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Instability of biological nitrogen removal in a cokes wastewater treatment facility during summer

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Abstract

Failure in nitrogen removal of cokes wastewater occurs occasionally during summer season (38 °C) due to the instability of nitrification process. The objective of this study was to examine why the nitrification process is unstable especially in summer. Various parameters such as pH, temperature, nutrients and pollutants were examined in batch experiments using activated sludge and wastewater obtained from a full-scale cokes wastewater treatment facility. Batch experiments showed that nitrification rate of the activated sludge was faster in summer (38 °C) than in spring or autumn (29 °C) and the toxic effects of cyanide, phenol and thiocyanate on nitrification were reduced with increasing temperature. Meanwhile, experiment using continuous reactor showed that the reduction rate in nitrification efficiency was higher at 38 °C than at 29 °C. In conclusion, the instability of full-scale nitrification process in summer might be mainly due to washing out of nitrifiers by fast growth of competitive microorganisms at higher temperature under increased concentrations of phenol and thiocyanate.

Keywords: Cokes wastewater; Nitrification; Pre-denitrification process; Temperature; Washing out

1. Introduction

Steel industries generate various wastewaters during the manufacture and processing of iron. Above all, cokes wastewater is considered the most toxic one to be treated before being discharged [1]. This wastewater is mostly generated in the cooling step after coking coals at high temperature (900–1100 °C) and in the liquid-stripping step of the produced coke oven gas (COG). Moreover, a considerable amount of condensed water is generated during the transport of COG through pipes to neighboring plants as heat source. These resulting wastewaters, designated as cokes wastewater, contain various toxic pollutants such as phenols, ammonia, thiocyanate and cyanide in high concentration range [2].

Although activated sludge process has been successfully used for treating various domestic and industrial wastewaters, the high concentration of toxic pollutants such as phenol and cyanide severely inhibit biological activities of activated sludge [3,4]. For this reason, many researchers have studied how to efficiently treat cokes wastewater biologically [1,2,5–8]. Among many proposed processes, a biological nitrogen removal (BNR) process can simultaneously remove phenols, ammonia, thiocyanate and cyanide. Particularly, a single-sludge process with recycle of nitrified effluent, i.e., pre-denitrification process, has been preferred in Korea because of its simplicity and economic benefits [9].

The pre-denitrification process consists of two distinct microbial reactions under anoxic or oxic condition. In anoxic condition, heterotrophic denitrifiers convert nitrite or nitrate into nitrogen gas using phenols as a carbon source, thus most of phenols are removed in this step [10]. Additionally, very toxic free cyanide can be removed to some degree by anaerobes [11]. Since free cyanide is known to be the most toxic pollutant to nitrifiers, it must be removed below 0.1 mg/L before inflowing into nitrification step [12]. In oxic condition, autotrophic nitrifiers convert ammonia into nitrite or nitrate, meanwhile autotrophic

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thiocyanate-oxidizing bacteria convert thiocyanate into ammonia and sulfate [13]. These consecutive microbial reactions can remove most of pollutants within the cokes wastewater.

However, a full-scale pre-denitrification process has often been unstable due to instability of nitrification reaction during summer season (38 °C). Therefore, the objective of this study was to examine why the nitrification process is unstable especially in summer. For it, we investigated the effects of pH, nutrients and concentrations of toxic pollutants on nitrification according to temperature.

2. Materials and methods

2.1. Activated sludge and wastewater

Activated sludge used in this study was collected from an aeration tank of a full-scale wastewater treatment facility of a cokes manufacturing plant in a steel company, Korea. It was impossible to collect influent flowing into the aeration tank where nitrification reaction occurs. Thus, test solutions were prepared similarly to the influent by dissolving the exact quantities of phenol (Junsei), KCN (Acros), KSCN (Junsei) and NH_4Cl (Samjun) in effluent of nitrification process (notice that only these toxic compounds were absent in the effluent, as shown in Table 1). Additionally, 1 g/L of $NaHCO_3$ (Samjun) was added in the test solution to supply inorganic carbon for nitrifiers, except the experiment examining effect of bicarbonate concentration.

2.2. Batch experiments

Batch experiments for nitrification reaction were carried out in 500 mL Erlenmeyer flasks (Pyrex) filled with 200 mL of test solution containing 50 mg/L of ammonia (NH_4^+) and other pollutants such as free cyanide, phenol and thiocyanate. To examine the effect of pH on nitrification according to temperature (20, 29, 38 and 45 °C), test solutions containing only 50 mg/L ammonia were adjusted to pH 6.0, 6.5, 7.0, 7.5, 8.0, 8.5 and 9.0, respectively. To examine the effects of pollutants on nitrification according to temperature (20, 29 and 38 °C), test solutions containing 50 mg/L ammonia and a pollutant (for free cyanide, 0, 0.1 and 0.2 mg/L; for phenol, 0, 100 and 200 mg/L; for thiocyanate, 0 and 200 mg/L) were adjusted to pH 8.0. Each flask was inoculated with activated sludge in the range of 2700–3400 mg/L, and then agitated on a thermostatic shaker at 200 rpm and constant temperature. During batch experiments, dissolved oxygen concentration was above 1 mg/L, and the solution pH was continuously maintained at desired value using 1 M NaOH or 1 M HCl solution. One-milliliter samples were intermittently removed from the flask to analyze ammonia, phenol and thiocyanate concentrations.

2.3. Continuous reactors

To investigate the microbial interaction between various microorganisms within activated sludge according to temperature, two continuous reactors were operated with same test solution at 29 and 38 °C, respectively. The continuous reactor was a double-jacketed glass column with an inner diameter of 10 cm and a height of 20 cm. The working volume was 500 mL and dosage of activated sludge was 2860 mg/L. The used test solution consisted of 50 mg/L ammonia, 100 mg/L phenol and 100 mg/L thiocyanate. Air was injected into the bottom part of the reactor (2 L/min) providing also mixing. Meanwhile, the flow rate of the test solution was 0.35 mL/min, i.e., hydraulic retention time (HRT) was about 1 day. During the experiments, the solution pH was maintained at 8.0, and effluents from the reactors were sampled to analyze ammonia concentration.

2.4. Analytical methods

Each sample collected from batch and continuous experiments was centrifuged at 3500 rpm for 3 min with a centrifuge (MF550, HANIL), and then the supernatant was used for analysis. Ammonia was analyzed with phenate method, phenol with chloroform extraction method, thiocyanate with reaction with ferric nitrate and cyanide with pyridine–pyrazolone method after distillation using a spectrophotometer (Spectronic 21, MILTON ROY Co.) [14]. Nitrite and nitrate concentrations were analyzed with an ion chromatograph (DX-120, DIONEX Co.).

3. Results and discussion

3.1. Effect of pH on nitrification according to temperature

Not only pH but also temperature affects biological nitrification reaction [15,16]. Thus, the effects of these parameters on nitrification should be examined together. Effects of pH on nitrification were examined by batch experiments at 20, 29, 38 and 45 °C, since full-scale pre-denitrification process has been operated in the temperature range from 20 (in winter) to 38 °C

Table 1
Compositions of influent and effluent of nitrification process in a full-scale cokes wastewater treatment facility

	COD	Phenols	Total N	NH_4^+	NO_2^-	NO_3^-	SCN^-	Total CN
Influent (mg/L)	~400	~15	~200	~40	ND	ND	~80	~13
Effluent (mg/L)	300	ND	58	ND	2.59	38.0	ND	10.33

	Free CN^-	Total organic carbon	Inorganic carbon	PO_4^{3-}	SO_4^{2-}	F^-	Cl^-	Fe
Influent (mg/L)	<0.1	~120	~40	<5	~500	~100	~1000	~5
Effluent (mg/L)	ND	80.3	24.6	3.2	1035	89.4	1150	5.13

ND, not detected.

(in summer) according to the seasonal variation. The test solution contained 50 mg/L of ammonia, but toxic pollutants such as phenol, cyanide and thiocyanate were absent. Nitrification of ammonia by activated sludge depended on both pH and temperature (Fig. 1a–d). At 20 °C, ammonia was completely nitrified to nitrite or nitrate in the pH range of 7.5–8.5 in 12 h, but not at pH 6.0. At 38 °C, ammonia was completely nitrified in the pH range of 7.5–8.0 in 4 h, but not below pH 6.0 or above pH 9.0. At 45 °C, nitrification occurred most favorably at pH 7.0, but not below pH 6.0 or above pH 9.0. At a fixed pH of 8.0, meanwhile, the nitrification rate of ammonia increased in the order 45 < 20 < 29 < 38 °C, which means that the optimum temperature was 38 °C. However, the optimum temperature at a fixed pH of 9.0 was 29 °C.

To numerically examine the effects of pH and temperature on nitrification, the specific initial nitrification rate was calculated by using initial decline slope of ammonia concentration. Temperature and pH were co-dependent (Fig. 2). At lower pH, nitrification was less dependent on temperature, but its initial rate was very slow. At higher temperature, meanwhile, nitrification was strongly dependent on pH, and its initial rate was very fast at pH 7. Interestingly, the present optimum condition for nitrification by activated sludge was 38 °C and pH 8.0, and initial nitrification rate was 8.2 mg/g h.

Although there is much information in the literature about the influences of temperature and pH on nitrification, the reported optimum condition for nitrification varies considerably. Charley et al. reported an optimum temperature of 15 °C for ammonia oxidation in a steady state of nitrification kinetics of activated sludge at various temperatures between 10 and 35 °C [17]. Buswell et al. reported 30–36 °C as the optimum for *Nitrosomonas* [18]. Painter and Loveless reported 34–35 °C as an optimum for *Nitrobacter* [19], while Laudelot and Van Tichelen found that 42 °C was the best for the same organisms [20]. Neufeld et al. indicated little or no growth below 5 °C and above

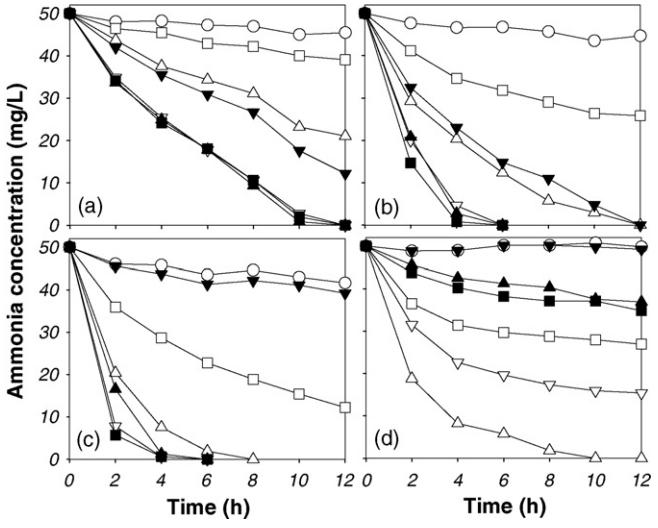

Fig. 1. Effects of pH on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C; (d) 45 °C. This study was a batch experiment. Concentration of activated sludge was 3350–3360 mg/L and ash content 19–21%. Symbols: (◯) pH 6.0; (□) pH 6.5; (△) pH 7.0; (▽) pH 7.5; (■) pH 8.0; (▲) pH 8.5; (▼) pH 9.0.

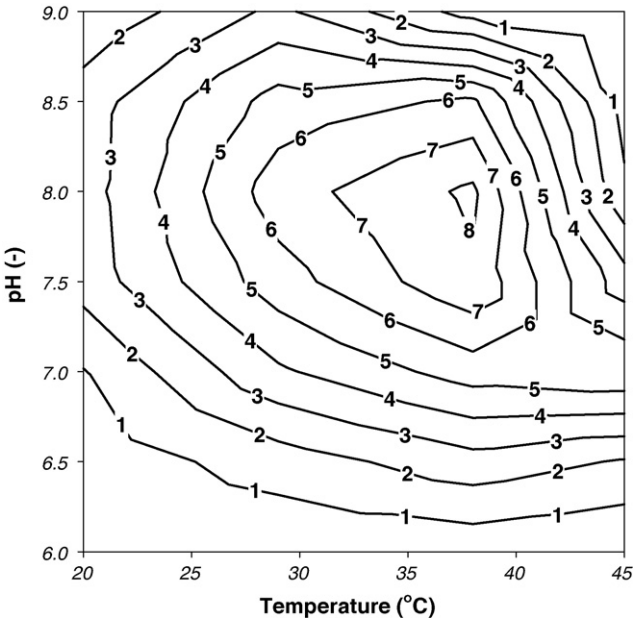

Fig. 2. Specific initial nitrification rate (mg/g h) according to pH and temperature.

45 °C for both *Nitrosomonas* and *Nitrobacter* [12]. Meanwhile, Antoniou et al. determined the dependence of the maximum specific growth rate of nitrifiers on temperature and pH [21]. By using a nonlinear regression scheme, an optimum pH of 7.8 was determined and the effective maximum specific growth rate was found to be a monotonically increasing function of temperature in the range of 15–25 °C. Painter and Loveless reported that pH 7.5–8.0 was optimum value for nitrifiers, expect at 16 °C, where the highest growth rate was achieved at pH 8.5 [15]. No nitrification was observed over a 7-week period at pH 6.0 at any temperature (16–25 °C). In conclusion, the effects of temperature and pH on nitrifiers vary due to the differences in composition and strength of the activated sludge used. It is natural that nitrification occurs more efficiently at a given condition if the activated sludge has previously been acclimatized to the condition. Therefore, results obtained from different conditions cannot be applied to actual industrial process. For this reason, activated sludge and wastewater obtained from full-scale facility were used in this study.

In the begin of this study, high temperature in summer was suspected as a major cause of unstable nitrification, but batch experiments showed that nitrification reaction with the used activated sludge was more favorable in summer than other seasons. In addition, the optimum pH for nitrification was 8.0 in the range of 20–38 °C, which was the operating condition of full-scale predenitrification process. Finally, neither temperature nor pH was the main cause of instability of nitrification process in summer.

3.2. Effect of nutrients on nitrification according to temperature

The influent flowing into nitrification step contained below 50 mg/L inorganic carbon and 5 mg/L phosphate, thus it was suspected that lack of nutrients might cause instability of nitri-

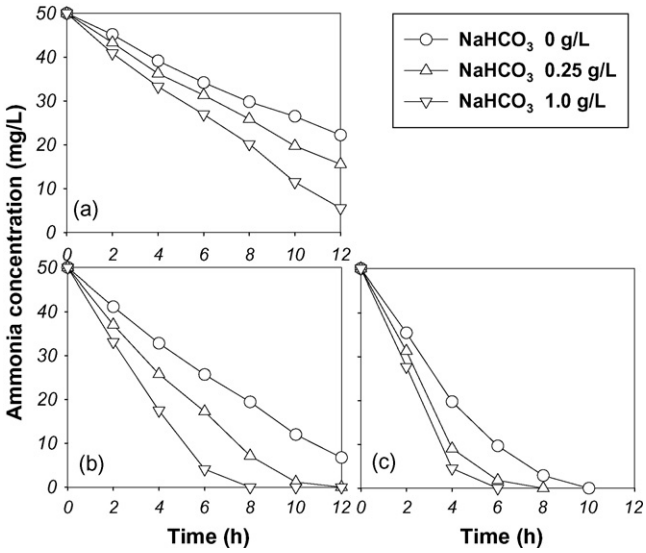

Fig. 3. Effect of bicarbonate ($NaHCO_3$) on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C. This study was a batch experiment. Concentration of activated sludge was 2720 mg/L and ash content 17%.

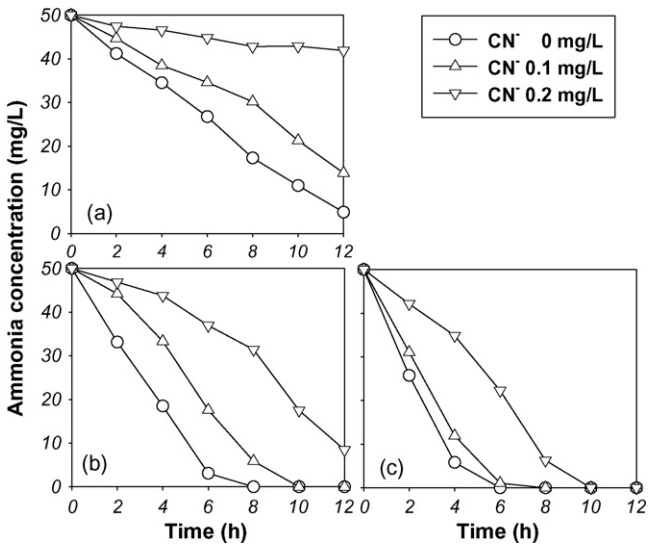

Fig. 4. Effect of free cyanide on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C. This study was a batch experiment. Concentration of activated sludge was 2720 mg/L and ash content 17%.

fication process in summer. Fig. 3 shows the effect of bicarbonate concentration on nitrification according to temperature (20–38 °C), where added inorganic carbon was in the form of $NaHCO_3$. At given temperature, nitrification rate increased with increasing bicarbonate concentration, but nitrification reaction also occurred without additional bicarbonate at all temperatures. For given bicarbonate concentration, as temperature was increased from 20 to 38 °C, nitrification rate increased. Meanwhile, addition of phosphate only slightly enhanced the nitrification rate since phosphate was micronutrient for nitrifiers (data not shown). In general, 5 mg/L of phosphate is sufficient in nitrification process [16]. In conclusion, sufficient nutrients such as bicarbonate and phosphate should be supplied to nitrification process, but the lack of these components might be not the main cause of instability of nitrification process in summer.

3.3. Effect of toxic compounds on nitrification according to temperature

Among various toxic compounds, free cyanide is known to be most toxic to nitrifiers [12,22]. Small amount of free cyanide affected nitrification reaction at all temperatures (Fig. 4). At given temperature, 0.2 mg/L of free cyanide caused serious inhibition to nitrification reaction, especially at 20 °C. However, increasing temperature reduced the negative effect of free cyanide on nitrification, i.e., 0.1 mg/L of free cyanide did not nearly inhibit nitrification at 38 °C. These results might be explained by enhanced microbial activity and evaporation of free cyanide at higher temperature. Thus, free cyanide below 0.1 mg/L was not the main cause of instability of nitrification process in summer. However, free cyanide above 0.2 mg/L can significantly inhibit nitrification in summer, but less than in other seasons.

Phenol is also known to be toxic to nitrifiers next to free cyanide [4,12]. About 200 mg/L of phenol seriously inhibited nitrification at all temperatures, but 100 mg/L of phenol inhibited it only at 20 °C (Fig. 5). Interestingly, phenol could be degraded by activated sludge (Fig. 6) since it contained various heterotrophic bacteria capable of degrading phenol under oxic condition [3,4]. As temperature was increased, the removal rate of phenol increased. This result might be explained by enhanced microbial activity and evaporation of phenol at higher temperature. However, 3 h were needed for complete removal of phenol even at 38 °C. Thus, 200 mg/L of phenol could inhibit nitrification reaction, but phenol below 100 mg/L did not inhibit it at higher temperature. As a matter of fact, there was no possibility that phenol above 50 mg/L flowed into nitrification process since most of phenol was degraded in denitrification process (Table 1).

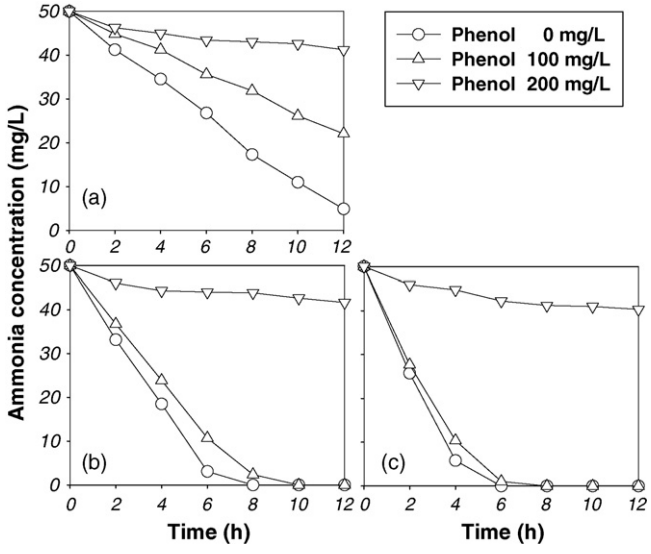

Fig. 5. Effect of phenol on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C. This study was a batch experiment. Concentration of activated sludge was 2720 mg/L and ash content 17%.

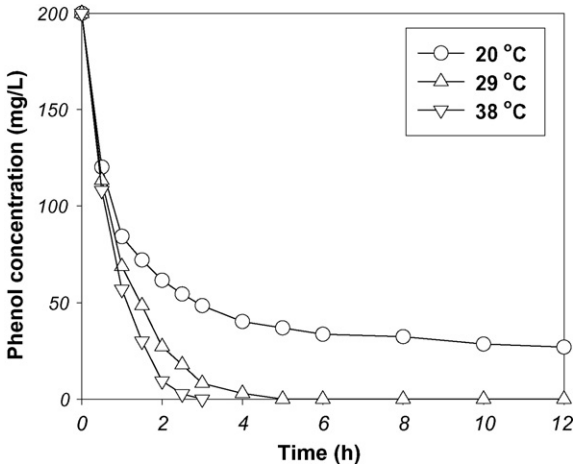

Fig. 6. Degradation of phenol during nitrification at various temperatures. This study was a batch experiment.

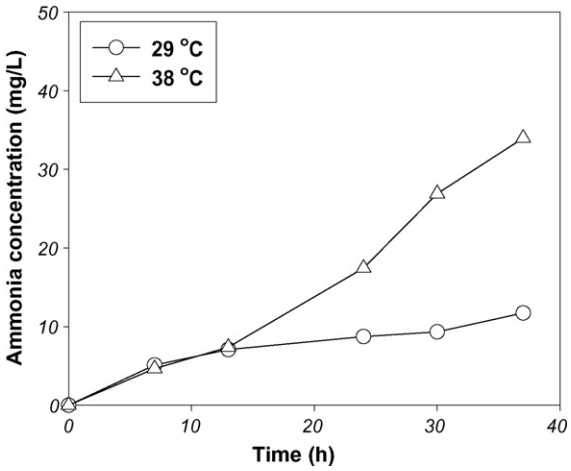

Fig. 8. Effect of temperature on nitrification in continuous flow reactor. Concentration of activated sludge was 2825 mg/L and ash content 19%.

Therefore, the instability of nitrification process in summer was not due to toxic effect of phenol on nitrifiers.

About 200 mg/L of thiocyanate seemed to inhibit nitrification reaction (Fig. 7), but it was due to production of ammonia during microbial degradation of thiocyanate itself (data not shown). As temperature was increased, degradation rate of thiocyanate increased, and its negative effect on nitrification decreased. It is well known that various bacteria within activated sludge can degrade thiocyanate into ammonia, sulphate and bicarbonate under oxic condition [13,23]. Though most of thiocyanate is flowed into nitrification process, thiocyanate below 100 mg/L generally flows into nitrification process due to the dilution effect of pre-denitrification process. Therefore, the negative effect of thiocyanate on nitrifiers was not the cause of instability of nitrification process in summer.

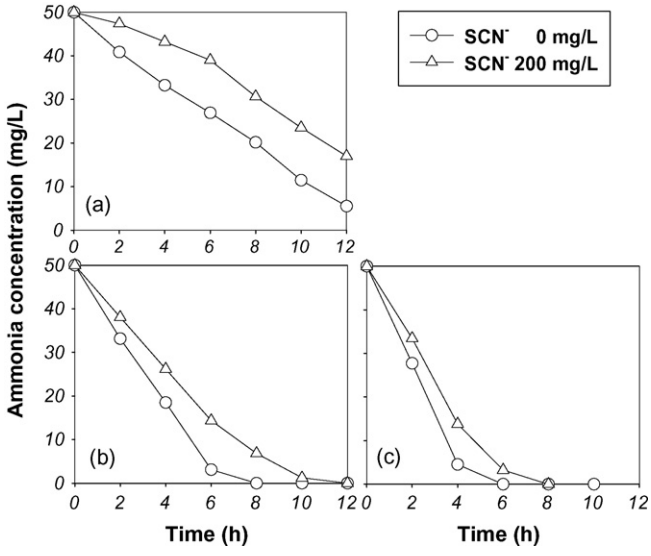

Fig. 7. Effect of thiocyanate on nitrification at: (a) 20 °C; (b) 29 °C; (c) 38 °C. This study was a batch experiment. Concentration of activated sludge was 2720 mg/L and ash content 17%.

3.4. Washing out experiment using continuous reactor

Lastly, it was suspected that microbial interaction between various microorganisms within activated sludge might cause the instability of nitrification process in summer. To identify it, two continuous reactors were operated with same test solution at 29 and 38 °C, respectively. The HRT of 1 day caused washing out of microorganisms from the reactors, thus microorganisms having slow growth rate may have washed out faster than those having faster growth rate. Nitrification efficiency decreased with increasing operation time due to washing out of nitrifiers (Fig. 8). Importantly, the reduction rate in nitrification efficiency was higher at 38 °C than at 29 °C. This result is contrary to that from batch experiments, where nitrification rate was faster at 38 °C than at 29 °C under all conditions. Therefore, the cause of unstable nitrification in summer can be explained as follows: the increasing temperature may more enhance the growth rate of other microorganisms such as heterotrophic phenol-degrading bacteria and autotrophic thiocyanate-degrading bacteria than that of nitrifiers. In general, it is known that loss of oxygen by heterotrophic bacteria is much higher than autotrophic bacteria [16], and the carbon source of thiocyanate-degrading bacteria is inorganic carbon, similarly to nitrifiers [23]. As a result, the exhaustion of oxygen and inorganic carbon by excess multiplication of these bacteria may inhibit growth of nitrifiers and lead to its washing out.

4. Conclusions

Batch experiments showed that nitrification rate of activated sludge was faster in summer (38 °C) than in spring or autumn (29 °C) and the toxic effects of cyanide, phenol and thiocyanate on nitrification were reduced with increasing temperature. Meanwhile, experiments using continuous reactor showed that the reduction rate in nitrification efficiency was higher at 38 °C than at 29 °C. In conclusion, the instability of nitrification process in summer was due to washing out of nitrifiers by fast growth of competitive microorganisms at higher tempera-

ture under increased concentrations of phenol and thiocyanate. Therefore, preventing abnormal influx of these pollutants may be one way to operate pre-denitrification process stably in summer.

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