Effect of ozonation on sludge reduction in a SBR plant

A. Chiavola, M. Naso, E. Rolle and D. Trombetta

Department of Hydraulics, Transportation and Roads, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Rome, Italy (E-mail: *massimiliano.naso@uniroma1.it*)

Abstract This paper provides new insights on the application of the ozonation process for the reduction of activated sludge production in a Sequencing Batch Reactor. The study was performed on two identical lab-scale SBRs plant, fed with domestic sewage: a fraction (1/3 of the working volume) of the activated sludge from one reactor (Exp SBR) was periodically subjected to ozonation for 30 minutes at 0.05 g O_3/gSS and then recirculated before the beginning of the cycle; the other reactor was used as control and therefore managed at the same sludge retention time but without the application of ozonation. The effects of the recirculation of the ozonated sludge to the Exp SBR were evaluated in terms of biological nitrogen and carbon removal efficiencies, Mixed Liquor Volatile and Suspended Solids (MLSS and MLVSS, respectively) concentrations, effluent quality and sludge settleability. Besides, characterization of the ozonated sludge was carried out for different oxidant dosages (0.05, 0.07 and 0.37 g O_3/gSS) and durations of the ozonation process (10, 20 and 30 minutes). The results show that at 0.05 g O_3/gSS and 30 minutes contact time MLVSS as well as MLVSS/MLSS ratio do not change appreciably. Ozone dosage must be increased much further to obtain a relevant effect.

Keywords Activated sludge; biodegradability; ozonation; sludge reduction

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Introduction

For the final disposal of the excess biological sludge, landfilling represents the most common solution currently adopted in wastewater treatment plants, particularly in Italy, due to the lower related costs, as compared to the alternative technologies, and the wide availability of landfill plants. However, the very restrictive constraints which must be respected by the landfilled sludge according to the new legislation, are determining an appreciable increase of the treatment and disposal costs. Therefore, the investigation of alternative solutions is receiving major interest, as well as the evaluation of all the strategies aimed at reducing the biological sludge production at source. Several methods have been already proposed in order to address such a problem, some of which seem to be quite efficient and economically sustainable. An innovative system has been developed which couples activated sludge process with disintegration of sludge recycle achieved through the application of mills, ultrasounds, heat, alkali or ozone (Yasui *et al.*, 1996; Deleris *et al.*, 2000; Wei *et al.*, 2003). Among these alternatives, partial ozonation of a fraction of the returned activated sludge stream has been demonstrated to be one of the most cost effective technologies with the highest disintegration capability (Huysmans *et al.*, 2001).

The application of ozone induces bacteria cell damage and the release of colloidal and soluble materials, part of which are biodegradable (Yeom *et al.*, 2002). By carefully controlling the ozonation process, reduction of the net sludge production can be achieved. Besides, the recirculation of the ozonated sludge stream to the oxidation tank, causes an increase of the organic loading factor in the influent, which may positively affects biological nitrogen removal (Ahn *et al.*, 2002a, b). Despite the numerous studies recently carried out on this topic, there are still numerous aspects which need to be further investigated in order to provide a better understanding of the effects of the

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ozonation process on both sludge characteristics and treatment plant efficiencies (Kamiya and Hirotsuji, 1998; Lee *et al.*, 2005; Yoon and Lee, 2005).

The present paper shows the results obtained through an experimental work aimed at investigating the effect of the ozonation process in a Sequencing Batch Reactor (SBR) plant. Ozone dosage and duration of the oxidation process were fixed and the long term effects of the recirculation of the ozonated sludge on biological nitrogen and carbon removal, effluent quality, sludge settleability and activated sludge concentration in the reactor determined. Besides, different oxidant dosages and durations of the ozonation process were applied to sludge samples collected from the waste stream; their effects were evaluated in terms of variations of soluble and particulate COD fractions, ammonia nitrogen concentration, total and volatile suspended solids, biological respirometric activity.

Materials and methods

Lab-scale plant

Two identical Sequencing Batch Reactors (SBRs), one used for process control (Control SBR) and the other one for the ozonation studies (Exp SBR), were set up in laboratory scale. At regime conditions both worked through 6 daily cycles, each one lasting 4 hours. Phase duration of each operating cycle is shown in Table 1. Each plant had a working liquid volume of 6 L and was operated at 26 ± 1 °C.

At the beginning of the cycle, 2 L influent was fed to each reactor; an equal volume of supernatant was drawn at the end of the settle phase. The hydraulic retention time (HRT) was fixed to 12 hours.

Peristaltic pumps were used to supply influent feed and to draw supernatant and excess sludge. During the aerobic react phase, aeration was provided by means of a compressor connected to porous stones located close to the bottom of the reactors. The dissolved oxygen (DO) concentration was always above 2 mg/L. Pumps, aeration and mixing systems were controlled by a timer.

The feed solution was the influent stream to the full-scale municipal wastewater treatment plant of the city of Rome, after screening and degritting (780,000 P.E. and 354,000 m^3/d as average flow rate). The average Chemical Oxygen Demand (COD) and ammonia concentrations in the feed solution were approximately 200 mg COD/L and 20 mg NH_3-N/L, respectively. Due to the very low organic loading in the feed, a static fill was adopted for each operating cycle in order to expose biomass to higher substrate concentration at the beginning of the following react phase. The feed solution was stored into refrigerator at 4 °C under mixed conditions. Activated sludge from the oxidation tank of the full-scale treatment plant was used as seed for both reactors. The initial concentration of the seed was 4000 mg MLVSS/L. During the first 30 d of the experimental activity, since the effects of the ozonation process on the activated sludge concentration in the reactor were unknown, the sludge retention time (SRT or Θ_c) in the Exp SBR was maintained very high (no sludge waste was applied beside samplings). Afterwards it was fixed at 20 d. In the Control SBR, SRT was always kept equal to 20 d, corresponding to a

Table 1 Operating conditions of the lab-scale SBRs

Phase	Duration (min)
Static fill	7
Anoxic react	33
Aerobic react	120
Settle	40
Draw	10
Idle	30

sludge waste flow rate of 300 mL/d. In the Exp SBR, 700 mL of activated sludge was collected three times per week at the end of the react phase, subjected to ozonation and then recirculated to the reactor at beginning of the next cycle. Long term effects on Exp SBR performances were evaluated at the following ozonation conditions: ozone dosage of 0.05 gO_3/gSS, corresponding to 20 gO_3/Nm^3, (35% generator power), 1.5 atm of gas flux, 30 minutes as contact time.

Both reactors were continuously monitored by measuring the following parameters: MLSS, MLVSS in the reactors, ammonia nitrogen, NO_2-N, NO_3-N, total and different COD fractions in both the influent and the effluent and at the end of the anoxic phase, Sludge Volume Index (SVI), Total and Volatile Suspended Solids (TSS and VSS, respectively) in the effluent.

Track studies were also carried out within typical operating cycles, in order to determine removal patterns and kinetic parameters in the presence and absence of recirculation of ozonated sludge. Samples of mixed liquor were collected at regular intervals during the fill and the react phases, filtered and then analyzed. pH and Oxygen Uptake Rate (OUR) were also measured.

Tests of sludge characterization

Samples of the excess sludge drawn from the Control SBR were used to investigate the effects on the sludge characteristics of different durations (10, 20 and 30 minutes) of the ozonation process and of the oxidant dosages (0.05, 0.07 and 0.37 gO_3/gSS). Particularly, total, soluble and particulate COD fractions, TSS and VSS concentrations, and OUR were measured on sludge samples before and after ozonation for the different conditions.

The observed growth yield, Y_{obs}, of the ozonated sludge was also calculated. Therefore, sludge sample was firstly maintained under aeration for 12 h in order to establish endogenous conditions and then spiked with the influent feed so as to reproduce the same organic loading factor of the lab-scale reactor. Nitrification process was inhibited by adding thiourea to the mixed liquor before the test. Y_{obs} was finally calculated by the following equations based on the total amount of COD removed (ΔCOD) and the OUR related to the exogenous substrate consumption (OUR_{ex}):

$$Y_{obs} = \frac{Y_H}{1 + k_d \Theta_c} \qquad Y_H = \frac{\Delta COD - \int_0^t OUR_{ex}}{\Delta COD}$$

where k_d is the constant of endogenous decay, calculated to be equal to 0.03 d^{-1}.

Ozone system

The ozonation process was performed with the ozone generator BMT802M, supplied by Air Liquide Italia. The sludge collected from the Exp SBR was transferred to a 1 L contact chamber, where it was maintained for a prefixed duration under the ozonating flux. The ozone transfer efficiency was computed by in and off-gas measurements using an ozone detector. The transfer efficiency was always over 90%.

Analytical methods

Analyses of MLSS, MLVSS, COD, NH3-N, NO2-N, NO3-N concentrations in mixed liquors, influents and effluents were performed according to standard methods (*Standard Methods*, 1998). BOD measurement were also carried out by using FTC90 by Velp. pH and ORP were measured directly in each reactor by using pH and ORP meters (HI8417 and HI3230B by Hanna Instruments, respectively). OUR measurements were conducted by an automatic DO/OUR meter (UCT Chemical Engineering High Tech Micro Systems).

Results and discussion

Long-term effects

Figure 1 shows MLSS and MLVSS concentration time profiles and MLVSS/MLSS ratio measured throughout the experimental activity in the Exp SBR for an ozone dosage of 0.05 gO_3/gSS (35%) and 30 minute contact time. It can be noted that mixed liquor concentration did not change appreciably with time, even when sludge waste was introduced. The cryptic growth seems to be compensated by the amount of biomass been destroyed in the oxidation treatment, giving a net contribution to biomass growth close to zero.

It is noteworthy that during the first 30 d, no sludge waste was applied (except for the samples collected for the analyses), whereas in the last 60 d Θ_c was fixed at 20 d. Therefore, ozonation was less effective during the last period of observation, because the constant profile of the mixed liquor concentration must be attributed to both effects: sludge waste and oxidation of the return sludge stream. The result might be related to the reduction of the MLVSS/MLSS ratio from 0.63 to 0.47 (as average value) observed in this period. The higher inert fraction being present in the influent may have acted as a shield which protected microorganism cells from oxidant action.

In the Control SBR, a net decrease of MLVSS concentration was observed until the steady state mixed liquor concentration, corresponding to a Θ_c of 20 d, was achieved.

A lower O_3 dosage of 0.025 gO_3/gSS (17% generator power) was applied for a short period giving the effects shown in Figure 2. A net increase of MLVSS concentration was observed, reflecting the reduced effectiveness of the oxidation process. The bacterial cells react to low ozone dosage by increasing the anti-oxidant production (such as glutathione); then, such compounds protect cell against sub-lethal doses of ozone (Dziurla, 2005).

Sludge settleability improved with time in the Exp SBR due to ozonation. The settling rate, shown in Figure 3 increased from 0.9 to 2.03 mL/min. In the same reactor, the SVI decreased from 70 mL/g to about 40 mL/g, whereas remained basically constant in the Control SBR (equal to about 60 mL/g). The effluent quality was also improved by ozonation, and average SST concentration decreased from 25 mg/L to 5 mg/L. The microscopic observation of the activated sludge before and after the oxidation treatment confirmed the effectiveness of ozone: filamentous bacteria were damaged, free suspended cells increased as well as small size flocs.

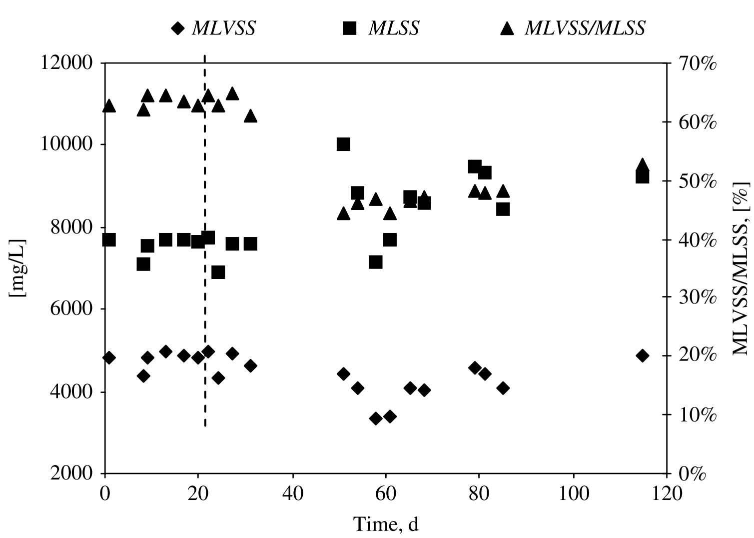

Figure 1 MLSS and MLVSS concentration and MLVS S/MLSS ratio in Exp SBR

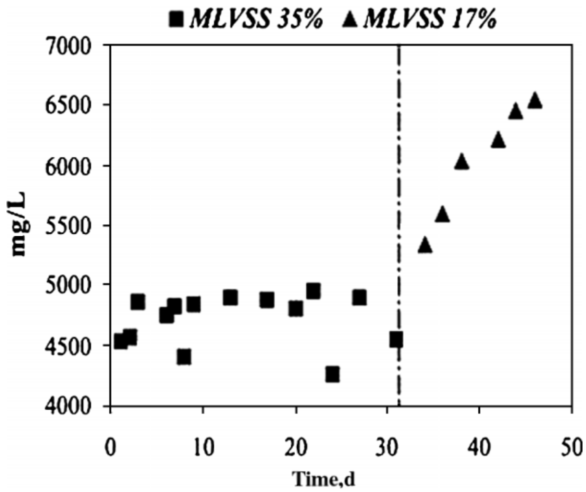

Figure 2 MLVSS concentration in Exp SBR for 0.05 gO_3/gSS (35%) and 0.025 gO_3/gSS (17%)

Figure 4 shows soluble COD (i.e. filtrate at 1.2 μm) concentration measured in the activated sludge before and after the ozone treatment. It can be noted that a very high increase was achieved due to the oxidation of particulate matter into soluble compounds; the recirculation of the ozonated sludge into the reactor at beginning of the next cycle resulted in augmentation of influent organic loading of about 35% (as average). Nonetheless, such an increase did not appreciably affected COD removal efficiency which was about 90% in both SBR plants.

Filtrate ammonia nitrogen in the activated sludge increased as well as due to ozonation at 0.05 gO_3/gSS. When a lower dosage was used (of 0.025 gO_3/gSS), still an increase was observed although much lower, probably because ozonation was unable to achieve break down of protein molecules. The recirculation of ozonated sludge to the reactor determined an increase of the ammonia nitrogen influent loading. The nitrification process efficiency was negatively affected, as compared with that measured in the Control SBR (Figure 5).

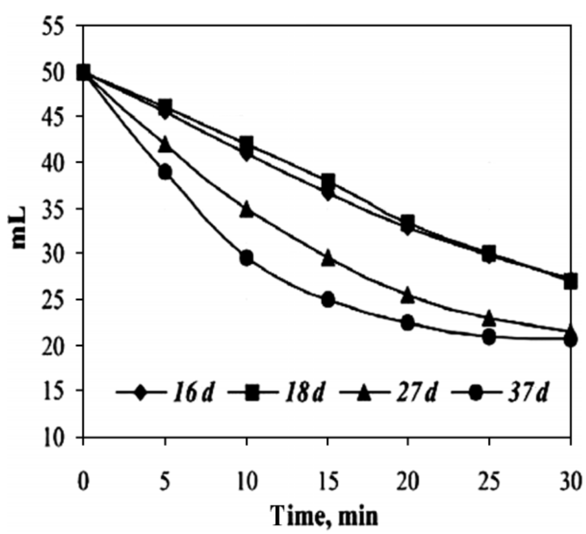

Figure 3 Settling rate in Exp SBR

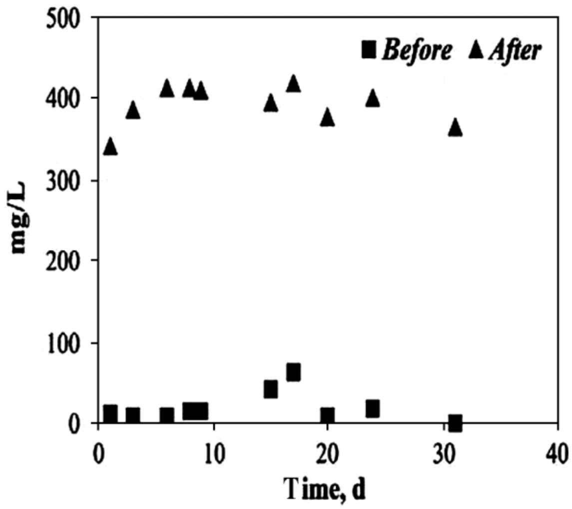

Figure 4 Soluble COD concentration in the activated sludge before and after ozone treatment

However, such an effect remained still very limited, and nitrogen removal efficiency was always about 98% in both reactors. It must be pointed out that domestic sewage used as feed was always characterised by a very low nitrogen load (in the range of 25–15 mg/L as soluble ammonia). An increase of NO_2-N and, especially of NO_3-N was observed after ozonation due to the partial oxidation of the released ammonia.

Several track studies were performed during the experimental activity with the aim of investigating time profiles of different parameters within the operating cycles. Figure 6 shows soluble COD concentration during two track studies carried out in the Control SBR and in the Exp SBR after recirculation of ozonated sludge.

A considerable increase of soluble COD in the feed was observed in the Exp SBR as a consequence of ozonation; nonetheless, degradation rate was still very fast, and complete COD removal was achieved by the end of the anoxic phase. Conversely, in the Control SBR, despite a fast removal rate, residual COD of about 35 mg/L remained in the reactor and did not undergo any degradation either in the following aerobic react phase. The different results can be related to the ability of ozone to oxidize complex

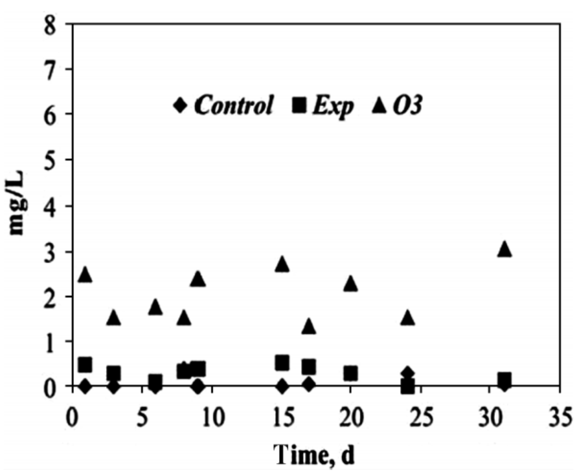

Figure 5 Soluble ammonia nitrogen in the activated sludge at the end of the react phase and after ozone treatment in SBRs

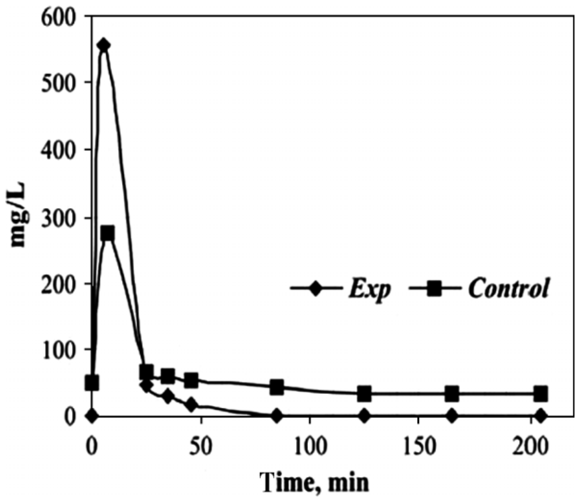

Figure 6 Soluble COD during track studies in Exp SBR after ozonation and in Control SBR

and/or inert soluble compounds into more biodegradable materials. An improvement of denitrification process efficiency was observed due to the raised availability of biodegradable COD.

Sludge characterization

With prolonged ozonation time from 10 to 30 minutes, soluble COD/total COD (SCOD/TCOD) percentage ratio raised for ozone dosages of 0.05 gO_3/gSS and also of 0.07, due to the release of organic materials by broken cells (Table 2).

At much higher ozone dosage (0.37 gO_3/gSS), solubilization did not change appreciably with duration. SCOD/TCOD ratio increased only for 10 and 20 minutes of treatment; longer ozonation resulted in oxidation of the released soluble materials, and the ratio lowered.

The increase of soluble COD from cell oxidation caused higher OUR values in the treated sludge at 0.05 and 0.07 gO_3/gSS; with prolonged ozonation above 20 minutes, bacterial respirometric activity diminished due to reduced availability of organic substrate. At higher ozone levels, dosage had major influence than contact time: OUR decreased very rapidly with time and after 20 minutes of the aerobic test, the biomass turned into endogenous conditions. Figures 7, 8 and 9 show OUR profiles measured at 0.05, 0.07 and 0.37 gO_3/gSS respectively, for different durations.

Determinations of Y_{obs} of ozonated sludge at 0.05 gO_3/gSS after 10, 20 and 30 minutes contact time gave approximately the same result, that was 0.26 mg O_2/mg COD removed. The same determination performed on sludge sample collected before the ozonation, had given very similar value.

Table 2 O_3 dosage and Contact Time based SCOD/TCOD increase (%)

Dosage Time	0′	10′	20′	30′
0.05	0	3.2	4.7	14.9
0.07	2.7	2.8	2.5	4.9
0.37	2.7	3	3.7	2.6

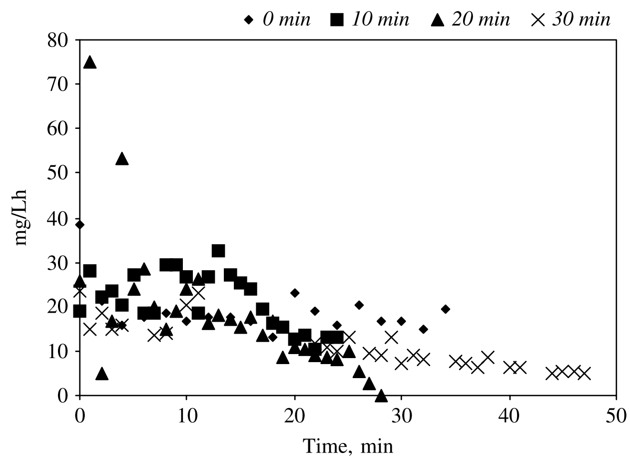

Figure 7 OUR profiles at 0.05 gO_3/gSS for different durations

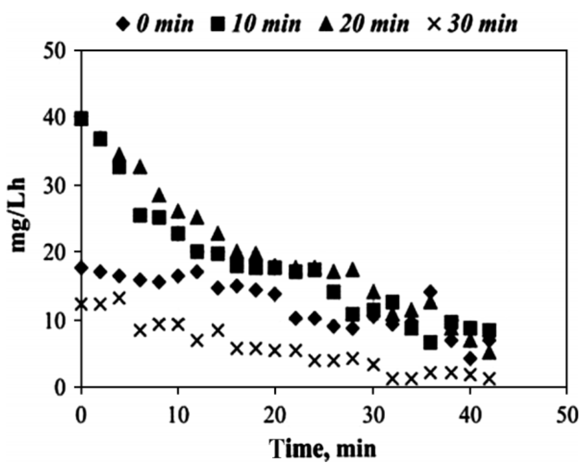

Figure 8 OUR profiles at 0.07 gO_3/gSS for different durations

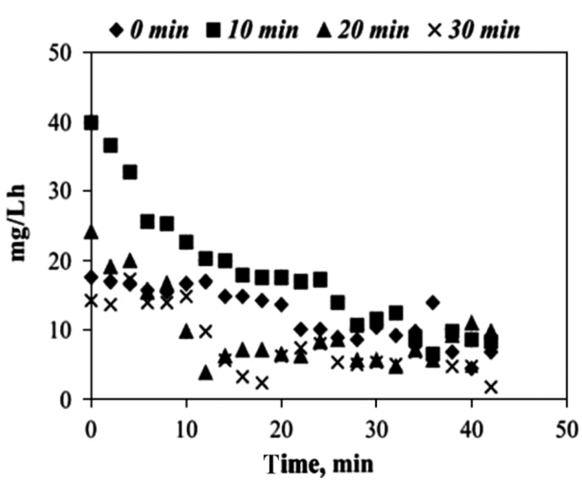

Figure 9 OUR profiles at 0.37 gO_3/gSS for different durations

Conclusions

From the results obtained in the present experimental work it is possible to draw the following conclusions. Ozonation at 0.05 gO_3/gSS and 30 minute contact time did not achieve the aim of reducing sludge production in the SBR plant. Soluble COD concentration rose as a consequence of oxidation of particulate matter. Then, cryptic growth gave rise to biomass production which compensated for MLVSS that been destroyed by ozonation. However, the effects of the oxidation treatment strictly depended on the composition of the influent stream used as feed for the SBR: this was frequently rich in particulate matter which probably reduced ozone efficiency. Ammonia nitrogen increase was also observed in the ozonated sludge. Nonetheless, nitrogen and carbon loading in the influent remained still very low despite the addition of NH_3 and COD with the recirculated sludge. Therefore, removal efficiencies were not modified appreciably. Ozonation was also able to improve sludge settleability by reducing abundance of filamentous bacteria within microbial population.

Tests performed under different ozonation conditions showed that ozone dosage must be increased much further to achieve both sludge disintegration and soluble COD oxidation. At high ozone levels, duration has less effect than dosage; therefore, ozonation can be performed for a shorter time, giving raise to reducing costs.

It can be concluded that to pursue zero excess sludge production, ozonation conditions should be properly selected depending upon specific wastewater characteristics and system operation, and eventually dynamically adjusted as a function of variations of the influent stream.

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References

Ahn, K.H., Park, K.Y., Maeng, S.K., Hwang, J.H., Lee, J.W., Song, K.G. and Choi, S. (2002). Ozonation of wastewater sludge for reduction and recycling. *Wat. Sci. Tech.*, **46**(10), 71–77.

Ahn, K.H., Yeom, I.T., Park, K.Y., Maeng, S.K., Lee, Y.H., Song, K.G. and Hwang, J.H. (2002b). Reduction of sludge by ozone treatment and production of carbon source for denitrification. *Wat. Sci. Tech.*, **46**(11–12), 121–125.

Déléris, S., Etienne, P., Audic, J.M., Roustan, M. and Debellefontaine, H. (2000). Effect of ozonation on activated sludge solubilization and mineralization. *Ozone Sci. Eng.*, **22**, 473–486.

Dziurla, M.A. (2005). Variations of respiratory activity and glutathione in activated sludges exposed to low ozone doses. *Wat. Res.*, **39**, 2591–2598.

Huysmans, A., Weemaes, M., Fonseca, P.A. and Verstraete, W. (2001). Ozonation of activated sludge in the recycle stream. *J. Chem. Tech. Biotech.*, **76**(3), 321–324.

Kamiya, T. and Hirotsuji, J. (1998). New combined system of biological process and intermittent ozonation for advanced wastewater treatment. *Wat. Sci Tech.*, **38**(8–9), 145–153.

Lee, J.W., Cha, H.Y., Park, K.Y., Song, K.G. and Ahn, K.H. (2005). Operational strategies for an activated sludge process in conjunction with ozone oxidation for zero excess sludge production during winter season. *Wat. Res.*, **39**, 1199–1204.

Standard Methods for the Examination of Water and Wastewater (1998). 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Wei, Y., Van Houten, R.T., Borger, A.R., Eikelboom, D.H. and Fan, Y. (2003). Minimization of excess sludge production for biological wastewater treatment. *Wat. Res.*, **37**, 4453–4467.

Yasui, H., Nakamura, K., Sakuma, S., Iwasaki, M. and Sakai, Y. (1996). A full-scale operation of a novel activated sludge process without excess sludge production. *Wat. Sci. Tech.*, **34**(3–4), 395–404.

Yeom, I.T., Lee, K.R., Lee, Y.H., Ahn, K.H. and Lee, S.H. (2002). Effects of ozone treatment on the biodegradability of sludge for municipal wastewater treatment plants. *Wat. Sci. Tech.*, **46**(4–5), 421–425.

Yoon, S.H. and Lee, S. (2005). Critical operational parameters for zero sludge production in biological wastewater treatment process combined with sludge disintegration. *Wat. Res.*, **39**, 3738–3754.