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**Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing**

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37 **Abstract**

38 Phenolic compounds in wastewaters are difficult to treat using the conventional  
39 biological techniques such as activated sludge processes because of their bio-toxic and  
40 recalcitrant properties and the high volumes released from various chemical, pharmaceutical  
41 and other industries. In the current work, a modified heterogeneous Advanced Fenton  
42 Process (AFP) is presented as a novel methodology for the treatment of phenolic wastewater.  
43 The modified AFP, which is a combination of hydrodynamic cavitation generated using a  
44 liquid whistle reactor and the AFP is a promising technology for wastewaters containing high  
45 organic content. The presence of hydrodynamic cavitation in the treatment scheme  
46 intensifies the Fenton process by generation of additional free radicals. Also, the turbulence  
47 produced during the hydrodynamic cavitation process increases the mass transfer rates as  
48 well as providing better contact between the pseudo-catalyst surfaces and the reactants.

49 A multivariate design of experiments has been used to ascertain the influence of  
50 hydrogen peroxide dosage and iron catalyst loadings on the oxidation performance of the  
51 modified AFP. Higher TOC removal rates were achieved with increased concentrations of  
52 hydrogen peroxide. In contrast, the effect of catalyst loadings was less important on the TOC  
53 removal rate under conditions used in this work although there is an optimum value of this  
54 parameter. The concentration of iron species in the reaction solution was measured at 105  
55 min and its relationship with the catalyst loadings and hydrogen peroxide level is presented.

56 **Key words:** Hydrodynamic cavitation; Advanced Fenton Process (AFP); Phenol; Multivariate  
57 analysis; Wastewater treatment

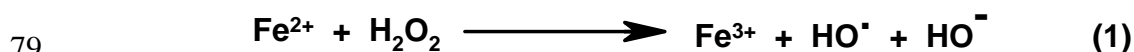
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## 60 1. Introduction

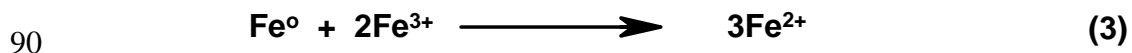
61 Certain aromatic or phenolic compounds in wastewaters exhibit biotoxicity and  
62 recalcitrance to conventional biological oxidation process and consequently prove difficult to  
63 treat. With an increase in the stringent water quality regulations due to environmental  
64 concerns there is a huge demand for upgrading current water treatment technologies and the  
65 development of novel and more economical processes that can effectively deal with soluble  
66 toxic and non-biodegradable organic content in wastewater. Advanced oxidation  
67 technologies [1,2] have proven to be highly effective, though they have limitations of high  
68 investment cost for installation and operational costs due to the consumption of large  
69 amounts of energy/reagents in the process. These factors often limit the use of these  
70 alternative technologies even when cheaper processes are much less effective. Advanced  
71 oxidation processes (AOP's) are based on the formation of highly reactive hydroxyl radical  
72 species which act as an oxidant for the mineralisation of target compounds present in the  
73 aqueous solution. Among AOP's Fenton's reagent, which is a highly economical and  
74 effective treatment in terms of removing organic pollutants from industrial effluents, is one of  
75 the better chemical oxidation processes [3].

76 In a conventional Fenton process, iron salts in the presence of hydrogen peroxide  
77 under acidic milieu produce very highly reactive hydroxyl radicals (equation 1) which then  
78 react with the pollutant to degrade the organic molecules present in the solution.



80 The use of zero-valent iron metal has been shown to be effective for the removal of  
81 toxic organic pollutants from water. In one sense, it is a cost effective treatment process  
82 which employs the direct use of metals and reduces the process cost by replacing metal salts.  
83 Zero-valent iron has been used for the degradation of azo dyes [4,5], phenol [6-8],  
84 chlorophenols [9] and nitro aromatic compounds [10]. In the AFP [8], zero-valent iron acts

85 as a catalyst in place of ferrous salts. Initially, iron metal pieces produce ferrous ions and  
86 hydrogen gas when subjected to acid conditions (equation 2). The ferrous ions then produce  
87 hydroxyl radicals in a similar way to the normal Fenton reaction (equation 1). However, in  
88 the AFP the ferric iron is reduced to ferrous by interaction with zero valent iron (equation 3)  
89 and the cycle continues as long as there is hydrogen peroxide present.



91 Hydrodynamic cavitation has been shown to be effective for the production of highly  
92 reactive free radicals due to the creation of high temperature and pressure and generation of  
93 intense turbulence and liquid circulation currents, which can be effectively harnessed for  
94 wastewater treatment applications [11-13]. Apart from a few reports [11,12] for synthetic  
95 effluents, use of hydrodynamic cavitation reactors in real industrial wastewater treatment  
96 applications has been rarely investigated possibly due to the lower intensity of cavitation  
97 generated in the reactors. The best approach for utilizing the impressive properties of  
98 hydrodynamic cavitation is to use it in combination with advanced oxidation processes and  
99 exploit the synergistic effects expected due to a common mechanism of destruction. The  
100 present work reports the use of hydrodynamic cavitation in combination with the advanced  
101 Fenton process. In continuation of our earlier work [6,14] dealing with establishing efficient  
102 treatment strategies for destruction of pollutants, phenol has been selected as a model  
103 pollutant. The outcome of different operating parameters on the extent of degradation has  
104 been established while the effectiveness of the treatment performance of the process  
105 described has been determined by monitoring the decrease of the total organic carbon (TOC)  
106 content in the solution at regular time intervals. Additionally, the amount of oxidant and  
107 catalyst, which produces the best results in terms of pollutant destruction has been optimized  
108 using multivariate analysis.

## 109 **2. Materials and methods**

### 110 *2.1 Experimental set-up*

111 Hydrodynamic cavitation was generated using a Liquid Whistle Reactor (LWR)  
112 which is coupled to a positive displacement pump and is employed in a comprehensive  
113 system containing the motor, base, variable frequency drives, pressure and flow measuring  
114 devices. The system consists of a feed vessel tank with a 5 L capacity, a plunger pump  
115 (Giant Industries, Model P220A, USA) with a power consumption of 3.6 kW and having a  
116 speed of 1750 rpm and a mixing chamber comprising of an orifice (orifice area,  $7.74 \times 10^{-7}$   
117  $\text{m}^2$ ) and a blade (length, 0.0268 m; width, 0.0222 m; thickness, 0.0015 m). The pump has a  
118 maximum discharge pressure of up to 2000 psi (13788 kPa). The distance between the  
119 orifice and blade is adjustable and the backpressure valve connected at the end of the mixing  
120 chamber influences the pressure. Aqueous phenol solution was circulated through the orifice  
121 chamber and subsequent iron chamber at a fixed flow rate of  $8.67 \times 10^{-5} \text{ m}^3/\text{s}$  for a desired  
122 contact time. A schematic representation of the intensified hydrodynamic cavitation  
123 generated by the LWR in conjunction with the AFP is shown in Figure 1.

### 124 *2.2 Experimental methodology*

125 All experiments were carried out with 4 L of “synthetic” phenol wastewater for a  
126 period of 1–2 h reaction time with zero-valent iron pieces (unless specified otherwise, 80 g;  
127 50 pieces of 1 cm  $\times$  2 cm, L-shaped having thickness of 0.10 cm) and  $\text{H}_2\text{O}_2$  (usually 2000  
128 mg/L unless specified otherwise). Dilute solutions of sulphuric acid (2 M) and sodium  
129 hydroxide (2 M) were used for the adjustment of pH. The temperature was maintained  
130 constant at  $35 \pm 3 \text{ }^\circ\text{C}$  using an external cooling ice bath. At defined time intervals, samples  
131 were taken and analysed for TOC and total dissolved iron content present in the solution. The  
132 experimental runs were repeated 3 times to check the reproducibility of the data and the

133 reported values are the average of these individual runs. The variation observed in the  
134 experimental data was in the range  $\pm 2\%$ .

135 The extent of mineralisation was determined by direct injection of the filtered samples  
136 into the heated persulphate-type (100 °C) TOC analyser (Model 700, OI Analytical). The  
137 total dissolved iron content present in the solution after the reaction was measured by a  
138 calorimetric process in a DR/2000 Spectrophotometer (HACH) after proper dilution using the  
139 FerroVer Iron reagent. The FerroVer Iron reagent combines 1,10-phenanthroline with a  
140 reducing agent which converts any iron present into the +2 oxidation state ( $\text{Fe}^{2+}$ ). The 1,10-  
141 phenanthroline then reacts with  $\text{Fe}^{2+}$  to form an orange coloured complex, the intensity of  
142 which, measured at 510 nm, is directly proportional to the amount of  $\text{Fe}^{2+}$  present in the  
143 sample. The pH of the solution was determined using a Hanna pH meter.

144

### 145 **3. Results and discussion**

146 The current study evaluates the phenol degradation in a hydrodynamically enhanced  
147 advanced Fenton process. The various important operating parameters which affect the  
148 efficacy of the process include: operating pressure of the hydrodynamic cavitation reactor;  
149 location of the catalyst bed relative to the hydrodynamic cavitation reactor; initial phenol  
150 concentrations; and dosage of hydrogen peroxide. The effects of each of these operating  
151 parameters on the extent of TOC removal are discussed below.

#### 152 *3.1 Effect of inlet pressure:*

153 Figure 2 shows the extent of TOC mineralization obtained as a function of the  
154 operating pressure in the hydrodynamic cavitation reactor in the presence of a zero valent  
155 iron bed downstream of the orifice. Using our experimental set-up, it should be noted here  
156 that without the use of an iron catalyst bed, hydrodynamic cavitation alone resulted only in  
157 marginal reduction in the TOC. This indicates that presence of iron, acting as a pseudo

158 catalyst, is a requirement for obtaining reasonable extents of phenol degradation or TOC  
159 removal. Figure 2 also shows the extent of degradation obtained in the absence of the orifice  
160 and blade i.e. without any hydrodynamic cavitation. It can be seen that about 40% reduction  
161 of TOC is obtained in 80 min of treatment time without the input of hydrodynamic cavitation  
162 and it only marginally increases at the 300 psi operating pressure. A substantial increase in  
163 the extent of TOC removal is however obtained when the inlet pressure is increased to 1500  
164 psi (without the blade) where maximum contribution from hydrodynamic cavitation is  
165 expected. This required inlet pressure for the onset of cavitation effects is also dependent on  
166 the geometry of the cavitation chamber and it has been shown that with a proper optimization  
167 of the geometry of the setup, onset of cavitation can be obtained at inlet pressures as low as  
168 15 psi [16]. The acceleration in degradation of organic contaminants with increasing pressure  
169 at 1500 psi (10340 kPa) can be attributed to the enhancement of the hydroxyl radical  
170 production as a result of the intensification of cavitation activity. Bubble dynamics studies  
171 [17] have indicated that the cavitation intensity quantified in terms of the pressure pulse  
172 generated at the collapse of the cavity increases as a result of an increase in the inlet pressure  
173 of the system. It should be noted that the cavitation intensity is also dependent on the  
174 recovered pressure but in the present case the change in the recovered pressure was only  
175 marginal as compared to the change in the inlet pressure and hence the cavitation intensity  
176 is dominantly affected by the changes in the inlet pressure. Since there is elevated  
177 cavitation collapse intensity at higher inlet pressures, a higher temperature and pressure  
178 pulse is generated resulting in enhanced dissociation of the water molecules trapped in the  
179 cavity thereby leading to more hydroxyl radicals.

180         Use of a blade just adjacent to the orifice, at same operating pressure, results in  
181 further, but minimal, increase in the extent of TOC removal observed in the reactor. This  
182 increase can be attributed to the fact that the system acts as multiple orifices resulting in a

183 greater number of cavitation events and hence the overall cavitation intensity is greater  
184 resulting in enhanced degradation. Superior degradation with higher inlet pressures and  
185 multiple orifices is consistent with other literature reports. Vichare et al. [16] and Sivakumar  
186 and Pandit [18] have shown that an increase in the upstream pressure and use of multiple  
187 orifices on the plate raises the extent of degradation of potassium iodide and rhodamine B  
188 respectively.

189 To maximize the amount of degradation of the effluent stream in the present case, all  
190 further experiments were performed at an operating pressure of 1500 psi (10340 kPa) with  
191 both orifice and blade in place. It should also be noted here that applying 1500 psi (10340  
192 kPa) may not be feasible on an industrial scale of operation where a modification in the  
193 design of the hydrodynamic cavitation unit (use of multiple orifice plates where the number  
194 of holes can be as high as 30 to 50) is recommended to get similar effects at much lower inlet  
195 pressures. The work of Vichare et al. [16] is recommended in order to get a greater insight  
196 into optimization of hydrodynamic cavitation reactors.

### 197 3.2 *Effect of catalyst bed location in the experimental set-up*

198 Hydrodynamic cavitation and the Fenton oxidation process using iron as catalyst  
199 operates in a sequential manner as described above. Thus the location of the iron bed should  
200 also play an important role in the extent of observed synergistic effects. It is expected that  
201 the catalyst bed should be subjected to the influence of cavities generated downstream of the  
202 orifice to get maximum benefits. The acceleration/enhancement in the process performance  
203 with respect to the catalyst bed location is due to the continuous cleaning of the active  
204 catalyst surface by the impingement of the liquid jet stream with high force at the iron metal  
205 surface and also by the collapsing microbubbles at the reactive sites on the surface generated  
206 by the hydrodynamic cavitation. The flow rate of the solution through the iron metal surface  
207 can thus significantly enhance the treatment performance through changing the contact time.



208 Keeping this in mind, the effect of catalyst bed location (two positions; 23 and 50 cm from  
209 the orifice) on the TOC removal rates has been investigated. Experiments were carried out at  
210 each location with 4 L of phenol wastewater (initial concentration 2.5mM), pH adjusted to  
211 2.5, initial H<sub>2</sub>O<sub>2</sub> concentration of 2000 mg/L, initial pressure of 1500 psi and 50 iron metal  
212 pieces as catalyst in the modified AFP. Each experiment with the catalyst bed located close  
213 and far from the orifice was carried out in triplicate and the reported TOC values are the  
214 average values (the observed variation in each set was within  $\pm 2\%$ ). It has been observed  
215 that the extent of TOC mineralisation was marginally higher (however not within the limits of  
216 the experimental errors for these experimental runs) when the catalyst bed was located near  
217 the orifice (57%) as compared to that observed at a location away from the orifice (53%).  
218 Similar results were obtained with measurements of the total dissolved iron content  
219 (concentration was 252 mg/L for near location and 243 mg/L for location away from the  
220 orifice). The results indicate that the operating conditions in the present work are such that  
221 the intensity of hydrodynamic cavitation generated in the system is sufficient (due to very  
222 high inlet pressures into the cavitation chamber, it is expected that the cavitation intensity  
223 will be high) to maintain the active cavitation zone over a distance of 50 cm away from the  
224 point of generation (orifice) and only a marginal decay in the intensity of cavitation is  
225 observed as indicated by a decrease in the TOC removal rates. Still, the location of the  
226 catalyst bed in the system is an important design parameter especially in the case of large  
227 scale industrial wastewater treatment plants where higher distances are expected and where  
228 low operating pressures are used (a proper design of the experimental setup also allows  
229 generation of cavitation activity at much lower operating pressures and hence much lower  
230 operating costs). More work is indeed required on a larger scale of operation and with  
231 varying designs of cavitation chamber for generation of different cavitation intensities for  
232 optimisation of the relative location of the catalyst bed and orifice.

### 233 3.3 *Effect of initial phenol concentration*

234 The effect of initial phenol concentration on the mineralisation of TOC content has  
235 been investigated in the range of 0.5 mM – 1.5 mM at a pH 2.5, H<sub>2</sub>O<sub>2</sub> concentration of 2000  
236 mg/L and at a pressure of 1500 psi with the modified AFP. Figure 3 shows the corresponding  
237 mineralisation ratios obtained at different initial concentrations of phenol wastewater using  
238 iron metal pieces acting as a pseudo catalyst. In the first 10 min of the reaction, the solution  
239 turned brown in colour, which can be attributed to the formation of quinones and the solution  
240 got progressively darker within the next 5 min, indicating an accumulation of quinones or  
241 iron complexes. Further treatment for 10 min changed the dark solution to colourless. The  
242 pH of the solution remained constant throughout the experiment. It is evident from Figure 3  
243 that maximum TOC removal was obtained at a low phenol concentration of 0.5 mM  
244 (approximately 58%) and the TOC removal marginally decreased with an increase in the  
245 phenol concentration. The extent of TOC removal in 105 min of treatment time was 54%, and  
246 51% for the initial phenol concentrations of 1.5 mM and 2.5 mM respectively. The observed  
247 results are consistent with the literature reports indicating better efficacy of both Fenton  
248 chemistry as well as cavitation phenomena at lower pollutant concentration [19-22]. It  
249 should be also noted here that the actual number of moles of phenol degraded are higher at  
250 2.5mM concentration as compared to 1.5 mM initial concentration. This also means that the  
251 extent of corrosion of the zero valent iron pieces and hence the extent of dissolved iron  
252 appearing into the solution increases. The observed results are consistent with our earlier  
253 observations with phenol degradation using the individual operation of advanced Fenton  
254 process [6].

### 255 3.4 *Variation of total iron content concentration*

256 The iron content in the solution also increased with longer treatment time due to  
257 continuous leaching during the flow and also with operating pressure and initial concentration

258 of phenol. The trends in variation of the iron content of the stream with the treatment time  
259 and initial concentration of phenol are shown in Figure 4. It can be seen that a maximum  
260 value of about 330 mg/L of iron in solution was observed for 90 minutes of treatment time at  
261 initial phenol concentration of 2.5mM. An increase in the treatment time or initial phenol  
262 concentration shows higher amounts of degradation of phenol and results in the dissolution of  
263 more iron. These results are in good agreement with our earlier studies [6,8] and the detailed  
264 discussion into the chemistry aspects of the advanced Fenton process can be referred to in our  
265 earlier work [6]. It should also be noted that the dissolved iron could easily be removed using  
266 a coagulation technique and hence does not represent any additional problem in terms of  
267 wastewater treatment. The outlet samples after treatment contained less than 10 mg/L iron  
268 following the coagulation treatment.

### 269 3.5 *Effect of Hydrogen Peroxide concentration:*

270 The concentration of hydrogen peroxide plays a crucial role in determining the  
271 overall efficacy of the degradation process especially for Fenton chemistry. Usually the  
272 loading of hydrogen peroxide should be adjusted in such a way that the entire amount is  
273 utilized in the process as the residual hydrogen peroxide contributes to COD and also is  
274 harmful to micro-organisms (important if the technique is used as a pre-treatment strategy for  
275 conventional aerobic oxidation). The effect of hydrogen peroxide concentration is shown in  
276 Figure 5 and it can be clearly seen that extent of degradation increases with the hydrogen  
277 peroxide concentration over the range 500 to 2000 mg/L. The observed trend is again  
278 consistent with the literature reports [23,24]. It has been established that the extent of  
279 increase in the TOC removal does not decrease with an increasing hydrogen peroxide  
280 concentration over the range investigated in the present work. An optimum hydrogen  
281 peroxide ratio must be selected as beyond a certain concentration, any excess might act as a  
282 scavenger for hydroxyl radicals and also contribute to excess COD in the pollutant stream.

283 Thus, proper selection of the operating concentration of the oxidant is necessary and  
284 multivariate analysis (discussed below) provides some guidelines on the selection of the  
285 optimum operating parameters.

### 286 3.6 *Factorial design of experiments for the modified AFP*

287 The use of a multivariate design of experiments has proven to be an important tool for  
288 obtaining valuable and statistically significant models of phenomena by performing a well  
289 planned set of experiments. Using this technique, it is possible to assess the importance of  
290 each individual variable and the interaction effects between them, thereby yielding the most  
291 desirable response. Application of this statistical technique has been reported for the  
292 treatment of pollutants by photocatalytic oxidation [25] and the Fenton/sono-Fenton  
293 technique [14, 25]. We now discuss the use of multivariate design of experiments to evaluate  
294 the importance of iron metal catalyst used in the combination of hydrodynamic cavitation and  
295 advanced AFP, and the hydrogen peroxide dosage in the TOC removal of phenol wastewater.

296 The influence of different variables in the modified advanced Fenton process was  
297 investigated using an experimental design methodology. The variables studied with this  
298 method include hydrogen peroxide dosage and different amounts of zero valent iron metal  
299 pieces acting as catalyst in our process. A complete  $3^2$  experimental design [26,27] was  
300 performed and employed different amounts of iron (25, 50 and 100 pieces, corresponding to  
301 low, medium and high amounts) and hydrogen peroxide (500 mg/L, 1000 mg/L and 2000  
302 mg/L, representing the low, medium and high amounts respectively). The results for all the 9  
303 experimental runs are presented for both experimental and calculated values in Table 1. The  
304 initial pH was adjusted to 2.5, by the addition of appropriate amounts of  $H_2SO_4$  solution (0.1  
305 M). The objective was to minimize the hydrogen peroxide concentration in the process that  
306 accompanied high efficiency of degradation of phenol and the organic by-products formed in  
307 the reaction.

308 Table 1 shows the factorial design of the experiment, along with the real values for  
309 the independent variables (-1, 0 and 1 for low, medium and high levels respectively). The  
310 response variables selected were TOC conversion at 15 min, 60 min and 105 min of treatment  
311 time, with the objective of studying the influence of the independent variables on the activity  
312 and the amount of iron dissolved from the catalyst during the process, to determine the  
313 influence of the independent variables on the modified AFP. The values of these variables,  
314 as well as the calculated values obtained from the model are also shown in Table 1. The  
315 experimental values can be used to construct a matrix and assuming a second order  
316 polynomial model and a Levenberg-Marquad algorithm for nonlinear regression, predictive  
317 equations for the response variables were obtained (equations 4 to 7 in Table 2), where X and  
318 Y represent the catalyst and hydrogen peroxide concentration respectively, and  $Z_1$  to  $Z_3$   
319 correspond to TOC conversion at 15, 60 and 105 minutes respectively and  $Z_4$  the total iron  
320 dissolved after 105 minutes treatment time. The influence of the independent variables and  
321 their combination is related to the value and sign of the coefficients of the polynomial  
322 expressions. Values in parenthesis describe the relative error of each coefficient. Based on  
323 the experimental values, Origin software (version 6.1) was used to predict the equations that  
324 quantitatively describe each variable and to build the surface response curves.

### 325 3.7 *Influence of process variables on the performance of the modified AFP*

326 The conversion of TOC values at 15, 60 and 105 minutes was selected for the study of  
327 the performance of the novel heterogeneous system in the mineralization of the aqueous  
328 phenol solution. Equations 4 to 7 (Table 2) fit the experimental data obtained and it has been  
329 observed that the predicted values of the extent of degradation using these equations perfectly  
330 match the experimentally observed values. Considering the influence of the variables with  
331 the coefficients of the equations shown above, it is notable that the presence of quadratic  
332 terms in all the equations and the responses are graphically represented by the surface

333 response curves. The amount of catalyst (X) is important in all the reaction times, although a  
334 negative effect of an excess of catalyst ( $X^2$ ) becomes important with the reaction time. An  
335 excess of hydrogen peroxide ( $Y^2$ ) has a positive effect also and the synergistic effect of the  
336 catalyst (X) and hydrogen peroxide ( $Y^2$ ) becomes important at the reaction time of 105  
337 minutes.

338 The graphical representation of the surface response curves of TOC removal for 15  
339 min, 60 min and 105 min is depicted in Figure 6. The three surfaces are in the same shades  
340 of grey to make a comparison between them easy. The 3D-response surface at 15 minutes  
341 (Figure 6a) clearly shows no significant increase in the TOC conversion with increasing  
342 catalyst loadings. Similar results were observed with the 3D response surface plots at 60 min  
343 (Figure 6b) and at 105 min (Figure 6c). Importantly, the maximum TOC conversion was  
344 obtained for elevated concentrations of hydrogen peroxide. The 3D response surface at 105  
345 min clearly shows an enhanced TOC conversion with increasing concentration of hydrogen  
346 peroxide and this beneficial effect of hydrogen peroxide concentration on the TOC removal  
347 rates is also seen for the other two time intervals investigated in the present work as shown in  
348 Figures 6a and 6b. This implies that the higher the amount of hydrogen peroxide (over the  
349 range selected in the present work) in conjunction with continuous generation of iron species  
350 in the reaction solution can produce more oxidising species, such as hydroxyl radicals, which  
351 can mineralise phenol solution. The same inference can also be obtained from the values of  
352 coefficients for each of these operating variables. From equation 6, it is clearly seen that the  
353 principal influence corresponds to hydrogen peroxide concentration (Y). It is seen that other  
354 variables such as X, XY,  $X^2$ ,  $Y^2$  and the combination of catalyst pieces and hydrogen  
355 peroxide concentration ( $XY^2$  and  $X^2Y$ ) has less effect on the TOC removal rates since the  
356 relative error is bigger than the coefficients.

357 Overall, it can be said that for 15 min, 60 min and 105 min of reaction time, the  
358 influence of the catalyst loadings is negligible and the results seem to be only dependent on  
359 hydrogen peroxide concentration in the modified AFP. However, it should be noted that the  
360 presence of iron metal catalyst is necessary for mineralization of phenol as preliminary  
361 experiments indicated that the combination of hydrodynamic cavitation and hydrogen  
362 peroxide (without iron metal catalyst) does not result in any TOC removal. Thus, even if  
363 catalyst loading does not play a significant role in deciding the extent of degradation, its  
364 presence in the system is equally important.

365 A change in the behaviour is observed in the 3D response surface at 15 min, 60 min  
366 and 105 minutes. Maximum values of TOC conversions are seen with catalyst amounts  
367 ranging from medium to high (0 to 1) and at a hydrogen peroxide concentration of 2000  
368 mg/L. For all the catalyst loadings employed, relative maximum values are obtained around  
369 this hydrogen peroxide concentration (2000 mg/L).

370 The amount of dissolved iron was determined at different concentrations of hydrogen  
371 peroxide. Figure 7 shows the amount of total dissolved iron in the solution after 105 minutes  
372 of phenol wastewater treatment by the combination of hydrodynamic cavitation and the AFP.  
373 Not surprisingly the more iron pieces present the greater the amount of iron that dissolves and  
374 maximum values are obtained with low concentrations of hydrogen peroxide. It should be  
375 pointed out that high concentration of hydrogen peroxide can retard corrosion of iron metal  
376 surfaces (passivation) as it can act as an electron donor at anodic sites [8] and this can explain  
377 why the lower iron content at higher concentration of hydrogen peroxide is observed.

378 Considering the coefficients of Equation 7, the major influence corresponds to  
379 changes in the amount of iron metal pieces in the reaction medium ( $X$ ,  $X^2$ ). Only high levels  
380 of hydrogen peroxide ( $Y^2$ ) or the combination of hydrogen peroxide and catalyst ( $XY^2$  and  
381  $YX^2$ ) have an appreciable influence in the degree of dissolution. In all these cases, an

382 increase in the individual variable or in the combination of both of them results in an increase  
383 in the amount of iron in solution as shown by plus signs before the coefficients. The 3D  
384 response surface corresponding to Equation 7 for the total dissolved iron content in the  
385 solution after 105 min of treatment time is shown in Figure 7 and there is a strong correlation  
386 between catalyst loadings and the degree of iron dissolution. The amount of catalyst used at  
387 high concentration of hydrogen peroxide seems to have a negligible influence on the  
388 dissolved iron content, while at a lower concentration of hydrogen peroxide the response  
389 surface shows a relative maximum. Equation 7 fits the experimental values, in terms of total  
390 iron dissolved in the solution.

391

#### 392 **4. Conclusions**

393 Zero valent iron is a promising catalyst for the treatment of phenolic aqueous  
394 solutions by the combination of hydrodynamic cavitation induced by the liquid whistle  
395 reactor with the AFP (modified AFP). Use of hydrodynamic cavitation enhances the efficacy  
396 of the AFP by keeping the iron surface active with the continuous impingement of the liquid  
397 jet stream flowing over the catalyst surface and at the same time providing additional free  
398 radicals for oxidation.

399 The current work has clearly shown that the modified AFP results in degradation of  
400 phenol and is indeed suitable for industrial wastewater applications. The efficacy of the  
401 treatment scheme is enhanced by high operating pressures, an increase in the oxidant dosage  
402 and a lowering of the pollutant concentration. The position of the catalyst bed with respect to  
403 the hydrodynamic cavitation unit is also important and it should be within the zone of  
404 influence of the cavities generated at the orifice.

405 The factorial design of experiments results in a removal of 50 – 60% TOC after 105  
406 min of treatment time with the modified AFP with an optimal H<sub>2</sub>O<sub>2</sub> concentration of 2000



407 mg/L (high value) and with 50 pieces of iron catalyst (mid value). The hydrogen peroxide  
408 dosage plays a more vital role than the catalyst amount in the modified AFP.

409 Thus, the combination of hydrodynamic cavitation along with the advanced Fenton  
410 process offers a viable treatment scheme for industrial wastewater and the current work has  
411 described optimisation of the operating parameters with the aim of cost reduction by a  
412 combination of experimental and statistical analysis.

413

#### 414 **Acknowledgements**

415 We wish to acknowledge support from the University of Abertay Dundee (UAD) for  
416 this work. Also, AGC and DHB wish to acknowledge funding from Scottish Enterprise  
417 under the Proof of Concept extension (POC+). PRG also wishes to acknowledge the support  
418 of Department of Science & Technology, India and the Royal Society, UK for sponsoring the  
419 visit to the University of Abertay Dundee under the India UK Science Networks Scheme.  
420 DHB also thanks the EU Cost D32 Action for travel support.

421

#### 422 **References**

- 423 1. P.R. Gogate, A.B. Pandit, *Adv. Env. Res.* 8 (2004) 501
- 424 2. P.R. Gogate, A.B. Pandit, *Adv. Env. Res.* 8 (2004) 553.
- 425 3. R.J. Bigda, *Chem. Eng. Prog.* 91 (1995) 62
- 426 4. S. Nam, P. G. Tratnyek, *Water Res.*, 34 (2000) 1837
- 427 5. J. Cao, L. Wei, Q. Huang, L. Wang, S. Han, *Chemosphere*, 38 (1999) 565
- 428 6. D. H. Bremner, A. E. Burgess, D. Houllmare, K-C. Namkung, *Appl. Catal. B:*  
429 *Environ.* 63 (2006) 15
- 430 7. J. Rima, E. Aoun, K. Hanna, Q.X. Li, *Journal De Physique*, 124 (2005) 81
- 431 8. K.C. Namkung, A. E. Burgess, D. H. Bremner, *Environ. Tech.* 26 (2005) 341

- 432 9. C-J. Liao, T-L. Chung, W-L. Chen, S-L. Kuo, *J. Mol. Catal. A: Chem.*, 265  
433 (2007) 189
- 434 10. A. Agrawal, P.G. Tratnyek, *Environ. Sci. Technol.*, 30 (1996) 153
- 435 11. M. Sivakumar, A.B. Pandit, *Ultrason. Sonochem.* 9 (2002) 123.
- 436 12. K.M. Kalumuck, G.L. Chahine, *J. Fluids Eng.* 122 (2000) 465.
- 437 13. P.R. Gogate, A.B. Pandit, *Rev. Chem. Eng.* 17 (2001) 1.
- 438 14. R. Molina, F. Martínez, J. A. Melero, D. H. Bremner, A. G. Chakinala, *Appl. Catal.*  
439 *B: Environ.* 66 (2006) 198.
- 440 15. A.G. Chakinala, P.R. Gogate, A. E. Burgess, D. H. Bremner, *Ultrason. Sonochem.* 14  
441 (2007) in press.
- 442 16. N.P. Vichare, P.R. Gogate, A.B. Pandit, *Chem. Eng. Tech.* 23 (2000) 683
- 443 17. P.R. Gogate, A.B. Pandit, *AIChE J.* 46 ( 2000) 1681.
- 444 18. M. Sivakumar, A.B. Pandit, *Ultrason. Sonochem.* 9 (2002) 123.
- 445 19. B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, *Water Res.* 33 (1999) 2110
- 446 20. F.J. Benitez, J.L. Acero, F. J. Real, F.J. Rubio, A.I. Leal, *Water Res.* 35 (2001) 1338
- 447 21. D. Peters, *Ultrason. Sonochem.* 8 (2001) 221
- 448 22. J. Dewulf, H. Van Langenhove, A. De Visscher, S. Sabbe, *Ultrason. Sonochem.* 8  
449 (2001) 143
- 450 23. Y.W. Kang, K-Y. Hwang, *Water Res.* 34 (2000) 2786
- 451 24. F.J. Rivas, F.J. Beltran, J. Frades, P. Buzeda, *Water Res.* 35 (2001) 387
- 452 25. M. Pérez, F. Torrades, J. Peral, C. Lizama, C. Bravo, S. Casas, J. Freer, H. D.  
453 Mansilla, *Appl. Catal. B: Environ.* 33 (2001) 89.
- 454 26. F. Torrades, M. Pérez, H. D. Mansilla, J. Peral, *Chemosphere*, 53 (2003) 1211
- 455 27. G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experiments, an Introduction to*  
456 *Design, Data Analysis and Model Building*, John Wiley and Sons, New York, 1978.

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459 **List of Figures:**

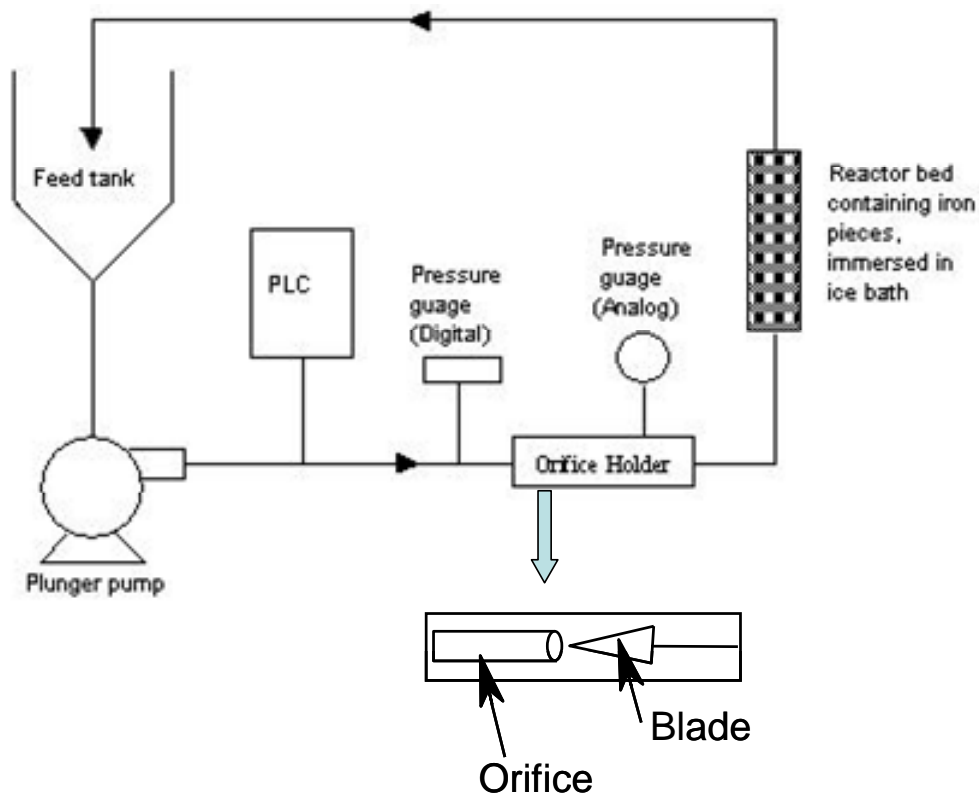
- 460 1. Schematic representation of the experimental setup with expanded view of  
461 arrangement of orifice and blade
- 462 2. Effect of inlet pressure in the hydrodynamic cavitation reactor on the TOC removal  
463 ratio. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub> 2000  
464 mg/L; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having thickness of 0.10 cm);  
465 orifice area 0.012 in<sup>2</sup>.
- 466 3. Effect of initial phenol concentration on the TOC removal ratio using the modified  
467 AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub> 2000  
468 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having  
469 thickness of 0.10 cm); orifice area 0.012 in<sup>2</sup>.
- 470 4. Variation of total iron content of solution with treatment time and initial phenol  
471 concentration. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub>  
472 2000 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having  
473 thickness of 0.10 cm); orifice area 0.012 in<sup>2</sup>.
- 474 5. Effect of hydrogen peroxide concentration on the TOC removal ratio using the  
475 modified AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub>  
476 2000 mg/L; pressure 1500 psi; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having  
477 thickness of 0.10 cm); orifice area 0.012 in<sup>2</sup>.
- 478 6. Response surfaces for TOC conversion of phenolic wastewater by the modified  
479 advanced Fenton process at a) 15 min, b) 60 min and c) 105 min.
- 480 7. The surface response curve of the total dissolved iron content after 105 min of  
481 treatment time.

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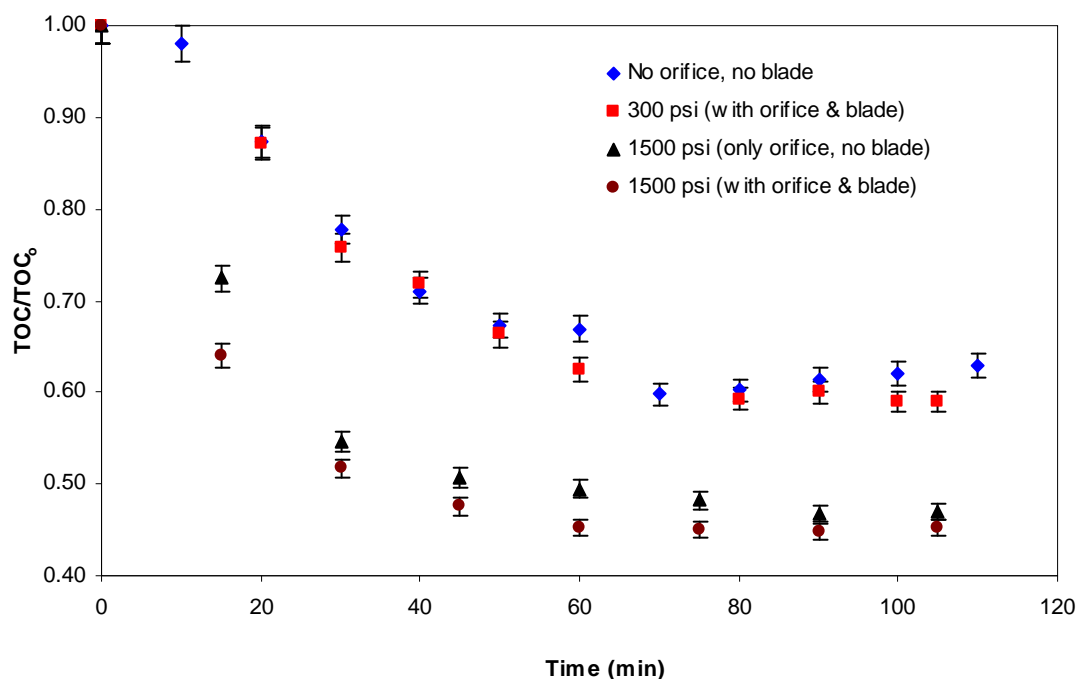
483 **List of Tables:**

484 Table 1: Factorial design of experiments

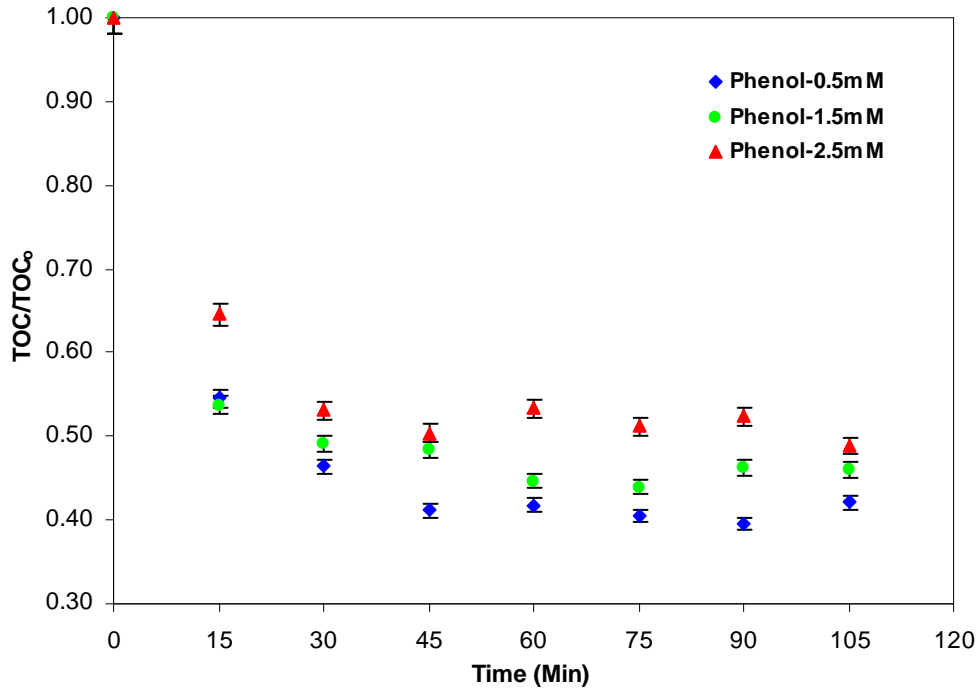
485 Table 2: Predicted equations obtained by factorial design of experiments



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487 Figure 1: Schematic representation of the experimental setup with expanded  
488 view of arrangement of orifice and blade

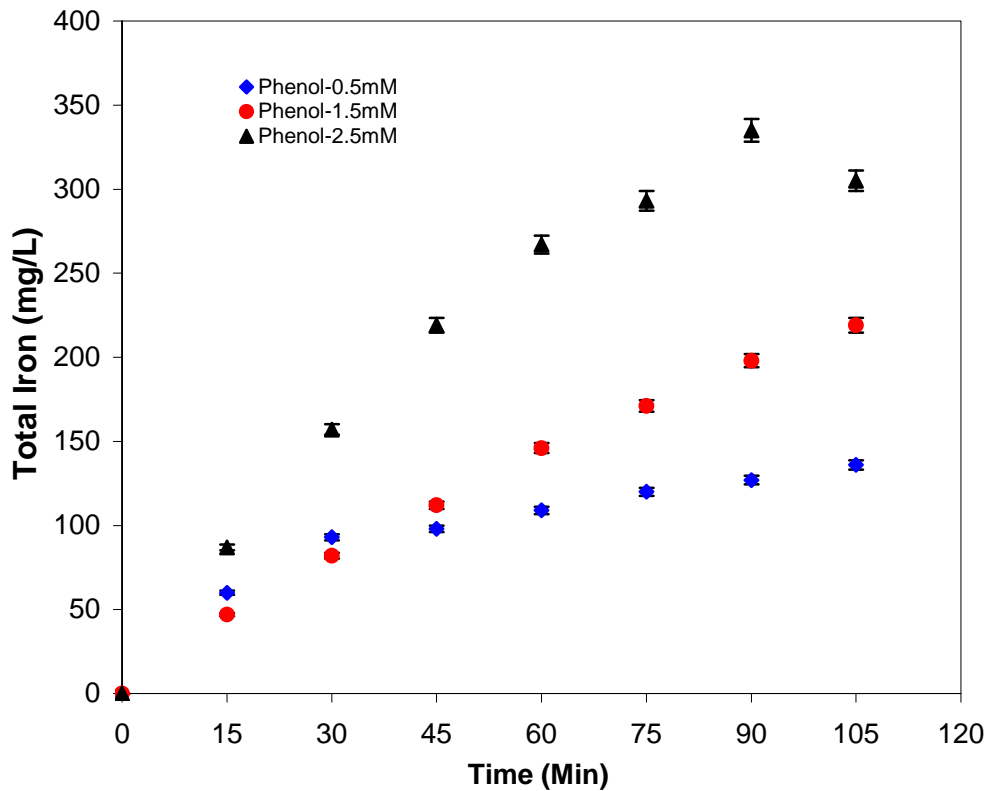


489  
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491 removal ratio. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub>  
492 2000 mg/L; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having thickness of 0.10  
493 cm); orifice area 0.012 in<sup>2</sup>.



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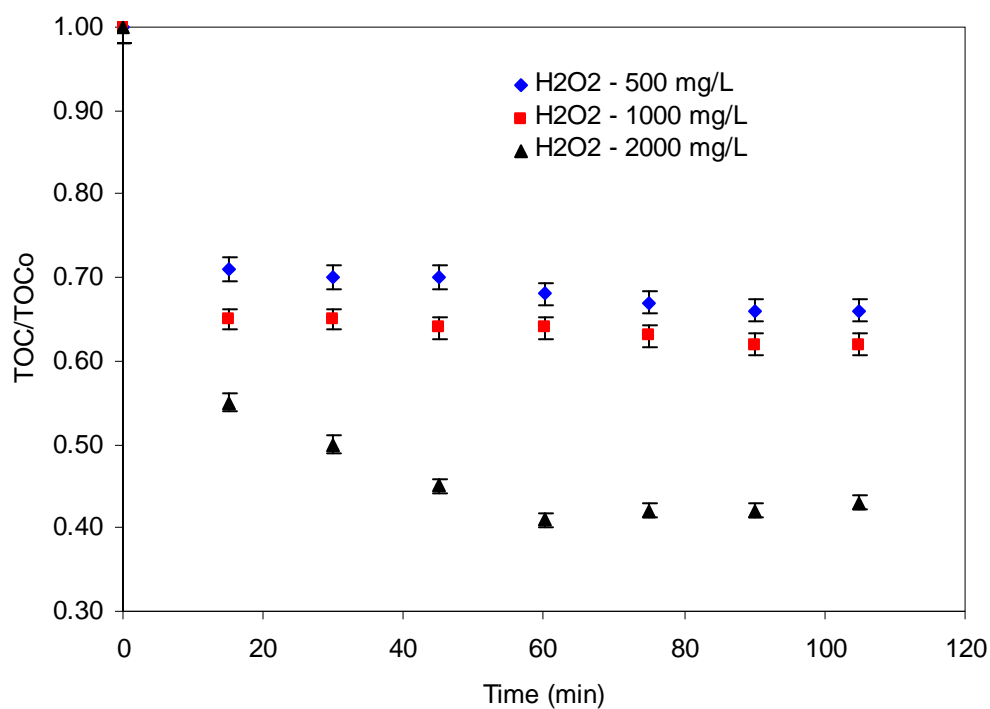
495 Figure 3: Effect of initial phenol concentration on the TOC removal ratio using the modified  
 496 AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub> 2000 mg/L;  
 497 pressure 1500 psi; iron 80 g (50 pieces of 1 cm x 2 cm, L-shaped having thickness of 0.10  
 498 cm); orifice area 0.012 in<sup>2</sup>.  
 499



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501 Figure 4: Variation of total iron content of solution with treatment time and initial phenol  
 502 concentration. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub> 2000

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504 0.10 cm); orifice area 0.012 in<sup>2</sup>.  
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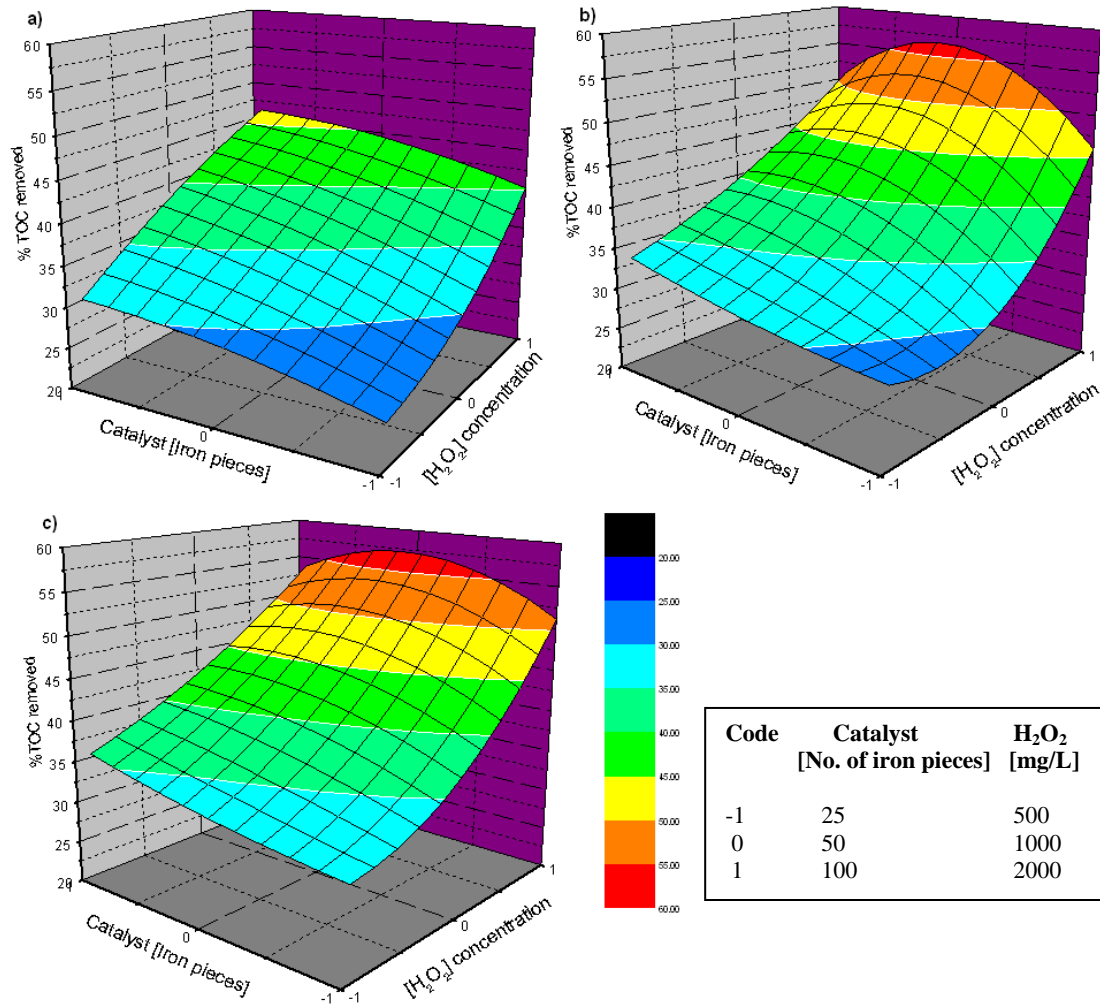


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507 Figure 5: Effect of hydrogen peroxide concentration on the TOC removal ratio using the  
508 modified AFP. Experimental conditions: pH 2.5; phenol concentration 2.5 mM, H<sub>2</sub>O<sub>2</sub> 2000  
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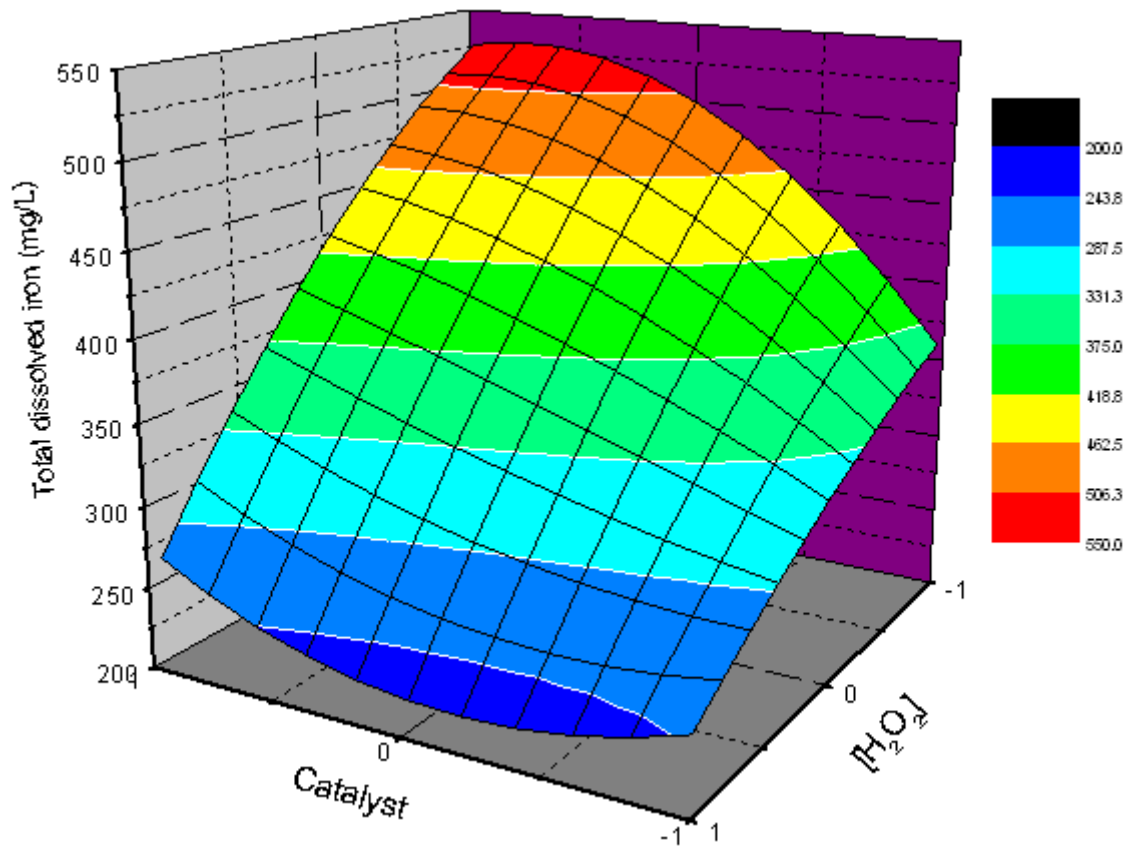
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517 Figure 6: Response surfaces for TOC conversion of phenol wastewater by the modified

518 advanced Fenton process at (a) 15 min, (b) 60 min and (c) 105 min.

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521 Figure 7: The surface response curve of the total dissolved iron content after 105 min of  
 522 treatment time.

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Table 1:

[Catalyst] (X)	[H <sub>2</sub> O <sub>2</sub> ] (Y)	X <sub>TOC</sub> <sup>15'</sup> (%) (Z <sub>1</sub> )		X <sub>TOC</sub> <sup>60'</sup> (%) (Z <sub>2</sub> )		X <sub>TOC</sub> <sup>105'</sup> (%) (Z <sub>3</sub> )		Fe <sub>Total</sub> <sup>105'</sup> (mg/L) (Z <sub>4</sub> )	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
-1	-1	25	25.1	29	29.6	30	30.7	370	365.9
-1	0	30	29.7	32	30.6	38	36.2	310	316.9
-1	1	40	40.2	45	46.0	50	51.2	250	247.2
0	-1	29	28.6	32	30.6	34	32.4	500	511.1
0	0	35	35.8	36	39.1	38	41.6	406	388.0
0	1	45	44.5	59	56.5	60	57.2	219	223.8
1	-1	30	30.2	33	33.7	35	35.8	536	530.1
1	0	40	40.0	42	40.2	45	42.9	425	434.4
1	1	46	46.3	49	50.1	52	53.2	280	276.9

526

527

Table 2:

$$Z_1 = 35.8(\pm 0.9) + 4.95(\pm 0.8)X + 7.9(\pm 0.8)Y + 0.3(\pm 0.6)XY - 1.2(\pm 0.8)X^2 + 0.83(\pm 0.8)Y^2 -$$

$$0.1(\pm 1.0)X^2Y - 2.2(\pm 1.0)XY^2 \quad (4)$$

$$Z_2 = 39.1(\pm 3.7) + 4.8(\pm 3.5)X + 12.9(\pm 3.8)Y + 1.1E-10(\pm 2.5)XY - 3.7(\pm 3.6)X^2 + 4.4(\pm 3.5)Y^2 -$$

$$4.7(\pm 4.5)X^2Y - 2.7(\pm 4.3)XY^2 \quad (5)$$

$$Z_3 = 41.6(\pm 4.3) + 3.3(\pm 4.1)X + 12.4(\pm 4.4)Y - 0.8(\pm 2.9)XY - 2.0(\pm 4.2)X^2 + 3.1(\pm 4.1)Y^2 -$$

$$2.9(\pm 5.2)X^2Y - 1.5(\pm 5.0)XY^2 \quad (6)$$

$$Z_4 = 388.0(\pm 18.9) + 58.8(\pm 17.5)X - 143.6(\pm 17.0)Y - 33.6(\pm 12.3)XY - 12.4(\pm 17.6)X^2 -$$

$$20.6(\pm 17.7)Y^2 + 50.6(\pm 20.8)X^2Y - 10.3(\pm 21.4)XY^2 \quad (7)$$

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530