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**Title****Kinetic modeling of advanced starch oxidation with ozone in basic solutions****Authors**

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Starch; ozone; kinetic model; advanced oxidation process; semi-batch reactor

## Abstract

The growing use of ozone ( $O_3$ ) in the last years to clean and enhance the physicochemical properties of starches, widely used as additives in food, beverage, and pharmaceutical industries, calls for a better understanding of their oxidation process. High pH, however, decomposes  $O_3$  rapidly, forming highly-oxidant radicals, thus increasing the complexity of the reaction system. In this study, a kinetic model for the ozonation reaction of starch in an alkaline medium was developed and experimentally validated. Firstly, the concentration of hydroxyl radicals ( $\bullet OH$ ) over the reaction time is evaluated through the degradation of pCBA (a probe compound) to later evaluate and model the oxidation process of starch based on Chemical Oxygen Demand (COD) measurements.

By using a semi-batch reactor containing alkaline solutions at pH=13, different  $O_3$  concentrations (0-42.30 g/Nm<sup>3</sup>) and temperatures (20-60°C), a pseudo first-order kinetic model was proposed to model the pCBA-ozone reaction. This model estimates the  $\bullet OH$  formation, being [ $\bullet OH$ ] constant and proportional to the  $O_3$  continuous dose. Therefore, under the conditions studied,  $\bullet OH$  is a non-limiting reactant independent of temperature. The activation energy was estimated at 14.2±2.1 and 14.5±0.6 KJ/mol for 21.15 and 42.30 g $O_3$ /Nm<sup>3</sup>, respectively. Then, COD data were used to propose a kinetic model for ozone-starch oxidation in alkaline media, where besides  $O_3$  concentration and temperature, starch concentration (600-1700 mg/L) was also varied. According to the results, higher temperatures and longer reaction times resulted in a greater COD reduction, being it more pronounced at lower initial starch concentration. The activation energy of the ozone radicals-starch reaction was estimated at 8.1±0.4 KJ/mol, being significantly lower than those reported for the reaction between pCBA and  $\bullet OH$ .

## Introduction.

The application of ozone ( $O_3$ ), a powerful oxidant, has considerably increased in recent years. It is commonly used to remove pollutants from effluents (Wang and Bai, 2017) and purify water (Brodowska, Nowak, and Smigielski, 2018), but also to clean and disinfect food processing lines (Ávila-Sierra et al., 2020, 2021; Medina-Rodríguez et al., 2020) and other surfaces and environments, especially after the advent of the COVID-19 pandemic (Epelle et al., 2023), to preserve foods (Pandiselvam et al., 2019a) or eliminate odors (Pandiselvam et al., 2019b). As a disinfectant, ozone has several advantages over traditional disinfectants like chlorine (Pascual, Llorca, and Canut, 2007) since  $O_3$  decomposes quickly into oxygen without leaving residues (Castanha, Matta Junior, and Augusto, 2017; Catal and Ibanoglu, 2014), preserving foods, and avoiding the presence of contaminants in process effluents. As a cleaning agent,  $O_3$  is effective in removing fatty (Chang, Chung, and Han, 2001; Jurado-Alameda et al., 2012; Vicaria et al., 2016), proteinaceous (Jurado-Alameda et al., 2014) and starchy deposits (Ávila-Sierra et al., 2020) adhered to hard surfaces. The cleaning of these deposits commonly requires high temperatures and/or strong alkaline formulations (Vicaria et al., 2017). Recently, Ávila-Sierra et al. (2020, 2021) studied the removal of starch from stainless steel using an advanced ozone-based oxidation process in high alkaline media, where the formation of hydroxyl radicals seems to enhance both the cleaning performance and the biodegradability of the cleaning wastewaters, reducing their toxicity and Chemical Oxygen Demand (COD); however a kinetic study on the starch degradation with the ozone under such conditions was not performed and, as far as we know, there is no literature about it.

In the last years, the use of  $O_3$  has also gained considerable popularity for enhancing the physicochemical properties of starches (Sivaranjania et al., 2021; Maniglia et al., 2021) as they are widely used as additives in food, beverage, and pharmaceutical industries. Previous

works have studied the effect of ozone in starch-based solutions at different pH (3-10), temperatures, and reaction times, being ozone able to modify the carboxyl content, swelling power and water solubility of starches (Chan, Bhat, and Karim, 2009; Gozé et al., 2016; Maniglia et al., 2019); their carboxyl content increased at high pH, while their water solubility decreased (Pudjihastuti, Handayani, and Sumardiono, 2018). At 25°C, Klein et al. (2014) also evaluated the pasting properties and surface morphology of ozone-oxidized starches under different pH (3.5-9.5), where higher both pH and ozone concentration favored cross-linking between the depolymerized starch molecules. Clearly, these variations in starch properties show that ozone is an effective oxidizing agent for starches. However, there is very little research on the ozonation of starch at high temperatures in high alkaline media, where O<sub>3</sub> is quickly decomposed to yield radicals with stronger oxidizing power (Brodowska, Nowak, and Smigielski, 2018; Hien et al., 2020).

The oxidative action of ozone comes from two mechanisms: direct reactions with O<sub>3</sub>, or indirect reactions with hydroxyl radicals (Wang and Bai, 2017; Ghuge and Saroha, 2018; Hien et al., 2020). Hoigné (1997) and Elovitz & Von Gunten (1999) defined the hydroxyl radical ( $\bullet\text{OH}$ ) as a highly reactive and nonspecific oxidant formed from the O<sub>3</sub> decomposition. Hydroxyl radicals have higher oxidizing power than ozone molecules, with a standard redox potential of 2.8 V versus 2.07 V (Boczkaj and Fernandes, 2017). Elovitz and von Gunten (1999) defined  $R_{ct}$  as the ratio  $\bullet\text{OH}/\text{O}_3$  that increases with pH, reaching very high values around pH=9, suggesting that the O<sub>3</sub> concentration is very low compared to the  $\bullet\text{OH}$  concentration at high pHs (Elovitz, von Gunten and Kaiser, 2000). The direct reaction of ozone with other substances is selective, whilst hydroxyl radicals show faster non-selective reactions, attacking both organic and inorganic compounds (Boczkaj and Fernandes, 2017). Due to the selectivity criterion, incomplete mineralization of compounds commonly occurs in direct ozone reactions, whereas hydroxyl radicals can cause complete mineralization (Ghugue

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3 and Saroha, 2018; Boczkaj and Fernandes, 2017; Nawrocki and Kasprzyk-Hordern, 2010). As  
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5 a result of the improved performance, advanced oxidation processes, AOPs, have become  
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7 increasingly popular for wastewater treatment (Ghuge & Saroha, 2018) as they increase  
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9 degradation capacity, reduce operational time and costs, and allow the elimination of  
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11 recalcitrant pollutants (Ghuge and Saroha, 2018; Hien et al., 2020; Kasprzyk-Hordern, Ziolek,  
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13 and Nawrocki, 2003). Among all the AOPs, Fenton/photo-Fenton processes, ozonation, wet  
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15 air oxidation (WAO), electrocoagulation and photocatalytic oxidation are extensively used  
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17 (Ghuge and Saroha, 2018). Considering ozone-based AOPs, hydroxyl radicals can be  
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19 produced by using alkaline pH, UV, H<sub>2</sub>O<sub>2</sub>, catalytic and photocatalytic ozonation, non-  
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21 thermal DBD plasma and ozonation combination with Fenton and photo-Fenton (Beltrán,  
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23 2004; Hama Aziz et al., 2018; Hama Aziz, 2019 Hien et al., 2020).

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28 **Therefore, there is** a current need to better understand the oxidation process of starches  
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30 using ozone at high temperatures in alkaline conditions to improve its application for starch  
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32 modification and industrial cleaning. Since ozone chemistry is complex, measuring the  
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34 concentration of ozone and radicals may require indirect analytical methods using probe  
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36 compounds such as p-chlorobenzoic acid (pCBA) (Elovitz and von Gunten, 1999). In this  
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38 study, COD monitoring was used for investigating the kinetic of the starch-ozone reaction **in**  
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40 **alkaline media, where** the generation of hydroxyl radicals was assessed using pCBA. **The**  
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42 **influence of** ozone concentration and temperature were **evaluated** during ozonation **using a**  
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44 **semi-batch reactor.**  
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## Materials and methods.

### *Materials.*

Corn starch (Maizena®, 87.91 % cornstarch, 11,50 %, moisture, 0.29% fat, 0.3% protein) and 4-Chlorobenzoic acid 99% (pCBA; supplied by Across Organics™) were used in this work.

### *Ozonation Device.*

A semi-batch reactor (**Figure 1**) with an integrated ozonation system was used for ozonation experiments. The device allows the modification of ozone concentration, solution type, and temperature. It is composed by a jacketed tank (1L of capacity), a peristaltic pump (Heidolph, model 5006) supplying a 60L/h recirculation flow, a thermostatically controlled bath (P-Selecta, model Ultraterm), and a gas diffuser. Ozone was generated *in situ* from an oxygen stream using an ozone generator (Peripherals COM-AD, Anseros Germany). By recirculating the solution, a constant composition is maintained. The ozone concentration in the ozone-oxygen flow was determined for each assay by an analyzer (Anseros, Ozomat GM-6000-PRO, Germany). The volumetric flow of the ozone-oxygen gas flow was 40 NL/h. The residual ozone was eliminated passing through washing flasks with 5% KI aqueous solution before being released into the atmosphere.

### *Ozonation of Starch Solutions.*

Ozonation of aqueous alkaline starch solutions (600-1700 mg starch/L of NaOH solution pH13) was carried out in a semi-batch reactor for 120 minutes at different temperatures, ranging between 40–60°C, and an ozone concentration of 42.30 g/Nm<sup>3</sup>, applying ozone dosages between 0-0.47 g O<sub>3</sub>/L. The thermostatically controlled semi-batch reactor was filled with 1.2 L of the starch solution. Then, an oxygen current **was** introduced for 20 minutes, before ozonation began. Samples of 1 mL were extracted periodically from

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3 the tank. The residual ozone of the samples was eliminated by adding 0.2 mL of 0.2 g/L  
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5  $\text{Na}_2\text{SO}_3$  aqueous solution. At least three repeats were performed per experimental run.

### 6 7 ***Evaluation of Chemical Oxygen Demand (COD).***

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10 The COD value was analyzed according to Ávila-Sierra et al. (2020). Solution samples  
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12 of 1.5 mL were extracted periodically and added to 1.5 mL of distilled water and mixed with  
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14 the reagent solution. The reagent solution was formed by mixing 0.08 g  $\text{Hg}_2\text{SO}_4$  (Panreac), 4  
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16 mL of sulfuric acid reagent (10 g/L  $\text{Ag}_2\text{SO}_4$  dissolved in  $\text{H}_2\text{SO}_4$ ) and 1 mL of 0.5 N  $\text{K}_2\text{Cr}_2\text{O}_7$   
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18 aqueous solution. The vials were stirred and placed into a digester (150°C, 2h). After  
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20 digestion, the vials were cooled down to room temperature. Absorbance was measured at 620  
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22 nm. COD measurements were obtained by a calibration curve at different concentrations of a  
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24 0.85 g/L  $\text{KC}_8\text{H}_5\text{O}_4$  solution (Panreac, Spain).

### 25 26 27 ***Evaluation of Oxidizing Power: pCBA Method.***

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30 The measure of radical concentration in ozonated solutions was based on the pCBA  
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32 method described in Elovitz and von Gunten (1999). A 10 mg/L of pCBA in NaOH aqueous  
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34 solution (pH=13) was introduced in the semi-batch reactor, thermostatted at the temperature  
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36 of interest. Then, an oxygen current was introduced in the pCBA solution for 20 min, before  
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38 ozonation experiments. The variables analyzed were ozone concentration (0.00, 21.15 and  
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40 42.30 g/Nm<sup>3</sup>, corresponding to an ozone feed rate of 0, 0.846 and 1.692 g/h respectively)  
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42 obtaining applied ozone dosages between 0-0.47 g  $\text{O}_3$ /L, temperature (20, 40, 50, 60°C), and  
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44 time (0-80 min). To evaluate the radical concentration in the ozonated alkaline solution,  
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46 samples of 5 mL extracted periodically from the reactor and the pCBA concentration was  
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48 measured as a function of time by spectrophotometry (Cary 100 Bio UV–Visible, Varian) at  
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50 234 nm, using a calibration line (0-0.01 g pCBA/L). Experiments were performed at least  
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56 three times.

## Results and discussion.

As highlighted in the introduction, a high pH causes ozone to decompose rapidly, forming radicals. As a function of ozonation time, the concentration of hydroxyl radicals was firstly evaluated through the degradation of pCBA. Then, the process of starch oxidation was modeled using Chemical Oxygen Demand (COD) data.

### *Evaluation of the Concentration of Hydroxyl Radicals in Alkaline Medium.*

Figure 2 shows the  $[pCBA]/[pCBA]_0$  profiles as a function of both time and temperature at two ozone concentrations, 21.15 g/Nm<sup>3</sup> (Figure 2.a) and 42.30 g/Nm<sup>3</sup> (Figure 2.b). With increasing time and temperature, the concentration of pCBA decreases, decreasing faster at high ozone concentration. Elovitz and von Gunten (1999) predicted the ozone concentration using a first-order kinetic model. However, measuring the concentration of the hydroxyl radicals is more complex as the reactivity of radicals towards the water matrix leads to a minimal steady-state concentration, typically  $<10^{-12}$  M. Notwithstanding, the  $\bullet OH$  concentration can be measured indirectly by an  $\bullet OH$ -probe compound such as p-chlorobenzoic acid (pCBA), which is used due to its low reactivity with ozone ( $k_{O_3/pCBA} \leq 0.15$  M<sup>-1</sup>s<sup>-1</sup>) and rapid reaction with  $\bullet OH$  radicals ( $k_{\bullet OH/pCBA} = 5 \cdot 10^9$  M<sup>-1</sup>s<sup>-1</sup>) (Elovitz and von Gunten, 1999). Therefore, considering that ozone is mainly transformed into hydroxyl radicals ( $\bullet OH$ ) at high pH (Boczkaj and Fernandes, 2017), the reaction scheme for ozone decomposition and subsequent hydroxyl radical reaction with pCBA could be defined as:



where  $k_{pCBA}$  is the individual rate constant for the  $\bullet OH$ -pCBA reaction. Then, the kinetic model for this reaction is defined as:

$$-\frac{d[pCBA]}{dt} = k_{pCBA} [pCBA] [\bullet OH] \quad (\text{Eq.3})$$

where  $t$  is the reaction time.



Elovitz, von Gunten, and Kaiser (2000) found that for each temperature and ozone dose, the ratio  $[\bullet\text{OH}]/[\text{O}_3]$  remained constant over time, where  $\bullet\text{OH}$  exposure was unaffected by either reaction temperature or pH, while  $\text{O}_3$  exposure changed drastically, decreasing it as both temperature and pH increased. The fast  $\text{O}_3$  decomposition at high pH (Gounden, Singh, and Jonnalagadda, 2019) along with uninterrupted  $\text{O}_3$  gas flow into the alkaline solution leads to a continuous formation of hydroxyl radicals. Considering that hydroxyl radicals steady-state concentrations are usually very low, typically  $<10^{-12}$  M, it could be initially assumed that  $[\bullet\text{OH}]$  is constant for a fixed ozone continuous dose. Then, the integration of (Eq. 3) gives:

$$\ln \frac{[\text{pCBA}]}{[\text{pCBA}]_0} = -k_{\text{pCBA}} [\bullet\text{OH}] t \quad (\text{Eq.4})$$

Applying (Eq.4) to the experimental results,  $\ln([\text{pCBA}]/[\text{pCBA}]_0)$  shows a linear dependence over time as a function of both temperature and the initial  $\text{O}_3$  concentration ( $r^2$  values between 0.987-0.998; **Table 1**), suggesting that  $k_{\text{pCBA}} [\bullet\text{OH}]$ , and therefore  $[\bullet\text{OH}]$ , remains constant over the entire reaction for each temperature and  $\text{O}_3$  concentration assayed, being  $[\bullet\text{OH}]$  a non-limiting factor. Then, for each ozone dose evaluated, it is possible to estimate the activation energy ( $E_{\text{a1}}$ ) and  $k_0_{\text{pCBA}} [\bullet\text{OH}]$  for the  $\bullet\text{OH}$ -pCBA reaction, fitting the data to the Arrhenius equation using (Eq.5):

$$\ln(k_{\text{pCBA}} [\bullet\text{OH}]) = \ln(k_0_{\text{pCBA}} [\bullet\text{OH}]) - E_{\text{a1}}/R T \quad (\text{Eq.5})$$

$k_{\text{pCBA}} [\bullet\text{OH}]$  vs.  $1/T$  fits well (**Figure 3**), with  $r^2$  values between 0.957-0.998. The use of the parameters calculated reproduces the experimental results in a suitable form as shown in **Figure 2**.

The  $E_{\text{a1}}$  values obtained for each ozone dose used are similar ( $14.2 \pm 2.1$  and  $14.5 \pm 0.6$  KJ/mol for 21.15 and 42.30 g  $\text{O}_3/\text{Nm}^3$  respectively), finding analogous values to the results reported by Elovitz, von Gunten, and Kaiser (2000), where  $\bullet\text{OH}$  reactions activation energies varied between 5 and 10 KJ/mol. According to **Figure 3** and (Eq.5),  $k_0_{\text{pCBA}} [\bullet\text{OH}]$  is

independent of temperature but depends on the gas ozone concentration.  $k_{0_{\text{pCBA}}} [\bullet\text{OH}]$  is directly proportional to the concentration of ozone in the gas flow (**Figure 4**), according to (Eq.6).

$$k_{0_{\text{pCBA}}} [\bullet\text{OH}] = 28.9 [\text{O}_3] \quad r^2=0.9998 \quad (\text{Eq.6})$$

Therefore, under the experimental conditions used,  $[\bullet\text{OH}]$  is constant and proportional to the ozone dose, as it was previously assumed for (Eq. 4) deduction, and independent of temperature. In fact, a similar increase in the production of hydroxyl radicals with a raising ozone dose has been previously described by Ghuge (2018).

### ***Kinetic Modeling of Starch Oxidation with Ozone in Basic Solutions.***

**Modeling** the kinetic of ozonation of polysaccharides is complex. Previous research proposed a kinetic model to explain the depolymerization of  $\kappa$ -carrageenan by ozone using viscosity changes (Prasetyaningrum, Ratnawati, and Jos, 2017). In the present work, a model for the ozone-starch reaction in alkaline solution **at high pH** was proposed based on the COD measurements, being  $[\text{St}]$  (g/L) the starch concentration as a function of time,  $[\text{St}]_0$  (g/L) the initial starch concentration, and  $k_{\text{St}}$  the kinetic constant for the reaction:



$$-\frac{d[\text{St}]}{dt} = k_{\text{St}} [\bullet\text{OH}] [\text{St}]^\alpha \quad (\text{Eq.8})$$

$$\text{COD}(\text{mg O}_2/\text{L}) = 1.116 [\text{St}] (\text{mg/L}) \quad (\text{Eq.9})$$

The concentration of starch is proportional to the COD, allowing to evaluate simultaneously the pollutant load of the chemical solutions over time.

As previously demonstrated in section 3.1, for each  $\text{O}_3$  dose,  $[\bullet\text{OH}]$  was constant throughout the entire reaction at  $\text{pH}=13$ , being independent of temperature. Then, substituting (Eq.9) in (Eq.8) and considering  $\alpha=1$ , its integration results in:

$$-\ln \frac{\text{COD}}{\text{COD}_0} = k_{\text{St}} [\bullet\text{OH}] t \quad (\text{Eq.10})$$

If  $\alpha$  is not equal to 1, then:

$$\frac{\text{COD}}{\text{COD}_0} = \left[ 1 + \left( \frac{1.116}{\text{COD}_0} \right)^{1-\alpha} (\alpha - 1) k_{\text{St}} [\bullet\text{OH}] t \right]^{\frac{1}{1-\alpha}} \quad (\text{Eq.11})$$

Applying Eq.(11) to the experimental results, the best fitting was obtained at  $\alpha=0.3$  (**Figure 5**). The COD/COD<sub>0</sub> ratio decreased as both ozonation time and temperature increased, being this reduction more pronounced at low initial starch concentrations. According to the kinetic model proposed,  $k_{\text{St}} [\bullet\text{OH}]$  remains constant over the entire reaction at each temperature and starch concentration. Then,  $k_{\text{St}} [\bullet\text{OH}]$  (**Table 2**) could be fitted to the Arrhenius equation:

$$\ln (k_{\text{St}} [\bullet\text{OH}]) = \ln (k_{\text{St}0} [\bullet\text{OH}]) - E_{a2}/R T \quad (\text{Eq.12})$$

Applying Eq.(12) ( $r^2=0.993$ ),  $E_{a2}$  and  $k_{\text{St}0} [\bullet\text{OH}]$  were determined, being  $8.1 \pm 0.4$  KJ/mol and  $780.7 \pm 1.1$  (L/mg St)<sup>-0.7</sup> h<sup>-1</sup> respectively. These parameters fit the experimental results in a suitable form as shown in **Figures 5**. Comparing both models,  $\bullet\text{OH}$ -starch and  $\bullet\text{OH}$ -pCBA, the  $E_{a2}$  values estimated for the reaction between starch and  $\bullet\text{OH}$  were lower than those estimated for the  $\bullet\text{OH}$ -pCBA reaction.

Previous works have shown that ozone can modify the composition and structure of starch, given its ability to break the glucosidic bonds that bind glucose molecules, causing starch depolymerization, and oxidizing its hydroxyl and carbonyl groups to carboxyl groups (Castanha, Matta Junior, and Augusto, 2017; Catal and Ibanoglu, 2014). Similarly, it has been observed how hydroxyl radicals react with oligosaccharides and polysaccharides, being capable of breaking glucosidic bonds (Dai et al., 2017). The glucose oxidation by ozone generates different products, including acidic sugars, such as uronic (glucuronic acid), aldonic (gluconic acid) and aldaric acids (glucaric acid). The subsequent oxidation of these substances gives rise to other organic acids and compounds with fewer carbon atoms, the latter arising from their decarboxylation causing the release of CO<sub>2</sub> (Marcq et al., 2009). Analogously, successive oxidations of starch by hydroxyl radicals during its ozonation at alkaline pH are

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3 foreseeable and would be justified by the observed reduction of COD (**Figure 5**), being this  
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5 COD reduction also found in previous works on cleaning of starchy deposits (Ávila-Sierra et  
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7 al., 2020; 2021). Likewise, these oxidations and depolymerizations may change the properties  
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9 of starch after ozonation, e.g., gelatinization, pasting, retrogradation and solubility (Catal and  
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11 Ibanoglu, 2014), likely affecting the cleaning process of starches.  
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## Conclusions.

In this work, the concentration of hydroxyl radicals ( $\bullet\text{OH}$ ) over time is firstly evaluated through the degradation of pCBA (a probe compound) to later evaluate and model the ozonation process of starch in alkaline solutions based on Chemical Oxygen Demand (COD) measurements.

By using a semi-batch reactor containing alkaline solutions at high pH (pH=13), different  $\text{O}_3$  concentrations (0-42.30 g/Nm<sup>3</sup>) and temperatures (20-60°C), a pseudo first-order kinetic model was proposed to model the pCBA-ozone reaction. This model estimates the  $\bullet\text{OH}$  formation, being  $[\bullet\text{OH}]$  constant and proportional to the  $\text{O}_3$  continuous dose. Therefore, and under the conditions studied,  $\bullet\text{OH}$  is a non-limiting reactant independent of temperature. The activation energy was estimated at  $14.2\pm 2.1$  and  $14.5\pm 0.6$  KJ/mol for 21.15 and 42.30 g  $\text{O}_3/\text{Nm}^3$ , respectively. Then, a kinetic model for ozone-starch oxidation in alkaline media was proposed based on COD data. The best fit was obtained at  $\alpha=0.3$ . According to the results, higher temperatures and longer reaction times resulted in a greater reduction of COD, which was more pronounced at lower initial starch concentration. The activation energy of the ozone-starch reaction was estimated at  $8.1\pm 0.4$  KJ/mol, being significantly lower than those reported for the reaction between pCBA and  $\bullet\text{OH}$ .

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## References.

- Ávila-Sierra, A., Vicaria, J.M., Jurado-Alameda, E., and J.F. Martínez-Gallegos. 2020. "Removal of food soil by ozone-based oxidation processes: Cleaning and wastewater degradation in a single step." *Journal of Food Engineering* 272:109803. doi: 10.1016/j.jfoodeng.2019.109803.
- Avila-Sierra, A., Vicaria, J.M., Lechuga, M., Martínez-Gallegos, J.F., Olivares-Arias, V., Medina-Rodríguez, A.C., Jiménez-Robles, R., Jurado-Alameda, E. 2021. "Insights into the optimisation of the Clean-In-Place technique: Cleaning, disinfection, and reduced environmental impact using ozone-based formulations". *Food and Bioproducts Processing* 129: 124–133. doi: 10.1016/j.fbp.2021.08.003.
- F.J. Beltrán. 2004. "Ozone Reaction Kinetics for Water & Wastewater Systems." Lewis Publishers (Eds.), pp. 14-26. CRC Press, Boca Raton, USA
- Boczkaj, G., and A.Fernandes. 2017. "Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review." *Chemical Engineering Journal* 320: 608-633. doi: 10.1016/j.cej.2017.03.084.
- Brodowska, A.J., Nowak, A., and K. Smigielski. 2018. "Ozone in the food industry: Principles of ozone treatment, mechanisms of action, and applications: An overview." *Critical Reviews in Food Science and Nutrition* 58: 2176-2201. doi: 10.1080/10408398.2017.1308313.
- Castanha, N., Matta Junior, M.D., and P.E.D. Augusto. 2017. "Potato starch modification using the ozone technology." *Food Hydrocolloids* 66: 343-356. doi: 10.1016/j.foodhyd.2016.12.001.
- Castanha, N., Santos, D.N., Cunha, R.L., and P.E.D. Augusto. 2019. "Properties and possible applications of ozone-modified potato starch." *Food Research. International* 116: 1192-1201. doi: 10.1016/j.foodres.2018.09.064.

1  
2  
3 Catal, H., and S. Ibanoglu. 2014. "Effect of aqueous ozonation on the pasting, flow and  
4 gelatinization properties of wheat starch." *LWT-Food Science and Technology* 59: 577-582.  
5  
6 doi: 10.1016/j.lwt.2014.04.025.  
7

8  
9  
10 Chan, H.T., Bhat, R., and A.A. Karim. 2009. "Physicochemical and Functional Properties  
11 of Ozone-Oxidized Starch." *Journal of Agricultural Food Chemistry* 57: 5965–5970. doi:  
12 10.1021/jf9008789.  
13  
14

15  
16  
17 Chang, I.-S., Chung, C.-M., and S.-H. Han. 2001. "Treatment of oily wastewater by  
18 ultrafiltration and ozone." *Desalination* 133: 225-232. doi: 10.1016/S0011-9164(01)00103-  
19 5.  
20  
21

22  
23  
24 Dai, Y., Shao, C., Piao, Y., Hu, H., Lu, K., Zhang, T., Zhang, X., Jia, S., Wang, M., and S.  
25 Man. 2017. "The mechanism for cleavage of three typical glucosidic bonds induced by  
26 hydroxyl free radical." *Carbohydrate Polymers*. 178: 34-40. doi:  
27 10.1016/j.carbpol.2017.09.016.  
28  
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30  
31  
32 Elovitz, M.S., and U. von Gunten. 1999. "Hydroxyl Radical/Ozone Ratios During  
33 Ozonation Processes. I. The Rct Concept." *Ozone-Science Engineering* 21: 239-260. doi:  
34 10.1080/01919519908547239.  
35  
36

37  
38  
39 Elovitz, M.S., von Gunten, U., and H. Kaiser. 2000. "Hydroxyl Radical/Ozone Ratios  
40 During Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM  
41 Properties." *Ozone-Science Engineering*. 22: 123-150. doi: 10.1080/01919510008547216.  
42  
43

44  
45  
46 Gounden, A.N., Singh, S., and Jonnalagadda, S.B. 2019. "Non-catalytic and catalytic  
47 ozonation of simple halohydrins in water." *Journal of Environmental Chemical*  
48 *Engineering* 7(1): 102783. doi: 10.1016/j.jece.2018.11.028.  
49  
50

51  
52  
53 Epelle, E.I., Macfarlane, A., Cusack, M., Burns, A., Okolie, J.A., Mackay, W., Rateb, M.  
54 and Yaseen, M. 2023. "Ozone application in different industries: A review of recent  
55 developments". *Chemical Engineering Journal* 454(2): 140188. doi:  
56  
57  
58  
59  
60

1  
2  
3 [10.1016/j.cej.2022.140188](https://doi.org/10.1016/j.cej.2022.140188).

4  
5  
6 Gozé, P., Rhazi, L., Paus, A., and T. Aussenac. 2016. "Starch characterization after ozone  
7 treatment of wheat grains." *Journal of Cereal Science* 70: 207-213. doi:  
8 10.1016/j.jcs.2016.06.007.  
9

10  
11  
12 Ghuge, S.P., Saroha, A.K. 2018. "Catalytic ozonation for the treatment of synthetic and  
13 industrial effluents - Application of mesoporous materials: A review." *Journal of*  
14 *Environmental Management* 211: 83-102. doi: 10.1016/j.jenvman.2018.01.052.  
15  
16

17  
18  
19 Hama Aziz, K.H. (2019) "Application of different advanced oxidation processes for the  
20 removal of chloroacetic acids using a planar falling film reactor." *Chemosphere* 228: 377-  
21 383. doi: 10.1016/j.chemosphere.2019.04.160.  
22  
23

24  
25  
26 Hama Aziz, K.H., Mahyar, A., Miessner, H., Mueller, S., Kalass, D., Moeller, D.,  
27 Khorshid, I., Rashid, M.A.M. 2018. "Application of a planar falling film reactor for  
28 decomposition and mineralization of methylene blue in the aqueous media via ozonation,  
29 Fenton, photocatalysis and non-thermal plasma: A comparative study." *Process Safety and*  
30 *Environmental Protection* 113: 319-329. doi: 10.1016/j.psep.2017.11.005.  
31  
32

33  
34  
35 Hien, N.T., Nguyen, L.H., Van, H.T., Nguyen, T.D., Nguyen, T.H.V., Chu, T.H.H.,  
36 Nguyen, T.V., Trinh, V.T., Vu, X.H., Aziz, K.H.H. 2020. "Heterogeneous catalyst  
37 ozonation of Direct Black 22 from aqueous solution in the presence of metal slags  
38 originating from industrial solid wastes." *Separation and Purification Technology*. 233:  
39 115961. doi: 10.1016/j.seppur.2019.115961.  
40  
41

42  
43  
44 Hoigné, J. 1997. "Inter-calibration of OH radical sources and water quality parameters."  
45 *Water Science and Technology* 35: 1-8. doi: 10.2166/wst.1997.0072.  
46  
47

48  
49  
50 Jurado-Alameda, E., García-Roman, M., Altmajer-Vaz, D., and J.L. Jiménez-Pérez. 2012.  
51 "Assessment of the use of ozone for cleaning fatty soils in the food industry." *Journal of*  
52 *Food Engineering* 110: 44-52. doi: 10.1016/j.jfoodeng.2011.12.010.  
53  
54  
55  
56  
57  
58  
59  
60



- 1  
2  
3 Jurado-Alameda, E., Altmajer-Vaz, D., García-Román, M., and J.L. Jiménez-Pérez. 2014.  
4  
5 “Study of heat-denatured whey protein removal from stainless steel surfaces in clean-in-  
6  
7 place systems.” *International Dairy Journal* 38: 195-198. doi:  
8  
9 10.1016/j.idairyj.2014.01.006.  
10  
11  
12 Kasprzyk-Hordern, B., Ziolek, M., and J. Nawrocki. 2003 “Catalytic ozonation and  
13  
14 methods of enhancing molecular ozone reactions in water treatment.” *Applied Catalysis B-  
15  
16 Environmental*. 46: 639-669. doi: 10.1016/S0926-3373(03)00326-6.  
17  
18  
19 Klein, B., Vanier, N.L., Moomand, K., Pinto, V.Z., Colussi, R., Zavareze, E.R., and A.R.G.  
20  
21 Días. 2014. “Ozone oxidation of cassava starch in aqueous solution at different pH.” *Food  
22  
23 Chemistry* 155: 167–173. doi: 10.1016/j.foodchem.2014.01.058.  
24  
25  
26 Maniglia, B.C., Lima, D.C., Matta, M.D., Le-Bail, P., Le-Bail, A., and P.E.D., Augusto.  
27  
28 2019. “Hydrogels based on ozonated cassava starch: Effect of ozone processing and  
29  
30 gelatinization conditions on enhancing printability for 3D-printing applications.”  
31  
32 *International Journal of Biological Macromolecules* 138: 1087-1097. doi:  
33  
34 10.1016/j.ijbiomac.2019.07.124.  
35  
36  
37 Maniglia, B.C., Castanha, N., Rojas, M.L., and P.E.D. Augusto. 2021. “Emerging  
38  
39 technologies to enhance starch performance.” *Current Opinion in Food Science* 37: 26-36.  
40  
41 doi: 10.1016/j.cofs.2020.09.003.  
42  
43  
44 Marcq, O., Barbe, J.-M., Trichet, A., and R. Guillard. 2009. “Reaction pathways of glucose  
45  
46 oxidation by ozone under acidic conditions.” *Carbohydrate Research* 344: 1303-1310. doi:  
47  
48 10.1016/j.carres.2009.05.012.  
49  
50  
51 Medina-Rodríguez, A.C., Ávila-Sierra, A., Ariza, J.J., Guillamón, E., Baños-Arjona, A.,  
52  
53 Vicaria, J.M., and E. Jurado. 2020. “Clean-in-place disinfection of dual-species biofilm  
54  
55 (*Listeria* and *Pseudomonas*) by a green antibacterial product made from citrus extract,”  
56  
57 *Food Control* 118:107422. doi: 10.1016/j.foodcont.2020.107422.  
58  
59  
60

1  
2  
3 Nawrocki, J., and B. Kasprzyk-Hordern. 2010. "The efficiency and mechanisms of catalytic  
4 ozonation." *Applied Catalysis B-Environmental* 99: 27-42. doi:  
5  
6 10.1016/j.apcatb.2010.06.033.  
7  
8

9  
10 Pandiselvam, R., Manikantan, M.R., Divya, V., Ashokkumar, C., Kaavya, R., Kothakota,  
11 A., and S.V. Ramesh. 2019a. "Ozone: An Advanced Oxidation Technology for Starch  
12 Modification." *Ozone-Science Engineering* 41: 491-507. doi:  
13  
14 10.1080/01919512.2019.1577128.  
15  
16

17  
18 Pandiselvam, R., Subhashini, S., Banuu Priya, E.P., Kothakota, A., Ramesh, S.V., and S.  
19 Shahir. 2019b. "Ozone based food preservation: a promising green technology for enhanced  
20 food safety" *Ozone-Science Engineering* 41: 17-34. doi: 10.1080/01919512.2018.1490636.  
21  
22

23  
24 Pascual, A., Llorca, I., and A. Canut, 2007. "Use of ozone in food industries for reducing  
25 the environmental impact of cleaning and disinfection activities." *Trends Food Science and*  
26  
27  
28  
29  
30  
31  
32  
33  
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58  
59  
60

31  
32  
33 Prasetyaningrum, A., Ratnawati, R., and B. Jos. 2017. "Kinetics of Oxidative  
34 Depolymerization of  $\kappa$ -carrageenan by Ozone" *Bulletin of Chemical Reaction Engineering*  
35  
36  
37  
38  
39  
40  
41  
42  
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2  
3 Vicaria, J.M., Altmajer-Vaz, D., Luzón, G., Jiménez-Pérez, J.L., Moya-Ramírez, I., and E.  
4  
5 Jurado. 2016. "Experimental studies and modeling of a simplified CIP system using ozone  
6  
7 and linear alkylbenzenesulfonate." *Chemical Engineering Journal* 287: 130-138. doi:  
8  
9 10.1016/j.cej.2015.11.032.  
10  
11  
12 Vicaria, J.M., Jurado-Alameda, E., Herrera-Márquez, O., Olivares-Arias, V., and A. Ávila-  
13  
14 Sierra. 2017. "Analysis of different protocols for the cleaning of corn starch adhering to  
15  
16 stainless steel." *Journal of Cleaner Production* 168: 87-96. doi:  
17  
18 10.1016/j.jclepro.2017.08.232.  
19  
20  
21 Wang, J., and Z. Bai. 2014. "Fe-based catalysts for heterogeneous catalytic ozonation of  
22  
23 emerging contaminants in water and wastewater." *Chemical Engineering Journal* 312: 79-  
24  
25 98. doi: 10.1016/j.cej.2016.11.118.  
26  
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**Figures captions.**

**Figure 1.** Scheme of a semi-batch reactor with an integrated ozonation system. The device is composed of a (1) jacketed tank, (2) peristaltic pump, (3) thermostatically controlled bath and (4) gas diffusor.

**Figure 2** – Ozonation of pCBA solutions in semi-batch reactor. Influence of time and temperature. ● 20°C, ○ 40°C, ■ 50°C, □ 60°C. Ozone concentration: a) 21.15 g/Nm<sup>3</sup>, b) 42.30 g/Nm<sup>3</sup> Lines show the model proposed.

**Figure 3** – Dependence of  $k_{pCBA} [\cdot OH]$  with temperature. Ozone concentration in oxygen-ozone current: ■ 21.15 g/Nm<sup>3</sup>, □ 42.30 g/Nm<sup>3</sup>.

**Figure 4** – Dependence of  $k_{0pCBA} [\cdot OH]$  with ozone dose.

**Figure 5** – Ozonation of aqueous solutions of starch vs. temperature and time. pH=13. Starch concentration: ● 600 mg/L, ○ 1300 mg/L, ■ 1700 mg/L. (a) 40°C, (b) 50°C, (c) 60°C. — model proposed, Eq. (11). Bars errors show the standard deviation of three samples.

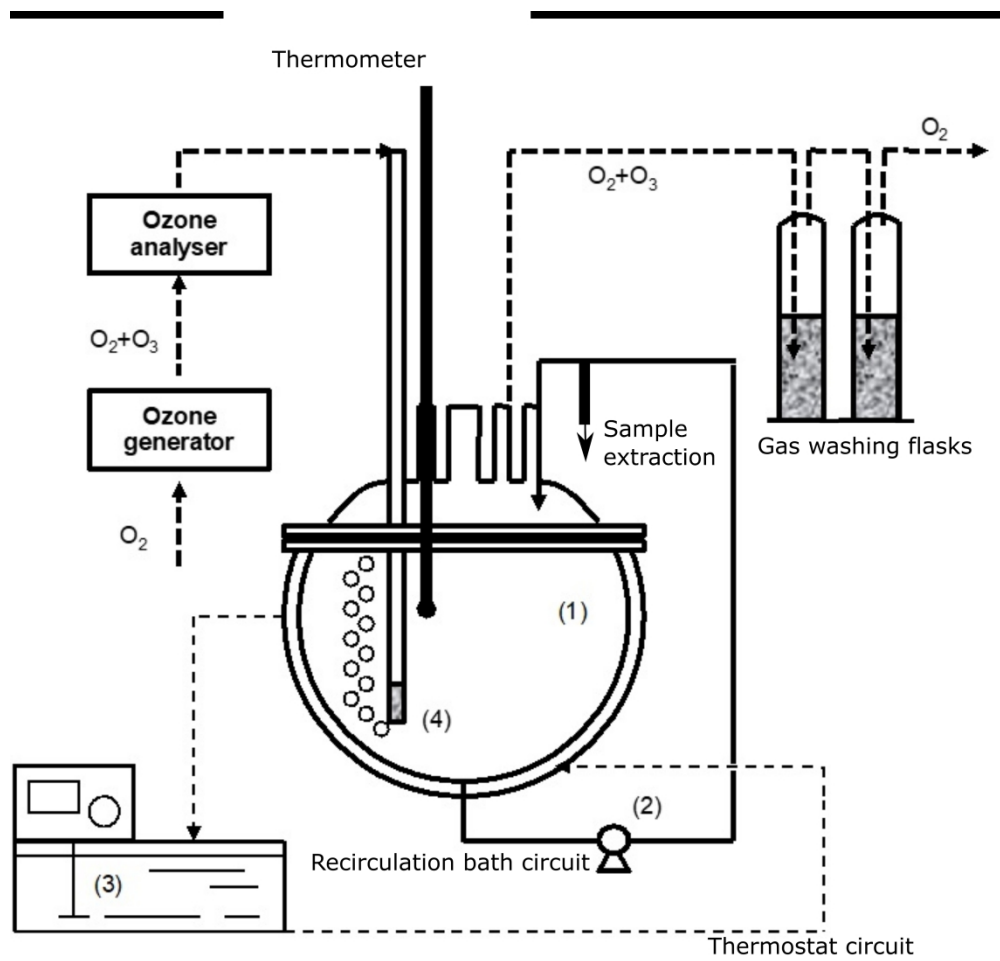


Figure 1. Scheme of a semi-batch reactor with an integrated ozonation system. The device is composed of a (1) jacketed tank, (2) peristaltic pump, (3) thermostatically controlled bath and (4) gas diffuser.

398x379mm (236 x 236 DPI)

Figure 2a.

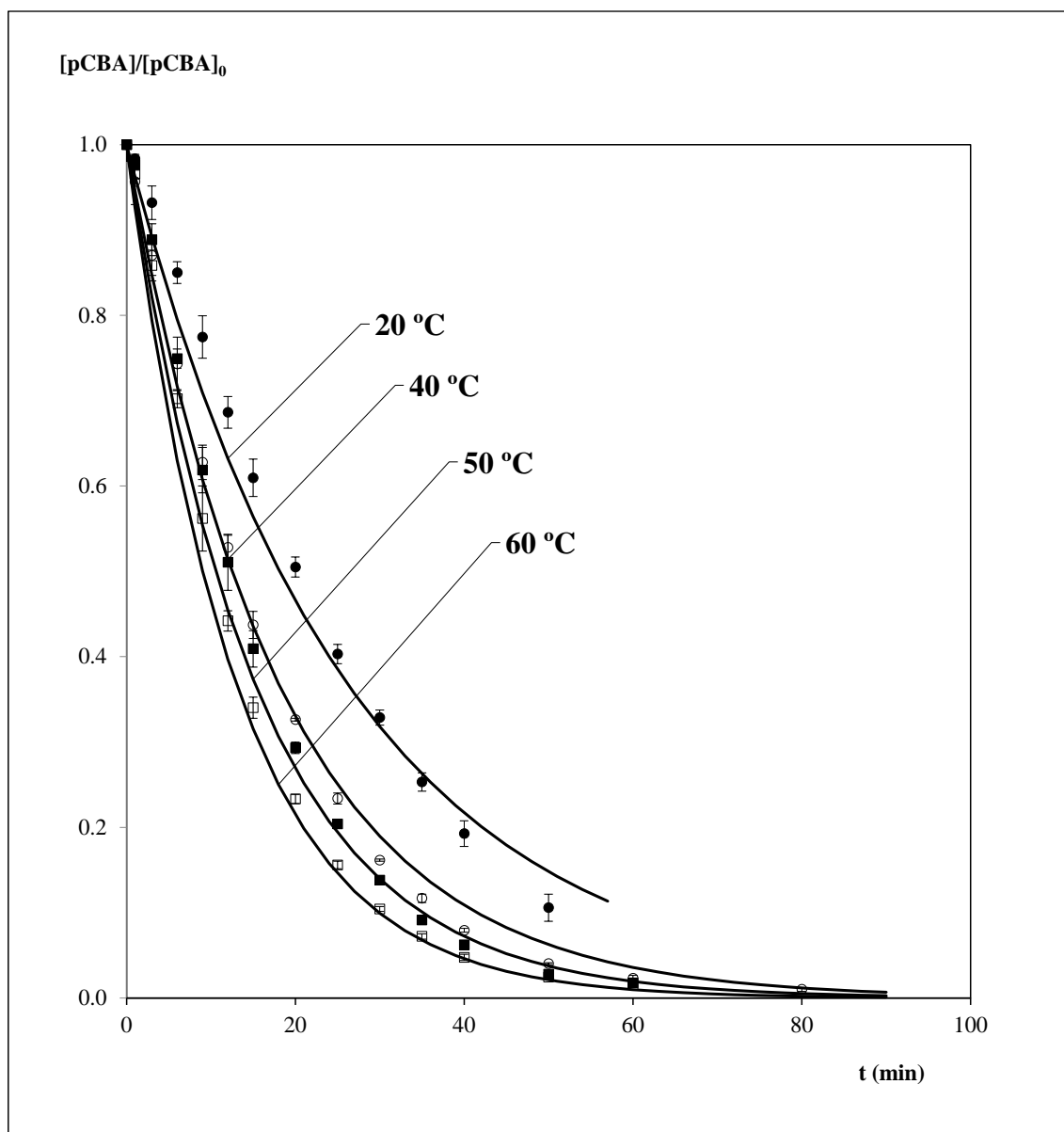
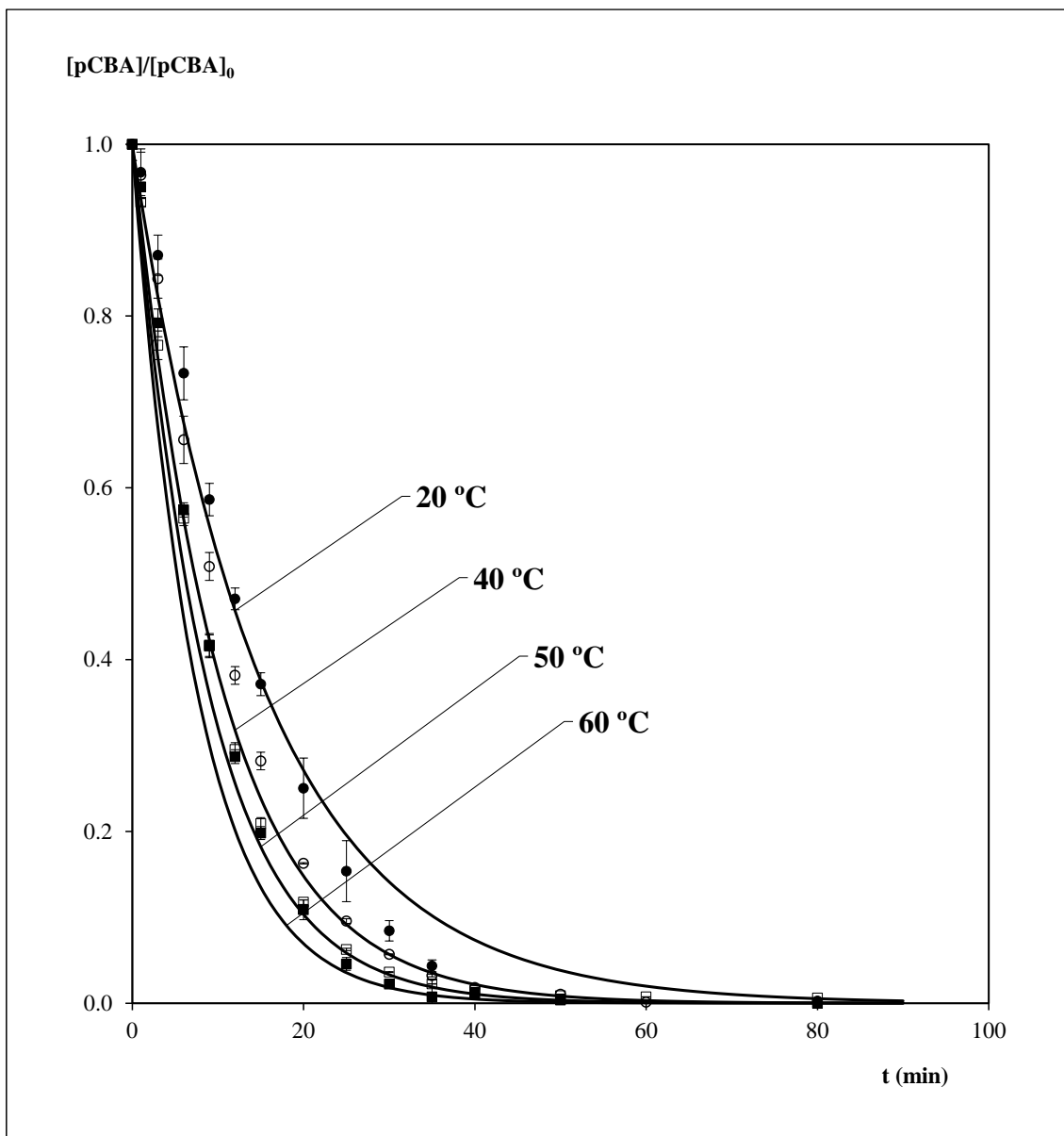
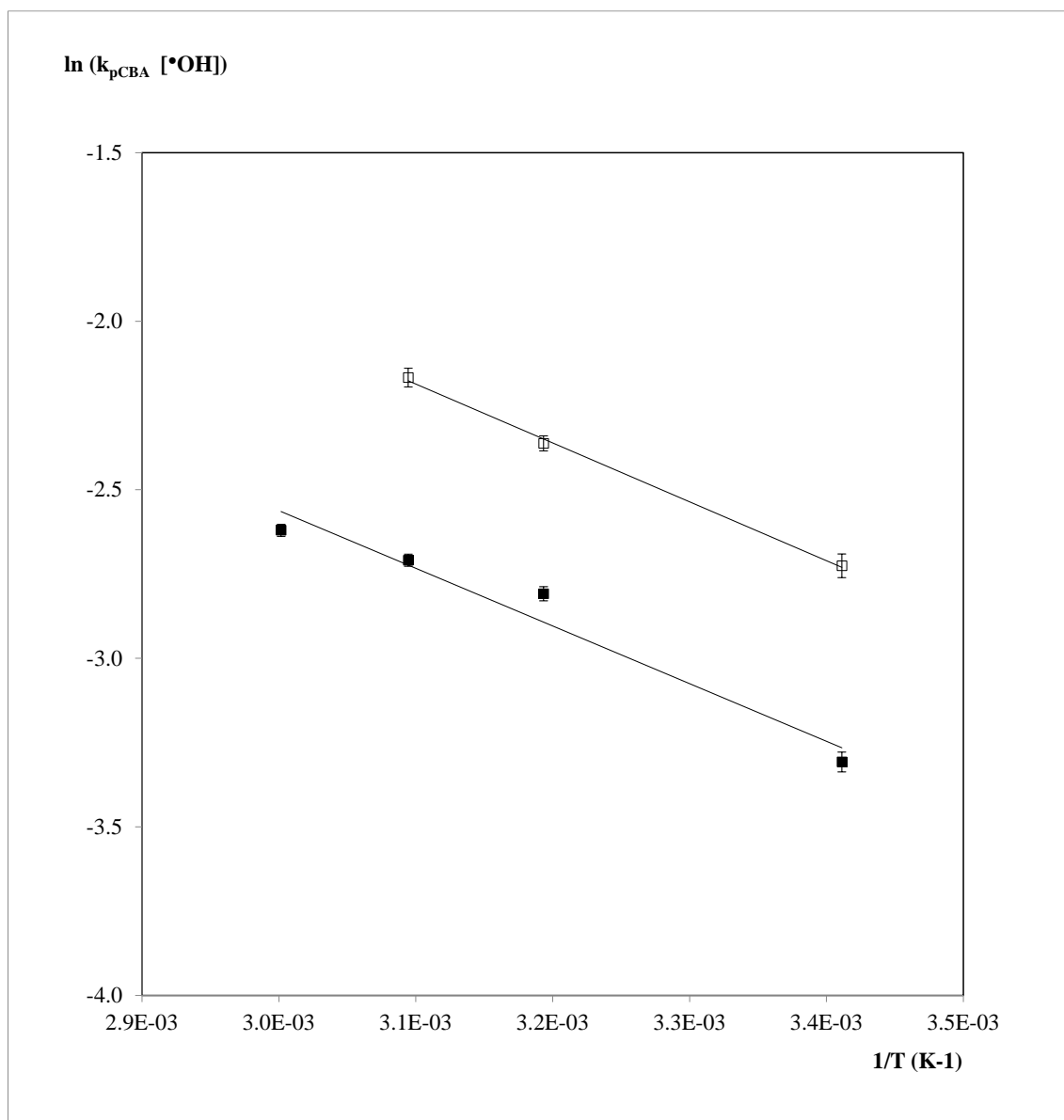


Figure 2b.



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**Figure 3.**



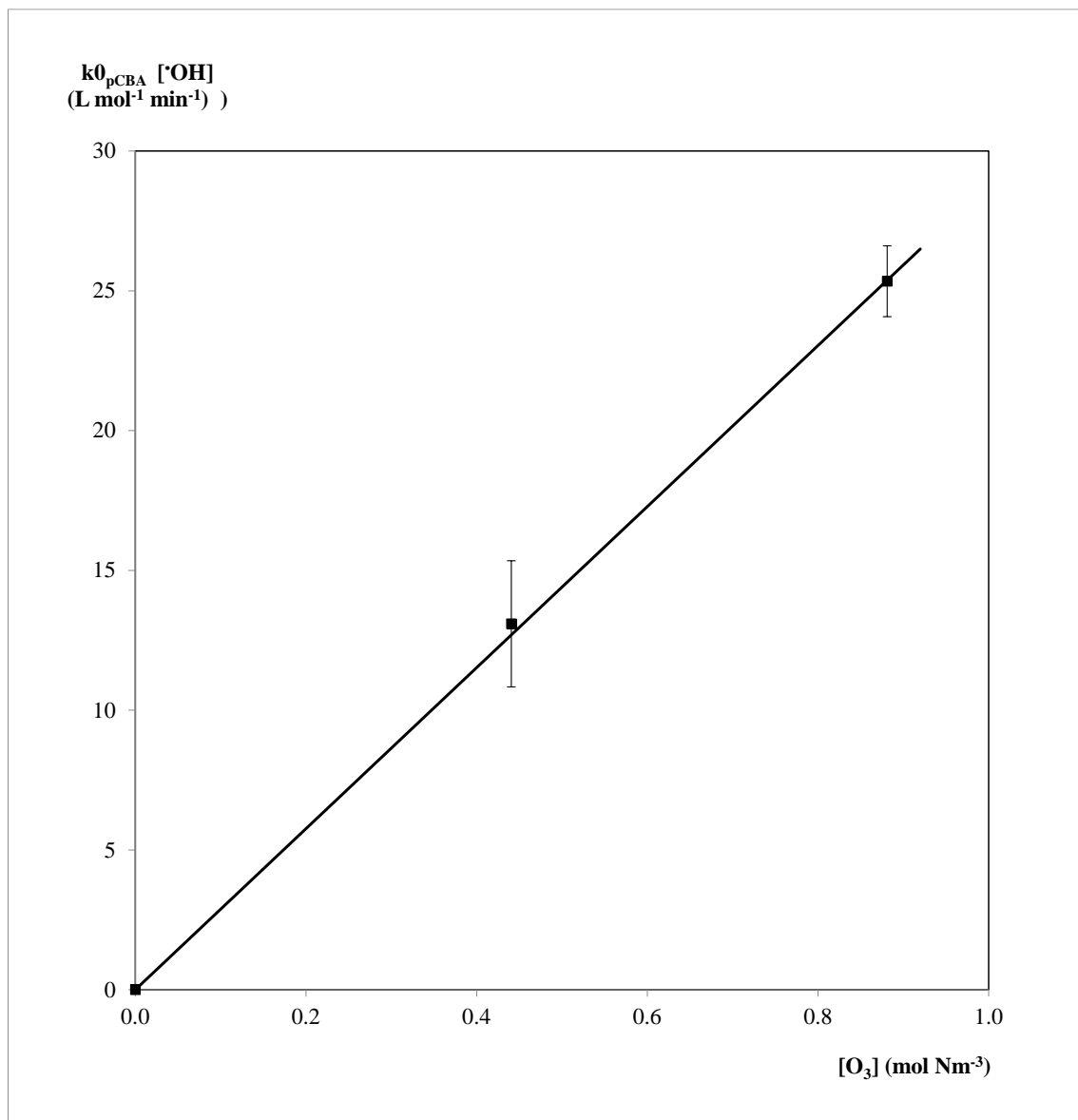
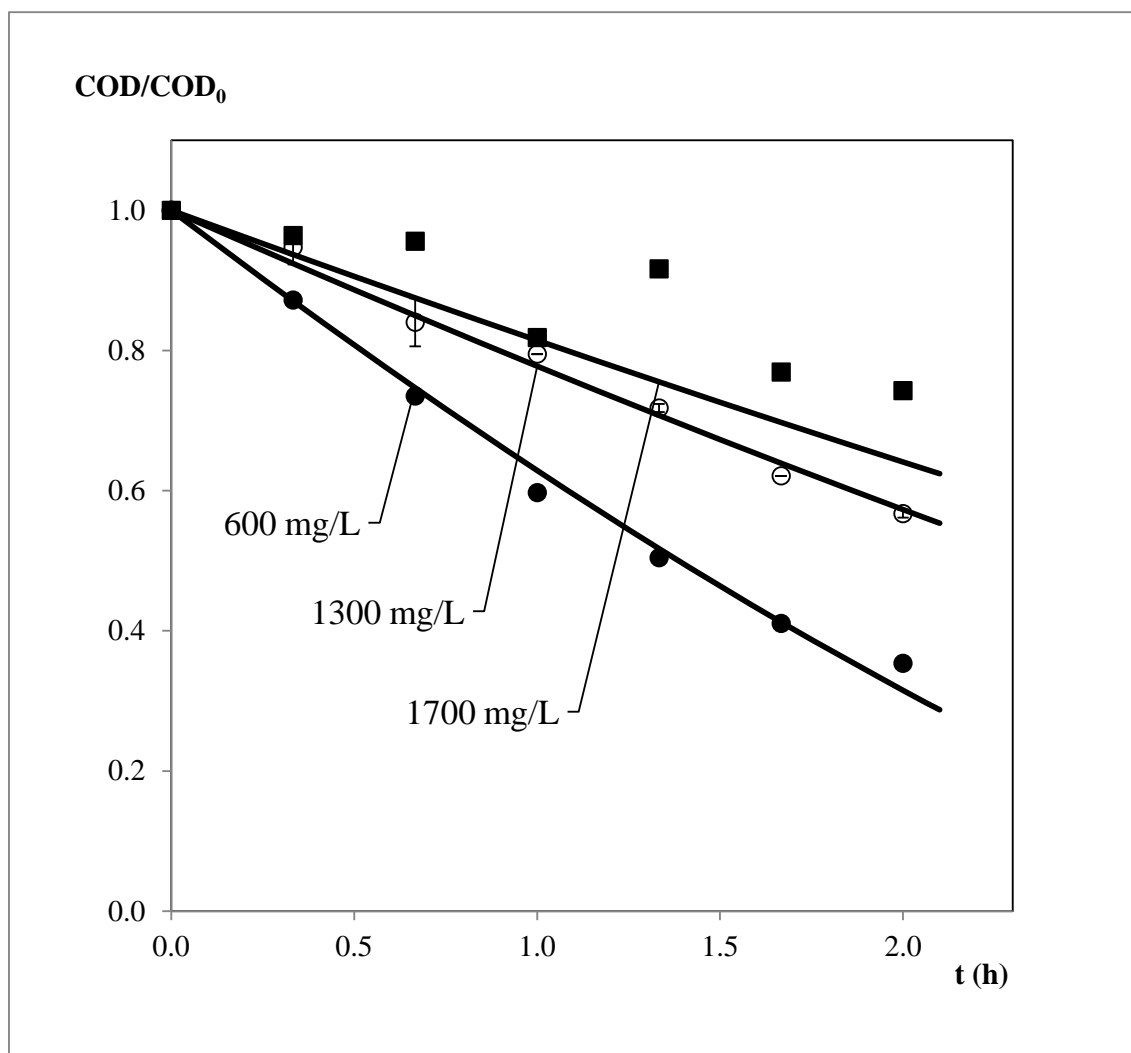
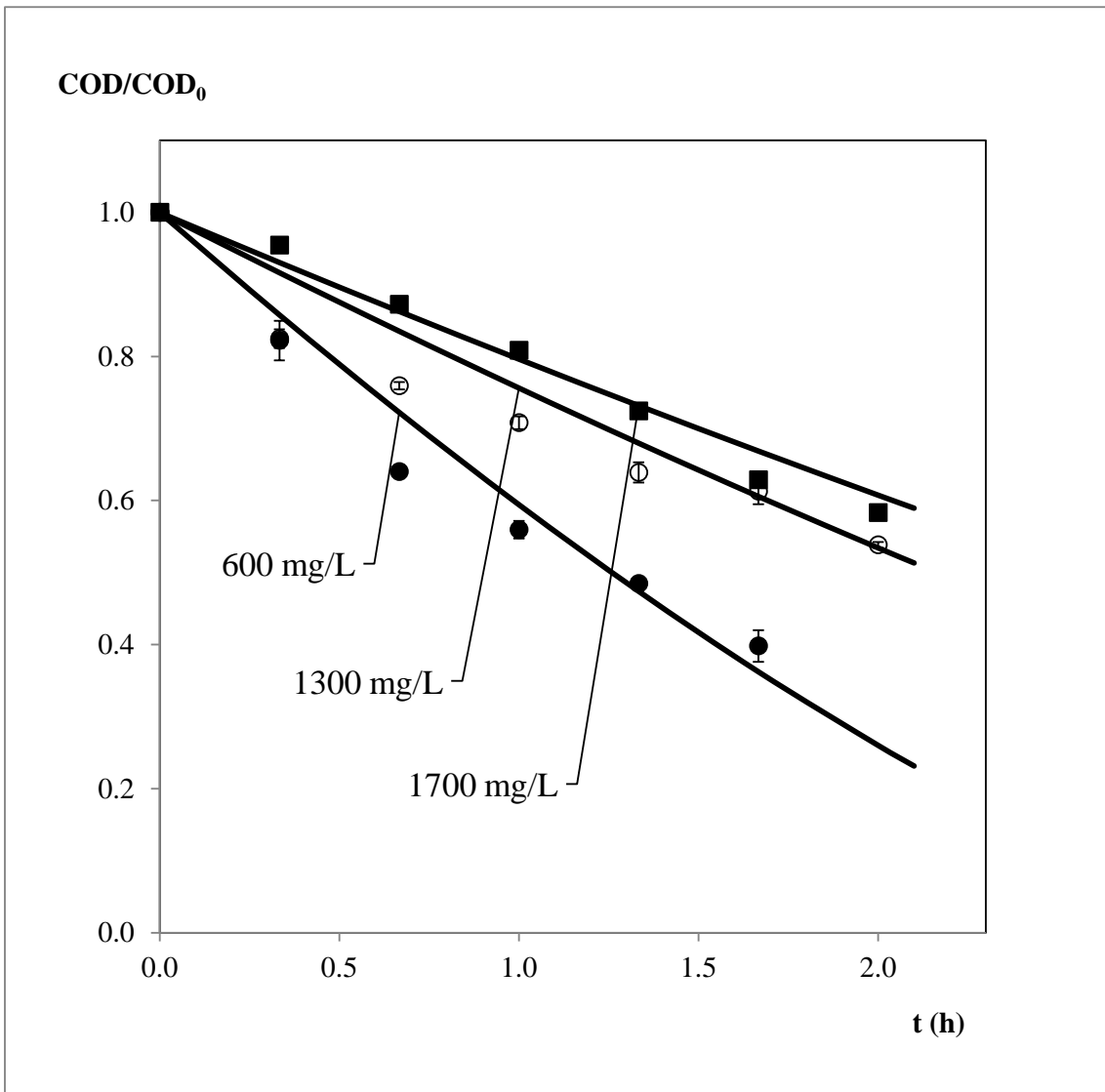
**Figure 4.**

Figure 5a.



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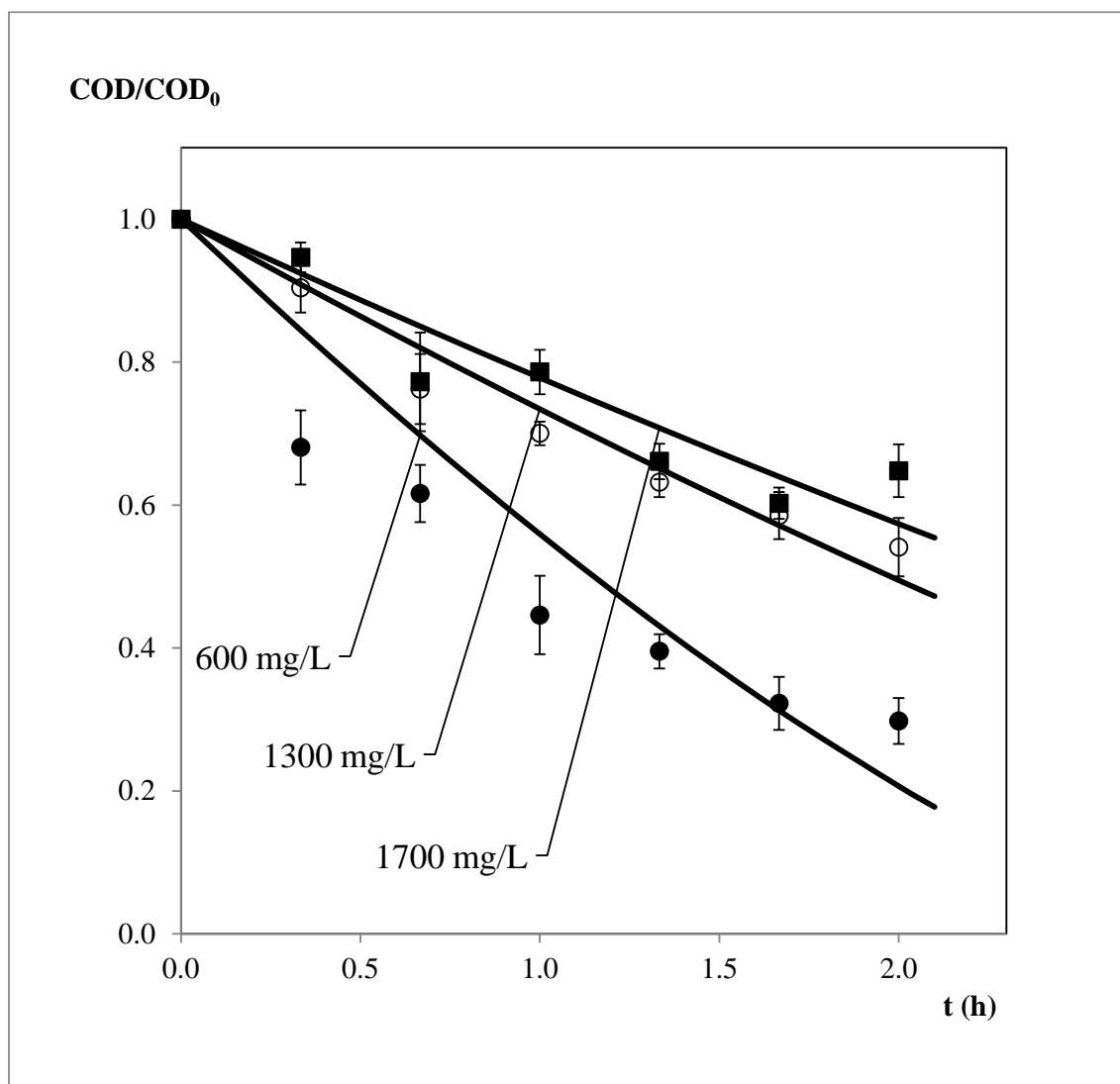
Figure 5b.



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Figure 5c.



Only

**Table 1.** Ozone decomposition. Kinetic parameters.

[O <sub>3</sub> ] (g Nm <sup>-3</sup> )	T (°C)	k <sub>pCBA</sub> [•OH] (L mol <sup>-1</sup> min <sup>-1</sup> )	r <sup>2</sup>
21.15	20	0.0366	0.987
	40	0.0603	0.994
	50	0.0666	0.995
	60	0.0728	0.996
42.3	20	0.0655	0.988
	40	0.0942	0.993
	50	0.1145	0.992

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**Table 2.** Starch oxidation with ozone. Kinetic parameters.

T (°C)	[St] <sub>0</sub> (mg L <sup>-1</sup> )	k <sub>St</sub> [•OH] (L mol <sup>-1</sup> min <sup>-1</sup> )	r <sup>2</sup>
40	600	34.6	0.991
	1300	35.1	0.991
50	600	38.4	0.943
	1300	38.6	0.956
	1700	38.9	0.938
60	600	42.2	0.891
	1300	41.6	0.955
	1700	42.2	0.890