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Experimental study on the abatement of ammonia and organic carbon with ozone

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ABSTRACT

Ammonia and organic carbon are commonly widespread substances both in municipal and in industrial wastewaters and are usually treated having recourse to biological processes. This work presents some preliminary results useful for the design of an oxidation treatment using ozone which has effect on both ammonia and organic carbon. In the first part of the paper the oxidation of relatively low concentrations of ammonia (20 mg/l) by means of ozone and halides (chloride, bromide) was investigated with the aid of on-purpose made solutions. The experimental findings pointed out that the reaction rate of an oxidation process involving ammonia and ozone (or ozone and halides) is different from a zero-order kinetics and is affected by the presence of free OH^- ions. In fact high pH values promote both the ozone (O_3) decomposition in $HO^\bullet$ radicals and the displacement of the ammonia equilibrium (NH_3/NH_4^+) toward NH_3. Chloride was found to have no effect on the ammonia oxidation, on the other hand, the joined effect of ozone and bromide results in a more effective and faster reaction, which generates lower amounts of nitrate in comparison with the oxidation due to the only ozone and/or $HO^\bullet$ radicals. In the second part of the work the oxidation of organic carbon (as potassium hydrogen phthalate) with ozone or bromide/ozone was investigated. In the process of the ozonation of organic carbon, bromide has no effect on the reaction rate, but it seems to slow down the process because of the competition between the oxidation of the potassium hydrogen phthalate and the formation of HOBr. The obtained results show that the oxidation stops when the residual concentration of organic carbon reaches a value equal to about 50% of the initial value.

Keywords: Ozone; Ammonia; Organic carbon; pH; Chemical equilibrium; Wastewater

1. Introduction

Organic and nitrogen-containing organic compounds are a large class of aqueous pollutants that are found in both surface waters and wastewaters. Their oxidation by ozone has been applied in several fields and for several purposes over the last few decades [1–3].

Focusing the attention on the simplest nitrogen-containing compound, the process of ammonia (NH_3/NH_4^+) oxidation with ozone and their rate constants are well-known since the mid-Seventies [4]. In the ozonation process, ammonia may be oxidized by both dissolved, non-dissociated ozone (O_3) and $HO^\bullet$ radicals (see Eqs. (1,2), Table 1), the major secondary oxidant coming from the ozone decomposition. The stability of ozone and its decomposition in $HO^\bullet$ radicals largely

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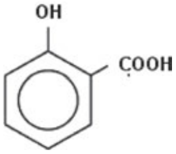
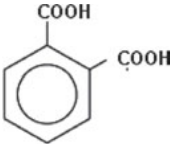
Table 1
Reactions and rate constants for processes occurring in ozonation

Eq.		k or pK_a (20°C)	Ref.
1	$NH_3 + 4O_3 \rightarrow H^+ + NO_3^- + H_2O + 4O_2$	20/0 $M^{-1}s^{-1}$	[4]
2	$NH_3 + HO^\bullet \rightarrow H^+ + NO_3^- + H_2O$	9.7×10^7 $M^{-1}s^{-1}$	[3]
3	$NH_3 + H^+ \leftrightarrow NH_4^+$	9.3	[4]
4	$NH_3 + HOBr \rightarrow NH_2Br + H_2O$ (a)	8×10^7 $M^{-1}s^{-1}$	[4,7]
	$NH_2Br + HOBr \rightarrow NHBr_2 + H_2O$ (b)		
	$NHBr_2 + HOBr \rightarrow NBr_3 + H_2O$ (c)		
	$2H_2O + NHBr_2 + NBr_3 \rightarrow N_2 + 3Br^- + 3H^+ + 2HOBr$ (d)		
5	$O_3 + OH^- \rightarrow HO_2^- + O_2$	70 $M^{-1}s^{-1}$	[3,16]
6	$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet -} + O_2$	2.8×10^6 $M^{-1}s^{-1}$	[3,16]
7	$Cl^- + O_3 \rightarrow OCl^- + O_2$	10^{-4}–10^{-3} $M^{-1}s^{-1}$	[6]
8	$3O_3 + NH_2Br \rightarrow 2H^+ + NO_3^- + Br^- + 3O_2$	40 $M^{-1}s^{-1}$	[3,7]
9	$O_3 + Br^- \rightarrow OBr^- + O_2$	160 $M^{-1}s^{-1}$	[3]
10	$Br^- + HO^\bullet \rightarrow Br^\bullet + OH^-$	10^{10} $M^{-1}s^{-1}$	[3]
11	$Br^- + Br^\bullet \rightarrow HOBr$	≈ 10^7 $M^{-1}s^{-1}$	[3]
12	$H^+ + OBr^- \leftrightarrow HOBr$	8.7	[3]
13	$HCO_3^- + HO^\bullet \rightarrow HCO_3^\bullet + OH^-$	8.5 x 10^6 $M^{-1}s^{-1}$	[16]
14	$HCO_3^- + H^+ \leftrightarrow H_2CO_3$	4.5	[16]
15	 salicilic acid	2.97 (carboxylate group) – 13.4	[14]
16	 phtalic acid	2.95–5.40	[14]

depends on the chemical composition of the aqueous phase, especially its pH, the type and the content of natural organic matter and its alkalinity [2,5]. Towards the end of the Seventies, Singer and Zilli (1975) and Hoigné and Barder (1978) - cited in [4] – focused their research on the effect of the non-dissociated ozone in the process of the ammonia oxidation and discovered that ammonia reacts with ozone only when is non-protonated (that is when ammonia is in the form NH_3) and NO_3- is the product. Both ammonia and nitrate are quite undesired species in the effluents and they must be removed before being discharged into receiving water bodies in order to prevent eutrophication.

As shown in Eq. 1, the reaction between ammonia and dissolved, non-dissociated ozone is very slow, with a rate constant of 20 $M^{-1}s^{-1}$ for non protonated NH_3 and an apparent rate constant of 1 $M^{-1}s^{-1}$ for the ensemble of NH_3/NH_4^+ species at pH 8 [3,6]. The apparent rate constant shows a decrease when the pH values are lower than 9.5, in accordance with the protonation of NH_3 to NH_4^+ (see Eq. 3). In fact, in the region of pH values lower than 9, a significant fraction of the ammonia nitrogen is masked as an ammonia ion (NH_4^+) because of the protonation. Hence, for pH values lower than 9, the apparent reaction rate constant for the total ammonia decreases by a factor of ten when pH is lowered by one unit. The decrease in the pH value also affects the ammonia oxidation via $HO^\bullet$ radicals. Therefore, because the process of the ammonia abatement through the oxidation with ozone is effective, it requires an elevation of the pH value and relatively high amounts of ozone [2].

In 1984 Haag and al. [4] discovered that the ammonia oxidation reported an enhancement in the presence of bromide ion, which acts as a catalyst in the depletion of ammonia. The authors suggested the ensemble of reactions as in Eq. (4), demonstrating that [4,7]:

- the ammonia oxidation process occurs via the formation of the bromoamine series;

- the reaction rate of the oxidation process with ozone and bromide is not significantly affected by the pH value of the system (that is the degree of the ammonia dissociation);
- ammonia is mainly converted to gaseous nitrogen instead of nitrate, thus allowing to employ the ozonation process in the ammonia abatement.

In recent years these observations have been successfully applied in some research concerning the treatment of spent brine, the oxidation of ammonia in exhaust process waters from thermal power plants and the oxidation of the natural organic matter, ammonia and nitrite in exhaust waters from aquaculture ponds located, in particular, in marine environments [7–12].

In a previous work [13] we studied the joined effect of ozone and bromide (the latter in a range of concentrations from 20 to 100 mg Br/l) on the abatement of ammonia amounts equal to about 40–50 mg/l. We demonstrated that the ammonia oxidation occurs according to a zero-order kinetics and we showed that a linear trend between the residual concentration of ammonia and the contact time is possible from the beginning of the process until the complete consume of the alkalinity content is achieved.

In the first part of the present work, some experimental tests were carried out on on-purpose made solutions containing ammonia (20 mg/l) and bromide (0–20 mg/l). The afore-mentioned tests were aimed to investigate the behavior of such systems and to understand the influence of the free OH^- and bicarbonate species on the ammonia oxidation rate. In fact, in the investigated systems, the alkalinity content is due not only to the presence of bicarbonate, but also to an amount of OH^- ions in excess with respect to the condition of neutrality (pH = 7). Some tests were also carried out in order to evaluate if the chloride ion is able to improve the reaction rate of the ammonia oxidation.

In the second part of the work, the effect of ozone (or ozone plus bromide) on the depletion of the organic carbon (as potassium hydrogen phthalate, $H_5C_8O_4K$) was investigated. The reaction rate constants of ozone with some groups of organic substances (e.g., carboxylic acids and phenols) were evaluated by Hoigné and Barder in 1983 [14]. Hoigné and Barder found that the rate constant values depend on the kind of chemical group attached to the molecule and the degree of dissociation of the dissolved substances. In particular, the second-order rate constants for carboxylic acids and for phenolic compounds increase with pH as does the degree of deprotonation of the dissolved substances, that is from 1 to 100 $M^{-1}s^{-1}$ for formic acid, from 0.2 to 2 $M^{-1}s^{-1}$ for glyoxalic acid and from 10^3 to 10^9 $M^{-1}s^{-1}$ for some phenolic compounds [14].

2. Materials and methods

2.1. Experimental set up and operative conditions

The ozone flow was produced from oxygen gas (99.95% v/v) in an ozonator Ozone Lab TM (Ozone Services division of Yanco Industries, Canada), see Fig 1. All tests were performed 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 oxygen flow, entering the ozonator, equal to 200 ml/min and a room temperature value equal to 22 ± 2°C. The reactor was dipped in a thermostatic bath (settled on 15°C) for the entire duration of the test, because the in-water ozone concentration is strongly dependent on the temperature value.

2.2. Batch tests

All tests were carried out on 250 ml ON-PURPOSE MADE solutions. In all the experiences the in-water ozone concentration was equal to 16 mg/l.

The effect of the ozone as the only oxidation agent and the combination of ozone + halides (chloride and bromide) on the oxidation of ammonia and the depletion of bicarbonate was evaluated using four sets of batch tests (see Table 2). The first set of tests was employed to investigate the effect of ozone as the only oxidant agent in the ammonia oxidation process. The second, third and fourth set of tests were used to investigate the combined effect of ozone and halides (chloride and bromide) on the ammonia abatement.

ON-PURPOSE MADE solutions were obtained by dissolving weighted amounts of salt in deionized water.

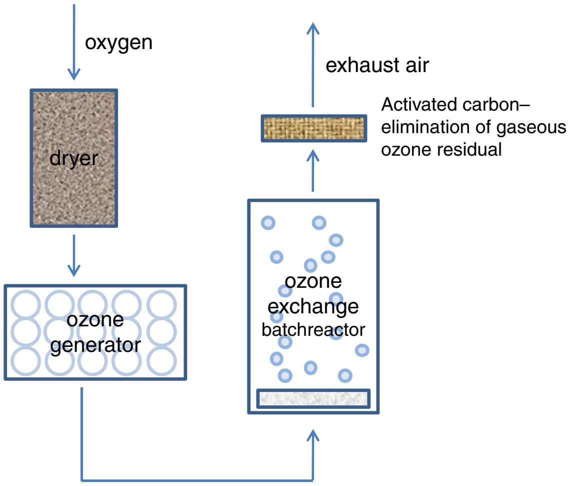


Fig. 1. Experimental set-up.

Table 2
Initial concentrations for the solutions employed in the ammonia abatement tests

Series	Name	Ammonia (mg/l)	Bicarbonate (mg/l)	Bromide (mg/l)	Chloride (mg/l)	Contact time (min)
First	A	20	200	0	0	0–30
Second	B	20	200	10	0	0–30
Third	C	20	200	20	0	0–30
Fourth	D	20	200	0	500*	0–30

*Over the chloride amount added as NH_4Cl.

Ammonia was introduced in the systems as NH_4Cl (ammonium chloride, puriss. p.a., ACS reagent, ≥99.5% (AT), Fluka), bicarbonate as $NaHCO_3$ (sodium bicarbonate, puriss. p.a., ACS reagent, reag. Ph.Eur., ≥99.7%, powder, Sigma Aldrich), bromide as KBr (potassium bromide, puriss. p.a., ACS reagent, ≥99.5% (AT), Sigma Aldrich) and chloride as NaCl (sodium chloride, puriss. p.a., ACS reagent, ≥99.5% (AT), Sigma Aldrich).

Weighted amounts of 1N NaOH solution (Sigma-Aldrich) were added in order to shift the system from the condition of neutrality and study the effect of OH^- on the ammonia depletion in an ozonation process.

The depletion rate of the organic carbon was evaluated taking advantage of five further series of batch tests (see Table 3). The organic carbon was introduced in the ON-PURPOSE MADE solutions as $H_5C_8O_4K$, (potassium phthalate monobasic, puriss. p.a., ≥99.5% (T), Sigma Aldrich), bicarbonate as $NaHCO_3$ (sodium bicarbonate, puriss. p.a., ACS reagent, reag. Ph. Eur., ≥99.7%, powder, Sigma Aldrich), bromide as KBr (potassium bromide, puriss. p.a., ACS reagent, ≥99.5% (AT), Sigma Aldrich).

2.3. Analytical methods

All the employed reagents were ACS grade (i.e., that fulfill the American Chemical Society requirements concerning product quality) and the flasks and the glassware were class A. All parameters (with the exception of pH value) were measured 24 h after the end of the ozonation. The pH value was measured using an Orion 420 pH-meter both at the end of the ozonation and 24 h later.

Ammonia was detected as blue indophenol by means of a VIS-UV spectrophotometer (690 nm).

Nitrate was made to react with 2,6 dimetilphenol, in the presence of a mixture of sulfuric and phosphoric acids, thus allowing its determination through a spectrophotometric method (385 nm).

Alkalinity (as the concentration of $CaCO_3$ equivalent) was measured by titration with a standard HCl solution (0.05 N) to a bicarbonate equivalent endpoint (pH 4.5) using an Orion 420 pH-meter. TOC was measured by high-temperature combustion analysis (TCM 480, Fisons Instruments). The ozone concentration in the water phase was determined by the indigo trisulfonate method [15].

3. Results and discussion

In Fig. 2a the trend of the residual concentration of ammonia vs. contact time for the solutions A, B, C and D is shown. In the systems examined, ammonia disappeared progressively as the contact time increased. In particular, the reaction rate of the ammonia disappearance rose as the concentration of bromide increased. On the other hand (see system D), the introduction of an excess of chloride (500 mg/l more than the amount brought about by the ammonia chloride) did not seem to affect the ammonia disappearance rate, in fact the systems A and D showed an identical trend.

Table 3
Initial concentrations for the solutions employed in the organic carbon oxidation tests

Series	Name	Organic carbon (mg/l)	Bicarbonate (mg/l)	Bromide (mg/l)	Chloride (mg/l)	Contact time (min)
First	E	100	0	0	0	0–45
Second	F	100	200	0	0	0–90
Third	G	100	200	50	0	0–45
Fourth	H	50	200	0	0	0–90
Fifth	I	25	200	0	0	0–90

In a previous work [13] which involved some artificial systems with the same characteristics of those involved in the present experimentation (that is containing ammonia and bicarbonate or ammonia, bicarbonate and bromide), we demonstrated that the ammonia disappearance followed a zero-order kinetics. That trend could be observed from the beginning of the oxidation process until the complete depletion of the bicarbonate. On the contrary, in this work the ammonia oxidation rate did not follow a zero-order kinetics, in fact the oxidation rate was faster over the first fifteen minutes and slowed down during the last part of the process. In particular, for the system A the N-ammonia zero-order oxidation rate over the first fifteen minutes was equal to 1.98×10^{-4} $mM^{-1}s^{-1}$ (0.2144 mg ammonia l^{-1} min^{-1}), it lowered to 1.32×10^{-4} $mM^{-1}s^{-1}$ (0.1428 mg ammonia l^{-1} min^{-1}) during the second fifteen minutes and, eventually, it reached the rate of 0.888×10^{-4} $mM^{-1}s^{-1}$ (0.0960 mg ammonia l^{-1} min^{-1}) over the third fifteen minutes. This outcome could be due to the initial excess of OH^- ions. In the case of the presented experimentation, all the systems involved had an initial amount of OH^- ions (coming from a NaOH addition) in excess with respect to the condition of neutrality (pH = 7). This excess of OH^- ions affected the initial pH and alkalinity values of the system. In fact all the systems considered (A, B, C and D) had an initial pH value equal to about 8.10 and an alkalinity content ranging from 180 to 185 mg $CaCO_3$ eq/l. The alkalinity value found was due to the presence of bicarbonate (200 mg/l as $NaHCO_3$, that caused an alkalinity content equal to about 165 mg $CaCO_3$ eq/l) and an excess of OH^- ions (as NaOH). High pH values (due to free OH^- ions) promote both the ozone (O_3) decomposition in $HO^\bullet$ radicals (see Eqs. (5–6)) and the displacement of the ammonia equilibrium (NH_3/NH_4^+) toward NH_3 (see Eq. (3)). When the pH value of the system is almost equal (or slightly lower) to the ammonia basic dissociation constant (9.3), the increase of one unit in the pH value increases by a factor of ten the apparent reaction-rate constant for ammonia [2].

Using a mass balance carried out on the nitrogen forms present in the system without bromide (A) at the beginning of the tests (ammonia) and at the end of the process (ammonia and nitrate), the amount of nitrogen removed by stripping can be evaluated. These amounts were about 0.125 mg (in the volume of the ozonized water, 250 ml) for the first fifteen minutes and about 0.062 mg (in the volume of the ozonized water) for the next fifteen minutes.

As for the results of the second (B) and third (C) sets of tests, which were aimed to evaluate the combined effect of ozone and bromide (at the concentration values of 10 mg/l and 20 mg/l) in the ammonia oxidation process, they showed that, over the first ten minutes, the rate of the ammonia disappearance was faster than described by the zero-order law (see the points 5 min and 10 min for the systems B and C, Fig. 2a). This was probably due because, in the range of the pH values (7.0–8.0) in which the ozonation was carried out (see Fig 2c), the effect of the radical $HO^\bullet$ on the ammonia oxidation (see Eq. (2)) was still noticeable, if compared to that of HOBr (see Eq. (4a)). It has also to be taken into account that, in the same pH range, the oxidation of the ammonia due to

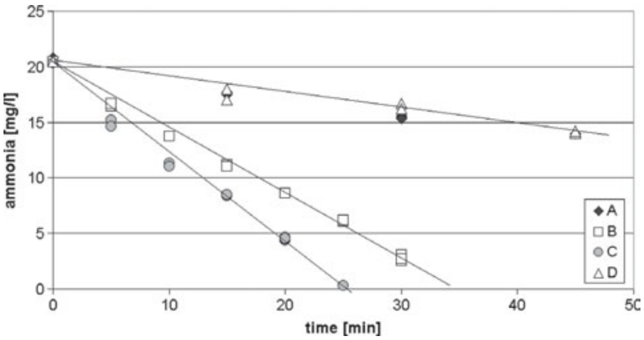


Fig. 2a. Residual value of ammonia vs. contact time for the systems A, B, C and D.

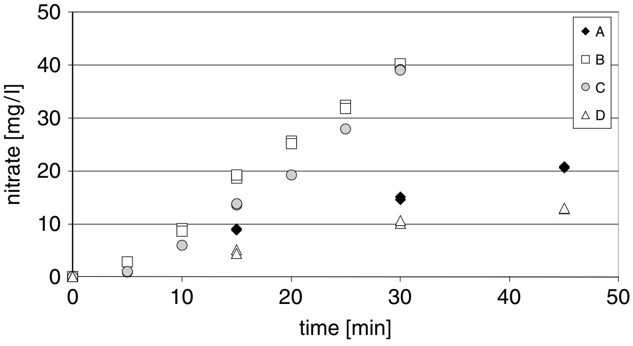


Fig. 2b. Generated nitrate vs. contact time for the systems A, B, C and D.

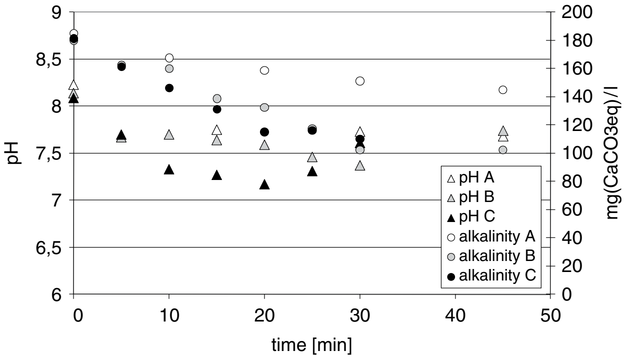


Fig. 2c. pH value and alkalinity content vs. contact time for the systems A, B and C.

the O_3 species is negligible (see Eq. (1)), second-order rate constant $k < 20\ M^{-1}s^{-1}$). The concentrations of bromide (10–20 mg/l) here employed were lower than those used in our previous work [13] and the results obtained seemed to confirm that the pH value affected both the dissociation of ozone in $HO^{\bullet}$ radicals and the protonation of the ammonia, thus enhancing the ammonia oxidation.

The results of the fourth series of tests were in line with the findings obtained by Tanaka and Matsumura [7]. The observed trend for the systems A and D showed that the decrease in the ammonia concentration did not change in the presence of chloride. This is because chloride consumes ozone (see Eq. (7)) at a constant rate ranging from $10^{-4}\ M^{-1}s^{-1}$ to $10^{-3}\ M^{-1}s^{-1}$, depending on the temperature and pH values of the system [6]. This is followed by a rapid protonation to HOCl and conversion to Cl_2. The reaction of ozone with Cl^- is an extremely slow process even in highly saline waters where the molar ratio of Cl^-/Br^- is generally about 500 [6,7].

Fig. 2b shows the trend of the nitrate generated in the oxidation process vs. contact time. Nitrate is the product of the direct oxidation of ammonia with ozone, as shown in Eq. (1). The systems A and D showed a nearly linear trend for the concentration of generated nitrate. On the other hand, the systems B and C, in which the ammonia oxidation process was stronger, showed a delay in the nitrate generation, but the more effective the process of direct oxidation, the higher the concentration of nitrate. Considering an identical amount of oxidized ammonia, the concentration of generated nitrate was lower where the oxidation is caused by HOBr, which converts ammonia to bromoamines and, then, to nitrogen gas (see Eq. (4)). The delay in the nitrate generation for the systems B and C could be due to the high reaction rate of the process responsible for the generation of the first bromoamine (see Eq. (4a)) compared to the reaction rate of the pathway responsible for the generation of nitrate from bromoamines (see Eq. (9)). The most important feature of the scheme shown in Eq. (4) was that the first step is rapid if compared to the last, and, therefore, NH_2Br was rapidly regenerated after it was destroyed by the reaction which also regenerated Br^-. Thus, nearly all of the total bromide present existed as NH_2Br (plus some $NHBr_2$) and the concentration of NH_2Br remained constant. This led to the formulation of a zero-order kinetics with respect to the ammonia concentration when O_3 concentration was maintained constant and when the direct reaction of NH_3 with ozone (or $HO^{\bullet}$ radicals) could be neglected [4].

Fig. 2c shows the trend of pH value and alkalinity vs. contact time for the systems A, B and C; pH and alkalinity values of the system D were quite similar to those of the system A. All the systems considered showed a decrease in the pH value linked to an increase in the contact time. The pH value showed an increase since the moment ammonia completely depleted on. The alkalinity content decreased as the time elapsed reaching a nearly constant value when the complete depletion of the ammonia took place. The pH values of the systems involving the oxidation of the ammonia in the presence of bromide was affected by two mechanisms. The first mechanism was responsible for an increase in the pH value, due to HOBr formation via $HO^{\bullet}$ radicals (see Eqs. (9–12)). The second mechanism was responsible for a decrease in the pH value, due to the oxidation of ammonia and intermediate bromoamines (see Eqs. (1, 4 and 8)).

The pH value measured at the end of the ozonation process was the result of these two opposite phenomena. The natural tendency of the pH value to increase, noticed in the presence of bromide, was inhibited by the release of H^+ ions into the system because of the progressive abatement of ammonia. A too fast decrease in the pH value was prevented by the reaction of H^+ with bicarbonate; in fact most of the H^+ ions from the ammonia oxidation were neutralized by the bicarbonate and, as shown in Fig. 2c, the mild decrease in the pH value was coupled with a stronger alkalinity disappearance.

Fig. 3a shows the trend of the residual concentration of organic carbon vs. contact time for the systems E, F, and G. It could be seen that the disappearance of organic carbon vs. time was more noticeable for the systems E and F than for the system G. Moreover, the disappearance kinetics of the organic carbon in the first thirty minutes for the system E was faster than for the systems F and G, but for contact times higher than thirty minutes, the organic carbon oxidation rate for the system E slowed down with respect to the oxidation rate for the system F (see Table 4).

Table 4
Zero-order rate constants and % depletion for the organic carbon in the systems E, F and G

System	0–15 min kinetic rate $mM^{-1}s^{-1}$	15–30 min kinetic rate $mM^{-1}s^{-1}$	30–45 min kinetic rate $mM^{-1}s^{-1}$	0–15 min % depletion	0–30 min % depletion	0–45 min % depletion
E	3.05×10^{-3}	1.39×10^{-3}	0.480×10^{-3}	30	43	48
F	2.28×10^{-3}	1.77×10^{-3}	1.20×10^{-3}	23	41	52
G	0.791×10^{-3}	0.804×10^{-3}	0.984×10^{-3}	8	16	26

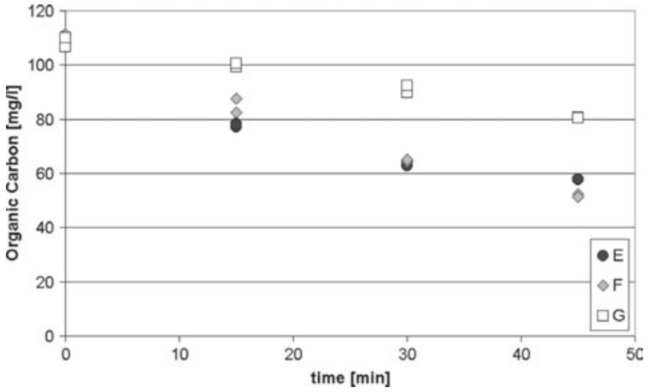


Fig. 3a. Residual organic carbon vs. contact time for the systems E, F and G.

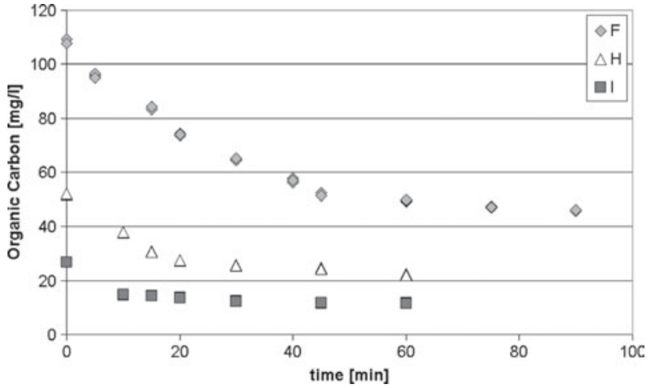


Fig. 3b. Residual organic carbon vs. contact time for the systems F, H and I.

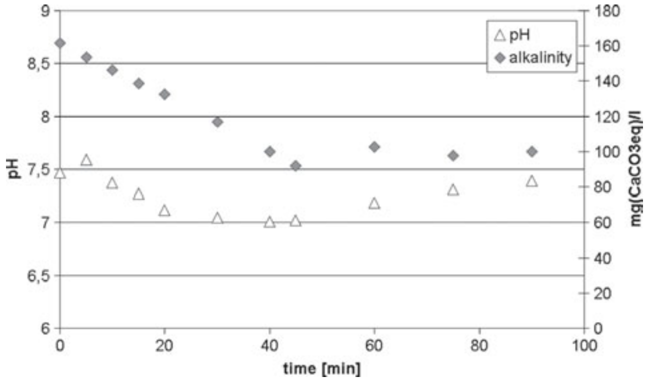


Fig. 3c. pH value and alkalinity content vs. contact time for the system F.

The oxidation rate in the systems E and F, where the phthalate consumption was more evident, changed with the contact time. For low contact times (lower than 30 min), the oxidation of the organic carbon was more effective in the system E, composed only by distilled water and potassium hydrogen phthalate, than in the system F. The better performance of the system E over the first fifteen minutes was explained because of the absence of bicarbonate. Being no scavenger effect against the $HO^{\bullet}$ species (see Eq. (13)), phthalate could be oxidized by $HO^{\bullet}$ radicals. For higher contact times (more than 30 min) the afore described trend reversed: the oxidation of organic carbon for the system F (made of distilled water, potassium hydrogen phthalate and bicarbonate) was more efficient than for the system with only distilled water and potassium hydrogen phthalate (E). In fact the oxidation of phthalate released H^+ ions into the system thus causing the displacement of the chemical equilibria. In the system E the release of H^+ ions was not buffered and, according to the results found by Hoigné and Barder (see Fig. 4) for some phenolic compounds, the non-dissociated species were more resistant to the ozonation than the dissociated ones [14]. Among the compounds examined in [14], salicylic acid was the most similar to potassium hydrogen phthalate. The diagram given in Fig. 4 shows that, on the one hand, the aromatic ring of the salicilate ion, in comparison with other substances belonging to the phenolic compounds, seemed to be somewhat activated for reactions with ozone because of the presence of the carboxylate group. On the other hand, the rate constant for salicylic acid increased with pH up to pH = 3. Above pH = 3, that corresponds to pKa value of the acid (see Eqs. (15–16)), the carboxylic group is highly dissociated. The phenolic group of the salicylic acid did not affect the value of the reaction rate constant, unless the ozonation was carried out in the presence of high pH values, far from those used in the experimental tests.

Moreover, the comparison of the results coming from the tests E, F and G and given in Fig. 3a showed that the

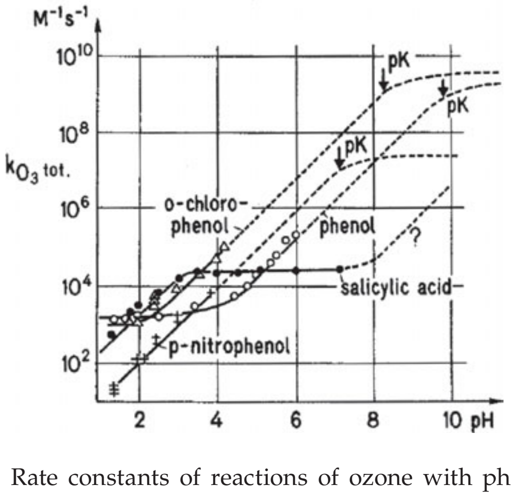


Fig. 4. Rate constants of reactions of ozone with phenolic compounds vs. pH (from [14]).

oxidation rate of the organic carbon in the presence of bromide ion (G series) was slower than in its absence and that could be due to the following reasons:

- a competition between the oxidation of potassium hydrogen phthalate and the formation of HOBr (see Eqs. (10,11));
- a possible ineffectiveness of HOBr over the phthalate oxidation.

Anyway, for contact times higher than 30 min, a remarkable slowdown in the oxidation kinetics of the organic carbon was observed. This behavior was understood employing two further series of tests (named H and I) which involved two series of systems characterized by the presence of bicarbonate (200 mg/l) and an initial phthalate concentration equal to a half (50 mg/l, H) or a quarter (25 mg/l, I) of the initial concentration tested in the series F.

Fig. 3b shows the trend of the residual concentration of organic carbon vs. contact time for the systems F, H and I. These three systems, which had different initial concentrations of organic carbon, showed a gradual reduction in the organic carbon amount and reached an asymptotic value of about 50% of the initial value. The organic carbon oxidation rate was almost identical for the three systems considered and the time required to reach the asymptotic value depended on the initial organic carbon concentration value.

Fig. 3c shows the trend of pH and alkalinity vs. contact time for the system F. The examined system showed a decrease in the pH value as the contact time increased. The pH value showed an increase when the asymptotic value of the residual organic carbon was reached. Both the alkalinity content and the organic carbon concentration decreased over time and eventually reached a nearly constant value.

The comparison of the results obtained in the three series of tests (F, H, I) highlighted that, regardless of the initial concentration, the ozonization process was able to oxidize about 50% of the initial organic carbon amount. Fig. 3b, which reports the organic carbon residual concentration vs. contact time, shows the achievement of an asymptotic value for the residual concentration. The lower the initial concentration of organic carbon, the faster was the achievement of the asymptotic value.

4. Conclusions

On the basis of the experimentation outcomes, the following remarks may be made. For the oxidation of ammonia with ozone or ozone plus bromide as oxidizing agents, the reaction rates are different from zero-order and are affected by the amount of free OH^- in the system. An excess of OH^- ions at the beginning of the process increases the reaction rates and makes them faster than described by the zero-order law. High pH values promote both ozone (O_3) decomposition in $HO^\bullet$ radicals and the displacement of ammonia equilibrium (NH_3/NH_4^+) toward NH_3.

The oxidation of ammonia in the presence of bromide is more effective, less dependent on the pH value and generates lower amounts of nitrate than in the presence of only ozone. In fact, considering an identical amount of oxidized ammonia, the amount of generated nitrate is lower where the oxidation is done by the hypobromous acid that converts ammonia to bromoamines and, eventually, to nitrogen gas.

Chloride ion (500 mg/l more than the amount brought about by the ammonia chloride) has no effect on the ammonia disappearance probably because of the slow rate constant of the reaction between ozone and chloride.

For the oxidation of the organic carbon, bromide ion has no effect on the rate constant, but it seems to slow down the process because of the competition between the oxidation of potassium hydrogen phthalate and the formation of HOBr. The obtained results show that the organic carbon oxidation stops when the residual concentration reaches a value equal to about 50% of the initial value. This is probably due to the formation of byproducts, having different molecular arrangement compared with the parent compound, and then refractory to further oxidations.

Further tests are needed to understand the behavior of ozone toward ammonia and organic carbon, when both of them are present at the same time in a wastewater.

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References

[1] EPA Guidance Manual Alternative disinfectants and oxidants (1999).

[2] J. Hoigné, Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Processes, The Handbook of Environmental Chemistry Part C, Springer-Verlag, Berlin Heidelberg, 5 (1998) 83–141.

[3] U. von Gunten, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Wat. Res., 37(7) (2003) 1443–1467.

[4] W.R. Haag, J. Hoigné and H. Bader. Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment, Wat. Res., 18(9) (1984) 1125–1128.

[5] C. von Sonntag, The basics of oxidants in water treatment. Part A: OH radical reactions, Water Sci. Technol., 55(12) (2007) 19–23.

[6] J. Hoigné, H. Barder, W.R. Haag and J. Staehelin, Rate constants of reactions of ozone with organic and inorganic compounds in water – III Inorganic compounds and radicals, Wat. Res., 19(8) (1985) 993–1004.

[7] J. Tanaka and M. Matsumura, Applications of ozone treatment for ammonia removal in spent brine, Adv. Environ. Res., 7 (2003) 835–845.

[8] M. Yang, K. Uesugi and H. Myoga, Ammonia removal in bubble column by ozonation in the presence of bromide, Wat. Res., 33(8) (1999) 1911–1917.

[9] S.T. Summerfelt, J.A. Hankins, A.L. Weber and M.D. Durant, Ozonation of a recirculating rainbow trout culture system II – Effects of microscreen filtration and water quality, Aquaculture, 158(1–2) (1997) 57–67.

[10] V. Krumins, J. Ebeling and F. Wheaton, Part-day ozonation for nitrogen and organic carbon control in recirculating aquaculture systems, Aquacult. Eng., 24 (2001) 231–241.

[11] S.T. Summerfelt, Ozonation and UV irradiation – an introduction and examples of current applications, Aquacult. Eng., 28 (2003) 21–36.

[12] M.S. Tango and G.A. Gagnon, Impact of ozonation on water quality in marine recirculation systems, Aquacult. Eng., 29 (2003) 125–137.

[13] B. Ruffino and M.C. Zanetti, Ammonia abatement by means of ozone in a system containing bicarbonates and bromides. In: Proceedings of the IWA – World Water Congress and Exhibition (2008) 1–9, CD-Rom.

[14] J. Hoigné and H. Barder, Rate constants of reactions of ozone with organic and inorganic compounds in water – II Dissociating organic compounds, Wat. Res., 17 (1983) 185–194.

[15] H. Barder and J. Hoigné, Determination of ozone in water by the indigo method, Wat. Res., 15 (1981) 449–456.

[16] J.L. Acero and U. von Gunten, Influence of Carbonate on the Ozone/Hyrogen Peroxide Based Advanced Oxidation Process for Drinking Water Treatment, Ozone Sci. Eng., 22 (2000) 305–308.