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Sludge Ozonation



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Full Scale Application of a Novel Sludge Ozonation Process for Achieving 40% and up to 80% Excess Sludge Reduction at a 25,000 m³/day Municipal Wastewater Plant

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Abstract

Although sludge ozonation in lab scale tests have tended to yield economic dosage rates in the regime of ≤ 0.1 kg O₃/kg SS removed, previous attempts to extend the approach to commercial scale installations have resulted in non-economical ozone dosage levels (Sievers et al, 2004; Yasui et al, 1996; Kobayashi et al, 2001; Sakai et al, 1997), requiring as much as 0.395 kg O₃ per kg SS removed (See Table 2). In this paper, we discuss a novel approach to sludge ozonation and report the results of full scale tests carried out at a 7 MGD (1100 m³/h) wastewater treatment facility which has been in operation since May 2006. A cost effective Ozone consumption value of 0.07 kg O₃/kg SS reduced was attained in the field, demonstrating the successful translation of bench scale type results to field applications using the Praxair approach.

Introduction

The activated sludge process is the most widely utilized method for wastewater treatment process due to its relatively low cost and relative ease of operation. The generation of excess sludge is an inevitable result of the biochemical processing of organic waste by microbial agents in the activated sludge process. Generally the excess sludge produced from the conventional aerobic biological wastewater treatment process ranges from 0.2-0.4 kg excess solids/kg COD removed depending on the Solids Retention Time (SRT), oxic state and microbial species distribution in the treatment system. The associated power and chemicals costs for solids handling and eventual disposal can be significant and as much as 40-60% of the costs of wastewater treatment are associated with the handling and disposal of excess solids (Tchobanoglous et al, 2003).

Several factors have emerged which increase the likelihood that sludge costs will continue to increase. For instance restrictions on the availability of landfills (In Germany f.e. TAsi 2001 (Verwaltungsvorschrift Technische Anleitung zur Verwendung, Behandlung und sonstigen Entsorgung von Siedlungsabfällen)), restrictions on the quality of biosolids used in land application and increasing citizen concerns over odor are causing sludge handling costs to increase. Recent regulatory pressures seem likely to increase the costs associated with sludge disposal. In the EU for instance,

while regulatory pronouncements like the Urban Waste Water Treatment Directive 91/271/EEC which requires that most of the EU populations be served by wastewater treatment facilities are leading to the generation of more excess sludge, other regulations like the Sewage Sludge Directive 86/278/EWG places restrictions on the agricultural application of sludge from the wastewater treatment process, while the landfill directive 1999/31/EC effectively limits the disposal routes for excess sludge (Perez-Elvira et al, 2006).

While the wastewater industry has traditionally focused on technologies that reduce the excess sludge generated at the back end of the wastewater treatment process, there has lately been a renewed interest in technologies focused on fundamentally reducing the generation of sludge in the aeration basin (WERF, 2004; Perez-Elvira et al, 2006).

Overview - Sludge Ozonation

Although several methods exist for achieving sludge minimization, the sludge ozonation process has been extensively studied and characterized, and has shown immense promise as a viable method for attaining consistent and reliable reduction of excess sludge (Yasui et al, 1996). The basic concept is the application of ozone to a side stream containing at a minimum, the equivalent portion of the excess sludge to be eliminated. The application of ozone to this stream causes the bacterial cells that come in contact with ozone to be lysed (Figure

1). Upon lysis, the cellular COD that is contained within the cells is leaked out, and the lysis products are then recycled back to the aeration basin where the bacteria feed on the released COD. The effective reduction in excess sludge is achieved when the COD generated from the lysed VSS (bacterial cells) is bio-oxidized in the aeration basin. The lysis COD when consumed, effectively generate a quantity of excess cells determined by the yield obtained within the wastewater treatment system.

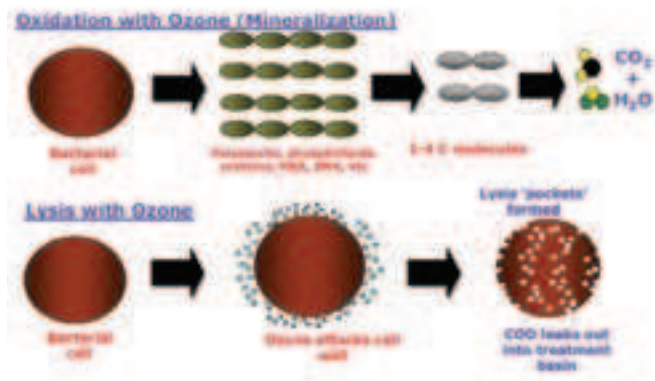


Figure 1. Principle of ozone lysis versus mineralization

While the conceptual case for sludge ozonation and other lysis based approaches is straightforward, and a significant amount of work has been done both at the lab and field scales, the sludge ozonation process has been slow to be adopted, largely because the amounts of ozone required to effect the sludge reduction are uneconomical. Ozone consumption values required to achieve cell lysis have ranged from about 0.165-0.395 Kg O₃/Kg TS removed (Yasui et al, 1996; Ried et al, 2002). Although the economical range of ozone consumption will necessarily depend on localized costs for sludge handling and disposal, we estimate that the range of ozone consumption that will be viable will be in the regime of ≤ 0.1 kg O₃/kg TS removed. The cost for sludge handling and disposal can vary between $< \text{€ } 80/\text{dry t TS}$ as a low cost range and $> \text{€ } 400/\text{dry t TS}$ as a high cost range. The operational cost for generating 1 kg ozone using oxygen can be estimated as $\text{€ } 1$ to 1.6. With an ozone consumption demand of 0.1 kg O₃/ kg TS removed, a total ozone demand of 100 kg ozone/ dry t TS is needed. This leads to operational costs of 100 to 160 €/dry ton TS.

Previous studies have indicated the possibility that sludge

ozonation can have a deleterious impact on several key operational parameters of the wastewater treatment process. Ried et al (2002) observed an increase in the effluent COD levels following sludge ozonation. Böhler & Siegrist (2004) have reported on the inhibition of nitrification and the improvement of denitrification observed during the sludge ozonation process. Raugust & Schwerdt (2004) reported about the possibility to completely eliminate filamental bacteria in the system.

Materials and Methods

Bench Scale Tests

Prior to commencing pilot tests in the field, initial bench scale tests were carried out in a 1.5" diameter sludge ozone contact unit. The bench scale tests were undertaken in order to establish the effects of different contacting configurations on the ozone dosage requirements, lysis effect of ozone contacting, COD release associated with the lysis process as well as the correlation of the COD release with the extent of VSS degradation achieved and the biodegradability of the COD released as a result of the lysis process.

Biodegradability was determined by comparing the oxygen uptake rates for the lysis products vs. a synthetic wastewater sample. Oxygen Uptake Rate (OUR) tests were carried out in a computerized N-CON Respirometer. Wastewater sludge samples were obtained from a municipal wastewater plant (Illinois, USA) with influent made up predominantly of sanitary wastewater. A 1L sample of synthetic wastewater was made up in distilled water by adding 16 g peptone, 11 g meat extract, 3 g Urea, 0.7 g NaCl, 0.4 g CaCl₂·2H₂O, 0.2 g MgSO₄·7H₂O, 2.8 g K₂HPO₄. The resulting wastewater was then diluted as required.

Full Scale Tests

The Lariana WWTP (25,400 m³/day; 10,000 kg/day COD removed – 2006 average) is located in Bulgarograsso (Como, Italy) and treats wastewater characterized by a predominant industrial (mainly textile) component: 62% as hydraulic flow rate and 75% as COD load during dry weather. The plant is a two-train aeration basin operation, with processes that includes an activated-sludge process for biological nitrogen removal (single sludge anoxic pre-denitrification - aerobic nitrification), followed by a sand filtration process for suspended solid removal, and final

effluent ozonation for the removal of color and surfactants. Prior to the commencement of the sludge ozonation process, all of the return activated sludge (RAS) was recycled to the anoxic pre-denitrification basin. The excess sludge is held in an aerobic holding tank and is then subsequently thickened and dewatered to about 19% dry solids content. The historical (2 year average) yield at the plant was 0.35 kg TS/kg COD removed.

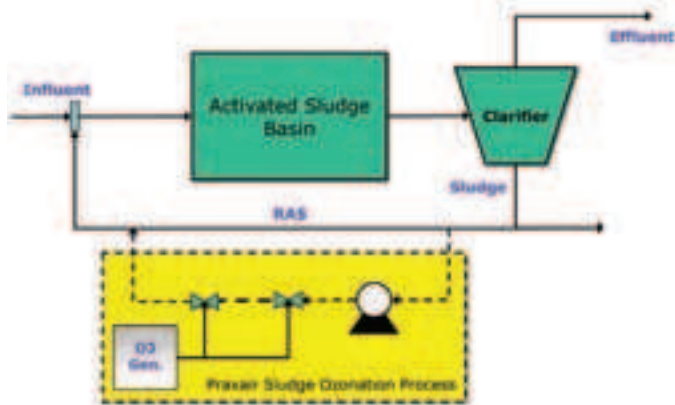


Figure 2. Generic schematic of the Praxair Sludge Ozonation Process

Praxair's sludge ozonation process Lyso™ comprises of an ozone supply system, a pump, and a gas liquid contacting system within which the sludge-ozone contact occurs (see Figure 2). The process requires that a portion of the RAS is passed through the sludge ozone contactor. System conditions are carefully controlled to ensure that an amount of ozone sufficient to implement the lysis of the bacterial cells is applied. An Allen Bradley SLC5/03 PLC system was used to provide automatic control of the process. Ozone was generated from pure oxygen. A 3-4 kg/h flow of a 7-8% w/w O₃ gas stream was applied to the portion of the RAS stream that flowed through the contactor. Because the primary RAS line at the Bulgarograsso plant is returned to an anoxic denitrification basin rather than to the nitrification basins, a separate RAS flow needed to be established for the sludge ozonation process as the high oxidic state of the ozonated sludge implies that this stream cannot be directly returned to an anoxic basin. Ozonated sludge was returned to both nitrification basins. Detailed microbiological and respirometric analyses were undertaken throughout the tests.

Results

Bench Scale Tests

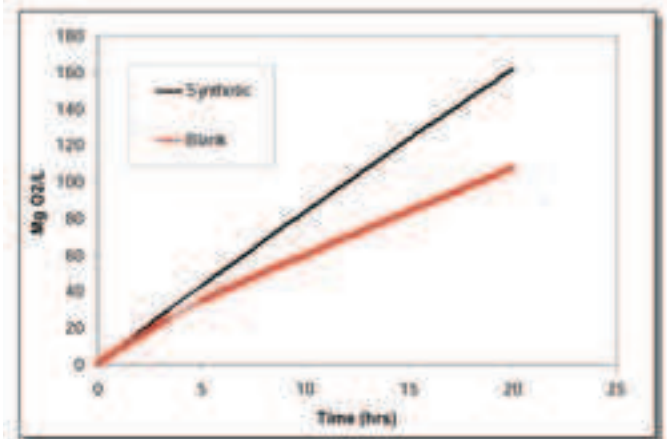


Figure 3. Baseline tests comparing OUR signature of sludge exposed to (synthetic) wastewater sample containing an ideal nutrient mix vs. a blank sample containing tap water.

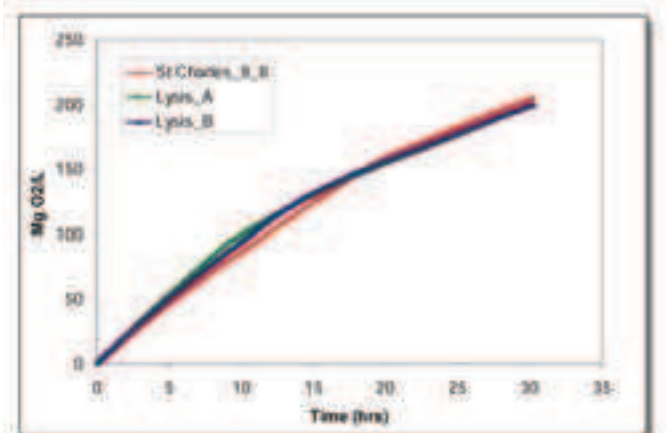


Figure 4. Extended 30-hour OUR profile of municipal wastewater and lysis COD products

An OUR baseline was determined by comparing the OUR of a synthetic wastewater containing an ideal nutrient mix with tap (blank) water (Figure 3). The endogenous respirometric rate for the sludge sample was determined from the OUR measurements obtained using the blank. Following the sludge ozonation process, lysis products were collected and the nutrient composition was analyzed (see Table 1). By comparing the relative proportions of Nitrogen and Phosphorus to the COD present in the lysis COD, it was determined that the nutrient composition of the lysis products was very similar to that of the idealized synthetic wastewater.

Table 1. Relative proportions of the composition of phosphorus and nitrogen compared to the COD present in wastewater influent, lysis products and synthetic wastewater formulations. Lysis products are derived from samples.

Substrate Sample ID	Reactive Phosphorus (mg/L PO ₄ ³⁻)	Nitrate (mg/L PO ₄ ³⁻)	Total Nitrogen (mg/L N)	NH ₃ (mg/L)	COD (mg/L)
Lysis Sample A	7%	1%	11%	6%	100%
Lysis Sample B	6%	0%	13%	8%	100%
Synthetic Raw Influent	5%	1%	16%	11%	100%
St. Charles Raw Influent	8%	1%	35%	20%	100%

Figure 4 above summarizes the results of the biodegradability tests that were run on the lysis products. The OUR results confirm the high biodegradability of the lysis product.

Full Scale Tests

Prior to the commencement of the sludge ozonation process, a comprehensive baselining study was undertaken during which the process conditions at the plant were measured and compared to the historical plant data. Broad agreement was observed between the results of the baselining exercise and the historical plant data. A plant wide biosolids inventory had also been established prior to the commencement of the tests, and a critical control feature was to maintain this solids inventory at constant levels in order to facilitate accurate accounting for the fate of the solids in the process. Solids inventory was therefore maintained at 80,000 kg and the extent of sludge reduction achieved was obtained by closing the solids balance. It was already established from the analysis of the previous 2 year operating data at the plant that the average yield was 0.35kg TS/kg COD removed. The current levels of sludge generation were compared against this historical baseline to determine the extent of sludge reduction achieved.

Discussion

The pilot test was carried out at a scale that was designed to allow for the effective treatment of up to 40% of the excess sludge. Praxair's approach to sludge ozonation differs from previous methods in its high selectivity (Fabiya & Novak, 2007) derived largely from the use of a plug flow approach that maximizes the use of ozone for cell lysis rather than wasteful consumption of ozone by the chemical oxidation of the lysis products. Our approach uses multiple injection loops for bringing the sludge and the ozone rich gas stream in contact. The

ozone consumption observed during the tests was approximately 0.07 kg of O₃ per kg TSS reduced. Table 2 provides a comparative summary of the ozone consumption values obtained during this study and other results from the literature.

Table 2. Comparative table of specific ozone consumption and the corresponding sludge reduction (derived from Sievers et al, 2004).

Reference	Ozone consumption kg O ₃ /kg TS _{reduced}
Yamui et al. (1996)	0.165
Sakai et al. (1997)	0.133 - 0.178
Kobayashi et al. (2001)	0.250
Sievers et al. (2004)	0.395
Praxair Approach	0.07

We observed significant reduction of foaming in the aeration basin process of the wastewater treatment operation as a result of the ozonation process. Prior to the commencement of the ozonation process, there was a persistent 20 cm foam layer at the top of the aeration basin causing solids to be frequently purged from the surface of the aeration tank and sent directly to an aerobic sludge holding tank that is connected to the aeration basin through an overflow weir. Following the commencement of the ozonation process, there was a significant reduction in the population of all filamentous microbial species, with the most significant reductions being observed in *Microthrix parvicella* and *Nocardia* species (see Figure 5). The impact of the sludge ozonation process on filamentous organisms was rapid and there was an effective control of the foaming within the first three weeks of operations.

Although previous studies (e.g., Ried et al, 2002) had indicated that there was a slight increase in the effluent COD during sludge ozonation, our bench scale tests

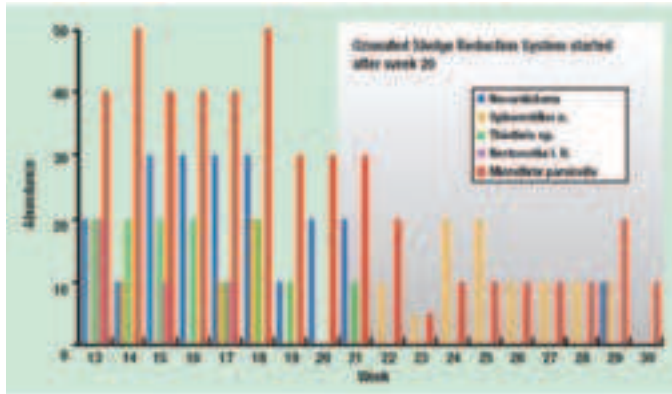


Figure 5. Plot showing impact of sludge ozonation on the incidence of filamentous bacterial species

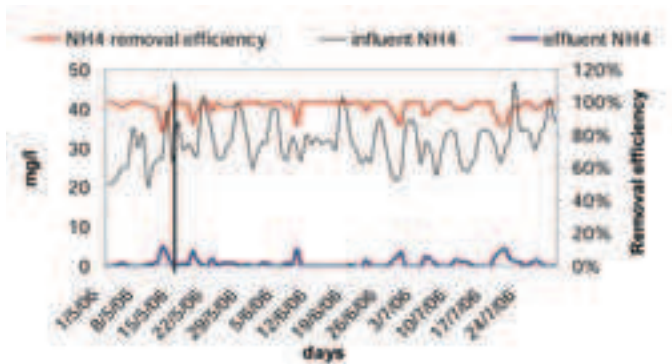


Figure 6. Effect of sludge ozonation on nitrogen removal. Solid black vertical line indicates commencement of sludge ozonation

Table 3. Summary of results obtained during the pilot tests.

	Base Case	With Ozone
Sludge Generated	2 Dry Tons / Day	0.4 Dry Tons / Day
% Dry Solids	0.18	0.22
SVI (mL/g)	80 - 100	50 - 60
Ozone Usage	0	0.07 kg Ozone / kg SS removed
Foaming	20 cm above liquid	Nil
Treatment	80 % COD removal	80 % COD removal
Capacity	60 % TN removal	60 % TN removal

suggested that the lysis products were sufficiently biodegradable and could be effectively removed in the aeration basin. Throughout the test period (May 2006 to March 2007) COD removal efficiency was maintained at the historical average of 80%. TN removal efficiency was also maintained at the historical pre-ozonation average level of 60% (See Figure 6 and Table 3). It is possible that the higher effluent COD levels that were observed in the

effluent could have been due to the lack of supplemental oxygen to use in the bio-oxidation of the lysis products in the basin. It should be noted that the concentration of ozone in most generators would typically be in the range of 7-14% w/w Ozone, with the rest of the stream being made up of pure oxygen. While previous methods viewed this ‘excess oxygen’ stream as a waste gas, our approach permits the dissolution of this ‘excess oxygen’. There is sufficient oxygen in this stream to provide all of the supplemental oxygen required for the oxidation of the lysis COD products in the basin. During the pilot, the residual DO level in the basin went from a value of about 1 mg/L to 2-3 mg/L following the commencement of the sludge ozonation process. It is conceivable that in addition to the benefits of reduced sludge handling and disposal costs, aeration power savings could be achieved in plants that have turn down capacity on their blowers based on the supplemental oxygen gains from the sludge ozonation process.

The impact of sludge ozonation on excess sludge generation occurs rapidly and net changes in the trends for sludge generation can be observed within a few weeks of operations (Figure 7).

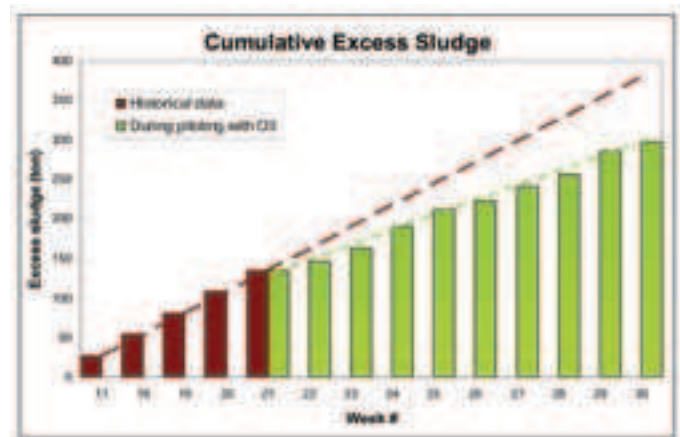


Figure 7. Trends in cumulative excess sludge production, before (weeks 17-21) and after (weeks 21-30) partial sludge recycle ozonation.

Conclusion

Ozonation of sludge is an effective method for achieving a reduction in excess sludge generated in the activated sludge process. It is possible using a high selectivity reactor to achieve economical levels of ozone consumption that make sludge ozonation a commercial viable approach for sludge minimization.

Results from our study indicate that sludge ozonation had no effect on the nitrification efficiency during full scale applications (Vergine et al, 2007) confirming the observations of other groups (e.g., Lebrun et al (2006), Raugust & Schwerdt (2004)). Our studies indicate that the COD released during the lysis process is highly biodegradable.

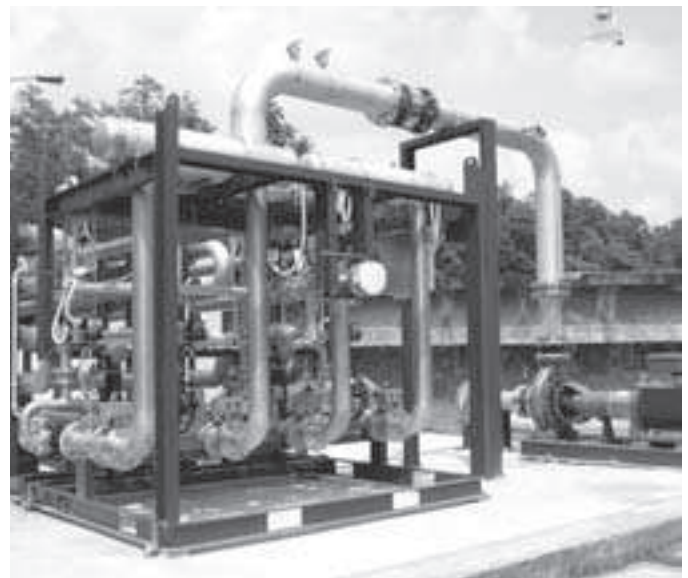
When optimally operated, the sludge ozonation process enables the realization of economical dosages and consumption levels of ozone in field tests. We did not observe a reduction in the COD and TN removal efficiencies at the plant, a result which was in agreement with the observations made at the bench scale regarding the very high biodegradability of the lysis products. Our experience also indicates that sludge ozonation can provide an effective means for biological foaming and bulking control in wastewater treatment operations.

The sludge ozonation process has been successfully applied for sludge reduction at a municipal wastewater treatment plant that handles some textile wastewater as well. The following results have been obtained (i) Sludge reduction up to 60% (ii) Elimination of foaming problems (iii) Improvement in process stability (iv) Improvement of dewatering (v) Improvement of settling (vi) Improvement of effluent quality (vii) Effective COD removal.

References

1. Böhler M., Siegrist H. (2004) Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking, *Wat. Sci. Technol.*, 49(10), 41–49.
2. Fabiyi, M & Novak, R (2007). System and method for eliminating sludge via ozonation. US Patent 7,309,432.
3. Kobayashi, T., Arakawa, K., Katu, Y., & Tanaka, T. (2001). Study on sludge reduction and other factors by use of an ozonation process in activated sludge treatment. *Proceedings of 15th Ozone World Congress, London 2001, International Ozone Association*, 321
4. Perez-Elvira, S., Nieto Diez, P and Fdz-Polanco, F. (2006). Sludge Minimization Technologies. *Reviews in Environmental Science and Biotechnology*. Volume 5, Number 4 / November, 2006, pp 375-398
5. Raugust G., Schwerdt J. (2004). 40% weniger – Reduzierung von Bioschlamm durch Ozonung. *Verfahrenstechnik* 38 (5) 16 - 17
6. Ried et al. (2002). Optimierungsmöglichkeiten beim Betrieb von biologischen Kläranlagen durch den Einsatz von Ozon. *Korrespondenz Abwasser* 49 (5) 648-661

7. Sakai et al. (1997). An activated sludge process without excess sludge production. *Wat. Sci. Tech.* 36 (11) 163-170
8. Sievers et al. (2004). Sludge treatment by ozonation – Evaluation of full-scale results. *Water Science & Technology* Vol 49 No 4 pp 247 – 253
9. Tchobanoglous, G., Burton, F., & Stensel, H. D (2003). *Metcalf & Eddy Wastewater Engineering: Treatment and Reuse*. McGraw Hill, NY.
10. Vergine, P., Menin, G., Canziani, R., Ficara, E., Fabiyi, M., Novak, R., Sandon, A., Bianchi, A., Bergna, G (2007). Partial Ozonation of Activated Sludge to Reduce Excess Sludge Production: Evaluation of Effects on Biomass Activity in a Full Scale Demonstration Test. *IWA Conference, Moncton, Canada*.
11. WERF Report (2004). Evaluation of Feasibility of Methods to Minimize Biomass Production from Biotreatment.
12. Yasui et al. (1996). A full-scale operation of a novel activated sludge process without excess sludge production. *Wat. Sci. Tech.* 34 (3-4) 395-404



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