

Application of excess activated sludge ozonation in an SBR Plant. Effects on substrate fractioning and solids production

M. Naso, A. Chiavola and E. Rolle

ABSTRACT

This paper provides new insights on the application of the ozonation process for the reduction of the activated sludge production in a sequencing batch reactor (SBR). The study was performed in two identical lab-scale SBRs plant, one for experimental activities (Exp SBR) and one used as control (Control SBR), both fed with domestic sewage. A fraction of the activated sludge collected from the Exp SBR at the end of the aerobic react phase was periodically subjected to ozonation for 30 minutes at three different specific dosages (0.05, 0.07 and 0.37 g O₃/gSS) and then recirculated before the beginning of the following cycle.

Recirculation of the ozonated sludge to the Exp SBR did not appreciably affect the efficiency of the biological nitrogen and carbon removal processes. Nonetheless, an improvement of the denitrification kinetic was observed. Mixed liquor volatile and suspended solids (MLSS and MLVSS, respectively) concentrations in the reactor decreased significantly with time for long term application of the ozonation treatment. Kinetic batch tests on unstressed sludge taken from Control SBR indicated that the different oxidant dosages (0.05, 0.07 and 0.37 g O₃/gSS) and durations of the ozonation process (10, 20 and 30 minutes) used remarkably affected chemical oxygen demand (COD) and organic nitrogen fractioning. In particular, soluble and biodegradable fractions seemed to be higher at lower dosage and longer contact time.

Key words | activated sludge, biodegradability, ozonation, sludge reduction, solubilisation

M. Naso

A. Chiavola

E. Rolle

Department of Hydraulics,
Sapienza University of Rome,
Transportation and Roads,
Via Eudossiana 18,
00184 Rome,
Italy

E-mail: massimiliano.naso@uniroma1.it

INTRODUCTION

The treatment and disposal of excess sludge in an activated sludge system requires tremendous costs, amounting to approximately half the overall operational cost for domestic waste water treatment. Italian legislation recently imposed new critical restrictions about biosolids characteristics to be respected for the final disposal. The scientific community and stakeholders are pressed to address such a problem by investigating alternative solutions as well as evaluating all the strategies aimed at reducing the biological sludge production at source.

Ozonation is one of the promising technologies for reducing waste activated sludge biomass production (Huysmans *et al.* 2001). The disintegration of returned activated

sludge (RAS) by ozone leads to a significant reduction of excess sludge production causing increased solubilisation and improved mineralisation of the organic solids (Yasui & Shibata 1994; Sakai *et al.* 1997; Ried *et al.* 2002). Particularly, during the ozonation process, two effects take place simultaneously: a) death of microorganisms and disruption of cellular membrane with the cell lysis, and consequently release of intracellular compounds, and b) dispersion of disrupted activated sludge flocs into the bulk solution and solubilisation of particulate matter with the consequent release of soluble and colloidal substrates, part of which are biodegradable.

Studies suggest that ozonation could even lead to a process with no excess sludge production (Yasui *et al.* 1996).

Furthermore, ozonated sludge could be effectively utilised as an additional carbon source in a biological nitrogen removal process saving a great deal of cost for external carbon sources (Ahn *et al.* 2002a,b).

Chiavola *et al.* (2007) investigated the effects of the recirculation of the ozonated sludge on biological nitrogen and carbon removal, effluent quality and sludge settleability in an SBR (Wilderer *et al.* 2001). Short term observations (about 100 d operating time) seemed to indicate that the specific ozone dosage of 0.05 g O₃/gSS and 30 minute contact time was not able to achieve an appreciable reduction of sludge production in the SBR plant. It was assumed that the cryptic growth gave rise to biomass production which compensated MLVSS destroyed by ozonation. Besides, the high particulate matter content of the influent stream probably acted as a shield which protected microorganism cells from oxidant action.

The objectives of the present paper are to investigate on the long term effects on SBR performance of recirculation of ozonated excess sludge into the reactor. In this case, the evaluation is performed for different specific ozone dosages. Furthermore, on sludge samples collected from the wasted (unstressed) sludge stream of the Control SBR, kinetic batch tests are carried out with the aim of determining variations on COD and nitrogen fractioning for different durations and dosages of the ozonation process.

Based on the results obtained in all the studies performed by the same authors, final considerations are presented which can allow selection of best operative conditions of the ozonation process in the SBR plant.

MATERIALS AND METHODS

Lab-scale plant

Two identical 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 six daily cycles, each one lasting 4 hours. The operational parameters are reported in Table 1.

At the beginning of the cycle, 2 L of influent was fed to each reactor; an equal volume of supernatant was drawn at the end of the settle phase. Peristaltic pumps were used to supply influent feed and to draw supernatant and excess

Table 1 | Operating conditions and parameters of the lab-scale SBRs

Typical phase	Duration (min)	V _{Tot} = 6 L	Q ₂₄ = 12 L/d
Static fill	7	V _{Fill} = 2 L/cycle	T _c = 4 h
Anoxic react	33		
Aerobic react	120	V _{Res} = 4 L/cycle	SRT = 20 d
Settle	40		
Draw	10	N _{Cycle} = 6	HRT = 0.5 d
Idle	30		

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 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 m³/d as average flow rate).

The average COD and ammonia concentrations in the feed solution were approximately 130 mg COD/L and 10 mg NH₃-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 concentrations at the beginning of the following reaction phase. Activated sludge from the oxidation tank of the full-scale treatment plant was used as seed for both reactors. In the Exp SBR, 700 mL of activated sludge was collected three times per week (corresponding to 300 mL/d) at the end of the react phase, subjected to ozonation and then recirculated to the reactor at the beginning of the next cycle. Long term effects on Exp SBR performances were evaluated at two different ozone specific dosages: 0.05 g O₃/gSS_{treated}, (20 g O₃/Nm³ and 35% generator power) and 0.37 g O₃/gSS_{treated} (150 g O₃/Nm³ and 100% generator power). The length of the ozonation process was fixed at 30 minutes contact time.

Both reactors performance were continuously monitored by measuring the following parameters: MLSS, MLVSS in the reactors, ammonia nitrogen, NO₂-N, NO₃-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.

Kinetic studies were also carried out within typical operating cycles, in order to determine the removal rates in the presence and absence of recirculation of ozonated sludge. Samples of mixed liquor were collected at regular intervals during fill and react, filtered and then analysed. pH and oxygen uptake rate (OUR) were also continuously measured.

Tests of sludge fractioning

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 g O₃/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. Fractioning of COD was performed by following the method described by Mamais *et al.* (1993) and by respirometric test conducted as described by Andreottola *et al.* (2006). N_{org} fractions were determined by using a simplified approach based on conversion factors, $i_{N,xx}$, from COD into nitrogen according to ASM models.

In the following, COD and organic nitrogen (N_{org}) fractions will be indicated according to ASM #1 classification (Henze *et al.* 1986):

S_S	biodegradable soluble COD
S_{ND}	biodegradable soluble N_{org}
S_I	inert soluble COD
S_{NI}	inert soluble N_{org}
X_S	biodegradable particulate COD
X_{ND}	biodegradable particulate N_{org}
X_I	inert particulate COD
X_{NI}	inert particulate N_{org}

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

MLSS and MLVSS in the mixed liquor, COD, NH₃-N, NO₂-N, NO₃-N concentrations in the influents and effluents were performed according to standard methods (*Standard Methods 1998*). Biochemical oxygen demand (BOD) measurements were also carried out by using FTC90 by Velp. pH and oxydation-reduction potential (ORP) were measured directly in each reactor by using pH and ORP metres (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

Tables 2 shows the average COD and ammonia–nitrogen removal efficiency measured throughout the experimental activity in the Exp SRB in the cycles performed before and after recirculation of ozonated sludge at different oxidant dosages and 30 minute contact time. High values were obtained for both COD and ammonia removal efficiency, with average effluent concentrations of 19 and 1.5 mg/L, respectively. It can be noted that overall efficiency did not change appreciably as a consequence of the recirculation of ozonated sludge to the reactor, particularly for COD. Ammonia removal efficiency slightly decreased for increasing specific ozone dosages. As reported by Böhler & Siegrist (2004), at high ozone dosages nitrifying bacteria might be partially inhibited, whereas at low ozone dosage

Table 2 | COD and ammonia removal efficiencies before and after recirculation

E%	Before ozone	0.05 mg O ₃ /mgSS _{treated}	0.07 mg O ₃ /mgSS _{treated}	0.37 mg O ₃ /mgSS _{treated}
COD	86	89	86	89
NH ₃	97	98	98	78

they would be protected within the sludge flocs by heterotrophs which are more abundant. This would explain why nitrogen removal efficiency did not differ appreciably due to recirculation of sludge ozonated at lower dosage.

Table 3 lists the average values of the specific biomass growth rate, μ , calculated in the same conditions based on long term total biomass measurements. The application of ozonation caused a remarkable reduction of biomass growth rate, particularly at higher ozone dosage.

Figure 1 shows cumulated trends of MLSS and MLVSS measured over time in the Exp SBR plant. As can be seen, the long term application of the ozone treatment caused an appreciable reduction of solids production with respect to the measurements performed in the absence of recirculation. It can also be noted that increasing specific ozone dosages did not significantly change the solid trend. Comparison of these results with those obtained by the authors in their previous work (Chiavola *et al.* 2007) highlights that ozone treatment probably became effective after a long period of application. It must be remembered that in the present case the volume of ozonated sludge and the frequency of ozonation which corresponds to the frequency of the recirculation of the ozonated sludge to the reactor, are both very modest as compared to the total mixed liquor volume of the plant. Therefore, the mineralisation of part of the ozonated sludge can appreciably affect the solid production only after a significant period of time.

Figure 1 also shows a progressive decrease of the MLVSS/MLSS ratio due to the increasing inert fractions observed over time, particularly at 0.37 g O₃/gSS. A lower dosage of ozone was capable of determining partial solubilisation of the particulate matter, whereas higher dosage probably determined preferably mineralisation of the solubilised matter rather than further oxidation of particulate substances.

Figure 2 shows the results obtained in the kinetic study conducted on wasted sludge at different contact time and for 0.05 g O₃/gSS ozone dosage. It can be noted that both MLSS

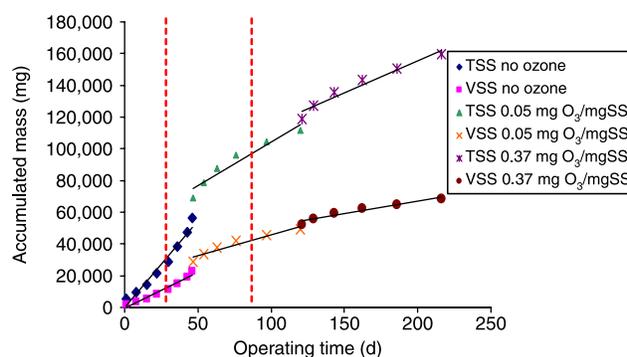


Figure 1 | Cumulative solids in Exp SBR before and after recirculation at different ozone dosages.

and MLVSS concentrations decreased almost linearly with the ozonation time. The pseudo-parallel trends seem to suggest that at this dosage the oxidation process affected both total solids and its volatile fraction in the same way.

Figures 3 and 4 show the effects of ozonation on nitrogen and COD fractioning determined in the kinetic studies for different dosages at 30 minutes contact time. As is well known, ozone treatment determines particulate matter conversion into soluble fractions. In the present case, the wasted sludge collected at the end of the aerobic react phase contained very low percentages of both S and S_N (0.8 and 0.3% of COD_{tot} and N_{tot} , respectively). The solubilisation effect was inversely proportional to the ozone dosage. For both COD and organic nitrogen, the particulate inert fraction increased significantly at higher ozone dosage; the inert soluble fraction was reduced appreciably only at the highest dosage. After 30 minutes contact time, the total soluble COD in the ozonated sludge accounted for approximately 20, 21 and 3% of COD_{tot} for 0.05 g O₃/gSS,

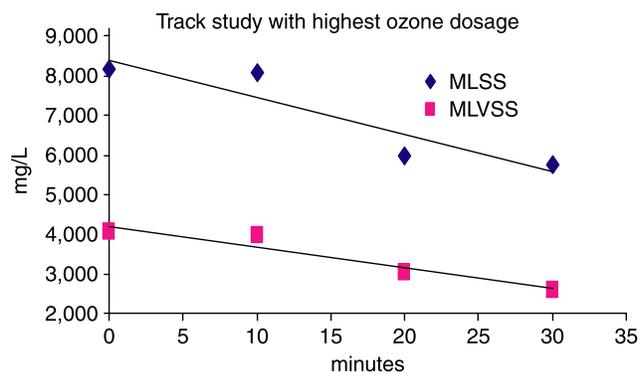


Figure 2 | Solids profile in the contact chamber with 0.05 mg O₃/mgSS.

Table 3 | Specific biomass growth rate before and after recirculation

	Before ozone	0.05 mg O ₃ /mgSS _{treated}	0.07 mg O ₃ /mgSS _{treated}	0.37 mg O ₃ /mgSS _{treated}
μ , d ⁻¹	0.054	0.032	0.021	0.009

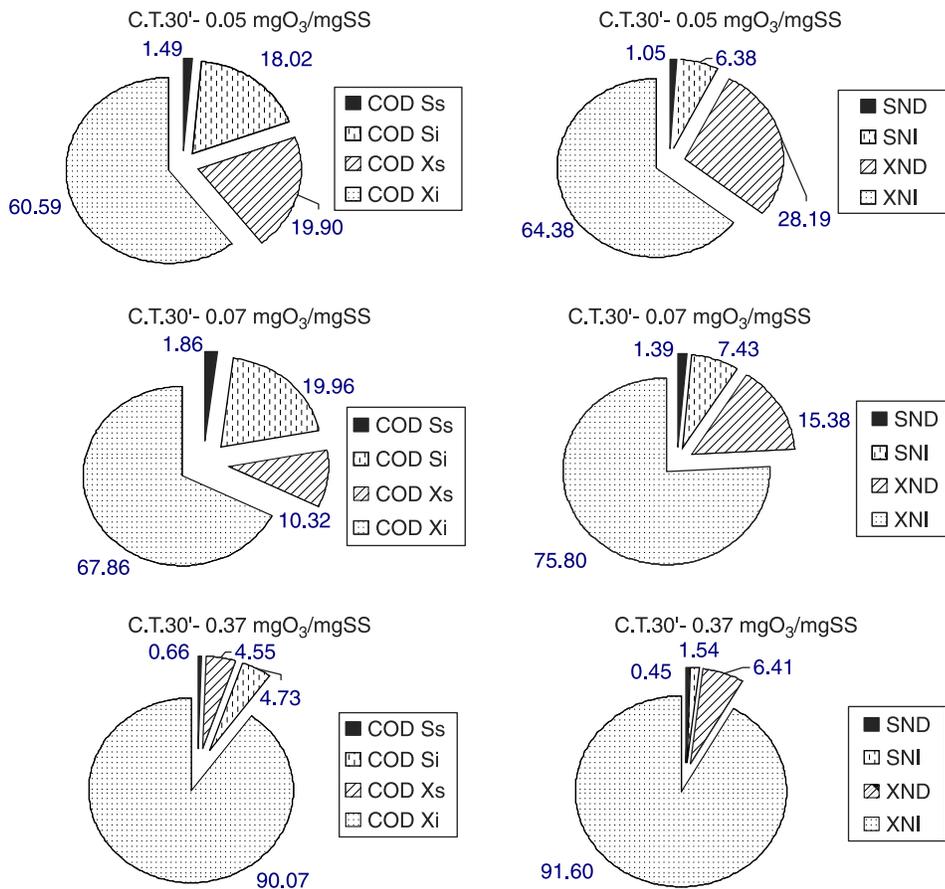


Figure 3 | Fractioning of COD and N_{org} for different dosages.

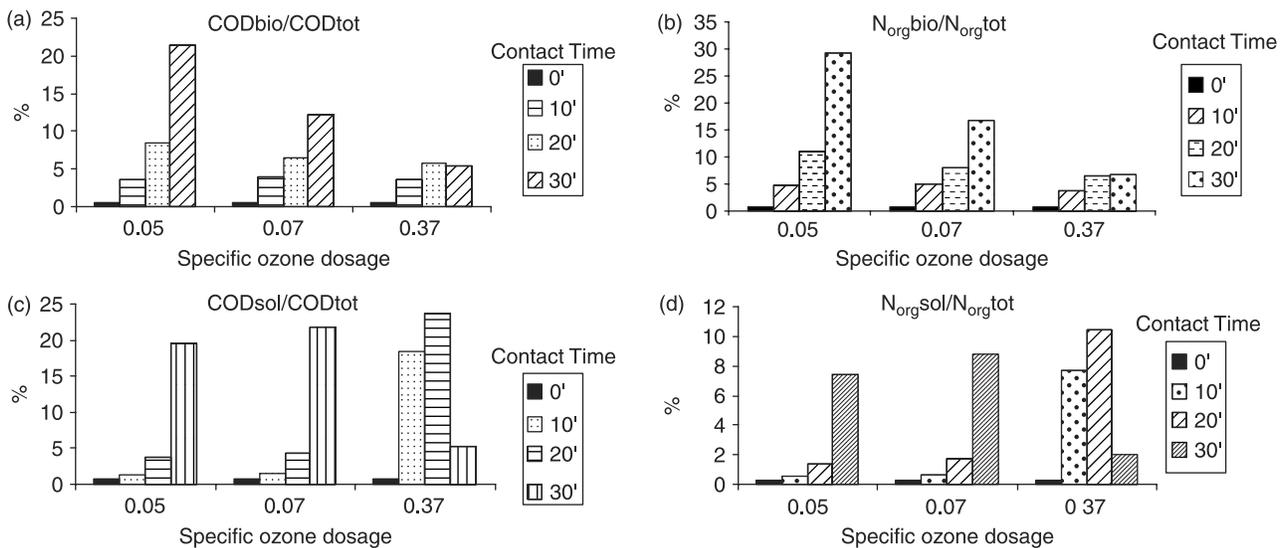


Figure 4 | Fractioning of COD and N_{org} for different dosages and contact times.

Table 4 | Maximum specific nitrate utilisation rate before and after recirculation

	0.37 mg O ₃ / mgSS _{treated}	0.05 mg O ₃ / mgSS _{treated}	Before ozone	Literature
k_{\max} , d ⁻¹ *	0.12	0.19	0.15	0.10

*In the cycle immediately after recirculation of ozonated sludge.

0.07 g O₃/gSS and 0.37 g O₃/gSS, respectively. The effects on organic nitrogen fractioning were quite similar.

Therefore, it can be concluded that a prolonged treatment of 30 minutes contact time resulted in oxidation of the released soluble materials and a decrease of solubilisation effect.

Dispersion of flocs aggregates in the bulk solution due to the oxidative treatment with the increase of soluble COD and N_{org} can be considered advantageous if associated to an increase of the biodegradability of the solubilised compounds. Therefore, in the evaluation of the capacity of excess sludge reduction, the measurement of the biodegradable fractions of lysate represents a key parameter. In fact, the reduction of sludge mass becomes effective when activated sludge in the reactor can accomplish oxidation of the solubilised compounds.

Figure 4 reports COD_{bio}/COD_{tot} and $N_{\text{bio}}/N_{\text{org}}$ ratio measured on wasted sludge from Control SBR which was treated at different ozone dosages and contact time. COD biodegradable fraction decreased for dosage increases and increased with ozone contact time, mainly at lower dosages (Figure 4a). For increasing specific ozone dosages, COD solubilisation efficiency decreased with time (Figure 4c) as already noted. As for biodegradable COD production, 0.37 g O₃/gSS seemed not to be convenient at any duration. For lower ozone dosages, optimal contact time was 30 minutes for both soluble and biodegradable COD production. Optimal time for the highest dosage was actually shorter, reaching most effective results at 20 minutes contact time.

No remarkable differences were appreciated in N_{org} fractions trends, although a direct proportion between biodegradable organic nitrogen release and durations was found (Figure 4b) at any dosages, as compared to the case of COD.

At higher ozone levels, dosage seemed to have a more major influence than contact time: longer ozonation resulted in oxidation of the released soluble materials.

The sludge lysate produced by the ozone treatment is recirculated into the Exp SBR, where the released

biodegradable fraction is subjected to oxidation. In the present case, when the biodegradable COD fraction was increased by the ozonation process it could be advantageously utilised as an additional carbon source to enhance the kinetic of the denitrification process. Data measured for the maximum specific nitrate utilization rate, k_{\max} , in the Exp SBR during a typical kinetic test, and presented in Table 4, confirmed the beneficial effect of the ozonation process at lower dosage on the removal rate of nitrate reduction.

CONCLUSION

The results obtained in the present experimental work and in the previous study conducted on the same topic suggest the following conclusions.

In the present case, the best ozonation conditions were found to be: 0.05 g O₃/gSS and 30 minutes contact time. These conditions allowed an appreciable reduction of solids production and increase of the readily biodegradable COD fraction to be achieved which, once introduced into the reactor through the recirculation of the ozonated sludge, had a beneficial effect on the kinetic of the denitrification process. Due to the low influent organic and nitrogen loadings applied to the SBR plant of this study, the incremented COD and N content in the influent did not affect the overall performance of the system.

Increasing the ozone dosage at 0.07 g O₃/gSS did not produce appreciable improvements. A much higher dosage of 0.37 g O₃/gSS and 30 minutes contact time had the same effects as 0.05 g O₃/gSS in terms of reduction of solids production. The application of such a high ozone level at different contact times evidenced that biodegradable COD was initially released and later oxidised, giving a net increase at 30 minutes being much lower than that measured for 0.05 g O₃/gSS and the same contact time.

Therefore, it can be concluded that in the present case, the application of ozonation can significantly reduce solids production with a modest increase of the operative treatment costs.

Further investigations need to be carried out with the aim of evaluating if better results can be obtained by increasing the volume of sludge to be subjected to ozonation.

ACKNOWLEDGEMENTS

The authors wish to thank Air Liquide Italia who supplied the ozone generator.

REFERENCES

- Ahn, K. H., Park, K. Y., Maeng, S. K., Hwang, J. H., Lee, J. W., Song, K. G. & Choi, S. 2002a Ozonation of wastewater sludge for reduction and recycling. *Water Sci. Technol.* **46**(10), 71–77.
- Ahn, K. H., Yeom, I. T., Park, K. Y., Maeng, S. K., Lee, Y. H., Song, K. G. & Hwang, J. H. 2002b Reduction of sludge by ozone treatment and production of carbon source for denitrification. *Water Sci. Technol.* **46**(11–12), 121–125.
- Andreottola, G., Foladori, P. & Vian, M. 2006 An integrated approach for the evaluation of bacteria damage and biodegradability increase in sonication of excess sludge. In *Proc. of IWA Specialized Conference Sustainable Sludge Management: state of art, challenges and perspectives*, Moscow, Russia, 29–31 May.
- Böhler, M. & Siegrist, H. 2004 Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking. *Water Sci. Technol.* **49**(10), 41–49.
- Chiavola, A., Naso, M., Rolle, E. & Trombetta, D. 2007 Effect of ozonation on sludge reduction in a SBR plant. *Water Sci. Technol.* **56**(9), 157–165.
- Henze, M., Grady, C. P. L., Gujer, W., Marais, G. v. R. & Matsuo, T. 1986 Activated Sludge Model No.1, IAWPRC Scientific and Technological reports, No.1, IAWPRC, London, ISSN 1010-707X.
- Huysmans, A., Weemaes, M., Fonseca, P. A. & Verstraete, W. 2001 Ozonation of activated sludge in the recycle stream. *J. Chem. Tech. Biotechnol.* **76**(3), 321–324.
- Mamais, D., Jenkins, D. & Pitt, P. 1993 A rapid physical-chemical method for the determination of readily biodegradable soluble COD in municipal wastewater. *Water Res.* **27**, 195–197.
- Ried, A., Stapel, H., Koll, R., Schettlinger, M., Wemhoner, F., Hamann-Steinmeier, A., Miethe, M. & Brombach, A. 2002 Optimierungsmöglichkeiten beim Betrieb von biologischen Klaranlagen durch den Einsatz von Ozon. *Korrespondenz Abwasser* **49**(5), 648–661.
- Sakai, Y., Fukase, T., Yasui, H. & Shibata, M. 1997 An activated sludge process without sludge production. *Water Sci. Technol.* **36**(11), 163–170.
- Standard Methods for the Examination of Water and Wastewater* 1998 20th edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Wilderer, P., Irvine, R. L. & Goronszy, M. C. 2001 *Sequencing Batch Reactor Technology*. IWA Publishing, London.
- Yasui, H., Nakamura, K., Sakuma, S., Iwasaki, M. & Sakai, Y. 1996 A full-scale operation of a novel activated sludge process without excess sludge production. *Water Sci. Technol.* **34**(3–4), 395–404.
- Yasui, H. & Shibata, M. 1994 An innovative approach to reduce excess sludge production in the activated sludge process. *Water Sci. Technol.* **30**(9), 11–20.