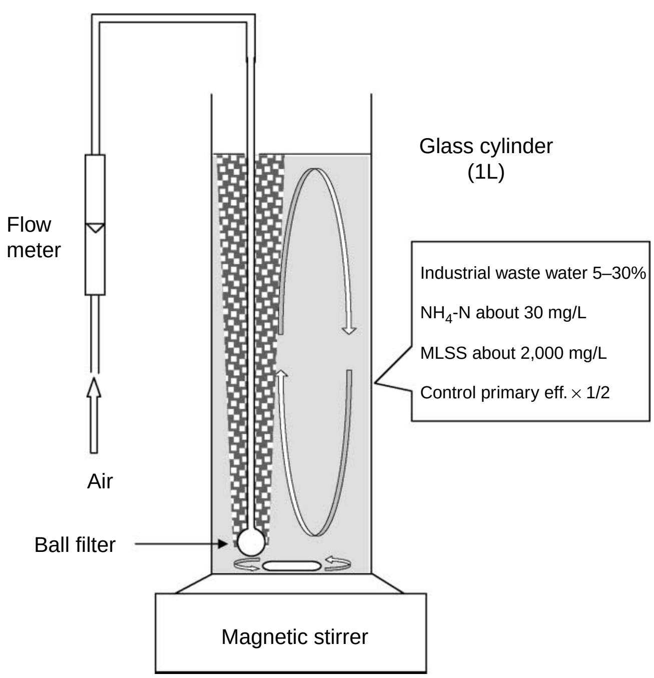

Figure 2 The test equipment for nitrification inhibition

The tests were conducted at room temperature with aeration of 100 mL/min for 3, 6 and 8 h. Ammonia-, nitrite-, and nitrate-nitrogens were measured with an ion-chromatography detector. COD, pH, DO and water temperature were observed.

Test results

Industrial waste waters of A to E factories with an ascending order by drainage volume were tested. Apart from C, a level of nitrification inhibition was increased in proportion to concentrations of industrial wastewaters added.

The volumes of industrial effluent from company A was 20% and E was 4% of the total volume industrial wastewater. These can be part of the cause of the inhibition of nitrification at the wastewater treatment plant. However, the materials that are inhibiting nitrification have not yet been specified.

Reduction of discharge of biopersistent substances

Industrial wastewaters include various types of chemical substances, most of which are difficult to decompose with activated sludge (Matsui *et al.*, 1975, 1989; Okawa *et al.*, 1989; Kozawa *et al.*, 1991). These substances are not treated with treatment plant and may be discharged into public waters. Typical chemical components contained in industrial wastewaters are raw materials, intermediates, by-products and additives. According to the biodegradability test of our activated sludge, the following empirical knowledge is accumulated: (a) natural organic substances are generally well degraded; (b) among synthetic chemicals, aliphatic alcoholic and carboxylic substances are also well degraded; however, more molecular weight substances become less degradable than lower molecular ones of the same groups when halogenated, biodegradation becomes difficult; (c) among aromatics, substituents of hydroxyl, amino and carboxyl help improvement of biodegradability while substituents of halogen, nitro and sulphonyl make the activated sludge degradability more difficult. Petrochemical wastewaters contain highly volatile substances which the biodegradability test of activated sludge needs to take account of. In general, wastewaters of oil refineries, ethylene production (C2) and propylene production (C3) are easily degraded due to their composition of alcohols, low molecular fatty acids, and low molecular hydrocarbons. However, wastewaters of polymer production contain hard compositions such as emulsions. Wastewaters of fine chemical

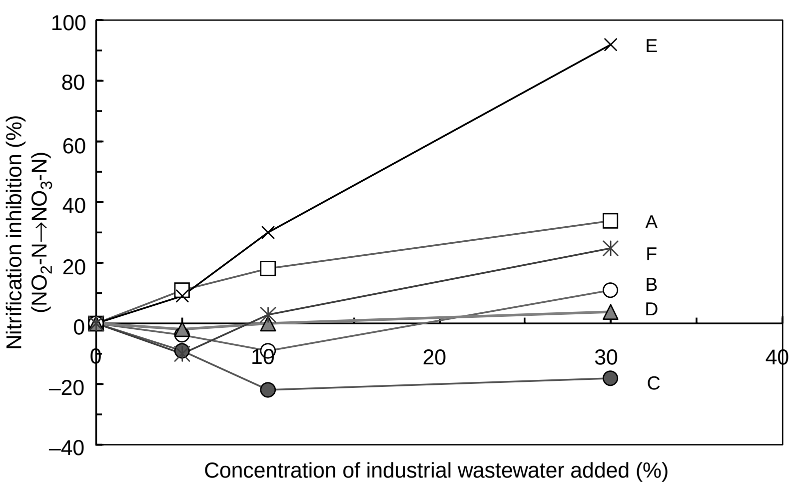

Figure 3 Concentration of industrial wastewater added and nitrification inhibition

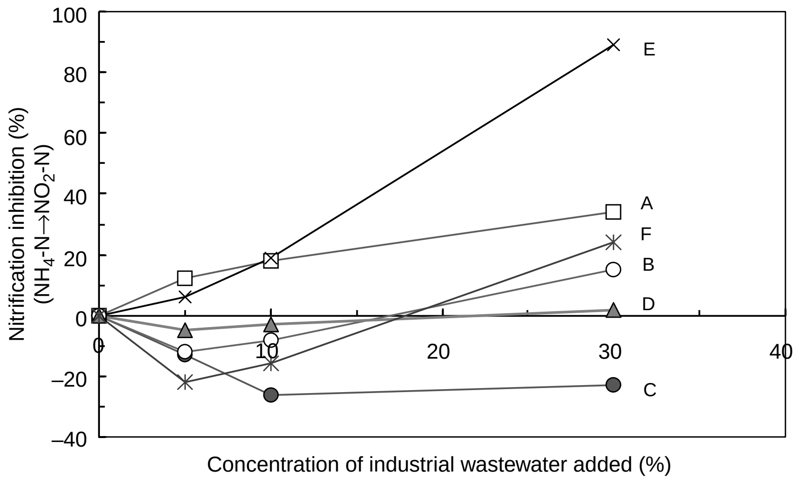

Figure 4 Concentration of industrial wastewater added and nitrification inhibition

processes contain various hard substances. We have attempted to reduce biopersistent substances that highly load to the Fukashiba Treatment Plant and affect its effluent quality in consultation with factories, as shown in Table 1.

Measures for compliance with the law on Pollutant Release and Transfer Register (PRTR)

The Japanese government issued the Law on Pollutant Release and Transfer Register (PRTR) aiming at 354 hazardous substances in 1999, which required public sewage treatment plants to report an inventory of hazardous substances designated by the Water Pollution Control Law and Sewerage Law. However, both laws cover only a part of the 354 hazardous substances (Table 2). Since the Fukashiba Treatment Plant receives various chemical wastestreams, it needs to expand monitoring capacity that can cover the 354 hazardous substances. We have started communication with factories over their

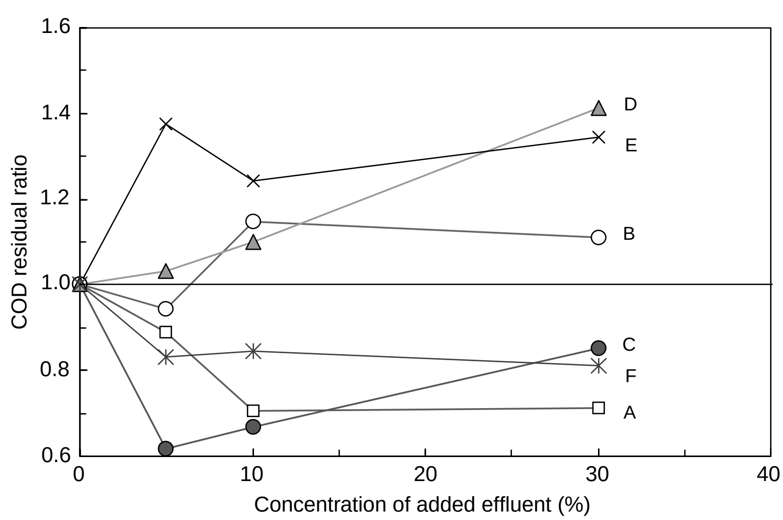

Figure 5 Relationship between concentration of added effluent and COD Residual ratio

Table 1 Method for reducing biopersistent substances

Reduction method	Biopersistent substances
Collection and recycling	Dinitrotoluene, diaminotoluene, polymerization stoppers, etc.
Modification of production process	Monomer process products of synthetic rubber
Modification of wastewater (hydrolysis)	Halogen compounds
Usage reduction and modification of raw materials	Xylene sulphonic acid, solvents
Remove (aeration, absorption and incineration)	Volatile organic substances, colouring substances

Table 2 Water quality standard when wastewater is released into sewerage systems

Target substances and items	Standard value for releasing wastewater (mg/L)
Sewage Law	
Phenols	10
Copper and its compounds	3
Zinc and its compounds	5
Iron and its compounds (soluble)	10
Manganese and its compounds (soluble)	10
Chromium and its compounds (soluble)	2
Fluorine and its compounds	15
Boron and its compounds	230
Cadmium and its compounds	0.1
Cyanogen compounds	1
Organophosphate	1
Lead and its compounds	0.1
Sexivalent chrome compounds	0.5
Arsenic compounds	0.1
Total mercury compounds	0.005
Alkyl mercury compounds	Must not be detected
Polychlorinated biphenyl	0.003
Trichloroethylene	0.3
Tetrachloroethylene	0.1
Dichloromethane	0.2
Carbon tetrachloride	0.02
1,2-dichloroethane	0.04
1,1-dichloroethylene	0.2
cis-1.2-dichloroethylene	0.4
1,1,1-trichloroethane	3
1,1,2-trichloroethane	0.06
1,3-dichloropropene	0.02
Tyraum	0.06
Simazine	0.03
Thiobencarb	0.2
Benzene	15
Selenium and its compounds	0.1
Dioxins	10 p(g/L)
Contract-based standard	
Temperature	Below 45 °C
Hydrogen ion concentration	$5 < pH < 9$
Biochemical oxygen demand	Below 600
Chemical oxygen demand	Below 600
Suspended solids	Below 600
Oil and fat content	Below 20
Content of ammonia nitrogen	Below 380
Directive standard	
Chemical oxygen demand	300
Chlorine compounds	20,000

reports of PRTR, and own analysis of chemicals in the reports since 2003. However, we can only conduct analysis of chemicals by established analytical methods that are applicable to limited species of chemicals after consultation with government laboratories and other analytical institutes. We found discrepancies between our estimation from inflow analyses and values of the PRTR reports of the factories as shown in Table 3. Epichlorohydrin and acetonitrile are typical cases of significant discrepancy. We have to make efforts of reducing discharge amounts of designated hazardous chemicals of PRTR with the cooperation of factories in the service area of the Fukashiba Treatment Plant. We are going to monitor behaviour of the chemicals in the plant to make our inventory.

Methods of pretreatment facilities in the factories

This section summarised methods of pretreatment facilities for the sewerage processes protection in 23 factories that discharge 1,000 m^3 or more of wastewater per day in fiscal year 2002.

Treatment methods are divided into the physical and chemical treatment process with a combination of neutralisation, sedimentation, flotation, separation and filtration, the physical and chemical treatment process plus biological treatment with catalytic oxidation and activated-sludge method, and the single biological treatment (Table 4).

Among 23 factories, seven factories treat their wastewater streams with their own centralised pretreatment facilities. Sixteen other factories independently treat their wastewater streams and discharge by their own single channels to the sewerage. The difference between the above pretreatment approaches is due to engineering and economic efficiencies. According to the standard of the Sewerage Law, the contract-based standard of Kasima Rinkai Specified Sewage Works (KRSSW), and the guidance of KRSSW, each factory tries to introduce and operate its own facilities, balancing between economy of discharge rate and compliance with the standards. The important guidance points of good operation and maintenance of the plant are keeping the capacity of COD_{Mn} removal rate at 80%, and the level of chloride concentration below 10,000 mg/L.

Table 3 Reported values and estimation from inflow analyses (t/year)

Substance name	Total of reported values on inflow	Estimation from inflow analysis
Epichlorohydrin	0	94.9
Ethyl benzene	1	0.5
Styrene	3.3	0.4
o-Dichlorobenzene	1.8	1.2
Acetonitrile	0	94.9
Formaldehyde	64	20
Linear alkylbenzene sulfonates	0.8	33
Dichloromethane	0.009	0.2
Benzene	3	5.3
Phenol	18.6	113.7

Table 4 Methods of pretreatment facilities in the factories

Treatment method	Number of factories
Physical and chemical treatment	16
Physical and chemical treatment + biological treatment	6
Biological treatment	1

Conclusions

When wastewater from petrochemical complexes is treated in the plant, it is judged that the operation for limiting nitrification must be continued due to the occurrence of unknown substances of those inhibiting nitrification, possibly with combined chemical effects of substances. It could be possible to modify the current operation of limiting nitrification to complete nitrification with an increase in SRT, aeration capacity, etc. However, we have to determine engineering solutions to overcome poor settling of the activated sludge due to changes in complete nitrification. The increase in aeration capacity requires more electricity consumption which leads to economic issues of the plant. The Kashima petrochemical complex conducts yearly inspections of all production processes during the summer for 1–2 months, which creates a 50% reduction of inflow volume, and a significant decrease in inflow concentration. These large operational changes introduce instability of the activated sludge performance every summer. Nitrification bacteria are understood to be the most sensitive species among the activated sludge bacteria. We are not sure how to overcome this difficulty for modification to complete nitrification. We will continue to find factors inhibiting nitrification through analysis of various data, and introducing activated carbon and activated sludge methods to reduce the effects of bioresistant substances for compliance of the PRTR activities. However, it is required to continue to determine these effects through data analyses. In addition, it may be required to conduct tests and research for new treatment methods.

References

Koazwa, T., Wueki, T., Kobayashi, H. and Matsui, S. (1991). Management of toxics for the Fukashiba industrial wastewater treatment plant of the Kashima petrochemical complex. Second international conference on waste management in the chemical and petrochemical industries – toxic management. 17–20 June 1991, New Orleans, USA.

Matsui, S., Murakami, T., Sasaki, T., Hirose, Y. and Iguma, Y. (1975). Activated sludge degradability of organic substances in the waste water of the Kashima petroleum and petrochemical industrial complex in Japan. *Prog. Water Tech.*, **7**(3/4), 645–659.

Matsui, S., Okawa, Y. and Ota, R. (1989). The Fukashiba industrial wastewater treatment plant for the Kashima petrochemical complex (II) – biodegradability of 37 organic substances and 28 process wastewater. *Wat. Sci. Tech.*, **20**(10), 201–210.

Okawa, Y., Shinozuka, S., Ota, R. and Matsui, S. (1989). Experience of 16 years operation and maintenance of the Fukashiba industrial wastewater treatment plant for the Kashima petrochemical complex (I) – operation and maintenance. *Wat. Sci. Tech.*, **20**(10), 193–200.