



Influence of water matrix on copper-catalysed continuous ozonation and related ecotoxicity



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ABSTRACT

The continuous ozonation of a mixture of carboxylic acids (formic, acetic, oxalic and maleic) has been performed under non-catalytic and copper-catalysed ozonation using a synthetic water matrix and a real sewage treatment plant (STP) effluent. The aim was to study the effect of water matrix on catalytic performance, particularly considering the toxicity of treated water to aquatic organisms. The non-catalytic ozonation of carboxylic acids in synthetic water resulted in a low reduction (36%) of the total organic carbon (TOC), the main feature being the accumulation oxalic acid due to the partial oxidation of maleic acid. Catalytic ozonation, adding copper concentration of 20 $\mu\text{g L}^{-1}$, achieved a TOC reduction of 75%, mainly due to the total depletion of oxalic acid. In wastewater effluent, the same general pattern was found with oxalic acid as the main by-product and its almost complete removal in catalytic ozonation. However, to attain the latter it was necessary to use copper concentrations as high as 100 $\mu\text{g L}^{-1}$. Copper proved to be a good catalyst for the oxidation of oxalic at near neutral pH, with short reaction times and matrix with high scavenging rate. The aquatic toxicity of treated mixtures was studied by means of five standard species placed on different trophic levels: *Vibrio fischeri*, *Pseudomonas putida*, *Pseudokirchneriella subcapitata*, *Tetrahymena thermophila* and *Daphnia magna*. The results showed that copper in STP effluent was less toxic than in synthetic water, an effect attributed to copper complexation with organic and inorganic compounds present in the matrix. The reduced biological availability could also explain the lower catalytic effect observed in real wastewater.

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1. Introduction

Ozone is widely used in drinking water and wastewater reclamation treatments due to its high disinfection power and oxidation potential [1]. The direct ozonation of organic compounds results in many refractory oxidation by-products, particularly carboxylic acids [2]. Different ozone-based processes have been developed to improve ozone oxidation performance in order to increase the degree of mineralization. These technologies include O_3/OH^- , $\text{O}_3/\text{H}_2\text{O}_2$, and O_3/UV and belong to the group of advanced oxidation process (AOP) based on the generation of hydroxyl radicals (OH^\bullet). Contrary to ozone, OH^\bullet reactions are not selective, but their

concentration depends on the scavenging rate of the water matrix [3–5].

Catalytic ozonation has also been proposed to increase the degree of mineralization and reduce ozone consumption [6,7]. Different transition metals and oxides have been studied as ozonation catalysts [3]. Among them, copper has shown a significant catalytic effect in the degradation of carboxylic acids [4,8–12]. It has been noted that the performance of catalytic ozonation strongly depends not only on the catalyst itself, but on the composition of water matrix [2,12]. Moreover, most catalytic ozonation studies have been carried out in batch or semi-batch conditions, but more relevant data would be obtained from continuous ozonation devices. Contrary to batch processes in which a well-defined reaction time is established, continuous treatments display a statistical distribution of residence times [13].

Catalytic ozonation is able to remove certain pollutants, but can generate new compounds as oxidation by-products and from the leaching of catalyst active phases, which may be more hazardous

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than the original mixture [6,14]. Treated water is a complex mixture of organic and inorganic compounds, whose ecotoxicological impact cannot be predicted by simple chemical determinations due to the potential interactions among pollutants [14]. The chemical analyses in which regulations are based identify and quantify trace metals in an aquatic environment. However, they do not provide direct indication of the potential effects of the metals on the biota [15]. Thus, ecotoxicological bioassays are required to provide a holistic direct estimation of the environmental hazard of a given mixture. In particular, metal ecotoxicity is directly affected by physico-chemical parameters such as pH, alkalinity, hardness and dissolved organic and suspended matter, which alter its speciation and bioavailability [16,17], and, indirectly, through synergistic or antagonistic effects [18,19]. Therefore, aquatic toxicological assessment should include a battery of different species representative of the different taxa in the trophic chain [20], with emphasis on organisms placed at the bottom, like phytoplankton and zooplankton, where damage caused by metals primarily occur [21]. Many ozonation catalytic studies have been carried out in ultrapure water neglecting the effects on catalyst performance of the organic and inorganic species present in real matrices. Similarly to the influence of water matrix composition over metal ecotoxicity through the bioavailability concept, the same behaviour could be applied to the influence of water matrix on copper catalytic availability.

The aim of this study was to explore the effect of the water matrix on the non-catalytic and copper-catalysed continuous ozonation of a mixture of carboxylic acids (formic, acetic, oxalic and maleic acid). These compounds are present in ozonated water as reaction intermediates or final ozone-refractory by-products. We used homogeneous catalyst due to simplicity of application in continuous processes, but in view of the low concentration used, the results could be extrapolated to the effect of active phase leaching in heterogeneous catalysis. The ecotoxicity of ozonated water was tracked using a battery of bioassays composed of five single species tests: *Vibrio fischeri*, *Pseudomonas putida*, *Pseudokirchneriella subcapitata*, *Tetrahymena thermophila* and *Daphnia magna*.

2. Materials and methods

2.1. Materials

Formic, acetic, oxalic and maleic acid and copper ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) of analytical degree were purchased from Fluka. The initial carboxylic acid mixtures were prepared with a concentration of 7 mg L^{-1} each. These organic acids and concentrations have been chosen because they have been previously identified and quantified as the main final ozonation by-products in a previous work dealing with the ozonation of pharmaceutical and personal care products in the same STP effluent [22]. These acids were the main responsible of the relative low mineralization degree achieved in direct ozonation runs.

In order to study the effect of the water matrix over the ozonation performance, two different matrices were used: a synthetic matrix and wastewater from the effluent of a sewage treatment plant (STP) located in Alcalá de Henares (Madrid, Spain). Synthetic water was prepared with the required amount of NaHCO_3 in ultrapure water to equal the alkalinity and pH values of the STP effluent. Ultrapure water was obtained from a Millipore Milli-Q system with a resistivity of at least $18 \text{ M}\Omega \text{ cm}$ at 25°C . The STP treats a mixture of domestic and industrial wastewater from facilities located near the city and has a nominal capacity of $3000 \text{ m}^3 \text{ h}^{-1}$ of raw wastewater. Details on

wastewater characterization are included as supplementary data (Table S1).

2.2. Experimental procedure and analytical methods

The experiments were carried out in continuous mode in a cylindrical reactor made of Pyrex (internal diameter of 6 cm and working height of 51 cm) with a total working volume of 1.44 L operated in co-current mode (Scheme 1). Water flow rate was 142 mL min^{-1} (Gilmont rotameter) and gas flow was 390 mL min^{-1} (Aalborg mass flow controller) with different inlet ozone concentrations (Anseros ozone generator COM-AD-02). Inlet and outlet ozone gas concentration (Anseros ozone GM-PRO analyser), dissolved ozone in the reactor exit (Mettler Toledo-Thomton dissolved ozone sensor), pH and temperature (Easyferm Plus VP 120 Hamilton pH sensor) were constantly monitored and recorded (Keithley 2700 Data Acquisition System). Copper solution was continuously added to the inlet stream at different flows (Harvard 11 plus infusion pump) to achieve the desired final concentration. In order to ensure homogeneity a nine-loop glass coiled pipe was used. The dilution ratio was always lower than 1%.

For every set of working conditions, samples were withdrawn for analysis at the column outlet once the stationary state was reached. This was accomplished after circulating four times the hydraulic retention time after a constant ozone value was obtained both in liquid and gas phases at the column outlet. The retention time distribution curve yielded an average retention time of 10.3 min and was analysed using the continuous stirred tank reactor CSTR in series model according to the procedure described in the literature [23]. The equivalent value of 1.13 tanks obtained indicated that the column can be approached to a perfect CSTR. It is generally accepted that short columns with intense gas phase hydrodynamics can be assimilated to a CSTR due to the bubble back mixing [24]. Assuming CSTR behaviour, the amount of ozone consumption at the stationary state $dC_{\text{O}_3}^{\text{liq}}/dt = 0$ can be obtained from the following mass balance (Eq. (1)) in which F_{O_3} is the rate of ozone entering the system in the gas phase (gas, in) or existing either in the exhaust gases (gas, out) or dissolved in water (liquid, out):

$$\text{Consumed } \text{O}_3 = F_{\text{O}_3}^{\text{gas,in}} - F_{\text{O}_3}^{\text{gas,out}} - F_{\text{O}_3}^{\text{liq,in}} \quad (1)$$

The concentration of organic acids was measured using a Dionex DX120 Ion Chromatograph (IC) with conductivity detector. Oxalic and maleic acid concentrations were determined using an IonPac AS9-HC analytical column ($4 \times 250 \text{ mm}$) with ASRS-Ultra suppressor, whereas acetic, glyoxalic and formic acids were measured with an IonPac ICE-AS6 analytical column ($9 \times 250 \text{ mm}$) with AMMS ICE II suppressor. Total organic carbon (TOC) analyses were performed on a Shimadzu TOC-V_{CSH} total carbon organic analyser equipped with an ASI-V autosampler. The concentration of copper was determined by Agilent 7700x ICP-MS operating at 3 MHz in helium cell gas mode.

2.3. Aquatic toxicity bioassays

The ecotoxicity of water samples was assessed by means of five bioassays using *V. fischeri*, *P. putida*, *P. subcapitata*, *T. thermophila* and *D. magna*. The battery of tests allowed the combination of acute and chronic assays and the combined use of prokaryotes and eukaryotes at several trophic levels. All these bioassays were conducted according to standard operational guidelines [25–29]. More details about the aquatic toxicity tests procedure are presented in supplementary data.

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