WATER RESEARCH 43 (2009) 195–203

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Analysis of the mechanism of sludge ozonation by a combination of biological and chemical approaches

Sang-Tian Yan[a,1], *Li-Bing Chu*[b,1], *Xin-Hui Xing*[a,*], *An-Feng Yu*[a], *Xu-Lin Sun*[c], *Benjamin Jurcik*[c]

[a]*Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*
[b]*Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China*
[c]*Air Liquide Laboratories, Tsukuba-shi, Ibaraki-Pref. 300-4247, Japan*

ARTICLE INFO

Article history:
Received 8 May 2008
Received in revised form
30 September 2008
Accepted 30 September 2008
Published online 11 October 2008

Keywords:
Sludge reduction
Ozonation
Ozone dosage
Biological response
Radical scavenger

ABSTRACT

Using the practical sludge obtained from municipal sewage treatment plants, the mechanism of the sludge ozonation process was systematically investigated by a combination of biological and chemical approaches, including analysis of the changes in biological response by CFU and PCR-DGGE, bio-macromolecular activity and radical scavenging activity. The results indicated that after the sludge was exposed to ozone at less than 0.02 g O_3/g TSS, the DGGE fingerprint remained constant and there was still some enzyme activity, indicating that the sludge solubilization was the main process. At greater than 0.02 g O_3/g TSS, the bacteria began to be broken down and ozone was used to oxidize the bio-macromolecules such as proteins and DNA released from the sludge. Bacteria belonging to 'G-Bacteria' were able to conserve their DNA in the presence of less than 0.08 g O_3/g TSS. At levels higher than 0.10 g O_3/g TSS, the disintegration of the sludge matrix became slow and the microbes lost most of their activity, and ozone was used to transform the bio-macromolecules into small molecules. However, at levels higher than 0.14 g O_3/g TSS, the ozone failed to oxidize the sludge efficiently, because several radical scavengers such as lactic acid and SO_4^{2-} were released from the microbial cells in the sludge.

1. Introduction

Excess sludge produced by biological wastewater treatments such as activated sludge system, has recently become a large issue. Treatment and disposal of excess sludge may account for up to 60% of the total operational costs of a plant (Spellman, 1997). Techniques for reducing excess sludge have gained much attention, and one promising technique is the sludge ozonation process (Wei et al., 2003). Ozone is a strong chemical oxidant capable of destroying the cell walls of microorganisms and solubilizing or oxidizing them to organic substances. Up to now, the ozonation process has been employed to reduce excess sludge directly in the activated sludge processes (Yasui and Shibata, 1994; Ahn et al., 2002; Bohler and Siegrist, 2004; Cui and Jahng, 2004) or as a pretreatment technique prior to anaerobic sludge digestion (Muller et al., 1998; Scheminski et al., 2000; Weemaes et al., 2000).

A comparison of different studies evaluating sludge ozonation is difficult since different types of sludge and evaluation methods have been used in the different studies as described above. In addition, in different sludge ozonation systems, the input ozone dosage is in a relatively wide range, from 0.04 to

* *Corresponding author*. Tel./fax: +86 10 62794771.
E-mail address: xhxing@tsinghua.edu.cn (X.-H. Xing).
[1] These authors contributed equally to this work.
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doi:10.1016/j.watres.2008.09.039

1.2 g O_3/g TSS, and the TSS disintegration efficiency ranges from 35% to 60%. TSS disintegration efficiency also seems to increase slowly when the ozone dosage is higher than around 0.15 g O_3/g TSS. The efficiency of the ozonation process is dependent upon both the mass transfer and reaction kinetics of ozone. Due to the low solubility of ozone gas in water, the rate of ozone mass transfer and ozonation efficiency for chemicals can be significantly improved by using microbubble ozone systems, as reported in our previous study (Chu et al., 2007). Sludge ozonation efficiency, especially the sludge disintegration step can be sped up, and very low ozone gas can be maintained by the microbubble system, as shown in our recent study (Chu et al., 2008). However, even for the microbubble ozone system, no distinct change in sludge disintegration and solubilization efficiency was observed when more than 0.16 g O_3/g TSS ozone was applied. Since ozone is an expensive reagent, optimization of the ozonation process is a crucial point for process engineering (Wei et al., 2003).

The sludge ozonation process has been suggested as the sequential decomposition processes of suspended solids disintegration, solubilization of the solids (cells) and mineralization of the soluble organic matter released from the microbial cells (Ahn et al., 2002). The interaction between bacterial cells and ozone has been studied in pure bacterial cultures. The results of these studies suggest that the reaction sequence occurs as follows: oxidation of lipids and sulfhydryl compounds within 3–5 min of exposure of the cells to ozone, followed by decreased culturability after 10 min of exposure and the leakage of nucleic acids from the cells after 15 min of exposure (Komanapalli and Lau, 1996). However, with the increase of ozone dosage during ozonation, changes that occur in the biological response and microbial activities of sludge are not well understood.

Staehelln and Hoignè (1985) have suggested that soluble biodegradable by-products or inorganic soluble oxidant scavengers produced following ozonation of sludge may compete to react with ozone. Sludge contains various types of microbes that can release a wide range of soluble substrates following their destruction during the ozonation process. These soluble substrates may then affect the efficiency of the ozonation process. Therefore, examining the relationship between the biological response and the formation of soluble substrates capable of acting as scavengers at certain ozone dosages is essential for the understanding of the sludge ozonation process.

Previous studies evaluating sludge reduction by ozone have primarily focused on operating conditions and process parameters. In this study, we focus on two aspects that have not been thoroughly considered in the previous studies. The first is the mechanism by which the effects of sludge ozonation change with increasing dosage of ozone. To accomplish this, we systematically investigated the biological response of the sludge matrix to different dosages of ozone by a combination of biological and chemical approaches, including analysis of the changes in the microbial population and biomacromolecule enzymatic activities. The second one is to examine the limitations of the ozone reaction. Specifically, we evaluated the effects of solutes released by the destruction of microbes in the sludge matrix, and analyzed the radical scavenging activities to determine if they interfere with the ozone reaction and hinder the further reduction of sludge. A better understanding of the reaction mechanism of the sludge ozonation process as well as the limitation of ozonation will be helpful in the effort to design and optimize an economic sludge reduction process.

For accomplishing the above study, a microbubble ozone system (Chu et al., 2008) was used to treat the sludge obtained from a real municipal wastewater treatment plant.

2. Materials and methods

2.1. Sludge sources

The sludge used in this study was mainly obtained from the Qinghe (QH) municipal wastewater treatment plant in Beijing, China. The plant adopts an A^2/O (anoxic–anaerobic–oxic) process. The initial total suspended solid (TSS) concentration was 3500–5000 mg/L, with a 65–70% volatile suspended solid (VSS) concentration. For comparison, sludge taken from Gaobeidian (GBD) municipal wastewater treatment plant (Beijing, China) at 3200–3600 mg/L TSS with 72–78% of VSS was also used, and this plant adopts an inverted A^2/O process to treat the sewage containing around 10% industrial wastewater.

2.2. Experiment setup

In this study, a microbubble generator produced by Kyowa Engineering Co., Ltd. (Japan) that consisted of a recycling pump, a gyratory accelerator and an ejector was employed. The principle of microbubble generation has been described elsewhere (Chu et al., 2007). The experimental conditions in this study were identical to those of our recently conducted study (Chu et al., 2008). Briefly, approximately 8 L of sludge was fed into the ozonation reactor, which was operated in semi-batch mode and fed ozone gas continuously at a concentration of approximately about 115 mg/L. The ozone and sludge contact time was controlled at from 0 to 100–180 min according to the initial TSS concentration. In order to compare the results obtained under the different conditions, the ozone dosage (g O_3/g TSS) (initial TSS concentration) was used. The ozone dosage was calculated from the difference in the amount of ozone at the inlet and the outlet of the ozonation reactor per dry weight of initial TSS (Chu et al., 2008). For example, for the sludge of 3000 mg TSS/L, when the contact time was increased from 0 to 100 min, the corresponding ozone dosage was from 0 to 0.27 g O_3/g TSS.

2.3. Batch assay for analyzing the limitation of the sludge ozonation

A batch ozonation experiment with dyestuff CI Reactive Black 5 (RB 5) was conducted to study the limitation of the sludge ozonation induced by the soluble recalcitrant compounds. 300 mL of untreated sludge and treated sludge (0.20 g O_3/g TSS) were collected. The sludge samples were centrifuged ($12{,}000 \times g$, 10 min). 200 mL supernatant of the sludge was collected and RB 5 dyestuffs (100 mg/L) were added. Deionized water containing 100 mg/L RB 5 was used as a control. Different samples were kept in contact with ozone for about