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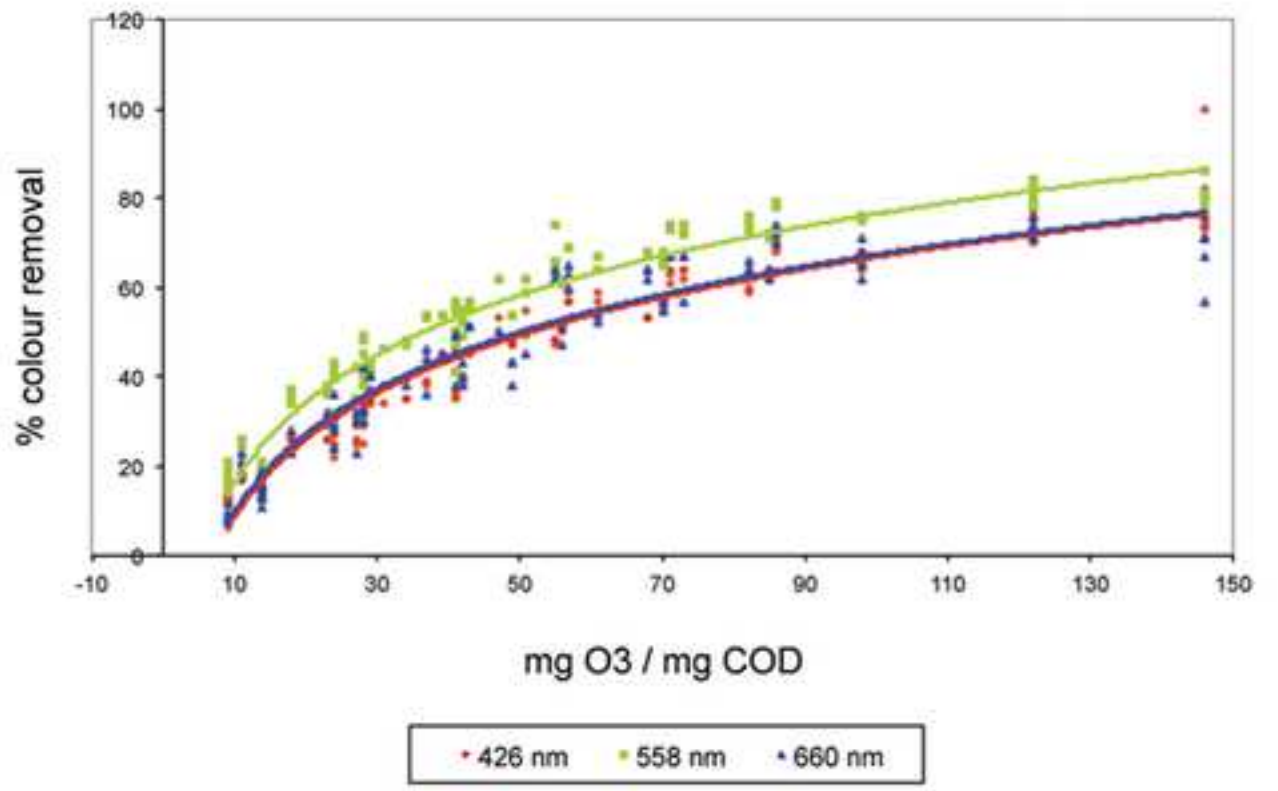
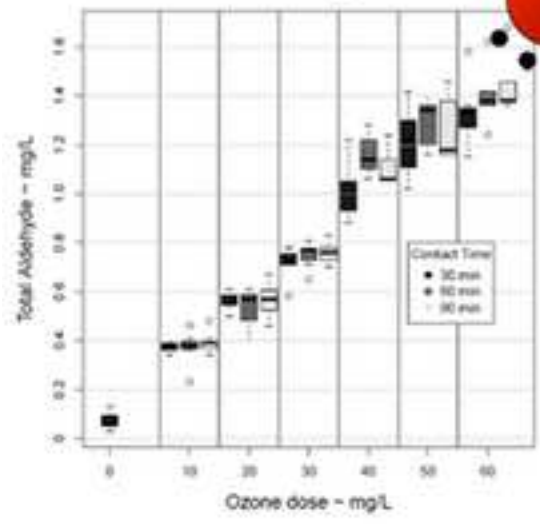
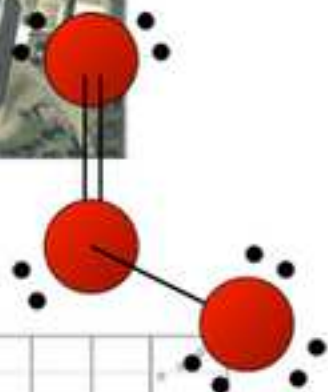
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Highlights

- We tested high dose ozonation (10÷60 mg O₃ L⁻¹) on a treated effluent
- Complete colour removal was needed
- At 60 mg O₃ L⁻¹ aldehyde concentration ranged between 0.72 and 1.02 mg L⁻¹
- Glyoxal and methylglyoxal concentrations were directly related to colour removal
- Colour removal can be used for predicting glyoxal and methylglyoxal concentration



ABSTRACT

A series of experimental tests has been conducted to investigate the efficiency and the by-product generation of high dose ozonation (10 to 60 mg O₃ L⁻¹) for complete colour removal from a treated effluent with an important component of textile dyeing wastewater. The effluent is discharged into an effluent-dominated stream where no dilution takes place, and thus, the quality requirement for the effluents is particularly strict. Three contact times were adopted: 30, 60 and 90 min. Colour was measured as absorbance at 426, 558 and 660 nm wavelengths. The experimental work showed that at 50 mg L⁻¹ colour removal was complete and at 60 mg O₃ L⁻¹ the final aldehyde concentration ranged between 0.72 and 1.02 mg L⁻¹. Glyoxal and methylglyoxal concentrations were directly related to colour removal, whereas formaldehyde, acetaldehyde, acetone and acrolein were not. Thus, the extent of colour removal can be used to predict the increase in glyoxal and methylglyoxal concentrations. As colour removal can be assessed by a simple absorbance measurement, in contrast to the analysis of specific carbonyl compounds, which is much longer and complex, the possibility of using colour removal as an indicator for predicting the toxic potential of ozone by-products for textile effluents is of great value.

1 **Colour removal and carbonyl by-production in high dose ozonation for**
2 **effluent polishing**

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18

19 **ABSTRACT**

20 A series of experimental tests has been conducted to investigate the efficiency and the by-
21 product generation of high dose ozonation (10 to 60 mg O₃ L⁻¹) for complete colour
22 removal from a treated effluent with an important component of textile dyeing wastewater.
23 The effluent is discharged into an effluent-dominated stream where no dilution takes place,
24 and thus, the quality requirement for the effluents is particularly strict. Three contact times
25 were adopted: 30, 60 and 90 min. Colour was measured as absorbance at 426, 558 and
26 660 nm wavelengths. The experimental work showed that at 50 mg L⁻¹ colour removal was
27 complete and at 60 mg O₃ L⁻¹ the final aldehyde concentration ranged between 0.72 and
28 1.02 mg L⁻¹. Glyoxal and methylglyoxal concentrations were directly related to colour
29 removal, whereas formaldehyde, acetaldehyde, acetone and acrolein were not. Thus, the
30 extent of colour removal can be used to predict the increase in glyoxal and methylglyoxal
31 concentrations. As colour removal can be assessed by a simple absorbance
32 measurement, in contrast to the analysis of specific carbonyl compounds, which is much
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34 the toxic potential of ozone by-products for textile effluents is of great value.

35

36 **Keywords:** Ozonation; colour removal; carbonyl by-products

37

38 **1. Introduction**

39 In effluent-dominated streams (Schmidt, 1993) advanced processes to polish treated
40 effluents must be adopted to reduce the impact of discharge on the receptor. In reality,
41 where the base flow of the stream is essentially made of effluents from wastewater
42 treatment plants, the flow of the receptor is too low to allow any significant dilution of the
43 residual input load; the aim of wastewater treatment should be to produce an effluent
44 quality as close as possible to an acceptable river water quality.

45 The present study has been carried out at the Bulgarograsso Wastewater Treatment Plant
46 (WWTP)(province of Como, Northern Italy), fed on mixed (industrial and urban)
47 wastewater and discharged into the stream Lura, which remains dry for most of the year
48 (Canobbio et al., 2009). The industrial flow is approximately 70% of the total inflow and
49 approximately 60% of the organic load fed to the WWTP and derives primarily from textile
50 dyeing industries. Consequently, it is characterised by high concentrations of surfactants
51 (especially non-ionic ones) and is quite strong in colour. The Bulgarograsso WWTP
52 includes a biological section consisting of pre-denitrification and biological oxidation
53 followed by sand filtration and chemical oxidation by ozone. In terms of removal rates, its
54 performance is satisfactory when compared with the discharge limits but is still insufficient
55 when considering that its effluent becomes river water in practice. The most serious
56 problems arise from the presence of residual colour that is not completely removed in the
57 present operative conditions. The chief procedure in colour removal is based on ozonation,
58 which is performed at 10-15 mg L⁻¹ with a 90-min average contact time and is designed to
59 remove especially colour and non ionic surfactants.

60 In textile dyeing effluents the colour is related to the residual, non exhausted dyestuffs
61 which are discharged, not being or being only partially removed in conventional activated
62 sludge treatment plants. In the case of centralized WWTP, a wide variety of dyestuffs can
63 be found, according to the different fabrics and processes performed by each factory.
64 Synthetic dyes are reported as one of the largest groups of organic pollutant in
65 wastewaters (Pan et al., 2011). Azo compounds, having the -N=N- group as
66 chromophore, represent about half of the whole dyestuff production in the world (Liu et al.,
67 2007) and are recognized, along with antraquinone dyes, as non-degradable by the
68 conventional activated sludge process (Wei Chu & Chi-Wai, 2000). They are thus a major
69 component in biologically treated effluents from the textile dyeing industry. Normally the
70 input of coloured effluents does not cause direct toxicity to the receiving water course, but

71 the visual impact is strong and some consequences of the influence on the light
72 penetration are likely to occur, even if till now they've not been documented.

73 Based on the kind of fabrics processed by the textile industries in Bulgarograsso area, it
74 can be estimated that most dyestuffs in wastewater belong to the class of reactive dyes,
75 most of which are azo-compounds, and that these are absolutely prevailing in the treated
76 effluent, due to their limited degradation during activated sludge process.

77 In the case of the Bulgarograsso WWTP, as well as in many similar plants, discharging
78 into effluent dominated streams, greater colour removal is needed, and the most suitable
79 solution to the problem seems to be the increase in ozone dose in the final polishing of the
80 effluent. Ozone is known for being highly efficient in removing colour from wastewater,
81 especially because of its high affinity for double bonds, which are responsible for colour in
82 the chromophore of most dyestuff molecules (Perkowski et al., 1996; Kos et al., 2000;
83 Antonelli et al., 2006). However, its dosage is often limited by the need to control the
84 formation of potentially toxic by-products.

85 Specific investigations have noted the potential ecotoxicity of ozonated effluents (Petala et
86 al.,2006) and pointed out that the toxicity of ozone-treated effluents on *Vibrio fischeri*
87 increased only for ozone doses of over 5.0 mg O₃ L⁻¹ and that ozonation influenced the
88 mutagenicity of secondary effluents (measured by Ames test) due to the possible
89 formation of intermediate by-products. (Petala et al., 2008)

90 The most frequently found (and most well-known) by-products of wastewater ozonation
91 are aldehydes (Bolzacchini et al., 2000; Silva et al, 2010; Melin & Odegaard, 2000; Huang
92 et al., 2005). In general, such compounds are considered to be hazardous in drinking
93 water: the WHO guidelines set a reference standard for formaldehyde at 0.9 mg L⁻¹, but no
94 such limit for aldehyde concentration in drinking water exists in Europe. In aquatic
95 medium, aldehydes absorb UV light and form very reactive organic free radicals.
96 Acetaldehyde has moderate acute toxicity to aquatic organisms.

97 According to the U.S. EPA database, acute toxicity values range from over 1 mg L⁻¹ to
98 100 mg L⁻¹, and the LC50 for fish is over 10 mg L⁻¹. The main aldehydes formed by
99 ozonation are formaldehyde (H₂CO), acetaldehyde (C₂H₄O), glyoxal (C₂H₂O₂) and
100 methylglyoxal, all of which are potentially carcinogenic and mutagenic and have been
101 observed to cause tumours in experimental animals (Bull & Koppfler, 1991). Italian law
102 sets limits for total aldehyde concentrations in wastewater for discharge and for re-use at 1
103 mg L⁻¹ and 0.5 mg L⁻¹, respectively, and this may be an important constraint when high
104 doses of ozone are needed to remove recalcitrant pollutants (Mezzanotte et al., 2005)
105 Many data exist regarding ozonation by-products at low ozone doses, while doses of over
106 10 mg L⁻¹ have been less studied. On the other hand, kinetic studies and detailed analyses
107 have been conducted on pure solutions of selected dyestuffs (De Souza et al., 2010, Koch
108 et al., 2002). The above considerations, along with the evidence of several
109 ecotoxicological surveys, have suggested the opportunity to investigate the quantitative
110 relationships between ozone dose, contact time, colour removal and aldehyde formation
111 on real effluent samples in order to assess the performance of the process in presence of
112 all the possible factors affecting colour removal and by-product generation.
113 In this view, a series of experimental tests was performed to define the ozone dose
114 needed to achieve complete colour removal from Bulgarograsso WWTP, representative of
115 common situations in industrial districts, and to assess the potential by-product generation
116 corresponding to the tested ozone dose.

117

118 **2. Materials and methods**

119 2.1 Experimental Design

120 Twelve samples, representative of the ordinary inflow conditions at the Bulgarograsso
121 WWTP, were collected, as described above, at different times. On average, COD was 70 ±
122 30 mg L⁻¹, absorbance at 426, 558 and 660 nm was 0.145 ± 0.038, 0.104 ± 0.027 and

123 0.049 ± 0.015, respectively, total aldehydes below the L.O.D. and pH 7.4÷7.5. The high
124 variability of the effluent chemical composition depends on the fact that industrial
125 wastewaters derive from small and medium size factories working for third parties and with
126 a certain discontinuity of industrial processes and production.

127 Each sample was ozonated at 10, 20, 30, 40, 50 and 60 mg L⁻¹ ozone doses and three
128 different contact times (30, 60, 90 min) were tested for each dose. At least 6 replicates
129 were completed for each combination of dose and contact time.

130 Removal efficiency has been evaluated using a two-way ANOVA model, considering both
131 ozone dose and contact time as treatments. To observe differences among specific
132 treatments, a posteriori comparisons were made using Tukey's HSD tests.

133

134 2.2 Experimental Tests

135 In the ozonation trials, a pressurised dry air-fed ozone generator (model TP 1/1 A/O₂,
136 Ozono Elettronica Internazionale) was used. Ozone was injected through a ceramic
137 porous diffuser into a 10 L contact reactor where mixing was optimised by magnetic
138 stirring. Ozone production and the working time of the ozone generator were set to obtain
139 the expected ozone concentration in the sample. Excess residual ozone was removed by
140 bubbling it into two in-series bottles filled with saturated KI solutions.

141

142 2.3 Sampling

143 The ozone treatment trials were carried out on samples collected at the outlet of sand
144 filtration of the Bulgarograsso WWTP. Samples (30 L) were collected in plastic containers
145 and transferred to the laboratory for analytical determination and ozone treatment.
146 Analyses and treatments were performed the same day of sampling to minimise the
147 chemical and biological degradation of the effluent components.

148

149 2.4 Analyses

150 COD, colour and total aldehyde concentration were analysed in the collected samples
151 prior to the ozone experimental trials. The analyses of the total aldehyde concentration
152 and colour were repeated after ozone treatment.

153 COD and total aldehyde analyses were performed according to the APHA Standard
154 Methods (APHA, 1998) and Italian standard methods (APAT-IRSA, 2003), respectively.

155 Colour was determined by absorbance at 426, 558 and 660 nm on 0.45- μ m filtered
156 samples by a Hach Lange DR3900 Visible Spectrophotometer.

157 After ozonation, the samples were further investigated by identifying the aldehydes
158 formed. The concentrations of formaldehyde, acetaldehyde, acetone, glyoxal,
159 methylglyoxal and acrolein were determined by HPLC-UV, after derivatisation with 2,4-
160 Dinitrophenylhydrazine (DNPH) (USEPA, 1996).

161 Such compounds have been chosen based on their toxicity, according to the literature
162 data (Bull & Koppfler, 1991).

163

164 **3. Results and discussion**

165 3.1 Colour removal

166 The various tested doses and contact times were evaluated to assess the optimal
167 operation parameters to obtain a nearly complete colour removal, thus minimising the
168 impact of the effluent input on the receiving water body. To obtain a better quantifiable
169 objective, a series of colour measurements has been performed at the three reference
170 wavelengths. The absorbance thresholds for non-detectable colour in the treated effluent
171 have been found at 0.012 (426 nm), 0.009 (558 nm) and 0.05 (660 nm). It is interesting to
172 observe that the threshold below which colour is not detectable is neither the same in
173 untreated and treated samples nor for different treatment doses, apart from consistently
174 being lower for the 660 nm wavelength. In contrast, absorbance is always much higher at

175 426 nm than at the other wavelengths; at 558 and 660 nm, absorbance is, on average,
176 57% and 33% of that of the 426 nm value. The influence of the starting quality must also
177 be taken into account. The starting COD is a chief component of ozone demand, and the
178 extent of its oxidation by ozone affects the overall effect of ozonation, including colour
179 removal. To overcome the problem and try to obtain a general interpretation to the
180 experimental data, the percent removal of colour at the three tested wavelengths has been
181 plotted against specific ozone dose for the three wavelengths. In Figure 1, percent colour
182 removal has been reported as a function of absolute ozone dose ($\text{mg O}_3 \text{ L}^{-1}$) and of
183 specific ozone doses referred to initial COD ($\text{mg O}_3 \text{ mg COD}^{-1}$) and initial absorbance (mg
184 O_3 ($\text{absorbance unit} \cdot 100$) $^{-1}$) for 426 nm wavelength. Further data, referred to 558 and 660
185 nm wavelength, are provided as supplementary material. Colour removal is well described
186 by logarithmic equations, as also reported in the literature (Sevimli & Sarikaya, 2002), with
187 a strong fitting in both cases. Colour and COD are normally co-variants in the starting
188 sample, even if ozone treatment affects their ratio because ozone is more efficient in
189 removing colour than COD. It is also true that, for common use, the measurement of
190 colour is much simpler and faster than COD analysis and the possibility of using
191 absorbance as reference parameter for setting ozone dose would be of great use.

192 To better understand the process, the specific roles of ozone dose and contact time have
193 been considered. Box-plots reporting the absorbance measured at the three tested
194 wavelengths as a function of ozone dose for the three contact times and the three tested
195 wavelengths are included in the Supplementary Material.

196 A two-way ANOVA model has subsequently been performed on the whole dataset. The
197 results are summarised in Table 1. The model shows high significance for all the three
198 wavelengths (always $p < 0.0001$). It can easily be observed that the role of contact time is
199 nearly negligible ($p = \text{non-significant}$ for all the three wavelengths), while colour removal is
200 significantly different among the different ozone doses ($p < 0.0001$ for all the three

201 wavelengths) and increases with increasing ozone doses. Tukey's HSD tests performed
202 on ozone doses at 426 nm show that every dose increase causes a significant (always
203 $p < 0.0001$) increase in colour removal, except for the highest dose increase (from 50 to 60
204 mg L^{-1}), which does not involve any further significant removal. At both 558 and 660 nm,
205 the increase of ozone dose results in a significantly increased removal of absorbance at
206 every step from 10 to 30 $\text{mg O}_3 \text{ L}^{-1}$. Over such a threshold, a significant improvement
207 takes place only when the ozone dose is raised from 30 to 50 $\text{mg O}_3 \text{ L}^{-1}$ ($p = 0.006$ at 558
208 nm and $p = 0.002$ at 660 nm) but not for any further dose increase. According to various
209 Authors (Wu & Wang, 2001; Chu & Ma, 2000), the decreasing efficiency of growing ozone
210 doses can depend on the low molecular diffusion of dissolved ozone. This could explain
211 the fact that over 50 mg L^{-1} no improvement in colour removal takes place. Below such
212 threshold, the presence of intermediates could justify the growing ozone consumption with
213 increasing ozone doses (Sevimli & Sarikaya, 2002) and a consequently lower efficiency in
214 colour removal.

215 Neglecting contact time, as it has been shown to be not relevant, the average colour unit
216 removal per $\text{mg O}_3 \text{ L}^{-1}$ is 0.0018 ± 0.0004 , 0.0016 ± 0.0005 and 0.0006 ± 0.0002 for 426, 558
217 and 660 nm absorbance, respectively. Of course, the observed specific colour removal
218 cannot be generalized, being strongly affected by the specific concentrations of the
219 different dyestuffs as well as by the overall properties of the treated effluent, but provide a
220 useful indication.

221 As previously described, in the present case, the 426 nm wavelength absorbance plays a
222 major role in the colour detectability.

223

224 3.2 Aldehyde production

225 The total amount of aldehydes has been determined in all samples, and the results are
226 reported in Figure 2 as a function of ozone dose and contact time. A two-way ANOVA

227 model has been performed on the results, which were highly significant ($F_{20, 129} = 177.066$;
228 $p < 0.0001$).

229 In contrast to the results concerning colour, both the ozone dose and contact time have
230 been shown to significantly affect aldehyde production ($p < 0.0001$ for ozone dose and
231 $p = 0.007$ for contact time). Tukey's HSD test applied to ozone doses shows that with every
232 dose increase from 0 (no dose) to $60 \text{ mg O}_3 \text{ L}^{-1}$, the increase in aldehydes is significant
233 (always $p < 0.0001$). Tukey's HSD test applied to contact times shows that the production of
234 aldehydes significantly increases when contact time is raised from 30 to 60 min ($p = 0.03$),
235 but not when contact time grows from 60 to 90 min.

236 Considering the specific ozone dose, referred both to COD ($\text{mg O}_3 \text{ mg COD}^{-1}$) and to
237 absorbance ($\text{mg O}_3 (\text{unit absorbance} \cdot 100)^{-1}$), the correlation is not so strict. This can be
238 explained by the unspecificity of COD and colour measurements. As aldehydes are
239 derived from only a small fraction of COD and dye residues, the identification of the
240 involved fractions would need further, more specific investigations.

241 Upon analysing the whole dataset, the aldehyde concentrations in the treated samples
242 ranged from 0.09 to 1.02 mg L^{-1} . At $60 \text{ mg O}_3 \text{ L}^{-1}$, the aldehyde concentration ranged from
243 0.72 to 1.02 mg L^{-1} , practically complying with Italian law standards (1 mg L^{-1} in treated
244 effluents), and otherwise acceptable from a toxicological point of view.

245 The experimental data show that in the present case study an increase in contact time
246 would be useless for colour removal and negative for aldehyde production (even if
247 differences are very small) apart from being more expensive.

248

249 3.3 Speciation of carbonyl compounds

250 Carboxylic acids and aldehydes are the main products of wastewater ozone oxidation
251 (Wert et al, 2007; Tripathi et al., 2011), but aldehydes are more important from a

252 toxicological point of view. Figure 3 reports the concentration of the analysed aldehydes at
253 different O₃ doses after 90 min of treatment.

254 According to Wert et al. (2007), formaldehyde was found to be the predominant carbonyl
255 compound generated during drinking water ozonation. In our study, however, glyoxal was
256 found to be the main carbonylic by-product. Among the analysed carbonyl compounds, a
257 correlation to ozone dose was established for glyoxal and methylglyoxal, while no
258 significant trend could be observed for the remaining compounds. For glyoxal and
259 methylglyoxal, a linear correlation between ozone dose and concentration existed, in
260 addition to the influence of contact time, as shown in Figure 4. Concentrations generally
261 increased for increasing contact time from 30 to 60 min and then decreased upon increase
262 in contact time to 90 min. From a statistical basis, however, differences were not
263 significant. The secondary (when not negligible) role of the contact time in the production
264 of formaldehyde, acetaldehyde, glyoxal or methylglyoxal concentration agrees with the
265 results reported by Silva et al. (2010) and Tripathi et al. (2011).

266 From a chemical point of view, the obtained results have been rationalised based on the
267 reactivity of azo dyes during ozonation. In fact, the analysed samples, collected after a
268 complete treatment sequence, were characterised by a low COD value chiefly due to the
269 presence of residual azo dyes. Glyoxal was found to be the main oxidation product, in
270 agreement with the results obtained by Rivera-Utrilla et al. (2002) in the oxidation of
271 sulphonaphtalene with ozone in the presence of ter-butyl alcohol (a suppressor of OH
272 radical). A direct attack of ozone on the activated aromatic ring caused a ring opening and
273 easily lead to formation of glyoxal. Additionally, in the case of radical reaction, the OH-
274 radical addition reaction of the aromatic compounds with highly activated aromatic rings
275 resulted in the formation of a hydroxycyclohexadienyl radical, also termed aromatic-OH
276 adduct and an important end product is glyoxal. A significant linear regression between

277 colour removal and glyoxal and methylglyoxal formation can be established, as shown in
278 Figure 5.

279

280 **4. Conclusions**

281 In our experimental conditions, it was not possible to establish the main mechanism of
282 ozone reaction; either direct ozone reaction or OH⁻ radical formation were presumably in
283 action and were responsible for both colour removal and aldehyde production.

284 In fact, even if it is well known that colour removal by ozone is more efficient in strongly
285 alkaline conditions (for the prevailing of hydroxyl radicals) (Balcioglu & Arslan, 2001), it
286 was decided to operate without adjusting pH. The choice was made considering that
287 significant differences in the process performance have been reported for pH around 11
288 (Sevimli & Sarikaya, 2002; Balcioglu & Arslan, 2001), while smaller increases from
289 neutrality seem to have negligible effects. At full scale, and considering the strong buffer
290 potential of wastewater, raising pH from neutrality to 11 would involve unsustainable costs
291 which would be further increased by the need for re-adjusting it around neutrality before
292 the final discharge.

293 The final aldehyde concentration was acceptable even in the highest dose trials. However,
294 glyoxal and methylglyoxal concentrations grew linearly with increasing ozone dose. The
295 obtained data show that the extent of colour removal can be used for predicting the
296 increase in glyoxal and methylglyoxal concentrations. Even if aldehydes could potentially
297 derive from a variety of compounds, in textile dyeing effluents, after a complete treatment
298 sequence of mechanical and biological treatments, it is likely that the major involved
299 component is the residual dyestuff one. Moreover, colour removal is an indicator of the
300 extent of oxidation reactions. Colour removal can be assessed by a simple absorbance
301 measurement, as opposed to the analysis of specific carbonyl compounds, which is much
302 longer and complex. So, the possibility of using colour removal as an indicator for

303 predicting the aldehyde related toxic potential of ozone treated effluents containing azo
304 dyes is of great value.

305

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310

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CAPTIONS TO FIGURES

Figure 1 - Percent removal of colour (as absorbance at 426 nm wavelength) as a function of ozone dose and specific ozone doses referred to COD and to initial absorbance

Figure 2 - Box plot representation of aldehyde concentration as a function of ozone doses for the three contact times (30, 60 and 90 min).

Figure 3 - Concentration ($\mu\text{mol/L}$) of formaldehyde, acetaldehyde, acetone, acrolein, glyoxal and methylglyoxal as a function of ozone doses (90' contact time).

Figure 4 - Box plot representation of aldehyde concentration as a function of ozone doses for the three contact times (30, 60 and 90 min).

Figure 5 - Glyoxal and methylglyoxal concentration as a function of percent colour removal.

Fig.1

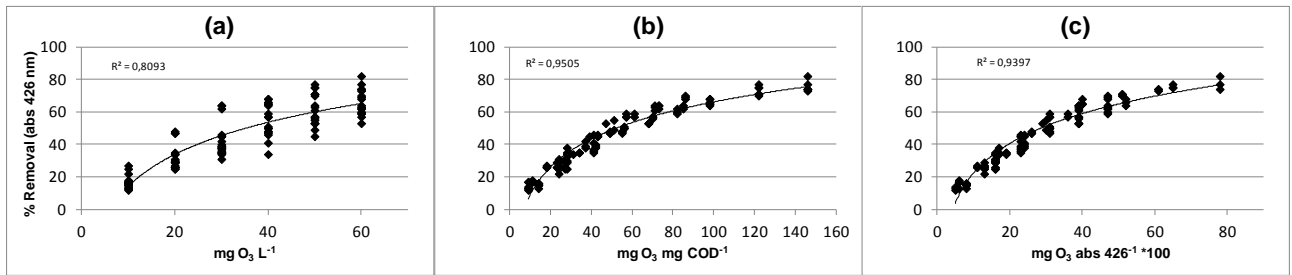


Fig.2

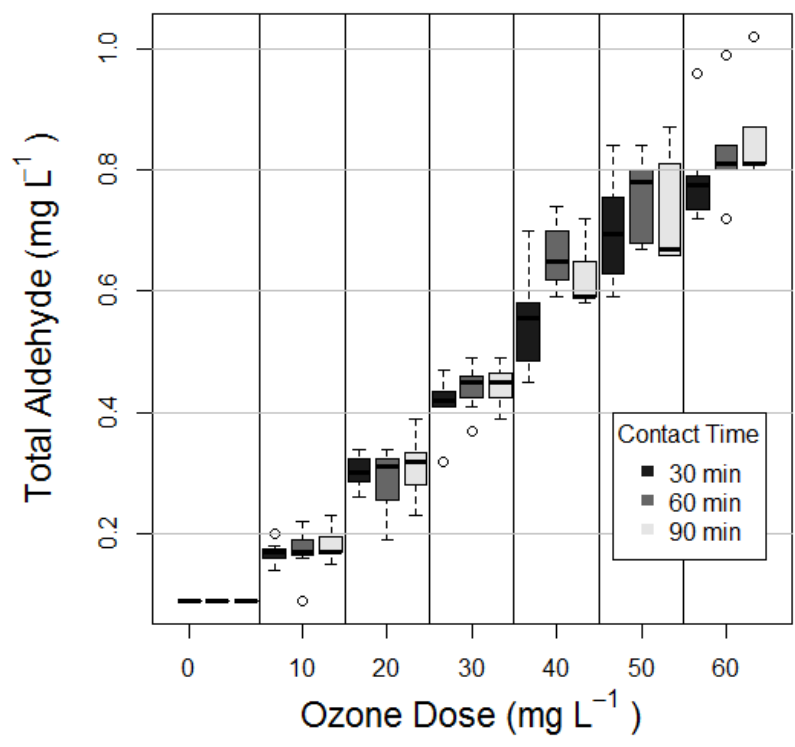


Fig.3

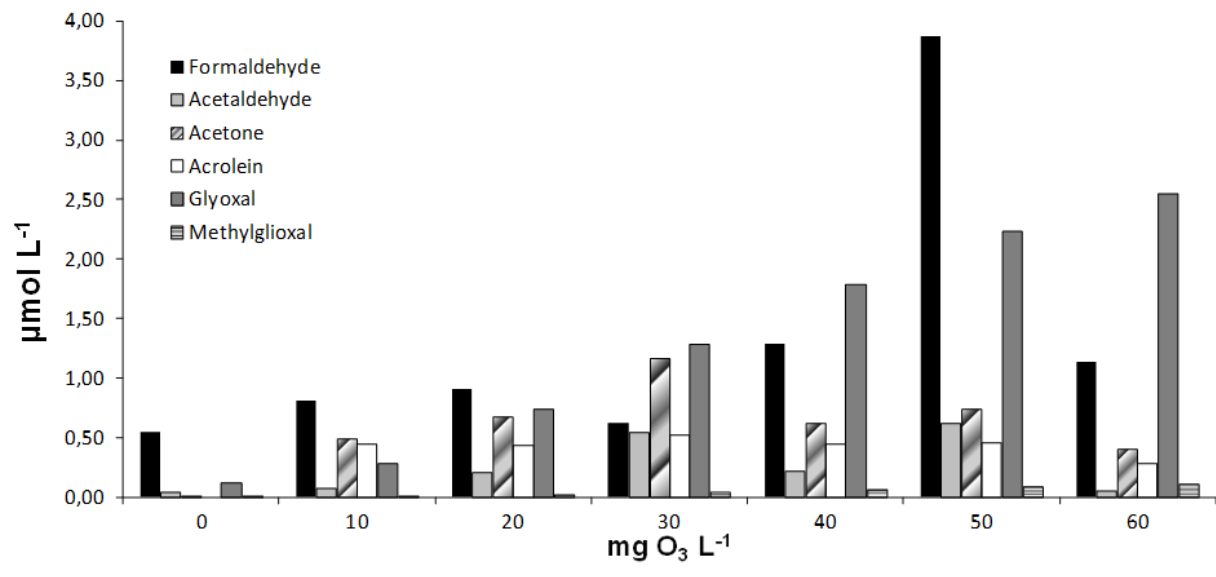


Fig.4

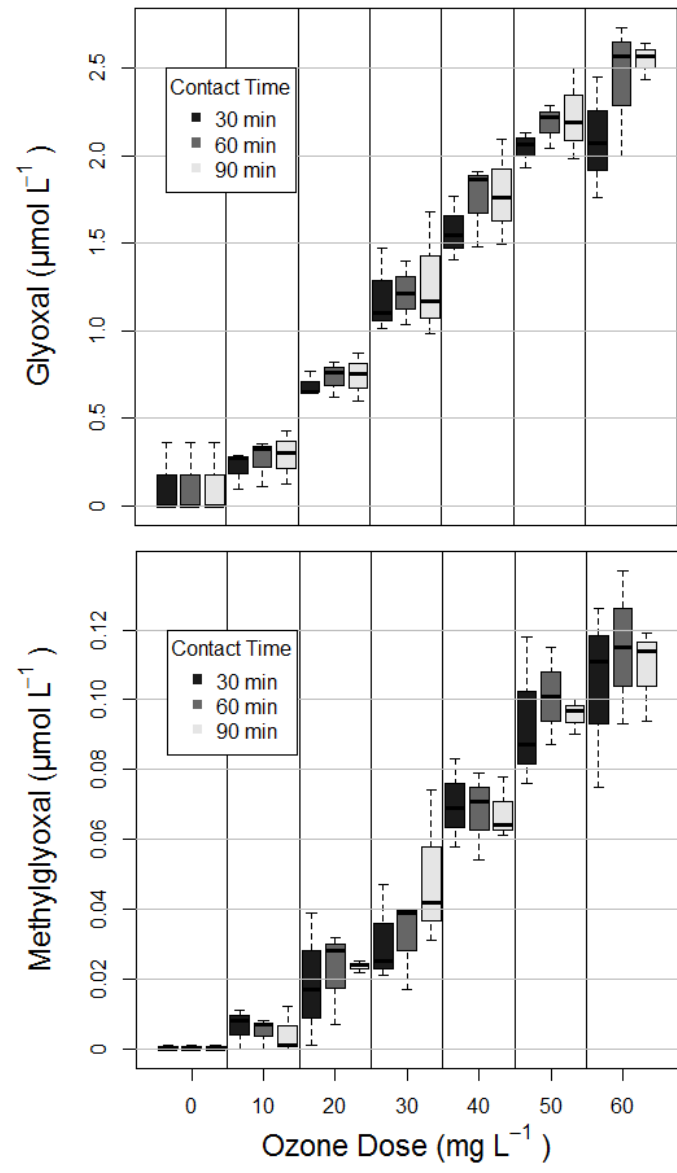
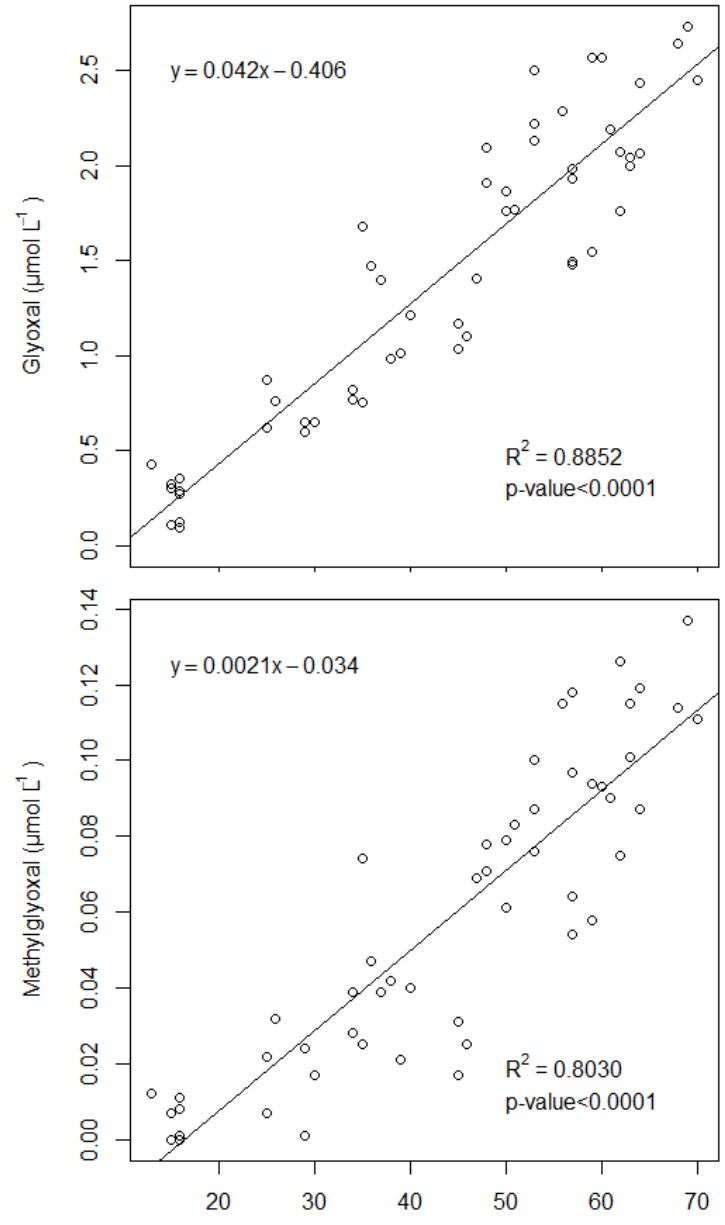


Fig.5



CAPTIONS TO TABLE

Table 1 - Two-way ANOVA table for colour removal at the three wavelengths.

Table 1

Source	Degrees of freedom (df)	Sum of squares (SS)	Mean square (MS)	F-ratio	P-value
<i>426 nm (F_{17, 99} = 40.944; p<0.0001)</i>					
Ozone dose	5	0.0461	0.0092	136.692	< 0.0001
Contact time	2	0.0004	0.0002	2.734	0.070
Interaction	10	0.0005	0.0000	0.712	0.711
Residual	99	0.0067	0.0001		
Total	116	0.0536			
<i>558 nm (F_{17, 99} = 19.183; p<0.0001)</i>					
Ozone dose	5	0.0266	0.0053	64.196	< 0.0001
Contact time	2	0.0001	0.0001	0.763	0.469
Interaction	10	0.0003	0.0000	0.360	0.961
Residual	99	0.0082	0.0001		
Total	116	0.0352			
<i>660 nm (F_{17, 99} = 16.222; p<0.0001)</i>					
Ozone dose	5	0.00601	0.0012	54.557	< 0.0001
Contact time	2	0.00002	0.0000	0.553	0.577
Interaction	10	0.00004	0.0000	0.189	0.997
Residual	99	0.00218	0.0000		
Total	116	0.00825			

Electronic Supplementary Material (online publication only)

[Click here to download Electronic Supplementary Material \(online publication only\): Supplementary aldehydes 18.10.docx](#)