Journal of Environmental Management 226 (2018) 289–297

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Index for nitrate dosage calculation on sediment odor control using nitrate-dependent ferrous and sulfide oxidation interactions

Zihao He, Rong Huang, Yuhai Liang**, Guangwei Yu*, Yunxiao Chong, Lin Wang

Department of Environmental Science and Engineering, College of Natural Resource and Environment, South China Agricultural University, Guangzhou, 510642, China

ARTICLE INFO

Keywords:
Sediments remediation
$n_{NO3}/n_{(S+Fe)}$ ratio
Nitrate reduction
Sulfide/ferrous oxidation
Microbial diversity

ABSTRACT

Nitrate-driven sulfide and ferrous oxidation have received great concern in researches on sediments odor control with calcium nitrate addition. However, interrelations among sulfide oxidation, ferrous oxidation and their associated microbes during the nitrate reduction process are rarely reported. In this work, a $n_{NO3}/n_{(S+Fe)}$ ratio (mole ratio of NO_3^- concentration to S^{2-} and Fe^{2+} concentration) was first introduced as an index for calcium nitrate dosage calculation. Then certain amount of calcium nitrate was added to four sediment systems with various sulfide and ferrous initial concentration to create four gradients of $n_{NO3}/n_{(S+Fe)}$ ratio (0.6, 0.9, 1.5 and 2.0) for treatment. Furthermore, the significant variations of sulfide and ferrous oxidation, microbial diversity and community structure were observed. The results revealed that at low $n_{NO3}/n_{(S+Fe)}$ ratio (0.6 and 0.9) systems, sulfide seemed prior to ferrous to be oxidized and no obvious ferrous oxidation occurred. Meanwhile, sulfide oxidizing associated genus *Sulfurimonas* sp. became dominant in these systems. In contrast, sulfide and ferrous oxidation rate increased when $n_{NO3}/n_{(S+Fe)}$ ratio reached 1.5 and 2.0 (two and three times of theoretically required amount for sulfide and ferrous oxidation), which made *Thiobacillus* sp. more dominant than *Sulfurimonas* sp. Hence, when $n_{NO3}/n_{(S+Fe)}$ ratio of 1.5 and 2.0 were used, sulfide and ferrous could be simultaneously oxidized and no sulfide regeneration appeared in two months. These results demonstrated that for sulfide- and ferrous-rich sediment treatment, the nitrate consumed by ferrous oxidation should be taken into account when calculating the nitrate injecting dosage. Moreover, $n_{NO3}/n_{(S+Fe)}$ ratio was feasible as a key parameter to control the oxidation process and as an index for calcium nitrate dosage calculation.

1. Introduction

Rivers in South China areas have been serving as the receiving waterbody of domestic sewage, industrial wastewater and agricultural runoff for a long time. As a result, sediment accumulation and odor problem mainly caused by Acidified Volatile Sulfide (AVS) has become a universal phenomenon in urban rivers in these areas, which seriously threatens the aquatic ecosystem and public health (Wang et al., 2016). Thus, solutions for fast and efficient remediation for the contaminated sediment have received much attention in recent years, especially for odor control, which has been considered an urgent issue demanding prompt actions from the local government.

It is generally agreed that the reduction of sulfate and ferric iron in anaerobic sediments primarily leads to the accumulation of AVS, including Iron (II) Sulfide (FeS) and unpleasant hydrogen sulfide (H_2S), and gives rise to black-color sediments and odor problem (Babin et al., 1999; Zhang et al., 2009; Jing et al., 2013; He et al., 2017). Therefore, the oxidation of sulfide is the key process to eliminate sediment odor smell and improve overlying water quality (Liang et al., 2016; Qiu et al., 2017). Compared with ex-situ remediation process such as dredging and capping (Jing et al., 2013), the in-situ sediment bioremediation with adding nitrate (NO_3^-), as a cost-effective approach, has attracted much more research attention since 1976 due to its low cost and low toxicity (Ripl, 1976; Murphy et al., 1999; Zhang et al., 2009; Perelo, 2010; Shao et al., 2010; Chen et al., 2013; Xu et al., 2014; He et al., 2017).

Though lots of researches related to sulfide odor control are conducted, a standard for the calculation of calcium nitrate dosage has not been set up by now. For example, in Babin's research (2003), a 30% nitrate residual was set as the requirement of nitrate addition. In Xu's research (Xu et al., 2014), calcium nitrate solution was injected at a dose of 45.3 g N per m^2 surface sediment once in a month. In our previous studies, the dosage was calculated according to the dry weight of sediment (Wang et al., 2016; He et al., 2017). Shao et al. (2009, 2011)

* Corresponding author.
** Corresponding author.
E-mail addresses: liangyuhai@scau.edu.cn (Y. Liang), yuguangwei@scau.edu.cn (G. Yu).

https://doi.org/10.1016/j.jenvman.2018.08.037
Received 27 July 2017; Received in revised form 28 June 2018; Accepted 7 August 2018

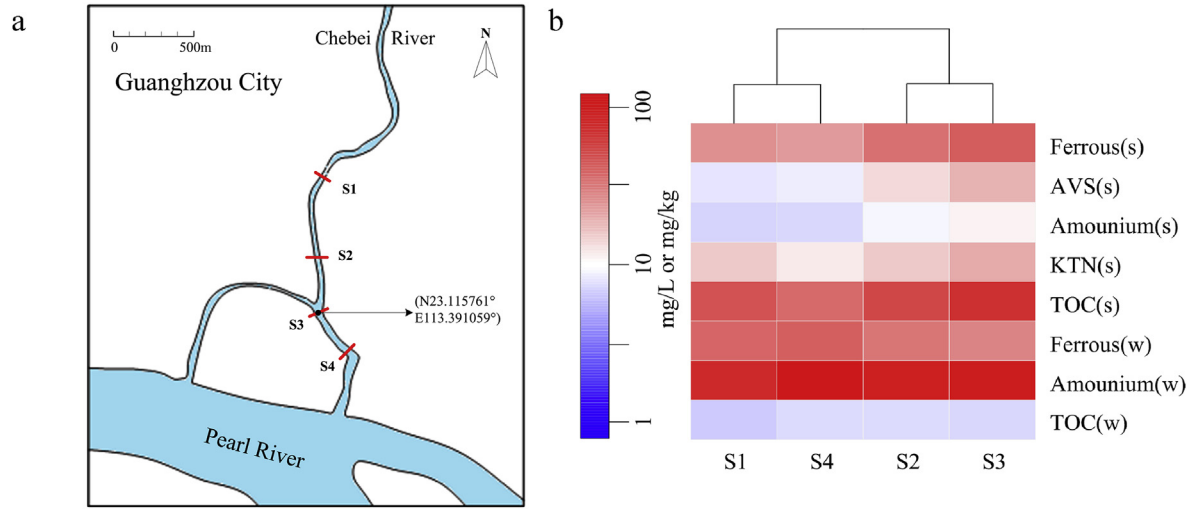

Fig. 1. Location of the four sampling sites in Chebei River in Guangzhou city(a) and the concentration of main pollutants in sediments and interstitial water(b). Note that (s) means concentration in sediments with a unit of mg/g, (w) means concentration in interstitial water with a unit of mg/L.

and Zhang et al. (2009) also conducted experiment on adding nitrate by means of NO_3^- concentration (with unit of mmol/L or mg/L). Obviously, most recent researches have been conducted based on experimental results, and the absence of a standard for calcium nitrate injecting dosage calculation might limit the future application of this technology.

Generally, the required amount of calcium nitrate depends on the purpose of the engineering application. For instance, for organic pollutant biodegradation, due to the long reaction time (even longer than two years in some cases), more calcium nitrate were needed (Babin et al., 2003). In contrast, since sulfide could be removed in weeks or a month (Shao et al., 2010; Yamada et al., 2012; Zhang et al., 2015; He et al., 2017), the required amount of calcium nitrate is less for odor control. However, our previous research confirmed that when calcium nitrate dosing is insufficient, sulfide could not be completely oxidized and would regenerate soon (Yu et al., 2015; Wang et al., 2016). But when nitrate was excessive, potential secondary pollution resulted from the release of surplus nitrate into overlying water would happen (Zhang et al., 2015; Liu et al., 2017). Therefore, the quantification of calcium nitrate dosage is primary and vital for the application of this technology under different purposes.

It is widely accepted that after calcium nitrate addition into sulfide-rich sediments, autotrophic sulfide-driven denitrification is the main process for nitrate consumption (Dolejs et al., 2015; Zhang et al., 2015; He et al., 2017). The process could be represented by the following equation (Cardoso et al., 2006; Zhang et al., 2009; Yang et al., 2012):

$$S^{2-} + 1.6NO_3^- + 1.6H^+ \rightarrow SO_4^{2-} + 0.8N_2 + 0.8H_2O \quad \triangle G^\circ = -744\,kJ\,mol^{-1} \quad (1)$$

Hence, in wastewater treatment system, sulfide to nitrate (n_S/n_{NO3}) ratio (mol/mol) was utilized as an index for nitrate calculation (Dolejs et al., 2015). It seemed that the calculating method based on theoretical AVS removal should be more reasonable and accurate than those based on experimental results. However, in case that injecting nitrate based on nitrate to AVS ratio in the sediment treatment in the south China area, the actual amount of consuming nitrate was found larger than the theoretical value (Liu et al., 2015). It suggested that the calculation of nitrate dosing quantity depending on sulfide to nitrate (n_S/n_{NO3}) ratio (mol/mol) was not accurate. Therefore, there might be some matters besides sulfide in sediments that consume nitrate. In fact, with high sulfur and ferrous iron content is one typical characteristic of sediments in the south China area. During the process of sulfide-driven nitrate reduction, the oxidation of another alternative electron acceptor, ferrous iron (Fe^{2+}), is always observed and has drawn more attention recently. Juncher Jørgensen et al. (2009) and Vaclavkova et al. (2014) even confirmed the occurrence of microbial FeS_2 and FeS oxidation accompanied with nitrate reduction after nitrate addition in sediments, with sulfate and ferric hydroxide as an end product. Many nitrate-dependent Fe(II) oxidizing bacteria have been confirmed in *Proteobacteria* (Hedrich et al., 2011; Laufer et al., 2016). Futhermore, previous researches (Shao et al., 2009, 2011; Zhang et al., 2009; Shao et al., 2010; Chen et al., 2013; He et al., 2017) indicated that apparent variation occurred in *Proteobacteria*, in which *Thiobacillus* sp. and *Sulfurimonas* sp. played an important role in microbial community structure after nitrate addition into river/marine sediments. It is noteworthy that *Thiobacillus denitrificans* was affirmed to be able to oxidize sulfide and ferrous (and pyrite) simultaneously (Straub et al., 1996; Juncher Jørgensen et al., 2009; He et al., 2017). Hence, the reaction of nitrate -dependent ferrous oxidation could not be ignored, which would be represented by the following equation (Juncher Jørgensen et al., 2009; Hayakawa et al., 2013; Robertson et al., 2016):

$$Fe^{2+} + 0.2\,NO_3^- + 2.4H_2O \rightarrow Fe(OH)_3 + 0.1N_2 + 1.8H^+ \quad \triangle G^\circ = -101\,kJ\,mol^{-1} \quad (2)$$

Therefore, the nitrate consumed by ferrous oxidation should be taken into account when calculating the nitrate injecting dosage. The oxidation of ferrous was also suggested as the reason for the sediment color being transferred from black to brown (Babin et al., 2003; Rickard and Morse, 2005). This implies that the $n_{NO3}/n_{(S+Fe)}$ ratio was more appropriate for dosage calculation in the treatment of sulfide- and ferrous-rich sediments. However, few researchers emphasis on nitrate-dependent ferrous oxidation for sediment treatments when considering calcium nitrate dosage calculations (Juncher Jørgensen et al., 2009; Hayakawa et al., 2013).

Thus, the main purpose of this work is to verify the feasibility of $n_{NO3}/n_{(S+Fe)}$ ratio as an index for calcium nitrate dosage calculation for sulfide-, ferrous-rich sediment treatment.

2. Materials and methods

2.1. Sediments collection

Sediments samples were collected from the tributary inlet of Chebei River to the Pearl River in Guangzhou City (Wang et al., 2016; He et al., 2017). As shown in Fig. 1a, this area named urban village was with high population density that led to an overloaded sewage discharge and high