

# Kinetic modeling of advanced starch oxidation with ozone in basic solutions

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## Abstract

Ozonation of cornstarch at pH 13 was performed using a semi-batch reactor to analyse the influence of a continuous ozone-oxygen gas flow (40 NL/h) at different ozone concentrations (0-42.30 g/Nm<sup>3</sup>) and temperatures (20-60°C). A pseudofirst-order kinetic model was proposed to elucidate the reaction mechanisms associated with ozone at high pH conditions. The radical concentration remains constant and proportional to the ozone continuous dose, being a non-limiting factor independent of temperature (activation energy 14.2-14.5 KJ/mol). The oxidation kinetic of starch was studied monitoring the Chemical Oxygen Demand, finding a reduction in ozone concentration when both temperature and time increased (activation energy 8.1 KJ/mol). Therefore, the model proposed for the starch ozonation at high alkaline solutions provides a better understanding of the oxidation processes of common product additives such as starch, also making it possible to determine the environmental impact of such solutions by Chemical Oxygen Demand measurement.

## Title

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

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## Abstract

Ozonation of cornstarch at pH 13 was performed using a semi-batch reactor to analyse the influence of a continuous ozone-oxygen gas flow (40 NL/h) at different ozone concentrations (0-42.30 g/Nm<sup>3</sup>) and temperatures (20-60°C). A pseudofirst-order kinetic model was proposed to elucidate the reaction mechanisms associated with ozone at high pH conditions. The radical concentration remains constant and proportional to the ozone continuous dose, being a non-limiting factor independent of temperature (activation energy 14.2-14.5 KJ/mol). The oxidation kinetic of starch was studied monitoring the Chemical Oxygen Demand, finding a reduction in ozone concentration when both temperature and time increased (activation energy 8.1 KJ/mol). Therefore, the model proposed for the starch ozonation at high alkaline solutions provides a better

understanding of the oxidation processes of common product additives such as starch, also making it possible to determine the environmental impact of such solutions by Chemical Oxygen Demand measurement.

## Topical Heading.

Reaction Engineering, Kinetics and Catalysis

## Keywords

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

## Plain Language Summary (PLS)

Ozonation of cornstarch in basic media has been modelled using a pseudo-first order kinetic model. Ozonation has been monitored using Chemical Oxygen Demand, finding a kinetic model that explains the ozonation of starch in highly alkaline solutions.

## 1. Introduction.

In recent years, the ozone application, a powerful oxidant, has increased considerably, being commonly used in the elimination of pollutants in effluents<sup>1</sup> and water purification,<sup>2</sup> as well as other fields such as the food industry for cleaning and disinfection processes,<sup>3-4</sup> food preservation<sup>5</sup> or odor reduction.<sup>6</sup> Interest in the use of ozone to improve or modify the physicochemical properties of cereals has also increased significantly.<sup>7-9</sup>

The oxidative action of ozone is carried out through two mechanisms: direct reaction of ozone, or indirect reaction through hydroxyl radicals generated in its decomposition.<sup>1,10</sup> The oxidizing power of hydroxyl radicals is higher than that of ozone molecules, with a standard redox potential of 2.8 V versus 2.07 V respectively.<sup>11</sup> The direct reaction of ozone with other substances is selective, whilst hydroxyl radicals show faster non-selective reactions, attacking both organic and inorganic compounds.<sup>11</sup> Furthermore, in direct ozone reactions, incomplete mineralization of compounds commonly occurs due to the selectivity criterion,<sup>12-13</sup> whereas complete mineralization can be achieved with hydroxyl radicals.<sup>10-11</sup> Such enhanced performance is the main reason for the utilization of advanced oxidation processes, AOP, for the treatment of wastewater,<sup>10</sup> as the generation of hydroxyl radicals increases the ozone degradation capacity and reduces operational times and costs, also allowing the elimination of recalcitrant pollutants.<sup>10-13</sup> One of the approaches to generate hydroxyl radicals is working with ozone in alkaline pH solutions,<sup>11-14</sup> where ozone decomposes into radicals, mainly hydroxyl radicals, increasing the decomposition rate as pH and temperature increase.<sup>2</sup> Due to the ozone chemistry complexity, it is difficult to directly measure the ozone concentration and different radicals. To unify and generalize the interpretation of the O<sub>3</sub> decomposition, Hoigné (1997)<sup>15</sup> and Elovitz and von Gunten (1999)<sup>16</sup> defined OH\* as hydroxyl radical, a highly reactive and nonspecific oxidant, formed from the ozone decomposition.

Starches are widely used as additives in food, beverage and pharmaceutical industries. Previous works have studied the ozone effect in starch solutions at different pH (3-10), temperatures and reaction times, mainly oriented to the modification of starch properties to improve its applicability by modification of carboxyl content, swelling power or water solubility;<sup>17-19</sup> the value of carboxyl content and water solubility increased at higher pH, whilst the swelling power remained low.<sup>20</sup> In addition to the carbonyl and carboxyl contents, Klein et al.(2014)<sup>21</sup> also evaluated the pasting properties and the surface morphology of ozone-oxidized starch under different pH (3.5- 9.5) at 25 oC, where higher pH and ozone concentration favoured the cross-linking between the depolymerized starch molecules. All these variations of starch properties prove the effectiveness of ozone as an effective oxidizing agent for starch modification. However, the ozonation of starch at high temperatures and alkaline media, where ozone is transformed into radicals of high oxidizing power, has been barely studied.

Ozone is also used in foods as a disinfectant agent, showing several advantages over commonly used disinfectants such as chlorine.<sup>22</sup> Ozone quickly decomposes into oxygen without leaving residues,<sup>23-24</sup> without affecting food product safety, and avoiding the presence of contaminants in process effluents or reducing its

content of salts coming from other chemical substances. On the other hand, ozone can also be used as a cleaning agent applied to fatty,<sup>25-27</sup> protein<sup>28</sup> and starchy soiling agents.<sup>3</sup> Starch is considered as water-insoluble soil with removal problems according to the classification made by Basso et al.(2017).<sup>29</sup> The cleaning of starches commonly requires high temperatures and strong alkaline formulations.<sup>30</sup> Avila-Sierra et al.(2020)<sup>4</sup> also studied the influence of ozone incorporation under these conditions, where the enhancement of starch removal was attributed to the formation of hydroxyl radicals – cleaning by advanced oxidation process – also decreasing the chemical oxygen demand (COD) of the cleaning wastewater due to the starch degradation, thus reducing the effluent pollutant load.

Therefore, there is a current need to understand the oxidation process of starches using ozone at an elevated range of temperatures in alkaline conditions, to improve the applicability of ozone for starch modification and industrial cleaning purposes. This work aims to study the kinetics of the starch-ozone reaction through COD monitoring, where the generation of hydroxyl radicals in alkaline solutions was assessed using p-chlorobenzoic acid as a probe compound. Ozonation was performed using a semi-batch reactor to determine the influence of ozone concentration and temperature.

## 2. Materials and methods

### 2.1 Materials

Two solutions, one of corn starch (Maizena(r), 87.91 % cornstarch, 11,50 %, moisture, 0.29% fat, 0.3% protein) at different concentrations (600-1700 mg starch/L), and another of 4-Chlorobenzoic acid 99% (pCBA; supplied by Across Organics) at 10 mg/L, were prepared in NaOH aqueous solution (pH=13) and used for ozonation experiments.

### 2.2 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, type of solution, and temperature. It is composed by a jacketed tank (1L of capacity), a peristaltic pump (Heidolph, model 5006) that supplies a 60L/h recirculation flow, a thermostatically controlled bath (P-Selecta, model Ultraterm), and a gas diffuser. Ozone was generated in situ by an ozone generator (Peripherals COM-AD, Anseros Germany) from an oxygen stream. The recirculation flow keeps a constant composition into the solution tested. The ozone concentration in the ozone-oxygen flow was determined by an analyzer (Anseros, Ozomat GM-6000-PRO, Germany). The volumetric flow of the ozone-oxygen gas flow was 40 NL/h, and the concentration of ozone was defined for each assay. The residual ozone was eliminated passing through washing flasks with 5% KI aqueous solution before being released into the atmosphere.

### 2.3 Ozonation of starch solutions

Ozonation of aqueous starch solutions (600-1700 mg starch/L, NaOH solutions of pH13) was carried out in a semi-batch reactor for 120 minutes at different temperatures, ranging between 40–60°C, and different ozone concentrations (i.e. 0.00, 21.15 and 42.30 g/m<sup>3</sup>). The thermostatically-controlled semi-batch reactor was filled with 1.2 L of the starch solution. Then, an oxygen current is introduced for 20 minutes, before ozonation began. Samples of 1 mL were extracted periodically from the tank. The residual ozone of the samples was eliminated by adding 0.2 mL of 0.2 g/L Na<sub>2</sub>SO<sub>3</sub> aqueous solution. Experiments were performed at least in triplicate.

### 2.4 Evaluation of Chemical Oxygen Demand (COD)

The COD value was analysed according to Avila-Sierra et al.(2020).<sup>4</sup> Solution samples of 1.5 mL were extracted periodically, and added to 1.5 mL of distilled water and mixed with the reagent solution. The reagent solution was formed by mixing 0.08 g Hg<sub>2</sub>SO<sub>4</sub> (Panreac), 4 mL of sulfuric acid reagent (10 g L<sup>-1</sup>Ag<sub>2</sub>SO<sub>4</sub> dissolved in H<sub>2</sub>SO<sub>4</sub>) and 1 mL of 0.5 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> aqueous solution. The vials were stirred and placed into a digester (150degC, 2h). After digestion, the vials were cooled down to room temperature.

Absorbance was measured at 620 nm. COD measurements were obtained by a calibration curve at different concentrations of a 0.85 g L<sup>-1</sup>KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> solution (Panreac, Spain).

## 2.5 Evaluation of oxidizing power: pCBA method

The measurement of radical concentration in ozonated solutions was based on the pCBA method.<sup>16</sup> A 10 mg/L of pCBA in NaOH aqueous solution (pH=13) was introduced in the semi-batch reactor and was thermostatted at the temperature of interest. Then, an oxygen current was introduced in the pCBA solution for 20 min, before ozonation experiments. The variables analysed were ozone concentration (0.00, 21.15 and 42.30 g/Nm<sup>3</sup>), temperature (20, 40, 50, 60oC), and time (0-80 min). To evaluate the radical concentration in the ozonated alkaline solution, samples of 5 mL extracted periodically from the reactor and the pCBA concentration was measured as a function of time by spectrophotometry (Cary 100 Bio UV-Visible, Varian) at 234 nm, using a calibration line (0-0.01 g pCBA/L).

## 3. Results and discussion

As commented in the introduction, ozone is rapidly decomposed at high pH solutions, forming radicals. In this work, firstly the concentration of hydroxyl radicals was studied through the degradation of pCBA as a function of ozonation time. Then, COD was used to model the starch oxidation process.

### 3.1. Evaluation of the concentration of hydroxyl radicals in alkaline medium

**Figure 2** shows the [pCBA]/[pCBA]<sub>0</sub> profiles as a function of time and temperature at an ozone concentration of 21.15 g/Nm<sup>3</sup> (**Figure 2.a**) and 42.30 g/Nm<sup>3</sup> (**Figure 2.b**). The pCBA concentration decreases as time and temperature increase, where the concentration of pCBA also decreased more rapidly when the gas ozone concentration was higher. Elovitz and von Gunten (1999)<sup>16</sup> predicted the ozone concentration using a first-order kinetic model. However, the concentration of the hydroxyl radicals is more complex to measure as the reactivity of radicals towards the water matrix leads to a minimal steady-state concentration, typically <10<sup>-12</sup>M. Notwithstanding, the OH\* concentration can be measured indirectly by an OH\*-probe compound such as p-chlorobenzoic acid (pCBA), which is used due to its low reactivity with ozone (k<sub>O<sub>3</sub>/pCBA</sub> [?]<sub>0.15 M<sup>-1</sup>s<sup>-1</sup></sub>) and rapid reaction with OH\* radicals (k<sub>OH\*/pCBA</sub> = 5\*10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup>) Elovitz and von Gunten, 1999).<sup>16</sup> Based on the work carried out by Elovitz and Von Gunten (1999)<sup>16</sup> and considering that at high pH conditions, ozone is mainly transformed into hydroxyl radicals (OH\*),<sup>11,14</sup> the reaction scheme for ozone decomposition and subsequent hydroxyl radical reaction with pCBA could be defined as:



where k<sub>pCBA</sub> is the individual rate constant for the OH\*-pCBA reaction. Then, the kinetic model for this reaction is defined as:

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

where t is the reaction time.

Elovitz et al.(2000)<sup>31</sup> found that for each temperature and ozone dose, the ratio [OH\*]/[O<sub>3</sub>] remained constant over time for each temperature and ozone concentration assayed, where OH\*-exposure was unaffected by reaction temperature nor pH, whilst O<sub>3</sub>-exposure changed drastically, decreasing as both temperature and pH increased. In addition, taking into account the fast ozone decomposition at high pH,<sup>32</sup> thus yielding a continuous formation of hydroxyl radicals due to the uninterrupted O<sub>3</sub> gas flow into the alkaline solution, and considering that hydroxyl radicals steady-state concentrations are usually very low, typically <10<sup>-12</sup> M,<sup>16</sup> it could be initially assumed that [OH\*] is constant for a fixed ozone continuous dose. Then, the integration of (Eq. 3) gives as a result:

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

Applying (Eq.4) to the experimental results,  $\ln \left( \frac{[pCBA]}{[pCBA]_0} \right)$  shows a linear dependence against time at each temperature and initial gas ozone concentration assayed with  $r^2$  values between 0.987-0.998. It suggests that  $k_{pCBA} [OH]$  is constant over the entire reaction for each temperature and gas ozone concentration, demonstrating that  $[OH^*]$  is not limiting and that throughout the experimental time is constant at the temperature and ozone dose assayed. Then, at each ozone dose evaluated, it is possible to estimate the activation energy ( $E_{a1}$ ) and  $k_{pCBA} [OH]$  for the  $OH^*$ -pCBA reaction, fitting the data to the Arrhenius equation by means of (Eq.5):

$$\ln ( k_{pCBA} [OH] ) = \ln ( k_{pCBA} [OH] ) - \frac{E_{a1}}{RT} \text{ (Eq.5)}$$

$k_{pCBA} [OH]$  vs.  $1/T$  fits well as the (Eq.5) suggests (**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 can be observed in **Figure 2**.

The  $E_{a1}$  values obtained for each ozone dose used are similar (14.2-14.5 KJ/mol) for different ozone doses (21.15-42.30 g/Nm<sup>3</sup>, respectively), finding analogous values to the results showed by Elovitz et al.(2000),<sup>31</sup> where  $OH^*$  reactions activation energies between 5-10 KJ/mol were reported. According to **Figure 3** and (Eq.5),  $k_{pCBA} [OH]$  is independent of temperature but depends on the gas ozone concentration.  $k_{pCBA} [OH]$  is directly proportional to the concentration of ozone in the gas flow (**Figure 4**), according to (Eq.6)

$$k_{pCBA} [OH] = 28.9 [O_3] \quad r^2=0.9996 \text{ (Eq.6)}$$

therefore, in the experimental range assayed,  $[OH^*]$  is constant and proportional to ozone dose, as it is previously assumed for (Eq. 4) deduction, and independent on temperature. A similar increase in the production of hydroxyl radicals with raising ozone dose has also been previously described by Ghuge and Saroha (2018).<sup>10</sup>

### 3.2 Kinetic modeling of starch oxidation with ozone in basic solutions

Modelling the ozonation kinetic of polysaccharides is complex. Prasetyaningrum et al.(2017)<sup>33</sup> proposed a kinetic model to explain the depolymerization of  $\kappa$ -carrageenan by ozone using viscosity data. In the present work, a model for the ozone-starch reaction in alkaline solution was proposed, being  $[St]$  (g/L) the starch concentration as a function of time,  $[St]_0$ (g/L) the initial starch concentration and  $k_{St}$  the kinetic constant for the reaction:



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

In this work, the COD measurement of the starch solutions was used to determine starch concentration as a function of time, since starch concentration was found to be proportional to COD (Eq.9), allowing to evaluate simultaneously the pollutant load of the chemical solutions over time.

$$COD(mg O_2/L) = 1.116 [St] (mg/L) \text{ (Eq.9)}$$

As it was demonstrated in section 3.1, for each  $O_3$  dose,  $[OH^*]$  was constant at pH=13 throughout the entire reaction, being not dependent on temperature. Then, substituting (Eq.9) in (Eq.8), considering  $\alpha=1$ , and integrating, it results:

$$-\ln \frac{COD}{COD_0} = k_{St} [OH] t \text{ (Eq.10)}$$

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

$$\frac{COD}{COD_0} = \left[ 1 + \left( \frac{1.116}{COD_0} \right)^{1-\alpha} (\alpha - 1) k_{St} [OH] t \right]^{\frac{1}{1-\alpha}} \text{ (Eq.11)}$$

Applying Eqs.(10) and (11) to the experimental results, the best fitting was obtained considering  $\alpha=0.3$  in Eq.(11), **Figure 5**. The COD/COD<sub>0</sub> ratio decreased with increasing ozonation time and temperature, with

this reduction being more pronounced the lower the initial starch concentration. According to the kinetic model proposed,  $k_{St} [OH]$  is constant over the entire reaction at each temperature and starch concentration. Then,  $k_{St} [OH]$  could be fitted to the Arrhenius equation resulting:

$$\ln (k_{St} [OH]) = \ln (k_{St0} [OH]) - \frac{E_{a2}}{R T} \text{ (Eq.12)}$$

Applying Eq.(12),  $E_{a2}$  resulted being equal to 8.1 KJ/mol and  $k_{St0} [OH] = 781 \text{ (L/mg St)}^{-0.7} \text{ h}^{-1}$  ( $r^2=0.993$ ). These parameters fit the experimental results in a suitable form as it can be observed in **Figures 5** . Comparing both models,  $OH^*$ -starch and  $OH^*$ -pCBA, the  $E_{a2}$  values estimated for the reaction between starch and  $OH^*$  were lower than those estimated for the  $OH^*$ -pCBA reaction.

Previous works have shown that ozone is capable of modifying the composition and structure of starch, given its ability to break the glucosidic bonds that bind glucose molecules in starch, causing its depolymerization, and oxidizing its hydroxyl and carbonyl groups to carboxyl groups.<sup>23,34,35</sup> Similarly, it has been observed how hydroxyl radicals react with oligosaccharides and polysaccharides, being capable of breaking glucosidic bonds.<sup>36</sup> 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  $CO_2$ .<sup>37,38</sup> This  $CO_2$  formation has also been observed during the ozonation of different polysaccharides including starch.<sup>37</sup> Analogously, successive oxidations of starch by hydroxyl radicals during its ozonation at alkaline pH are foreseeable, and that would be justified by the observed reduction of COD (**Figure 5**) which we also found in previous work on cleaning starch dirt.<sup>3</sup> Likewise, these oxidations and depolymerizations cause modifications in the properties of starch after ozonation, for example in gelatinization, pasting, retrogradation and solubility,<sup>24,39</sup> and that could therefore affect the cleaning processes of these soils.

#### 4. Conclusions.

A pseudofirst-order kinetic model has been proposed to model the pCBA-ozone reaction in a semi-batch reactor at high pH (pH=13), different ozone concentrations (0-42.30 g/Nm<sup>3</sup>), and different temperatures (20-60°C). This model estimates the formation of oxidant radicals ( $OH^*$ ), where, under the experimental conditions assayed, the  $[OH^*]$  was constant and proportional to the ozone continuous dose, being  $OH^*$  a no limiting reactant, independent on temperature. The activation energy values for the  $OH^*$ -pCBA reaction were estimated between 14.2-14.5 KJ/mol.

A kinetic model for ozone-starch oxidation in a semi-batch reactor with continuous gas ozone inlet using a high alkaline solution was also proposed based on COD measurements. The best fit was obtained considering  $\alpha=0.3$ . According to the results, the COD reduction was greater with increasing temperature and time, with the decrease being more pronounced at lower initial starch concentrations. The activation energy of the ozone-starch reaction was estimated at 8.1 KJ/mol, being lower than the reported for the reaction between pCBA and  $OH^*$ .

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## Figures captions.

**Figure 1.** Scheme of a semi-batch reactor with an integrated ozonation system. The device is composed by 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  $k_{pCBA}$  [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  $k_0_{pCBA}$  [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.

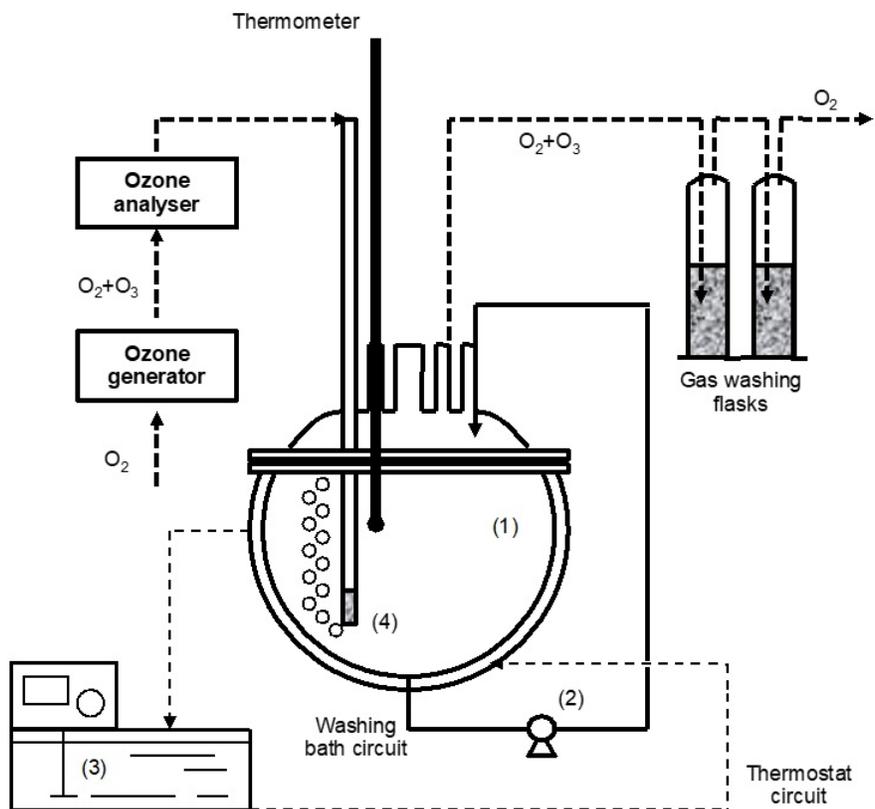


Figure 2a.

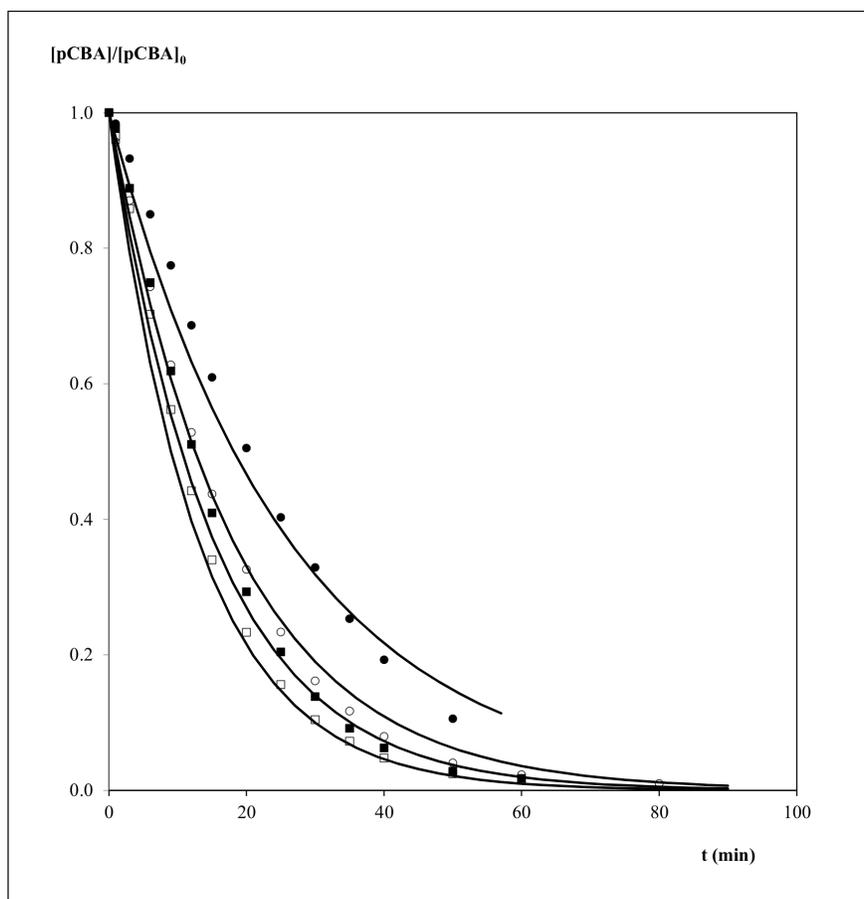
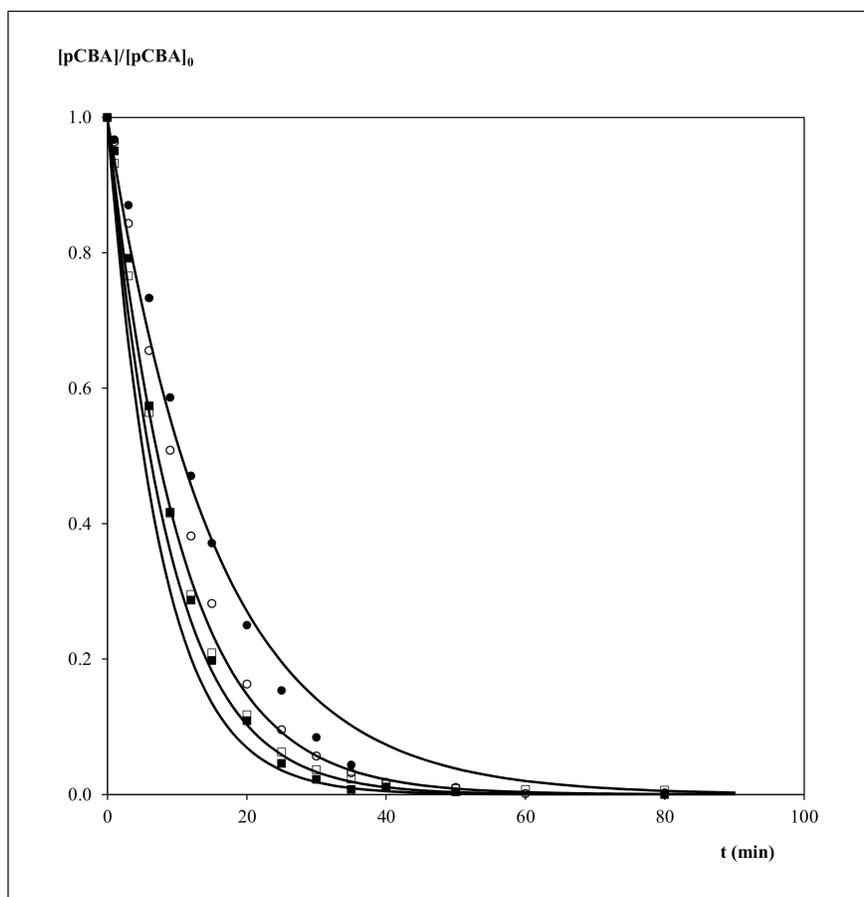
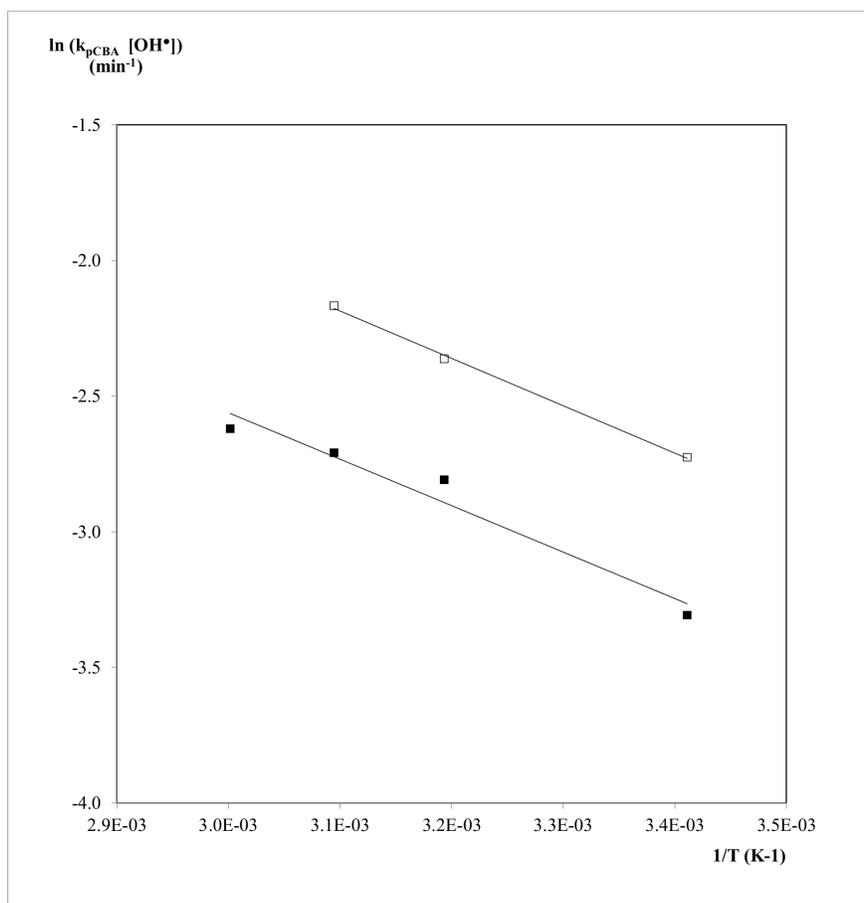


Figure 2b.



**Figure 3.**



**Figure 4.**

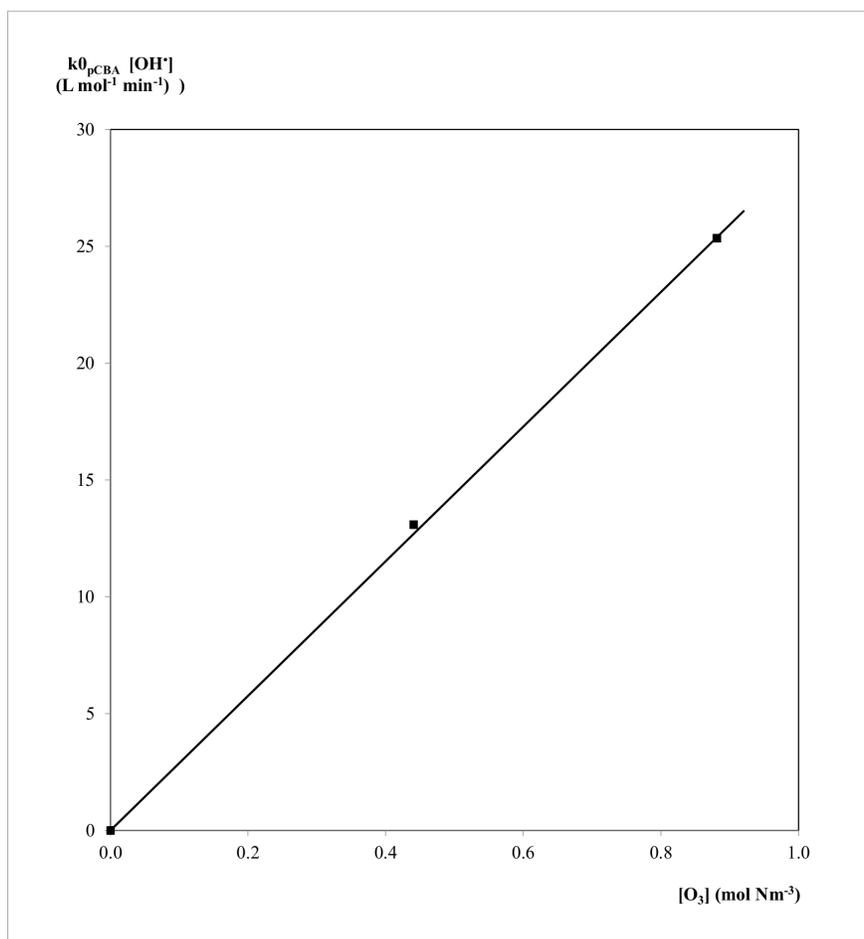


Figure 5a.

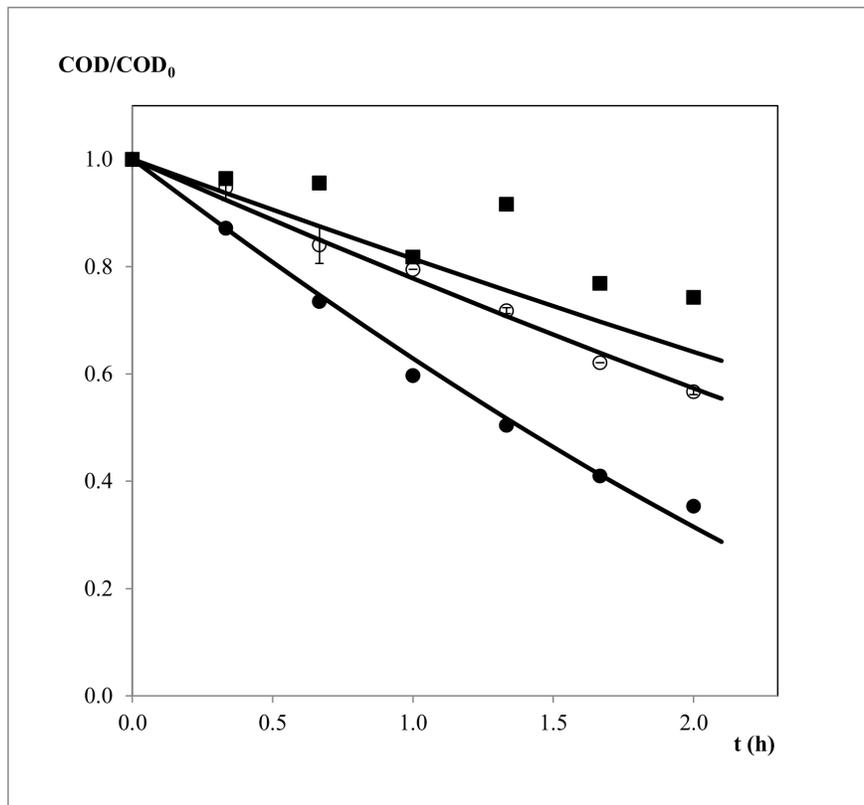


Figure 5b.

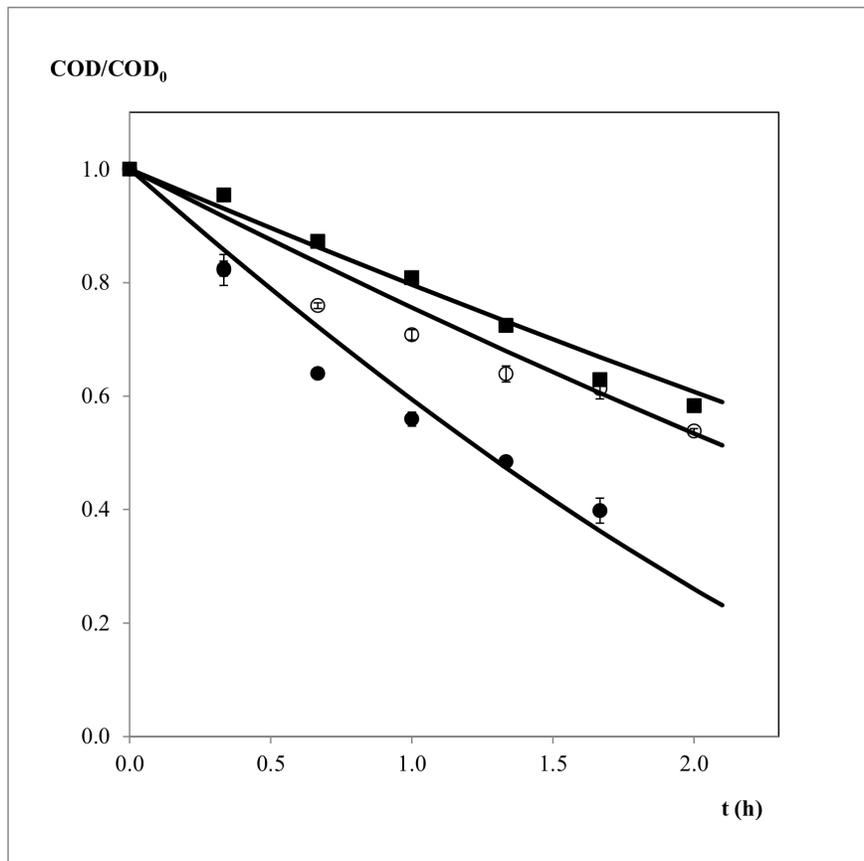


Figure 5c.

