Partial Ozonation of Activated Sludge to Reduce Excess Sludge Production: Evaluation of Effects on Biomass Activity in a Full Scale Demonstration Test.

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Abstract: Partial ozonation of the return sludge in activated sludge processes has been employed to reduce the excess sludge production and related disposal costs. However, it may have an impact on the microbial community which might affect the effluent quality. While previous lab scale studies have reported that ozonation could partly inhibit nitrifying bacteria, a number of workers have reported no effect of ozonation on the nitrification capacity. This paper presents the measurements of biomass activity in a demonstration test at a full-scale plant, designed at half of its full-scale potentiality. The WWTP (25,000 m^3/day), located near Como (Italy), treats wastewater characterized by a predominant industrial component. Ozonation permitted the reduction of as much as 40% of the excess sludge at ozone consumption values of 0.05-0.10 kg O_3/kg TS removed. The COD and TN removal capacities of the plant were not affected. Microbiological studies indicate that the elimination of foaming by the sludge ozonation process is due to the reduction of foam causing filamentous bacteria. Results from the monitoring of biomass activity indicate that the effects on nitrite oxidizing bacteria and heterotrophic bacteria were negligible, while there was a marked reduction in the activity of the ammonia oxidizing bacteria which almost halved. Monitoring the nitrification activity allowed the plant to meet the desired sludge reduction and biological foam control goals without affecting the nitrification efficiency of the process.

Keywords: excess sludge reduction, nitrification inhibition, ozonation, textile wastewaters.

INTRODUCTION

The activated sludge treatment of wastewaters produces excess sludge which needs further treatment and appropriate disposal. Recently, the increase of quality requirements of effluents and new sludge disposal regulations has limited the traditional disposal alternatives (i.e. agriculture and landfill) and made the cost of wastewater sludge management much higher. There is therefore a rising effort to develop and optimize technologies for minimizing excess sludge production in biological processes.

Previous work has shown that excess sludge production can be significantly reduced by partial ozonation of the return sludge of an activated sludge process. Ozonation also improves settling properties of the sludge and reduces bulking and scumming. However, ozonation, as any strategy employed for reducing sludge production, may have an impact on the microbial community which could influence the effluent quality. Although a significant amount of work has been done both at the lab and field scales to characterize the sludge ozonation process, adoption of the technology has been slow, largely because the dosages of ozone required to effect the sludge reduction in field tests have mostly been uneconomical (Sievers et al., 2004). Ozone consumption values required to effect sludge reduction have ranged from about 0.165-0.395 kg O_3/kg TS removed (Yasui et al., 1996; Sievers et al., 2004). It is estimated that the range of ozone consumption that will be viable will be in the regime of £ 0.1 kg O_3/kg TS removed. There have also been some issues related to the effect of sludge ozonation on the COD and Nitrogen removal capacity (Böhler & Siegrist, 2004, Lebrun et al., 2006).

In the case of textile industrial wastewaters, it is well documented that nitrification activity can be severely reduced due to toxicants and inhibitors present in the influent wastewater (e.g.: Rozzi et al., 1999; Bortone et al., 1997). While some lab scale studies have reported that sludge ozonation can negatively affect nitrification activity (e.g., Böhler and Siegrist, 2004), other workers have reported no effect of sludge ozonation on the nitrification capacity at full scale operations (e.g.: Lebrun et al., 2006).

This paper presents results from an ozonation demonstration plant designed at half of its maximum full-scale potentiality, developed by Praxair, Inc. that has been in operation from May 2006 till date (except for a 4 week shutdown in August for routine maintenance) on a WWTP (25,000 m^3/day), located near Como (Italy), that treats wastewater characterized by a predominant industrial component.

The full scale experimental program had the following objectives. (i) Investigating the effect of ozone induced lysis on the excess sludge (ii) Establishing the long-term effects of sludge Ozonation on the COD and TN removal efficiencies (iii) Establishing the scalability criteria of the sludge Ozonation process (iv) Determination of key economic parameters for the process (v) Establishing the impact of ozonation on sludge characteristics e.g., solids settling (SVI) and sludge dewatering characteristics (vi) Determination of the impact of sludge ozonation on system microbiology – effect on specific species and microbial populations as well as on the specific biomass activity. This paper mainly focuses on this last aspect.

MATERIALS AND METHODS

The ozonation process and the demonstration plant

The Lariana WWTP (25,400 m^3/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 operation each one including 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. Because of the severe foaming that was historically experienced at the plant, solids had to be frequently purged from the surface of the aeration tank and sent directly to an aerobic sludge holding tank. The historical (2 year average) yield at the plant was 0.35 kg TS/kg COD removed.

Praxair's sludge ozonation process comprises of an ozone supply system, a pump, and a gas liquid contacting system within which the sludge-ozone contact occurs. 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 effect the lysing of the bacterial cells is applied. An Allen Bradley SLC5/03 PLC system was used to effect automatic control of the process. A 3-4 kg/h flow of a 7% w/w O_3 gas stream was applied to the portion of the RAS stream that flowed through the contactor. Because the primary RAS line is returned to an anoxic basin rather than to the nitrification basins, a separate RAS flow needed to be established for the sludge ozonation process as the high oxic 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.

Prior to the commencement of the sludge ozonation process, a two-week 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.

Assessment of autotrophic biomass activity

Autotrophic biomass activity was assessed by means of the set-point titration technique. The measuring principle is the following: controlled amounts of an appropriate titrant are added to a batch sludge sample to maintain constant the level of a chemical species which takes part in the bioreaction under study. The reaction

rate is proportional to the measured titration rate via the reaction stoichiometry, while the amount of titrant dosed is proportional to the amount of substrate converted. When nitrification is the bioreaction to be studied, dissolved oxygen-stat (DO-stat) and pH-stat titration are especially useful. The reason is twofold: (i) the level of DO and pH are carefully controlled to the desired level and (ii) the reaction rates are easily calculated from their stoichiometric relation with titration rates. Specifically, the NaOH addition rate (r_{NaOH} in mmol/min) is used to assess the ammonium oxidation rate (r_{NH} in mg_N/min), while nitrite oxidation rate (r_{NO^2} in mg_N/min) is assessed from the O_2 addition rate (r_O in mg_{O^2}/min). The two-step nitrification model can be expressed by the following reaction equations:

$$(\frac{1}{Y_{AOB}} + i_{XB}) \cdot S_{NH} + \frac{3.42 - Y_{AOB}}{Y_{AOB}} S_O + \frac{1}{14}(i_{XB} + \frac{2}{Y_{AOB}}) S_{ALK} \rightarrow X_{AOB} + \frac{1}{Y_{AOB}} S_{NO2} \quad (1a)$$

$$\frac{1}{Y_{NOB}} S_{NO2} + \frac{1.14 - Y_{NOB}}{Y_{NOB}} S_O \rightarrow X_{NOB} + \frac{1}{Y_{NOB}} S_{NO3} \quad (1b)$$

where:

S_{NH}, S_{NO^2}, S_{NO^3}, S_{ALK}, S_O are concentrations of, respectively: ammonia (mg_N L^{-1}), nitrite (mg_N L^{-1}), nitrate (mg_N L^{-1}), alkalinity (mM) and dissolved oxygen (mg L^{-1});

X_{AOB}, X_{NOB} are biomass concentrations for, respectively: ammonium oxidising bacteria (AOB) and nitrite oxidising bacteria (NOB) (mg_{COD} L^{-1}); i_{XB} is the fraction of N in bacterial cells (0.086 g_N g_{COD}^{-1});

Y_{AOB}, Y_{NOB} are growth yield coefficients for, respectively, AOB (0.21 g_{COD} g_N^{-1}, Wiesman 1994) and NOB (0.06 g_{COD} g_N^{-1}, Wiesman 1994).

According to the reaction equation (1a), the relationship between ammonium oxidation rate and alkalinity consumption rate is:

$$r_{NH} = r_{NaOH} \cdot 14 \cdot \left(i_{XB} + \frac{1}{Y_{AOB}}\right) \cdot \left(i_{XB} + \frac{2}{Y_{AOB}}\right)^{-1}, \quad (2)$$

Similarly, the relationship between nitrite oxidation rate and dissolved oxygen consumption rate is deduced from the reaction equation (1b):

$$r_{NO2} = r_O \cdot \frac{1}{Y_{NOB}} \left(\frac{1.14 - Y_{NOB}}{Y_{NOB}}\right)^{-1}, \quad (3)$$

Both specific ammonium and nitrite oxidation rates of the activated sludge sample (r_{AOB}, r_{NOB}, in mg_N g_{VSS}^{-1} h^{-1}) are calculated by taking into account its biomass content in terms of volatile suspended solid (VSS, in g_{VSS}):

$$r_{NO2} = r_O \cdot \frac{1}{Y_{NOB}} \left(\frac{1.14 - Y_{NOB}}{Y_{NOB}}\right)^{-1}, \quad (3)$$

Similar titration tests for the study of nitrification were already described and validated (e.g. Massone et al. 1998, Pratt et al. 2003, for pH-stat titration; Ficara et al., 2000 and Artiga et al., 2005 for pH/DO-stat titration).

Set-point titration was performed by means of a prototype of the MARTINA instrument provided by SPES s.c.p.a (Fabriano, AN, Italy). A description of this apparatus can be found in Artiga et al., (2005). Sodium hydroxide (0.05 M) and hydrogen peroxide (0.1 M) were used as titrants.

Titration tests were conducted as follows. Sludge samples were freshly drawn from the return sludge line and mixed with treated effluent to achieve a suspended solid concentration within 2 and 3 gSST/L. A volume of 0.6-0.7 L of this suspension was poured into the MARTINA vessel and aerated for about 1 h to ensure endogenous conditions. Sludge temperature was maintained close to that of the activated sludge basin (±1°C). After

selecting the set-point levels for DO (7.5 mg L^{-1}) and pH (8.3), the titration experiment was started. A typical outcome of a titration experiment is shown in Figure 1. First, the endogenous respiration was monitored, then ammonium chloride was added to the sludge sample (3-6 mgN/L) to trigger nitrification (t1 in Figure 1). When ammonium was fully nitrified (t2, identified by the bending point on titration curves), sodium nitrite (3-6 mgN/L) was spiked to trigger nitratation (t3) and titration was continued until nitrite was fully oxidised (t4, identified by the bending point on the peroxide titration curves). Finally, allylthiourea was spiked (t5) to inhibit nitrification of ammonium produced by ammonification to assess the endogenous respiration rate. Titration rates required in eqs. (2) and (3) were estimated by linear regression on the titration curves.

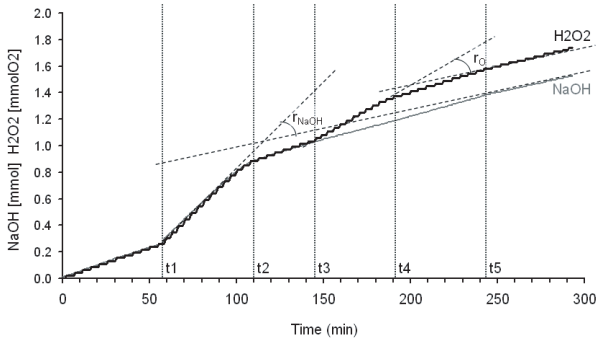

Figure 1 Outcome of a pH/DO-stat titration experiment for the assessment of specific ammonium and nitrite oxidation rates from NaOH titration rate (r_{NaOH}) and hydrogen peroxide titration rate (r_O).

Two measuring campaign were conducted, each one including 3 to 5 assessments of specific nitrification activities performed within a few days. The first one (C1, May 2006) was performed before starting the ozonation process to assess the baseline nitrification rate; the second one (C2, July 2006) after 7 weeks (i.e. about 3 times the sludge age) from ozonation start-up. During this second campaign return sludge was collected either before (sampling point S1) or after (sampling point S2) the ozone contactor.

Analytical methods

The determination of the COD, SST and nitrogen compounds present in the process were performed according to Standard Methods (APHA, 1998). In addition to these measurements, a number of additional parameters were routinely monitored, these being: aldehydes, surfactants, and color compounds (at specific wavelengths of 426, 558 and 660 nm) (data not shown). Samples were collected at various points in the process including the influent, effluent, nitrification basins, anoxic tank, as well as Pre-ozonated and ozonated RAS. Abundance of biological foaming (*Microthrix Parvicella* and *Nocardioforms*) were determined according to Jenkins et al. (2004).

RESULTS AND DISCUSSION

The main effects of return sludge ozonation were the disappearance of biological foaming and the reduction of excess sludge production. The COD and Total Nitrogen reduction capacity of the plant was not affected. There was an improvement in the dewatering characteristics of the sludge and as a consequence the dry solids content in the sludge increased from 19% to 22%. The activity of Nitrite oxidizing Bacteria was not significantly affected. However reduction of the activity of Ammonia Oxidizing Bacteria was observed. Each of these effects are hereafter discussed.

The effect of partial recycle sludge ozonation on biological foaming are shown in Figure 2. It can be readily observed that after 2 weeks (i.e.: 1 sludge age), microorganisms responsible for biological foaming have been reduced to non-harmful levels of abundance (always < 3).

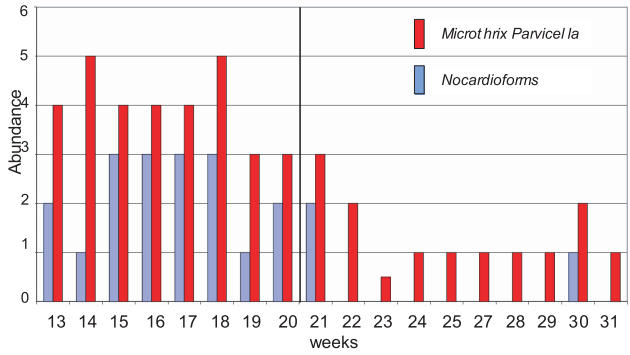

Figure 2 Abundance of filamentous organisms causing biological foaming before and after partial sludge recycle ozonation (the vertical line marks the start-up of the ozonation process).

Mass balance of solids in the process has been calculated from excess sludge purged and variation of biomass concentration in the biological tanks. The actual reduction in sludge production resulted as depicted in Figure 3. A comprehensive sludge balance was undertaken to ensure that all of the solids in the process were accounted for. The control strategy employed was to ensure that the solids quantity in whole system was maintained constant at a target value (i.e. 80,000 kg). The sludge removals from the plant were carefully measured both by closing the solids balance as well as by daily measurements of the solids quantities hauled away by trucks. An average biosolid generation reduction of about 39% was achieved during the test period. The average ozone consumption during the test period was 0.07 kg O_3/kg TS removed. Given that some of the ozone was consumed by the color and surfactant compounds in the RAS, the effective consumption would have been lower.

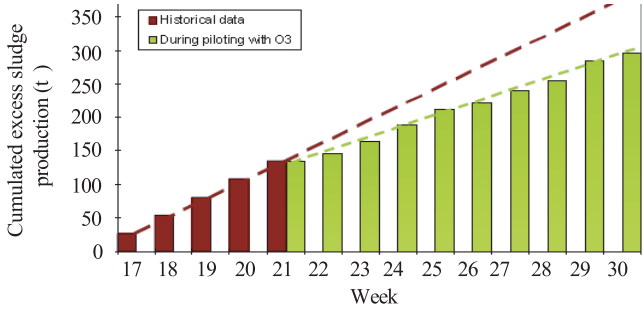

Figure 3 Cumulative excess sludge production, before (weeks 17-21) and after (weeks 21-30) partial sludge recycle ozonation.

Specific nitrification rates (ammonium oxidation rate r_{AOB}, nitrite oxidation rate r_{NOB}) measured before and 7 weeks after the start-up of the ozonation treatment are summarised in Table 1, where rates are referred to the reported temperature.

Table 1 specific nitrification rates (ammonium oxidation rate r_{AOB}, nitrite oxidation rate r_{NOB}) measured before and 7 weeks after the start up of the return sludge ozonation process.

Campaign/sampling point	Date (mm-dd)	r_{AOB} mgN/(h*gVSS)	r_{NOB} mgN/(h*gVSS)	Temperature (°C)
C1	05-02	2.32	2.73	22.3
	05-03	1.91	2.96	23.2
	05-08	1.91	2.86	24.0
	05-09	2.08	2.72	22.0
	05-09	2.06	2.87	23.2
	Mean±Standard dev.	***2.1±0.17***	***2.8±0.10***	***23.1***
C2/S1	07-04	0.98	2.38	29.4
	07-06	0.66	3.71	28.3
	07-20	1.18	2.59	28.0
	Mean±Standard dev.	***0.94±0.26***	***2.89±0.72***	***28.6***
C2/S2	07-04	0.75	1.88	29.1
	07-06	1.04	3.74	28.1
	07-20	1.16	3.00	28.3
	Mean±Standard dev.	***0.98±0.21***	***2.9±0.93***	***28.3***

The short term effect of the exposure of nitrifiers to ozone has been assessed, by measuring nitrification rates before (C2S1) and after the ozonation contactor (C2S2). In this case, the specific ammonium oxidation rate was not affected, while the oxidation rate of nitrites appears to be enhanced, possibly due to a more effective oxygen transfer into the inner layers of sludge flocs, where nitrite oxidisers are usually located (Wilen et al., 2004).

The specific ammonium oxidation rate approximately halved from C1 to C2, while the specific nitrite oxidation rate was almost the same (less than 10% reduction). Since temperature increased from about 23 to about 28 °C from May to July, nitrification rates (r) can be adjusted to temperature variations according to the usual expression: $r_T = r_{20°C} \times q^{T-20°C}$, where q can be assumed =1.08. The average reduction of nitrification activity due to return sludge ozonation can be estimated as about 70% for r_{AOB} and 35% for r_{NOB}. This suggests that the ozonation treatment exerts a significant long term effect on the treatment plant nitrification capacity in activated sludge processes treating textile wastewater. It is interesting to note that the reduction of AOB activity did not translate to a reduction in the nitrification capacity of the plant as might have been expected since no relevant effluent quality parameters were affected (see Figure 4). During the ozonation process, an actual nitrification rate of 0.6 mgN/(h gMLVSS) can be calculated by considering the average ammonium load reduction of 643 kgN/d and the average volatile solids concentration in the aeration basin (44,500 kgMLVSS/d). The values assessed by set-point titration are higher, since they are not limited by substrates availability (both dissolved oxygen and ammonium).

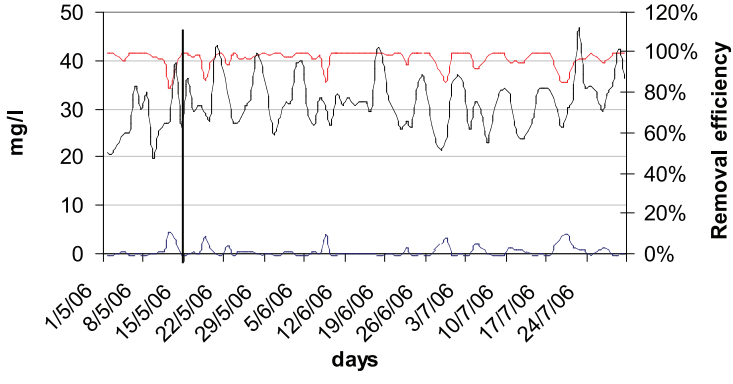

Figure 4 Influent and effluent Ammonium Nitrogen concentration over time. Vertical line marks ozonation start-up.

A second phase of testing commenced from September 2006, specifically to test the capacity of the system to maintain Nitrogen removal capacity through the winter months. The Nitrogen removal efficiency has been maintained consistently throughout the test period at the historical value of about 60% TN removal. Wastewater temperatures during the recent winter test period were in the range of 16^0C-20^0C.

CONCLUSIONS

Ozonation of a portion of the recycle sludge flow is important not only to reduce sludge production, but also to remove biological foams, which plagued the plant for years. Sludge ozonation enabled the reduction of excess sludge generation. Results from this study confirm the observation by Lebrun et al (2006) that sludge ozonation had no effect on the nitrification efficiency during full scale applications. The reduction of the activity of the Ammonia Oxidizing Bacteria should however be noted.

Textile wastewater contains toxicants and inhibiting compounds which can reduce the nitrification activity to low values. Given that any further impact on the nitrification capacity by sludge ozonation may impair the ability of the plant to meet its nitrogen removal targets, careful monitoring of nitrification activity is very important to ensure effluent compliance. Monitoring the nitrification activity in addition to the TN removal capacity of the plant can provide a valuable tool that can allow plants to be managed in a manner that permits the attainment of results planned both for sludge reduction and biological foam control without affecting the overall nitrification efficiency of the process.

ACKNOWLEDGMENTS

This work has been partially financed by Rivoira/Praxair, Lariana Depur S.p.A., Comodepur S.p.A. and CAP Gestione S.p.A.

REFERENCES

APHA, AWWA, WEF (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th Edition.

Artiga P., Gonzalez F., Mosquera-Corral A., Campos J.L., Garrido J.M., Ficara E., Méndez R. (2005). Multiple analyses reprogrammable titration analyser for the kinetic characterisation of nitrifying and autotrophic denitrifying biomass. *Biochem. Eng. J.,* **26**, 176-183.

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.

Bortone G., Gemelli S., Tilche A., Bianchi R., Bergna G. (1997) A new approach to the evaluation of biological treatability of industrial wastewater for the implementation of the "waste design" concept, *Wat. Sci. Technol.,* **36**(2-3), 81-90.

Ficara E., Rocco A. and Rozzi A. (2000) Determination of nitrification kinetics by the ANITA-DOstat Biosensor, *Wat. Sci. Technol.,* **41**(12),121-128.

Jenkins D., Richard M. G., Daigger G. T. (2004). *Manual on the causes and control of activated sludge bulking, foaming and other solid separation problems*. 3rd Edition, IWA publishing, CRC Press.

Lebrun, T., Rewcastle, M., Taylor, T., Churchley, J., Perrin, D. (2006). Full Scale Experience of Biolysis O Process for Biosolids Reduction on an Activated Sludge Plant. In: *Proceedings of the IOA-EA3G Conference, Zurich Switzerland. September 2006*.

Massone A., Gernaey K., Rozzi A., Verstraete W. (1998). Measurement of ammonium concentration and nitrification rate by a new titrimetric biosensor. *WEF Research Journal*, 70(3), 343-350.

Pratt S., Yuan Z., Gapes D., Dorigo M., Zeng R.J., Keller J. (2003). Development of a Novel Titration and Off-Gas Analysis (TOGA) Sensor for Study of Biological Processes in Wastewater Treatment Systems. *Biotechnol. Bioeng*. **81**, 482-495.

Rozzi A., Ficara E., Cellamare C., Bortone G. (1999). Characterization of textile wastewater and other industrial wastewaters by respirometric and titration biosensors. *Wat. Sci. Technol.,* **40**(1), 161-168.

Sievers, M., Ried, A., Koll, R. (2004) Sludge Treatment By Ozonation – Evaluation of Full Scale Results. *Wat. Sci. Technol.,* **49**(4), 247–253.

Wiesman U. (1994). Biological nitrogen removal from wastewater. *Ad. Biochem. Eng. Biotechnol.*, **51**, 113-154.

Wilen B-M., Gapes D., Keller J. (2004). Determination of external and internal mass transfer effects in nitrifying microbial aggregates. *Biotechnol. Bioeng.* **86**(4), 445-457.

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