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Biological Nitrogen Removal Using the Supernatant of Ozonized Sludge as Extra Carbon Source

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A sludge ozonation process with lab-scale anaerobic/oxic (A/O) system was used to investigate the utilization of the ozonized sludge (OS) supernatant as extra carbon source for denitrification. The optimal ozone dose for the sludge ozonation was 0.2 gO₃/gSS. The concentrations of SCOD, BOD, NH₃-N and TN in the supernatant increased respectively at this ozone dose. In the meantime, the sludge was significantly reduced. The OS supernatant had negative effect on nitrification because of low pH and alkalinity. After alkalinity adjustment, the A/O with the OS supernatant as the extra carbon source achieved a nitrogen removal rate of 78%, which was very close to the control experiment using glucose (79%).

Keywords Ozone, Sludge, Wastewater, Nitrogen Removal, Low Carbon Source

INTRODUCTION

Biological nitrogen removal (BNR) is widely used in modern municipal and industrial wastewater treatment. The availability of a suitable carbon source is critical for successful nitrogen removal. Wastewaters in China usually have high content of nitrogen and are short of carbon sources, which results in poor nitrogen removal efficiency. The commonly used solution for this problem is the pre-treatment (McCue et al., 2003) or the addition of extra carbon, which will increase the treatment cost.

On the other hand, the disposal of excess sludge accounts for 25%–60% of the total cost of wastewater treatment. The utilization of ozone to reduce excess sludge has drawn wide attention (Liu and Tay, 2001). Sakai et al. (1997) carried out a full-scale experiment on ozonation of the sludge and found

that excess sludge was reduced by 66%. The sludge reduction rate reported by Bohler and Siegrist (2004) was 46%. In general situation, the sludge is recycled to reactors for further treatment after ozonation (Yasui and Shibata, 1994). In recent years, there are also some experiments carried out to check whether the OS can be used as carbon source for BNR enhancement (Kampasa et al., 2007; Barlundhaug and Odegaard, 1996a, 1996b).

In this work, the excess sludge was disintegrated by ozone oxidation. The solubilized organic substances from the sludge were used as an extra carbon source for the denitrification in an A/O system. Glucose was also used as the extra carbon source as control. BNR efficiency of the A/O system was examined especially in terms of NH₃-N, TN for a long-term operation.

MATERIAL AND METHODS

Experiment System

The A/O system was composed of an anoxic tank (A) of 0.75 L and an aeration tank (O) of 2 L (Figure 1). A was equipped with an agitator providing a rotational speed of 40 r/min. O was filled with spherical aerobic fillers to improve BNR efficiency. The effluent (2.3 mL/min) from the system entered a settling tank where the sludge was separated and recycled to A. Hydraulic retention time (HRT), sludge retention time (SRT) and water internal recycle flow rate were controlled at 20 h, 3–5 d and 10 L/h, respectively.

The seed sludge taken from the Qinghe Sewage Treatment Plant of Beijing was screened, and then a part of it was filled into the A/O system, the other part was cultivated in low nitrogen condition for the sludge ozonation experiment. The A/O experiment was divided into 3 stages. At the start-up and stage 1, glucose was used as the extra carbon source. At stage 2, OS supernatant was circulated. To make the comparison, the influent maintained a C/N level of 8 and SCOD around 1000 mg/L during the whole experiment. SCOD,

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TABLE 1. Average Water Qualities of Simulated Wastewater at Different Stages

	Carbon source	SCOD (mg·L ⁻¹)	TN (mg·L ⁻¹)	NH ₃ -N (mg·L ⁻¹)
Start-up	Glucose	971.36	124.32	109.37
Stage 1	Glucose	979.83	125.92	114.19
Stage 2	OSR	956.86	131.61	109.40

OSR: ozonized sludge supernatant recirculated.

NH₃-N and TN removal efficiencies of the system were continuously examined. Table 1 shows the influent water qualities at different stages.

Choosing 8 as the influent C/N was based on our previous research results. The A/O system used in the experiment was equipped with spherical fillers and could achieve pretty high nitrogen removal efficiency at low C/N level (Yang et al., 2009; Li et al., 2007). Also, the research of Ruiz et al. (2006) shows when C/N < 10, high denitrifying activities could be got. When C/N > 10, most of the carbon source will be consumed by methanogenic activities. So, at C/N level of 8, the influence of other microorganisms could be depressed as much as possible and more accurate experimental results supposed to be got.

Sludge Ozonation

Excess sludge was periodically withdrawn from the settler, pumped into the ozonation reactor (inner diameter = 15 cm, height = 1.5 m). Because the sludge produced from A/O was not enough, some cultivated sludge was also added during stage 2. Gaseous ozone was generated from oxygen with an ozone generator (FSJ-220B, Ao-run Environment, Shanghai, China) and introduced into the reactor at its bottom. The ozone concentration at the reactor outlet was low in all experiments,

showing that the sludge consumed the ozone completely. The gas flow rate into the ozone reactor was set at about 20 L/h. Ozone dose was defined as the ratio of ozone (g) introduced into the reactor divided by the mass (g) of SS. The relationship between ozone dose and ozonation time at the gas flow rate of 20 L/h is shown in Figure 2.

Analysis

MLSS and MLVSS were measured following the Standard Methods (China Environmental Protection Bureau, 1997). DO and pH was measured with DO meter and pH meter, respectively. Gaseous ozone concentration was analyzed with the iodometric method (Xu and Zhao, 2003).

To determine the concentrations of SCOD, BOD and nitrogen compounds in the liquid samples, the supernatants were obtained by centrifuging sample suspensions at 4000 rpm for 5 min. SCOD (COD_{Cr}) was measured by rapid digestion measurement. BOD₅ was determined using OxiTop measure system. Ammonia and TN were analyzed using China standard methods. Repetitive trials for selected samples were done to validate the results.

RESULTS AND DISCUSSION

Effect of Ozone Dose on Sludge Solubilization and Reduction

Ozonation caused the release of sludge organics into liquid phase and the reduction of solid content of the sludge, represented by the decline of MLSS and MLVSS. Five samples were taken at different ozone doses as can be seen in Figure 3a (1: 0 gO₃/gMLSS; 2: 0.05 gO₃/gMLSS; 3: 0.10 gO₃/gMLSS; 4: 0.15 gO₃/gMLSS; 5: 0.20 gO₃/gMLSS).

Before ozonation, the sludge was well-settled, and the introduction of ozone caused the appearance of suspended matters as well as the increasing turbidity. As the ozone dose increased, the supernatant became pale yellow, and the volume of the sludge significantly reduced. The effect of ozone dose on the sludge lysis in terms of MLSS, MLVSS and

FIGURE 3. The effect of ozone dose on sludge reduction (color figure available online).

SCOD is shown in Figure 3b. With the increase of ozone dose, MLSS and MLVSS linearly decreased at the initial stage.

When the ozone dose was raised above 0.15 gO₃/gSS, both sludge solubilization and SS disintegration became insignificant. The phenomenon was similar to some other experiment results (Bohler and Siegrist, 2004; Weemaes et al., 2000). At ozone dose of 0.2 gO₃/gSS, MLSS and MLVSS decreased by 59 ± 4% and 69 ± 8%, respectively. During the course of the experiment, the supernatant SCOD increased and reached a level of 1.01 ± 0.07 g/L, which was caused by the release of organic compounds from the sludge ozonation. Some researchers have also found that a part of organic carbon like carbohydrate would be oxidized to CO₂ at high ozone doses (Zhang and Yang, 2009; Scheminske et al., 2000). In this experiment this part of organic carbon would act as an electron donor in denitrification, so it is not desirable to eliminate them. Therefore, an optimal ozone dose which leads to the maximum SCOD of the supernatant was decided.

Ozone Dose Optimization

To maximize the release of organic carbon from the sludge, the sludge was ozonized at different ozone doses. The ozonation process is generally described by the sequential decomposition reactions of floc disintegration, solubilization, and the subsequent oxidation of the released organics into carbon dioxide (mineralization) (Chu et al., 2009). They all would cause the changes in composition of the supernatant. Many researches showed that an ozone threshold exists in sludge ozonation (Dytczak et al., 2007; Yan et al., 2008). The reported optimal ozone dose range was 50–500 mgO₃/gSS (Wei et al., 2003).

During the course of ozonation, there are significant rises of the indexes like SCOD, nitrogen, phosphorus, proteins, polysaccharides and DNAs. Ammonia and Nitrate except

NO₂-N were found increased with the introduction of ozone in the experiment (Figure 4).

NO₂-N produced from sludge lysis was oxidized into NO₃-N by ozone soon after it was produced, which made the NO₂-N concentration rise first and fall afterwards. Because the nitrogen added was controlled at a relatively low level in the sludge cultivation to avoid the interference to A/O system, the concentration of nitrogen in the ozonation process remained at a low level.

It is also worth mentioning that in a BNR process, through nitrification and denitrification, nitrogen is transformed into gas. So, in a good operation system, low content of nitrogen can remain in sludge, and with sludge circulation the content will become even lower. In ideal condition, organic N in microorganisms will be the main form for nitrogen in sludge. But because the experiment was carried out not long enough, the decline of nitrogen content in sludge was not detected.

The changes of SCOD were divided into 3 distinct phases. When the ozone dose was below 0.05 gO₃/gSS (phase I), SCOD increased slowly because of the weak sludge lysis in this phase. SCOD increased linearly as the ozone dose increased from 0.05 to 0.15 gO₃/gSS (phase II). Because this phase was associated with high sludge reduction rates as shown in Figure 3b, the significant SCOD increased was believed to be due to cell damage and the release of the cytoplasm and intracellular matters into water. When ozone dose further increased above 0.15 gO₃/gSS (phase III), SCOD started to fall indicating mineralization of the released organics began playing the major role in this phase.

To determine the optimal ozone dose, a further experiment was carried out. The ozone dose was set in range of 0.16–0.28 gO₃/gSS in which the highest level of SCOD suppose to be got. The samples at the ozone dose interval of 0.2 gO₃/gSS in the range were got and checked. The changes

FIGURE 4. Relationships between ozone dose and quality changes of the sludge supernatant.

FIGURE 5. SCOD, BOD and biodegradability of the supernatant after ozonation of the sludge at different ozone doses.

of SCOD, BOD₅ and biodegradability (BOD₅/SCOD ratio) were shown in Figure 5.

At these ozone doses, the SCOD concentration maintained at 1000 ± 50 mg/L firstly, and then decreased gradually as the ozonation proceeded. The release of organics from sludge lysis and oxidation of organics into inorganic matter like CO₂ have opposite effects on the SCOD change. At ozone dose of 0.16–0.24 gO₃/gSS, the interaction of the two processes

made an equilibrium of the SCOD concentration. But the changes still occurred which can be represented by BOD₅ and biodegradability and at 0.20 gO₃/gSS the highest BOD₅ was obtained. Therefore, the ozone dose of 0.2 gO₃/gSS is desirable to produce the optimal denitrification carbon source through sludge ozonation. The changes of the sludge supernatant before and after the ozonation using the optimal ozone dose were shown in Table 2.

TABLE 2. Quality Parameters of the Supernatant Before and After Sludge Ozonation

Item	Before ozonation	After ozonation	Increase (%)
Total COD (mg/L)	124.2	1085	773.59%
Total BOD (mg/L)	53.9	927	1619.85%
NH ₃ -N (mg/L)	2.6	6.0	128.52%
NO ₃ -N (mg/L)	1.5	4.8	231.29%
NO ₂ -N (mg/L)	—	1.9	—
TN (mg/L)	3.4	13.0	278.2%
MLSS (g/L)	5.7	2.5	−56.37%
MLVSS (g/L)	3.4	0.8	−76.47

A/O Nitrogen Removal Experiment

The traditional BNR technology is a nitrification–denitrification process. During denitrification, carbon source is used as electron donors to transform nitrate to gaseous nitrogen. Besides the sufficiency of the carbon source, the nature of the carbon source also strongly influences the denitrification rate (Isaacs and Henze, 1995). To investigate

the denitrification behavior in the case of OS supernatant being used as the extra carbon source, about 100 mg/L NH₃-N were added to the supernatant of OS. The influent water qualities were similar at stage 1 and 2 except for the carbon source (Table 1), so that the influences of the OS on nitrogen removal efficiencies could be compared.

A 20-day start-up was operated first, after which the indexes (i.e., SCOD, TN, NH₃-N and sludge yield) were maintained stable. At stage 1, with glucose as the extra carbon source, the A/O system showed a good capability in removing SCOD and nitrogen (Figure 6). The average removal rates of SCOD, NH₃-N and TN were 84%, 85% and 79%, respectively. At stage 2, the OS supernatant was introduced to the A/O system as the extra carbon source. At this stage, although we had tried to keep the influent the same as that at stage 1, there were concentration fluctuations of SCOD and TN. NH₃-N, TN removal rates dropped significantly and no restoration was found in the next 10-day operation. This A/O system used in the experiment was equipped with spherical fillers to enhance its removal efficiency and resistance to impact load. The spherical fillers had been proved effective by the previous research. Therefore, the fluctuation of the influent was not supposed to be the cause for the reducing removal efficiency. The OS supernatant was suspected to have imposed some negative impact to the BNR process.

FIGURE 6. SCOD, NH₃-N and TN of the influent and effluent of the A/O system.

FIGURE 7. The comparison of alkalinity unadjusted and adjusted. (a) pH and alkalinity changes in the sludge ozonation. (b) NH₃-N and TN removal efficiencies with OS supernatant as carbon source (alkalinity unadjusted; alkalinity adjusted).

During the 41st–50th days, there was also a decline of nitrification rate. Nitrification is a process that consumes alkalinity but not COD. Using CaCO₃ to represent the alkalinity, nitrification needs 7.14 gCaCO₃ to transform 1 gNH₃-N to 1 gNO₃[−] (Li and Irvin, 2007). During sludge lysis, volatile fatty acids were produced and accumulated (Barlindhaug and Odegaard, 1996a), which could cause decrease in both pH and alkalinity of the OS supernatant (Figure 7a). With OS supernatant circulated, the influent to the A/O system had a pH of 5.7 and the alkalinity of 120 mg CaCO₃/L respectively, which were much lower than those in stage 1 (pH = 8.2, alkalinity = 310 mg CaCO₃/L).

The alkalinity of the influent was adjusted since the 51st day by adding calcium carbonate in sludge ozonation. The calcium carbonate maintained the pH and the alkalinity at constant levels during ozonation. At the same time, because CaCO₃ is weakly soluble, the influence of CaCO₃ addition on ozonation could be neglected. With alkalinity being adjusted, the pH and the alkalinity of the OS supernatant increased to 7.1 and 300 mg/L, respectively, and from then on, the removal rates of NH₃-N and TN increased gradually in the next 20 days (Figure 7b). TN removal rate reached a maximum 82% and an average 78% in the last 10 days.

The treatment efficiencies of stage 1 and stage 2 are shown in Table 3. When glucose was used as the carbon source (stage 1), the system was a conventional A/O. Sludge ozonation worked at stage 2. Because sludge produced in the A/O was not enough, external sludge was used at this stage, which made a negative growth of the sludge of the system.

CONCLUSIONS

This study investigated the feasibility of using ozonized sludge (OS) supernatant as an extra denitrification carbon

source for low C/N wastewater treatment. Results show that the OS supernatant can be used as an extra carbon resource at the optimal ozone dose of 0.2 gO₃/gSS. Extra alkalinity may need to be added into the OS supernatant because acid materials can be generated through ozonation. The A/O system with OSR can achieve similar nitrogen removal rate with that when glucose was used as the extra carbon source. Therefore, the ozonized sludge can substitute the traditional extra carbon source partly or totally to improve nitrogen removal during wastewater treatment.

But the economic feasibility of the technology still needs to be evaluated by practical operation or field test. The feasibility of using OS for other carbon demanding process is another interesting topic. But it needs to be realized that unlike nitrogen, most of the pollutants are removed through separation of sludge containing pollutants from water. Phosphorous (P) is very typical example. In this case, P will accumulate in sludge and ozonation will release it again. So, the pollutant being transformed to gas and removed during water treatment is a very important key for the reuse of OS.

TABLE 3. Treatment Efficiencies at Stage 1 and 2

	Stage 1	Stage 2
SCOD removal rate	84%	91%
TN removal rate	79%	78%
NH ₃ -N removal rate	85%	82%
Sludge yield	+0.4 gMLSS/gSCOD	−2.6 gMLSS/gSCOD

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