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(Article begins on next page)

1 **The role of boundary conditions in the bromide-enhanced ozonation**
2 **process for ammonia nitrogen removal and nitrate minimization**

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5 Barbara Ruffino ^{1,2,*} and Mariachiara Zanetti ¹

6 ¹Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, corso Duca
7 degli Abruzzi 24, 10129 Torino, Italy

8 ²CleanWaterCenter@PoliTo, Politecnico di Torino, corso Duca degli Abruzzi 24, 10129 Torino, Italy

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16 *Corresponding author

17 Barbara RUFFINO

18 DIATI, Department of Environment, Land and Infrastructure Engineering

19 Politecnico di Torino

20 Corso Duca degli Abruzzi, 24

21 10129 Torino, ITALY

22 Ph. +39.011.0907663

23 Fax +39.011.0907699

24 e-mail: barbara.ruffino@polito.it

25 **Abstract**

26 In this study we investigated the effect of some operating conditions, such as the ratio between ammonia
27 nitrogen (AN), ozone and bromide, the initial value of water pH, the amount of bicarbonate used as a
28 buffering substance and the possible interference of organic matter, in a bromide-enhanced ozonation
29 process for the removal of AN. One of the peculiarities of this process is that the oxidation of AN
30 proceeds through the generation of reaction intermediates (bromoamines) and ends with molecular
31 nitrogen (N₂) with none or limited generation of nitrate. The results of the ozonation tests carried out at
32 a lab scale demonstrated that nitrate generation could be lowered to less than 10% of the theoretical value
33 when three conditions coexist. Firstly, all the AN was present in the form of ammonium ion (NH₄⁺); this
34 happened when the pH of the system was lower than 8. Secondly, the ratio between bromide and ozone
35 species was optimized, so as to avoid the presence of free ozone and the consequent direct reaction with
36 AN. Finally, the acidification induced by the oxidation of AN was controlled with a buffering substance
37 (bicarbonate). The generation of inorganic bromoamines from the reaction between AN and bromide
38 inhibits the oxidation of bromide to bromate. In fact, in the tests carried out in this study the formation
39 of bromate was limited to values of less than 0.2% of the molar bromate yield.

40 Organic substances in the form of glucose or potassium hydrogen phthalate (KHP) did not affect the
41 removal rate of AN. Conversely, the presence of substances such as phenol and hydroquinone, that had
42 a higher reactivity towards ozone and HOBr, determined a reduced AN removal rate and a bromate
43 generation of one order of magnitude higher than that observed with KHP and glucose. Finally, all the
44 organic substances employed in the study seemed to have a positive effect in reducing the nitrate
45 generation (-30% of the value obtained with sole AN).

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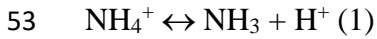
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49 **Keywords:** ozone, pH, bicarbonate, bromate, organic matter

50 **Introduction**

51 Ammonia (NH₃) and ammonium ion (NH₄⁺), which can be transferred to each other by a pH depending
52 equilibrium (shown in (1), pK_a = 9.23), are collectively named as ammonia nitrogen (AN).



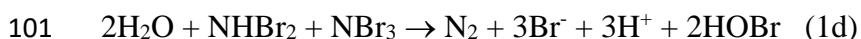
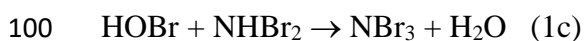
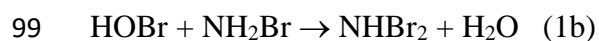
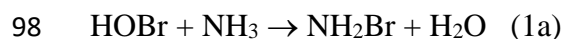
54 AN is present in almost all types of wastewater, from municipal, agricultural and industrial origin. High
55 concentrations of ammonia are especially found in wastewaters generated from the industry sector,
56 including electronic, petrochemical, pharmaceutical, fertilizer, food and steel manufacturing industries
57 (Lin et al., 2018). AN is a source of nitrogen, which is a nutrient for algae and other forms of plant life
58 when released into the environment, and thus contributes to eutrophication of receiving water bodies. In
59 addition, AN in fresh waters causes acute toxicity to fish species, already at concentrations of less than
60 10 mg/l (Park et al., 2015). For these reasons, processes for removal of AN from ammonia-rich streams
61 has gained increasing attention in recent years. Furthermore, because of the more and more stringent
62 discharge limits for AN that have been steadily imposed on wastewater treatment plants (WWTPs)
63 worldwide, AN needs to be removed from wastewater to very low concentration values before discharge
64 and preferably decomposed into harmless compounds.

65 The state-of-the-art treatment technologies for AN removal include traditional biological nitrification –
66 denitrification, anaerobic ammonium oxidation (ANAMMOX) and, especially for wastewaters from
67 industrial origin, air stripping (Hsieh et al., 2013; Yuan et al., 2016), chemical precipitation (Cheng et
68 al., 2016), eventually with the aim of recovering valuable compounds, ion exchange, adsorption, break-
69 point chlorination, reverse osmosis (Jin et al., 2013), electrodialysis and hollow fiber membrane contactor
70 and membrane distillation (Lin et al., 2018). Each of these technologies has its own limitation. For
71 example, due to the toxic nature of AN in industrial wastewater, biological treatments are often not
72 appropriate (Charmot-Charbonnel et al., 1999). Bacteria used in these processes are very sensitive and
73 cannot withstand wide ranges of pH and temperature, halogen compounds, cyanides, and other heavy
74 metals present in ammonia-containing water (Moussavi et al., 2009). Air-stripping creates additional air
75 pollution when AN is converted from liquid to gas phase. Chemical precipitation generates sludge, from
76 which the extraction of valuable products is not often possible, and leaves substantial amounts of AN in
77 exhaust waters even after recovering it from concentrated streams in the form of (NH₄)₂SO₄ (Ulbricht et
78 al., 2013). Ion exchange and reverse osmosis generates concentrated streams that have to be further
79 subjected to treatment.

80 In the last years, oxidation processes, where AN can be oxidized to molecular nitrogen, eventually
81 enhanced by using catalytic substances, have attracted increasing attention (Moussavi and

82 Mahdavianpour, 2016). Various metal oxide catalysts such as Co, Fe, Ni, Zn can improve the
83 performances of a conventional oxidation of AN with ozone (Ichikawa et al., 2014). The most efficient
84 catalysts (Co₃O₄, MgO and NiO) could increase the rate of AN decomposition up to 3-5 times and,
85 because of the high selectivity to gaseous products, including N₂ and N₂O, suppressed the formation of
86 soluble compounds such as nitrate. Recently, Chen and coauthors (2018) found that a catalyst with 8:2
87 MgO-Co₃O₄ molar ratio, calcined at 500°C for 3 hr, allowed to obtain an AN removal rate of 85.2% and
88 gaseous nitrogen selectivity of 44.8%.

89 Among the catalytic oxidation processes, ozonation enhanced by bromide can be included. The main
90 peculiarities of the role of bromide in an ozonation process were firstly discovered in early Eighties (Haag
91 et al., 1984). During ozonation, bromide is converted to hypobromous acid (HOBr). The mechanism of
92 the process is similar to that of ammonia breakpoint chlorination. The difference is that in an ozonation
93 process, HOBr can be continuously produced by the oxidation of bromide and bromide can be utilized
94 repeatedly. HOBr is known to be a stronger and more effective oxidant than the only ozone in the
95 oxidation of AN (von Gunten, 2003). The oxidation process of AN proceeds through the generation of
96 reaction intermediates (bromoamine) and ends with molecular nitrogen (N₂) as in the series of reactions
97 reported in Tanaka and Matsumura (2003):



102 Some patents, developed by Japanese inventors in the Nineties, used the basics of the bromide-enhanced
103 oxidation process for the treatment of wastewaters with a high content of AN deriving from the
104 deionization of cooling waters of power stations (Nitto Kikai KK and Permelec Electrode LTD, 1994;
105 Japan Organo CO LTD, 1997). However, the above-mentioned patents did not report the effect of the
106 operating parameters, that is both process parameters and the characteristics of the solution that
107 underwent the treatment, on the performance of the process in detail. Some years later, Yang and
108 coauthors (1999; 2000), by using water samples that reproduced the characteristics of the real
109 wastewaters from cooling towers (containing N-NH₄⁺, Na⁺, SO₄⁼ and very low amount of organic carbon,
110 1-4 mg/l), demonstrated that the formation of nitrate was mainly affected by the Br⁻/N ratio, N load, and
111 pH. The application of the bromide-enhanced ozonation process may be of great attractive for the
112 treatment of cooling waters, because aqueous bromine is often used as a primary biocide in cooling tower

113 disinfection applications. It is highly effective at inactivating bacteria responsible for forming biofilms,
114 such as *Pseudomonas aeruginosa* (Boal, 2016). In this case bromide should not be added for the
115 treatment.

116 Later, Tanaka and Matsumura (2003) treated real samples of spent brine that already contained bromide
117 at the concentration of 100 mg/l. They proved that increasing concentrations of bromide had positive
118 effect on AN removal and that a pH decrease slowed down the reaction. Brines, other than ammonia,
119 contained small amounts of organic matter (COD = 50 mg/l). Ozone had also effect on COD removal
120 but the competition between AN and organic carbon for the use of the oxidant (HOBr) was not
121 completely elucidated. More recently, Khuntia and coauthors (2013), using a batch apparatus equipped
122 with a fine diffuser to sparge ozone-enriched oxygen microbubbles, observed that the rate of oxidation
123 of ammonia by ozone becomes faster in the presence of bromide ions. Samples used for the tests were
124 on purpose made and contained only inorganic species such as NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, Na_2CO_3 , HCl . The
125 authors concluded that the advantage of using bromide is that the nitrate formed by the oxidation of
126 ammonia is ultimately converted to nitrogen.

127 As pointed out by the afore-mentioned experiences, the peculiarities of the bromide-enhanced ozonation
128 process could be used for a fast and effective treatment of effluents from industrial origin that contain
129 from moderate to high AN loads. However, for the application of the process at a real scale, the effect of
130 operating conditions needs to be elucidated, such as the initial pH of the water, the presence of buffering
131 substances, the ratio between AN, ozone and bromide, and the possible interference of organic matter on
132 the transformation of the species of concern (AN, nitrate). This work wants to identify, and subsequently
133 tune, the operating conditions that determine the minimization of nitrate generation in a bromide-
134 enhanced ozonation, with a regard to the problem of bromate formation. Secondly, it wants to provide
135 preliminary insights concerning the competition between AN and organic carbon for the use of the
136 oxidant (HOBr).

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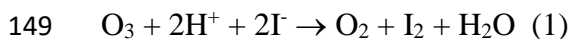
138 **2. Materials and Methods**

139 **2.1 Experimental set-up and ozone quantification**

140 Ozone was generated from oxygen gas (99.95% v/v) using an ozone generator (Ozone Lab TM, Ozone
141 Services Division of Yanco Industries, Canada). Fluxes of oxygen and ozone-enriched oxygen (after
142 ozone generation) of 200 ml/min were carried to and from the ozone generator through Teflon tubes. All
143 tests were carried out in batch modality in a 300 ml glass gas washing bottle equipped with a filter disc

144 for ozone diffusion. Volumes of solutions of 200 ml were subjected to ozonation treatments. All tests
145 took place at a room temperature value of $20 \pm 2^\circ\text{C}$.

146 The dose of ozone distributed to the solution was quantified by using the iodometric wet-chemistry
147 method (Rakness et al., 1996). The ozone enriched oxygen flow was bubbled through a 1% potassium
148 iodide (KI) solution. Ozone oxidizes iodide to iodine, according to reaction (1)



150 and the generated iodine was titrated with a 0.1 N solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$).

151 The concentration of ozone in water was quantified by using the method described in Bader and Hoigné
152 (1981), that is based on the reaction of ozone with potassium indigo trisulfonate ($\text{C}_{16}\text{H}_7\text{N}_2\text{O}_{11}\text{S}_3\text{K}_3$) and
153 the detection of the residual concentration of indigo at 600 nm.

154 155 **2.2 Experimental procedure and analytical parameters determination**

156 In this study four series of tests were carried out. The first series was aimed at investigating the effect of
157 $[\text{Br}^-]/[\text{O}_3]$ and $[\text{NH}_4^+]/[\text{Br}^-]$ ratios on AN depletion and generation of nitrate. Solutions were prepared by
158 dissolving NH_4Cl , NaHCO_3 (both of analytical grade and purchased by Sigma Aldrich) amounts in order
159 to obtain final concentrations of 200 mg NH_4^+/L (11.1 mM) and 1000 mg HCO_3^-/L (16.4 mM). Aliquots
160 of a 2000 mg/L solution of potassium bromide (KBr) were added in order to obtain bromide
161 concentrations that ranged from 44.3 to 282 mg Br^-/L (0.55 – 3.53 mM). $[\text{NH}_4^+]/[\text{Br}^-]$ ratios were in the
162 range 20.0 - 3.15 mM/mM. The generation of by-products (specifically bromate) was measured on the
163 system with $[\text{Br}^-] = 3.33$ mM.

164 The second series of tests was aimed at investigating the effect of the presence of sodium bicarbonate
165 (NaHCO_3), as a buffering agent, on the progress of AN oxidation and generation of nitrate. Solutions
166 were prepared by keeping constant the concentrations of NH_4^+ (200 mg/L, 11.1 mM) and bromide (88.6
167 mg/L, 1.11 mM), for a $[\text{NH}_4^+]/[\text{Br}^-] = 10.0$. Bicarbonate content was varied from 0 to 1000 (distributed
168 in two aliquots, 500 + 500) mg HCO_3^-/L .

169 The third series of tests was used for investigating the effect of the initial pH value of the solution on the
170 progress of the AN oxidation and generation of nitrate. Solutions were prepared by keeping constant the
171 concentrations of NH_4^+ (200 mg/L, 11.1 mM), bicarbonate (1000 mg/L, 16.4 mM) and bromide (136
172 mg/L, 1.70 mM), with a resulting $[\text{NH}_4^+]/[\text{Br}^-]$ ratio of 6.51. The natural pH of the solution
173 (approximately 8) was corrected to 9 by adding some drops of a 0.1 M NaOH solution.

174 A fourth series of tests was used to obtain preliminary information concerning the possible interference
175 of organic substances in the HOBr oxidation of AN. Five solutions containing AN (as NH_4Cl , 90.0 mg/L,

176 5.0 mM), bicarbonate (as NaHCO₃, 460 mg/L, 7.5 mM) and bromide (as KBr, 266 mg/L, 3.33 mM) were
 177 prepared. One solution was used as a reference. To each of the other four solutions an organic substance
 178 (glucose, potassium hydrogen phthalate (KHP), hydroquinone, phenol, all of analytical grade, purchased
 179 by Honeywell) was added to obtain a 0.5 M concentration. The compounds chosen for the test are
 180 representative of substances that are widely diffused into the environment. Specifically, phenolic
 181 compounds, like phenol and hydroquinone, have often been used as model compounds to describe
 182 substances that are naturally present in freshwater, as constituents of natural organic matter (NOM), or
 183 in wastewater, after conventional treatments, as effluent organic matter (EfOM) (Bond et al., 2009).
 184 Residual AN and alkalinity, nitrate and bromate were measured after a 30-min ozonation. Analytical
 185 parameters (AN, nitrate, pH, alkalinity, bromate) were determined according to Standards Methods
 186 (APHA, AWWA, WEF, 2005).

187

188 Table 1. Summary of the conditions used for the tests

Series of tests	N-NH ₄ ⁺ (mM)	HCO ₃ ⁻ (mM)	Br ⁻ (mM)	[N-NH ₄ ⁺ / Br ⁻]	pH	Organic (mM)
I	11.1	16.4	0.55 – 3.53	20.0 – 3.15	8	0
II	11.1	0 – 16.4	1.11	10.0	8	0
III	11.1	16.4	1.70	6.51	8 – 9	0
IV	5.0	7.5	3.33	1.50	NC	0.5

189 NC: not corrected

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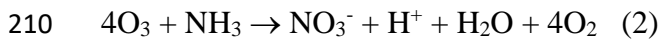
191 3. Results and Discussion

192 3.1 Effect of the [Br⁻]/[O₃] ratio on AN depletion and nitrate generation

193 It was verified, by using the iodometric wet-chemistry method, that the dose of ozone distributed to the
 194 solution, through the ozone-enriched flow (200 mL/min) with the employed set-up, was of 26.6 mg/min.
 195 The ozone concentration reached in the aqueous phase at steady-state, determined with potassium indigo
 196 trisulfonate, was of approximately 0.20 mM.

197 Figure 1 shows the trend of AN depletion in four solutions with an identical initial concentration of AN,
 198 equal to 200 mg NH₄⁺/L (11.1 mM), due to an oxidation process where ozone species (i.e. ozone and
 199 HO* radicals) and bromide were contemporaneously present in the system. For the systems shown in
 200 Figure 1, the [Br⁻]/[O₃] ratio was of 5.54, 8.51, 11.1 and 16.6 (mM Br⁻/mM O₃) for bromide
 201 concentrations of 88.6, 136, 177 and 266 mg/L (1.11, 1.70, 2.22 and 3.33 mM), respectively. It can be
 202 seen that processes from approximately 70 to 120-minute long, depending on the bromide concentration,
 203 were required to reduce the concentration of AN from 200 mg/L to zero. Then, the resulting AN removal

204 rates were of 1.80, 2.36, 2.62 and 2.79 mg NH₄⁺/L·min (0.100, 0.131, 0.145 and 0.155 mM/min) for [Br⁻]
205]/[O₃] ratios of 5.54, 8.51, 11.1 and 16.6 (mM Br⁻/mM O₃), respectively. As expected, the increase in
206 bromide concentration made the oxidation process faster. In fact, in an oxidation process with ozone and
207 bromide, it must be assumed that the oxidation of AN due to HOBr, also known as “active bromine”
208 (Khuntia et al., 2013), that proceeds through the generation of the series of bromoamines (see Equations
209 1 a-d), overcomes the direct oxidation of AN due to ozone, as described in Equation (2)



211 The rates of the two processes differ by several order of magnitude: $k_1 = 8 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$ (Haag and Hoigné,
212 1983; Haag et al., 1984; Tanaka and Matsumura, 2003), in the case of HOBr, vs. $k_2 = 1 \text{ M}^{-1}\text{s}^{-1}$ (at pH=8)
213 (Haag et al., 1984), in the case of the sole ozone.

214 The AN removal rates observed in this study were in good agreement with the capacity of ozone and
215 active bromine to oxidize AN found by Khuntia and coauthors (2013). They studied the effect of the
216 combination of bromide and ozone in the removal of AN and the consequent generation of nitrate. By
217 using an ozone dose of $5.6 \cdot 10^{-7} \text{ kg/s}$ (equivalent to 33.6 mg/min, approximately 25% higher than that
218 used in this study) and a molar ratio between AN and bromide of 18:1 (approximately 30 mg Br⁻/L) they
219 obtained an AN removal rate in the order of 1.3 mg NH₄⁺/L·min.

220 It can be observed that the oxidation process followed a zero-order kinetic, as described by Equation (3)

$$221 \quad [\text{AN}]_t = -m \cdot t + [\text{AN}]_0 \quad (3)$$

222 In a zero-order process the removal rate, m , is independent on the concentration of AN that remains in
223 the solution time after time. This result was in agreement with the findings of previous studies (Tanaka
224 and Matsumura, 2002; Ruffino and Zanetti, 2011; 2012), that had demonstrated that a bromide-aided
225 ozonation process, carried out on solutions containing concentrations of AN of more than 10 mg/l,
226 followed a zero order kinetic. Then, the removal rate, m , could be assumed as a constant value for almost
227 all the duration of the process. The starting pH of the three systems was in the order of 8.0 – 8.1 and it
228 decreased to 6.8-6.5 at the end of the process (data not shown).

229 Figure 2 shows the effect of the [Br⁻]/[O₃] ratio on the removal rate of AN (m , mg NH₄⁺/L·min). In the
230 presence of [Br⁻]/[O₃] ratios from 2.8 to 18 [mM Br⁻] / [mM O₃], the observed removal rates of AN were
231 in the range 1.4 - 3.0 mg NH₄⁺/L·min (0.078 – 0.166 mM/min). It is interesting to observe that the trend
232 of the AN removal rates could be fitted well by a line in the left part of the diagram, that is for [Br⁻]/[O₃]
233 ratios from 2.8 to approximately 11-12. Conversely, moving towards the right part of the diagram, that
234 is for [Br⁻]/[O₃] ratios of more than 11-12, the trend of the AN removal rates tended to an asymptote. The
235 trend of the AN removal rates shown in Figure 2 suggested that, above a fixed value of the [Br⁻]/[O₃]

236 ratio, all the ozone species (ozone and HO* radicals) available in the solution had reacted with bromide
237 to form the “active bromine” (i.e. HOBr) and that subsequent increases in the bromide concentration
238 were not able to further increase the oxidizing power of the solution. It can be stated/concluded that the
239 oxidizing power of the solution was limited by the amount of ozone able to dissolve in the solution. With
240 the employed set-up and oxygen flow (200 ml/min) and in the presence of the highest bromide
241 concentration, i.e. when all the ozone that was dissolved into the solution had reacted with the available
242 bromide to form active bromine, the specific consumption of ozone to remove AN was in the order of 60
243 mg O₃/mg NH₄⁺ (22.5 mmol O₃ / mmol NH₄⁺).

244 Additionally, Figure 2 shows the relation between the [Br⁻]/[O₃] ratio and the capacity of the process of
245 generating nitrate. For each test carried out at a different value of the [Br⁻]/[O₃] ratio, Figure 2 shows the
246 percentage of generated nitrate, compared to the theoretical value. The theoretical value of nitrate
247 concentration is the value that would be found if all the AN was oxidized to nitrate. As shown in Figure
248 2, an increase in bromide concentration, at a fixed dissolved ozone concentration value, determined a
249 decrease in the actual nitrate generation. The generation of nitrate decreased to less than 10% of the
250 theoretical value for [Br⁻]/[O₃] ratios higher than 6. As in the case of the removal rate of AN, even the
251 trend of the nitrate generation showed a plateau for [Br⁻]/[O₃] ratios of more than 10-12. The observed
252 trend can be justified because all the ozone species were involved in the formation of HOBr and could
253 not react with AN to form nitrate. As reported in Figure 2, for a [Br⁻]/[O₃] ratio equal to 1.5, the
254 generation of nitrate was approximately 40% of the theoretical value. This value was in good agreement
255 with the findings of Berne and coauthors (2004) that observed concentrations of nitrate of 105 μM and
256 260 μM (for [NH₄⁺]/[Br⁻] ratios of 2 and 5, respectively), after a complete depletion of the AN, which
257 were approximately 50% of the initial concentration of AN and, then, of the theoretical nitrate
258 concentration.

259

260 **3.2 Effect of bicarbonate concentration on AN depletion and nitrate generation**

261 As demonstrated from the results of Figure 2, even if nitrate was not formed (or was formed to a very
262 small extent), the oxidation of AN determined a release of H⁺ ions in the solution and a consequent
263 acidification. Previous studies demonstrated that the pH is a key parameter in the process of oxidation of
264 AN by active bromine and that the inhibition of AN oxidation started from pH values around 5.0 (Tanaka
265 and Matsumura, 2003). Consequently, in order to avoid a too fast acidification of the system, a buffering
266 agent must be added before the sparging of ozone begins.

267 Figure 3 shows the effect of increasing concentrations of sodium bicarbonate, NaHCO_3 , a buffering
268 substance, on both the performance of the AN oxidation process and the trend of the pH value in the
269 solution after treatments with durations from 15 to 120 minutes. This second series of tests was carried
270 out at a $[\text{Br}^-]/[\text{O}_3]$ ratio of 5.54. From the results of Figure 3 it can be observed that, without the presence
271 of a buffering source, the pH of the solution prepared for the test naturally assumed the value of 6 (see
272 the light blue bar). pH dropped to the value of 3.5 fifteen minutes after the beginning of the test. Without
273 bicarbonate, the removal rate of AN decreased from approximately $1.5 \text{ mg NH}_4^+/\text{L}\cdot\text{min}$, in the first
274 fifteen minutes of the test, to values of less than $0.5 \text{ mg NH}_4^+/\text{L}\cdot\text{min}$ in the remaining part of the test.
275 Amounts of bicarbonate in the order of 200 or 500 $\text{mg HCO}_3^-/\text{L}$ (i.e. $1 \text{ mg HCO}_3^-/\text{mg NH}_4^+$ or 2.5 mg
276 $\text{HCO}_3^-/\text{mg NH}_4^+$) were not sufficient to make the oxidation of AN complete (to bring the oxidation to
277 completion) without determining a decrease in the pH to values of less than 4.0. From Figure 3 it can be
278 seen that the addition of a dose of bicarbonate of $200 \text{ mg HCO}_3^-/\text{L}$ had been able to buffer the release of
279 H^+ for approximately 30 minutes (i.e. that dose could guarantee the depletion of approximately 25% of
280 the total amount of AN), while a concentration of 500 mg/l guaranteed a steady development of the
281 process for approximately 60 minutes.
282 In order to bring the removal of AN to completion without inducing an irreversible acidification of the
283 solution, the process described by the blue bars (Figure 3) was stopped after 60 minutes and a new amount
284 of bicarbonate was added to the solution. The dose added at minute 60th was such to bring the HCO_3^-
285 $/\text{NH}_4^+$ ratio (by weight, mg/mg) to 5. Ideally, after the addition, the overall concentration of bicarbonate
286 in the solution was of 1000 mg/L ($500 + 500 \text{ mg/L}$). The effect of the NaHCO_3 addition was the increase
287 in the pH value observed for the blue bars from 60 to 90 minutes (Figure 3).
288 Consequently, it could be calculated an overall bicarbonate specific consumption in the order of 5 mg
289 $\text{HCO}_3^-/\text{mg NH}_4^+$ to maintain the pH value in the range of neutrality for all the duration of the treatment.
290 These observations were in good agreements with the findings of a previous study that involved the
291 treatment of spent brine, where the initial concentrations of AN and bromide were of 13 mM and 106 (or
292 208) mg/l , respectively (Tanaka and Matsumura, 2003). The authors of this study observed that when all
293 the alkalinity was depleted, ammonia was difficult to be oxidized and the removal rate decreased from
294 approximately 0.8 mM h^{-1} to zero.
295 As shown in Figure 3, the decrease in the pH value had also a clear effect on nitrate generation. In the
296 systems where the oxidation of AN was not completely buffered (i.e 0; 200 and $500 \text{ mg NaHCO}_3/\text{l}$), the
297 generation of nitrate, expressed as the ratio between the actual and the theoretical concentration of nitrate,
298 increased to reach values in the order of 40% (see the series of light blue and red bars, Figure 3).

299 Conversely, where the pH was maintained at a nearly constant value for all the duration of the oxidation
300 process, with the aid of the buffer substance (see the blue bars), nitrate was generated at an approximately
301 constant rate that was in the order of 25% of the theoretical value.

302

303 **3.3 Effect of the initial pH value on AN depletion and nitrate generation**

304 Values of pH of more than 9.0 displaces the equilibrium between the forms of AN towards ammonia
305 (NH_3) and this species is removed preferentially by stripping (Luo et al., 2015). Figure 4 shows the effect
306 of the starting pH values of 8.0 and 9.0 on AN removal and the pH value found at the end of the test.
307 Tests were carried out in the presence of a $[\text{Br}^-]/[\text{O}_3]$ ratio of 8.51 (Br- concentration of 136 mg/l). As
308 expected, the progress of AN oxidation determined a decrease in the pH value in both systems. However,
309 the rate of AN removal for the system with a starting pH of 8.0 was approximately 10% faster than that
310 of the system with a starting pH of 9.0 (2.36 vs. 2.15 mg $\text{NH}_4^+/\text{L}\cdot\text{min}$). After 75 minutes, the residual
311 AN in the system with a starting pH of 9.0 was 24.3%, in that with a starting pH of 8 was only of 17.2%.
312 The increase in the pH at minute 60th, for the system with a starting pH of 8.0, was due to an addition of
313 NaHCO_3 , that was necessary because the residual amount of alkalinity was too low to guarantee the
314 completion of the process in the neutrality field.

315 As shown in Figure 4, the generation of nitrate seemed to be greatly affected by the starting pH of the
316 system. The generation of nitrate for the system with a starting pH of 8.0 was approximately 20% of the
317 theoretical value. Conversely, the more basic system registered a generation of nitrate in the order of 35-
318 37% of the theoretical value. The generation of nitrate between the two systems differed by
319 approximately 100%.

320 This result clarifies the role of the AN dissociation ($\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+$) on nitrate generation in an
321 oxidation process with both ozone and active bromine. At pH 9.0 approximately 60% of the AN is present
322 in the form of ammonia (NH_3), while at pH 8.0 the amount of ammonia is only of 6% and decreases to
323 less than 2% at pH 7.5. The observed results could be explained only if ammonia (NH_3) was directly
324 oxidized to nitrate, while the ammonium ion was involved in the process of bromoamine generation that
325 ends with the liberation of nitrogen gas (Rahmadi and Kim, 2014).

326

327 **3.4 Bromate generation potential**

328 It is well known that bromide during ozonation may be converted to bromate (BrO_3^-), classified as a
329 probable or likely human carcinogen (WHO, 2005), and for which many countries have established the
330 maximum allowable level in drinking water at 10 ug/L. Bromate is produced during ozonation through

331 a multistep process that involves the oxidation of bromide (Br^-), ensuing generation of HOBr and bromite
332 (BrO_2^-) and their reactions with ozone (Fischbacher et al., 2015; von Gunten, 2003; von Gunten and
333 Oliveras, 1998). Previous studies have revealed that many factors, including O_3 dosage, contact time,
334 pH, and Br^- and AN concentrations, influenced BrO_3^- formation during ozonation (Antoniou and
335 Andersen 2012; Lin et al., 2014; Pinkernell and von Gunten 2001).

336 Figure 5 relates the residual concentration of AN, after a 30 or 60-minute ozonation process, to the molar
337 bromate yield for the system containing $[\text{NH}_4^+] = 11.1 \text{ mM}$; $[\text{HCO}_3^-] = 16.4 \text{ mM}$ and $[\text{Br}^-] = 3.33 \text{ mM}$.
338 Molar bromate yield can be defined as the dimensionless ratio of molar bromate concentrations
339 normalized by the initial bromide level, $\text{BrO}_3^-/\text{Br}^-$, $\text{mmol L}^{-1}/\text{mmol L}^{-1}$ (Li et al., 2017).

340 Figure 5 shows that after a 30-minute process, the residual concentration of AN was in the order of 60%
341 of the initial concentration and the molar bromate yield was 0.07%, with a bromate concentration of
342 approximately 290 $\mu\text{g/L}$. After 60 minutes, the residual concentration of AN was of 16% and the molar
343 bromate yield rose to 0.15%, with a bromate concentration of 644 $\mu\text{g/L}$. These results demonstrate that
344 residual AN concentrations limited the generation of bromate to values much lower than 1% of the
345 potential generation, even in the presence of very high initial bromide concentrations (i.e. in the order of
346 100 mg/l or more). In fact, AN inhibits bromate formation by reacting with HOBr/OBr $^-$ and thus starting
347 the series of reactions that leads to the formation of amines with different degree of bromination (mono-
348 , di-, tri-bromoamine, see Reactions 1a – 1d). Bromoamines are cyclically formed, oxidized and
349 destroyed to regenerate HOBr and Br^- and release N_2 . The participation of HOBr/OBr $^-$ in the reactions
350 of formation of bromoamines prevents it to be further oxidized to BrO_3^- (Hofmann and Andrews 2001;
351 Heeb et al. 2014). The results concerning the generation of bromate observed in this study are in good
352 agreement with the findings of Berne and coauthors (2004) who observed delays in substantial bromate
353 generation that increased with the ratio between AN and bromide. Even in that case a residual presence
354 of AN in the solution inhibited the generation of bromate.

355 However, notwithstanding the well-known role of AN in the suppression of bromate generation, small
356 amounts of bromate have however been observed. This evidence suggests that radicals like CO_3^\bullet or
357 HCO_3^\bullet (coming from the bicarbonate introduced as a buffering agent) could be involved in the process
358 of generation of bromate and their effect should be more in-depth investigated (Yang et al., 2019).

359

360 **3.5 Interference of the presence of organic substances in AN depletion and nitrate generation**

361 As demonstrated in the previous sections, the bromide-enhanced ozonation process, if well regulated for
362 what concerns the initial pH value and the presence of buffer substances, could efficiently deplete AN

363 by keeping low the generation of nitrate. Moreover, the cyclical process of generation and destruction of
364 bromoamines, that involves HOBr/OBr⁻ species, prevents the further oxidation of such species to
365 bromate. However, the extension of the applicability of the enhanced ozonation process to systems that
366 contain substances different from the sole AN, for example organic compounds, requires a more in-depth
367 comprehension of the interferences that can occur.

368 To obtain some preliminary insights into the possible interference due to the presence of organic matter
369 in the process of oxidation of AN with ozone and bromide, tests were performed in the condition of
370 maximization of the amount of dissolved bromide ($[Br^-]/[O_3] > 12$). In this way, all the ozone species
371 (ozone and hydroxyl radicals) should have reacted with bromide to form “active bromine” and none (or
372 traces) of free oxidant (O₃ or HO^{*}) was available.

373 Figure 6 shows some preliminary results that concern the effect of the presence of organic substances in
374 the removal of AN in a bromide-enhanced ozonation process. It can be observed that, after 30 minutes,
375 the oxidant had consumed approximately 60% of the starting amount of AN in the system that did not
376 contain any organic substance. From Figure 6 it can be seen that glucose and KPH did not affect the
377 removal rate of AN, in fact the concentration of AN after a 30-min oxidation, in the systems that
378 contained the one or the other of these two substances, was of the same order of the AN concentration
379 found in the absence of organic substance. Conversely, the presence of hydroquinone and phenol slowed
380 down the AN removal. In fact, the residual amount of AN was of 60.1% (+50.2%, with respect to the
381 system containing the sole AN) and 63.6% (+58.8%) of the initial concentration for the systems that
382 contained hydroquinone and phenol, respectively.

383 The competition between the phenolic compounds and AN in the oxidation process takes probably place
384 in the very first stages of the process. It is well known that during oxidative processes (e.g., application
385 of ozone), the phenolic functional groups found in NOM are the main sink for the added oxidants, being
386 susceptible to chemical modifications during exposure to oxidants (Onnby et al., 2018). The apparent
387 second order rate constants for the reaction between phenol and ozone varies from 10³ to 10⁸ M⁻¹s⁻¹, in
388 the presence of pH values from pH 2 to 9 (Deborde and von Gunten, 2008). In the field of neutrality,
389 where the tests of the present study were carried out, the constant is in the order of 10⁶ M⁻¹ s⁻¹ and differs
390 for some orders of magnitude from that of the reaction between ozone and bromide (1.60 – 2.58·10² M⁻¹
391 s⁻¹, Liu et al., 2018). Phenol and compounds containing phenolic groups, like hydroquinone, are also
392 involved in reactions with HOBr and inorganic bromoamines. Recent studies demonstrated that HOBr
393 and bromoamines are highly reactive towards compounds containing phenolic groups. Apparent second-
394 order rate constant at pH = 7 in the order of 6.5·10⁴ M⁻¹ s⁻¹, 2.1·10² M⁻¹ s⁻¹ and 2.3·10¹ M⁻¹ s⁻¹ and were

395 measured for HOBr, monobromoamine and dibromoamine respectively (Criquet et al., 2015; Heeb et al.,
396 2017).

397 As shown in Table 2 the compresence of AN and an organic substance decreased the nitrate production
398 by approximately 30%. The presence of KHP or glucose seemed not to affect the generation of bromate
399 that was maintained on yield values in the order of 0.04-0.07%. Conversely, the addition of substances
400 such as phenol and hydroquinone determined a bromate generation of an order of magnitude higher than
401 that observed with KHP and glucose. Results obtained in previous works (Chon et al., 2015; Li et al.,
402 2017; Wu et al., 2018) proved that, at bromide concentrations in the order of few hundreds of micrograms
403 per liter, reactions between the most reactive parts of NOM and ozone/HO* limited bromate formation.
404 Conversely, the results found in this study demonstrate that, at high bromide concentration values, ready-
405 degradable substances like phenolic compounds were not only unable to suppress the generation of
406 bromate but seemed to be a cause for an enhanced generation. However, the series of mechanisms
407 responsible for this enhanced bromate generation deserves a more detailed investigation and has still to
408 be elucidated.

409

410 Table 2. Nitrate and bromate generation in systems containing ammonia (5 mM) and an organic substance
411 (0.05 mM)

	Ammonia only	KHP	glucose	phenol	hydroquinone
NO ₃ ⁻ /theor NO ₃ ⁻ (%)	8.65±0.33	6.00±0.37	6.17±0.14	6.07±0.53	5.73±0.65
Variation (%)	-	- 30.6	- 28.7	- 29.8	- 33.8
BrO ₃ ⁻ (mg/l)	0.298	0.179	0.238	3.28	1.66
BrO ₃ ⁻ molar yield (%)	0.070	0.042	0.056	0.77	0.39

412

413 **Conclusions**

414 This study demonstrated that a bromide-enhanced ozonation process could effectively remove AN and
415 minimize the generation of nitrate when all the ozone species reacted with bromide to form active
416 bromine (HOBr). With the set-up and oxygen flow (200 ml/min) employed in this study, the condition
417 of limiting ozone was realized for [Br⁻]/[O₃] ratios in the order of 12 or more. The generation of nitrate
418 could decrease to 10% or less of the theoretical generation value.

419 The pH value played a key role in the process for two main reasons. On the one hand, it affected the
420 equilibrium between ammonium ion and ammonia (NH₃ + H⁺ ↔ NH₄⁺). It was observed that, in the pH
421 range where ammonia is the predominant form, the reaction of direct oxidation of ammonia, with

422 generation of nitrate, competed with the reaction that generated bromoamines and ends with the liberation
423 of nitrogen gas. On the other hand, the oxidation of AN determined the release of H⁺ ions and a
424 consequent acidification of the solution. pH values below 5.0 resulted in a significant slowdown of the
425 reaction rate of AN oxidation and in an uncontrolled generation of nitrate. In order to avoid these
426 undesired effects, the addition of a buffering substance such as NaHCO₃ is compulsory. The
427 recommended ratio between HCO₃⁻/NH₄⁺ (by weight, g/g) is equal to 5.

428 The presence of AN inhibited the oxidation of bromide to bromate thanks to the generation of inorganic
429 bromoamines. The generation of bromate was limited to values of less than 0.2% of molar bromate yield.
430 However, even when a residual concentration of AN was present, secondary reaction pathways that lead
431 to the generation of bromate could not completely be excluded.

432 Organic substances in the form of KHP or glucose did not affect the removal rate of AN. Conversely, the
433 addition of substances such as phenol and hydroquinone, that have a higher reactivity towards ozone and
434 HOBr, determined a reduced AN removal rate and a bromate generation of one order of magnitude higher
435 than that observed with KHP and glucose. All the organic substances employed in this study seemed to
436 deplete the nitrate generation (-30% of the value obtained with sole AN). However, the role of organic
437 substances in nitrate and bromate generation was not completely elucidated yet.

438

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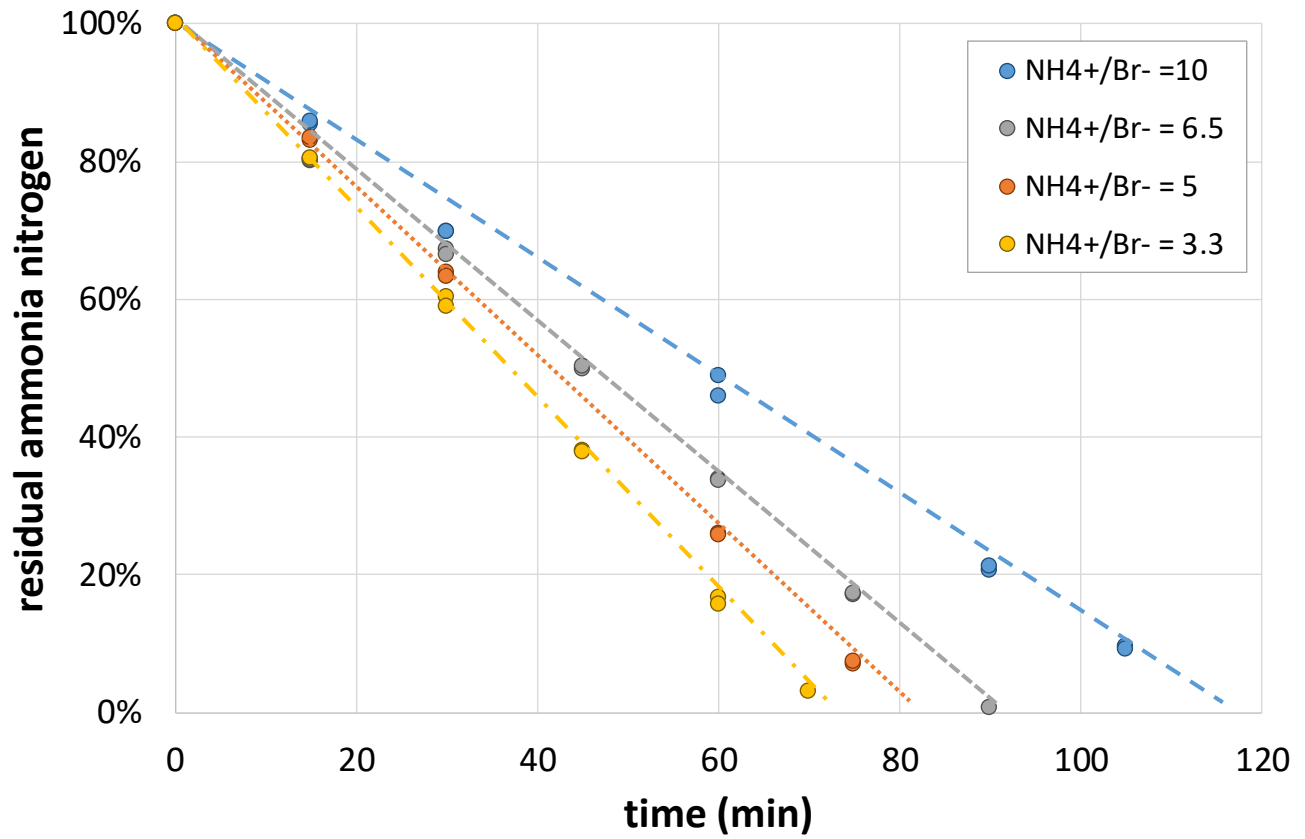
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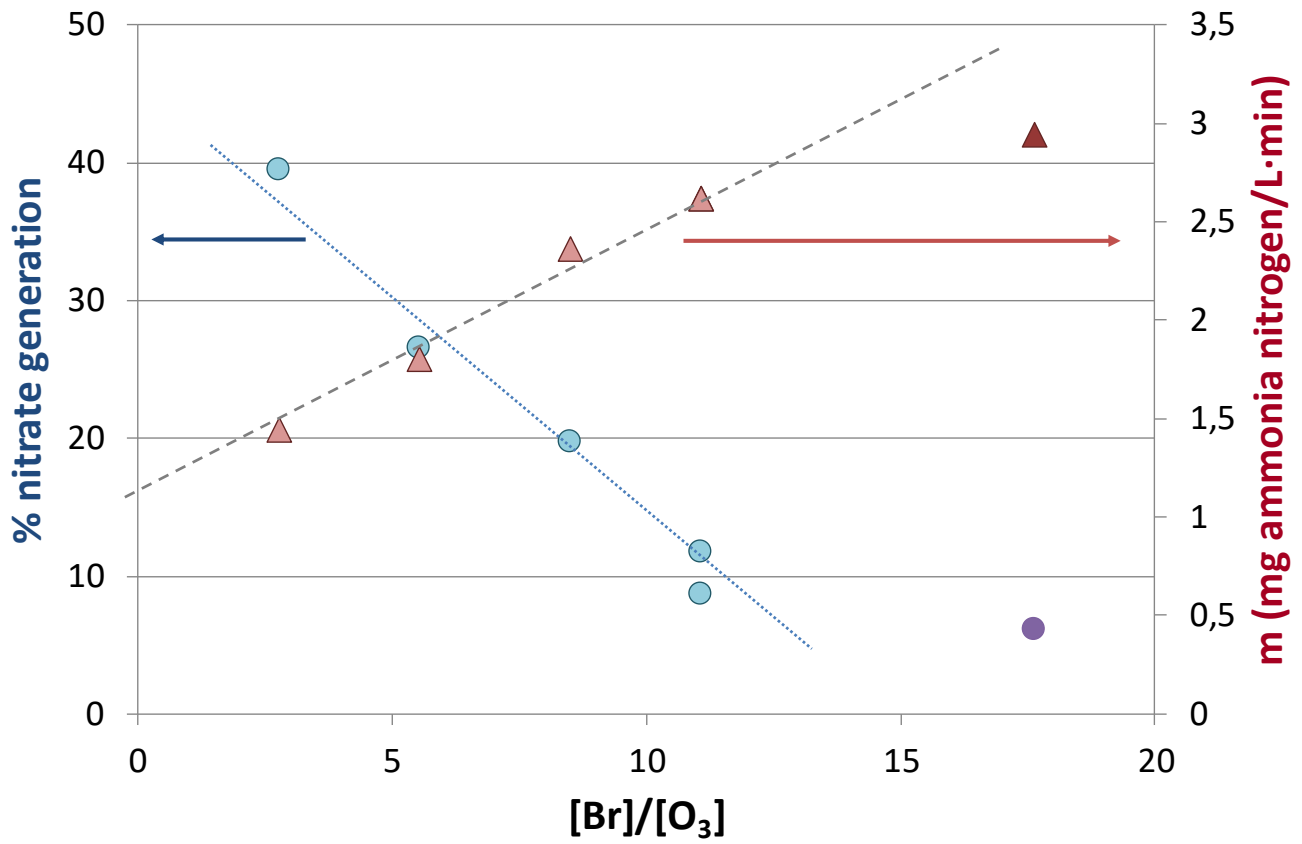


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Figure 1. Trend of AN depletion in time, $[\text{Br}^-/\text{O}_3] = 5.54; 8.51; 11.1$ and 16.6 mM/mM (test I)

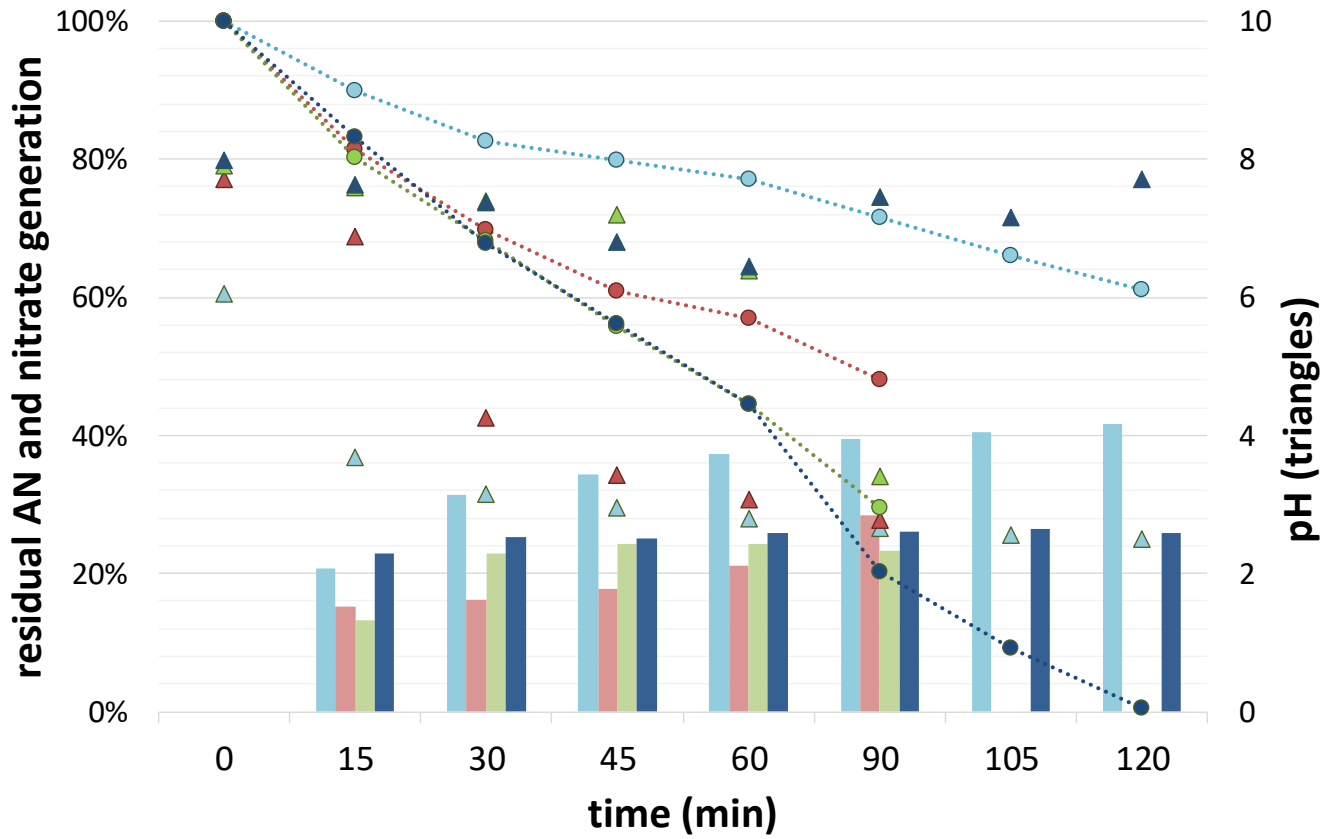
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568 Figure 2. Effect of the [Br-/O₃] ratio on AN removal rate (m, see Equation 2) and nitrate generation
569 (test I)

570



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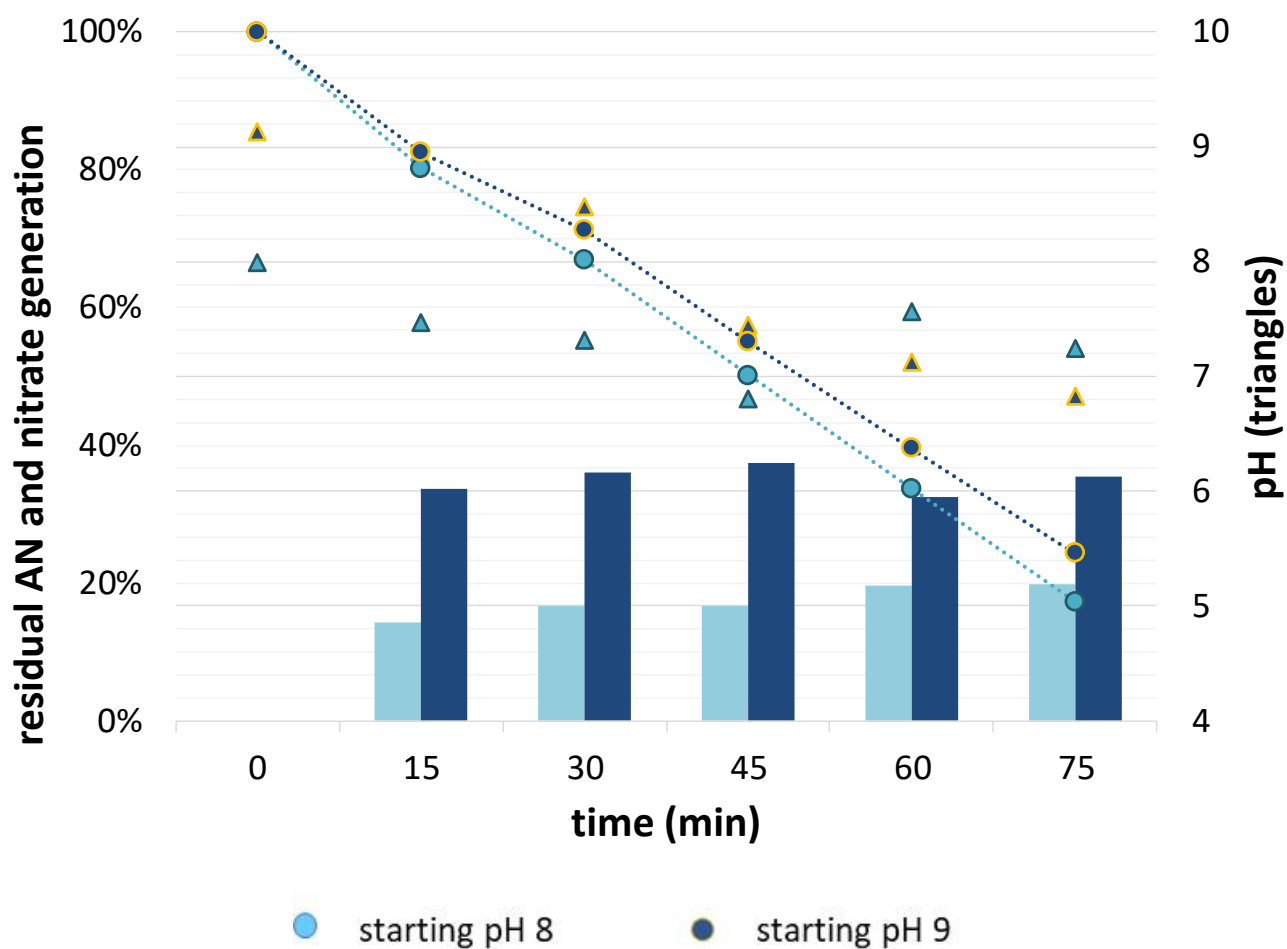
● 0 mg HCO₃⁻/l ● 200 mg HCO₃⁻/l ● 500 mg HCO₃⁻/l ● 500+500 mg HCO₃⁻/l

573

574

575 Figure 3. Effect of NaHCO₃ doses (0; 200; 500; 500+500 mg/L) on the progress of AN oxidation (dots
576 and dotted line), nitrate generation (bars) and pH (triangles) after ozonation. Test conditions: [NH₄⁺]
577 = 11.1 mM; [Br⁻] = 1.11 mM; [NH₄⁺]/[Br⁻] = 10.0, test II.

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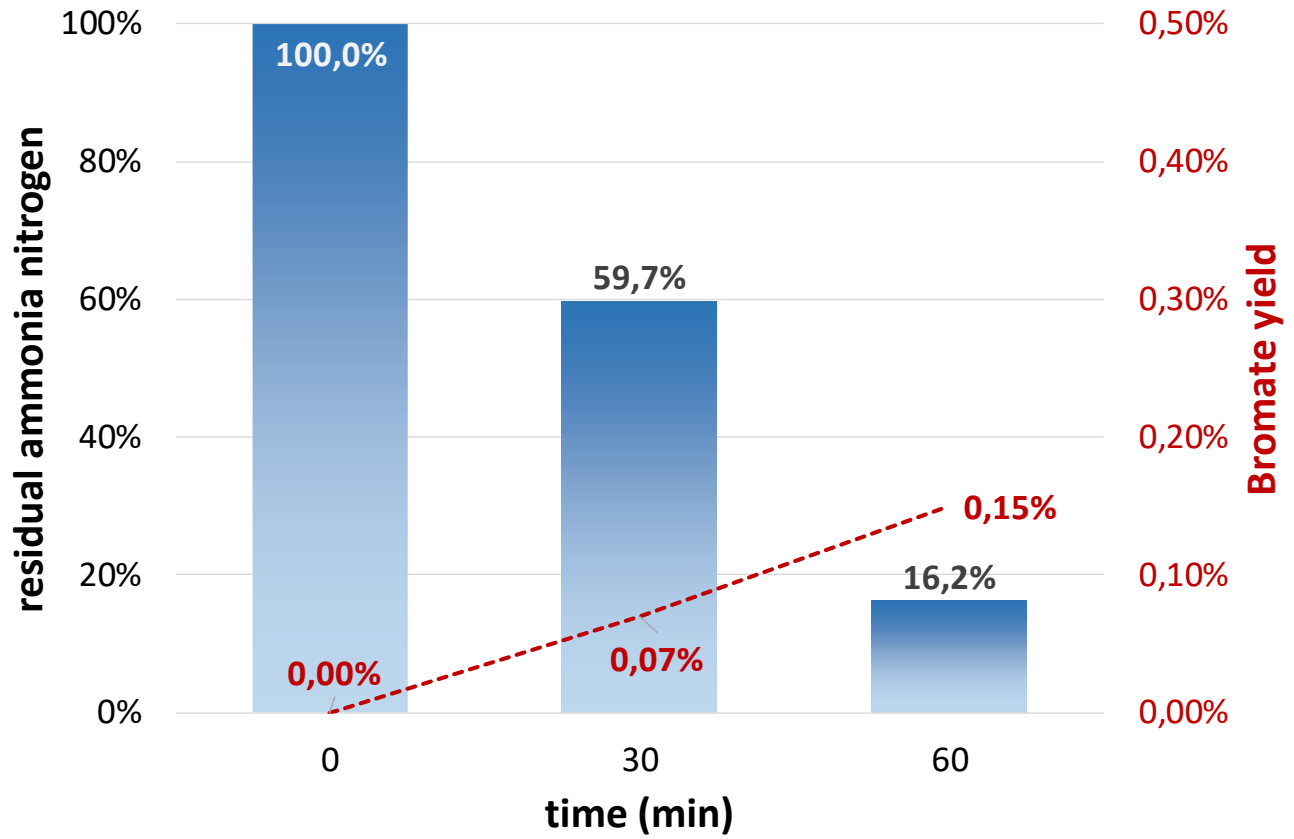


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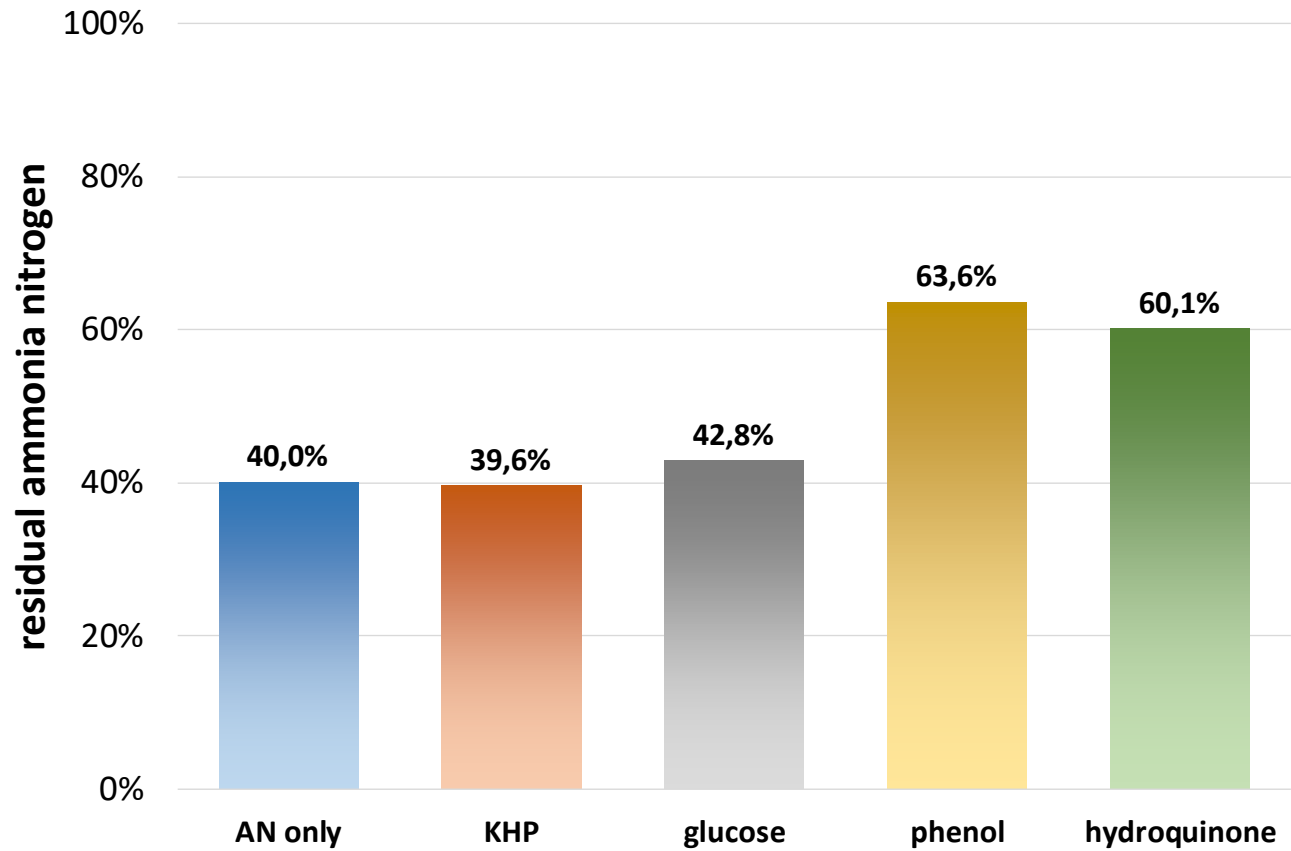
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582 Figure 4. Effect of the starting pH (8; 9) on the progress of AN oxidation (dots and dotted line), nitrate
583 generation (bars) and pH (triangles) after ozonation. Test conditions: $[\text{NH}_4^+] = 11.1 \text{ mM}$; $[\text{HCO}_3^-] =$
584 16.4 mM ; $[\text{Br}^-] = 1.70 \text{ mM}$; $[\text{NH}_4^+]/[\text{Br}^-] = 6.51$, test III.



585

586 Figure 5. Trend of residual ammonia nitrogen and bromate yield ($[\text{NH}_4^+] = 11.1 \text{ mM}$; $[\text{HCO}_3^-] = 16.4$
 587 mM ; $[\text{Br}^-] = 3.33 \text{ mM}$)



588

589

590 Figure 6. Residual ammonia nitrogen after a 30-minute ozonation in the presence of organic substances
591 (test IV)