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5	Determination of key operating conditions for the photocatalytic treatment of olive mill
6	wastewaters
7	
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17	
18	Abstract
19	The TiO ₂ -mediated photocatalytic treatment of olive mill wastewater (OMW) was investigated in a
20	batch type, laboratory scale photoreactor. UV-A irradiation was provided by a 400 W, high pressure
21	mercury lamp and Degussa P25 TiO_2 was used as the catalyst. A factorial design approach was used
22	to study the effect of various operating conditions such as initial organic loading, TiO ₂ loading, pH,
23	contact time and the addition of hydrogen peroxide on the conversion of COD and total phenols and
24	experimental models describing the respective removals were developed. Effluent decolorization as
25	well as process efficiency in terms of energy consumption were also evaluated. Finally, the acute
26	ecotoxicity of OMW samples prior to and after photocatalytic treatment was assessed.

Keywords: olive mill wastewater, TiO₂ photocatalysis, factorial design, energy consumption

30 **1. Introduction**

31 The foodstuff processing industry based on olive oil extraction is an economically important 32 activity for many regions of the Mediterranean Sea area. This process results in large quantities of 33 bio-recalcitrant effluents that come from the vegetation water and the soft tissues of the olive fruits 34 mixed with the water used at the different stages of oil production. All these wastewaters together with the industry washing waters make up the so called olive mill wastewater (OMW). Essentially, 35 OMW consists of water (80–83%), organic compounds (15–18%) and inorganic compounds (2%), 36 37 while the organic content varies broadly depending on many parameters such as the olive variety, 38 harvesting time, climatic conditions and the oil extraction process. OMW also contains phytotoxic 39 and biotoxic substances which prevent it from being disposed of. The phytotoxicity and strong 40 antibacterial action have been attributed mainly to the polyphenolic content (0.5–24 g/L) found in 41 OMW and secondarily to fatty acids present in olive oil residues [1]. The presence of these 42 recalcitrant organic compounds constitutes one of the major obstacles in the detoxification of 43 OMW.

Management of OMW and alike agro-industrial effluents is a complicated and pretty much 44 45 unresolved issue with serious socio-economic implications. Given the unique characteristics of 46 OMW (i.e. organic content of tens of g/L COD, seasonal and localized production involving small 47 to medium size ventures), it is likely that a sequence of processes rather than a single operation may 48 become the optimum treatment option. Such scheme could benefit from the integration of low-cost 49 technologies (i.e. sedimentation, filtration, coagulation), conventional biological processes (i.e. 50 aerobic and anaerobic) and the more costly advanced chemical oxidation to meet environmental 51 regulations for discharge [2]. In recent years, advanced oxidation processes (AOPs) have been 52 employed as alternative pretreatment methods aiming at reducing organic load and bio-recalcitrance 53 of these effluents. Among them, photocatalytic methods have attracted a great deal of attention 54 regarding OMW treatment. In a recent study, El Hajjouji et al. [3] studied the UV/TiO₂ treatment of OMW and found that oxidation for 24 h at 415 W intensity led to 94% phenols and 22% COD 55

56 removal respectively, while decolorization was 57%. Moreover, it was suggested that the 57 compounds responsible for the persistent effluent COD after UV/TiO₂ attack were mainly pectins. In another recent study [4], the effect of various operating factors was investigated for the 58 UV/H₂O₂/TiO₂ treatment of a synthetic solution containing 13 organic compounds typically found 59 60 in OMW. OMW has also been treated by UV irradiation combined with other techniques such as ultrafiltration and ozonation [5, 6]. Reports on solar photocatalytic and photo-Fenton processes have 61 also been published [7-9]. The possibility of reducing OMW phytotoxicity by means of solar 62 63 irradiation combined with the Fenton reagent was investigated by Andreozzi et al. [7] and it was 64 found that this process was not so efficient compared to other AOPs such as ozonation. On the other 65 hand, the photo-Fenton process successfully removed 85% COD and up to 100% of phenolic compounds at a pilot-plant solar photoreactor [8]. 66

The aim of this work was to study the photocatalytic oxidation of OMW regarding the effect of various operating conditions such as TiO_2 loading, initial organic loading, initial pH, contact time and the addition of hydrogen peroxide on the conversion of COD and total phenols (TPh). These parameters were chosen as they typically play a key role in dictating the performance of photocatalytic reactions. A factorial design methodology was adopted to determine in a systematic way the statistical significance of each parameter. Energy consumption of the process and ecotoxicity of OMW samples prior to and after treatment were also investigated.

74

75 **2. Experimental and analytical**

76 2.1. Materials

The OMW was provided by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. The effluent was subjected to filtration to remove most of its total solids. The effluent has a strong olive oil smell and a dark black-brown color with maximum absorbance in the visible region at λ =550 nm. Its main properties prior to and after filtration are given in Table 1. B1 Degussa P25 TiO₂ was kindly supplied by Degussa AG (anatase:rutile 75:25, 21 nm primary B2 crystallite particle size, 50 m²/g BET surface area) and it was used as received. Hydrogen peroxide, B3 as a 35% w/w solution, was supplied by Fluka.

84

85 2.2. Photocatalytic Experiments

UV-A irradiation was provided by a 400 W high pressure mercury lamp (Osram, HQL, MBF-U). The emission spectrum of the lamp consists of several spectral lines in the UV and visible region of which the main emission line exists at 366 nm [10]. Emission below 300 nm is impeded due to the reactor's material of construction (borosilicate glass). The photon flux emitted from the lamp was determined actinometrically using the potassium ferrioxalate method and was found to be 1.12 10⁻⁵ einstein/s.

92 Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor 93 described in detail elsewhere [11]. In a typical photocatalytic run, the original OMW was diluted 94 with distilled water to achieve the desirable initial organic loading. Afterwards, 350 mL of the effluent were loaded in the reaction vessel and the solution was slurried with the appropriate 95 96 amount of TiO₂. The resulting TiO₂ suspension was magnetically stirred for 30 min in the dark to 97 ensure complete equilibration of adsorption/desorption of OMW organic compounds onto the 98 catalyst surface which was about 10% in terms of COD. After that period of time, the lamp was 99 turned on (this was taken as "time zero" for the reaction), while air was continuously sparged in the 100 liquid and the reaction mixture was continuously stirred. Regarding the initial pH that took values 101 of 4.8 (natural pH of the diluted effluent) and 7 (after adjustment with a few drops of 1 M NaOH 102 solution), it should be noticed that the solution was not buffered to the aforementioned values. However, pH was monitored constantly throughout the reaction showing that only marginal 103 104 changes had occurred between the initial and final solutions. In those cases where experiments were 105 performed in the presence of hydrogen peroxide, the appropriate amount of 35% w/w solution of 106 H₂O₂ was added to achieve the desirable final concentration of H₂O₂. All experiments were

107 conducted at constant temperature of $28\pm2^{\circ}$ C. For each experimental run, 3 samples were taken, i.e. 108 the first at the beginning of the experiment (time zero), the second after 1 hour of treatment and the 109 third after 4 hours of treatment. The samples were filtered to remove solid particles and then 110 analyzed for their residual COD, total phenolic content (TPh) and color.

111

112 Analytical measurements

113 COD was determined by the dichromate method. The appropriate amount of sample was introduced 114 into commercially available digestion solution (0-1500 mg/L) containing potassium dichromate, 115 sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for 116 120 min at 150°C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was 117 measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

The total phenolic content was determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin-Ciocalteau reagent according to the procedures described in detail elsewhere [12]. Gallic acid monohydrate was used as standard to quantify the concentration of total phenols in OMW.

Sample absorbance was scanned in the 400-800 nm wavelength region on a Shimadzu UV 1240 spectrophotometer. Color was measured at λ =550 nm, which corresponds to the maximum absorbance in the visible region. Changes in sample absorbance at the wavelength of 550 nm were monitored to assess the extent of decolorization that had occurred during photocatalytic treatment.

H₂O₂ concentration in the OMW solution was monitored using Merck peroxide test strips (0-25 mg H_2O_2/L and 0-100 mg H_2O_2/L), while the pH was measured by a Toledo 225 pH meter during photocatalytic treatment.

The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of OMW samples. The inhibition of bioluminescense of *V. fischeri* was measured using a LUMIStox analyzer (Dr. Lange, Germany). Toxicity is expressed as EC_{50} , which is the effective concentration of a toxicant causing 50% reduction of light output during the designated time intervals at 15°C.

134 **3. Results and discussion**

135 *3.1. Effect of operating parameters*

136 In this work, a statistical approach was chosen based on a factorial experimental design that would 137 allow us to infer about the effect of the variables with a relatively small number of experiments 138 [13]. Five independent variables that may affect the photocatalytic treatment of OMW were taken 139 into account, namely initial COD concentration, TiO₂ loading, solution pH, treatment time and H₂O₂ concentration. The experimental design followed in this work was a full 2⁵ experimental set, 140 141 which required 32 experiments. The order each experiment was performed was selected randomly. 142 The design matrix of the experiments and the statistical analysis of these were made by means of 143 the software package Minitab 14. The values chosen for the independent variables and the results 144 obtained in terms of two measured response factors (dependent variables), namely concentration of COD oxidized in mg/L (response factor Y₁) and concentration of TPh removed in mg/L (response 145 factor Y₂) are presented in Table 2. Table 2 also shows percent removal of COD, TPh and color. 146

147 Statistical treatment of the response factors Y₁ and Y₂ according to the factorial design technique 148 involves the estimation of the average effect, the main effects of each individual variable as well as 149 their two and higher order interaction effect [13]. The average effect is the mean value of each 150 response factor, while the main and interaction effects are the difference between two averages: main effect= $\overline{Y_+} - \overline{Y_-}$, where $\overline{Y_+}$ and $\overline{Y_-}$ are the average response factors at the high and low level 151 152 respectively of the independent variables or their interactions. Estimation of the average effect, as well as the main and interaction effects was made by means of the statistical package Minitab 14 153 154 and the results are summarized in Table 3.

A key element in the factorial design statistical procedure is the determination of the significance of the estimated effects. For the assessment of the significance of the main and interaction effects in un-replicated factorial designs, Minitab uses the Lenth's pseudo-standard error (PSE) [13, 14]. Lenth's PSE is an estimate of the standard error of the effects and for its calculation the median, m, 159 of the absolute values of the effects is first determined and then $PSE=1.5 \times m$. Any estimated effect 160 exceeding $2.5 \times PSE$ is excluded and, if needed, m and PSE are recalculated. Then, a margin of 161 error (ME) is given by ME= $t \times PSE$, where t is the (1 - alpha/2) quantile of a t-distribution with 162 degrees of freedom equal to the number of effects/3 [13, 14]. The present study was done for a 163 confidence interval of 95%, therefore alpha=0.05. The calculated values of PSE and ME for the two response factors according to the Minitab software are also given in Table 3. All estimated effects 164 165 greater than the ME can be considered significant. On the other hand, all other effects whose values 166 are lower than the ME can be attributed to random statistical error.

A very useful pictorial presentation of the estimated effects and their statistical importance can be accomplished using the Pareto chart of the effects. The Pareto chart displays the absolute values of the effects in the ordinate, while a reference line is drawn at the margin of error, and any effect exceeding this reference line is potentially important. The Pareto charts of the effects for the COD and TPh oxidation are shown in Figs. 1 and 2 respectively.

As can be seen in Fig. 1, there are basically only two effects which are statistically important for 172 COD oxidation, namely, in decreasing order of significance: the reaction time, and the initial 173 174 concentration (influent) of COD. These effects are the most important factors affecting the 175 oxidation of COD. The presence of oxidant, TiO₂ loading and the initial solution pH, along with all interactions, are not significant and may be explained as random noise. Both significant effects are 176 177 positive indicating that an increase in their level brings about an increase in the amount of COD oxidized. The slightly positive (but still insignificant) effect of hydrogen peroxide on degradation 178 179 may be due to the low H₂O₂:COD concentration ratio employed in this work, i.e. the additional 180 oxidizing species generated by the dissociation of H₂O₂ lead to a measurable but marginal enhancement of degradation. In photocatalytic reactions, conversion invariably increases with 181 182 increasing TiO₂ concentration up to a point above which it levels off; this corresponds to the point 183 where all catalyst particles are fully illuminated. At higher concentrations, a screening effect of 184 excess particles occurs, thus hindering light penetration; this usually results in conversion reaching

185 a plateau, while at excessive catalyst concentrations conversion may also decrease due to increased light reflectance [4, 11]. It appears that the catalyst concentrations employed in this work fall within 186 this range, thus having a slightly negative but not statistically important influence on COD 187 188 conversion. A change in initial pH from 4.8 to 7 has no effect on conversion and this is consistent 189 with the results of Silva et al [4] who found that the photocatalytic treatment of a synthetic OMW in the pH range 3.5-8 gave almost identical final conversions. It should be noticed here that the point 190 of zero charge of Degussa P25 TiO₂ is at pH=6.8; for the range of pH values in question, the 191 192 catalyst ionization state would remain unchanged (e.g. positively charged) and consequently would 193 not affect the degree of adsorption/reaction onto the surface.

Based on the variables which are statistically significant, a model describing the experimental
response Y₁ was constructed:

196

197
$$Y_1 = 601.75 + 184.5X_4 + 92X_1 \tag{1}$$

198

199 where Y_1 is the mass of COD oxidized (mg/L), X_i are the transformed forms of the independent 200 variables according to:

201
$$X_{i} = \frac{Z_{i} - \left(\frac{Z_{high} + Z_{low}}{2}\right)}{\left(\frac{Z_{high} - Z_{low}}{2}\right)}$$
(2)

and Z_i are the original (untransformed) values of the variables. The coefficients that appear in equation (2) are half the calculated effects, since a change of X=-1 to X=1 is a change of two units along the X axis.

The model predicts a linear dependency of the mass of COD oxidized on the operating variables. Not only this, but it also indicates that the contact time (x_4) is the most significant variable in terms of COD removal, because its effect has the highest value and its about two times greater than the effect of influent organic loading (x_1) . Therefore, the factorial design analysis shows that 209 photocatalytic treatment is more efficient, in terms of mass of pollutants removed, at increased 210 organic loadings, thus implying that the concept of severe OMW dilution (usually with other 211 industrial [15] or municipal wastewaters [16]) prior to treatment may be revisited. This undoubtedly 212 enhances the use of TiO₂-mediated photocatalysis for OMW treatment.

Regarding TPh removal, the Pareto chart of the effects (Fig. 2) shows that contact time, influent COD and their interaction have a significant positive effect. On the other hand, the interactions of initial COD, TiO₂ and H₂O₂ loading as well as the interaction between TiO₂ loading and initial H₂O₂ concentration have a significant negative effect on TPh removal.

217 The following experimental model describes the TPh removal in mg/L:

218

219 $Y_2 = 113.53 + 34.16X_4 + 30.91X_1 - 22.34X_1X_2X_5 - 18.97X_2X_5 + 15.91X_1X_4$ (3)

220

221 It can be observed from eqn 3 that, contrary to eqn 1, the effect of the contact time is not much 222 greater than the effect of the influent COD. Moreover, the effect of TiO₂ loading has an indirect negative effect on TPh removal through its interaction with initial COD and H₂O₂ concentrations. 223 224 On the assumption that TPh are represented by gallic acid monohydrate, the stoichiometry of its 225 reaction to carbon dioxide and water dictates that 100 mg of gallic acid would require 102 mg 226 oxygen for the complete oxidation; therefore, Y₂ in Table 2 practically corresponds to the concentration of COD oxidized due to the phenolic fraction of the effluent. Comparison between Y₁ 227 and Y₂ clearly shows that TiO₂ photocatalysis is a non-selective oxidation process, attacking 228 229 simultaneously TPh and other organics.

In terms of color removal, decolorization mainly takes place during the first hour of treatment under almost all experimental conditions. As seen in Table 2, decolorization is always greater than 80%, and in most cases it is over 95%, at low influent COD; conversely, for influent COD of 5100 mg/L color removal typically varies between 40 and 70%. Interestingly, complete decolorization coincides with equally high levels of TPh removal, thus implying that the OMW dark color ismainly due to the presence of phenolic compounds and their polymerized derivatives.

236 The validation of the mathematical model was based on the calculation of the residuals, which are 237 the observed minus the predicted values according to the model, for the two response factors. The 238 values of the calculated residuals for the two response factors were plotted in a normal probability plot and the results are shown in Figs. 3 and 4. For both responses, almost all data points lie close to 239 240 a straight line and within the 95% confidence interval lines. These results indicate that the 241 calculated residuals follow a normal distribution with mean values near zero. According to the 242 above observations, it can be concluded that there is a good agreement between the experimental 243 values and the mathematical model developed and the observed differences (i.e. the residuals) may 244 be readily explained as random noise.

Eventually, the development of empirical mathematical models with relatively few experiments to describe OMW mineralization and TPh degradation is of great importance. Based on these models, an indicative view for scaling-up the process can be obtained.

248

249 *Energy consumption*

AOPs based on artificial light may be associated with increased operating costs, a major fraction of which is related to energy consumption. Bolton *et al* [17] introduced the concept of specific electric energy consumption per unit mass of pollutant (e.g. COD) degraded (E_{EM}):

253

254

$$E_{EM} = \frac{Pt}{V(COD_0 - COD)} \tag{4}$$

255

where *V* is the effluent volume in liters, *t* is the treatment time in hours, *P* is the lamp power in kW, *COD*₀ and *COD* is the concentration in g/L before treatment and after time *t* respectively. Eqn (4) assumes that the reaction is zero-order with respect to COD, i.e. the removal rate is directly proportional to the rate of electric energy consumption. Although a thorough kinetic analysis was 260 outside the scope of this work, an attempt was made to evaluate the apparent order of reaction with 261 respect to COD concentration based on the experimental data of Table 2. If the reaction were firstorder, COD conversion would remain constant for runs performed at different initial COD values 262 and all other variables being identical; conversely, for zero-order kinetics an increase in initial COD 263 264 would result in a similar conversion decrease. In most cases (e.g. see runs 1 and 11, 2 and 12, 5 and 20, 6 and 22, 7 and 14, 9 and 19, 15 and 23, 26 and 32, 28 and 31), a 5-fold COD increase (i.e. from 265 266 1000 to 5100 mg/L) yields a decrease in the conversion by about 4-5 times, thus implying that the 267 apparent reaction rate is near zero-order.

268 Applying eqn (4), it is evident that photocatalytic treatment is more efficient, in terms of energy 269 consumption, at high influent COD values and short treatment times. For instance, comparing runs 270 29 and 17 energy consumption is 4.5 and 1.8 kWh/g COD removed after 1 h at 1000 and 5100 271 mg/L influent COD respectively; these values become 11 and 5 kWh/g COD removed after 4 h of 272 treatment (runs 13 and 18). This fact comes to boost the conclusion, drawn from the factorial design 273 analysis, that photocatalytic treatment is more efficient when working at increased organic loadings. Similar arguments can be inferred for TPh removal; energy consumption is 26.5 and 9 kW/g TPh 274 removed after 1 h and 61 and 14.2 kW/g TPh removed after 4 h at 1000 and 5100 mg/L influent 275 276 COD respectively (applying again eqn (4)). These values are seemingly greater than those for COD 277 as the phenolic content comprises only a fraction of the total organic content.

278

279 *Acute toxicity*

The untreated effluent was highly ecotoxic to *V. fischeri* with an EC_{50} value of 12%. Changes in ecotoxicity were found to depend strongly on the residual organic matter following treatment. For instance at the conditions of run 23, the resulting effluent with a residual organic content of about 200 mg/L COD was non-toxic and this can be attributed to the complete removal of TPh. Conversely, when the experiment was performed at increased influent COD (run 15), the ecotoxicity of the treated effluent remained nearly unchanged ($EC_{50}=15\%$), thus indicating that the

residual 4150 mg/L COD (including about 200 mg/L TPh) contain various toxic species.

287

288 4. Closing remarks

Diluted wastewater from the olive oil industry was treated by TiO_2 photocatalysis with emphasis given on the effect of various operating conditions on treatment efficiency with regard to COD and TPh removal as well as decolorization. In order to evaluate the importance of the various parameters involved in a coherent way, a factorial design methodology was followed. The conclusions drawn from this study can be summarized as follows:

294

(1) COD removal was positively affected mostly by contact time and secondly by influent COD. All other variables had no significant statistical importance to COD removal response. TPh removal was positively affected by contact time and influent COD, while there was a negative effect through the interaction of influent COD, TiO₂ and H₂O₂ concentrations.

(2) Simple, empirical models were developed and adequately simulated quantitatively the amount
of COD and TPh removed as a function of the most statistically significant effects for the range of
operating variables in question. These models may provide a useful tool for scaling-up and making
an economic analysis for an industrial application of the proposed process.

303 (3) Energy consumption per unit mass of pollutant removed is lower for high influent COD,
 304 indicating that TiO₂ photocatalysis can be a promising process for OMW treatment.

305 (4) Monitoring ecotoxicity during photocatalytic treatment showed that OMW was almost
 306 completely detoxified at low influent COD, while toxicity was only slightly reduced at increased
 307 organic loadings.

308

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Properties	Before filtration	After filtration
COD, g/L	47	40
Total phenols (TPh), g/L	8.1	3.5
Total solids, g/L	50.3	0.6
TOC, g/L	16.9	14
pН	4.6	4.4
Conductivity, mS/cm	17	18

Table 1. Properties of OMW samples used in this study.

Table 2. Design matrix of the 2^5 factorial experimental design and observed response factors (Y₁:

348 mg of COD removed per liter; Y₂: mg of TPh removed per liter) as well as percent removal of

349	COD, TPh and color.
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Run order	X ₁ , [COD] ₀ , mg/L	X ₂ [TiO ₂], g/L	X ₃ pH	X ₄ Reaction time, h	X5 [H2O2], mg/L	Y ₁ COD oxidized, mg/L	Y ₂ TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal
1	1000	2	7	1	500	286	72	29	77	95
2	1000	2	7	4	500	906	102	92	99	99
3	5100	0.5	7	1	0	790	49	15	11	9
4	1000	0.5	4 8	1	500	382	67	37	73	89
5	5100	0.5	7	1	500	400	144	8	27	38
6	5100	2	48	4	500	950	73	18	20	61
7	5100	0.5	7	4	0	860	155	17	34	28
8	5100	2	4.8	1	500	730	78	15	22	46
9	5100	2	7	1	0	370	66	7	12	18
10	5100	0.5	7	4	500	550	282	11	53	50
11	5100	2	7	1	500	390	78	8	19	63
12	5100	2	7	4	500	810	169	17	42	74
13	1000	2	4.8	4	0	412	75	42	85	93
14	1000	0.5	7	4	0	758	101	74	99	95
15	5100	0.5	4.8	4	500	950	205	19	43	58
16	1000	0.5	7	1	0	256	57	25	61	77
17	5100	2	4.8	1	0	630	125	12	24	39
18	5100	2	4.8	4	0	970	322	18	63	66
19	1000	2	7	1	0	254	67	25	55	76
20	1000	0.5	7	1	500	288	67	32	73	96
21	1000	0.5	7	4	500	820	109	91	99	99
22	1000	2	4.8	4	500	752	101	81	99	94
23	1000	0.5	4.8	4	500	798	104	78	99	93
24	1000	0.5	4.8	1	0	78	72	7	60	70
25	1000	2	4.8	1	500	360	70	39	71	82
26	1000	0.5	4.8	4	0	918	113	92	95	96
27	5100	0.5	4.8	1	500	660	126	13	27	47
28	5100	2	7	4	0	570	216	11	41	43
29	1000	2	4.8	1	0	252	43	26	49	64
30	5100	0.5	4.8	1	0	550	89	11	18	45
31	1000	2	7	4	0	636	102	62	85	97
32	5100	0.5	4.8	4	0	920	134	18	27	52

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Effect	Value of	fEffect
	COD removal	TPh removal
Average Effect	601.75	113.53
Main Effects		
X ₁	184	61.81
X2	-43.75	-7.19
X3	-85.5	2.44
X4	369	68.31
X5	50.5	3.81
Two-factor Interactions		
x ₁ x ₂	11.25	0.06
X ₁ X ₃	-117	-1.56
X1 X4	-111.5	31.81
x ₁ x ₅	-78	-3.94
X ₂ X ₃	-18.75	-4.31
X ₂ X ₄	-27.25	1.81
X2 X5	85.75	-37.94
X3 X4	-9.5	11.19
X3 X5	-56	22.44
X4 X5	11	-12.94
Three-factor Interactions		
X ₁ X ₂ X ₃	-63.75	-13.81
$X_1 X_2 X_4$	64.75	6.31
X1 X2 X5	26.75	-44.69
$X_1 X_3 X_4$	-38.00	9.94
X1 X3 X5	-26.50	24.44
$X_1 X_4 X_5$	1.50	-11.44
X ₂ X ₃ X ₄	73.25	-4.81
X2 X3 X5	60.25	4.19
X2 X4 X5	60.30	-20.44
X3 X4 X5	60.00	8.69
Four-factor Interactions		
X ₁ X ₂ X ₃ X ₄	-10.75	-4.06
X1 X2 X3 X5	67.25	14.19
X1 X2 X4 X5	-47.75	-20.44
X1 X3 X4 X5	2.50	8.94
X2 X3 X4 X5	-16.75	8.69
Five-factor Interactions		• •
x ₁ x ₂ x ₃ x ₄ x ₅	39.25	9.44
Lenth's PSE	73.69	13.03
ME	163.5	28.91

Table 3. Average and main effects of the independent variables and their two and higher order

interactions of the 2^5 factorial design on the response factors Y_1 and Y_2 .

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357

358 **Fig. 1.** Pareto chart of the effects for COD oxidation. White bars: positive effects; hatched bars:

359 negative effects. The dotted line is drawn at the margin of error (ME).

- **Fig. 2.** Pareto chart of the effects for TPh oxidation. White bars: positive effects; hatched bars:
- 361 negative effects. The dotted line is drawn at the margin of error (ME).
- Fig. 3. Normal probability plot of the residuals at 95% confidence interval for the response factor
 Y₁.
- **Fig. 4.** Normal probability plot of the residuals at 95% confidence interval for the response factor
- $365 \quad Y_{2.}$
- 366
- 367



Figure 1



Figure 2



Figure 3



Figure 4