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Ozone II: Characterization of In Situ Ozone Generation Using Diamond Electrodes

Ozone can be widely used for oxidation of diverse water constituents and mineralization of organic compounds and therefore for their elimination in drinking and process water as explained before in the review Ozone I: Characteristics/Generation/Possible Applications by Heim C. and Glas K., BrewingScience 2011 [1]. Electrolytic ozone generation in situ using boron-doped diamond electrodes is a relatively new and promising technology. The current article describes the formation of ozone directly from water with a DIACHEM® electrode. Ozone concentrations in water depend on the applied current on the one hand and on the water matrix on the other hand. The influence of organic and inorganic components on residual ozone concentrations in several water matrices was also investigated. The results form the basis to find reasonable applications of the described technology in the food and beverage industry.

Descriptors: ozone, oxidation, diamond electrode, water quality

1 Introduction

Ozone is highly reactive due to its oxidative potential of +2.07 V. In water ozone is unstable and decomposes to oxygen in a radical chain reaction. During this chain reaction, several radicals, primarily hydroxyl radicals, are formed. Hydroxyl radicals show even higher reactivity towards organic and inorganic water components, as their oxidation potential (+2.8 V) is even higher than that of ozone. Their reactivity, however, is much more unspecific compared to ozone reactions with higher selectivity towards organic double bonds, activated aromatic systems and non-protonated amines. Thus, ozone and its decay products are able to quickly oxidize organic and inorganic compounds [2–6]. A detailed description of ozone characteristics, current technologies for ozone production and possible applications was already given in a review article [1].

The application of so-called Advanced Oxidation Processes (AOPs) has been gaining more and more importance in water treatment for mineralization and elimination of dissolved matter, to achieve a higher bio-degradability of organic pollutants and for disinfection reasons during the last several years [7]. Ozonation is an already established technology for wastewater and drinking water treatment as well as for disinfection of swimming pools. Currently, its applicability within cleaning-in-place systems in the beverage industry is under investigation [8].

A rather new method for ozone generation in this field is the electrolytic production using diamond electrodes that emerged in the 80s of the last century [9]. The characteristic of these non-catalytic electrodes is the suppression of anodic oxygen formation due to the required high overvoltage. Conductivity is achieved through doping of the crystalline diamond layer with boron. At the anode, the major process is the formation of hydroxyl radicals followed by the generation of other oxidizing compounds. The desired quantities of ozone and hydroxyl radicals for the oxidation of unwanted materials can be adapted through variation of the current [7, 9]. Thus, depending on the current density, ozone can be generated directly from water (in situ). The dissolved ozone vesicles are sputtered through a nozzle to even smaller gas vesicles, in order to increase the solubility. Basic processes of the formation of ozone at the diamond electrode are displayed in figure 1.

Compared to other ozonation methods this technology can be characterized as follows [7, 9–11]:

- Ozone generation takes place in situ. Compared to classical generators, there is no need to introduce gaseous ozone into water, what may reduce losses.
- Higher ozone concentrations can be achieved compared to classical generators, as ozone is produced at low temperatures. The amount of ozone is limited by its solubility in water, the overall electrode surface and the current density.
- Ozonation with diamond electrodes can be considered an environmentally friendly method for water treatment, as it can be undertaken in absence of additional chemicals.
- Because oxidizing agents break down to oxygen molecules, no unwanted disinfection by-products arise directly from the application of ozone. However, products from cross-reactions of ozone and inorganic and organic water constituents (depending on their concentration) may be of concern.
- In contrast to other ozone-generating electrodes (e.g. PbO_2), diamond electrodes have a higher current efficiency and better stability as no battery back-up is needed.
- Due to the fact that several electrodes can be combined in electrode stacks to achieve optimum ozone amounts, high flexibility is given.

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Tables and figures see Appendix

- Complete mineralization of organic material is possible under optimum current densities and high energy consumption. Typical conditions using lower energy entries lead to better biodegradability of organic pollutants through partial oxidation.

The aim of this research was the characterization of the diamond electrode as a relatively new technology for ozone production. Different current densities and water qualities were tested in order to determine the dependency of ozone formation on these factors. The results will help to develop proper applications of the technology as an AOP to support cleaning and disinfection processes in the food and beverage industry.

2 Materials and methods

The ozone reactor

Experiments were conducted with a CONDIAPURE® test facility (CONDIAS GmbH, Itzehoe, D) using a DIACHEM® electrode stack (CONDIAS GmbH, Itzehoe, D) that was integrated into an optically accessible glass reactor with a total height of 253 mm and 42 mm diameter (Esau & Hueber GmbH, Schrobenhausen, D).

The test facility included a pump (PY-2071, Speck Pumpen, Hilpoltstein, D) with a maximum capacity of 17 L/min and a DC source with a maximum output current of 10 A and a maximum output voltage of 35 V. Ozonation was carried out at constant recirculation flow rates of 4 L/min at 20 °C in a 3 L batch vessel. Current densities of 42, 208 and 333 mA/cm^2 were applied.

Electrode stack

In situ ozone generation was undertaken using the DIACHEM® electrode stack with a single cathode- and anode-pair and a surface of 24 x 50 mm^2 per electrode. The electrode substrate material was niobium, coated with a 1–5 µm thick boron-doped diamond layer.

Sample vessel

Water samples with a total volume of 3 L were prepared in a glass vessel that was connected to the ozone reactor with an inlet and outlet tube. The solution was ice-cooled to keep the temperature at 20 ± 1 °C during electrode operation.

Sampling

Samples were taken from the outlet tube at 0, 1, 2, 3, 5, 7.5, 10, 15, 20 and 30 minutes ozonation. After 30 minutes the electrode was turned off and ozone degradation was monitored for a maximum of 20 minutes at different time points.

Each ozone sample drawing reduced the total reaction volume in the batch vessel by approximately 20 mL. The resulting higher volume flow generally leads to a better agitation of the oxidant in the batch vessel and therefore to a higher ozonation rate due to higher turnover rates. Therefore ozone concentrations in the present experiments were corrected for the volume difference.

Ozone measurement

Residual ozone concentrations were quantified after certain time intervals based on the decolorization of indigo disulfonate in the presence of ozone [12]. Briefly, the absorption of the sample was measured in a spectrophotometer at 610 nm after reaction with 1 mM indigocarmin solution in 0.31 M phosphoric acid. Absorption values were subtracted from blank samples and compared to a standard curve. Each sample was analyzed in duplicate.

Water matrices

All experiments were carried out in synthetic water of three different qualities: The first water corresponds to a soft drinking water (‘soft water’, total hardness 0.9 mmol/L), the second water simulates a hard tap water with a total hardness of 3.6 mmol/L (‘hard water’). Additionally, 2.5 mg/L BSA (albumin from bovine serum 96 %, FLUKA, Buchs, Ch) and 2.5 mg/L humic acid (Roth, Karlsruhe, D) were added to the third water matrix (‘hard water + organics’). A detailed description of the water properties is given in table 1.

3 Results and discussion

Experiments were conducted to determine the effect of different water matrices on residual ozone concentrations during electrolytic ozone generation. Therefore, a synthetic soft water with no organics and synthetic hard water with and without organics were employed (see Table 1). Ozone was produced at different current densities (42, 208 and 333 mA/cm^2) using the DIACHEM® diamond electrode and residual ozone values in water were measured photometrically. After 30 minutes of ozonation the electrode was turned off and residual ozone concentrations were monitored for several minutes. The ozone reactor was run in batch mode.

As shown in figure 2, ozone concentrations reflect a logarithmic growth rate during the first minutes of ozonation followed by a plateau phase with approximately constant ozone concentrations. In ‘soft water’ maximum concentrations are the following: 0.51 mg/L during the application of 42 mA/cm^2, 2.63 mg/L at 208 mA/cm^2 and 4.83 mg/L at 333 mA/cm^2, respectively. The curves for ozone decay display a strong initial ozone decay during the first minute after the time point when the electrode was turned off, followed by a first order decomposition with half-life times of approximately 5–12 minutes. The initial decay period might even be longer for higher initial ozone concentrations compared to lower ones. However, to receive reliable information about half-life times, ozone decomposition should be followed for a longer time period. According to literature data, ozone decomposition strongly depends on the water quality, its pH and temperature [5]. High pH values can accelerate ozone decay reactions and waters containing few ions under high current densities give higher ozone rates [5, 13]. The effect of organic matter is still unknown as organic molecules can either accelerate the decomposition of ozone through their ozone- and hydroxyl radical-mediated oxidation or inhibit the decay [5]. In general, ozone decomposition is faster in waters containing compounds that lead to ozone consumption, in contrast to highly pure water [14, 15]. Our data show that using high current densites (333 mA/cm^2) results in a slower ozone decay in water containing organic material compared to the water qualities without organic components (data not shown). This would suggest a rather inhibiting effect of organics on the ozone decay after turning off the electrode. Further experiments have to be undertaken to examine the effects of the organic matrix on ozone decomposition rates.

A comparison of the maximum ozone concentrations for different currents results in a linear correlation with $R^2 = 0.991$ for ‘soft water’ and $R^2 = 0.999$ for ‘hard water’. It can also be noticed that for ‘hard water’ containing a certain organic load, this correlation only appears for current densities above 84 mA/cm^2, whereas lower current densities do not reflect the linear correlation and apparently result in higher residual ozone concentrations. Beside that, ozone concentrations at 42 mA/cm^2 were of very poor reproducibility. Therefore higher current densitites are recommended to achieve practicable ozonation rates. This can be seen from the following results.

Comparing different water matrices by the observation of residual ozone concentrations in the water phase gives insight into the consumption of ozone through different water components (Fig. 3), as reacting ozone concentrations cannot be measured directly. In general, for water matrices low in inorganic and organic material, higher ozone concentrations could be measured during ozonation. Applying a current density of 208 mA/cm^2 (Fig. 3 a) resulted in a maximum ozone concentration of 2.63 mg/L in ‘soft water’, 2.21 mg/L in ‘hard water’ and 1.73 mg/L in ‘hard water + organics’, respectively. Using 333 mA/cm^2 instead caused an increase in the maximum ozone amounts up to 4.83 mg/L in ‘soft water’, 3.02 mg/L in ‘hard water’ and up to 2.79 mg/L in ‘hard water + organics’, respectively (Fig. 3 b). Ozone concentrations appeared to be the highest in ‘soft water’ where no organic material was added and concentrations of inorganic ions were relatively low. As shown by the comparison with ‘hard water’, an increase of inorganic molecules might lead to ozone consumption due to oxidation reactions. Further addition of organic material as shown in ‘hard water + organics’ clearly reduced residual ozone concentrations compared to the ‘hard water’ without organic molecules at 208 mA/cm^2, whereas at 333 mA/cm^2 the decrease between the two water qualities was not as considerable. The reason for this difference is not clear yet, but it has to be taken into account that not only ozone can react with water constituents, but also other highly reactive oxidation agents such as OH radicals and hydrogen peroxide. In the presence of organic material not only oxidation of unsaturated double bonds and substituted aromatic systems takes place, but there might also be cross-reactions with inorganic ions, especially in bromide- and chloride-rich waters. Further analysis of so-called disinfection by-products such as chlorate, bromate and halogenated organic compounds can provide important information on whether these reactions might be more relevant when high currents are applied.

The achieved residual ozone concentrations of up to almost 5 mg/L in soft water should generally be sufficient to oxidize inorganic molecules of low oxidation state and organic compounds in natural water or even wastewater matrices. According to literature data, degradation of organic material strongly depends on the amount of total organic carbon (TOC) in the water, whereas ozone/TOC ratios below 1 mg ozone/mg TOC cannot be used for complete mineralization [16]. At low ozone concentrations, organic molecules are saturated and oxidized, and therefore a higher degree of biodegradability can be achieved. This would allow an application of the diamond electrode in the area of wastewater treatment in combination with biological processes for a successful removal of organic as well as inorganic pollutants. It may also be of importance to introduce water recycling processes in the food and drinking industry.

Several publications report disinfection effects of ozonated water on micro-organisms: Compared to other commonly used oxidative disinfection methods, ozonation could be shown to be the most efficient one to damage the surface of *Escherichia coli* bacteria [17]. Coliform bacteria were reported to be killed within 15 minutes using ozone doses of only 0.6 mg/L [16]. Another study showed that ozonated water could be successfully used against several food-related micro-organisms, including yeasts and fungal spores [18]. Its integration into cleaning and disinfection processes in breweries is already under investigation [19]. Our data clearly shows that, with the diamond electrode, ozone values produced in different water matrices can be sufficient to render anti-microbial effects. This may support the idea of adding or, on the long term, of replacing classical cleaning and disinfection processes by an integrated ozonation step. Disinfection of drinking water used for food manufacturing seems possible as well. Nevertheless, further experiments are needed for verification.

Foodstuffs themselves as well as the different manufacturing processes are strictly regulated and well-controlled. The application of ozone as a disinfectant in drinking water is highly regulated by limiting values for ozone itself and several problematic disinfection by-products for its use in drinking water. In general, product quality should not be affected by the ozonation. Also the application of ozone within industrial processes must be safe for the operator, as ozone is toxic depending on its concentration and the exposure time. As a strong oxidizing agent it has to be considered that ozone can also lead to corrosion of the processing equipment. During food processing, ozone or ozonated water do not need an approval because they can be considered as manufacturing additives that do not appear in the product [8]. To exclude an impact of problematic disinfection by-products or of residual ozone on the product, further research is necessary.

4 Conclusion / Summary

The described experiments form a basis to develop various industrial procedures using the diamond electrode for ozonation purposes. They clearly show that ozone concentrations in water can directly be influenced by variation of the current and the water quality. The ozone concentrations that can be achieved with this technology provide possibilities for successful treatment of organic material or micro-organisms in aqueous solutions. Therefore, various applications for the food and beverage industry can be postulated:

- application of ozonated water as a cleaning agent and disinfectant for surfaces or integrated in “cleaning in place” processes,
- treatment of wastewater for reuse,

- disinfection of drinking water for use in food processing.

However, as food quality underlies strict regulation, further research has to be conducted to verify the applicability of the proposed technology.

Acknowledgement

This work was conducted within the project NADINE ("Nanomodifizierte Diamantelektroden für Inlinedesinfektionsprozesse in unterschiedlichen Einsatzgebieten") funded by the BMBF and the project "Entwicklung eines Verfahrens zur Desinfektion von Brauereianlagen mittels ozonhaltigen Wassers" funded by the BMWi.

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Received 26 August 2011, accepted 20 September, 2011

Appendix

Table 1 Detailed parameters and ingredients of the applied water matrices

Parameter	Unit	‚Soft water‘	‚Hard water‘	‚Hard water + organics‘
Total hardness	mmol/L	0.9	3.6	3.6
Chloride	mg/L	20	250	250
Bromide	mg/L	0.1	1.0	1.0
Nitrate	mg/L	10	50	50
Sulfate	mg/L	60	200	200
Iodide	mg/L	–	0.1	0.1
pH	–	8.9	8.7	8.8

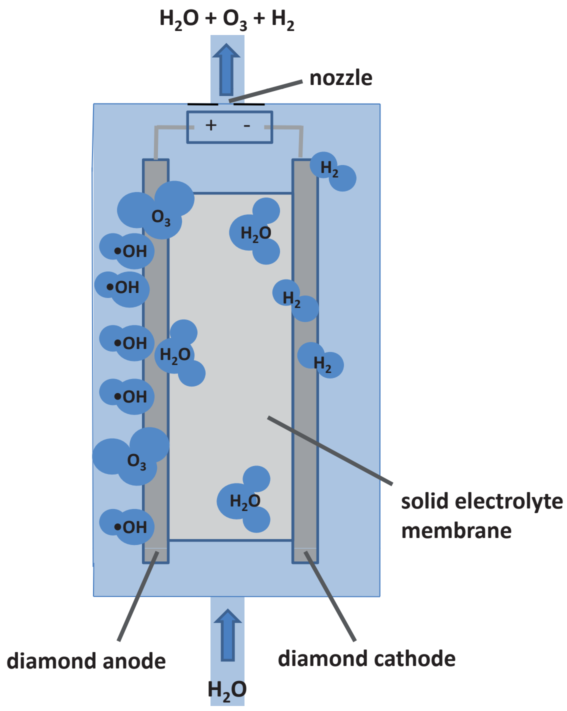

Fig. 1 Formation of hydroxyl-radicals and ozone at the diamond electrode

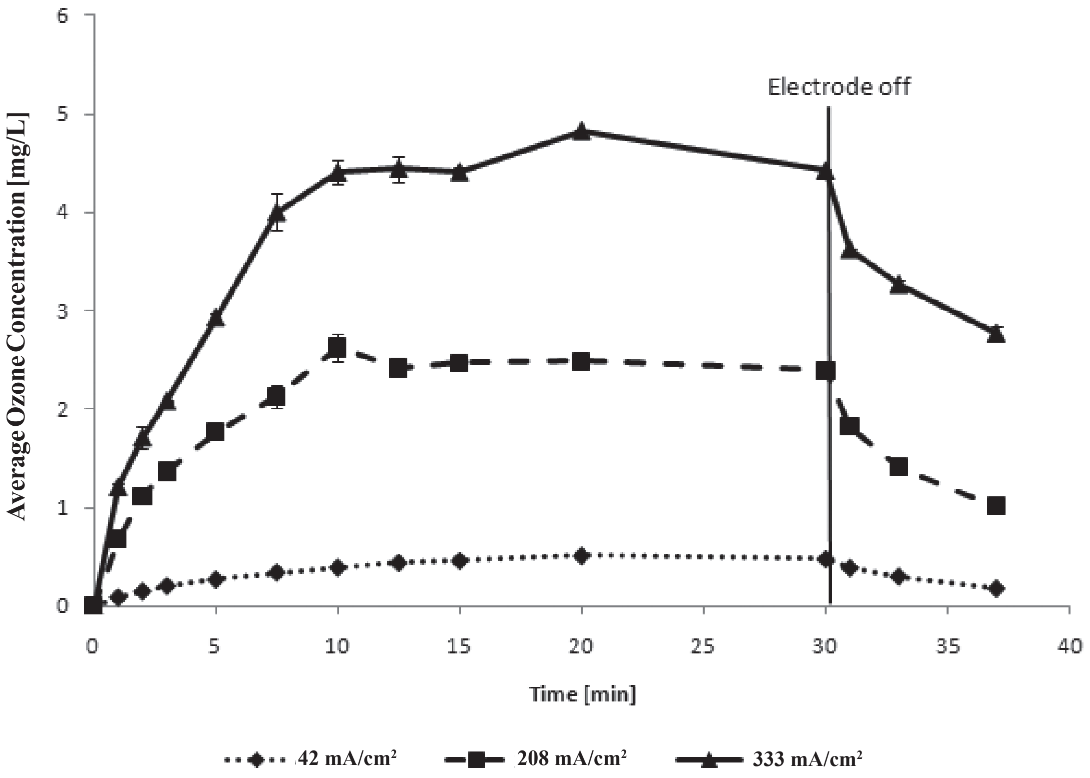

Fig. 2 Ozone formation and degradation in ‘soft water’ using different current densities at 20 °C. Average ozone concentrations were calculated from duplicate measurements

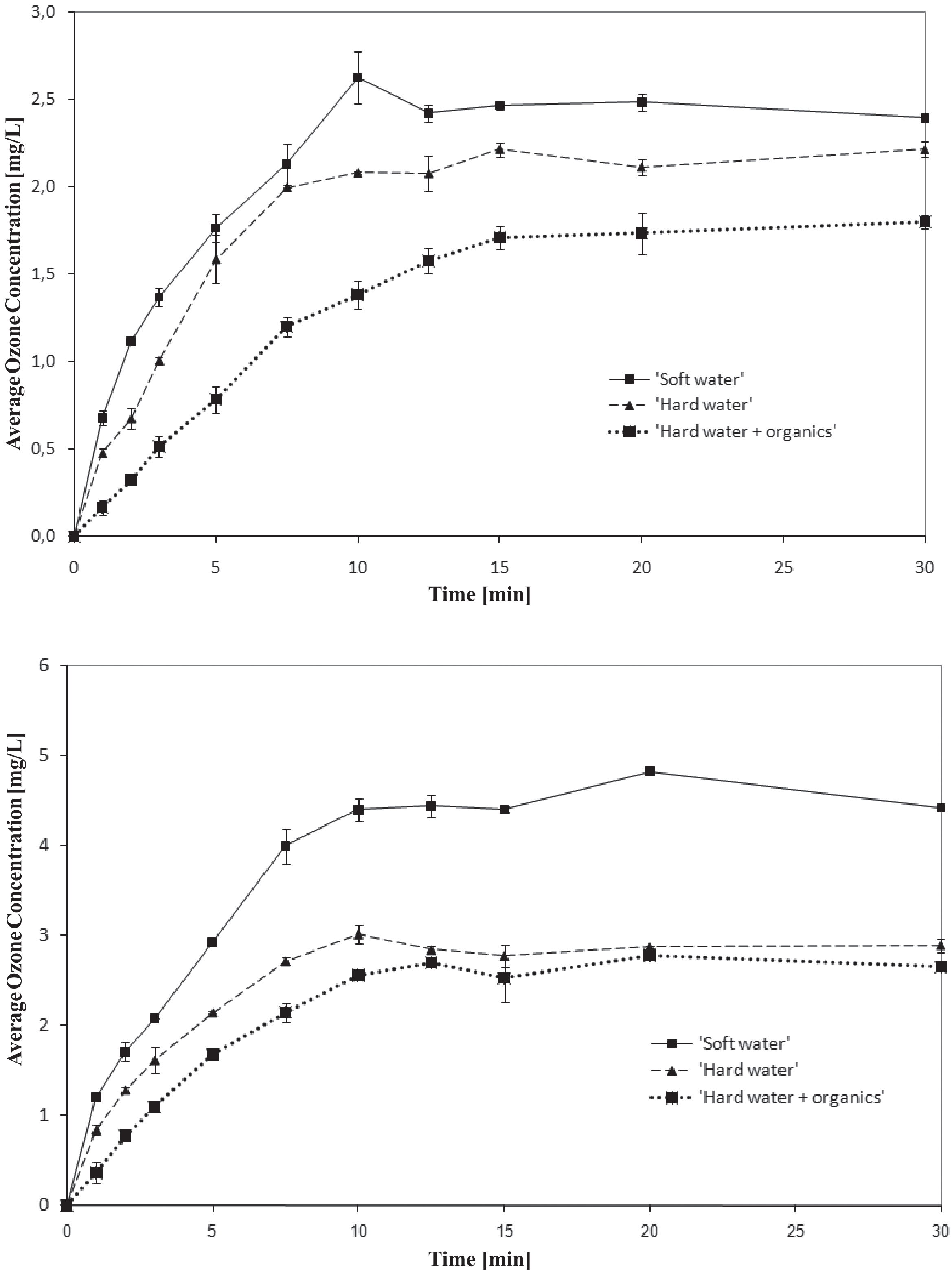

Fig. 3 **Ozone formation in different water matrices at 20 °C;**
a) 208 mA/cm^2,
b) 333 mA/cm^2.
Average ozone concentrations were calculated from duplicate measurements