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Free radicals formation induced by the ozonation of humic substances in aqueous medium

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Abstract

This laboratory study was designed to investigate the mechanism of the formation of the OH radicals during the ozonation of humic substances solutions. The evaluation of the formation of these radical species was performed by using 1,1,2-trichloro ethane (TCA) as a probe. The apparent removal of TCA observed during the ozonation treatment implies the production of secondary species that catalyze the generation of OH radicals from ozone. These species are formed by a reaction between H_2O_2, formed in-situ, and O_3 and by a radical mechanism involving reactive humic substances sites.

Keywords: OH radicals formation; Ozonation

1. Introduction

Surface waters contain between 2 and 10 mg l^{-1} of total organic carbon (TOC). The brownish color of the water is usually ascribed to the humic substances which are liable to obnoxious tastes and odors and to the reviving of microorganisms in the water distribution network [1].

Ozone is used in water treatment for disinfection, for decolorization and as a pretreatment process for the removal of organic matter. The ozonation of natural water containing humic substances induced a large consumption of ozone but the treatment with ozone does not remove organics to any significant extent [2].

Because of their chemical structure, humic substances reactions with ozone are mechanistically very complex. Organic compounds react with molecular ozone as well as indirectly with OH radicals generated by the decomposition of O_3 [3] [4]. The mechanism can be summarized by 4 main reactions:

$$SH_i + O_3 \rightarrow \cdots \rightarrow OH\cdot \quad (1)$$

$$SH_p + OH\cdot \rightarrow \text{products} + O_2\cdot^- \quad (2)$$

$$SH_s + OH\cdot \rightarrow \text{products} \quad (3)$$

$$SH_d + O_3 \rightarrow \text{products} + O_2 + H_2O_2 \quad (4)$$

This mechanism mainly involves initiator SH_i (reaction (1)) and promotor SH_p (reaction (2)) sites of humic substances (HS) and is affected by the presence of radical scavengers sites SH_s (reaction (3)) in the medium. In addition to these reactions, there is also the direct reaction of O_3 with organics SH_d (reaction (4)) [5].

The formation of OH radicals during the ozonation process is of greatest interest because

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these entities are extremely reactive ($k = 10^7$ to 10^{10} l mol^{-1} s^{-1}) [6]. The presence in water of organic micropollutants (pesticides, chlorinated solvents, hydrocarbons, etc.), non-reactive with molecular ozone or other chemical oxidants, can be removed by reactions involving the radical pathway. The ozonation efficiency will depend on the capability to produce radical entities during the oxidation process of water containing humic substances. The aim of this study is to investigate the different pathways of production of these radicals during ozonation of humic substances solutions. As OH radicals have a short life (about 10^{-6} s), a probe was used in order to show the formation of the radical species.

2. Experimental procedure

2.1. Preparation of the solutions

Humic substances were dissolved in ultrapure water (MilliQ, Millipore) buffered with phosphate ions (pH 7, $\mu = 5\ 10^{-3}$ mol l^{-1}). The humic substances studied are commercial humic substances from Aldrich.

2.2. Reactors

Humic substances were ozonated in a 1.8 l semi-batch reactor with ozone produced from oxygen. Ozone flux was measured at the inlet and at the outlet of the reactor with a washing vessel containing potassium iodide (20 g l^{-1}). The reactor is equipped with a valve for sampling and a stirrer.

2.3. Ozone measurement

Ozone concentration in the aqueous phase was measured by a spectrophotometric method using indigo trisulfonate [7], ozone in the gas phase was analyzed by iodometric method.

2.4. 1,1,2-trichloroethane (TCA)

TCA was extracted from 5 ml water with 3 ml pentane containing dibromomethane as internal standard. The concentration of TCA was determined by gas chromatography (Perkin Elmer, Model 9 000) using a DB5 capillary column ($l = 25$ m; $\phi = 0.25$ μm) and a ECD detector. Temperatures of oven, injector and detector were 75, 175 and 300°C, respectively.

2.5. Hydrogen peroxide

The determination of H_2O_2 concentrations was performed by a fluorometric method [8]. This method is based on the reaction between H_2O_2 and *p*-hydroxy phenylacetic acid and is catalyzed by horseradish peroxidase.

3. Results and discussion

The study of free radical formation from ozonation reactions of HS was carried out using TCA as an OH radical probe. TCA was chosen because of its reactivity with OH radicals ($k = 10^7$ l mol^{-1} s^{-1}) [6] and because it does not react with molecular ozone. However, TCA is a volatile compound and the stripping should be taken into account during the ozonation process. As OH radicals are the most reactive species among the organic and inorganic radicals formed during the ozonation of humic substances solutions, we considered only the OH radical attack in the removal of TCA.

Fig. 1a and Fig. 1b illustrate data taken during a typical ozonation experiment. Parallel to these experiments, a blank was performed in order to evaluate the stripping of the TCA during the bubbling of the gas in the solution. Different runs were carried out using the combinations: O_3/TCA; O_2/TCA/HS; O_2/TCA.

Fig. 1a shows the TCA disappearance curves versus time for these 3 runs (upper curves), the results indicate that no significant difference arises from these different experiments confirming the non-reactivity of ozone with TCA.

A positive effect in TCA removal was observed as soon as humic substances were introduced in the medium. Thus, these results indicate that the ozonation of humic substances contributed to the removal of TCA by the formation of intermediate species. As the concentration of OH radicals can not be measured directly, their formation was correlated with global parameters such as the disappearance of humic substances through the UV absorbance at 254 nm, H_2O_2 and O_3 residual concentration in the aqueous phase.

Fig. 1b shows that H_2O_2 accumulates at the beginning of the ozonation of the humic substances and reaches its maximum after 10 min. Then, H_2O_2 decreases and becomes very weak after 30 min. This time corresponds to the stabilization of the absorbance of the solution measured at 254 nm and of the concentration at the steady state of ozone in the aqueous phase.

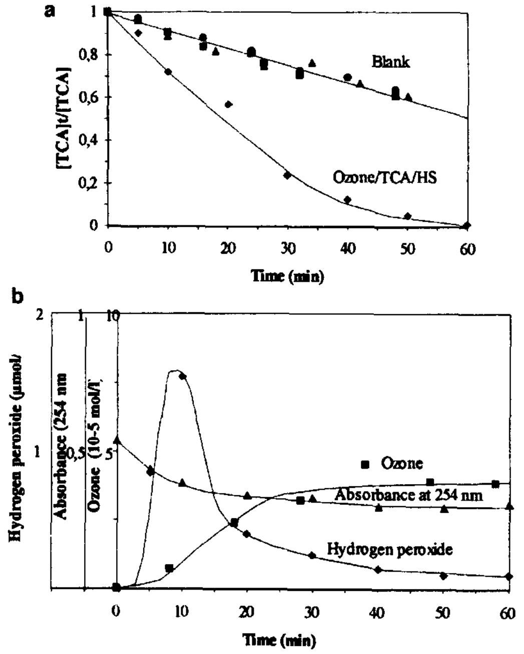

Fig. 1. (a) TCA removal during ozonation of humic substances solutions. (b) Evolution of ozone concentration in the aqueous phase, of the absorbance at 254 nm and hydrogen peroxide concentration formed in-situ ($[HS]_0 = 10$ mg l^{-1}; $[TCA]_0 = 10^{-5}$ mol l^{-1}; $Q(O_3) = 1.1 \times 10^{-4}$ mol min^{-1}).

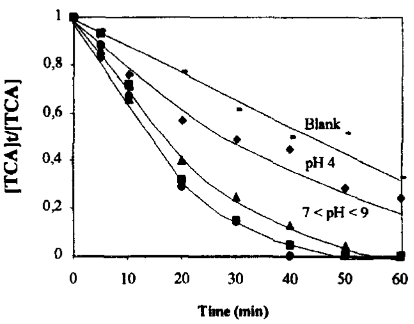

Fig. 2. Influence of pH on TCA removal ($[HS]_0 = 10$ mg l^{-1}; $[TCA]_0 = 10^{-5}$ mol l^{-1}; $Q(O_3) = 1.1 \times 10^{-4}$ mol min^{-1}).

In order to evaluate the influence of different parameters on the radical formation during the ozonation of humic substances, we studied the influence of pH, the formation of H_2O_2 and the ozonation time.

3.1. Influence of pH on the formation of radicals

The pH has a strong influence on the ozonation mechanism. At basic pH (pH > 8) hydroxide ions can:

- act as initiators of the decomposition of ozone with the production of OH radicals [9],
- increase the dissociation of H_2O_2 to its conjugate base, HO_2^- reacts with O_3 to give, via a radical mechanism, OH radicals [9],
- modify the reactivity of humic substances with ozone.

Results, shown in Fig. 2, show that the removal of TCA by ozonation of humic substances is hardly influenced by pH up to the neutrality, but strongly decreases at acidic pH (pH 4). In all these experiments the transfer of ozone is not affected by pH. The consumption of ozone by humic substances is the same at pH 4 and pH 9, the concentration in the solution at the steady state (up to 30 min ozonation) is 4 10^{-5} mol l^{-1} which is very close to the one obtained with pure water at the same pH ($[O_3] = 5.2$ 10^{-5} mol l^{-1}). On the other hand, the H_2O_2 residual concentration measured in the medium is slightly influenced by pH. The residual concentration at its maximum was 2.8 10^{-6}

mol l^{-1} at pH 9 and decreases gradually to 0.74 10^{-6} mol l^{-1} at pH 4.

The fact that H_2O_2 residual concentration at the steady state is very small (< 3 10^{-6} mol l^{-1}) explains the weak influence of pH in the basic medium. In our experiment, the production of radicals is essentially affected by pH below the neutrality due to the protonation of acidic groups contained in the humic substances structure which modify their reactivity with ozone.

3.2. *Influence of H_2O_2 in the TCA removal*

To evaluate the participation of H_2O_2 in the formation of OH radical during the ozonation of humic substances, an experiment was carried out with $KMnO_4$ in the medium as an inhibitor. $KMnO_4$ is an oxidant which does not react with ozone but which reacts very weakly with organic compounds at neutral pH and at 20°C. The reaction of $KMnO_4$ with H_2O_2 is very slow but can be catalyzed in the presence of phosphate ions.

When 10^{-4} mol l^{-1} of $KMnO_4$ was added in the medium, we noticed that a part of the radical reactions was inhibited. The removal of the TCA for 30 min of ozonation are respectively 60% and 75% with and without $KMnO_4$ (e.g., 40% for the stripping) which implies that the reactions between H_2O_2 and O_3 are important in the radical pathway during the ozonation process of humic substances solutions. During these experiments, no change in transfer and in the concentration of ozone at the steady state was observed.

3.3. *OH radicals formation in function of the degree of oxidation of the humic substances*

The formation of OH radicals was studied for an extend ozonation time corresponding to an advanced oxidation degree of organic matter. The experiments of ozonation was rerun with a new injection of 10^{-5} mol l^{-1} of TCA in the preozonated solution of humic substances. The results, reported in Table 1, indicate that TCA was removed only during the first run. No removal of TCA, except by stripping, was observed for the 2nd injection of the organic compound in the medium. A 3rd and a 4th TCA dose was added to verify the reproducability of the result with the 2nd TCA addition.

Table 1
Removal of TCA and H_2O_2 formation for different cumulated ozonation time

Run number	1	2	3	4
Ozonation time (h)	0.5	2	2.5	3.5
TCA removal by ozonation	76%	42%	44%	44%
H_2O_2 (μmol l^{-1})	1.6	0	0	0
TCA removal by stipping	40%	41%	41%	38%

During this experiment, H_2O_2 is formed only at the beginning of the ozonation of humic substances, for a prolonged time no H_2O_2 was detected.

It is established that the consumption of O_3 by humic substances is very rapid during the first stage of ozonation [10,11]. In our experiments, all ozone reactive sites of humic substances were consumed within the first 30 min. After this time, the production of radical species stops and the disappearance rate of TCA returns to the one observed during the stripping. This reaction time corresponds to the accumulation curve of H_2O_2 in the medium, to the removal of the color and to the decrease of the absorbance at 254 nm.

3.4. *ESR measurement*

UV absorbance and the color of humic substances solutions reflect the degree of aromaticity of the humic substances and particularly hydroxylated and semi-quinonic groups. In order to show the influence of these groups on the production of OH radicals during the ozonation process, a measurement by ESR was performed at different ozonation times of a very concentrated humic substances solution ($[SH]_0 = 400$ mg l^{-1}).

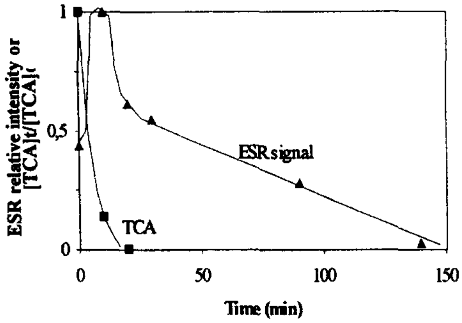

Fig. 3. TCA removal and ESR signal during the ozonation of humic substances solutions.

The semi-quinonic groups are responsible for forming organic radicals, these radicals are very stable when humic substances are on their solid form [12] but their concentration decreases within a short time in solution. The irradiation of a humic substances solution caused an increase of the free radical concentration but when the light was switched off, the free radical concentration returned to the same value as that obtained prior to irradiation. In our experiment the ESR signal was recorded after 15 min irradiation time in liquid nitrogen with a high pressure mercury lamp (HPK, Philips).

If we assumed that the formation of these radicals is essentially due to the presence of quinonic groups in the structure of humic substances [12], we can observe in Fig. 3 that the quantity of these groups increases at the beginning of the ozonation, probably due to the electrophilic attack of ozone on phenolic group leading to a pseudo-quinonic group. Then, for a higher ozone dose, we observed a decrease of the quinoic groups corresponding to the break down of the aromatic cycle with probably the formation of carboxylic acids.

4. Conclusion

This study shows that the ozonation of humic substances in solution leads to the formation of radical species. The formation of OH radicals in the medium can be provided by two main mechanisms:

- The direct reaction of ozone with organic compounds producing secondary oxidant such as hydrogen peroxide that further reacts with ozone to produce OH radicals.
- The reaction of ozone with the humic substances that gives radical intermediates.

It is difficult to dissociate these two mechanisms and the OH radicals observed in our experiments are probably formed simultaneously by these two mechanisms.

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