



Characterization of odor emission from alternating aerobic and anoxic activated sludge systems using real-time total reduced sulfur analyzer



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HIGHLIGHTS

- Odorous volatile sulfurs emitted from AAA system characterized.
- VSC peaks right after start of aeration for AAA system observed.
- More sulfur emission during air-on period than air-off observed.
- Effect of dimethyl sulfoxide in influent on sulfur generation studied.
- Odor control schemes for both air on and off periods suggested.

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ABSTRACT

Anaerobic biodegradation of sulfur-containing compounds always generates volatile sulfur compounds (VSCs) including H₂S, methyl mercaptan, and dimethyl sulfide (DMS). VSC emissions from wastewater treatment plants (WWTPs) result in odor complaints from people living nearby. To control odor-causing compounds in WWTPs, it is important to know the odor emission quantity particularly with continuous monitoring. Since modified activated sludge processes always include anaerobic, anoxic and aerobic conditions for nutrient removal, odor emission from these different environmental settings is expected.

In this study, continuous monitoring of VSCs from the headspace of an alternating aerobic and anoxic (AAA) activated sludge process via total reduced sulfur (TRS) analyzer was performed. There is clear pattern of the initial TRS peak immediately after the initiation of the aeration in the AAA system and TRS concentration begins to drop through the remaining air-on cycle. On the other hand, during the air-off period, TRS concentrations increase with time. In particular, a clear inflection point in the TRS profile could be observed after complete removal of nitrate during air-off, meaning more VSCs formation. Since the highest odor emission occurs after the initiation of aeration, the future control of exhausted air should only deal with air collected during the initial aeration period (e.g., 30 min), a similar concept for the treatment of first flush in combined sewer overflow. In addition, application of a control scheme to initiate aeration immediately after denitrification is completed during air-off should be beneficial in reducing odor emission.

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1. Introduction

The odor-causing gaseous compounds are produced and emitted in wastewater treatment plants (WWTPs) from each step of the treatment process. The emitted odors from WWTPs, in particular from sludge handling processes, have become a significant source of environmental annoyance, since odor-related complaints from communities surrounding WWTPs have been constantly increasing during the last decades (Karageorgos et al., 2010; Choi

et al., 2012). The cost for controlling odor is expensive, exemplified by the fact that Philadelphia had spent USD 2.5 million a year to minimize the effect of the odor on neighboring community (Cheng et al., 2009).

Main odorous compounds generated include volatile sulfur compounds (VSCs), reduced nitrogen compounds and volatile fatty acids in WWTPs (Wang et al., 2012). Among them, VSCs such as H₂S, methyl mercaptan, dimethyl sulfide (DMS), and dimethyl disulfide are known as main odorous compounds due to their extremely low odor threshold levels (e.g., H₂S 0.7 ppbv and DMS 0.3 ppbv; Devai and DeLaune, 1999; Lehtinen and Veijanen, 2011). Unfortunately, the generation of VSCs is unavoidable due to various anaerobic

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conditions encountered in WWTPs where inorganic sulfate and sulfur-containing organic compounds are transformed to H_2S and other reduced sulfur compounds, e.g., DMS. Compound to the problem is the fact that as urbanization accelerates, WWTPs are located closer to the residential areas (Karageorgos et al., 2010), resulting in increasing number of odor complaints as in the case of Metropolitan Seoul, Korea (Choi et al., 2012).

Each of different treatment unit processes in WWTPs may release different odorants (Easter et al., 2005). A potential odor source would be the aeration basins due to its stripping effect on previously accumulated reducing sulfur compounds present in the influent as well as in the return activated sludge (RAS). There have been many studies regarding VSC emission from aeration tanks (CDM, 2003; Cheng et al., 2005; Kim et al., 2006; Wu et al., 2006; Beghi et al., 2012). For example, DMS emitted from aeration basins with aqueous concentration varying from 5 to $1260 \mu\text{g L}^{-1}$ was found to be responsible for odor problem (Cheng et al., 2005). In fact, significant odor problems from VSCs (e.g., DMS) have been encountered in well aerated activated sludge tanks in Philadelphia WWTP since 1980s (Glindemann et al., 2005) and in the residential area near an industrial science park in Taiwan (Wu et al., 2006). The presence of 200 ppbv H_2S and 8 ppbv DMS was also reported in aeration tanks of Concord WWTP (Amirhor et al., 2006). Thus, unlike layman's wisdom that odor generation only occurs under anaerobic conditions, aerobic conditions in aeration basins also release odorants.

In addition, domestic WWTPs also receive wastewater from various sources which may contain a number of odorants and odor-causing precursors such as volatile organic compounds and sulfur-containing compounds (Glindemann et al., 2007; Cheng et al., 2009; Lei et al., 2010). These precursors are transformed to VSCs while wastewater is being treated. For example, dimethyl sulfoxide (DMSO), which is used commonly in photo-electronics, semi-conductor (Hwang et al., 2007) and thin-film transistor liquid crystal industries (Lei et al., 2010; Fukushima et al., 2013; Wu et al., 2014) is discharged into a WWTP and can cause "canned corn-like" nuisance odor in the form of DMS as the case of Philadelphia's Northeast WWTP (Glindemann et al., 2005; Cheng et al., 2007). This is due to the fact that 95% of about 150 tested strains of microorganisms (prokaryotes, eukaryotes, aerobes and anaerobes) are able to carry out the 2-electron transfer of DMSO reduction to DMS (Alef and Kleiner, 1989).

A variety of modified activated sludge processes used nowadays all provide anaerobic, anoxic and aerobic conditions for biological nutrient removal and these different conditions may also favor odor generation. For example, under anoxic conditions with measurable dissolved oxygen (DO) in bulk water but undetected DO inside sludge flocs, the microbial reduction of DMSO to DMS can occur (Glindemann et al., 2007; Bamforth, 2014). Even under high DO conditions in the aeration tank, average DMS concentration of $250 \mu\text{g L}^{-1}$ was found (Cheng et al., 2005). The presence of DMS in aeration tanks is due to the fact that DMSO can be reduced via 2-electron transfer to DMS as mentioned before. Also DMSO can be used as a terminal electron acceptor and eventually reduced to DMS (Zinder and Brock, 1978) in the presence or absence of O_2 (Griebler and Slezak, 2001). All the studies reported in the literature have focused on sporadic manual sampling and odor analysis to quantitate odorants level in headspace of in the mixed liquor of a bioreactor. Continuous monitoring of a bioreactor has not been performed to investigate odor emission characteristics of the reactor under different operating conditions.

Consequently, the present study was undertaken to monitor VSC emission from an alternating aerobic and anoxic (AAA) system by using a real-time total reduced sulfur (TRS) analyzer. The VSC emissions during both air-on and air-off periods in an AAA system were monitored. In addition, in order to assess the impact of sulfur

contents in the feed on the odor emission from the AAA system over time, 30 mg L^{-1} DMSO was added into the feed of the AAA system and headspace TRS and DMS were monitored.

To the best of our knowledge, this is the first attempt to continuously monitor TRS profiles during air-on and air-off period in an AAA system.

2. Materials and methods

2.1. Experimental set-up

A lab-scale AAA system consisted of a reactor (4 L), a settling basin (3.8 L) and a feed tank (40 L) for supplying feed to the AAA system (Fig. 1). The content in the feed basin, stored for about 3-d feeding for deliberately providing anaerobic conditions, was gently stirred to maintain wastewater composition homogeneous. The feed tank was covered to minimize loss of odorants generated during the storage.

The AAA system was operated in a cyclic mode of 2 h air-on and 2 h air-off. During air-on cycles, air was supplied to the bioreactor at the rate of 800 mL min^{-1} ; the range of the DO in the system was measured from 2 to 3 mg L^{-1} . It was hypothesized that the accumulated sulfide compounds from feed as well as from RAS could be stripped out of the mixed liquor in the beginning of the air-on cycle. During air-off cycles, the content of the reactor was mixed with a motor-driven stirrer. The hydraulic retention time (HRT) and solids retention time (SRT) of the system were maintained at 8 h and 15 d, respectively. The SRT was controlled by wasting appropriate amount of MLSS ($2000\text{--}3000 \text{ mg L}^{-1}$) from the reactor. The RAS was recycled to the head of the AAA basin at 100% of the influent flow rate. The upper part of the AAA reactor was sealed with a cover while the gas in the headspace was continuously withdrawn at 620 mL min^{-1} to a real-time TRS analyzer. A vent was made in the cover to allow fresh air to flow into the head space during the air-off, and to allow air emission through the surface of the bioreactor to flow out. Additional gas samples were also collected from the headspace for gas chromatographic analysis of DMS. System pH and ORP were continuously monitored using ORP (Mettler Toledo Type Pt4805-5c-DPAS-K8S/325, Woburn, Massachusetts) and pH probes (Mettler Toledo Type HA405-DXK-S8/225) installed on the bioreactor. The pH and ORP signals were transferred to a PC using a data acquisition and control program (LabView 8.0, NI-Korea, Seoul, Korea).

2.2. Sample preparation and analysis

2.2.1. Wastewater samples

Wastewater used in this study was collected from the primary effluent of a local WWTP. Once the wastewater was delivered (twice a week) to the laboratory, COD, TN, and TP were analyzed according to the Standard Methods (APHA, 2005). NH_4^+ , NO_3^- , SO_4^{2-} , and PO_4^{3-} were analyzed using Dionex ion chromatography (ICS-90, USA). S^{2-} was measured according to the Standard Methods (APHA, 2005). The same water quality parameters were analyzed for the effluent from the system.

2.2.2. Real-time TRS analyzer

VSCs present in the headspace gas from the AAA system were continuously monitored using a real-time TRS analyzer (M102E, Eco-S&E, Korea). The TRS analyzer can be operated in two different modes; one is for the range less than few ppmv, and the other for the higher range than 1 ppmv. In this study, the analyzer was calibrated with the standard H_2S gas with the R^2 of >0.99 for the range of 0–1000 ppbv, since the TRS concentration was not over the range under normal operation of the AAA system. Therefore, any

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