Effect of water temperature and pH on the concentration and time of ozone saturation

Efeito da temperatura e do pH da água na concentração e no tempo de saturação por ozônio

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Abstract

Ozone has been used for many years to disinfect water due to its oxidizing potential. Since it decomposes quickly into molecular oxygen, leaving no residue, it has important advantages for use. The decomposition of ozone is affected by the temperature and pH of the medium, low pH values and temperatures increasing its half-life, which can result in more efficient disinfection. With the objective of increasing the effectiveness of ozonation, this study investigated the effect of temperature (8 ºC and 25 ºC) and pH (3.0 and 6.0) of the water on the saturation time and gas concentration, employing two initial gas concentrations (13.3 and 22.3 mg L⁻¹). The concentration of ozone saturation increased as the temperature and pH of the medium decreased, as also with the higher initial gas concentration (C). The highest saturation concentrations were obtained at pH 3.0 and 8 ºC (4.50 and 8.03 mg L⁻¹ with C of 13.3 and 22.3 mg L⁻¹, respectively). This higher ozone content could result in greater decontamination efficiency of the food products washed with this water.

Keywords: Ozonation; Saturation concentration; Saturation time.

Resumo

O ozônio tem sido usado, por muito tempo, na água como desinfetante, devido ao seu potencial oxidante. Visto que possui capacidade de se decompor rapidamente em oxigênio molecular, não deixando resíduo, apresenta vantagens importantes para uso. A decomposição do ozônio é afetada pela temperatura e pelo pH do meio, sendo que baixos níveis de pH e de temperatura aumentam sua meia-vida, o que pode levar a uma desinfeção mais eficiente. Com o objetivo de aumentar a eficiência da ozonização, este trabalho investigou o efeito da temperatura (8 ºC e 25 ºC) e do pH (3,0 e 6,0) da água no tempo de saturação e na concentração do gás, empregando duas concentrações iniciais de gás (13,3 e 22,3 mg L⁻¹). A concentração de saturação do ozônio aumentou conforme a temperatura e o pH do meio diminuíram, bem como com uma maior concentração inicial do gás (C). As maiores concentrações de saturação 4,50 e 8,03 mg L⁻¹ foram obtidas em pH 3,0 e à 8 ºC, com em C de 13,3 e 22,3 mg L⁻¹, respectivamente. Este maior teor de ozônio pode resultar em maior eficiência de descontaminação dos produtos alimentícios, quando higienizados com água submetida a esse tratamento.

Palavras-chave: Ozonização; Concentração de saturação; Tempo de saturação.

1 Introduction

Ozone (O₃) is a highly reactive and unstable gas, causing it to decompose rapidly under normal environmental conditions. Its oxidation potential (2.07 mV) is 1.5 times higher than that of chlorine, lower only than that of fluorine (3.06 mV). Considering the highly oxidant characteristics and efficiency of ozone as a fumigation, sanitization and antimicrobial agent,
it has attracted great interest in the food industry since its discovery (SILVA et al., 2011). Owing to its greater effectiveness, ozone can be used as an alternative to chlorine; its rapid decomposition into oxygen and the absence of residues being important advantages for application in the food area (TJAHJANTO et al., 2012).

Ozone gas has been classified by the U.S. Food and Drug Administration (FDA) as a Generally Recognized as Safe (GRAS) substance, and in particular as a safe sanitizer of water and food. Ozonation started to be used to treat water in Brazil in 1983, but there is no existing legislation to guide applications in the food area (FREITAS-SILVA et al., 2013).

Besides the broad spectrum of microbial inactivation (LI et al., 2012, 2013) and pest control (KEIVANLOO et al., 2014), ozone has demonstrated a potential use in the degradation of mycotoxins (EL-DESOUKY et al., 2012; FREITAS-SILVA et al., 2013).

Ozone can be used as a gas or dissolved in water and the presence of water increases its reactivity and can improve the results (EL-DESOUKY et al., 2012). On the other hand, its low stability in aqueous media (half-life between 20 to 30 minutes) poses a limitation on its use (KHADRE et al., 2001; DI BERNARDO; DANTAS, 2005).

Giving priority to the greater reactivity of the gas, studies have been investigating the application of aqueous ozone in the food area, such as the washing of Brazil nuts (FREITAS-SILVA et al., 2013) and apples (ACHEN; YOUSEF, 2001), production of corn starch (RUAN et al., 2004), washing of fish filets (KIM et al., 2000) and the treatment of wheat grains (TROMBETE et al., 2016, 2017).

The effectiveness of ozonation depends on the process of introducing (gas solubility) and maintaining (reduced decomposition rate) the gas in the water, which is directly related to the generation time and to the temperature and pH of the medium. High temperatures accelerate the decomposition rate besides reducing its water solubility (DI BERNARDO; DANTAS, 2005). Ozone is also more stable in aqueous solutions with low pH values (KHADRE et al., 2001).

In the light of these aspects, the aim of this study was to analyse the effect of the water temperature and pH value on the ozone saturation time and concentration, employing two initial gas concentrations.

### 2 Material and methods

The ozone was synthesized from industrial grade oxygen (99.5% purity). The potassium indigotrisulphonate \(\text{C}_{51}\text{H}_{12}\text{N}_{3}\text{O}_{18}\text{S}_{3}\text{K}_{2}\); 80-85% purity), phosphoric acid, monosodium dihydrogen phosphate and glacial acetic acid were of analytical grade.

2.1 Preparing the solutions to determine the ozone

The indigo stock solution was prepared by dissolving 770 mg of potassium indigotrisulphonate in 500 mL of deionized water and 1 mL of concentrated phosphoric acid contained in a 1000 mL volumetric flask. The volume was completed with deionized water. The indigo reagent was prepared by diluting 20 mL of the stock solution, 10 g of \(\text{NaH}_2\text{PO}_4\) and 7 mL of concentrated \(\text{H}_3\text{PO}_4\) by completing the volume with deionized water in a 1000 mL volumetric flask.

2.2 Generating the ozone

The ozone gas was generated by passing the oxygen through a model 3RM ozone generator (Ozone & Life, São José dos Campos, Brazil). Inside the device, the oxygen was subjected to a dielectric discharge produced by applying a high voltage between two parallel electrodes separated by a dielectric element (glass), and a free space for dry air to flow. In this free space, electrons were generated with sufficient energy to break the oxygen molecules, forming ozone.

2.3 Determining the ozone concentration

The ozone concentration in the water was quantified using the method described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2012). This method is based on the ability of ozone to transform indigo (blue colour) into isatin (colourless). 50 mL of indigo reagent was added to each of two 100 mL volumetric flasks, the volume of one being completed with deionized water (blank) and of the other with the ozonated sample. The absorbance of both solutions was measured at 600 nm. The ozone concentration in the water \((\text{mg L}^{-1})\) was calculated as indicated by the Equation 1 below:

\[
\text{mg L}^{-1} = \frac{(100 \times \Delta A)}{(f \times b \times V)}
\]

where \(\Delta A\) is the difference in absorbance between the sample and the blank, \(b\) is the length of the cell (cm), \(V\) is the sample volume (50 mL) and \(f=0.42\) (sensitivity factor of 20,000/cm for the change of absorbance per mole of added ozone per litre).

2.4 Saturation kinetics of ozone in water

The ozone saturation time and concentration in the water were determined by injecting the gas (bubbling) at initial concentrations of 13.3 and 22.3 mg L\(^{-1}\) into a 1000 mL volume of deionized water. The effects of water temperature (8 °C and 25 °C) and pH (3.0 and 6.0, adjusted with glacial acetic acid) on the gas saturation were assessed. The ozone was injected and quantified after 0, 1, 2, 3, 5, 7, 15, 20, 30, 40 and 60 minutes. The experiment was carried out in quadruplicate using...
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a fully randomized design. The data on both saturation time and concentration were fitted to four mathematical models: sigmoidal (SIGM); segmented linear regression with plateau (LiRP), segmented quadratic regression with plateau (QRP); and segmented logarithmic with plateau (LgRP) (Table 1) to ascertain the best fit. The mathematical modelling was carried out using the nlstools package (Tools for nonlinear regression analysis), version 1.0-2. The coefficient of determination ($R^2$) and the residual standard error (SE) were calculated according to Equations 2 and 3.

$$R^2 = \frac{\sum_{i=1}^{N} (C_{\text{m}} - C_{\text{exp},i})^2 - \sum_{i=1}^{N} (C_{\text{exp}} - C_{\text{pre},i})^2}{\sum_{i=1}^{N} (C_{\text{m}} - C_{\text{exp}})^2}$$

(2)

$$SE = \sqrt{\frac{\sum_{i=1}^{N} (C_{\text{exp},i} - C_{\text{pre},i})^2}{N - n}}$$

(3)

where $C_{\text{m}}$ is the mean ozone concentration, $C_{\text{exp},i}$ is the ozone concentration in the i-th time interval, $C_{\text{pre},i}$ is the ozone concentration predicted by the model at the i-th time, $N$ is the number of experimental points and $n$ is the number of parameters in the model.

3 Results and discussion

Figure 1 presents the ozone levels determined during the water saturation process as a function of the gas exposure time under different temperature and pH conditions (8 °C and 25 °C; pH 3.0 and 6.0) and gas injection concentrations ($C$) (13.3 and 22.3 mg L$^{-1}$).

The SE and $R^2$ values of the regression models (SIGM, LiRP, QRP and LgRP) are reported in Table 2. The fits of all the models were considered good, with $R^2$ values ranging from 87.95% to 99.47% and low SE values. However, of the four mathematical models, the segmented regression models with plateau better represented the behaviour of the ozone concentration as a function of time (higher $R^2$ and lower SE values) than the sigmoidal model. In addition, by using the segmented

![Figure 1. Saturation kinetics of ozone in water injected at rates of 13.3 mg L$^{-1}$ (a) and 22.3 mg L$^{-1}$ (b). ■ 25 °C and pH 6.0; ▲ 25 °C and pH 3.0; ▼ 8 °C and pH 3.0; ● 8 °C and pH 6.0.](http://bjft.ital.sp.gov.br)
regression models it was possible to calculate the ozone saturation time and concentration in the water.

The ozone gas concentration in the aqueous medium increased with longer exposure time (Figure 1). The treatments starting from a C value of 13.3 mg L⁻¹ were best represented by the LgRP regression model in the majority of cases, while for the treatments with a C value of 22.3 mg L⁻¹, the QRP regression showed the best fits (Table 2).

Table 3 reports the saturation times (t) and saturation concentrations (C) for the treatments with the two gas injection levels. At the injection concentration of 13.3 mg L⁻¹, the t values were near each other for all treatments, varying from 16.44 min to 17.70 min, while the C values ranged from 3.51 to 4.50 mg L⁻¹, and the highest ozone level was obtained at the lowest temperature (8 °C) and lowest pH value (3.0). This finding was in agreement with previous reports in the literature (KUNZ et al., 1999; JUNG et al., 2017).

The temperature and pH had an important effect on the ozone concentration in the water. As observed by Chitrakorn (2008), this effect may be related to the different rates of gas decomposition in different media, since the decomposition rate of the gas increases with increasing temperature and pH value of the medium. At pH values above 8.0, ozone is rapidly decomposed due to the presence of hydroxyl ions (JUNG et al., 2017). Therefore, the higher the temperature and pH value, the lower the half-life of the gas. Once incorporated in the liquid, the ozone must remain as such for a certain period of time to achieve its oxidizing effect, but its half-life is generally shorter than this requirement (KHADRE et al., 2001), and hence the control of the temperature and pH value is essential in order to extend the half-life.
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Table 3. Saturation times and concentrations and the C/C ratios at injection concentrations of 13.3 and 22.3 mg L\(^{-1}\).

<table>
<thead>
<tr>
<th>(C_0) (mg L(^{-1}))</th>
<th>Treatment</th>
<th>(t_{sat}) (min)</th>
<th>(C_{sat}) (mg L(^{-1}))</th>
<th>(C_{sat}/C_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3 mg L(^{-1})</td>
<td>25 °C and pH 6.0</td>
<td>16.44</td>
<td>3.5131</td>
<td>0.2641</td>
</tr>
<tr>
<td></td>
<td>25 °C and pH 3.0</td>
<td>16.96</td>
<td>4.1449</td>
<td>0.3116</td>
</tr>
<tr>
<td></td>
<td>8 °C and pH 6.0</td>
<td>16.93</td>
<td>3.9898</td>
<td>0.3000</td>
</tr>
<tr>
<td></td>
<td>8 °C and pH 3.0</td>
<td>17.70</td>
<td>4.5012</td>
<td>0.3384</td>
</tr>
<tr>
<td>22.3 mg L(^{-1})</td>
<td>25 °C and pH 6.0</td>
<td>27.94</td>
<td>5.2618</td>
<td>0.2361</td>
</tr>
<tr>
<td></td>
<td>25 °C and pH 3.0</td>
<td>15.57</td>
<td>6.0279</td>
<td>0.2703</td>
</tr>
<tr>
<td></td>
<td>8 °C and pH 6.0</td>
<td>26.04</td>
<td>7.8178</td>
<td>0.3506</td>
</tr>
<tr>
<td></td>
<td>8 °C and pH 3.0</td>
<td>19.03</td>
<td>8.0357</td>
<td>0.3603</td>
</tr>
</tbody>
</table>

\(C_{sat}\): saturation concentration (mg L\(^{-1}\)); \(C_0\): initial injection concentration (mg L\(^{-1}\)); \(t_{sat}\): saturation time (min).

Although it was observed that the greatest \(O_3\) concentration retained occurred at the lowest pH value, according to Di Bernardo and Dantas (2005), this factor may not have a direct influence on the efficiency of the disinfection process of the gas. The reason given by those authors for this suggestion was that at higher pH values, the formation of hydroxyl radicals occurs, which have strong oxidation power. Conversely, at values below neutral pH, the disinfection efficiency can be attributed to molecular ozone. In other words, in an acidic medium, the oxidation will mainly operate via molecular ozone, called the direct reaction. In contrast, in an alkaline medium, the oxidation will be predominantly via hydroxyl radicals, called the indirect reaction (ASSALIN; DURÁN, 2007). However, according to Jung et al. (2017), if the ozone degradation is very fast, the residual ozone concentration will always be low, causing a reduction in the Ct value (disinfectant concentration \(\times\) contact time) required for disinfection, thus affecting the efficiency of the process.

In the present study, when \(C\) was 13.3 mg L\(^{-1}\), the \(C\) value at pH=3.0 and T=25 °C was lower than that obtained by Kunz et al. (1999). These authors injected 14.96 mg of ozone L\(^{-1}\) into deionized water at 26 °C and pH 2.0 and found a saturation concentration of 5.75 mg L\(^{-1}\). This can be explained by the difference in pH between the two studies.

Further evidence of the great instability of ozone is provided by the large difference between the injected gas content and the saturation concentration. At a \(C\) value of 13.3 mg L\(^{-1}\), only 26% to 34% of the injected ozone was quantified in the water. The lowest value occurred with the highest temperature (25 °C) and the highest pH (6.0). It is likely that under conditions where the ozone decomposition is faster (high pH and temperature), the decomposition rate was predominant in relation to the injection concentration, thus resulting in the observed values.

This difference between \(C\) and \(C\) was also found in other studies. Santos et al. (2016) applied 10.13 mg L\(^{-1}\) of ozone to water and the residual saturation concentration was 5.0075 mg L\(^{-1}\), corresponding to approximately 50% of the concentration initially injected. Silva et al. (2011) obtained saturation concentration values between 42% and 45% of the injected concentration.

Besides the effect of self-decomposition, the low solubility of ozone in water can also explain the large difference between \(C\) and \(C\) (DI BERNARDO; DANTAS, 2005). Ozone is only partially soluble in water, and as is true for the majority of gases, its solubility increases as the temperature decreases or the mixture is pressurized (Henry’s Law). For this reason, according to the authors, the concentrations of dissolved ozone do not generally exceed 5 ppm, since the treatments are normally carried out at atmospheric pressure and near room temperature.

When a \(C\) value of 22.3 mg L\(^{-1}\) was used, the saturation times increased from 15.57 min to 27.94 min, and the highest \(O_3\) level (8.03 mg L\(^{-1}\)) was also obtained at the lowest temperature (8 °C) and lowest pH value (3.0). The values for \(C\) were about 24% and 36% of the injected concentration.

Both \(t\) and \(C\) depended on the initial gas concentration. The greater the \(C\) value, the longer the saturation time and the higher the ozone concentration in the water. The \(C\) at 8 °C, pH 3.0 and \(C\) 22.3 mg L\(^{-1}\) was about 80% higher than at \(C\) value of 13.3 mg L\(^{-1}\). Other authors have also determined the saturation time and concentration of ozone by using different initial gas concentrations. As verified in the present work, Roberto et al. (2016) found that the \(C\) increased when the initial ozone concentration increased. In relation to the saturation time, Silva et al. (2011) also observed no reduction in \(t\) when the ozone initial concentration was increased.

\section*{4 Conclusion}

The ozone saturation concentration in deionized water increased as the temperature and pH value of the medium decreased and as the initial ozone concentration increased. At 8 °C and pH 3.0, the saturation times were 17.70 min and 19.03 min and the saturation concentrations...
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were 4.50 and 8.03 mg L⁻¹ for initial concentrations of 13.3 and 22.3 mg L⁻¹, respectively. This higher ozone content may result in greater decontamination efficiency of the food products washed with this water.

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