

1 **Title**

2 **Removal of food soil by ozone-based oxidation processes: cleaning and wastewater**
3 **degradation in a single step**

4

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15 **Abstract**

16 The cleaning of heat-treated cornstarch adhered to stainless steel is analyzed in a
17 simulated Cleaning-In-Place system. The effects of temperature (20-60 °C), cleaning
18 time (30-120 minutes), and ozone (0.00-42.30 g/Nm³) on both detergency and chemical
19 oxygen demand (COD) are analyzed. Two mathematical models are proposed to
20 evaluate the detergency and COD fitting satisfactorily the experimental results. The
21 highest detergency is obtained at 60°C and 120min, reaching 68 and 88% when the
22 ozone concentration is 0.00 and 42.30 g/Nm³, respectively. Ozone diminishes the COD
23 in the wastewater. Higher ozone concentration, cleaning time and temperature produces
24 the greater reduction of COD/Detergency ratio. So, ozone promotes starch degradation,
25 reducing the contamination charge of the wastewater during the cleaning process

26 providing new possibilities for the optimization of cleaning processes in starch end-user
27 industries by combining cleaning and depuration processes in a single step.

28

29 **Keywords**

30 Food cleaning; starch; ozone; Chemical Oxygen Demand; Fouling; Cleaning in Place

31

32 **1. Introduction**

33 Starches are commonly used in food and pharmaceutical industries for
34 thickening, gelling, bulking, and as a water retention agent (Singh et al., 2003). Within
35 the wide variety of starches cornstarch is the most important one, representing more
36 than 80% of the worldwide market (Jobling, 2004). In these industries, cleaning
37 processes are crucial in order to achieve high quality products and good hygienic
38 conditions of devices (Liu et al., 2002). Cleaning protocols must be optimized, affecting
39 many factors such as properties and concentration of the fouling agent, substrate
40 properties, temperature, cleaning agents, hydrodynamic forces and time (von Rybinski,
41 2007). The use of specific cleaning protocols could reduce energy consumption as well
42 as improving other parameters such as surface protection and biodegradability of the
43 wastewater.

44 Starches present strong adhesion forces to hard surfaces (Lam and Newton,
45 1991). These forces depend on the interaction between the fouling and the substrate
46 material (Liu et al., 2002). Based on the soil classification proposed by Fryer and
47 Asteriadou (2009), made according to soil type and cleaning method, Goode et al.,
48 (2013) categorized starch soils as Type 3 deposits, thus requiring hot chemical cleaning
49 for their removal (Fryer and Asteriadou, 2009). When starch is heated in water, its
50 structure breaks down and water molecules bind with the hydroxyl groups of

51 amylopectin and amylose by hydrogen bonds. This process causes a greater starch
52 solubility and swelling (Soto and Oliva, 2012). High-temperature and alkaline media are
53 commonly used for cleaning carbohydrates (Chisti, 2014) as strongly alkaline solutions
54 can achieve significant starch removal (Jurado et al., 2015a) by changing microstructure
55 and physico-chemical properties of starches (Han and Lim, 2004) as well as the
56 isoelectric point of stainless steel (Mauermann et al., 2012). Thus, as both starches and
57 steel are negatively charged at alkaline pH, electrostatic repulsive forces dominate
58 facilitating the removal (Otto et al., 2016).

59 The rheological properties of starch gels and pastes are influenced by surfactants
60 (Biliaderis, 2009). However, when Vicaria et al. (2017) studied starch soiling removal
61 at alkaline pH, it was found that the use of surfactants (e.g. fatty ethoxylated alcohol,
62 alkylpolyglucoside, linear alkyl benzene sulfonate and amine oxide) did not improve the
63 elimination of heat-treated starch. On the other hand, when enzymes, ozone and fatty
64 alcohol ethoxylate surfactant were included, higher detergency values were reached at
65 lower temperatures than normally used in the food industry (Vicaria et al., 2019).

66 Advanced Oxidation Processes (AOPs) are wastewater treatment technologies of
67 high interest. They combine high effectiveness of pollutant removal through oxidation
68 reactions with highly efficient generation of hydroxyl radicals, often aided by catalytic
69 and photocatalytic processes (Gagol et al., 2018). Oxidation of hardly degradable
70 organic contaminants is observed when hybrid processes are used as, for example,
71 hydrodynamic or acoustic cavitation combined with the Fenton process, ozonation,
72 hydrogen peroxide, UV irradiation, catalysts or persulfates, a highly promising method
73 (Shah et al., 2018; Fernandes et al., 2018, 2019a). Ozone has a strong oxidant potential
74 useful for the removal of organic and even inorganic residuals via the formation of
75 highly reactive hydroxyl radicals. Radicals react unselectively and very fast with

76 organic materials and living microorganisms being a good alternative for disinfection of
77 food installations (Boczka and Fernandes, 2017a). Hybrid processes are developed for
78 increase the ozonation effectiveness as, for example, photocatalytic processes
79 (Fernandes et al., 2019b), cavitation combined with AOPs (Gagol et al., 2018) or
80 combined application of ozone and H₂O₂ (Boczka et al., 2017b). However, the effect of
81 ozone during the cleaning process requires further knowledge to know application
82 conditions and concentrations to avoid harmful radical levels. Ozone can remove starch
83 fouling by modifying its properties (Chan et al., 2009), producing polysaccharide
84 depolymerisation (Wang et al., 1999) and forming viscous pastes at moderate
85 temperatures (Castanha e al., 2019). From an environmental point of view, ozone can
86 increase the biodegradability of wastewaters (Guzel-Seydim et al., 2004) reducing their
87 chemical oxygen demand, and replacing other chemicals with a higher environmental
88 impact such as chlorine (Pascual et al., 2007). Furthermore, ozone is able to generate an
89 initial degradation of the surfactants (Vicaria et al 2016), helping the wastewater
90 treatment. Therefore, the use of ozone could provide a new opportunity of improvement
91 combining soil cleaning process, degradation of the wastewater, and even disinfection.

92 The kinetic of cleaning-in-place devices is still poorly understood, and a direct
93 selection of cleaning protocols is not always possible. The understanding of the fouling
94 removal, their modelling and final prediction (e.g. by experimental design), is critical
95 for optimizing the cleaning performance. Although detergency is essential, the
96 environmental impact of processes is also becoming ever more important (Fryer and
97 Asteriadou, 2009), and so a combined optimization of removal effectiveness and
98 environmental impact of the cleaning process deserves study. Although different
99 researchers have studied the use of ozonation in alkaline solutions to degrade chemical
100 compounds or to disinfect (Woo et al., 2019; Cheng et al., 2019; Wu et al., 2019), it has

101 not been reported the effect that ozone used in basic condition and high temperatures
102 generates in the starchy dirt, both in detergency and in chemical oxygen demand
103 (COD). The novelty of this work is to report about the removal of heat-treated
104 cornstarch adhered to stainless steel using ozone. The combined effects of temperature,
105 ozone and cleaning time on both detergency and COD are analyzed in order to optimize
106 and predict the best cleaning parameters by means of an experimental design analysis
107 and multi-objective optimization.

108

109 **2. Materials and methods.**

110 **2.1 Substrate, foulant and fouling procedure**

111 Wads of stainless steel fibers (AISI 410) with a diameter of 2.0-2.1 cm, weight
112 of 0.80-0.81g and fiber width of 0.51mm, are used as the substrate. The substrate is the
113 surface where the foulant is retained. A total of eight wads per cleaning test are put into
114 the Bath-Substrate-Flow device (BSF). This substrate is selected due to the difficulty to
115 remove starch from it, making it possible to better analyze the effect of the experimental
116 conditions on the cleaning process.

117 Heat-treated cornstarch gel is the fouling agent. The composition of the
118 cornstarch powder (0.37% protein, 0.42% fat, 90.37% carbohydrates, 7.84% moisture,
119 0.99% ashes), the preparation of the fouling agent and the soiling procedure are detailed
120 in a previous work (Jurado-Alameda et al., 2015b). The fouling agent is prepared as
121 follows: a cornstarch water suspension (8% wt./wt. Maizena®) is heated at 70°C for 1h
122 and cooled at room temperature for at least 12h to obtain the gel. The soiling procedure
123 is: stainless steel wads are fouled with the soil by submersion in the starch gel and are
124 dried at 60°C for 12h in an oven. The eight dried soiled wads used in each cleaning test

125 have a total starch mass of 2.0 ± 0.1 g. Starch adhered to stainless steel simulates fouling
126 conditions in industrial equipment when starch has been heat-treated.

127

128 **2.2 Cleaning device.**

129 The starch removal is studied in a modified Bath-Substrate-Flow device (BSF)
130 (Jurado-Alameda et al., 2016). This device simulates an industrial Cleaning-In-Place
131 system, allowing modification of the main factors in the cleaning process such as
132 temperature, chemical agent, fouling agent, flow rate, and substrate. A diagram of the
133 modified BSF, including an ozonation system, is represented in **Figure 1**. The BSF
134 device has a jacketed tank (1) containing the cleaning solution (volume 1L); a pump
135 (model 5006, Heidolph) (2) supplying a 60L/h recirculation flow; a column (3) with a
136 capacity of 50mL (diameter = 2.5cm, height = 8.5cm) where the soiled substrate is
137 placed; a thermostatically controlled bath (4) (model Ultraterm, P-Selecta) and a gas
138 diffuser (5). The ozone generator (Anseros Peripherals COM-AD, Germany) generates
139 the ozone in situ by an oxygen stream. In the ozone-oxygen mixture, concentration of
140 ozone is measured by an analyzer (Ozomat GM-6000-PRO, Anseros, Germany) (the
141 lines of ozone generator-reactor and reactor-ozone analyzer are made of PTFE). The
142 volumetric flow of the ozone-oxygen gas flow is 40 NL/h, and the concentration of the
143 ozone inflow is modified in each assay. The residual ozone is eliminated by passing it
144 through washing flasks with 5% KI aqueous solution before being released into the
145 atmosphere.

146

147 **2.3 Cleaning procedure.**

148 NaOH aqueous solution (0.60 wt./wt.) is selected for this study as the chemical
149 agent base for the cleaning process; lower pH have been found not being able to remove

150 starch in previous studies, where detergency is negligible with or without ozone (Jurado
151 et al., 2015a; Vicaria et al., 2017). The cleaning tests are carried out between 20 and
152 60°C for 30, 60, 90 and 120 minutes. Different concentrations of ozone (0.00, 21.15 and
153 42.30 g/m³) in the gas flow are assayed in order to analyze its influence on the cleaning
154 process.

155 Before each cleaning assay, the system is filled with 1.2 L of the
156 thermostatically-controlled washing solution. Oxygen or oxygen-ozone flows are
157 sparkled into the cleaning solution 20 min before the cleaning operation in order to
158 achieve an initial ozone concentration in the solution. The fouled wads are placed in the
159 column and then the pump is turned on. At this moment, the cleaning assay begins.
160 Samples of cleaning solution (3 mL) are extracted periodically from the tank during the
161 test. The residual oxidants of the samples are eliminated adding 0.2 mL of Na₂SO₃
162 solution (0.2 g/L) to the sample (1mL). Na₂SO₃ neutralizes the residual oxidants. When
163 the cleaning process finishes, the wads are removed from the column and dried in an
164 oven at 60°C for 24h. The detergency (De, %) is calculated dividing the difference in
165 the wads weight before and after the cleaning test by the mass of the starch at the
166 beginning of the assay. After each test, the BSF is cleaned with water (3 cycles) at 50°C
167 for 5 min.

168 **2.4 Chemical Oxygen Demand method (COD).**

169 The COD method is carried out by mixing 0.08 g Hg₂SO₄ (Panreac), 4 mL of
170 sulfuric acid reagent (10 g Ag₂SO₄ dissolved in 1 L H₂SO₄) and 1 mL of 0.5N K₂Cr₂O₇
171 aqueous solution. 1.5mL of distilled water and 1.5 mL of the sample are then added to
172 the later reagent. The vials are shaken and introduced into a reactor at 150°C for 2h.
173 After digestion, the vials are cooled at room temperature. Absorbance is measured at
174 620 nm. The evaluation of the results is carried out by means of a calibration curve at

175 different concentrations of known COD prepared with a standard solution of potassium
176 hydrogen phthalate (dissolving 0.85 g of phthalate in 1 L of distilled water).

177 The samples extracted periodically from the tank are analyzed determining their
178 COD values. No interference in the COD method is detected using Na₂SO₃ solution to
179 remove the residual oxidants.

180 **2.5 Experimental design and mathematical modeling.**

181 A multifactorial model is carried out in order to determine the effect of the
182 variables tested on the removal of starch, as well as on the reduction in the COD of the
183 cleaning wastewater. Time (t), concentration of ozone ([O₃]) and temperature (T) are the
184 input variables. Time of cleaning is tested from 30 to 120 min with two intermediate
185 levels (60 and 90 min), ozone concentration with three levels (0.00, 21.15 and 42.30
186 g/m³) and temperature at 20, 40 and 60 °C. Among the factors that play a fundamental
187 role in the detergency of hard surfaces (Durr and Wildbrett, 2000), the substrate and the
188 soiling agent are not modified. Consequently, 36 experimental runs are conducted in a
189 random order.

190 A multivariate analysis is applied to the input variables ([O₃], T, t) using
191 multiple regression with an advanced statistical software (StatGraphics 5.1, Stat-point
192 Technologies, Inc., Warrenton, VA, USA). Quadratic models for De and COD, Eq. (1)
193 and Eq. (2), are proposed, respectively; the statistical significance of each term in the
194 models is assessed by ANOVA analysis. Every term in the polynomial is associated
195 with a p-value obtained by the Fisher's statistical test at a confidence level of 95%.

196

$$197 \quad De = \alpha_0 + \alpha_1 \cdot T + \alpha_2 \cdot [O_3] + \alpha_3 \cdot t + \alpha_{11} \cdot T^2 + \alpha_{12} \cdot T \cdot [O_3] + \alpha_{13} \cdot T \cdot t + \alpha_{22} \cdot [O_3]^2$$
$$198 \quad \quad \quad + \alpha_{23} \cdot [O_3] \cdot t + \alpha_{33} \cdot t^2 \quad \quad \quad \text{Eq. (1)}$$

$$199 \quad COD = \alpha_0 + \alpha_1 \cdot T + \alpha_2 \cdot [O_3] + \alpha_3 \cdot t + \alpha_{11} \cdot T^2 + \alpha_{12} \cdot T \cdot [O_3] + \alpha_{13} \cdot T \cdot t + \alpha_{22} \cdot [O_3]^2$$

200 $+ \alpha_{23} \cdot [\text{O}_3] \cdot t + \alpha_{33} \cdot t^2$ Eq. (2)

201

202 Non-significant terms are removed from the model by stepwise backward selection.

203 Finally, the reduced models for De and COD are optimized to determine the best

204 conditions with each single variable. Data fitness is assessed by the determination of r^2

205 coefficient. Absolute optimums, maximization of detergency and minimization of COD

206 are validated experimentally in the BSF, as well as the experimental error and deviation

207 between the predicted and experimental values.

208 **2.6 Multi-objective optimization.**

209 The study of independent variables allows us to identify minimums and

210 maximums of little relevance. However, a joint study of the two output variables

211 provides much more information. For this, a Pareto Front is created by the ϵ -constraint

212 technique, which consists of maximizing/minimizing one single variable while another

213 is fixed (Halsall-Whitney and Thibault, 2006). In this case, the detergency value is

214 fixed, and COD is reduced to a minimum value, by means of decreasing the time, the

215 ozone concentration and the temperature values needed to achieve such De and COD

216 values. The optimization problem can be defined as follows:

217 a) Fixing (De) and reducing (t,[O₃],T).

218 b) Minimizing COD and reducing (t,[O₃],T).

219 Both optimization problems were restricted to:

220 $30 \leq t \text{ (min)} \leq 120$

221 $30 \leq T \text{ (}^\circ\text{C)} \leq 60$

222 $0 \leq [\text{O}_3] \text{ (g/Nm}^3\text{)} \leq 42.30$

223 For this purpose, the GRG non-linear algorithm implemented by Solver Tool of MS
224 Excel software is selected (detailed information about GRG algorithm can be consulted
225 at <http://www.solver.com>).

226

227 **3. Results and discussion.**

228 **3.1 Influence of temperature, ozone and cleaning time on detergency.**

229 Firstly, the influence of an oxygen flow of 40 NL/h (without ozone) on the
230 removal of starch is analyzed. The assays made at different temperatures for 120
231 minutes indicate that, in absence of ozone, the same detergency is obtained in the
232 presence of oxygen flow as in its absence (data not shown). Hence, considering that the
233 conditions used for all the experiments are similar (same device and gas flow), the
234 bubbles produced at 40 NL/h in all assays do not affect the cleaning results.

235

236 **3.1.1 Detergency analysis.**

237 As an example, **Figure 2a** shows the detergency obtained through 120 min at
238 different temperatures (20-60°C) and ozone concentrations (0.00 and 42.30 g/Nm³).
239 Increasing temperature raises starch cleaning with or without ozone treatment;
240 temperature plays an important role in cleaning processes, especially in relation to solid
241 fouling (Goode et al., 2013) and it is generally found that the higher the cleaning
242 temperature, the higher the detergency and energy consumption. The starch removal,
243 both in the presence and absence of ozone, increases rapidly during the first 30 minutes
244 of the cleaning process (**Figure 2a**) - likely influenced by the effect of drag, swelling
245 and solubilization-, followed by a gradual declining of the deterrent rate until reaching
246 an inflection point around 60 minutes. From that point, detergency remains practically
247 constant or increases until final 120 minutes. These results lead to the conclusion that

248 due to the deterative rate decreases after 30 minutes, a suitable cleaning time would be
249 below 60 min, conditioned to reach the desired degree of cleaning within that time.
250 When the cleaning results obtained with and without ozone are compared (**Figure 2a**), a
251 similar behavior is found at both 20 and 40°C, obtaining values after 120 min of 33%
252 and 63% approx., respectively. However, at 60°C the behavior is quite different.
253 Detergency reached higher values when ozone (42.30 g/Nm³) is used for all the times
254 analyzed. Thus, the highest detergency (88%) is obtained at 60 °C and ozone (42.30
255 g/Nm³), compared to 68% obtained in the absence of ozone current.

256 At alkaline pH, ozone decomposes into radicals, mainly hydroxyl radicals,
257 increasing this decomposition with raising pH. These radicals are non-selective and
258 have stronger oxidation mechanism than that of ozone, giving rise to an advanced
259 oxidation process (Boczkaj and Fernandes, 2017a). Castanha e al. (2019) observed that
260 the ozonated potato starch had a less compact structure due to the cleavage of their
261 glycosidic bonds and the presence of electronegative groups. Klein et al.(2014)
262 evaluated the starch properties associated with ozone treatment in aqueous solution
263 finding that the ozonation in basic media produced the cross-linking between the
264 depolymerised starch. The formation of intermolecular crosslinks between ozone gas
265 and amylose molecules is accompanied by the depolymerization of amylopectin chains
266 (Oladebeye et al., 2013). So, the chemical changes generated by ozone in the starch
267 during the cleaning protocol increase the starch detergency due to the amylose is more
268 soluble than amylopectin. For the ozonation of potato starch.

269

270 **3.1.2 COD analysis.**

271 **Figure 2b** shows the COD values obtained when the cleaning assays are made at
272 different temperatures (20-60°C) and cleaning times, up to 120 min, in the presence and

273 absence of ozone (0 and 42.30 g/Nm³). As it is expected, there is a direct relationship
274 between the COD and the starch concentration in the wastewater for the ozonation
275 assays (**Figure 2a** and **2b**).

276 When detergency and COD results are compared jointly, it is observed that,
277 throughout the 120 min of experimental time, COD is lower for the cleaning assays
278 made with ozone, although the detergency obtained in this case is almost equal (at 20-
279 40 °C) to that one without ozone or even higher (at 60 °C). Therefore ozone causes an
280 important increase of wastewaters degradation, being more significant with increasing
281 temperature (when higher detergency values are also obtained). In addition, almost the
282 same time profile can be observed with De and COD, especially at washing times
283 higher than 60 minutes, where a practically constant stage is reached. Hence, in spite of
284 that at 20 and 40°C detergency is not improved, there would be a beneficial degradation
285 of the cleaning waste reducing the associated sewage treatment cost.

286 As commented in **section 3.1.1**, at 60 °C, detergency is higher with ozone,
287 raising until 60 min and remaining practically constant or slowly increasing up to 120
288 min. These results suggests that ozone increase the detergency and reduces the COD of
289 the wastewater. Leifeld et al.(2018) also used ozone with wastewater obtained from
290 starch processing, finding reductions of about 30-70% in COD after the ozonation
291 processes. The toxicity tests indicated that the structural modification of organic
292 components of wastewater reduced the toxicity after ozonation. Chan et al.(2011) also
293 demonstrated that ozonation is a clean technology that required limited downstream
294 purification processes

295

296 **3.2 Application of experimental design to detergency and COD results.**

297 Two factorial models are used for De and COD as described in section 2.5.
 298 **Table 1** shows the model statistical analysis via ANOVA. De and COD have 5 and 6
 299 significant effects respectively (p-value smaller than 0.05) and two reduced
 300 mathematical models are obtained **Eq.(3)** and **(4)**:

301

$$302 \quad De_{\text{model}} = -23.5330 + 0.8550 \cdot T - 0.3379 \cdot [\text{O3}] + 0.6885 \cdot t + 0.0115 \cdot T \cdot [\text{O3}] - 0.0027 \cdot t^2 \quad \mathbf{Eq. (3)}$$

$$303 \quad COD_{\text{model}} = -429.561 + 19.6828 \cdot T - 6.9233 \cdot [\text{O3}] + 15.1282 \cdot t + 0.1824 \cdot [\text{O3}]^2$$

$$304 \quad -0.0592 \cdot [\text{O3}] \cdot t - 0.0593 \cdot t^2 \quad \mathbf{Eq. (4)}$$

305

306 where De_{model} and COD_{model} are the De and COD calculated by the mathematical model,
 307 respectively. In both cases, r^2 and r^2 adjusted indicates that the model explains over 94%
 308 of the data variability (**Table 1**). For both models, the correlation matrix shows a
 309 perfectly orthogonal design with a random distribution of real and calculated values
 310 (**Fig 3a** and **3b** with r^2 values of 0.9514 and 0.9369 respectively).

311 **Table 1** demonstrates a significant impact of temperature, time and ozone on
 312 detergency. An increase of temperature, cleaning time and ozone concentration has a
 313 general positive influence on starch removal. Regarding the single effects, temperature
 314 and time show the most important ones in the cleaning process. Temperature and ozone
 315 also exhibit a positive interacting effect on detergency. However, at low temperatures
 316 there is not an improvement of the starch removal with ozone (as discussed in section
 317 3.1.1), being the parameter α_2 negative in order to represent such behavior. Regarding
 318 the quadratic effects, only the washing time displays negative influence on detergency
 319 due to detergency rate tends to lower at high times, even detergency becoming constant
 320 (as previously commented in section 3.1.1), and then the removal is not improved.
 321 Similar to mentioned above for detergency, both temperature and cleaning time show

322 the effects with the greatest influence on COD increase, obviously linked to the starch
323 amount present in the wastewater. On the other hand, ozone has the most influential
324 effect on the reduction of COD, helping the degradation of cleaning wastewater (as
325 mentioned in section 3.1.2).

326 **Figures 4a, b and c** shows the contour plots for the detergency indicated by the
327 mathematical model (**Eqs.(3)** and **(4)**) at different ozone concentrations. With the same
328 temperature and experimental time, higher detergency is obtained when ozone
329 concentration is increased. For example, to reach a detergency close to 60% after 75
330 min it is necessary to clean at 55, 49 and 46 °C using an ozone concentration of 0.00,
331 21.30 or 42.30 g/Nm³, respectively. It is also observed that the maximum detergency
332 (87%) is achieved at the highest temperature, time and ozone concentration (60°C, 120
333 min and 42.30 g/Nm³ respectively). **Figures 4d, e and f** shows the contour plots for
334 COD indicated by the mathematical model (**Eq.(3)** and **(4)**) at different ozone
335 concentrations. As expected, for each ozone concentration assayed, the COD values are
336 higher when higher detergency values are obtained (at higher temperatures and longer
337 experimental times). However, it is observed that although greater detergency is
338 obtained when ozone is used in the washing process, COD values are lower under these
339 conditions. Clearly, the incorporation of ozone in the washing process reduces the
340 wastewater COD, producing a partial degradation of the substances.

341 As commented previously in **section 3.1.2**, a relationship is found between COD
342 values, detergency, and ozone concentration in the cleaning process. A parameter called
343 " COD_{model} / De_{model} " is defined to analyze this effect being defined as the COD value
344 divided by detergency, both calculated by **Eq.(3)** and **(4)**. If this parameter decreases, it
345 would indicate that a COD reduction is also taking place in the washing process, thus
346 leading to a reduction in wastewater contamination. **Figures 5** shows the COD_{model}

347 $/De_{\text{model}}$ calculated as a function of time and temperature at different ozone
348 concentrations. As it can be observed, for ozone concentration equal to 0 g/Nm^3 (**Figure**
349 **5a**), at low temperature and short experimental time, the parameter value is the highest,
350 being reduced when time and temperature increases suggesting the starting point of a
351 chemical degradation of the starch. An important part of the starch removed from the
352 substrate appears as small pieces in suspension at low experimental times, although
353 these pieces ends up dissolving in the wastewater when the washing time increases,
354 being this process accelerated when the temperature increases. However, COD_{model}
355 $/De_{\text{model}}$ coefficient is practically constant to 25 throughout almost all the range
356 analyzed.

357 When ozone is used, lower $COD_{\text{model}} /De_{\text{model}}$ values are obtained due to the
358 attack of ozone radicals on starch, this effect being more pronounced when a higher
359 concentration of ozone and higher values of time and temperature are used. **Figure 5b**
360 shows the $COD_{\text{model}} /De_{\text{model}}$ values obtained at different time-temperature values when
361 the ozone concentration assayed is 21.15 g/Nm^3 . $COD_{\text{model}} /De_{\text{model}}$ values are lower
362 than in the absence of ozone, and even lesser with 42.30 g/Nm^3 of ozone (**Figure 5c**).

363 The mathematical models predict satisfactorily the cleaning of starch and the
364 wastewater degradation, demonstrating that the use of ozone in the washing process
365 increases not only the detergency with temperature, but also the pre-depuration of the
366 cleaning solution: the lowest value of COD per unit of detergency is obtained (COD_{model}
367 $/De_{\text{model}}$) at the highest ozone concentration.

368

369 **3.3 Multi-objective optimization of the cleaning process.**

370 COD is minimized according to cleaning parameters such as ozone
371 concentration, time and temperature in the cleaning test, whereas detergency values are

372 fixed, as described in section 2.6. **Table 2** shows the minimum value of COD (COD_{min})
373 and conditions to reach a given detergency between 40% and 86.7%. For these
374 conditions, the minimum value of COD (COD_{min}) is always obtained at 120 min.
375 **Figure 6** shows that COD_{min} and temperature present a linear increase with detergency.
376 Regarding the use of ozone, **Table 2** indicates that to reach detergency values between
377 40-60%, a slight increase in the ozone concentration (from 32.7 to 36.9 g/Nm³) is
378 needed to attain the COD_{min} . To achieve detergency values higher than 60%, it is always
379 necessary to work with ozone concentrations of 42.30 g/Nm³, reaching detergency
380 values close to 90%.

381 Therefore with this multi-objective optimization it could be possible to approach
382 the research results to the industrial end-users needs, making a CIP protocol adequate to
383 their requirements. So, as a function of the detergency level required in the cleaning
384 process, the values of temperature, time, and ozone concentration could be optimized
385 (minimized) depending on the final COD required. The economic estimation of the
386 different cleaning protocols is suitable in order to be more realistic in industrial
387 applications.

388

389 **4. Conclusions.**

390 The cleaning of heat-treated starch adhered to a stainless steel surface is studied
391 in a cleaning device that simulates a CIP system, analyzing the influence of time (30-
392 120 minutes), ozone concentration (0.00-42.30 g/Nm³), and temperature (20-60 °C)
393 using alkaline solutions. An increase in detergency is obtained when ozone is used at
394 high temperature. The highest detergency is obtained at 60°C and 120 min, reaching 68
395 and 88% with ozone concentrations of 0 and 42.30 g/Nm³, respectively. COD values
396 show similar behavior to detergency values, being lower when ozone is used. Two

397 mathematical models are proposed and verified to evaluate the detergency and COD
398 using an experimental design. The multi-objective optimization shows the temperature
399 and ozone concentration to minimize COD for a detergency value. COD/De is lower
400 when ozone is used obtaining a greater reduction using the higher the concentration of
401 ozone, cleaning time and temperature. Therefore, under the conditions assayed, ozone
402 not only enhances starch removal but also allows its degradation through an advanced
403 oxidation process, reducing the contamination charge of water after the cleaning
404 process, hence combining cleaning process and wastewater treatment in a single step.
405 However, more research is needed to be able to incorporate these experimental
406 conditions into the industry since it is necessary to evaluate, for example, the risk of
407 oxygenated organic compounds formation and the environmental impact they would
408 cause on the environment (Makos et al., 2019) and the economic cost of replacing this
409 technology with existing ones.

410

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414

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1 **Figure captions.**

2

3 **Figure 1.** BSF device including an ozonation system: (1) jacketed tank, (2) pump, (3)
4 column, (4) thermostatically controlled bath and (5) gas diffuser. **1a) Schematic**
5 **diagram, 1b) Photography.**

6

7 **Figure 2 -** Influence of temperature and ozone on detergency and COD. $[O_3] = 0 \text{ g/Nm}^3$
8 (filled symbols), $[O_3] = 42.30 \text{ g/Nm}^3$ (hollow symbols). 20°C (circles), 40°C (squares),
9 60°C (triangles). **2a) Detergency results, 2b) COD results.** **The error bars represent $\pm\text{SD}$**
10 **of at least 3 replicates.**

11

12 **Figure 3.** Distribution of the model and experimental values: **3a) Detergency, 3b) COD**

13

14 **Figure 4.** Contour plots for De (%) and COD (mgO_2/L) of cleaning wastewater from
15 mathematical model (Eqs.(3) and (4)). Influence of temperature, ozone concentration
16 and cleaning time. Detergency graphs: **a) $[O_3] = 0.00 \text{ g/Nm}^3$, b) $[O_3] = 21.15 \text{ g/Nm}^3$, c)**
17 **$[O_3] = 42.30 \text{ g/Nm}^3$. COD graphs: d) $[O_3] = 0.00 \text{ g/Nm}^3$, e) $[O_3] = 21.15 \text{ g/Nm}^3$, f) $[O_3]$**
18 **$= 42.30 \text{ g/Nm}^3$ (lines show the model results)**

19

20 **Figure 5-** Influence of temperature and cleaning time on $\text{COD}_{\text{model}} / \text{De}_{\text{model}}$. Ozone
21 concentration: **a) 0.00 g/Nm^3 , b) 21.15 g/Nm^3 , c) 42.30 g/Nm^3** (lines show the model
22 results)

23

24 **Figure 6.** Multi-objective optimization. Dependence of COD_{min} and the temperature
25 needed to reach the COD_{min} as a function of the detergency required. $t=120 \text{ min}$. ■
26 COD_{min} , ● T (lines show the model results)

27

Figure1a

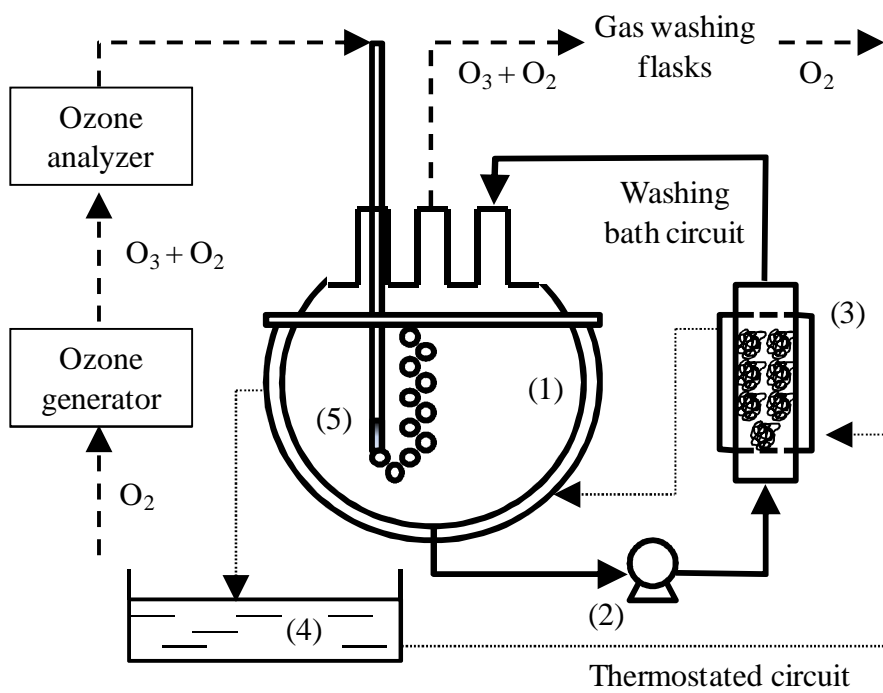


Figure 1b



Figure 2a.

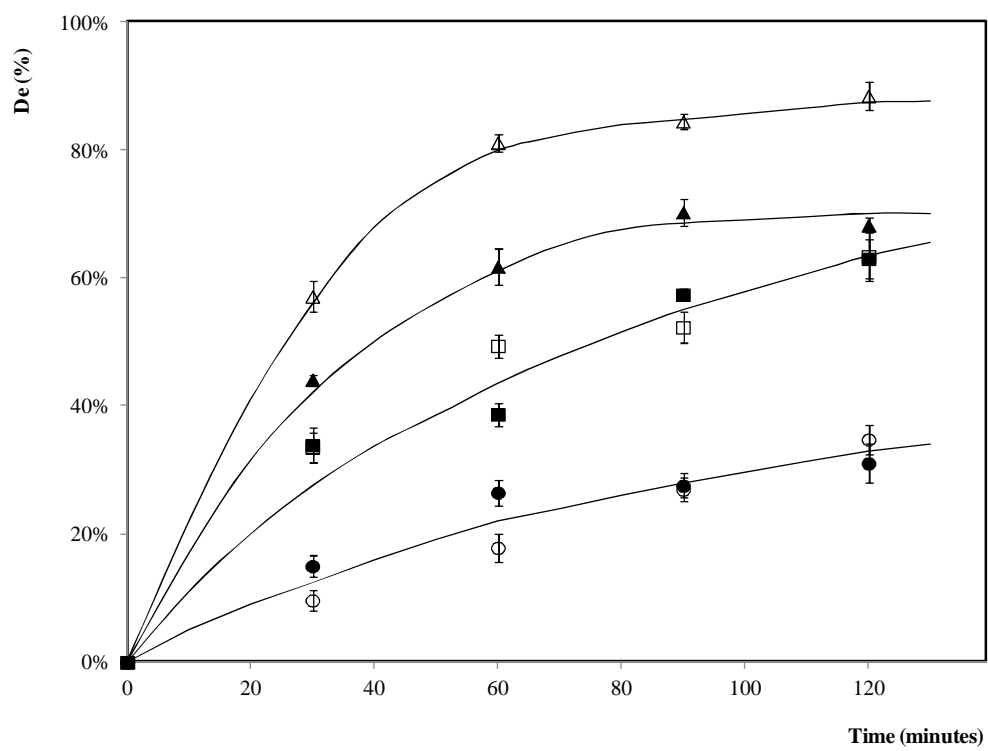


Figure 2b.

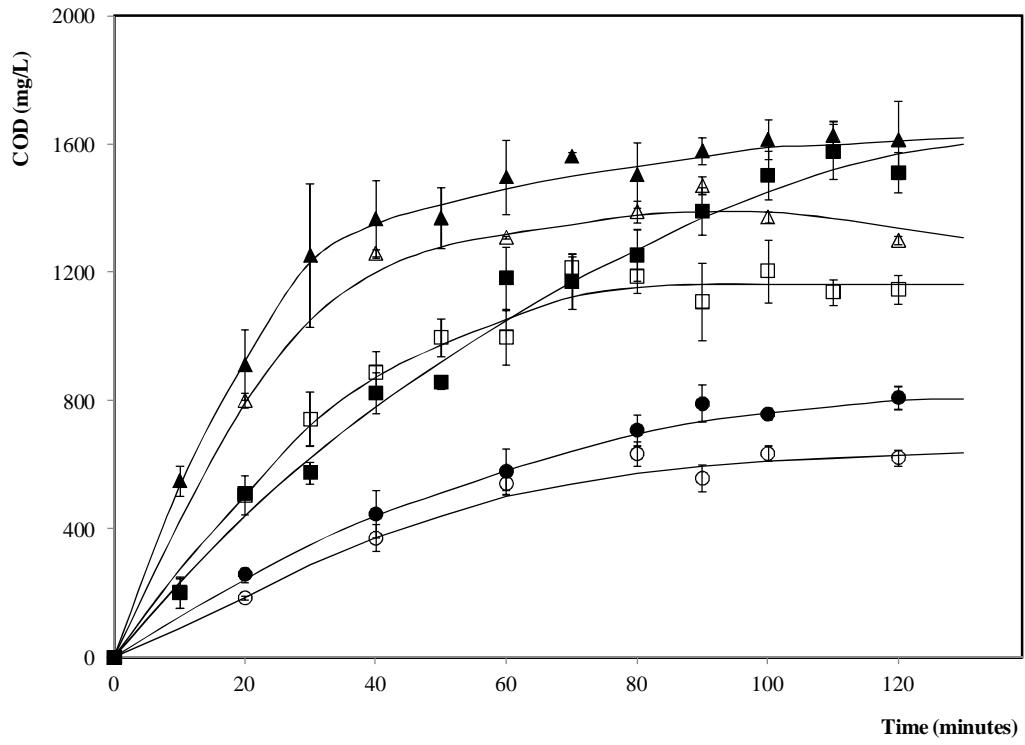


Figure 3a.

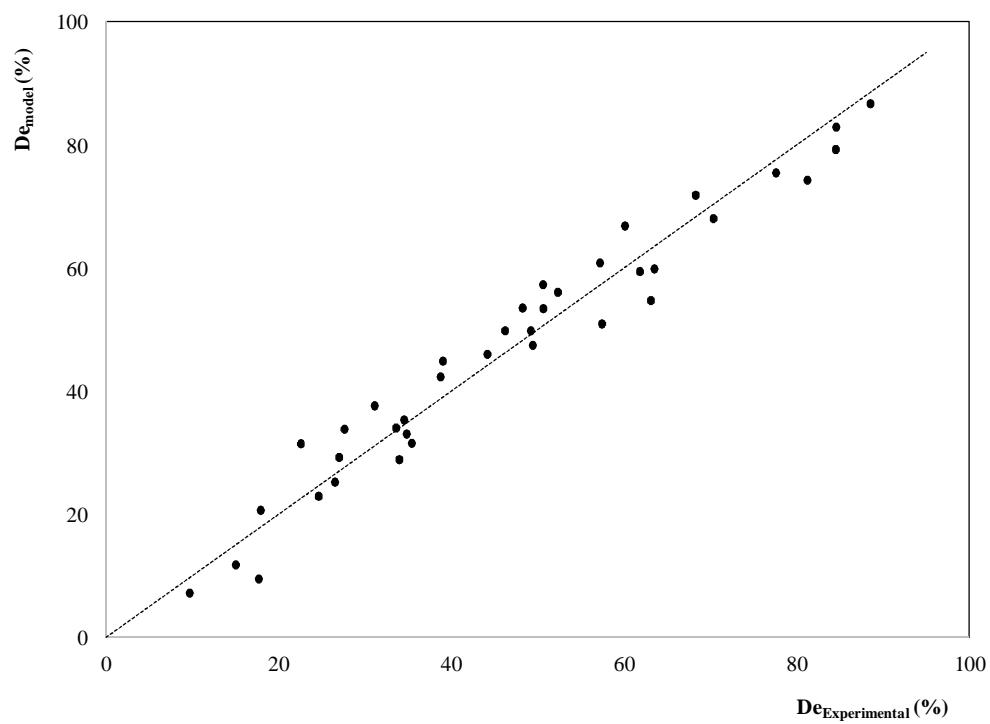


Figure 3b.

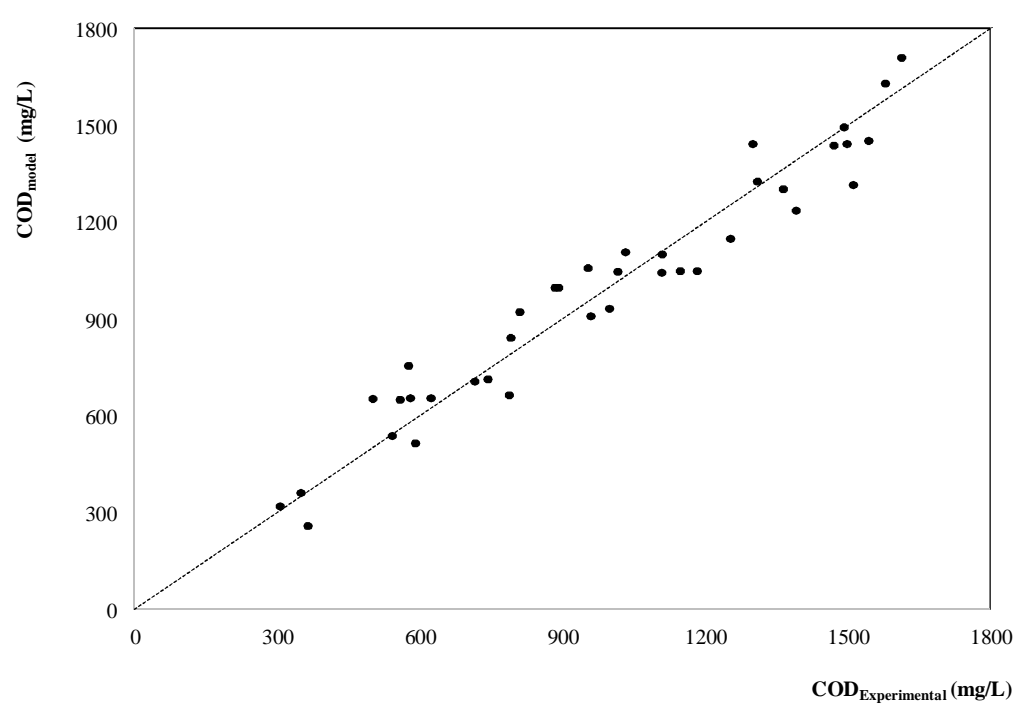


Figure4abc

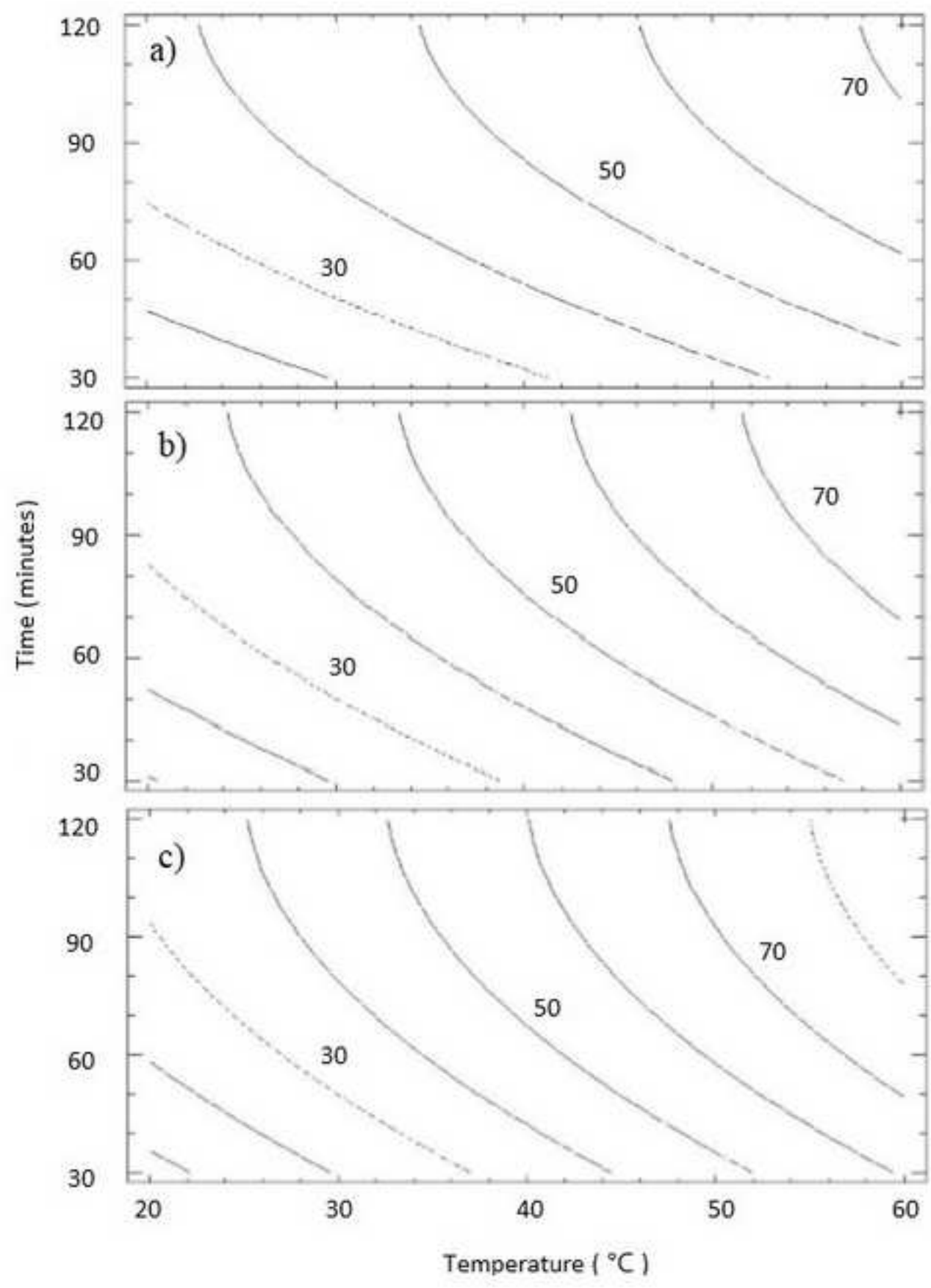


Figure4def

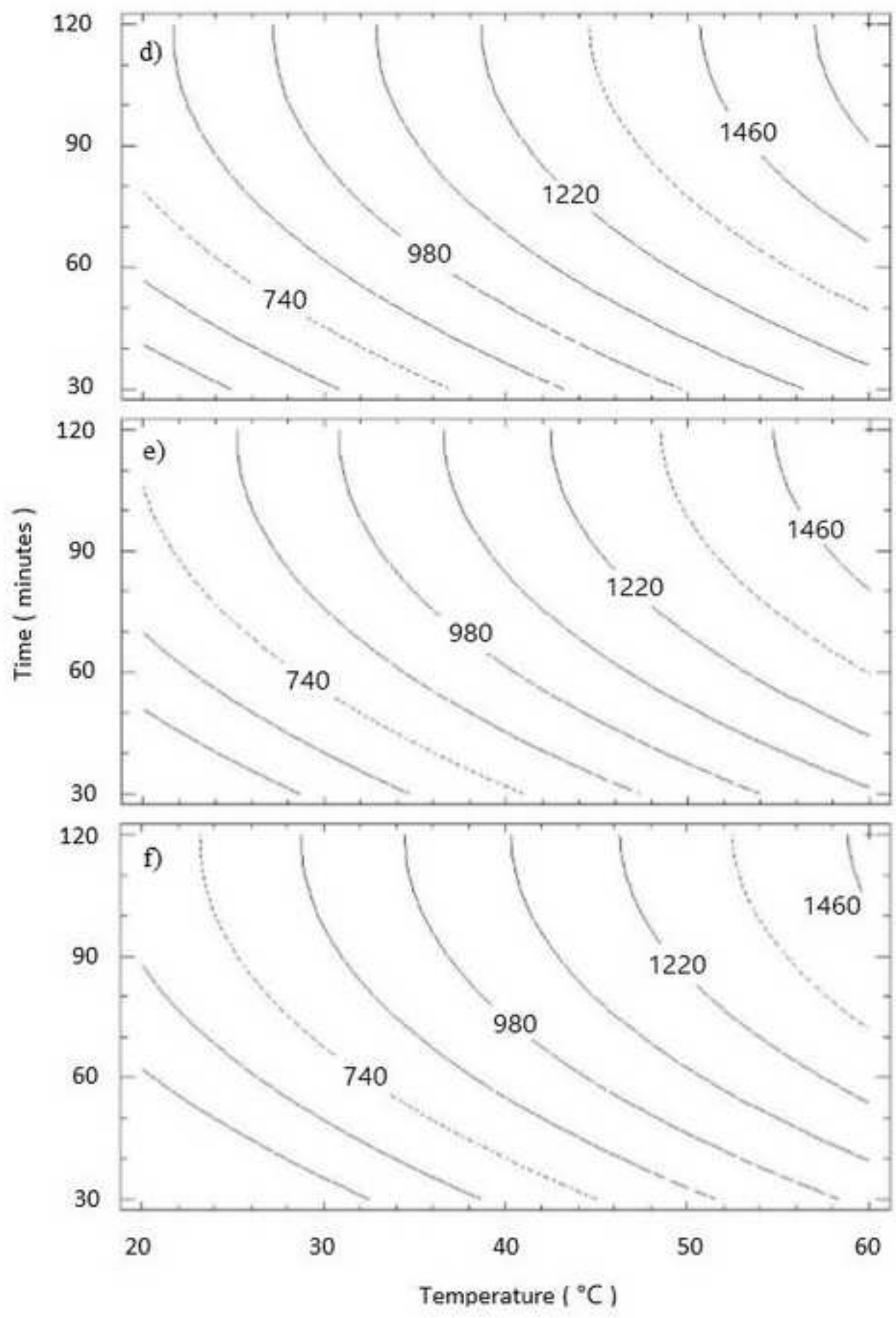


Figure 5a.

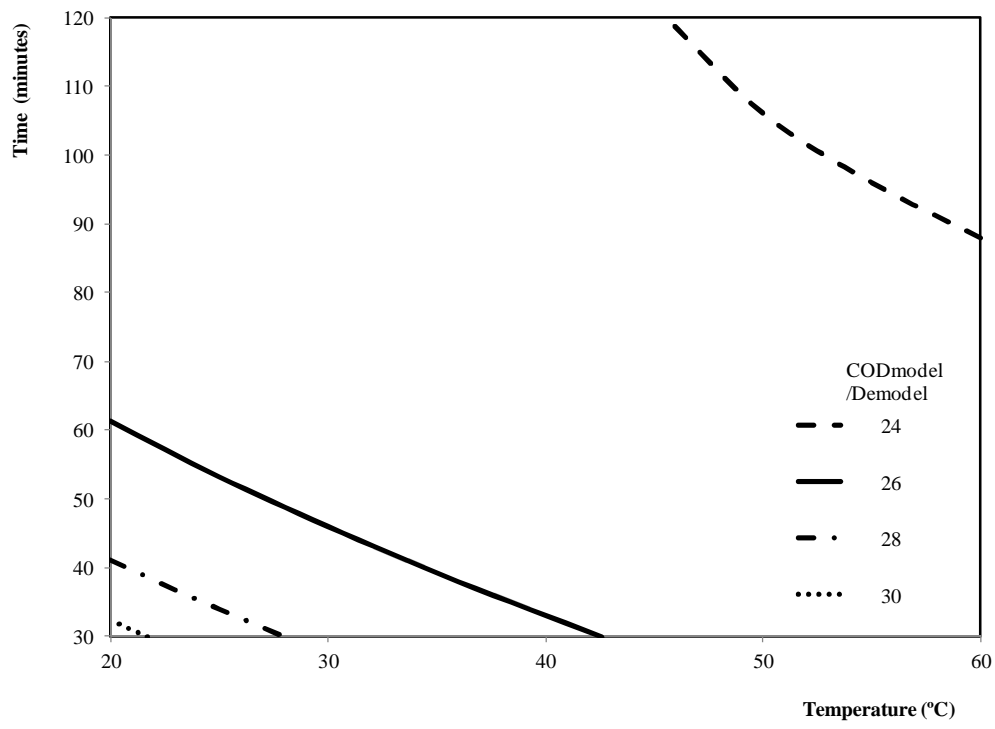


Figure 5b.

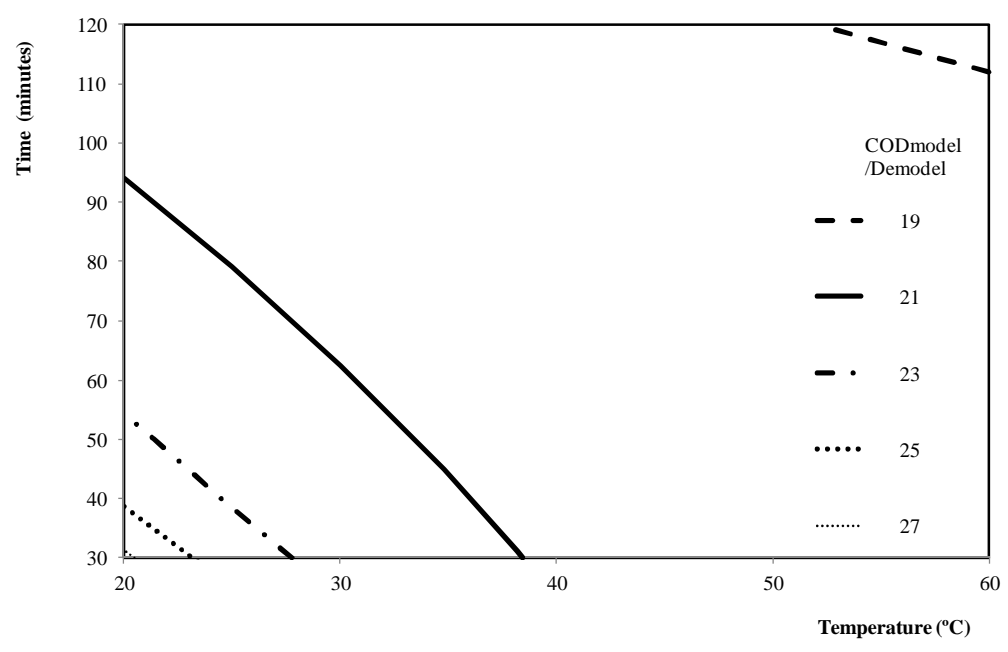


Figure 5c.

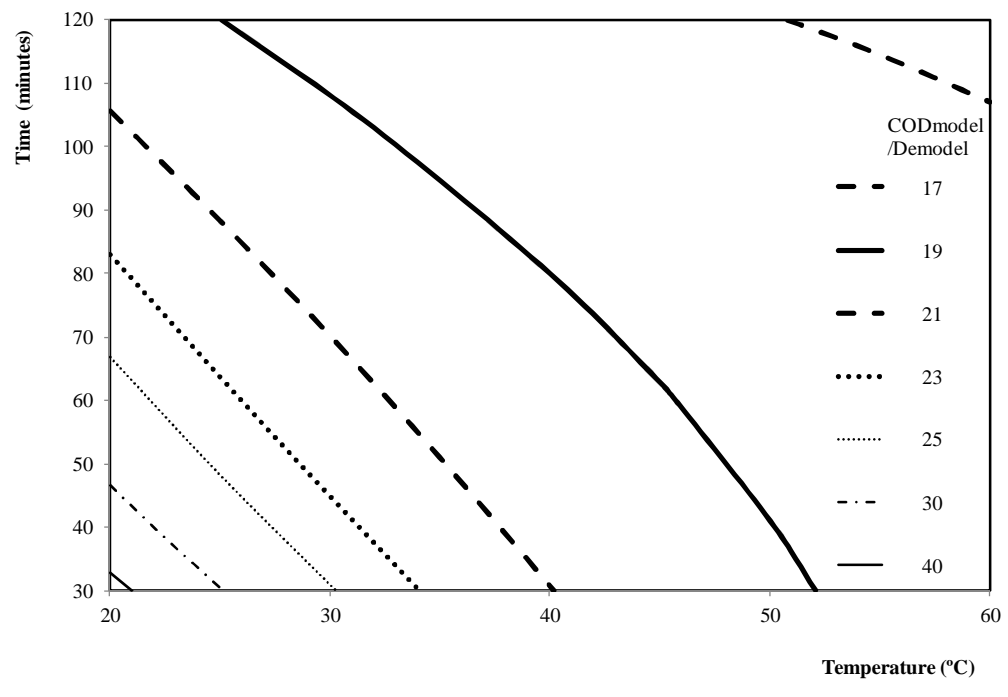


Figure 6.

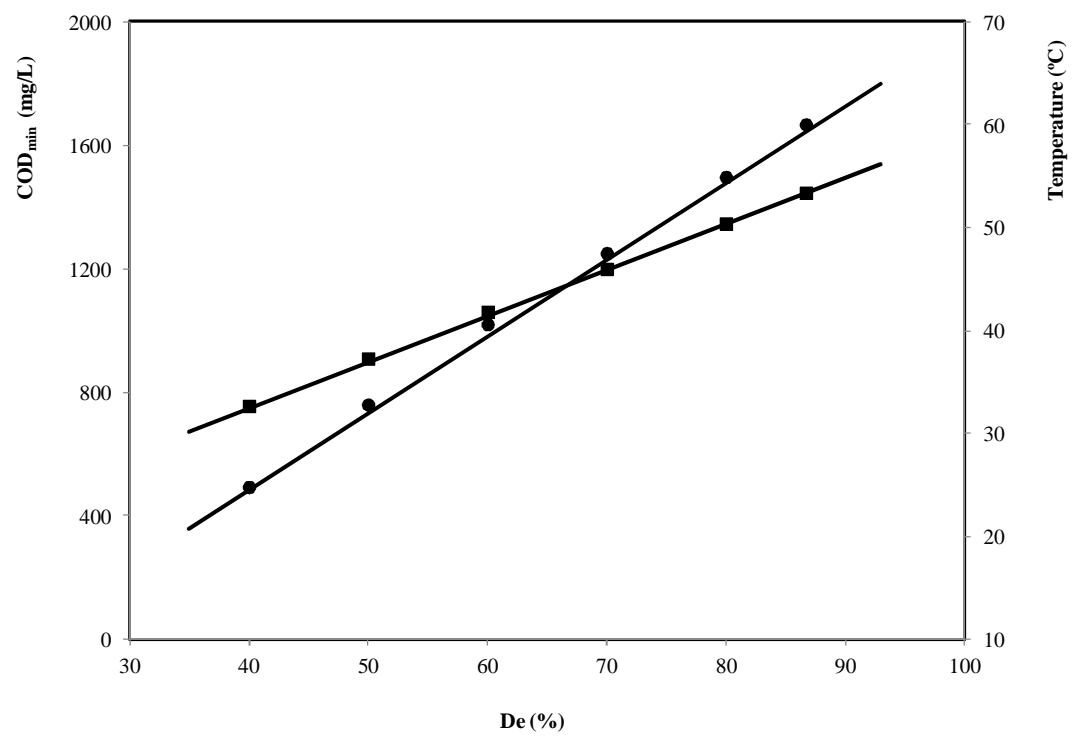


Table 1. Mathematical model Eqs.(1-2) for De and COD results. Coefficients and effects.

Model terms	Detergency		COD		De Effects	COD Effects
	Coefficient value	(p-value)	Coefficient value	(p-value)	Value	Value
α_0	-23.5330		-429.5610			
T	0.8550	0.0000	19.6828	0.0000	43.9120	787.3310
[O3]	-0.3379	0.0168	-6.9233	0.0005	5.1331	-154.2690
t	0.6885	0.0000	15.1282	0.0000	25.8407	447.6360
T ²	0.0000	ns	0.0000	ns	0.0000	0.0000
T·[O3]	0.0115	0.0005	0.0000	ns	9.7131	0.0000
T·t	0.0000	ns	0.0000	ns	0.0000	0.0000
[O3] ²	0.0000	ns	0.1824	0.0191	0.0000	163.2130
[O3]·t	0.0000	ns	-0.0592	0.0436	0.0000	-112.7030
t ²	-0.0027	0.0050	-0.0593	0.0019	-10.8360	-240.3610
r ²	95.2		94.5			
r ² (df)	94.4		93.4			

ns: Non significant at 95% confidence level ($p > 0.05$)

r² (df): r² adjusted to the degrees of freedom.

Table 2. Multi-objective optimization. Pareto front. COD_{min} for each detergency. t=120 min

De (%)	COD_{min} (mg O₂/L)	T (°C)	[O₃] (g/Nm³)
40.0	755	24.8	32.7
50.0	910	32.8	34.9
60.0	1061	40.6	36.9
70.0	1200	47.5	42.3
80.0	1346	54.9	42.3
86.7	1445	60.0	42.3