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

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Abstract

The decoloration of reactive dye C.I. Reactive Blue 19 (RB 19) using combined ultrasound with the Fenton process has been investigated. The effect of varying the concentrations of hydrogen peroxide and iron sulphate, initial pH, ultrasonic power, initial dye concentration and dissolved gas on the decoloration and degradation efficiencies was measured. Calibration of the ultrasound systems was performed using calorimetric measurements and oxidative species monitoring using the Fricke dosimeter and degradations were carried out with a 20 kHz probe type transducer at 2, 4, 6, 8 W cm^{-2} of acoustic intensity at 15, 25, 50, 75 mg L^{-1} initial dye concentrations. First order rate kinetics was observed. It was found that while the degradation rate due to ultrasound alone was slow, sonication significantly accelerated the Fenton reaction. While the results were similar to those reported for other dyes, the effects occurred at lower concentrations.

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

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

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1. Introduction

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

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

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + \cdot OH \quad (1)$$

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

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

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

2. Experimental Procedure

2.1. Materials

Reactive Blue 19 (RB 19) was purchased from Sigma Aldrich (UK) and was used as received; its structure is shown in Fig. 1. $FeSO_4.7H_2O$ (analytical grade) was obtained from BDH Laboratory Supplies (England). Hydrogen peroxide (analytical grade) 35% w/v, H_2SO_4 and NaOH were obtained from Fisher Scientific (UK). All solutions were prepared with distilled water. Gases were obtained from BOC and were used without further purification.

2.2. Procedure

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

glass reactor was equipped with a water circulating jacket for maintaining reaction temperature to ± 1 °C. Sonication was performed with a Sonic processor L500-20 ultrasonic generator (20 kHz, 200W, Sonic Systems) equipped with titanium probe transducer (23820T). The tip of the horn was 1 cm in diameter and was placed 1.5 cm into the liquid layer (Fig. 2). At 5 min time intervals, samples were taken from the reactor and analyzed by UV/visible spectrophotometry (Agilent 8453) using detection wavelengths of 256 and 594 nm. Each experiment was performed in duplicate. Sonication was conducted in the presence of air with no added gas except when the effect of dissolved gas was being investigated. In these experiments, the initial solution was vigorously purged with Argon, O_2 or N_2 for 20 min prior to ultrasonic irradiation and a gas flow of *approx*. 1 ml min^{-1} was maintained throughout the experiment.

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

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

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

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

where A is the absorbance, l is the path length (cm), ε is the molar extinction coefficient (L mol^{-1} cm^{-1}) and C is the dye concentration (mol L^{-1}).

2.3. Instrumentation

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

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

2.4. Effects of acoustic intensity and sonolysis

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

Energy input, $q = mc\ dT/dt$ (4)

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

2.5. Oxidizing species determination

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

$Fe^{+2} + \cdot OH \rightarrow Fe^{+3} + OH^{-}$ (5)

The Fricke solution was prepared with 0.001 M ($FeSO_4.7H_2O$) and 0.005 M (H_2SO_4). The concentration of Fe^{+3} formed during irradiation was measured by a UV/Visible spectrophotometry at wavelength of 304 nm.

3. Results and Discussion

3.1. Decolorization of RB 19 in different systems

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

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

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

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

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

radicals [8, 9]. The decolorization rate increased as the H_2O_2 concentration increased from 0.05 mM to 0.5 mM although further increase in concentration did not lead to the further increase in decoloration. This can be explained since only a comparatively small amount of additional hydrogen peroxide decomposed to generate hydroxyl radicals and the undecomposed hydrogen peroxide may act as a scavenger for ·OH resulting in the generation of hydroperoxy radicals (Eq. 6) that are less reactive than the hydroxyl radicals. At these higher H_2O_2 concentrations, hydroxyl radicals react with the peroxide in preference to the RB19 so the degradation rate is reduced.

$$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \quad (6)$$

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

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

where k is the first order rate constant (min^{-1}) and t is reaction time in min. The relationship between hydrogen peroxide concentration and first order rate constant is shown in Fig. 4(c).

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

The pH values investigated were 2.5, 3.5, 4.5, 5.5 at a fixed $FeSO_4$ concentration of 3 mg L^{-1}, H_2O_2 concentration of 0.5 mM and ultrasonic intensity of 8 W cm^{-2}. It can be seen from Fig. 5(a) that the decoloration rate increased with decreasing pH, reaching a maximum at pH 3.5 after which the rate decreased. Zhang *et al.* [8, 13] reported that the rate of decolouration was relatively insensitive to pH below pH=6 although the reduction of chemical oxygen demand was maximized at pH=3. Similar results on other dyes have been reported [10]. The pH is an important parameter in Fenton reactions and it has often

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

$$\cdot OH + H^+ + e^- \rightarrow H_2O \quad (8)$$

Under these conditions, the rate of production of hydroxyl radicals is relatively slow since iron mainly exists as $[Fe(H_2O)_2]^{+2}$. Iron is present in solution in catalytic amounts and a further limitation on the rate of ·OH production is the slow regeneration of Fe^{+2} after reaction (1). [18].

These effects are less important as the pH rises and so the rate and extent of decolouration rises. However, above pH = 4, other effects come into play which reduce the rate [19-21]. The concentration of Fe^{+2+} in solution is reduced since Fe^{+3} species are more stable in solution. Solid oxyhydroxides such as $Fe(OH)_3$ can also precipitate. Thus, lower concentrations of ·OH are generated and decolouration is less effective. These effects combine to give an optimum value of pH = 3.5 in this work as reported previously with other dyes.

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

The effect of iron sulphate concentration on RB 19 dye decoloration was investigated with H_2O_2 concentration fixed at 0.5 mM, pH value at 3.5 and ultrasonic intensity of 8 W cm^{-2}. It was observed that the degradation of RB 19 increased with increasing Fe^{+2} concentrations in solution (Fig. 6(a)) although the decoloration rate decreased when the iron sulphate concentration was above 3 mg L^{-1}. High concentrations

of iron sulphate would produce too many ferrous ions in solution, resulting in scavenging of the ·OH radicals according to reaction (9) [9, 18] in preference to reaction with the dye.

$$Fe^{+2} + \cdot OH \rightarrow Fe^{+3} + OH^{-} \quad (9)$$

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

3.5. Decay of UV/Visible absorption spectra

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

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

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

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

3.7. The effect of dissolved gases on RB 19 decolorization

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

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

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

$$H_2O +))) \rightarrow \cdot H + \cdot OH \quad (10)$$

Under oxygen atmosphere the degradation rates were higher as compared to argon and nitrogen, since oxygen promotes the formation of ·OH radicals as in Eq. (12).

$$O_2 \rightarrow 2O \quad (11)$$

$$O + H_2O \rightarrow 2\cdot OH \quad (12)$$

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

3.8. Effect of ultrasonic powers on RB 19 decolorization

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

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

3.9. RB 19 degradation studies

Attempts to identify the intermediates/end products after the treatment of RB 19 were made using LC/MS. Samples at different time intervals were collected during the combined ultrasound and Fenton process when initial RB 19 concentration was 200 mg L^{-1}, H_2O_2 concentration was 0.5 mM, $FeSO_4$ concentration was 3 mg L^{-1}, pH was 3.5 and ultrasonic intensities of 8 W cm^{-2}. From the results of this oxidation process, it can be 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 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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415

Figure Captions

Fig. 1. Structure of RB 19 dye

Fig. 2. Experimental setup

Fig. 3. Decolorization of RB 19 by with/without H_2O_2, $FeSO_4$ by sonolysis ($C_{0=}$ 25 mg L^{-1}, H_2O_2 conc. 0.5 mM, $FeSO_4$ 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 ($C_{0=}$ 25 mg L^{-1}, $FeSO_4$ 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. ($C_{0=}$ 25 mg L^{-1}, $FeSO_4$ 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 ($C_{0=}$ 25 mg L^{-1}, $FeSO_4$ conc. 3 mg L^{-1}, H_2O_2 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 ($C_{0=}$ 25 mg L^{-1}, H_2O_2 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 ($C_{0=}$ 25 mg L^{-1}, H_2O_2 conc. 0.5 mM, $FeSO_4$ 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 (H_2O_2 conc. 0.5 mM, $FeSO_4$ conc. 3 mg L^{-1}, pH 3.5, US power = 8 W cm^{-2})

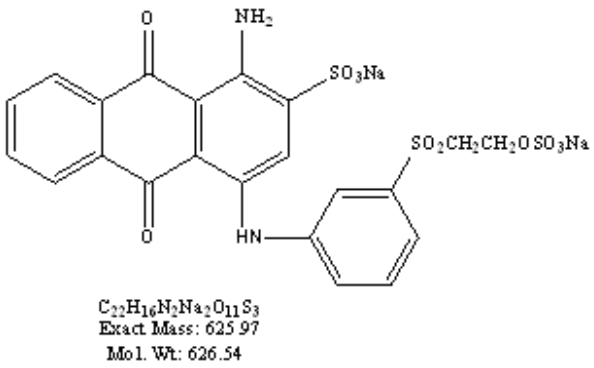
Fig. 8 (b). The effect of initial dye concentration on the rate constant

Fig. 8 (c). First order kinetic plot of RB 19 degradation by combined ultrasound and Fenton process at different dye concentrations (H_2O_2 conc. 0.5 mM, $FeSO_4$ 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}, H_2O_2 conc. 0.5 mM, $FeSO_4$ 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}, H_2O_2 conc. 0.5 mM, $FeSO_4$ conc. 3 mg L^{-1}, pH 3.5)

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



$C_{22}H_{16}N_2Na_2O_{11}S_3$
Exact Mass: 625.97
Mol. Wt: 626.54

Fig. 1.

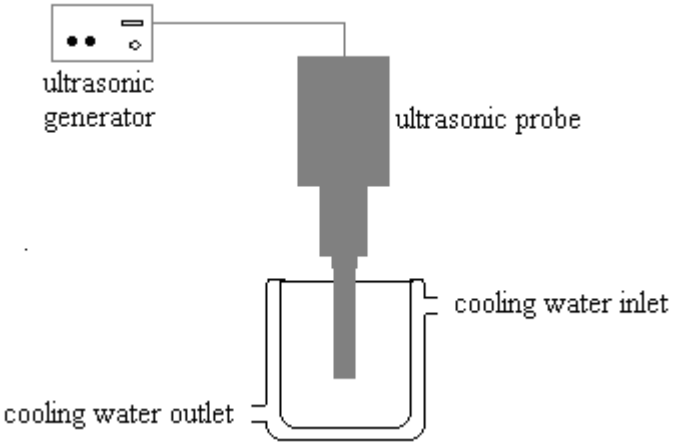


Fig. 2.

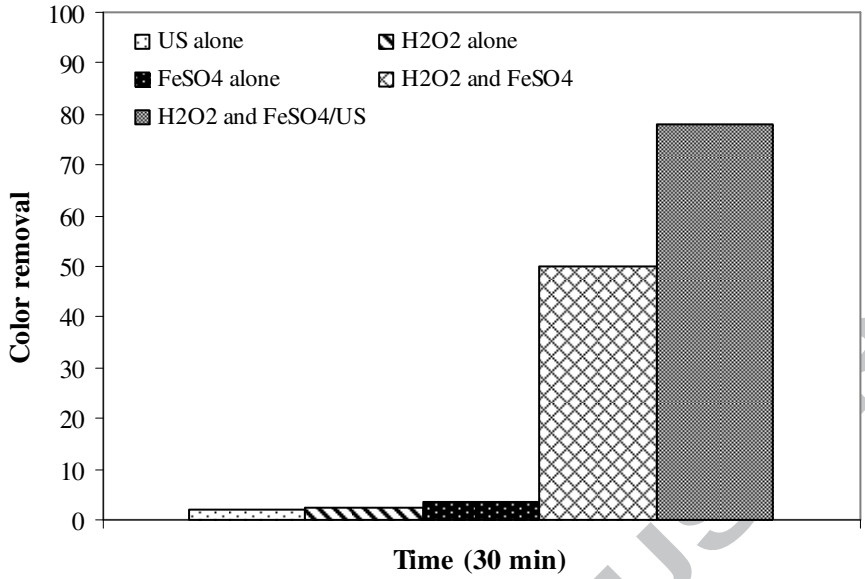


Fig. 3

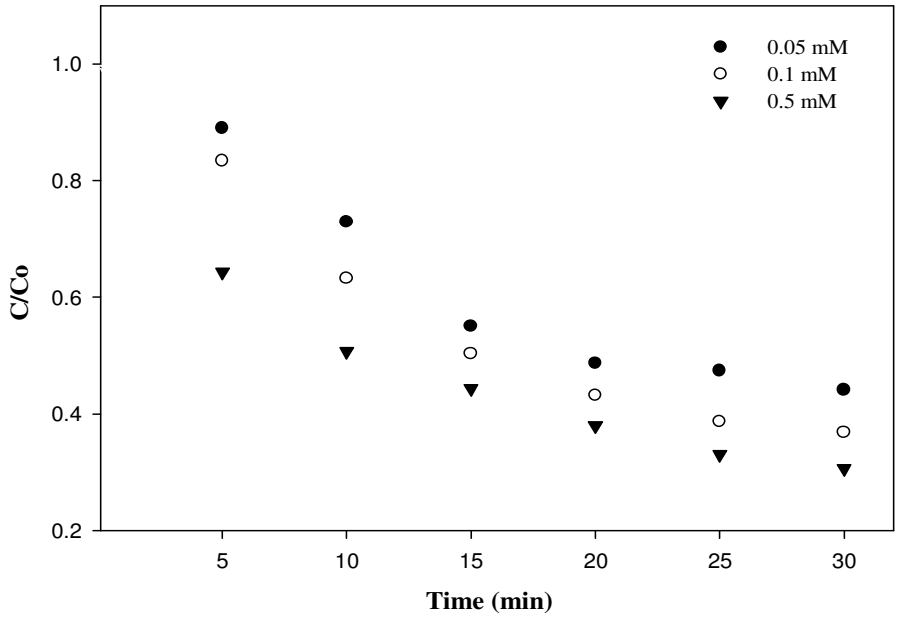


Fig. 4 (a).

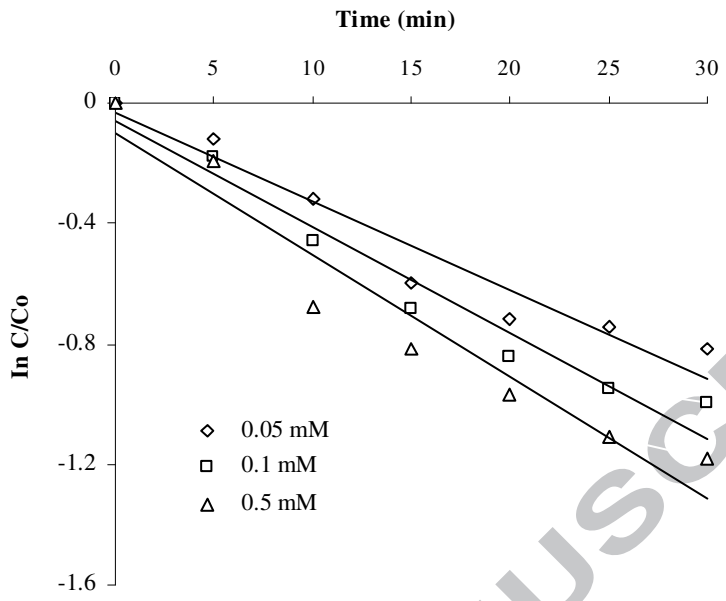


Fig. 4 (b).

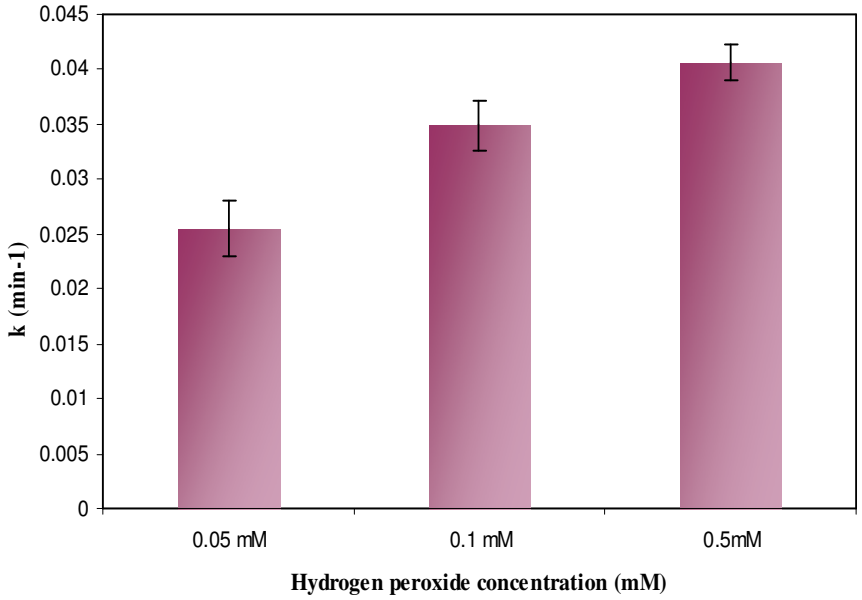


Fig. 4 (c).

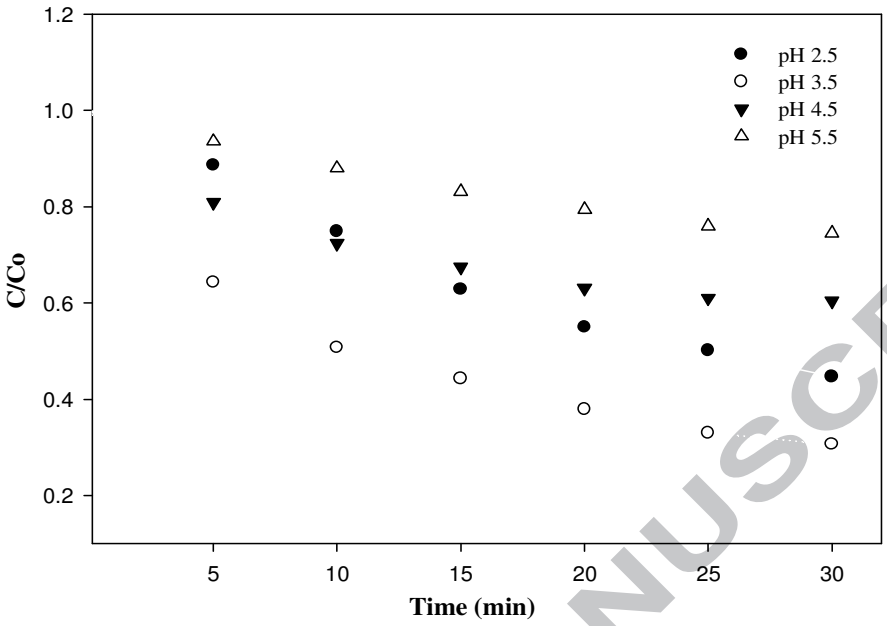


Fig. 5 (a).

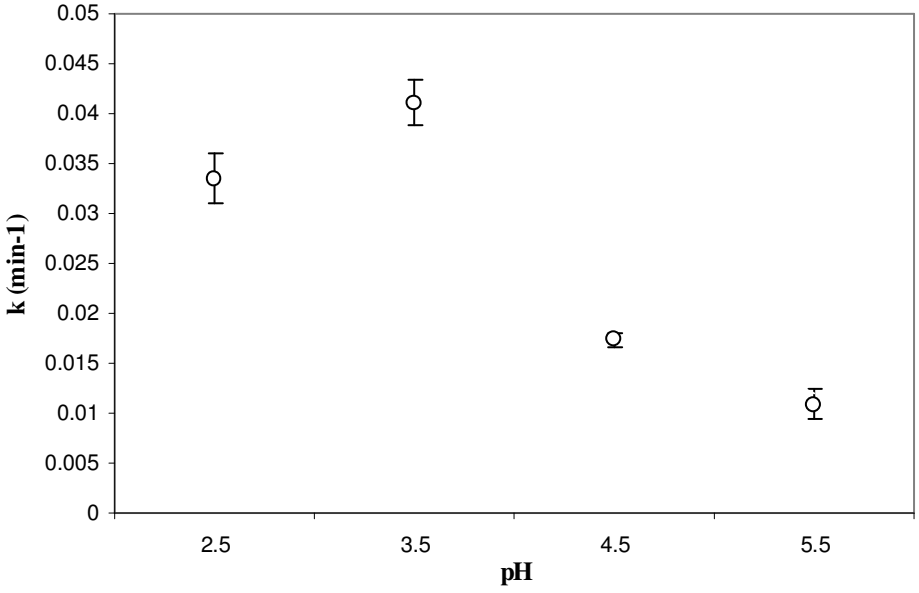
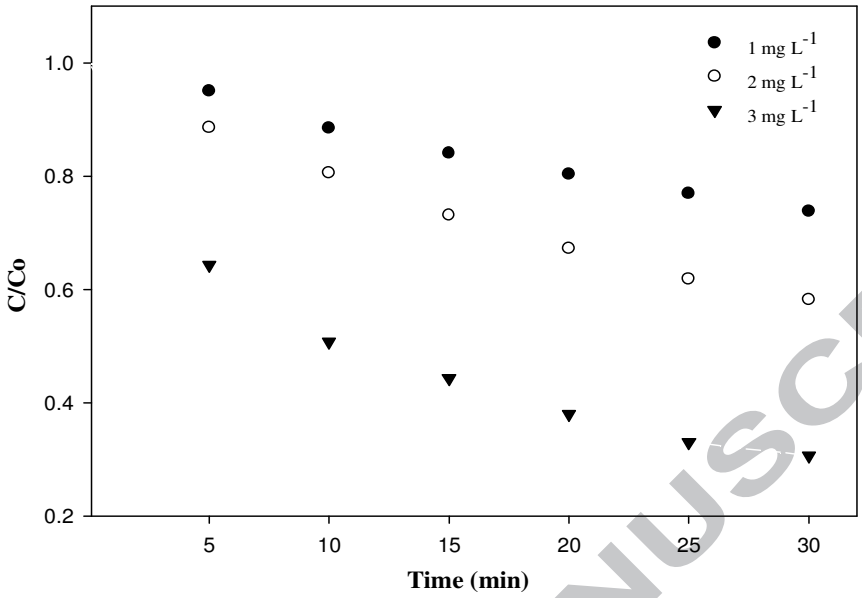


Fig. 5 (b).



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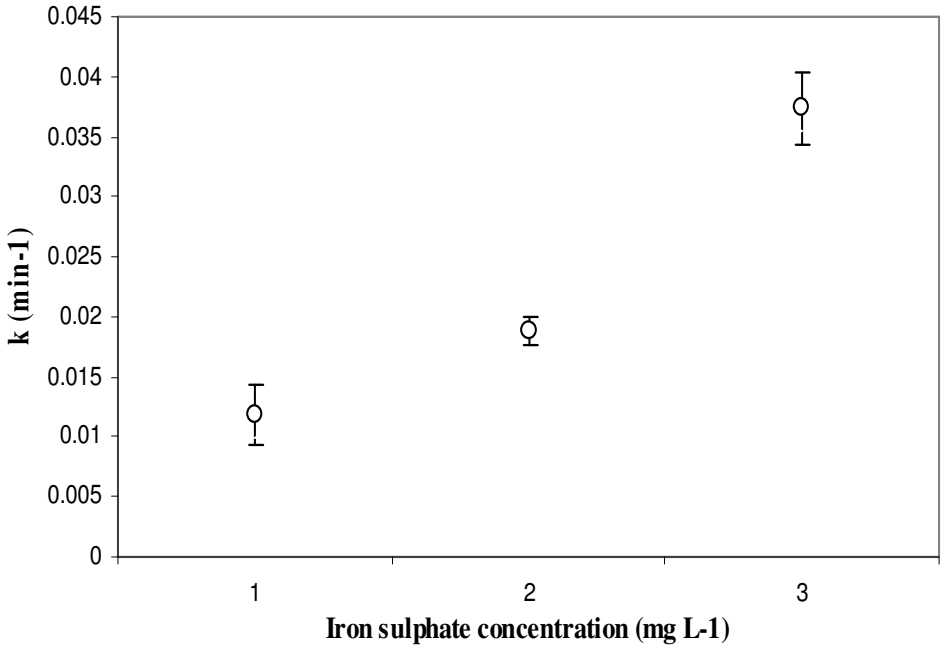

Fig. 6 (b).

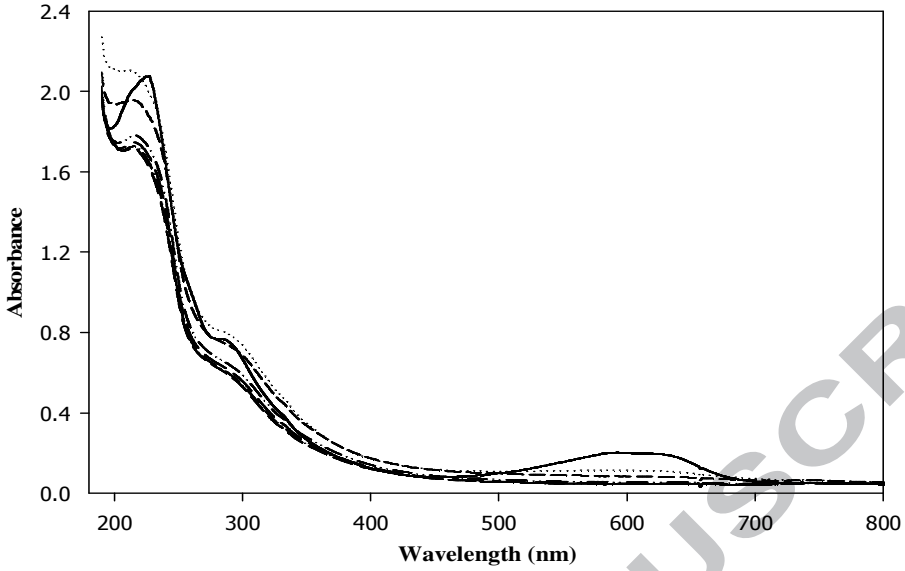

Fig. 7.

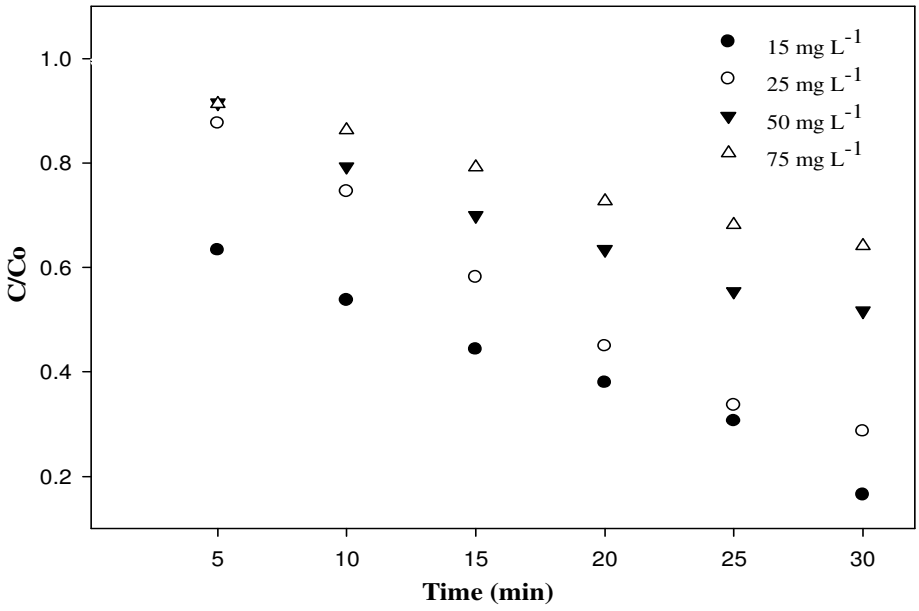

Fig. 8 (a).

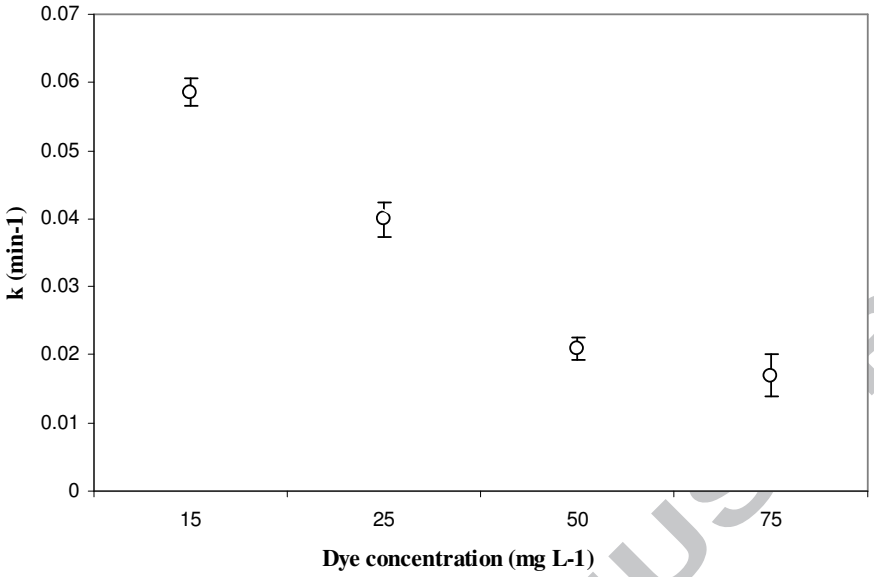

Fig. 8 (b).

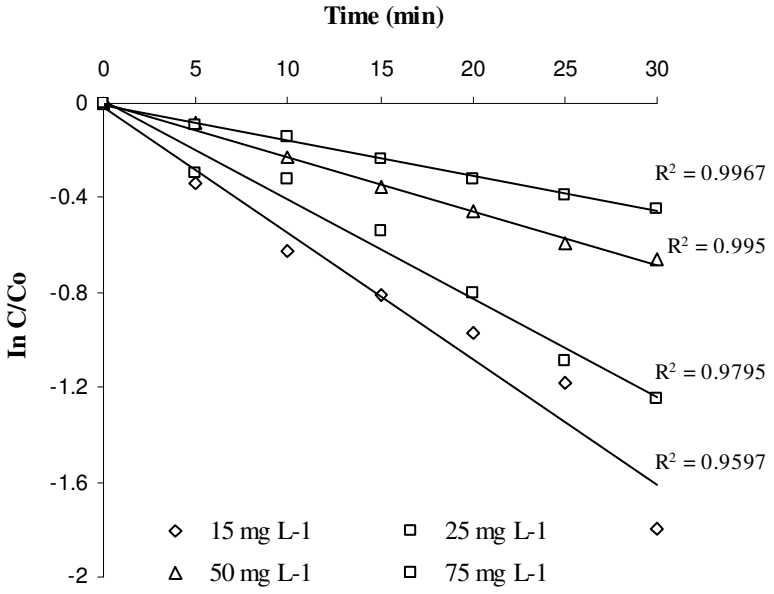

Fig. 8 (c).

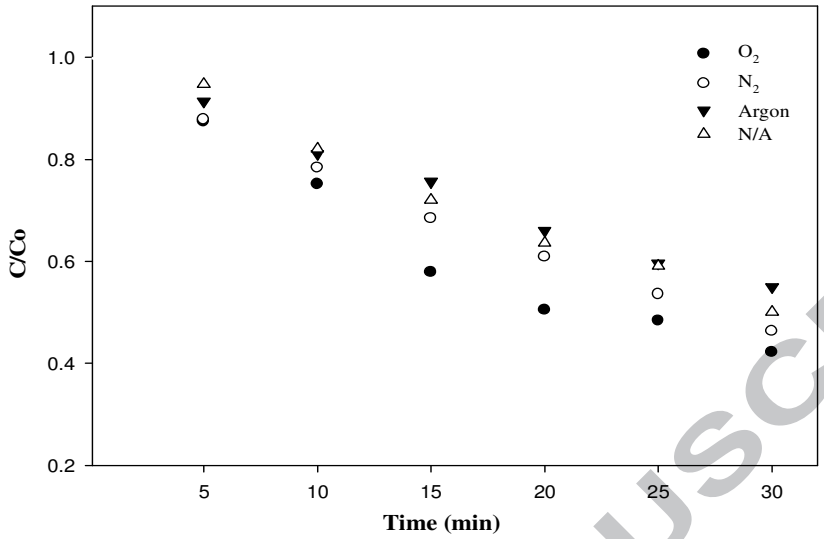

Fig. 9.

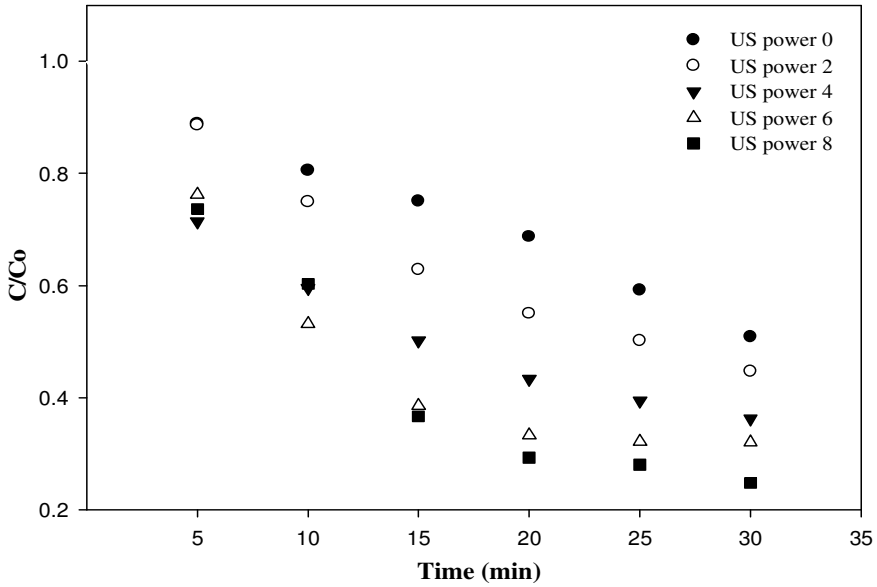

Fig. 10 (a).

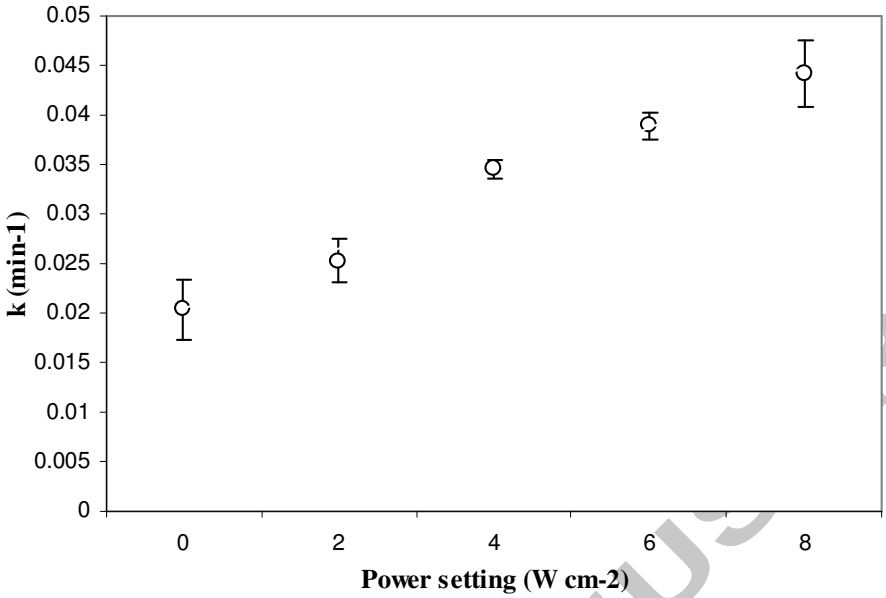

Fig. 10 (b).

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 min^{-1}(US)**	**k min^{-1} (US) - k min^{-1} (no US)**	**k 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