Nitrification preservation in activated sludge during curative bulking chlorination

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Abstract The bulking that occurs in biological wastewater treatment plants using activated sludge is very often controlled by the injection of sodium hypochlorite into the return activated sludge (RAS) stream. In the present study undertaken at two pilot plants fed with synthetic wastewater, the impact of the pass frequency of the sludge at the chlorine dosing point on the nitrifying flora is analysed. The pass frequency is one for the pilot plant 1 and two for the pilot plant 2. A dose of chlorine of 4.85 ± 0.05 g/kg/MLVSS per day was applied at both pilots. The preservative effect on nitrifying activity of the lowest concentration of chlorine at the dosing point and therefore of the highest pass frequency was evidenced. Among other tools, a simple method of measurement of the oxygen uptake rate enabled us to monitor the effect of chlorination on nitrification before recording an increase in the ammonia concentration in the bulking.
Keywords Bulking; chlorination; nitrification; respiration

Introduction

Biological wastewater treatment using the activated sludge process is frequently affected by the excessive growth of filamentous micro-organisms (Eikelboom *et al*., 1998), or bulking. The high sludge volume index thus produced increases the risk of the loss of sludge with the treated water. Bulking can be controlled by various methods, and its effects can be reduced by the addition of flocculation-coagulation reagents (polymers, ferric chloride, etc.) or of ballast (talc, clay, etc.). The most widely used and the most effective curative method uses an oxidizing agent such as chlorine, mainly in the form of sodium hypochlorite, preferably injected at the level of the RAS stream (Jenkins *et al*., 1986). This method does have disadvantages (degradation of the treatment performance at high doses), especially as far as maintenance of the nitrifying activity is concerned. The treatment doses applied, expressed in terms of grams of active chlorine per kilo of MLVSS per day, are still empirical. Occasionally, doses considered to be harmless to nitrification prove to be deleterious, in particular in connection with the sludge return flow capacity of the plant. The general aim remains to optimise chlorination operations in accordance to the load, the presence of ammonia, the type of bulking, the daily dose, and the pass rate at the dosing point as found in wastewater treatment plants. To determine the efficiency of the bulking control and the preservation of nitrification, the level of chlorination at the dosing point was the parameter studied. This was determined by the daily dose of chlorine and by the number of daily sludge passes at the dosing point, which varied with the RAS flow rate. In this study the effect of a dose of chlorine, considered to have an adverse effect on nitrification for two pass frequencies, is analysed.

Material and methods

Experimental set-up : Two pilot plants (P1 and P2)(aeration tank of 100 L, clarifier of 50 L) were each seeded with one half of the activated sludge from a similar pilot plant (P0). The P0 sludge came from an urban WWTP and was acclimatised to a synthetic effluent VIANDOX®, with the addition of nitrogen (NH_4Cl at 13 g/L) and of phosphorus (HK_2PO_4 at

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1.43 g/L) and diluted by tap water. The period of acclimatisation to the organic load of 0.07 kg BOD/kg MLVSS per day was three months. Five weeks after the start of acclimatisation, *Nostocoida* type II, presumed to be *Trichoccus* according to Seviour *et al*. (2002), developed. The sludge volume index (SVI) reached over 1,000 mL/g but rapidly dropped back to values of 250 mL/g 15 days after the start of the proliferation. The SVI remained at that level until the start-up of P1 and P2. On dividing the sludge, the daily input at each P1 and P2 remained identical to that of the P0 plant, which resulted in a doubling of the F/M both in carbon and in nitrogen over a period of 10 days prior to the start of chlorination. No extraction was performed making it possible to find a low F/M of the order of 0.06 kg BOD/kg MLVSS/day. Chlorination was then undertaken at the RAS stream at a daily dose of 4.9 and 4.8 g of Cl_2/kg MLVSS/day respectively in P1 and P2. The chlorine concentrations at the injection point never exceeded 25 mg/L. The daily pass rates of the sludge at the dosing point were set at once for P1 and twice for P2, defined as being the ratio between the mass of sludge passing the dosing point in 24 hours and the total SS inventory in the system. At the end of the experiment, a chlorine shock that occurred in P1 on the tenth day was reproduced in P2 on the sixteenth day. Figure 1 the chlorination set-up and Tables 1 and 2 show the operational characteristics

The SVI was monitored according to Stobbe (1964). The COD in the treated effluent was measured by the HACH micro-method.

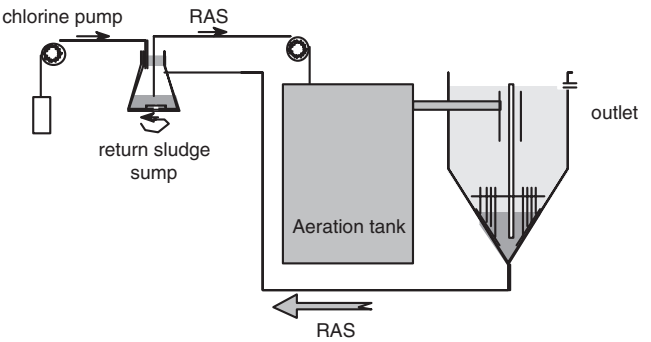

Figure 1 Experimental set-up. The RAS sump is hermetically closed to create a negative pressure to draw up sludge

Table 1 Influent characteristics

Parameter	COD	BOD	KN	NH_4-N	PO_4-P	DBO/NH_4-N/PO_4-P
Viandox (g/l)	210	85	8,75	1.9	1.1	100/2.23/1.29
Effluent (mg/L)	420	170	43.5	29,8	5	100/17.5/3.5

Table 2 Operating parameter

Parameters	Pilot 1	Pilot 2
Aeration tank	100 L	100 L
Clarifier	50 L	50 L
Recirculating sump	0.40 L	0.40 L
Feed frequency	3 min every 30 min	3 min every 30 min
Clean water flow (L/min)	0.7	0.7
Viandox flow (L/min)	0.0013	0.0013
Return sludge flow (L/min)	0.07	0.14
MLSS (g/L)	2.95	2.80
MLVSS in aeration tank (g/L)	2.48	2.20
MLVSS in recirculating sump (g/L)	4.06	4.09
Sludge volume in clarifier (L)	1 to 2	1 to 2
F/M (g BOD/kg MLVSS.day)	0.06	0.06

Measurement of the autotrophic oxygen uptake rate

The method employed was adapted from that proposed by Surmacz-Gorska *et al*. (1996). Each of the two measuring devices consists of a 500 ml Erlenmeyer flask placed on a magnetic stirrer. Particular attention is paid to the constancy of temperature and speed of agitation. Part of the volume of sludge extracted each day is placed under continuous aeration for at least 1.5 hour to reach a stabilised OUR on the scale of the measurement time. During the period without extraction (10 days), this sludge is returned to the aeration tank after each test. The NH_4-N load from this re-injection represents 3.5% of the daily nitrogen load. For measurement purposes, the flasks are filled with sludge and hermetically closed by the oxygen probe of a YSI 57 oxymeter. The drop in oxygen is recorded on a data recorder. The oxygen concentration is initially of the order of 8 mg/L. When this reaches 4 mg/L, 0.5 ml of ammonium chloride (30 g/L of NH_4-N) are added. When the oxygen concentration reaches 1 mg/L, the data are analysed. The slopes of the linear regression straight lines of each part (before and after the addition of NH_4) are calculated. The difference between the slope values makes it possible to determine the oxygen consumption required for nitrification. The oxygen uptake rate measured prior to the addition of ammonia can be assimilated to an oxidation of the carbon substrate (slow, bio-absorbed substrates + endogenous uptake) insofar as the residual ammonia concentrations in the pilot plant are practically nil. Each test was performed twice and the deviations between the values obtained were on average 2% with maximum deviations of 4%. In the method proposed by Surmacz-Gorska, allylthiourea (ATU) is used to inhibit the oxygen uptake of the nitrifying flora. Numerous tests using ATU performed on sludges with a high F/M, considered as non-nitrifying, show drops in the oxygen uptake rate of the order of 10% to 25% (unpublished data). This therefore shows that ATU does not inhibit only the nitrifying populations and cannot therefore be used to determine the share of oxygen uptake related to nitrification as against the oxygen uptake rate as defined in the protocol.

Measurements of the nitrification uptake rates

1 ml of a solution of NH_4Cl at 30 g/L is added to 1 litre of sludge from each pilot plant after an aeration time of at least 1.5 hours. Aeration is maintained then after $t = 0$; 5; 10; 15; 20 and 30 minutes, 50 ml of sludge is collected and the nitrification blocked in a 50 ml Falcon tube by 50 µl of ATU at 20 mmol/L. The tubes are centrifuged for 10 minutes at 1,000 g. The supernatant is analysed on the same day, or kept at 4°C. Quantification of the NO_3-N, NO_2-N and NH_4-N is performed according to classic colorimetric methods (AFNOR 1994) using a Bran and Luebbe Traacs analyser. The linear regression straight line of the concentrations is calculated according to time.

In situ hybridisations are performed according to the FISH method of Manz *et al*. (1992) to monitor certain nitrifying populations. The NEU probe (Wagner *et al*., 1995) coupled to the Cy3 fluorophore is hybridised with 40% of formamide. No competitor is used within the framework of this study. The slides are kept at –20°C before observation under a Leica Laborlux microscope fitted with an epifluorescence device. The samples taken after the oxygen uptake test are fixed in pure ethanol (v/v).

Results

Chlorine dose

The overall chlorine mass dose as shown in Figure 2 (ratio between the mass of chlorine added in 24 hours and the mass of MLVSS in the system) is on average between 4.9 and 4.8 g of chlorine per kg of MLVSS per day for P1 and P2, respectively.

The chlorination dose at the dose point is defined as the ratio between the mass flow rate of chlorine injected and the mass flow rate of the MLVSS passing the injection point. The

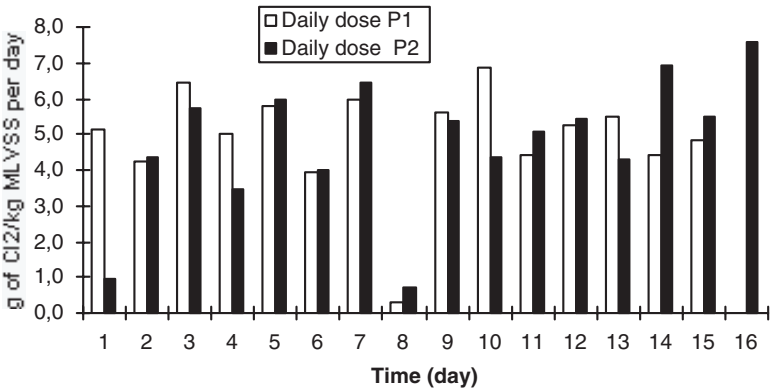

Figure 2 Overall chlorine mass dose versus time

various doses obtained in the course of the day are shown in Figure 3. On average, they range from 3.8 g to 1.9 g of Cl_2/MLVSS for P1 and P2 respectively. For practical reasons, however, the loads of chlorine may vary over the course of the day. This was the case for P1 where a dose at the injection point of over 7 g of Cl_2/kg of MLVSS was added on the tenth day over a time period of 7.5 hours.

Sludge volume index

Observation of the evolution of the sludge volume index (Figure 4) evidences a decrease of more or less the same proportions in both pilot plants as from Day+5 after the start of chlorination. The SVI is stabilised at around 250 ml/g during the sludge acclimatisation period and reaches values close to 150 ml/g at the end of the experiment.

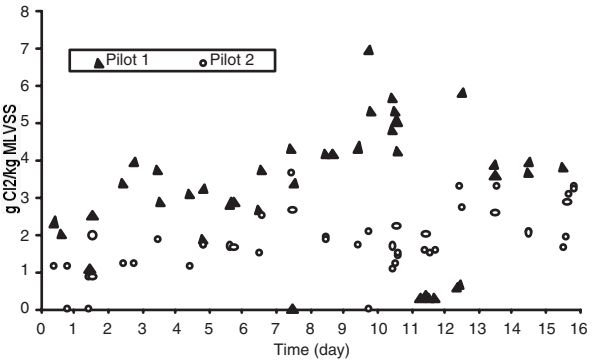

Figure 3 Dosing point chlorine dose

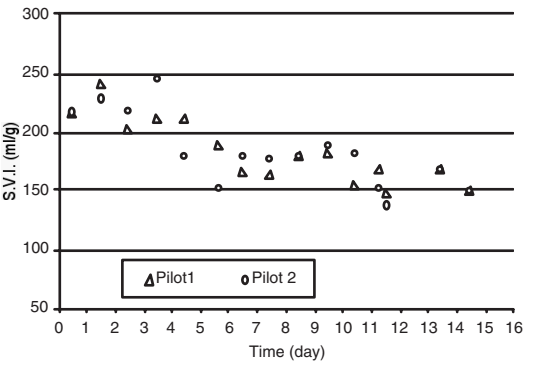

Figure 4 SVI vs time

COD at the exit of the pilot plants

The COD values measured at the exit of the pilot plants are relatively stable in both plants, evidencing maintenance of the efficiency of the treatment. This result also indicates that the treatment doses applied at the dose point have no adverse effect on flocculation, which matches the usual recommendations (Jenkins *et al.*, 1986).

Autotrophic oxygen uptake rate due to nitrification (OUR) and nitrification uptake rate (NUR)

The oxygen uptake rate due to nitrification and the NH_4-N concentrations at the exit of the two pilot plants are shown in Figure 5.

The increase of the uptake rates observed over the ten days prior to the implementation of chlorination can be explained by the absence of extraction over that period. The drops recorded after the start of chlorination are partly related to the treatment. Graph 6 shows the rates of disappearance of ammonia (NUR) and the concentrations at the exit in ammonia nitrogen.

The ratio between the nitrogen uptake rate and the nitrification rate is between 2.3 and 3.0 for both plants as long as the nitrification rate remains stable at a disappearance of around 6 mg of NH_4-N per hour and per litre. For P1, the nitrification rate is close to the uptake rates. The drop in the uptake rates after the start of chlorination can be partly explained by the resumption of extractions. The real effect of chlorination is therefore probably slightly masked by this effect during the first few days following the start of chlorination. Nevertheless, in the P1, the uptake rates due to nitrification dropped more than at

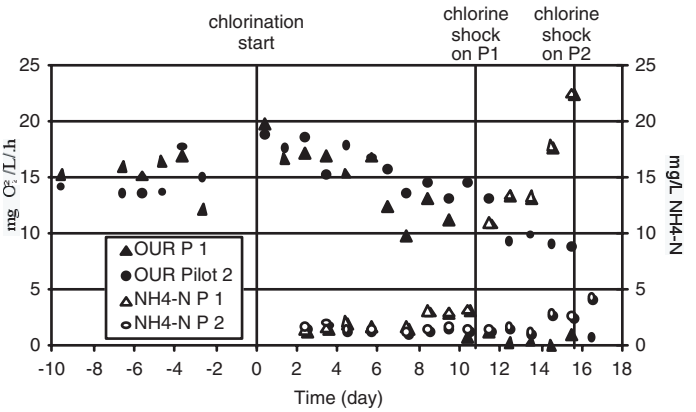

Figure 5 Autotrophic respiration and treated effluent NH_4-N concentration

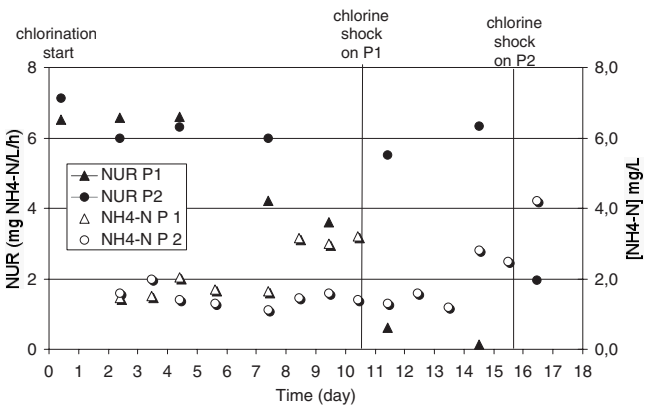

Figure 6 Nitrogen uptake rate and NH_4-N concentration

P2. This observation is even more flagrant for the values of the nitrification rates. As far as the relationship between the nitrogen concentration in the treated effluent and the uptake rate values is concerned, it can be noted that despite the drop in the NUR at both P1 and P2, the quality of the treatment is not degraded in the treated effluent as far as ammonia is concerned. The degradation in the quality of the bulking for this parameter occurs at P1 8 days after the start of chlorination, namely one day after the drop in the nitrification rate. Figure 7 shows the concentrations in NO_2-N from spot measurements taken at the exit from the pilot plants. The nitrate concentrations at the treated effluent remained under 1 mg/L throughout the experiment.

An overall increase in the nitrite concentration at the exit was recorded, especially at P2. This contributes to the fact that there is practically no drop in the speed of disappearance of the ammonia, which even increases (Figure 6). One hypothesis is that at P1 the ammonia-oxidizing and nitrite-oxidizing populations are affected simultaneously, where at the P2 plant only the nitrite-oxidizing populations are affected. Unfortunatly, it was not possible to establish any correlation between the nitrification activity and the number of hybridised bacteria by counting the clusters which responded positively to *in situ* hybridisation of the NEU probe on 6 samples from P1, taken before and after the loss of nitrification. The number of bacteria responding positively to the probe is more or less the same before and after the tenth day of chlorination. On the other hand, it would appear that the intensity of fluorescence is less after the tenth day. In the absence of any means of measuring that intensity, it was impossible to exploit that result.

Discussion

OUR due to nitrification and autotrophic NUR

The oxygen uptake rates related to carbon and nitrification increase slightly on the day of starting chlorination, even before the addition of the chlorine (Figure 5). The increase in the nitrifying microflora, with the temperature of the pilot plants at 16 ± 1°C, may explain this increase, due to the absence of extraction. After the start of chlorination, there was a drop in the nitrification uptake rates and in the speed of the disappearance of ammonia as from Day 6. These two factors (Figures 5 and 6) are therefore predictive with respect to the exit value of ammonia, which for P1 increases at Day+8. The correlation is less distinct at P2 for the NUR parameter. Whereas the oxygen uptake rates due to nitrification decrease from Day5 after the start of chlorination, the ammonia consumption rates (NUR) remain stable and fall off only after the chlorine shock of Day16. The dramatic drop in the efficiency of

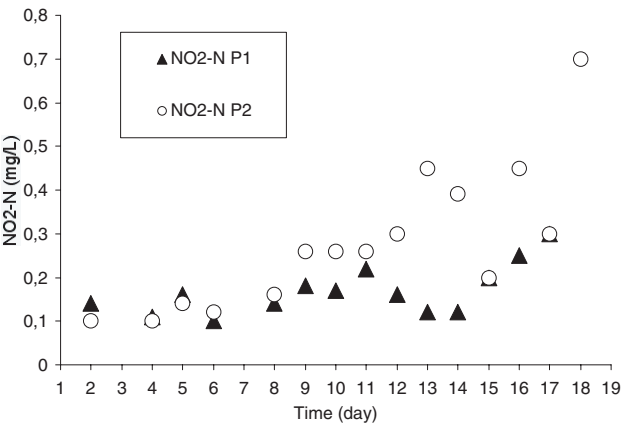

Figure 7 NO_2-N concentrations in the treated effluent

nitrification in P1 is detected quite simultaneously to the unfortunate chlorine shock which occurred in the afternoon of Day 10 (analyses were performed in the morning). A similarly shock was performed deliberately at P2 on Day 16 and showed that the chlorine shock at the P1 plant on Day 10 was in fact fatal for nitrification. Meanwhile, it was presumed that at the P2 plant only the nitrating phase was affected which is confirmed by the NO_2-N concentration increase in the treated effluent at P2 (Figure 7). There was therefore still a nitrifying and oxygen consuming activity (Figure 6). It was evidenced that a dose of chlorine at the dosing point of less than 2 g/kg of MLVSS for 24 hours (Day 7) was not sufficient to impact nitritation but still sufficient to affect nitratation. On the other hand, after a longer period of chlorination (at Day+13), all the nitrification is affected and the ammonia concentration at the exit starts to rise. Furthermore, Figure 6 shows that the NH_4-N concentration exceeds the normal value (2 mg/L) as soon as the nitrification uptake rate drops below 12 mg of O_2 consumed per hour and per litre of sludge. This observation was valid at both P1 and P2.

Conclusion

The daily chlorine dose, calculated as being the ratio between the amount of chlorine injected in 24 hours and the quantity of sludge, was 4.9 g/kg of MLVSS per day for the P1 plant and 4.8 g for the P2 plant. On average, the chlorine dose at the dosing point was 3.8 g/kg of MLVSS for P1 and 1.9 g/kg of MLVSS for P2. No nitrate was recorded in the treated effluent and the COD values measured remained stable. The chlorine doses applied in this study failed to cause any significant change in the heterotrophic biomass. With a chlorine dose at the injection point of between 3 and 4 g per kilo of MLVSS and at between 15° and 17°C, the loss of efficiency of nitrification occurred 8 days after the start of the treatment, whereas for a dose of essentially between 1 and 2 the efficiency of nitrification was maintained for 13 days. The impact of the recirculation rate is therefore crucial to preserve nitrification. The effect of this dose is, however, visible on the nitratation phase as from the 8th day. It should also be specified that peaks over the value of 2 occurred at the P2 plant and were probably sufficient to have a noticeable impact on nitratation at the onset (Day7) but more certainly at Day 13. The use of ATU is not recommended to determine oxygen uptake rates due to nitrification as it increases the OUR result. The method for measuring the oxygen uptake rate as presented in this study appears to be valuable for monitoring the effect of chlorination on nitrification. This method has the advantage of being simple to implement and above all of providing information in real time on the nitrification potential. The information obtained does not, however, clearly reveal the partial loss of nitratation. This measurement should, therefore, be coupled with the measurement of the treated effluent nitrite content.

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