The role of boundary conditions in the treatment of high-load ammonia wastewaters with ozone

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Abstract. This work presents some recent developments concerning the treatment of industrial wastewaters containing high loads of ammonia nitrogen using an ozonation process. It is well known that the direct oxidation of ammonia nitrogen generates nitrate. Nitrate is an unwanted reaction product because of its high eutrophication potential. Towards late Seventies it was demonstrated that an ozonation treatment enhanced by bromide ion may inhibit the generation of nitrate. The depletion of ammonia nitrogen proceeds through the formation and destruction of species that belong to the family of bromoamine, to finally generate nitrogen gas.

Ozonation tests carried out at a lab scale in batch modality demonstrated that the nitrate generation could be lowered to less than 10% of the theoretical value when two conditions coexist. Firstly, all the ammonia nitrogen was present in the form of ammonium (NH_4^+); this happens when the pH of the system is less than 8. Secondly, the ratio between dissolved ozone and bromide must be carefully calibrated, so as to avoid the presence of free ozone and the consequent direct reaction with ammonia nitrogen.

Keywords: bromide, ammonia nitrogen, nitrate, pH, buffering agents

1.   Introduction

The presence of ammonia (NH_3) and ammonium ion (NH_4^+)
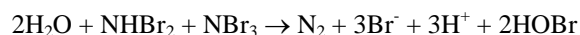
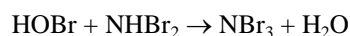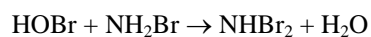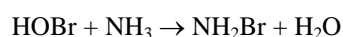$$NH_4^+ \leftrightarrow NH_3 + H^+ \ (pKa = 9.23)$$
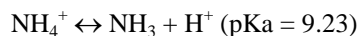
which are collectively called ammonia nitrogen, in municipal, agricultural, and industrial wastewaters may cause eutrophication of receiving water bodies. In addition, ammonia nitrogen in fresh waters causes acute toxicity to fish species, already at concentrations of less than 10 mg/l (Park *et al.*, 2015). Therefore, ammonia nitrogen needs to be removed from wastewater and preferably decomposed into harmless compounds.

The more conventional treatment for wastewater containing ammonia nitrogen is the biological nitrification, followed by denitrification. In fact, even nitrate is cause of eutrophication and it is more harmful than ammonia nitrogen. Moreover, nitrate is very water-soluble, so it moves readily with surface runoff into rivers or with water leaching through the soil profile into the groundwater. However, biological processes for the removal of ammonia nitrogen and nitrate are not applicable to wastewater with high salinity content or toxic compounds, like heavy metals. Consequently, other methods must be investigated, especially when it is necessary to deal with high ammonia nitrogen concentrations.

The conventional oxidation by ozone may be enhanced by using various metal oxide catalysts such as Co, Fe, Ni, Zn (Ichikawa *et al.*, 2014). The most efficient catalysts (Co_3O_4, MgO and NiO) could increase the rate of ammonia nitrogen decomposition up to 3-5 times and, because of the high selectivity to gaseous products, including N_2 and N_2O, suppressed the formation of soluble compounds such as nitrate.

Among the catalytic oxidation processes, ozonation enhanced by bromide can be included. Since the early Eighties it is known that the yield of oxidation of ammonia nitrogen with ozone improves if the process is carried out in the presence of bromide (Haag *et al.*, 1984). The improvement consists in a faster oxidation rate and avoided nitrate generation. In the ozonation process, the bromide ion reacts with molecular ozone and/or OH radicals to generate hypobromous acid (HOBr). HOBr is known to be an oxidant stronger and more effective than the only ozone in the oxidation of ammonia nitrogen (von Gunten, 2003). The oxidation process of the ammonia nitrogen proceeds through the generation of reaction intermediates (bromoamine) and ends with molecular nitrogen (N_2), that is the final product of reaction, as described by the series of reactions reported in Tanaka and Matsumura (2003):

$$HOBr + NH_3 \rightarrow NH_2Br + H_2O$$

$$HOBr + NH_2Br \rightarrow NHBr_2 + H_2O$$

$$HOBr + NHBr_2 \rightarrow NBr_3 + H_2O$$

$$2H_2O + NHBr_2 + NBr_3 \rightarrow N_2 + 3Br^- + 3H^+ + 2HOBr$$

Therefore, the above-described process is capable of minimizing or completely inhibiting the formation of nitrate.

Some patents, developed by Japanese inventors in the Nineties, use the basics of the bromide enhanced oxidation for the treatment of wastewater with a high content of ammonia nitrogen deriving from the deionization of the cooling waters of power stations (JP06269785, 1994;

JP09239384, 1997). However, the above-mentioned patents did not deal with the effect of the operating parameters (both process variables and characteristics of the solution that underwent the treatment) on the development of the process.

This study wants to investigate the effect of the ratio between bromide and ozone [Br⁻]/[O₃] and the influence of the pH on the efficacy of the bromide enhanced ozonation in the removal of ammonia nitrogen and in avoiding the generation of nitrate.

2. Materials and Methods

Ozone was generated from oxygen gas (99.95% v/v) using an ozone generator (Ozone Lab TM, Ozone Services Division of Yanco Industries, Canada). All tests were carried out in batch modality in a 300 ml glass reactor equipped with an ozone diffuser and all fluxes (oxygen and ozone) were carried through Teflon tubes. All tests took place in the presence of an ozone/oxygen flow, entering the ozone generator, equal to 200 ml/min and a room temperature value of $20 \pm 2°C$.

Analytical parameters (ammonia nitrogen, nitrate, pH, alkalinity) were determined according to Standards Methods (APHA, AWWA, WEF, 2005). The concentration of ozone in water was quantified by using the method described in Bader and Hoigné (1981), that is based on the reaction of ozone with potassium indigo trisulfonate ($C_{16}H_7N2O_{11}S_3K_3$). The dose of ozone distributed to the solution was of 26.6 mg/min and the resulting ozone concentration in the aqueous phase was of approximately 0.20 mM.

In this study three series of tests were performed. The first series was aimed at investigating the effect of the ratio [Br⁻]/[O₃] on the ammonia nitrogen depletion and nitrate generation. Solutions were prepared by dissolving NH_4Cl, $NaHCO_3$ (both of analytical grade and purchased by Sigma Aldrich) amounts in order to obtain final concentrations of 200 mg NH_4^+/L (11.1 mM) and 1000 mg HCO_3^-/L (16.4 mM). Potassium bromide (KBr) was added in order to obtain concentrations that ranged from 44.3 to 282 mg Br⁻/L. This generated [Br⁻]/[O₃] ratios from 2.8 to 18 mM/mM and [NH_4^+]/[Br⁻] ratios from 20.0 to 3.15 mM/mM.
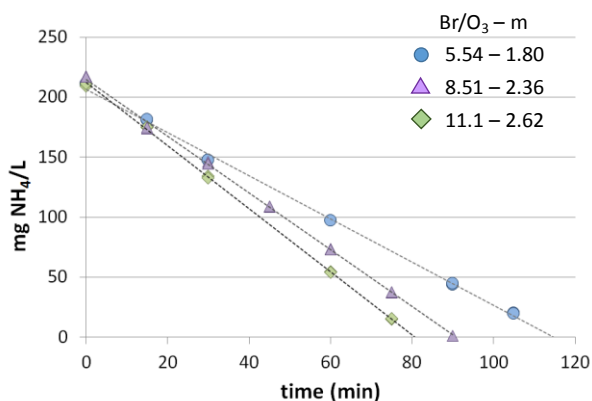
The second series of tests was aimed at investigating the effect of the presence of a buffer species ($NaHCO_3$) on the progression of the ammonia nitrogen oxidation and on the generation of nitrate. Solutions were prepared by keeping constant the concentrations of NH_4^+ (200 mg/L, 11.1 mM) and bromide (88.6 mg/L, 1.11 mM), for a [NH_4^+]/[Br⁻] = 10.0 and [Br⁻]/[O₃] = 5.54. Bicarbonate content was varied from 0 to 1000 (distributed in two aliquots 500 + 500) mg HCO_3^-/L.

The third series of tests was aimed at investigating the effect of the initial pH value of the solution on the progression of the ammonia nitrogen oxidation and on the generation of nitrate. Solutions were prepared by keeping constant the concentrations of NH_4^+ (200 mg/L, 11.1 mM), bicarbonate (1000 mg/L, 16.4 mM) and bromide (136 mg/L, 1.70 mM), with resulting [NH_4^+]/[Br⁻] and [Br⁻]/[O₃] ratios of 6.51 and 8.51, respectively. The natural pH of the solution (approximately 8.00) was corrected to 9.00 by adding some drops of a 0.1 M NaOH solution.

3. Results and Discussion

Figure 1 shows the depletion of ammonia nitrogen over time due to the oxidation with ozone species (ozone and HO* radicals) and HOBr, also known as "active bromine" (Khuntia *et al.*, 2013). In the three cases the ratio between bromide and ozone (mM Br⁻/mM O₃) was of 5.54, 8.51 and 11.1 and the resulting removal rates were of 1.80, 2.36 and 2.62 mg NH_4^+/L·min, respectively.

The starting pH of the three systems was in the order of 8.0 and it decreased to 6.8-6.5 towards the end of the process.

As it was demonstrated in previous studies (Tanaka and Matsumura, 2002; Ruffino and Zanetti, 2011), when the oxidation process involved high concentrations of ammonia nitrogen (> 10 mg/l), it followed a zero order rate, as in (1)

$$[A]_t = -mt + [A]_0 \quad (1)$$

that is the removal rate was independent on the residual concentration of ammonia nitrogen in the solution. Then,
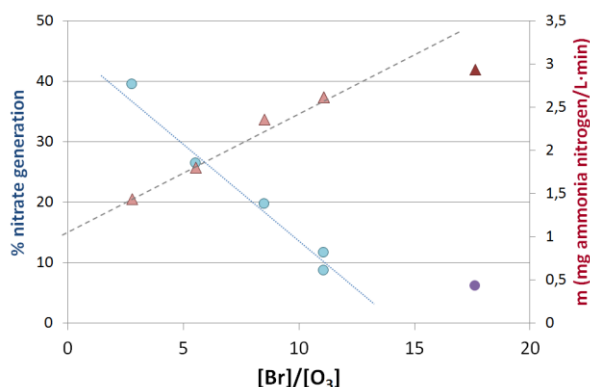

Figure 1. Depletion of ammonia nitrogen in time [Br-/O₃] = 5.54; 8.51; 11.1 mM/mM (on the left)

Figure 2. Effect of the [Br-/O₃] on the ammonia nitrogen removal rate and on the nitrate generation (on the right)

the removal rate (m) can be assumed as a constant value for almost all the duration of the process.

Figure 2 shows the effect of the ratio between the concentration of bromide and the concentration of dissolved ozone on the removal rate of ammonia nitrogen (m, mg NH_4^+/L·min). The ratio between bromide and ozone was varied from 2.8 to 18 [mM Br^-] /[mM O_3]. The observed removal rates of ammonia nitrogen were in the range 1.4 - 3.0 mg NH_4^+/L·min. The trend was initially linear and then tended to an asymptote, thus suggesting that, for the highest value of the ratio, all the ozone species had reacted with bromide to form "active bromine" (i.e. HOBr).

These results were in good agreement with the capacity of ozone and active bromine to oxidize ammonia nitrogen found by Khuntia and coauthors (2013). They studied the effect of the combination of bromide and ozone in the removal of ammonia nitrogen and the consequent generation of nitrate. By using an ozone dose of $5.6 \cdot 10^{-7}$ kg/s (equivalent to 33.6 mg/min, approximately 25% higher than that used in this study) and a molar ratio between ammonia nitrogen and bromide of 18:1 (approximately 30 mg Br-/L) they obtained an ammonia nitrogen removal rate in the order of 1.3 mg NH_4^+/L·min.

As shown in Figure 2, an increase in bromide concentration determined a decrease in nitrate generation. For a ratio between bromide and ozone equal to 1.5, the generation of nitrate was approximately 40% of the theoretical value (i.e. the concentration that would be found if all ammonia nitrogen was oxidized to nitrate). Berne and coauthors (2004) observed final concentrations of nitrate of 105 μM and 260 μM (for $[NH_4^+]/[Br^-]$ ratios of 2 and 5, respectively), which were about 50% of the initial concentration of ammonia nitrogen. Figure 2 shows that the generation of nitrate decrease to less than 10% of the theoretical value for $[Br^-]/[O_3]$ ratios higher than 6. Even in the case of nitrate generation, an asymptote may be observed for high $[Br^-]/[O_3]$ ratios. The reason of the observed trend was probably because all the ozone species

were involved in the formation of HOBr and could not react with ammonia nitrogen to form nitrate.

Even if nitrate was not formed (or was formed to a very small extent), the oxidation of ammonia nitrogen determined a release of H^+ ions in the solution and a consequent acidification. Previous studies demonstrated that pH is a key parameter in the process of oxidation of ammonia nitrogen by active bromine and that the oxidation resulted to be inhibited at very low pH values (Tanaka and Matsumura, 2003). In order to avoid a too fast acidification of the system a buffering agent must be added before the diffusion of ozone starts.

Figure 3 shows the effect of the presence of a buffering species (sodium bicarbonate, $NaHCO_3$) on the progression of the ammonia nitrogen oxidation. Without the presence of a buffering source, the pH of the solution prepared for the test naturally went to 6. The pH value dropped to 3.5 fifteen minutes after the beginning of the test. Without sodium bicarbonate, the removal rate of ammonia nitrogen decreased from approximately 1.5 to values of less than 0.5 mg NH_4^+/L·min.

Concentrations of the buffer agents in the order of 200 or 500 mg HCO_3^-/L were not sufficient to complete the oxidation of ammonia nitrogen in conditions close to neutrality. From Figure 3 it can be seen that the addition of 200 mg HCO_3^-/L could buffer the release of H^+ for approximately 30 minutes (i.e. they can guarantee the depletion of approximately 25% of the total amount of ammonia nitrogen), while a concentration of 500 mg/l guaranteed a steady development of the process for approximately 60 minutes. The increase in the pH value highlighted by the trend of the blue bars from 60 to 90 minutes (Figure 3) was due to the addition of an amount of $NaHCO_3$, corresponding to 500 mg HCO_3^-/L, after 60 minutes from the beginning of the test. This was done to
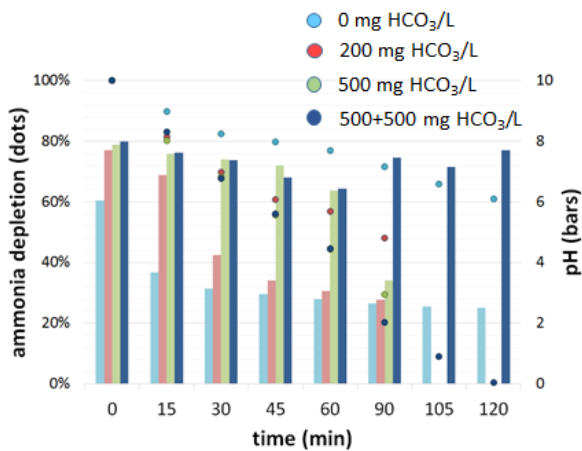

Figure 3. Effect of the presence of $NaHCO_3$ (0; 200; 500; 500+500 mg/L) on the progression of the ammonia nitrogen oxidation (on the left)
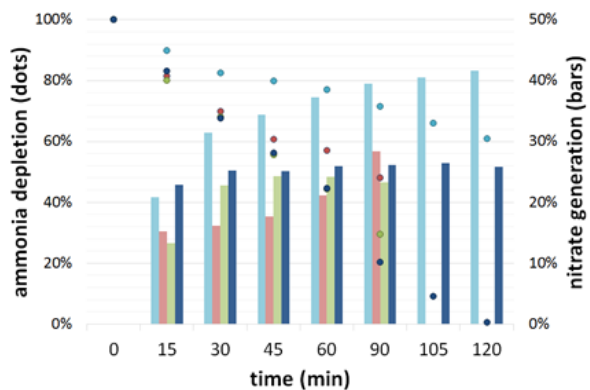
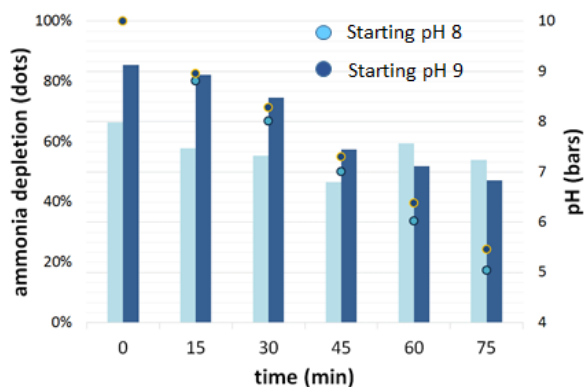**Figure 4.** Effect of $NaHCO_3$ on nitrate generation (on the right)

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Figure 5. Effect of the starting pH on the ammonia nitrogen removal (on the left)
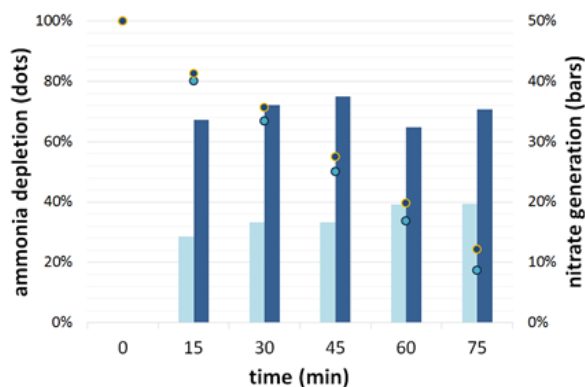
Figure 6. Effect of the starting pH on nitrate generation (on the right)

guarantee the completion of the oxidation process in the optimal pH conditions (i.e. close to neutrality).

As shown in Figure 4, the decrease in pH had a clear effect on the nitrate generation. In the systems where the oxidation of ammonia nitrogen was not completely buffered, the generation of nitrate (expressed as the ratio between the actual and the theoretical concentration of nitrate) increased (see the series of the light blue and red bars, Figure 4). Conversely, where the pH maintained a nearly constant value for all the duration of the oxidation process (see the blue bars), nitrate was generated at an approximately constant rateFigure 5 shows the effect of the starting pH on the ammonia nitrogen removal and nitrate generation. The test was carried out in the presence of a ratio between bromide and ozone of 8.51 (Br-concentration of 136 mg/l). The two systems differed for only one pH unit. As expected, the progression of the ammonia nitrogen oxidation determined a decrease in the pH in both systems. However, the rate of ammonia nitrogen removal for the system with starting pH of 8 was approximately 10% faster than the rate for the system with starting pH of 9 (2.36 vs. 2.15 mg NH_4^+/L·min).

After 75 minutes, the residual ammonia nitrogen in the system with starting pH of 9 was 24.3%, in that with starting pH of 8 was only of 17.2%. The increase in the pH at minute 60th, for the system with starting pH of 8, was due to an addition of $NaHCO_3$, that was necessary because the residual amount of alkalinity was too low to guarantee the completion of the process in the neutrality range. The generation of nitrate seemed to be greatly affected by the starting pH of the system. The generation of nitrate for the system with starting pH of 8 was approximately 20% of the theoretical value. Conversely, the more basic system registered a generation of nitrate in the order of 35-37% of the theoretical value. The generation of nitrate between the two systems differed by approximately 100%.

This result suggests the role of the ammonia nitrogen dissociation ($NH_3 \leftrightarrow NH_4^+$) on the nitrate generation in an

oxidation process with both ozone species and active bromine. At pH 9 approximately 60% of the ammonia nitrogen is present as ammonia (NH_3), while at pH 8 the amount of ammonia is only of 6% and decreases to less than 2% at pH 7.5. The observed results could be explained only if ammonia was directly oxidized to nitrate, while the ammonium ion was involved in the process of bromoamine generation that ends with the liberation of nitrogen gas.

4. Conclusions

This study demonstrated that the process of ozonation of ammonia nitrogen aided by bromide has some peculiarities:

1. a well-conducted process was capable to minimize the generation of nitrate. The generation of nitrate can probably be 15-20% (or less) of the potential generation value, if all the ozone is used for the formation of HOBr. In this way the direct oxidation reaction between ozone and ammonium ion is prevented. The yield of HOBr generation can be maximized by removing all the substances ozone inhibiting ("scavenger") from the solution.

2. the pH plays a key role in the process. For pH values of more than 8 the equilibrium between ammonia and ammonium ion is shifted towards NH_3 (pKa = 9.23). In this pH range the reaction of direct oxidation of ammonia (with generation of nitrate) competes with the oxidation reaction mediated by HOBr. On the other hand, pH values below 5-6 result in a significant slowdown of the reaction rate of ammonia nitrogen oxidation. The role of pH in nitrate generation was not completely investigated yet.

3. it is important that the process of ozonation is stopped when a residual concentration of ammonium ion is still present in the wastewater. The presence of ammonium ion prevents the irreversible oxidation of bromide to bromate

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