JOURNAL OF ENVIRONMENTAL SCIENCES

ISSN 1001-0742 CN 11-26250X

May 1, 2014 Volume 26 Number 5 www.jesc.ac.cn



Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates





Sponsored by Research Center for Eco-Environmental Sciences Chinese Academy of Sciences

CONTENTS

Aquatic environment

A review of environmental characteristics and effects of low-molecular weight organic acids in the surface ecosystem
Min Xiao, Fengchang Wu·····935
Review on water leakage control in distribution networks and the associated environmental benefits
Qiang Xu, Ruiping Liu, Qiuwen Chen, Ruonan Li ······955
Synthesis of carbon-coated magnetic nanocomposite (Fe3O4@C) and its application for sulfonamide antibiotics removal from water
Xiaolei Bao, Zhimin Qiang, Jih-Hsing Chang, Weiwei Ben, Jiuhui Qu962
Removal of phosphate from wastewater using alkaline residue
Yubo Yan, Xiuyun Sun, Fangbian Ma, Jiansheng Li, Jinyou Shen, Weiqing Han, Xiaodong Liu, Lianjun Wang970
Immunotoxic effects of an industrial waste incineration site on groundwater in rainbow trout (Oncorhynchus mykiss)
Nadjet Benchalgo, François Gagné, Michel Fournier ·····981
Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates (Cover story)
Zhilong Ye, Yin Shen, Xin Ye, Zhaoji Zhang, Shaohua Chen, Jianwen Shi991
Adaptation of microbial communities to multiple stressors associated with litter decomposition of Pterocarya stenoptera
Gaozhong Pu, Jingjing Tong, Aimeng Su1, Xu Ma, Jingjing Du, Yanna Lv, Xingjun Tian 1001
Effect of alkalinity on nitrite accumulation in treatment of coal chemical industry wastewater using moving bed biofilm reactor
Baolin Hou, Hongjun Han, Shengyong Jia, Haifeng Zhuang, Qian Zhao, Peng Xu ····· 1014
Distribution and seasonal variation of estrogenic endocrine disrupting compounds, N-nitrosodimethylamine,
and N-nitrosodimethylamine formation potential in the Huangpu River, China
Ai Zhang, Yongmei Li, Ling Chen 1023
Effects of ferrous and manganese ions on anammox process in sequencing batch biofilm reactors
Xiaoli Huang, Dawen Gao, Sha Peng, Yu Tao ······ 1034

Atmospheric environment

Shilei Long, Jianrong Zeng, Yan Li, Liangman Bao, Lingling Cao, Ke Liu, Liang Xu, Jun Lin, Wei Liu, Guanghua Wang, Jian Yao, Chenyan Ma, Yidong Zhao	Characteristics of secondary inorganic aerosol and sulfate species in size-fractionated aerosol particles in Shanghai	
Guanghua Wang, Jian Yao, Chenyan Ma, Yidong Zhao	Shilei Long, Jianrong Zeng, Yan Li, Liangman Bao, Lingling Cao, Ke Liu, Liang Xu, Jun Lin, Wei Liu,	
1-vehicle VOCs composition of unconditioned, newly produced cars Krzysztof Brodzik, Joanna Faber, Damian Łomankiewicz, Anna Gołda-Kopek	Guanghua Wang, Jian Yao, Chenyan Ma, Yidong Zhao 1	1040
Krzysztof Brodzik, Joanna Faber, Damian Łomankiewicz, Anna Gołda-Kopek	In-vehicle VOCs composition of unconditioned, newly produced cars	
ulfur evolution in chemical looping combustion of coal with MnFe ₂ O ₄ α xygen carrier	Krzysztof Brodzik, Joanna Faber, Damian Łomankiewicz , Anna Gołda-Kopek	1052
anar evolution in enemieta rooping combastion of coar with him e ₂ of on gen carrier	Sulfur evolution in chemical looping combustion of coal with MnFe ₂ O ₄ oxygen carrier	
Baowen Wang, Chuchang Gao, Weishu Wang, Haibo Zhao, Chuguang Zheng	Baowen Wang, Chuchang Gao, Weishu Wang, Haibo Zhao, Chuguang Zheng	1062
and evolution in chemical recepting contraction of coal with third e ₂ of on/gen carrier	Sulfur evolution in chemical looping combustion of coal with MnFe ₂ O ₄ oxygen carrier	1032

Terrestrial environment

-microbe associated bioremediation of phenanthrene and pyrene contaminated soil by SDBS-Tween 80 mixed surfactants
Venjun Zhou, Lizhong Zhu ····· 1071
al uptake of energy sugarcane (Saccharum spp.) in different metal mine tailings with soil amendments
Yongguan Zhu, Yuebin Zhang, Yunxia Liu, Shaochun Liu, Jiawen Guo, Rudan Li, Songlin Wu, Baodong Chen 1080
omoting integrated floating bed and its experimental performance in eutrophication remediation
o, Yunguo Liu, Guangming Zeng, Xinjiang Hu, Xin Li, Dawei Huang, Yunqin Liu, Yicheng Yin 1090
Smoting integrated floating bed and its experimental performance in eutrophication remediation b, Yunguo Liu, Guangming Zeng, Xinjiang Hu, Xin Li, Dawei Huang, Yunqin Liu, Yicheng Yin

Environmental biology

Environmental health and toxicology

Primary neuronal-astrocytic co-culture platform for neurotoxicity assessment of di-(2-ethylhexyl) phthalate Yang Wu, Ke Li, Haoxiao Zuo, Ye Yuan, Yi Sun, Xu Yang 1145
Environmental catalysis and materials
Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation
Jinjun Tu, Zhendong Yang, Chun Hu, Jiuhui Qu ······ 1154
Effects of particle composition and environmental parameters on catalytic hydrodechlorination of trichloroethylene
by nanoscale bimetallic Ni-Fe
Jianjun Wei, Yajing Qian, Wenjuan Liu, Lutao Wang, Yijie Ge, Jianghao Zhang, Jiang Yu, Xingmao Ma
Heterogeneous Fenton-like degradation of 4-chlorophenol using iron/ordered mesoporous carbon catalyst
Feng Duan, Yuezhu Yang, Yuping Li, Hongbin Cao, Yi Wang, Yi Zhang
Photocatalytic removal of NO and NO2 using titania nanotubes synthesized by hydrothermal method
Nhat Huy Nguyen, Hsunling Bai ······ 1180
Efficient dechlorination of chlorinated solvent pollutants under UV irradiation by using the synthesized TiO2 nano-sheets in aqueous phase
Landry Biyoghe Bi Ndong, Murielle Primaelle Ibondou, Zhouwei Miao, Xiaogang Gu,
Shuguang Lu, Zhaofu Qiu, Qian Sui, Serge Maurice Mbadinga ····· 1188
Biogenic C-doped titania templated by cyanobacteria for visible-light photocatalytic degradation of Rhodamine B
Jiao He, Guoli Zi, Zhiying Yan, Yongli Li, Jiao Xie, Deliang Duan, Yongjuan Chen, Jiaqiang Wang
Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent
Genlin Zhang, Lijuan Yi, Hui Deng, Ping Sun ····· 1203
Serial parameter: CN 11-2629/X*1989*m*277*en*P*29*2014-5

Journal of Environmental Sciences 26 (2014) 1014-1022



Available online at www.sciencedirect.com

www.jesc.ac.cn

Journal of Environmental Sciences



Effect of alkalinity on nitrite accumulation in treatment of coal chemical industry wastewater using moving bed biofilm reactor

Baolin Hou, Hongjun Han*, Shengyong Jia, Haifeng Zhuang, Qian Zhao, Peng Xu

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China, E-mail: hbl527@163.com

ARTICLE INFO

Article history: Received 22 June 2013 revised 31 October 2013 accepted 07 November 2013

Keywords: alkalinity nitritation coal chemical industry wastewater moving bed biofilm reactor DOI: 10.1016/S1001-0742(13)60517-3

ABSTRACT

Nitrogen removal via nitrite (the nitrite pathway) is more suitable for carbon-limited industrial wastewater. Partial nitrification to nitrite is the primary step to achieve nitrogen removal via nitrite. The effect of alkalinity on nitrite accumulation in a continuous process was investigated by progressively increasing the alkalinity dosage ratio (amount of alkalinity to ammonia ratio, mol/mol). There is a close relationship among alkalinity, pH and the state of matter present in aqueous solution. When alkalinity was insufficient (compared to the theoretical alkalinity amount), ammonia removal efficiency process with increasing alkalinity dosage ratio. Ammonia removal efficiency rose with increasing alkalinity dosage ratio. Ammonia removal efficiency rose with increasing alkalinity dosage ratio. Nitrite accumulation could be achieved by inhibiting nitrite oxidizing bacteria (NOB) by free ammonia (FA) in the early period and free nitrous acid in the later period of nitrification when alkalinity was not adequate. Only FA worked to inhibit the activity of NOB when alkalinity addition was sufficient.

Introduction

With human progress and the improvement of living standards, an increasing amount of contaminants containing nitrogen have been discharged into the environment. The large amount of nitrogen discharged into water bodies has undermined the nitrogen cycle in nature, causing world-wide eutrophication that occurs repeatedly. Nitrogen removal has been a hot and difficult research issue in the environmental protection area. Numerous new theories and technology have been developed on the basis of traditional treatment theories and processes. Several typical new theories and processes have emerged such as: nitrogen removal via nitrite pathway (Hellinga et al., 1998; Van Hulle et al., 2007), anaerobic ammonium oxidation (Mulder et al., 1995; Strous et al., 1998), the combination of partial nitrification to nitrite and anaerobic ammonium oxidation (CANON) (Strous et al., 1999; Third et al., 2001)

* Corresponding author. E-mail: han13946003379@163.com

and the enhanced biological nitrification bacteria process (Salem et al., 2002), drawing a considerable amount of attention of scholars. New nitrogen removal theories and processes have shown great advantages compared to traditional theories and technology, especially nitrogen removal via the nitrite pathway and CANON, which are both based on partial nitrification to nitrite. The nitrite pathway is a more practical process among these new processes. Theoretically, nitrogen removal via nitrite yields a 25% reduction in oxygen demand and 40% reduction in carbon source requirement for denitrification.

Coal chemical industry wastewater is discharged in the processes of coal gasification and coal chemical production (Yang et al., 2006; Wang et al., 2010), the composition of which is very complex, containing various toxic compounds and a large number of refractory organic and inorganic contaminants, with poor biodegradability (Marañón et al., 2008). The wastewater characteristics vary significantly according to the coal quality used in the production. More than 244 kinds of organic compounds have been detected in the wastewater. Phenolic compounds are the main pollutants. The wastewater also contains polycyclic aromatic hydrocarbons, heterocyclic compounds, long-chain hydrocarbons, ammonia, cyanide and thiocyanate (Nakhla et al., 1990; Gai et al., 2008; Felföldi et al., 2010; Yu et al., 2010). Although the wastewater is pretreated via ammonia-stripping, it also contains a high concentration of ammonia. Nitrogen removal was unsatisfactory in the suspended activated sludge process due to the presence of toxic and inhibitory matter and limited available carbon sources (Kumar et al., 2000). Under high concentrations of phenolic compounds and inhibitors, nitrifying bacteria were out-competed in the suspended activated sludge system by the fast growth of heterotrophic microorganisms (Kim et al., 2007). However, the moving bed biofilm reactor has proved to be an effective process to remove both organic contaminants and ammonia in the treatment of coal chemical industry wastewater (Li et al., 2011). Considering the limited carbon source characteristic and complex composition of coal chemical industry wastewater, nitrogen removal via a nitrite pathway that requires less carbon source is a desirable method for the treatment of coal chemical industry wastewater. Alkalinity plays a vital role in nitrification, especially carbonate alkalinity. Alkalinity is not only the inorganic carbon source of heterotrophic nitrifying bacteria, but also balances the acid-base level of the mixture, affecting the state of matter present in aqueous solution. In this context, a moving bed biofilm reactor (MBBR) was adopted to treat coal chemical industry wastewater to investigate the effects of variations of nitrogen and alkalinity on the treatment process. The study involved five operation phases with different alkalinity dosage ratios. The effect of alkalinity on nitrification to nitrite and nitrite accumulation were the key issues to be investigated. The evolution of NH_4^+-N removal and nitrite accumulation were studied by raising the alkalinity dosage ratio stepwise.

1 Materials and methods

1.1 Experimental apparatus

The MBBR was a cylindrical Plexiglas reactor with an internal diameter of 120 mm and height of 450 mm. The effective volume of the MBBR was 4.85 L, followed by a 0.5 L settling tank. The suspended carriers used in the MBBR were circular polyethylene flakes, with a diameter of 22 mm and thickness of 1.5 mm. The density of the carriers was about 0.86 g/cm³, lower than that of water. The density of carriers with attached wet biofilm was 1.11 g/cm³. The filling ratio (volumetric filling in empty reactor) was 35%.

1.2 Inoculum and wastewater characteristics

Seed was collected from a full-scale coal chemical industry wastewater treatment plant in Harbin, China. The sludge was gray-black and the settling characteristic was good with a sludge volume index of 83.

Real coal chemical industry wastewater used in this study was obtained from the full-scale wastewater treatment facility of a coal chemical plant in Harbin, China. The characteristics of the wastewater as following: COD 895–1109 mg/L with mean value 1065 mg/L, total phenol 198–249 with mean 226 mg/L, NH_4^+ -N 92–118 mg/L with mean 108 mg/L, and pH 6.5–7.5 with mean 7.16. Considering the fluctuations in the parameters of the real wastewater, the main parameters in the influent were controlled by adding tap water into the real wastewater. The concentration of ammonia was adjusted by adding ammonia chloride. Sodium bicarbonate was added to control alkalinity.

1.3 Experiment operation

Initially, the reactor ran for 30 days as a batch system after being inoculated with the seed sludge obtained from the full-scale facility, followed by a continuous flow process. A stable biofilm was formed on the carriers, with the biomass of 0.28 g VSS/g. During batch culture, the reactor was fed with the real wastewater diluted by adding tap water, with the COD concentration increasing stepwise from 500 to 1000 mg/L in three steps. The hydraulic retention time was 36 hr in the continuous flow process during the experimental period. The motion of carriers was driven by aeration introduced at the bottom of the reactor and the dissolved oxygen (DO) concentration was kept around 1.8 mg/L. The experiment operation was divided into 5 phases (**Table 1**) and the temperature was controlled at $(25 \pm 2)^{\circ}$ C throughout the experiment.

Table 1 Operational conditions				
Phase	Time (days)	COD (mg/L)	Total phenols (mg/L)	NaHCO ₃ (dosage ratio)
I	1–15	1002.65 ± 11.72	208.99 ± 5.24	_
II	16-30	501.95 ± 7.37	114.26 ± 5.38	_
III	31-45	504.28 ± 9.44	115.50 ± 5.66	2:1
IV	45-60	1000.46 ± 9.51	210.66 ± 6.89	2:1
V	61–75	998.78 ± 8.45	209.72 ± 5.83	0.5:1
	76–90			1:1
	91-105			1.5:1
	106-120			2:1
	121-135			2.5:1

*Dosage ratio: defined as the molar ratio of sodium bicarbonate to ammonia

Jesc. ac. ch

1.4 Specific oxygen uptake rate test

Specific oxygen uptake rate (SOUR) is an important parameter to assess the activity of activated sludge. Table 2 lists the substrate solutions for SOUR measurement. The SOUR test was conducted to investigate the distribution characteristics of the two kinds of nitrifying microorganism, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). Activated sludge from different samples was first separately maintained at 20°C and was continuously aerated to saturate it with a sufficient DO concentration. Then the activated sludge was centrifuged at the speed of 1400 r/min for 3 min. The centrifuged sludge samples were rinsed to wash out the NH_4^+ , NO_2^- and $NO_3^$ adsorbed on the sludge. The substrate solutions (Table 2) were aerated for 2 hr to saturate the DO concentration at 20°C. The pretreated sludge and substrate solution were mixed into a 300 mL dissolved oxygen bottle, and the initial mixed liquor volatile suspended solids (MLVSS) was kept at 200 \pm 20 mg VSS/L. Then each bottle was sealed carefully with a rubber stopper equipped with an IntelliCAL LDO probe (101, HACH, USA), without air bubbles inside. The mixtures were then incubated at 20°C and stirred with a magnetic stirrer. The DO concentration in each bottle was continuously monitored. The SOUR of each sample equaled the linear regression slope of the DO drop vs. time divided by the VSS concentration in the bottle. All batch tests were preformed in triplicate.

The substrate solution for SOUR measurement of AOB was without an organic carbon source or nitrite (**Table 2**). A 20-mmol NaClO₃ was added to the mixed solution as inhibitor to selectively prevent nitrite from being oxidized to nitrate (Belser and Mays, 1980; Hynes and Knowles, 1983). Allylthiourea (5 mg/L) was added into the feed solution for SOUR measurement of NOB as a selective inhibitor to keep ammonia from being oxidized to nitrite (Wood et al., 1981; Chung et al., 2006), because a small

amount of ammonia might be left in the sludge or arise from endogenous nitrification. 100 mg/L COD was supplied by the coal chemical industry wastewater in terms of feed solution for SOUR measurement of heterotrophic microorganisms. Both selective inhibitors were added into the feed solution for SOUR measurement of heterotrophic microorganisms due to coal chemical industry wastewater including ammonia and nitrite. The endogenous respiration rate of the activated sludge was tested as blank. The substrate solution for blank measurement was without organic compounds, ammonia or nitrite, having minerals only. The net SOUR of each kind of microorganism was calculated by subtracting the SOUR caused by the endogenous respiration rate from the measured SOUR.

1.5 Analytical methods

COD, NH_4^+ -N, NO_2^- -N, NO_3^- -N were measured daily in accordance with standard methods (APHA, 1998). Bicarbonate alkalinity was determined by a distillation method. pH and DO were measured using a pHC101 probe and IntelliCAL LDO probe, both of which were connected to a multifunction meter (HQ30d, HACH, USA).

2 Results and discussion

2.1 Relationships among alkalinity, pH and ion form

Generally, pH is in the range of 6.5–8.5 in common biological wastewater treatment systems, the alkalinity of which is composed of carbonate alkalinity (CO_3^{2-} , HCO_3^{-} and CO_2). There is also a buffer capacity in the carbonate balance system. The relationship between alkalinity and pH in the carbonate system is shown in **Fig. 1**.

The dissociation equilibrium in a carbonate solution

	Compound	Heterotrophic microorganism	AOB	NOB	Blank
Electron donor	Coal chemical industry wastewater (mg/L)	100	_	_	_
	NH ₄ Cl (mg/L)	_	100	_	-
	NaNO ₂ (mg/L)	-	_	100	-
Buffer	KH ₂ PO ₄ (mg/L)	0.85	0.85	0.85	0.85
	K ₂ HPO ₄ (mg/L)	2.1	2.1	2.1	2.1
	Na2HPO4·7H2O (mg/L)	3.3	3.3	3.3	3.3
Inorganic salt	MgSO ₄ ·7H ₂ O (mg/L)	2.2	2.2	2.2	2.2
	CaCl ₂ (mg/L)	2.7	2.7	2.7	2.7
	FeCl ₃ ·6H ₂ O (mg/L)	0.25	0.25	0.25	0.25
	KCl (mg/L)	3.2	3.2	3.2	3.2
	MnSO ₄ ·H ₂ O (mg/L)	1.6	1.6	1.6	1.6
	NaHCO ₃ (mg/L)	800	800	800	800
Inhibitor	NaClO ₃ (mmol)	20	20	-	-
	Allylthiourea (mg/L)	5	_	5	-
				°	



8

system can be described as following Reaction (1).

$$\operatorname{CO}_2 + \operatorname{H}_2 \operatorname{O} \longleftrightarrow \operatorname{H}_2 \operatorname{CO}_3 \longleftrightarrow \operatorname{H}^+ + \operatorname{HCO}_3^- \longleftrightarrow 2\operatorname{H}^+ + \operatorname{CO}_3^{2-} (1)$$

 CO_2 in water mainly exists in dissolved gas molecule form. Only a small part of CO_2 dissolved in water reacts with water to form carbonic acid. The sum of the two is referred as to free carbon dioxide. The first dissociation equilibrium constant can be calculated by Eq. (2):

$$K_1 = \frac{[\mathrm{H}^+][\mathrm{HCO}_3^-]}{\mathrm{H}_2\mathrm{CO}_3^-} = \frac{[\mathrm{H}^+][\mathrm{HCO}_3^-]}{[\mathrm{CO}_2] + [\mathrm{H}_2\mathrm{O}]}$$
(2)

$$K_1 = 4.45 \times 10^{-7}$$
 at 20°C.

The second dissociation equilibrium constant of HCO_3^- can be calculated by Eq. (3)

$$K_2 = \frac{[\mathrm{H}^+][\mathrm{CO}_3^{2^-}]}{\mathrm{HCO}_3^-}$$
 $K_2 = 4.69 \times 10^{-11} \text{ at } 20^\circ \mathrm{C}.$ (3)

The proportions of CO_2 , HCO_3^- and CO_3^{2-} change with the variation of pH as shown in **Fig. 2**.

Ammonia is the energy and nitrogen source of nitrifying bacteria. Free ammonia (FA) is the real growth substrate



Fig. 2 Variation of form proportion with pH in carbonate system

of AOB, while a high concentration of FA shows an inhibitory effect on the activity of AOB and NOB. Forms of nitrogen in ammonia solution include NH_3 and NH_4^+ , between which there is dissociation equilibrium (Reaction (4)).

$$NH_3 + H_2O \Longleftrightarrow NH_4^+ + OH^-$$
(4)

The proportion of FA can be estimated using Eq. (5).

$$\frac{C_{\rm FA}}{C_{\rm TNH_3}} = \frac{10^{\rm pH}}{K_{\rm b}/K_{\rm w} + 10^{\rm pH}}$$
(5)

where, $K_{\rm b}$ is the dissociation equilibrium constant ($K_{\rm b} = 10^{-4.7}$ at 20°C). $K_{\rm w}$ is the ion product constant of water, ($K_{\rm w} = 1 \times 10^{-14}$ at 20°C).

Free nitrous acid (FNA) is the feed of NOB; it can also inhibit the growth and activity of both AOB and NOB. The concentration of FNA (C_{FNA}) at different pH can be calculated by Eq. (6):

$$\frac{C_{\rm FNA}}{C_{\rm TNH_2}} = \frac{1}{1 + K_a \times 10^{\rm pH}}$$
(6)

where, K_a is the dissociation equilibrium constant of nitrous acid ($K_a = 10^{-4.5}$ at 20°C). The proportion of FA and FNA as a function of pH can be calculated by Eqs. (5) and (6) (**Fig. 3**).

Alkalinity plays an important role in terms of both growth substrate and environment for microorganisms, especially in establishing a balanced system for the growth of AOB and NOB in the control of nitritation.

2.2 SOUR

The SOUR experiments were performed to assess the microbial distribution for sludge obtained from different periods. The proportions of the three kinds of microorganisms in activated sludge could be estimated according to the SOUR. **Figure 4** shows the decline of DO concentration per unit biomass and time of sludge collected from



Fig. 3 Proportion of FA and FNA in the corresponding system.



different phases for three kinds of electron donors. After blank correction, the slope of each line represented the SOUR of the different microbial groups.

For organics (expressed as COD) oxidation, the SOURs of suspended and attached activated sludge in MBBR were 9.110 mg O₂/(g VSS·hr) and 9.360 mg O₂/(g VSS·hr), respectively, both higher than that of raw sludge (6.692 mg $O_2/(g VSS \cdot hr)$), which demonstrated that the ability for organic contaminant (mainly phenolic compounds) degradation of activated sludge in the MBBR was promoted after domestication. The SOUR difference of suspended and attached activated sludge was not significant. The SOURs for the ammonia oxidation by suspended and attached sludge in the MBBR were 3.5 and 4 times higher than that of the original sludge respectively, suggesting that the biomasses of AOB in suspended and attached activated sludge were 3.5 and 4 times higher, assuming AOB in different sources with similar activity. For nitrite oxidation, the SOUR of raw sludge was estimated to be 3.5 times higher than that of the sludge in the MBBR. The distribution ratio of AOB to NOB was 1.65 assuming similar microbial activity, implying the presence of more AOB compared to NOB. In comparison, the ratios for suspended and attached activated sludge were calculated to be 18.67 and 25.73, indicating that AOB was dominant in the MBBR. The results indicated that there was a significant difference in microbial distribution for different activated sludge. In addition, AOB was more easily adapted for attached growth to the carrier. NOB was gradually eliminated by heterotrophic microorganisms and AOB via the synergetic inhibition of FA and FNA (Park et al., 2010a), when carbon source and DO were the limiting factors.

2.3 Ammonia removal efficiency

Treatment effectiveness during the first four phases is shown in **Fig. 5**. Removal of COD and total phenols stabilized after operation for about 7 days, and removal efficiency of COD and total phenols reached 81% and 90%

respectively. However, ammonia removal efficiency was no more than 20%. COD and total phenol concentrations were reduced by half in the second phase by dilution with tap water. Removal of COD and total phenols were still stable and rose slightly, while ammonia removal was not enhanced yet. The SOUR test indicated that the sludge contained a certain amount of AOB. Ammonia removal efficiency was not promoted by diluting the contaminant concentrations, implying that toxic compounds in the coal chemical industry effluent were not the key factor inhibiting nitrification.

Sodium bicarbonate was added to supplement alkalinity from the third phase on, with the dosage ratio of 2:1. Ammonia removal efficiency ascended rapidly from 20% to 88% after adding sodium bicarbonate. Augmentation of the pollutant concentration in the influent induced a sudden rise of NH_4^+ -N in the effluent (IV phase), while NH_4^+ -N removal efficiency returned to the normal level (88%) in 4 days. The result suggested that alkalinity played a vital role in ammonia removal and was an important factor affecting AOB. The investigation also demonstrated that the toxicity of coal chemical industry wastewater was not the main inhibitory factor for nitrification.

The evolution of NH_4^+ -N in the influent and effluent on heightening the alkalinity dosage ratio stepwise is illustrated in **Fig. 6**. NH_4^+ -N removal efficiency dropped from 90% to 31% rapidly when the alkalinity dosage ratio varied between 2.0:1 and 0.5:1. NH_4^+ -N removal efficiency ascended to 72% and then fell to 40% when the alkalinity dosage ratio rose to 1.0:1. The level of NH_4^+ -N in the effluent at the dosage ratio of 1.5:1 was similar to that at the dosage of 1.0:1. When alkalinity was sufficient (dosage ratio $\ge 2.0:1$), NH_4^+ -N removal efficiency stabilized at around 89%.

NH⁴₄-N removal increased first and then decreased, stabilizing at a low level when alkalinity addition was insufficient. Each 1.0 mol ammonia nitrification consumes 2.0 mol alkalinity theoretically, according to the nitri-



fication chemical equation. Alkalinity consumption will attenuate the buffering capacity of the mixture, and result in a diminution of pH. On one hand, the fall of pH lowered the FA concentration, which was the real feed for AOB (Bagchi et al., 2010). According to the Monod equation, the reaction rate changes from a zero-order reaction to a pseudo first-order reaction when the substrate concentration decreases, especially when less than the saturation constant, causing the reduction of NH_4^+ -N removal. On the other hand, the drop of pH attenuated the microbial activity of AOB, hindering nitrification. A peak was observed in terms of NH₄⁺-N removal efficiency at each alkalinity dosage ratio when it increased from 0.5:1 to 1.5:1 stepwise. The peak removal efficiency exceeded the theoretical amount of NH₄⁺-N removal (calculated by the ratio of alkalinity to sufficient alkalinity). It was difficult to give a definite reason for the peak, and this requires further study. NH₄⁺-N removal was stable when alkalinity was adequate due to the successful nitrification, and this environmental condition was suitable for the growth and metabolism of nitrifying bacteria.

2.4 Nitrite accumulation

Nitrite accumulation is the primary step for biological nitrogen removal via nitrite. The evolution of nitrite accu-

mulation throughout the experiment is illustrated in Fig. 7. The nitrite accumulation rate was very low when no extra alkalinity was added (phases I and II), and a small amount of nitrite accumulation was obtained at the end of phase II. 84% nitrite accumulation emerged with sufficient alkalinity addition (phases III and IV), which suggested that alkalinity was not only essential for ammonia removal, but also played a vital role in nitrite accumulation. The nitrite accumulation rate dropped to 37% in a short period of time when the alkalinity dosage ratio declined from 2:1 to 0.5:1. The nitrite accumulation rate continued to decrease and was stable at 30% when the alkalinity dosage ratio rose to 1.0:1. The nitrite accumulation rate rose to 84% and then dropped to 75% when the alkalinity dosage ratio increased to 1.5:1. The nitrite accumulation rate reached 96% when alkalinity addition was adequate (dosage ratio $\ge 2.0:1$).

One of the essential requirements for nitrite accumulation is taking measures to suppress the activity of NOB but with no effect on AOB. According to the SOUR test, AOB was dominant compared to NOB in the reactor. However, the small amount of NOB would attenuate nitrite accumulation because nitrite oxidation to nitrate was much easier than ammonia oxidation to nitrite in the two-step nitrification. AOB are inhibited by FA in the range of 10– 150 mg/L, while NOB are more sensitive to FA in the range of 0.1–1.0 mg/L (Anthonisen et al., 1976; Park and





Fig. 7 Variations of nitrite accumulation rate at different alkalinity dosage ratios.

Bae, 2009); and it was found that NOB could be inhibited completely by impeding the respiration if the FA level was higher than 6.0 mg/L (Vadivelu et al., 2007). The inhibitory concentrations of FNA for AOB and NOB were 0.4 mg/L and 0.02 mg/L respectively (Vadivelu et al., 2006a, 2006b). Therefore, the activity of NOB could be suppressed by the double inhibitions of sensitivity difference to FA and FNA. A triple inhibition was formed when combined with low DO concentration. The pH of the influent was around 7.0 without sodium bicarbonate addition. Although the total ammonia in the influent was about 100 mg/L, the proportion of FA was small (Fig. 3, Eq. (5)), and was not up to the level to inhibit NOB, resulting in a low nitrite accumulation rate. When a small amount of sodium bicarbonate was added, pH in the influent rose and FA reached the concentration range that inhibited NOB, inducing the increase of nitrite accumulation rate. pH was decreased by the H⁺ generated in the nitrification. The inhibition of FA toward NOB then disappeared due to the fall of pH, and the nitrite accumulation rate dropped. The biological activity of NOB was inhibited by the FA in the influent when the alkalinity dosage ratio was 1.5:1, leading to the increase of nitrite accumulation rate. The consumption of alkalinity during the nitrification reaction lowered the pH. The inhibitory effect of FA on NOB continued to weaken and even disappeared because of the continuous decrease of pH, and the nitrite accumulation rate declined accordingly. With the continuous diminution of pH, the proportion of FNA in the accumulated nitrite rose and arrived at the inhibitory level to NOB (Torà et al., 2010). Then nitrite accumulation no longer declined. When alkalinity addition was sufficient, FA was sufficient to inhibit NOB, and the nitrite accumulation rate was maintained at a high level (Park et al., 2010b). It was · Jose . ac . ch found that the inhibitory effects of FA and FNA on NOB

were temporary. When inhibition terminated, the activity of NOB revived.

3 Conclusions

pH affected the form of NH_4^+ -N and nitrite present in aqueous solution, and there was a negative correlation between the two. Alkalinity plays an important role in terms of both growth substrate and environment for microorganisms, especially in establishing a balanced system for the growth of AOB and NOB in the control of nitritation.

The biomasses of AOB in suspended and attached activated sludge were 3.5 and 4 times higher than that of the original sludge. The distribution ratio of AOB to NOB was about 1.65 in the raw sludge, while the ratios for suspended and attached activated sludge were calculated to be 18.67 and 25.73, indicating that AOB was dominant in the MBBR.

Alkalinity was a vital factor in ammonia removal. NH_4^+ -N removal efficiency rose from 13% to 88% when adequate sodium bicarbonate was added. NH_4^+ -N removal increased first and then decreased, stabilizing at a low level when alkalinity addition was insufficient. A peak was observed in terms of NH_4^+ -N removal efficiency at each alkalinity dosage ratio when it increased from 0.5:1 to 1.5:1 stepwise. The reason for the peak removal needs to be further studied. Generally, NH_4^+ -N removal efficiency increased with the increase of the alkalinity dosage ratio.

Nitrite accumulation could be achieved via the double inhibition of FA and FNA at low DO concentration when alkalinity addition was not sufficient. Initially, inhibition by FA toward NOB was employed to realize nitrite accumulation. The fall of pH enhanced the inhibitory effect of FNA on NOB along with the nitrifying process. Only the inhibitory effect of FA on NOB worked when alkalinity was adequate. The inhibitory effects of FA and FNA on NOB were temporary. When inhibition terminated, the activity of NOB revived.

Acknowledgments

This work was supported by the State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. 2013DX10) and the National Water Special Funds of China (No. 2008ZX07207).

REFERENCES

- Anthonisen, A.C., Loehr, R.C., Prakasam, T.B., Srinath, E.G., 1976. Inhibition of nitrification by ammonia and nitrous acid. J. Water Pollut. Control Fed. 48(5), 835–852.
- APHA, 1998. Standard Methods for Examination of Water and Wastewater (20th ed.). American Public Health Association, Washington DC, USA.

- Bagchi, S., Biswas, R., Nandy, T., 2010. Alkalinity and dissolved oxygen as controlling parameters for ammonia removal through partial nitritation and ANAMMOX in a single-stage bioreactor. J. Ind. Microbiol. Biot. 37(8), 871–876.
- Belser, L.W., Mays, E.L., 1980. Specific inhibition of nitrite oxidation by chlorate and its use in assessing nitrification in soils and sediments. Appl. Environ. Microb. 39(3), 505–510.
- Chung, J., Shim, H., Park, S.J., Kim, S.J., Bae, W., 2006. Optimization of free ammonia concentration for nitrite accumulation in shortcut biological nitrogen removal process. Bioproc. Biosyst. Eng. 28(4), 275–282.
- Felföldi, T., Székely, A.J., Gorál, R., Barkcs, K., Scheirich, G., Andrs, J. et al., 2010. Polyphasic bacterial community analysis of an aerobic activated sludge removing phenols and thiocyanate from coke plant effluent. Bioresource Technol. 101(10), 3406–3414.
- Gai, H., Jiang, Y., Qian, Y., Kraslawski, A., 2008. Conceptual design and retrofitting of the coal-gasification wastewater treatment process. Chem. Eng. J. 138(1-3), 84–94.
- Hellinga, C., Schellen, A.A.J.C., Mulder, J.W., van Loosdrecht, M.C.M., Heijnen, J.J., 1998. The SHARON process: An innovative method for nitrogen removal from ammonium-rich waste water. Water Sci. Technol. 37(9), 135–142.
- Hynes, R.K., Knowles, R., 1983. Inhibition of chemoautotrophic nitrification by sodium chlorate and sodium chlorite: A reexamination. Appl. Environ. Microb. 45(4), 1178–1182.
- Kim, Y.M., Park, D., Lee, D.S., Park, J.M., 2007. Instability of biological nitrogen removal in a cokes wastewater treatment facility during summer. J. Hazard. Mater. 141(1), 27–32.
- Kumar, M.S., Vaidya, V.N., Shivaraman, N., Bal, A.S., 2000. Biotreatment of oil-bearing coke-oven wastewater in fixed-film reactor a viable alternative to activated sludge process. Environ. Eng. Sci. 17(4), 221–226.
- Li, H.Q., Han, H.J., Du, M.A., Wang, W., 2011. Removal of phenols, thiocyanate and ammonium from coal gasification wastewater using moving bed biofilm reactor. Bioresource Technol. 102(7), 4667–4673.
- Marañón, E., Vázquez, I., Rodríguez, J., Castrillón, L., Fernández, Y., López, H., 2008. Treatment of coke wastewater in a sequential batch reactor (SBR) at pilot plant scale. Bioresource Technol. 99, 4192–4198.
- Mulder, A., Van de Graaf, A.A., Robertson, L.A., Kuenen, J.G., 1995. Anaerobic ammonium oxidation discovered in a denitrifying flidized bed reactor. FEMS Microbiol. Ecol. 16, 177–184.
- Nakhla, G.F., Suidan, M.T., Pfeffer, J.T., 1990. Control of anaerobic gac reactors treating inhibitory wastewaters. Res. J. Water Pollut. C. 62(1), 65–72.
- Park, S., Bae, W., 2009. Modeling kinetics of ammonium oxidation and nitrite oxidation under simultaneous inhibition by free ammonia and free nitrous acid. Process Biochem. 44(6), 631–640.
- Park, S., Bae, W., Rittmann, B.E., 2010a. Multi-species nitrifying biofilm model (MSNBM) including free ammonia and free nitrous acid inhibition and oxygen limitation. Biotechnol. Bioeng. 105(6), 1115–1130.
- Park, S., Bae, W., Rittmann, B.E., 2010b. Operational boundaries for nitrite accumulation in nitrification based on minimum/maximum substrate concentrations that include effects of oxygen limitation, pH, and free ammonia and free nitrous acid inhibition. Environ. Sci. Technol. 44(1), 335–342.

- Salem, S., Berends, D., Heijnen, J.J., van Loosdrecht, M.C.M., 2002. Model-based evaluation of a new upgrading concept for N-removal. Water Sci. Technol. 45, 169–176.
- Strous, M., Fuerst, J.A., Kramer, E.H.M., Logemann, S., Muyzer, G., van de Pas-Schoonen, K.T. et al., 1999. Missing lithotroph identified as new planctomycete. Nature 400(6743), 446–449.
- Strous, M., Heijnen, J.J., Kuenen, J.G., Jetten, M.S.M., 1998. The sequencing batch reactor as a powerful tool for the study of slowly growing anaerobic ammonium-oxidizing microorganisms. Appl. Microbiol. Biotechnol. 50(5), 589–596.
- Third, K.A., Sliekers, A.O., Kuenen, J.G., Jetten, M.S.M., 2001. The CANON system (completely autotrophic nitrogen-removal over nitrite) under ammonium limitation: Interaction and competition between three groups of bacteria. Syst. Appl. Microbiol. 24, 588– 596.
- Torà, J.A., Lafuente, J., Baeza, J.A., Carrera, J., 2010. Combined effect of inorganic carbon limitation and inhibition by free ammonia and free nitrous acid on ammonia oxidizing bacteria. Bioresource Technol. 101(15), 6051–6058.
- Vadivelu, V.M., Keller, J., Yuan, Z.G., 2006a. Effect of free ammonia and free nitrous acid concentration on the anabolic and catabolic processes of an enriched *Nitrosomonas* culture. Biotechnol. Bioeng. 95(5), 830–839.

Vadivelu, V.M., Keller, J., Yuan, Z.G., 2007. Effect of free ammonia on

the respiration and growth processes of an enriched Nitrobacter culture. Water Res. 41(4), 826–834.

- Vadivelu, V.M., Yuan, Z., Fux, C., Keller, J., 2006b. The inhibitory effects of free nitrous acid on the energy generation and growth processes of an enriched *Nitrobacter* culture. Environ. Sci. Technol. 40(14), 4442–4448.
- Van Hulle, S.W.H., Volcke, E.I.P., Teruel, J.L., Donckels, B., van Loosdrecht, M.C.M., Vanrolleghem, P.A., 2007. Influence of temperature and pH on the kinetics of the Sharon nitritation process. J. Chem. Technol. Biot. 82(5), 471–480.
- Wang, W., Han, H.J., Yuan, M., Li, H.Q., 2010. Enhanced anaerobic biodegradability of real coal gasification wastewater with methanol addition. J. Environ. Sci. China 22(12), 1868–1874.
- Wood, L.B., Hurley, B.J.E., Matthews, P.J., 1981. Some observations on the biochemistry and inhibition of nitrification. Water Res. 15(5), 543–551.
- Yang, C.F., Qian, Y., Zhang, L.J., Feng, J.Z., 2006. Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater. Chem. Eng. J. 177(2), 179–185.
- Yu, Z.J., Chen, Y., Feng, D.C., Qian, Y., 2010. Process development, simulation, and industrial implementation of a new coal-gasification wastewater treatment tnstallation for phenol and ammonia removal. Ind. Eng. Chem. Res. 49(6), 2874–2881.

Jese Be of



Editorial Board of Journal of Environmental Sciences

Editor-in-Chief

Hongxiao Tang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Associate Editors-in-Chief

Jiuhui Qu	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao	Peking University, China
Nigel Bell	Imperial College London, United Kingdom
Po-Keung Wong	The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment Baoyu Gao Shandong University, China **Maohong Fan** University of Wyoming, USA Chihpin Huang National Chiao Tung University Taiwan, China Ng Wun Jern Nanyang Environment & Water Research Institute, Singapore Clark C. K. Liu University of Hawaii at Manoa, USA **Hokyong Shon** University of Technology, Sydney, Australia Zijian Wang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China Zhiwu Wang The Ohio State University, USA Yuxiang Wang Queen's University, Canada Min Yang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China **Zhifeng Yang** Beijing Normal University, China Han-Qing Yu University of Science & Technology of China **Terrestrial environment Christopher Anderson** Massey University, New Zealand **Zucong Cai** Nanjing Normal University, China Xinbin Feng Institute of Geochemistry, Chinese Academy of Sciences, China Hongqing Hu Huazhong Agricultural University, China Kin-Che Lam The Chinese University of Hong Kong Hong Kong, China Erwin Klumpp Research Centre Juelich, Agrosphere Institute Germany Peijun Li Institute of Applied Ecology, Chinese Academy of Sciences, China

Michael Schloter German Research Center for Environmental Health Germany Xuejun Wang Peking University, China Lizhong Zhu Zhejiang University, China Atomospheric environment Jianmin Chen Fudan University, China Abdelwahid Mellouki Centre National de la Recherche Scientifique France Yujing Mu Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. China Min Shao Peking University, China James Jay Schauer University of Wisconsin-Madison, USA Yuesi Wang Institute of Atmospheric Physics, Chinese Academy of Sciences, China Xin Yang University of Cambridge, UK **Environmental biology** Yong Cai Florida International University, USA Henner Hollert RWTH Aachen University, Germany Jae-Seong Lee Sungkyunkwan University, South Korea **Christopher Rensing** University of Copenhagen, Denmark **Bojan Sedmak** National Institute of Biology, Ljubljana Lirong Song Institute of Hydrobiology, the Chinese Academy of Sciences, China Chunxia Wang National Natural Science Foundation of China Gehong Wei Northwest A & F University, China Daqiang Yin Tongji University, China Zhongtang Yu The Ohio State University, USA

Environmental toxicology and health Jingwen Chen Dalian University of Technology, China Jianving Hu Peking University, China Guibin Jiang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China Sijin Liu Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China Tsuyoshi Nakanishi Gifu Pharmaceutical University, Japan Willie Peijnenburg University of Leiden, The Netherlands **Bingsheng Zhou** Institute of Hydrobiology, Chinese Academy of Sciences, China Environmental catalysis and materials Hong He Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China Junhua Li Tsinghua University, China Wenfeng Shangguan Shanghai Jiao Tong University, China Yasutake Teraoka Kyushu University, Japan Ralph T. Yang University of Michigan, USA Environmental analysis and method Zongwei Cai Hong Kong Baptist University, Hong Kong, China Jiping Chen Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China Minghui Zheng Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China Municipal solid waste and green chemistry Pinjing He Tongji University, China **Environmental ecology Rusong Wang** Research Center for Eco-Environmental Sciences,

Chinese Academy of Sciences, China

Editorial office staff

Managing editor	Qingcai Feng		
Editors	Zixuan Wang	Suqin Liu	Zhengang Mao
English editor	Catherine Rice	(USA)	

Copyright[®] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)

(http://www.jesc.ac.cn)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via http://www.elsevier.com/locate/jes.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at http://www.jesc.ac.cn. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at http://www.jesc.ac.cn.

Journal of Environmental Sciences (Established in 1989) Vol. 26 No. 5 2014

CN 11-2629/X	Domestic postcode: 2-580		Domestic price per issue RMB ¥ 110.00	
Editor-in-chief	Hongxiao Tang	Printed by	Printed by Beijing Beilin Printing House, 100083, Chi	
	E-mail: jesc@263.net, jesc@rcees.ac.cn		http://www.elsevier.com/locate/jes	
	Tel: 86-10-62920553; http://www.jesc.ac.cn	Foreign	Elsevier Limited	
	P. O. Box 2871, Beijing 100085, China		Local Post Offices through China	
	Environmental Sciences		North Street, Beijing 100717, China	
Edited by	Editorial Office of Journal of	Domestic	Science Press, 16 Donghuangchenggen	
	Sciences, Chinese Academy of Sciences	Distributed by		
Sponsored by	Research Center for Eco-Environmental		Elsevier Limited, The Netherlands	
Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China	

