Pre-ozonation in the activated sludge process: fate of nitrogen species
J. H. Garcia-Orozco, A. Vargas-Martinez and M. A. Ayala-Arnez

ABSTRACT
The objective of this research was to include ozonation prior to an activated sludge treatment and investigate the effect on the nitrogen species, their fate and the consequences of this oxidation upon the biomass. Three parallel treatment systems were used: the base system, where feed went directly to the activated sludge reactor, and two others, where the influent was ozonated at two different dosages, 15 and 25 mg/L of influent, prior to the biological reactors. The results from the ozonation chamber show a high oxidation capacity of the entering ammonia and organic nitrogen, proportional to the ozone dose. The oxidation product was nitrate. No de-nitrification was expected because a high oxygen concentration (4 mg/L) was maintained in the reactors. The reactors receiving ozonated influent showed a lower assimilation of nitrogen by the biomass. The sludge nitrogen content resulted in 11, 9.3 and 7.4% dry-weight corresponding to no-ozone, low ozone and high ozone dosages, respectively. In spite of the lower ammonia available in the ozonated flows, the corresponding reactors showed a higher specific nitrification rate. The ozonated system also performed better in terms of chemical oxygen demand (COD) and biochemical oxygen demand (BOD5) removals, besides showing a higher true biomass yield coefficient.

Key words | activated sludge, nitrification, nitrogen species, ozonation

INTRODUCTION
Most of the biological treatment systems in urban areas serve combined sewers and are subject to sub-optimal conditions for an efficient elimination of inhibitory or toxic compounds as well as emerging contaminants, which later are discharged into the environment. The need arises for a more robust design or redesign of the conventional treatment processes in use.

The integration of an ozone-activated sludge waste water treatment has been recognized to improve the performance of the treatment system. Ozone increases the biodegradability of the waste water components, attributed to the oxidation power and its high reactivity towards organic and inorganic compounds. This process has been investigated in a number of situations dealing with biorefractory compounds (Heinzle et al. 1995; Scott & Ollis 1996; Beltran et al. 1999).

Recognising the potential of the dual processes for better contaminant elimination, is necessary to turn the attention to the nutrients in the biological process, in this case the nitrogen compounds. In a biological aerobic waste water treatment, nitrogen can be assimilated and eliminated by a consortium of microorganisms, through nitrification and de-nitrification.

On the other hand, the assimilation of nitrogen by the biomass results in a relatively high weight fraction of nitrogen in terms of the volatile suspended solids (VSS). In activated sludge the average weight percentage of nitrogen associated with the biomass usually ranges between 9 and 12% (Ekama & Wentzel 2008).

Considering the advantages of pre-ozonation found by previous researchers, the purpose of this research was to implement an ozonation pretreatment in an activated sludge waste water treatment and trace the transformations of the nitrogen species: ammonia nitrogen (N-NH₃), nitrates (N-NO₃), nitrites (N-NO₂), organic nitrogen (N-Org) and nitrogen assimilated into biomass (N-MLSS), in the activated sludge treatment.
Ozonation

The effects of wastewater pre-ozonation in the activated sludge performance have been reported extensively; these scenarios dealt with the use of ozone in treating recalcitrant or toxic components in wastewater (Riveras et al. 2000; Lin et al. 2001; Benitez et al. 2003; Bettazzi et al. 2006). One of the main results in all the studies was the increased biodegradability of a wastewater subjected to ozonation, measured by the increase of the biological oxygen demand (BOD₃) / chemical oxygen demand (COD) ratio, resulting in a more efficient biological treatment, i.e., a higher kinetic constant. Other results are concerned with the values of the stoichiometric coefficients as well as operational parameters related to the biomass like SVI (sludge volume index) and settling rate; these show differences between the ozonated and non-ozonated influents, depending on the type of waste, treatment mode and ozone dosages. However, very little attention has been given to the impact on the nitrogen species and on the nutrient availability to the biomass.

A few studies deal with the effect of ozonation on the nitrogen species and consequences thereof. Beltran et al. (1999) reported an increased rate of ammonia oxidation in a combined preozonation-activated sludge reactor. The authors attributed this fact to an increased nitrifying activity in a less inhibitory environment, due to ozonation and not to the ozone activity.

Recently, the emphasis of ozonation is either the direct ozonation of sludge in order to reduce its net production (Boehler & Siegrist 2007; Richardson et al. 2009) or the combined ozonation-biodegradation in the same vessel (van Leeuwen et al. 2009). Some aspects of de-nitrification and nitrification are dealt with as a result of cell lysis.

Experimental Procedures

During this investigation, waste water was obtained from the influent to the university campus Waste Water Treatment Plant. The wastewater characterization is shown in Table 1. The experimental biological reactors were seeded with sludge from the same treatment plant, which consists of four completely mixed reactors in series, with a total detention time of 13 h and a treatment capacity of 15 L/s.

The experimental set up consisted of three parallel reactors, 9 L each, with an integrated settler. One of the reactors received straight influent while the others were preceded by the ozonation contactor, rectangular in shape, with a capacity of 1.2 L, divided into five chambers. A diffuser was installed in each of these chambers. The ozonated air was provided by a Clear Water Ozone Generator, Model CD 10/AD, with a variable generation capacity (0.13–1.28 g O₃/h). The ozone dose was controlled through the ozone activity. The intention was to help the biological activity, not to treat the wastewater with ozone.

The ozone dosage was constant, independent of the organic loading. The ozonated wastewater flow rate to each contactor by adjusting the wastewater flowrate. Each ozone flow was corroborated using an iodometric method, APHA/AWWA/WEF (1992) Method 2350 E.

After a few ozonation trials, using O₃ up to 200 mg/L, two different dosages were chosen; a ‘high dose’ of 25 mg O₃ per litre of influent, and a ‘low dose’ of 15 mg O₃ per litre of influent. The criterion was to use the smallest possible dose at the highest possible BOD₃/COD ratio, taking advantage of an effective biodegradability increase produced by the ozone application. The intention was to help the biological treatment, not to treat the wastewater with ozone.

The combined continuous degradation experiment considered four different average organic loadings to the biological system (0.50, 0.73, 1.00 and 1.45 d⁻¹ COD base). No nutrient addition or pH adjustment was done. The ozone dosage was constant, independent of the organic loading. The ozonated flows to the reactors showed concentrations of ozone in the order of 0.45 mg/L (Method 8311 Accuvac-Indigo, HACH).

The following equipment was used to monitor the process and perform the waste water analysis: HACH Spectrophotometer, Model DR2800; HANNA Dissolved oxygen meter, Model HI 9145; ORION Potentiometer, Model 290A Plus and a HACH Digester Reactor, Model DRB200. The analytical procedure for BOD₃ was according

### Table 1 | General Waste Water Characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/L)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>491</td>
<td>46.4</td>
</tr>
<tr>
<td>BOD₃</td>
<td>228</td>
<td>11.9</td>
</tr>
<tr>
<td>TSS</td>
<td>294</td>
<td>125</td>
</tr>
<tr>
<td>VSS</td>
<td>227</td>
<td>73.1</td>
</tr>
<tr>
<td>N-NH₃</td>
<td>45.4</td>
<td>4.2</td>
</tr>
<tr>
<td>N-ORG</td>
<td>23.8</td>
<td>1.9</td>
</tr>
<tr>
<td>N-NO₃</td>
<td>3.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Tot-N</td>
<td>75</td>
<td>4.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.37</td>
<td>0.2</td>
</tr>
<tr>
<td>T (°C)</td>
<td>25</td>
<td>0.9</td>
</tr>
</tbody>
</table>

These values represent averages from samples taken throughout the experimentation. BOD₃, biochemical oxygen demand; COD, chemical oxygen demand; N-NH₃, ammonia nitrogen; N-NO₃, nitrate nitrogen; N-ORG, organic nitrogen; Tot-N, Total Nitrogen; TSS, total suspended solids; VSS, volatile suspended solids.
to APHA/AWWA/WEF (1992) Method 5210 B, and for the nitrogen species and COD, following the HACH’s procedures.

At steady state, a series of water samples were taken and analysed for nitrogen species (N-Total, N-NO₃ and N-NH₃). Water samples for the influent were collected from the feeding tank, from the effluents of the ozone contactors, and the effluents from each of the biological reactors. Organic nitrogen (N-Org) was defined and calculated by the difference N-Org = N-Total – (N-NO₃ + N-NH₃). No nitrite was detected in the influent or during the degradation experiments, so it is not considered in the rest of the document.

In order to complete the nitrogen accounting, the determination of the biomass nitrogen content was carried out separately, reported as N-MLSS, and was referred to as a final effluent concentration.

All measurements were carried out with unfiltered samples and the numbers reported are the result of two independent samples and a triplicate analysis in each sample. Although four organic loadings were used in the experimentation, only one (0.50 d⁻¹, COD base) is used to illustrate the effect of the ozone pretreatment on the nitrogen species. This organic loading (F/M) is represented by the hydraulic residence time in the reactors of τ = 16 h.

RESULTS AND DISCUSSION

Ozonation

The applied dosages resulted in a COD reduction proportional to the ozone dose. The average reductions were 9 and 19% with respect to the influent, for low and high ozone dose, respectively. Data expressed as BOD₅ were not suitable for this indicator, since some of the effluent values increased instead as a result of the ozonation.

As reported before (Beltran et al. 1999), the average BOD₅/COD ratios for the wastewater going to the three reaction systems were: 0.46, 0.52 and 0.55, corresponding to the control reactor, the low dose and the high dose ozonation, respectively. A higher level could be reached by increasing the ozone dose; however, the intention again was to use the pre-oxidation to increase the biodegradability with as little ozone as possible.

The percent carbon degradation in the reactors increased from 77 to 86% and finally to 90% (in terms of COD), as the ozone dosage was increased. Similar results were obtained for higher organic loadings.

Nitrogen species

Total nitrogen (Tot-N)

This is defined as the sum of all species present in the liquid phase plus the nitrogen assimilated into the biomass (N-MLSS), expressed per unit volume of water going through the reactor, i.e., Tot-N = N-NH₃ + N-NO₃ + N-Org + N-MLSS. Since no detectable nitrite was found and no de-nitification was expected to occur, most of the nitrogen was accounted for. The diminishing trend in Tot-N is attributed to experimental bias since the digestion methods used show less than 100% nitrogen recovery. See Figure 1.
Ammonia nitrogen (N-NH$_3$)

This is the more susceptible of the nitrogen forms in the treatment system. Its oxidation is directly related to the ozone dose and represents the most important influence on the treatment. As seen from Figure 1, even at these relatively low dosages, a high percentage of ammonia in solution is transformed. Given the small amounts of ozone supplied (0.31 and 0.52 mM), the extent of oxidation found cannot be explained by the common stoichiometry of oxidation; therefore a significant free radical chain reactions contribution must be taking place (Heinzle et al. 1995).

$$2\text{O}_3 + \text{H}_2\text{O} + \text{OH}^- \rightarrow 2\text{HO}^- + 2\text{O}_2 + \cdot\text{HO}_2$$

The remaining N-NH$_3$, once in the reactor, is either nitrified or incorporated in the sludge; as a result, just traces remain in the reactor effluents, with or without pretreatment. Comparing the pretreated influents, the extent of nitrification is inversely proportional to the ozone dose, due to the availability of N-NH$_3$; i.e., the amount nitrified is higher in the control reactor (no-ozone) since no ammonia had been previously oxidized.

Organic nitrogen (N-Org)

This concentration was calculated from the measurements of three parameters in the liquid phase, N-Tot, N-NH$_3$ and N-NO$_3$. Organic nitrogen is susceptible to oxidation by ozone, although with more difficulty compared to ammonia. Again, the higher the ozone dose the higher the oxidation percentage of N-Org. On the other hand, the role attributed to N-Org in the reactors is as a supplement to the ammonia assimilated by the sludge; so, as can be seen from Figure 1, the more ammonia available, the less N-Org is utilized. As a result, the larger percentage of N-Org elimination happens in the high ozone dose system, due to the ammonia pre-oxidation plus the assimilation into biomass. This condition becomes critical as the organic loading is increased using a high ozone dose; the N-Org is consumed almost completely, together with the N-NH$_3$, due to the biomass growth requirements. This would tend to limit the ozone utilized as pretreatment.

Nitrate (N-NO$_3$)

A few parts per million were found in the influent (less than 3); so, its presence is due to the oxidation of ammonia and organic nitrogen in the ozone reactor and to nitrification in the biological reactor. A higher concentration is present in the final effluents of the ozonated wastewater, this concentration being proportional to the ozone dose.

In the absence of de-nitrification, a relatively small percentage of the incoming nitrogen is eliminated from solution, except the amount absorbed by the biomass. The inclusion of an anoxic step in the treatment would increase the percentage of nitrogen eliminated, leading to better compliance with the total nitrogen discharge requirements and, at the same time, decreasing the impact caused by the use of energy during ozonation by saving aeration needs in the carbon oxidation.

Nitrogen assimilation (N-MLSS)

The analysis of the nitrogen content in the biomass was an independent measurement. A direct digestion of the MLSS was used, from which a dry weight percentage can be calculated, which can be related to the water flow through the reactors. The fraction of nitrogen in the biomass resulted in different values: 7.4, 9.3 and 11.1% of VSS for the high dose, low dose and control system, respectively. Since less readily available nitrogen finds its way to the biological reactor when ozone is used as pretreatment, less nitrogen is taken up by the biological solids. As the organic loadings were varied, no significant difference was found in these nitrogen weight fractions.

The 7.4% nitrogen found in biomass of the high ozone dose reactor (R1), normally corresponds to a very old sludge (Eckenfelder 2000); in this case the sludge age was in the order of 12 days for all the reactors. It seems contradictory that sludge with low nitrogen content, usually associated with a low activity, would in fact show higher activity in every respect. Moreover, as mentioned in Table 2, the reactors receiving the ozonated flow presented a higher true yield coefficient.

Looking at the ozone oxidation capability regarding N-Org, it is reasonable to assume a similar difficulty encountered by the cells. As shown in Figure 1, the biomass developed in the test reactors is capable of utilizing N-Org as a source of nitrogen for cell growth; however, it could come at an expense of energy or a re-conformation of the cell composition. It seems impossible to increase the ozone dosage indefinitely since nitrogen could become limiting. In these circumstances, we cannot assure the sludge viability with a lesser nitrogen content. Figure 1(a) shows both N-NH$_3$ and N-Org approaching this limit. However, as sludge age increases (F/M decreases), so does the nitrogen availability, since the need for nutrients becomes smaller. This could alleviate somehow the apparent nutrient deficiency.
Biodegradation alone is capable of reducing inhibition, without reaching the low levels found in the ozonated flows, from −63.6 to −14.1%.

No effort was made to identify the type of compounds coming out in the final effluents; hence an issue still remains: the effectiveness of this pre-treatment followed by the biological process in the elimination of possible emerging pollutants present in the influent. There are indications, however, that ozone is effective as a post-treatment acting upon certain chemicals present in activated sludge effluents. These chemicals are recognized pharmaceuticals, endocrine-disruptors and personal care products (Huber et al. 2005; Nakada et al. 2007).

### Treatment costs

Ozone’s main disadvantage in the treatment of wastewater is the associated operational cost. With the operational advantage of the ozonated system, a treatment plant upgrading scenario was created where the flow capacity of the model treatment plant was to be increased by 30%, and the options were: (A) to use O₃ with the same plant size (15 L/s) or (B) to implement a standard increase in size, to accommodate the new flow-rate. A simplified analysis was done, where capital and direct operational costs were included (electricity), i.e., ozonation tank and main ozonation equipment using the low dose for the option A and a parallel treatment train for option B. While the capital expense for option B was considerably larger (280,000 vs. 70,000 USD), the annual operational cost resulted higher for option A (140,000 vs. 110,000 USD), mainly due to the cost of ozone generation. Taking a 15 year horizon for the project, the net present value (NPV) for option A is higher by 8%, favouring option B. A shorter time horizon would benefit option A.

Outside this analysis, other operational advantages of option A remain: the effluents show less inhibition and turbidity and no odour, the sludge showed a slightly
improved SVI and faster settling rate. These could balance the higher NPV.

CONCLUSIONS

Ozonation causes oxidation of ammonia and organic nitrogen present in wastewater, decreasing the readily absorbable nitrogen, resulting in significant variations in the nitrogen content of the biomass. The higher the ozone dose, the lower the nitrogen content.

In spite of the low nitrogen content, the biomass activity is higher in terms of degradation; although the nitrogen content could represent a limit to the ozone dose in case a higher pre-oxidation level is desired. The test reactors presented a higher specific nitrification rate, as a result of ozonation.

The inhibition tests performed on the treated water in the intermediate stages support the higher degradability state of the ozonated flows. An important outcome is the fact that the final effluents of the pretreated wastewater resulted non-inhibitory. Another outcome is the higher true yield coefficient found for the sludge.

With the present technology the cost of electricity constitutes the main weighting factor in the use of ozone; however, with more stringent legislation regarding emerging contaminants, the new research regarding sludge reduction and the cost associated with sludge handling, this approach can become a viable option.

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