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Synergistic effects of combining ultrasound with the Fenton process in the degradation of Reactive Blue 19

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24 The rate and extent of decoloration of RB 19 increased with rising hydrogen peroxide
25 concentration, ultrasonic powers and iron sulphate concentration but decreased with
26 increasing dye concentration. An optimum pH value of pH=3.5 was found. The rate of
27 decoloration was higher when dissolved oxygen was present as compared with nitrogen
28 and argon confirming the solution phase mechanism of the degradation.

29

30 **Keywords:** Dye degradation; ultrasound promoted fenton process; ultrasonic cavitation;
31 dissolved gases; wastewater treatment

32

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35

36 1. Introduction

37 A variety of chemically different dyes are used for various industrial applications
38 such as textile dyeing, paper printing, leather, shoe polish, plastics, food coloring *etc.* A
39 significant amount of these dyes enter the environment as wastewater [1]. There are more
40 than 100,000 types of dyes commercially available and over 7×10^5 tonnes of dyestuff
41 are produced annually [2]. Reactive dyes are resistant to light, water and oxidizing agents
42 and are therefore difficult to degrade once released into aquatic systems. The presence of
43 very low concentrations of dyes in effluent can be highly visible and undesirable [3] on
44 aesthetic grounds. Their presence disturbs aquatic communities present in ecosystem by
45 obstructing light penetration and oxygen transfer into water bodies [4]. Moreover, they
46 can be toxic and carcinogenic [5-7].

47 A number of treatment techniques have been developed to remove dyes from the
48 wastewaters. Among these, advanced oxidation processes (AOPs) are effective in
49 degrading many reactive dyes. The Fenton process is a homogeneous advanced oxidation
50 process using an acidic mixture of hydrogen peroxide and ferrous ions [8, 9] to produce
51 highly oxidative hydroxyl radicals which react with dissolved species, removing colour
52 and lowering chemical oxygen demand. The $\cdot\text{OH}$ radicals (Eq .1), attack the unsaturated
53 dye molecule and the chromophore of the dye molecule is destroyed and decolorized [9].



55 The use of power ultrasound as an advanced oxidation process has been also
56 employed in the degradation of textile dyes [8, 10]. This is also generally based on the
57 formation of short-lived radical species generated in violent cavitation bubble collapses.
58 These radical species can diffuse out of the bubble into the bulk fluid medium where they
59 are able to react with solute molecules. A steady-state concentration of reactive radical
60 species in the liquid phase can be maintained by continuous irradiation with ultrasound.
61 Volatile solutes may evaporate into the bubble and be degraded by the harsh conditions
62 generated during cavitation. Non-volatile organic compounds present in the liquid phase
63 can undergo degradation mainly by reaction with powerful oxidizing agents such as $\cdot\text{OH}$
64 radicals produced [11]. The sonochemical enhancement of several AOPs has been
65 reported. A number of studies have reported the use of ultrasound for the decoloration
66 and degradation of textile dyes, but it has often been difficult to completely mineralize
67 the dye stuff using ultrasound alone [12].

68 The combination of ultrasound with other advanced oxidation process is a
69 convenient approach in degrading reactive dyes. There are a number of reports on the

70 combined use of ultrasound and Fenton process for the degradation of several textile dyes
71 [8, 9, 13, 14]. While Guimaraes *et al.* [15] showed that oxidation of Reactive Blue 19 can
72 be promoted by use of Fenton reagent and accelerated photochemically, the sono-Fenton
73 process has not previously been applied to the degradation of this dye. Given its
74 widespread use, [15, 16] the present study has focused on RB 19 dye to undergo
75 treatment with combined Fenton and ultrasonic processes. The effect of the various
76 experimental parameters including hydrogen peroxide and iron sulfate concentrations,
77 pH, initial dye concentrations and dissolved gases on color removal were investigated.

78

79 **2. Experimental Procedure**

80 **2.1. Materials**

81 Reactive Blue 19 (RB 19) was purchased from Sigma Aldrich (UK) and was used
82 as received; its structure is shown in Fig. 1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (analytical grade) was obtained
83 from BDH Laboratory Supplies (England). Hydrogen peroxide (analytical grade) 35%
84 w/v, H_2SO_4 and NaOH were obtained from Fisher Scientific (UK). All solutions were
85 prepared with distilled water. Gases were obtained from BOC and were used without
86 further purification.

87 **2.2. Procedure**

88 A stock solution of RB 19, prepared by dissolving 1 g of dye in 1 L of distilled
89 water, was diluted to give initial concentrations for each experiment of 25 mg L^{-1} (4×10^{-5}
90 mol L^{-1}). Sulphuric acid and sodium hydroxide were used to adjust the pH of the dye
91 solution. 100 mL volumes from the stock solution were placed in the glass reactor, and
92 the appropriate amount of hydrogen peroxide and iron sulphate added to the solution. The

93 glass reactor was equipped with a water circulating jacket for maintaining reaction
94 temperature to ± 1 °C. Sonication was performed with a Sonic processor L500-20
95 ultrasonic generator (20 kHz, 200W, Sonic Systems) equipped with titanium probe
96 transducer (23820T). The tip of the horn was 1 cm in diameter and was placed 1.5 cm
97 into the liquid layer (Fig. 2). At 5 min time intervals, samples were taken from the reactor
98 and analyzed by UV/visible spectrophotometry (Agilent 8453) using detection
99 wavelengths of 256 and 594 nm. Each experiment was performed in duplicate. Sonication
100 was conducted in the presence of air with no added gas except when the effect of
101 dissolved gas was being investigated. In these experiments, the initial solution was
102 vigorously purged with Argon, O₂ or N₂ for 20 min prior to ultrasonic irradiation and a
103 gas flow of *approx.* 1 ml min⁻¹ was maintained throughout the experiment.

104 The percentage (%) decolorization was found from equation (2)

$$105 \text{ Dye \% decolorization} = (1 - C_t / C_0) \times 100 \quad (2)$$

106 where C_t and C_0 are the concentrations (mg L⁻¹) of dye at reaction time t and prior to
107 sonication respectively [12]. The change in concentration in the solution was calculated
108 from the Beer-Lambert law [13].

$$109 A = l \varepsilon C \quad (3)$$

110 where A is the absorbance, l is the path length (cm), ε is the molar extinction coefficient
111 (L mol⁻¹ cm⁻¹) and C is the dye concentration (mol L⁻¹).

112 **2.3. Instrumentation**

113 The samples were collected at different time intervals and the degradation
114 products were identified using Liquid chromatography/mass spectrometry (LC/MS). The
115 mass spectrometry was performed using a microTOF electrospray time of flight (ESI-

116 TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) coupled to an
117 Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). The LC was
118 equipped with a Phenomenex Luna 5 μ C18 (2) column with stationary phase mesh size of
119 100 Å and dimensions (50 mm x 2 mm), connected directly to the MS. The other
120 experimental conditions were: nitrogen supplied at a pressure of 1 bar as a nebulising gas
121 and also used as the drying gas, with the flow rate of 8 L min⁻¹ at a temperature of 200°C,
122 water/acetonitrile was employed as mobile phase with a flow rate of 0.4 mL min⁻¹,
123 sample volume 1 μ l, injection temperature 25 °C. For the detection of positive/negative
124 ions a capillary voltage of -4000 V/ +4000 V was used.

125 **2.4. Effects of acoustic intensity and sonolysis**

126 The acoustic power dissipated by the horn into the solution in the reactor was
127 measured using the usual calorimetric method [17] employing a digital thermometer that
128 recorded the solution temperature every 5 min, over a 30 min interval. The overall power
129 input was estimated according to Eq. (4).

$$130 \text{ Energy input, } q = mc \, dT/dt \quad (4)$$

131 where m is the mass of water; c is the heat capacity of water and dT/dt is the temperature
132 gradient over time. The acoustic intensity (W cm⁻²) was determined by dividing the
133 power input (q) by the horn surface area (A).

134 **2.5. Oxidizing species determination**

135 The homogeneous system used to monitor radical activity was Fricke dosimetry,
136 in which iron II ions are oxidized (Eq. 5) by sonochemically generated species to iron III
137 [17]. When the ultrasound is irradiated into a Fricke solution Fe⁺² ions in the solution are
138 oxidized to Fe⁺³ ions as follows:



140 The Fricke solution was prepared with 0.001 M ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 0.005 M (H_2SO_4).

141 The concentration of Fe^{+3} formed during irradiation was measured by a UV/Visible
142 spectrophotometry at wavelength of 304 nm.

143

144 **3. Results and Discussion**

145 *3.1. Decolorization of RB 19 in different systems*

146 Experiments were performed using H_2O_2 alone, FeSO_4 alone, $\text{H}_2\text{O}_2 / \text{FeSO}_4$ and
147 ultrasound combined with $\text{H}_2\text{O}_2 / \text{FeSO}_4$ to observe independently the effects of different
148 parameters on RB 19 decoloration. Color removal over treatment times of 30 min was
149 less than 5% when H_2O_2 alone, FeSO_4 alone or ultrasound alone was used. Due to the
150 non-volatile and hydrophilic nature of reactive dyes, decoloration would be expected to
151 occur mainly in the bulk solution by radical reaction rather than inside the bubbles by
152 pyrolytic reaction. At a frequency of 20 kHz, the concentration of hydroxyl radicals
153 produced in the bulk solution by ultrasound alone was too low to affect the dye
154 decoloration. Also the limited oxidizing power of hydrogen peroxide ($E^0 = 1.78 \text{ V}$)
155 means that no color removal could be achieved by hydrogen peroxide alone. However, as
156 shown in Fig. 3, reduction in color was observed when the combined $\text{H}_2\text{O}_2 / \text{FeSO}_4$
157 system was used, resulting from the generation of hydroxyl ($\cdot\text{OH}$) radicals in the solution
158 as Equation (1). This contrasts with a related dye (CI Reactive Black 8) on which Zhang
159 and co-workers [13] showed ultrasound had no significant effect on decolourisation by
160 Fenton reagent although other systems have demonstrated a beneficial effect [8, 14, 15]
161 similar to that seen here.

162 Non-volatile organic compounds present in the liquid phase undergo degradation
163 mainly by reaction with these $\cdot\text{OH}$ radicals ($E^0 = 2.8 \text{ V}$). Further, the combined
164 ultrasound/ H_2O_2 / FeSO_4 system led to enhanced color removal, indicating an accelerating
165 effect due to cavitation [8]. The highest amount of decoloration of about 78% was found
166 in the coupled ultrasound and H_2O_2 / FeSO_4 system after 30 min of treatment, while only
167 50% of decolorization was obtained with H_2O_2 / FeSO_4 in the absence of ultrasound. A
168 detailed comparison with other published systems is complicated by the use of different
169 conditions but these results indicate that using ultrasound can enhance the action of the
170 H_2O_2 / FeSO_4 system so that each experimental parameter was studied to determine the
171 origin of the effects.

172 **3.2. Effect of hydrogen peroxide concentration on RB 19 dye decolorization**

173 The decoloration of RB 19 at different concentrations of hydrogen peroxide was
174 investigated (Fig. 4(a)) with a FeSO_4 concentration of 3 mg L^{-1} , pH of 3.5 and ultrasonic
175 intensity of 8 W cm^{-2} . As with previous studies using both homogeneous [13, 15] and
176 heterogeneous [14] sono-Fenton reactions, it was found that the rate of decoloration
177 increased with higher hydrogen peroxide concentration. It is notable that the
178 concentrations of hydrogen peroxide used here were lower than that used in previously
179 published studies and indicates that ultrasound may be applied at lower concentrations
180 than previously suggested and so useful in minimizing the amount of reagent necessary
181 for dye treatment. When hydrogen peroxide concentration was 0.05 mM the decoloration
182 efficiency was *approx.* 55 % after 30 min of reaction time.

183 When the hydrogen peroxide concentration was increased to 0.5 mM the
184 decoloration efficiency increased due to the higher concentrations of generated hydroxyl

185 radicals [8, 9]. The decolorization rate increased as the H₂O₂ concentration increased
186 from 0.05 mM to 0.5 mM although further increase in concentration did not lead to the
187 further increase in decoloration. This can be explained since only a comparatively small
188 amount of additional hydrogen peroxide decomposed to generate hydroxyl radicals and
189 the undecomposed hydrogen peroxide may act as a scavenger for ·OH resulting in the
190 generation of hydroperoxy radicals (Eq. 6) that are less reactive than the hydroxyl
191 radicals. At these higher H₂O₂ concentrations, hydroxyl radicals react with the peroxide
192 in preference to the RB19 so the degradation rate is reduced.



194 Fig. 4(b) illustrates the kinetics of RB 19 decoloration and demonstrates that it fits
195 a first order kinetic model as in Eq. (7).

$$196 \quad \ln (C_t/C_0) = -kt \quad (7)$$

197 where k is the first order rate constant (min⁻¹) and t is reaction time in min. The
198 relationship between hydrogen peroxide concentration and first order rate constant is
199 shown in Fig. 4(c).

200 **3.3. The effect of initial pH on the RB 19 dye decolorization**

201 The pH values investigated were 2.5, 3.5, 4.5, 5.5 at a fixed FeSO₄ concentration
202 of 3 mg L⁻¹, H₂O₂ concentration of 0.5 mM and ultrasonic intensity of 8 W cm⁻². It can be
203 seen from Fig. 5(a) that the decoloration rate increased with decreasing pH, reaching a
204 maximum at pH 3.5 after which the rate decreased. Zhang *et al.* [8, 13] reported that the
205 rate of decolouration was relatively insensitive to pH below pH=6 although the reduction
206 of chemical oxygen demand was maximized at pH=3. Similar results on other dyes have
207 been reported [10]. The pH is an important parameter in Fenton reactions and it has often

208 been reported that that the optimum pH is around pH = 3 is usually optimum for Fenton
209 oxidations [18, 19, 20]. Accordingly, the first order rate constant decreases linearly with
210 the increase of pH (> 3.5) as shown in Fig. 5(b). This variation of reaction rate with pH
211 arises from a complex mixture of factors. At low pH (< 2.5), the high concentration of H⁺
212 ions in solution dominates the reaction with ·OH (Eq. 8) [18].



214 Under these conditions, the rate of production of hydroxyl radicals is relatively
215 slow since iron mainly exists as [Fe(H₂O)₂]⁺². Iron is present in solution in catalytic
216 amounts and a further limitation on the rate of ·OH production is the slow regeneration of
217 Fe⁺² after reaction (1). [18].

218 These effects are less important as the pH rises and so the rate and extent of
219 decolouration rises. However, above pH = 4, other effects come into play which reduce
220 the rate [19-21]. The concentration of Fe⁺² in solution is reduced since Fe⁺³ species are
221 more stable in solution. Solid oxyhydroxides such as Fe(OH)₃ can also precipitate. Thus,
222 lower concentrations of ·OH are generated and decolouration is less effective. These
223 effects combine to give an optimum value of pH = 3.5 in this work as reported previously
224 with other dyes.

225 ***3.4. The effect of iron sulphate concentration on the RB 19 dye decolorization***

226 The effect of iron sulphate concentration on RB 19 dye decoloration was
227 investigated with H₂O₂ concentration fixed at 0.5 mM, pH value at 3.5 and ultrasonic
228 intensity of 8 W cm⁻². It was observed that the degradation of RB 19 increased with
229 increasing Fe⁺² concentrations in solution (Fig. 6(a)) although the decoloration rate
230 decreased when the iron sulphate concentration was above 3 mg L⁻¹. High concentrations

231 of iron sulphate would produce too many ferrous ions in solution, resulting in scavenging
232 of the $\cdot\text{OH}$ radicals according to reaction (9) [9, 18] in preference to reaction with the
233 dye.



235 The relationship between iron sulphate concentration loading and first order rate
236 constant is shown in Fig. 6(b) and indicates that the rate constant increases linearly with
237 the increase of iron loading. It should be noted that the concentration of Fe^{+2} used here is
238 lower than that used in other studies although where comparison is possible, the
239 degradation rate does increase with rising iron concentration under comparable
240 conditions in published studies.

241 **3.5. Decay of UV/Visible absorption spectra**

242 The change in UV/Visible absorption spectra for RB 19 decoloration as a function
243 of time was recorded (Fig. 7), using a H_2O_2 concentration of 0.5 mM, FeSO_4
244 concentration of 3 mg L^{-1} , pH 3.5 and ultrasonic intensity of 8 W cm^{-2} . As can be seen
245 from the spectra, before the oxidation, the absorption spectrum of RB 19 was
246 characterized by two main bands, in UV region (256 nm) and in visible region (594 nm).
247 The disappearance of the visible band was likely due to the fragmentation of
248 anthraquinone bond by oxidation and change in absorbance in UV region was considered
249 as evidence of aromatic fragment degradation in dye molecule and its degradation
250 products [8]. Initial radical attack occurs at the aromatic substituent on the anthraquinone
251 ring and at the carbonyl groups [22].

252

253

254 **3.6. The effect of initial dye concentration on RB 19 decolorization**

255 Fig. 8(a) illustrates the decoloration of RB 19 at different initial dye
256 concentrations when H_2O_2 concentration is 0.5 mM, FeSO_4 concentration is 3 mg L^{-1} , pH
257 value is 3.5 and ultrasonic intensity of 8 W cm^{-2} . It can be seen that higher initial dye
258 concentrations led to decreased decolorization rates. This may be due to insufficient
259 hydroxyl radical concentration to react with higher amounts of dye in solution. A
260 concentration of 75 mg L^{-1} corresponds to 0.12 mmol L^{-1} which is well in excess of the
261 expected generation of $\cdot\text{OH}$. Fig. 8(b) shows that the first order rate constant decreases
262 with the increase of initial dye concentration. This behavior is typical of such
263 sonochemical reactions.

264 A kinetic study using combined ultrasound and Fenton degradation processes was
265 undertaken by measuring the rate constant (k) for first, second and third order reactions.
266 The values confirmed that the order of reaction within the current experimental
267 conditions was first order as shown in Fig. 8(c) at different initial concentrations [23].
268 The correlation between $\ln(C_t/C_0)$ and irradiation time was linear (Fig. 8(c), the slopes
269 giving the apparent rate constant (k). The regression coefficient, R^2 , values ranged from
270 0.99 to 0.95, confirming that combined ultrasound and Fenton degradation process of RB
271 19 followed the first order reaction kinetics.

272 **3.7. The effect of dissolved gases on RB 19 decolorization**

273 Several authors have showed the dependence on the saturating gas of the
274 sonochemical treatment of organics in water [24, 25] although studies on dye systems are
275 rare. Zhang *et al.* showed [8] little difference in the degradation of CI Acid Orange 7
276 under nitrogen or oxygen. The nature of dissolved gas is an important parameter that

277 affects the sonochemical processes since it acts as nucleation sites for cavitation and also
278 influences the conditions such as final temperature achieved inside a collapsing cavitation
279 bubble [26]. Monatomic gases, with higher ratios of specific heat capacities, γ , such as
280 argon, promote increased temperature of collapse and hence higher levels of pyrolysis of
281 substances inside the cavitation bubbles. The physical properties, such as specific heat
282 ratio, of oxygen and nitrogen are similar and so similar temperatures are generated inside
283 collapsing bubbles. Any differences here are due to chemical effects. Thus, the gas
284 present in the solution plays a determinant role in the implosion conditions of the bubble
285 of cavitation and in the formation of radicals during the ultrasonic process.

286 Degradation of RB 19 was carried out under argon, nitrogen and oxygen with a
287 H_2O_2 concentration of 0.5 mM, FeSO_4 concentration of 3 mg L^{-1} , pH 3.5 and ultrasonic
288 intensity of 8 W cm^{-2} . The results showed that the dye decoloration was enhanced when
289 dissolved oxygen is present as compared with nitrogen or argon (Fig. 9). The lowest
290 degradation rate was measured under argon. In the presence of argon, the generation of
291 $\cdot\text{OH}$ is due only to the decomposition of vapor water (Eq. (10)). Evidence for this is the
292 generation of H_2O_2 under argon saturation compared with oxygen as dissolved gas [26].



294 Under oxygen atmosphere the degradation rates were higher as compared to argon and
295 nitrogen, since oxygen promotes the formation of $\cdot\text{OH}$ radicals as in Eq. (12).



298 These results are consistent with the reaction of RB 19 with hydroxyl radicals in solution
299 rather than through pyrolysis. If pyrolysis played a significant part in the degradation, a
300 faster rate under argon would be expected and this is not seen.

301 **3.8. Effect of ultrasonic powers on RB 19 decolorization**

302 The effect of ultrasonic power settings are shown in Fig. 10 (a) with optimized
303 conditions of other parameters. It can be seen that increase in ultrasonic intensities (0-8
304 W cm⁻²) increases the dye decoloration rate. This has commonly been reported in
305 sonochemical systems. The increase in ultrasonic powers would increase the mixing
306 intensity due to turbulence generated by cavitation bubble collapse as well as micro
307 jetting [8] in addition to yielding higher numbers of cavitation bubbles [17] and hence
308 higher yields of hydroxyl radicals. Fig. 10 (b) shows that the first order rate constant
309 increase with the increase of ultrasonic power settings.

310 By comparing the rate constant values of ultrasonic power settings with rate
311 constant values of Fricke dosimetry, it was found that in combined ultrasound and Fenton
312 process the production of ·OH radicals were almost 10 times more as compared to the
313 ·OH radicals produced by alone ultrasound process (Table 1) in Fricke dosimetry.

314 **3.9. RB 19 degradation studies**

315 Attempts to identify the intermediates/end products after the treatment of RB 19
316 were made using LC/MS. Samples at different time intervals were collected during the
317 combined ultrasound and Fenton process when initial RB 19 concentration was 200 mg
318 L⁻¹, H₂O₂ concentration was 0.5 mM, FeSO₄ concentration was 3 mg L⁻¹, pH was 3.5 and
319 ultrasonic intensities of 8 W cm⁻². From the results of this oxidation process, it can be
320 expected that the 5 min treatment resulted in the disappearance of dye molecule with

321 decreased peak areas of dye residues. The initial LC/MS results could not assist to
322 propose the degradation mechanism of dye therefore; further analysis will be required to
323 determine the low molecular weight compounds.

324 **4. Conclusions**

325 This study showed the first results on the effect of combined ultrasound and
326 Fenton's process on RB 19 dye removal. In general they demonstrate similar effects to
327 other dyes that have been subjected to the process although there are some differences. In
328 particular, significant decolourisation was detected at lower concentrations of iron and
329 peroxide than comparable studies on other dyes showing that the use of ultrasound can
330 save the cost and potential side effects of reagent use. Unlike some dye systems, a small
331 amount of degradation was detected using ultrasound alone although this was too slow to
332 be applied in practice. Using ultrasound accelerates the Fenton reaction by accelerating
333 the production of hydroxyl radicals. The decoloration of RB 19 dye was increased with
334 the increase of hydrogen peroxide concentration, ultrasonic power and iron sulphate
335 concentration but decreased by increasing the initial dye concentration. The process was
336 optimized at $\text{pH} = 3.5$. The decoloration of RB 19 follows first order rate constant. The
337 primary mechanism of reaction with hydroxyl radicals in solution rather than by pyrolysis
338 was confirmed since the rate of decoloration was higher when dissolved oxygen was
339 present as compared with nitrogen or argon.

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343

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Figure Captions

Fig. 1. Structure of RB 19 dye

Fig. 2. Experimental setup

Fig. 3. Decolorization of RB 19 by with/without H₂O₂, FeSO₄ by sonolysis (C₀= 25 mg L⁻¹, H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power =8 W cm⁻²)

Fig. 4 (a). The effect of hydrogen peroxide conc. on the decolorization of RB 19 (C₀= 25 mg L⁻¹, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power =8 W cm⁻²)

Fig. 4 (b). First order kinetic plot of RB 19 decoloration by different hydrogen peroxide conc. (C₀= 25 mg L⁻¹, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power = 8 W cm⁻²)

Fig. 4 (c). The effect of hydrogen peroxide concentration on the rate constant

Fig. 5 (a). The effect of pH on the decolorization of RB 19 (C₀= 25 mg L⁻¹, FeSO₄ conc. 3 mg L⁻¹, H₂O₂ conc. 0.5 mM, US power = 8 W cm⁻²)

Fig. 5 (b). The effect of different pH on the rate constant

Fig. 6 (a). The effect of iron sulphate addition on the decolorization of RB 19 (C₀= 25 mg L⁻¹, H₂O₂ conc. 0.5 mM, pH 3.5, US power = 8 W cm⁻²)

Fig. 6 (b). The effect of iron sulphate addition on the rate constant

Fig. 7. UV/Visible absorption changes with reaction time (C₀= 25 mg L⁻¹, H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power = 8 W cm⁻²)

Fig. 8 (a). The effect of initial dye concentration on the decolorization of RB 19 (H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power = 8 W cm⁻²)

Fig. 8 (b). The effect of initial dye concentration on the rate constant

Fig. 8 (c). First order kinetic plot of RB 19 degradation by combined ultrasound and Fenton process at different dye concentrations (H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power = 8 W cm⁻²)

Fig. 9. The effect of different gases on the decolorization of RB 19 ($C_{0=}$ 25 mg L⁻¹, H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5, US power =8 W cm⁻²)

Fig. 10 (a). The effect of ultrasonic powers on the decolorization of RB 19 ($C_{0=}$ 25 mg L⁻¹, H₂O₂ conc. 0.5 mM, FeSO₄ conc. 3 mg L⁻¹, pH 3.5)

Fig. 10 (b). The effect of ultrasonic power settings on the rate constant

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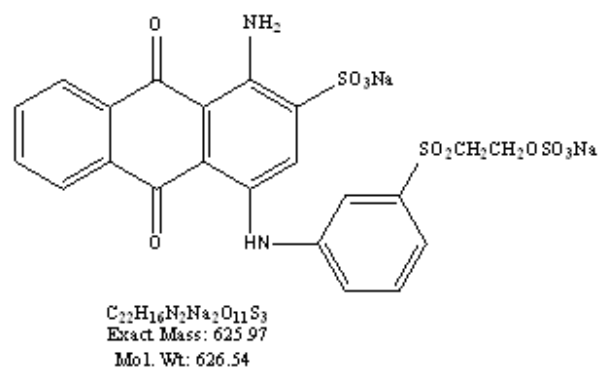


Fig. 1.

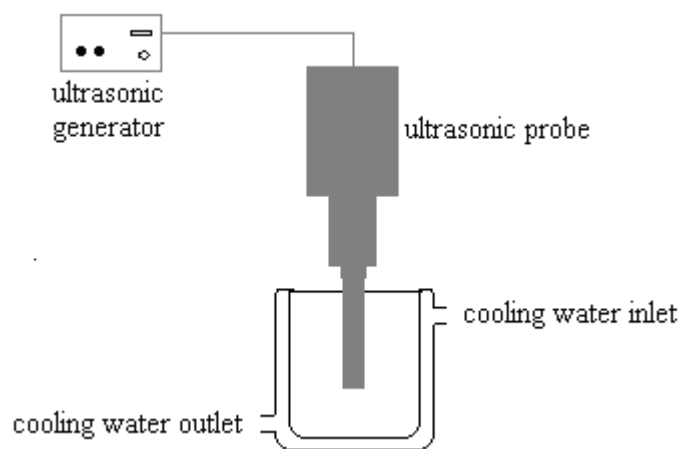


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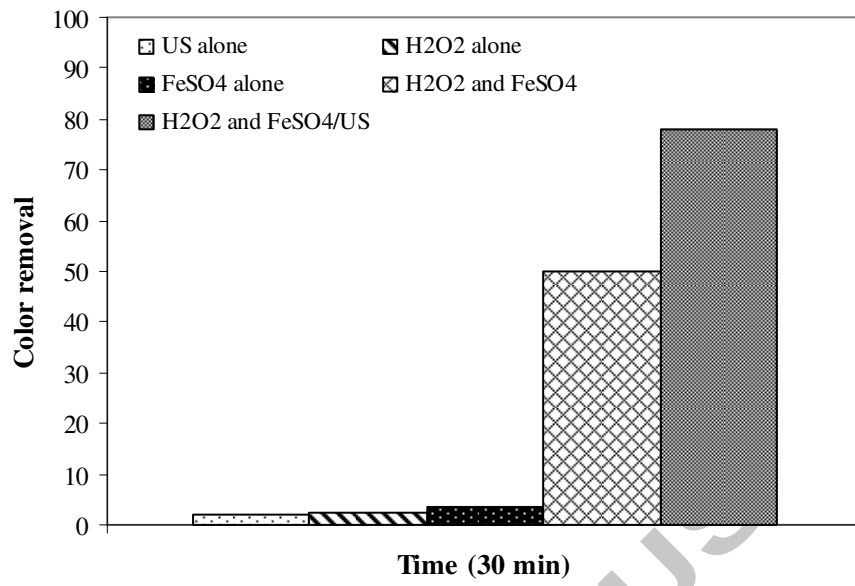


Fig. 3

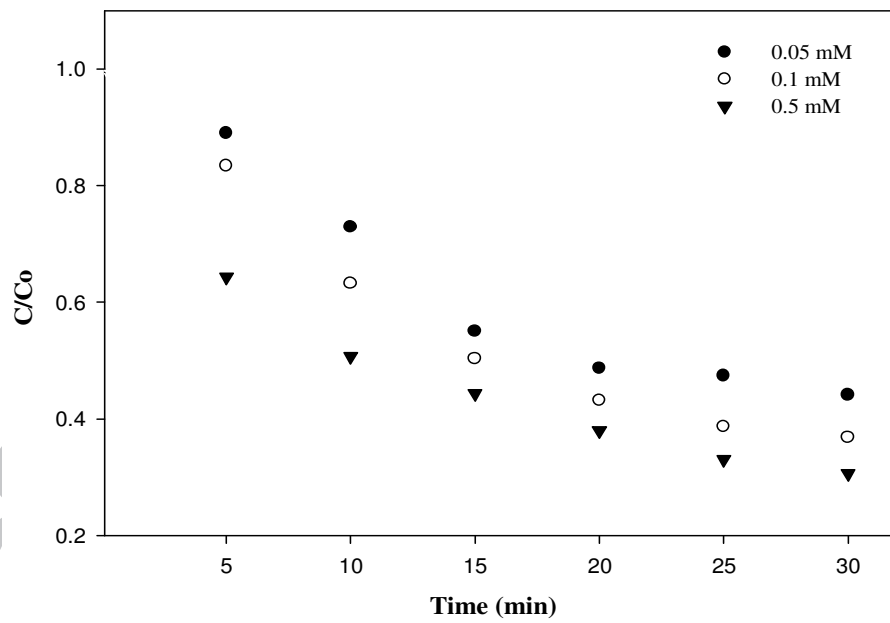


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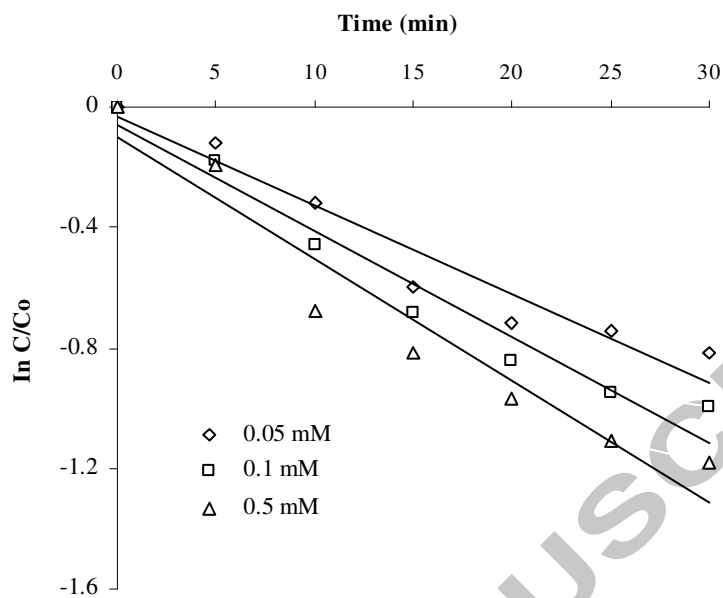


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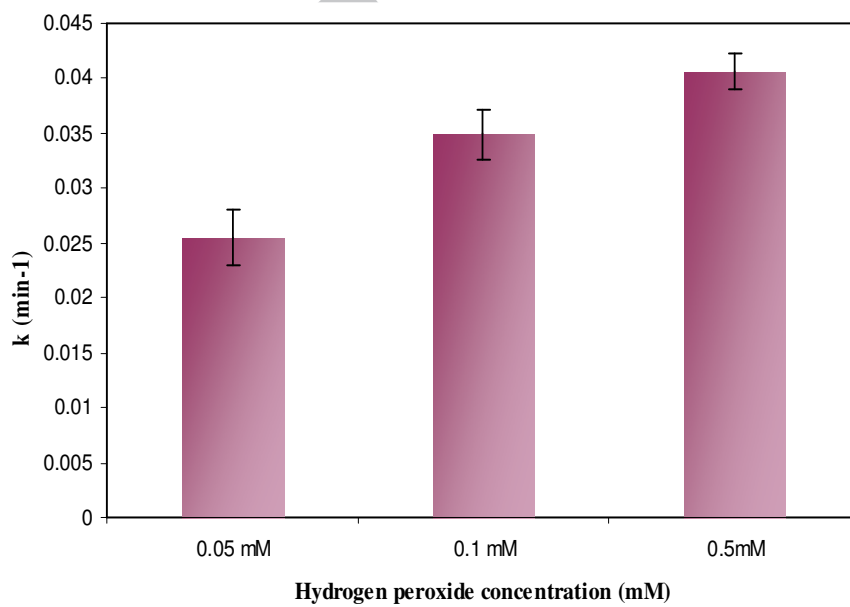


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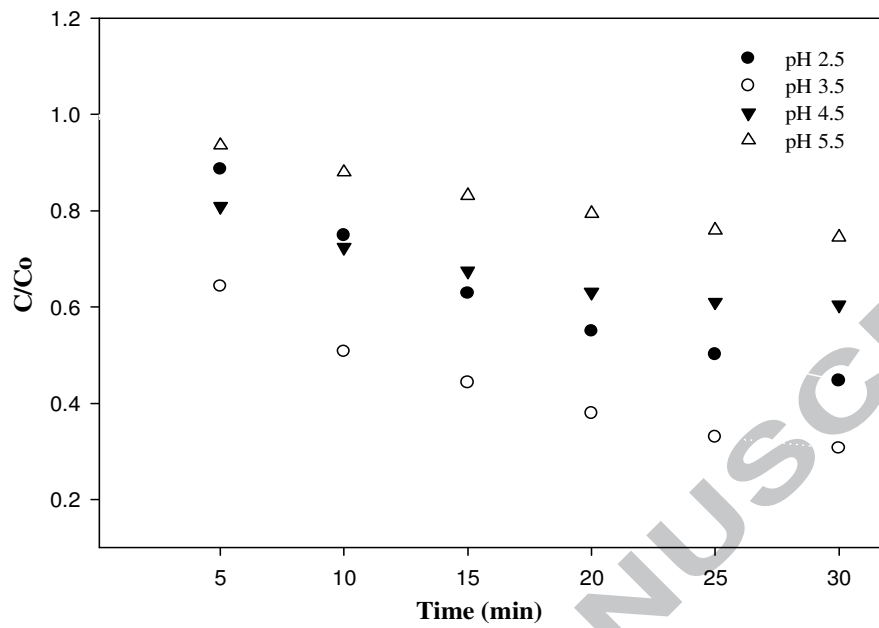


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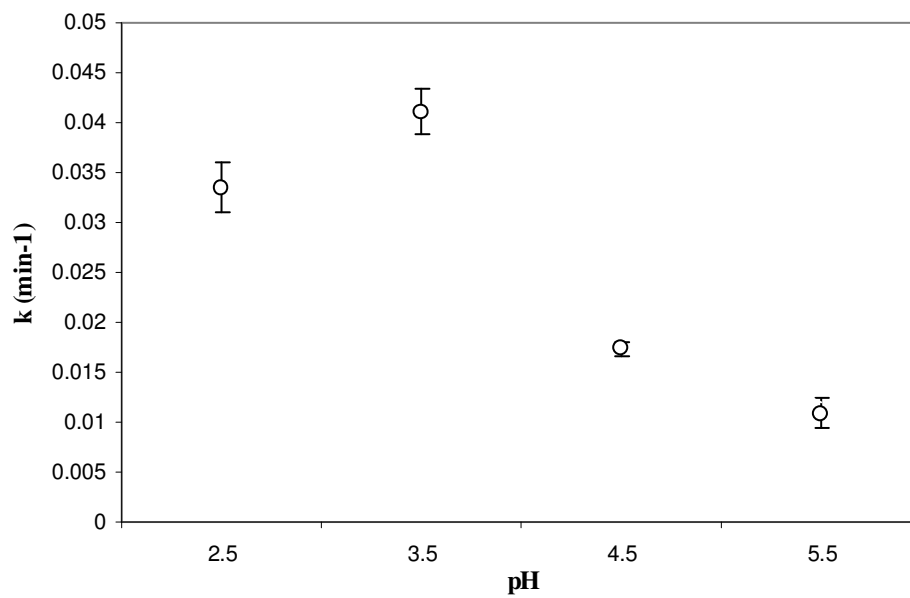


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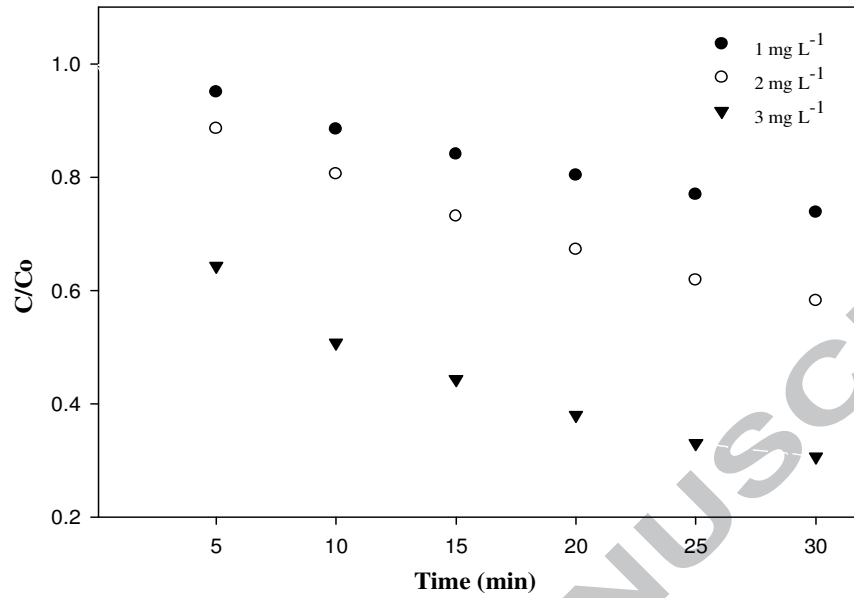


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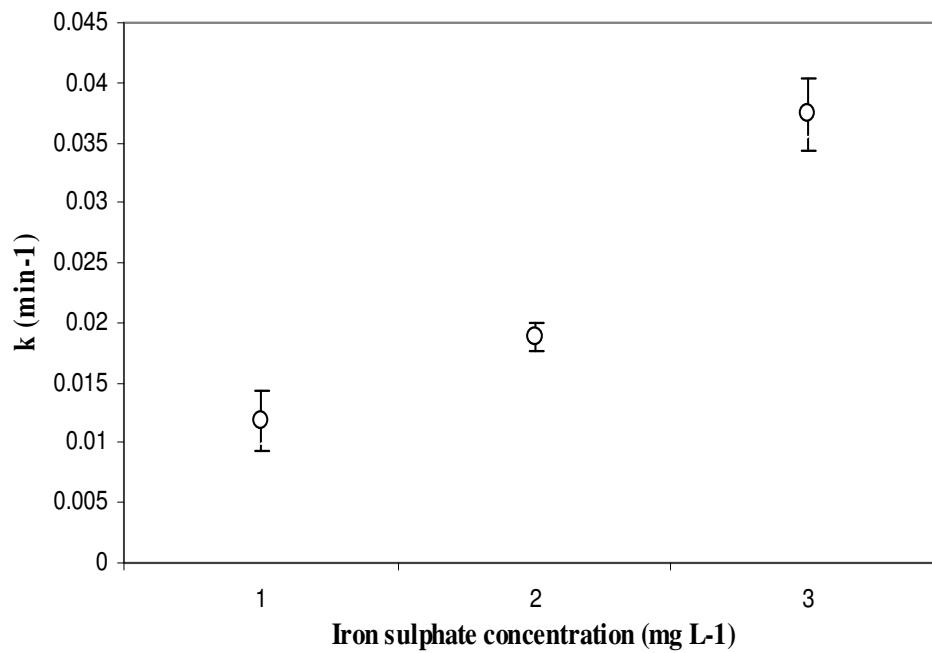


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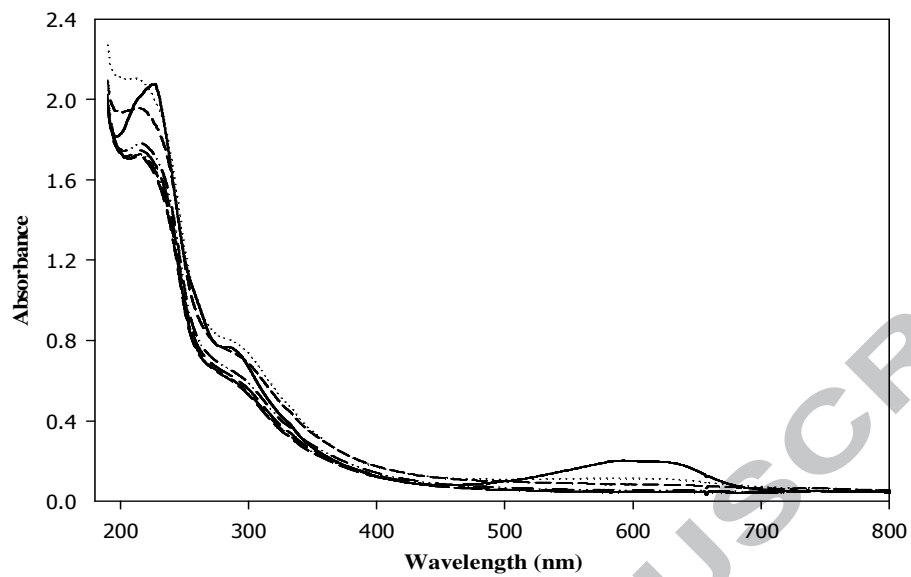


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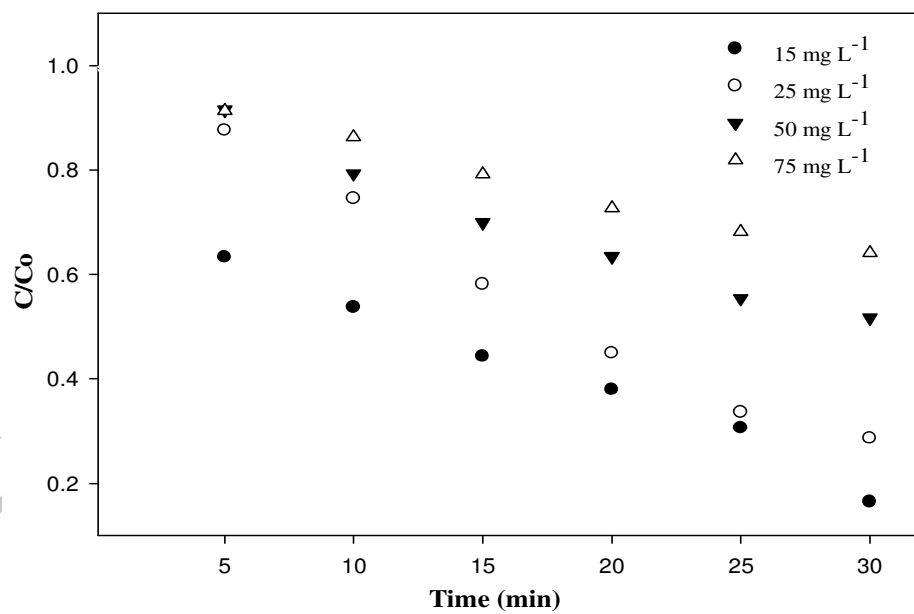


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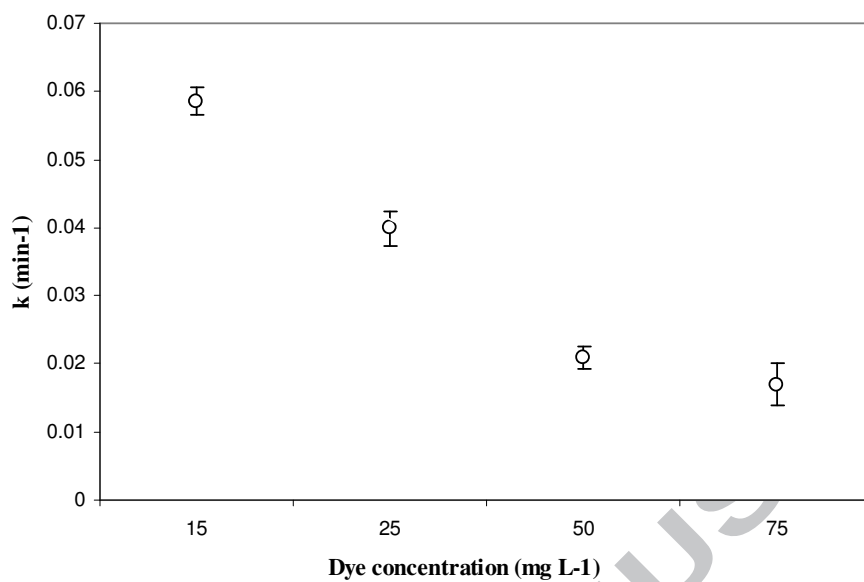


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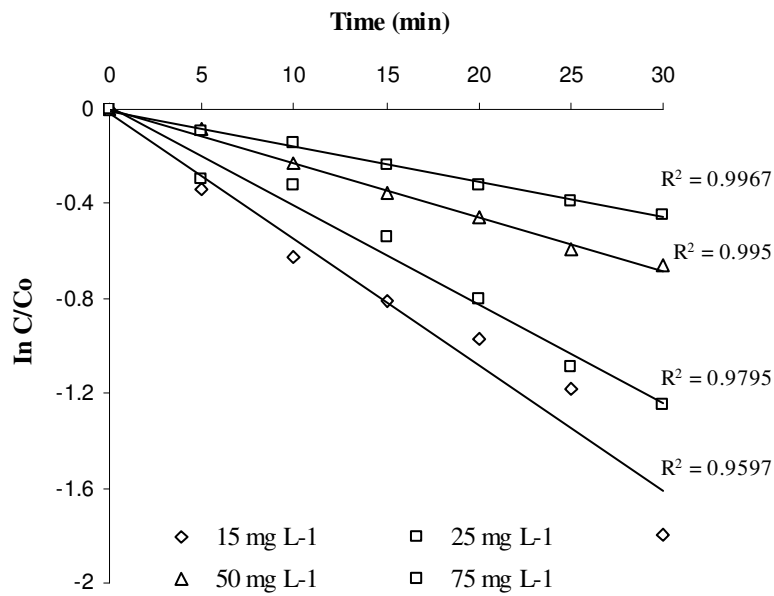


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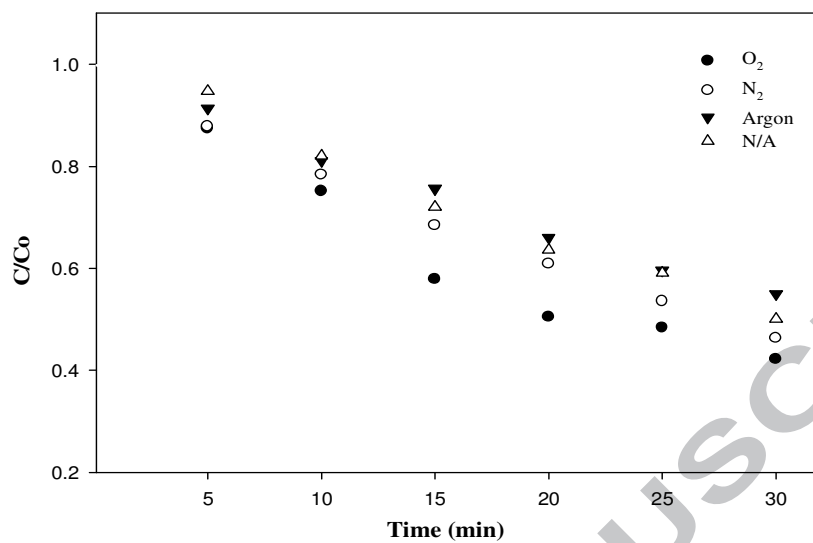


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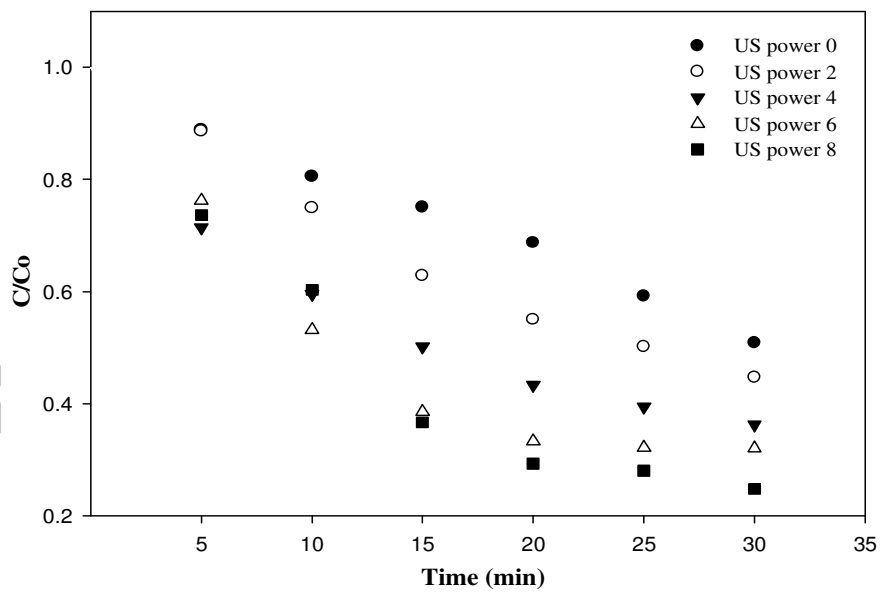


Fig. 10 (a).

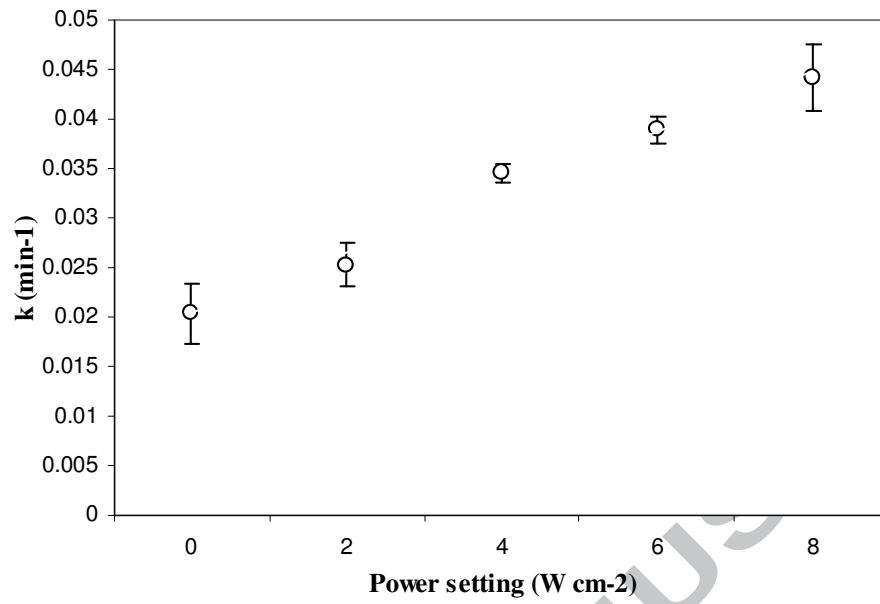


Fig. 10 (b).

Table.1: Comparison of rate constant (min^{-1}) values between US power settings (W cm^{-2}) and Fricke dosimetry

Ultrasonic power settings (W cm^{-2})	$k \text{ min}^{-1}$ (US)	$k \text{ min}^{-1}$ (US) - $k \text{ min}^{-1}$ (no US)	$k \text{ min}^{-1}$ (Fricke)
0	0.0204	--	--
2	0.0253	0.0041	0.00044
4	0.0345	0.0141	0.00105
6	0.0389	0.0185	0.0018
8	0.0442	0.0238	0.00235