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## FENTON OXIDATION OF REACTIVE BLACK 5: EFFECT OF MIXING INTENSITY AND REAGENT ADDITION STRATEGY

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### ABSTRACT

This study investigates the effect of mixing intensity and reagents addition strategy on Fenton's reagent degrading a common reactive diazo type dyestuff, Reactive Black 5. Within the experimental conditions used in the study, the effect of mixing intensity on TOC removal was observed to be both significant and complex. Using factorial analysis, it was found that if the reagents are added near to each other, higher mixing intensity will enhance the effectiveness of the degradation process. However, a very high mixing level may cause reduction in performance. It was also observed that the mixing intensity effect interacts with  $\text{Fe}^{2+}$  or/and  $\text{H}_2\text{O}_2$  dosage. The benefit of increasing mixing intensity appears to be higher for lower reagents dosage. The effect of reagents addition strategy was found to be inter-dependent with mixing intensity level. It was also deduced that proper chemical addition strategy could be used to reduce the mixing intensity requirement of the process.

Keywords: Fenton's reagent, AOPs, reactive dye, mixing intensity, reagent addition strategy

### INTRODUCTION

The last two decades of the twentieth century saw fast evolution of research devoted to the application of a new breed of chemical treatment, known as advanced oxidation processes (AOPs). Although making use of different reacting systems, the processes are all characterised by the same chemical feature, i.e. production and application of hydroxyl radicals ( $\text{HO}^\bullet$ ), an extraordinarily reactive species, as the oxidising agent. Hydroxyl radicals have an oxidation potential much higher than its nearest competitor, ozone, and is also characterised by unselective attack on pollutants with typical rate constants in the order of  $10^6$  to  $10^9 \text{ M}^{-1}\text{s}^{-1}$  [1]. These provide useful attributes for an oxidant used particularly in removing refractory and toxic organics such as those found in many industrial wastewaters [2].

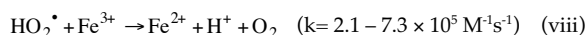
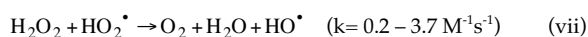
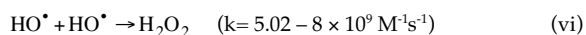
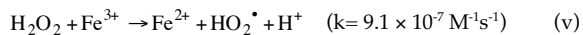
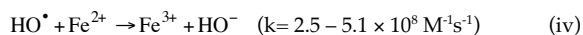
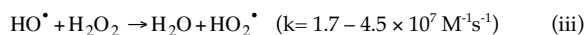
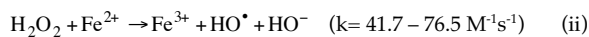
Fenton's reagent (FR), a combination of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ion is one of the most widespread AOPs available today. First discovered in 1894 by Fenton, two forms of mechanism have

been postulated by researchers with respect to the FR oxidation reactions. The study of Bray and Gorin in 1932 [3] suggested the formation of the ferryl ion ( $\text{FeO}^{2+}$ ),



while the involvement of  $\text{HO}^\bullet$  was suggested by Haber and Weiss [4] two years later (Equation (ii)).

Although direct experimental evidence for the formation of  $\text{FeO}^{2+}$  has not been obtained, the Bray-Gorin idea has been supported by many investigators who used it to account for the mechanism of the activity of the Fenton [3]. The Haber-Weiss pathway on the other hand, is more favoured by researchers as the formation and involvement of  $\text{HO}^\bullet$  has been well established through experimental observations. Therefore, with respect to the radical-chain mechanism, the following set of consecutive reactions has been widely accepted in the literature.



Numerous studies on the applications of FR with various pollutants and wastewater have been reported [5, 6, 7]. It has been well established that the process is affected by many factors that include pH, reagent dosage, type of Fe used, temperature, nature of the pollutant, and presence of oxygen and light (ultraviolet and visible).

In addition, there are several other factors that are potentially important in a design and operation of the full-scale unit. Studies on these factors, which include mixing intensity and reagents addition strategy, seem to be still lacking in the literature. Proper fluid mixing is an important factor that needs to be considered particularly for fast reactions such as those existing in FR system [8]. The benefit of fast reactions may not be acquired if the rate of mixing is lower than the rate of reaction, while over-mixing may be costly. With a complex system like FR, inadequate mixing along with inappropriate reagents addition strategy may cause improper distribution of the reagents and results in running the system away from its best reacting condition. As  $\text{HO}^\bullet$  scavenging can possibly take place in the presence of excessive reagents dosage, such conditions may also cause wastage of reagents which add cost to the process. Furthermore, it should also be noted that although the effect may seem insignificant in a small-scale laboratory study, they may have considerable impact in a bigger reactor.

Therefore, it is of interest to investigate the importance of the two factors and this paper presents the results of the study. A reactive dye, Reactive Black 5 (RB5), one of the most important reactive dyestuffs in term of quantity applied in Europe [9] was used in the study as a model pollutant with FR as the oxidant.

## MATERIALS AND METHODS

### Materials and Analysis

The chemicals used were of analytical grade and were supplied by BDH or Aldrich and used as received. Solutions were prepared using deionised water generated by Elsgat Spectrum deioniser. Dye and  $\text{Fe}^{2+}$  solutions were freshly

prepared prior to use while  $\text{H}_2\text{O}_2$  solution was used without any dilution. A stock solution of enzyme catalase for  $\text{H}_2\text{O}_2$  destruction was prepared and stored at below  $4^\circ\text{C}$ . The performance of the FR oxidation was characterised based on two parameters, namely colour and total organic carbon (TOC). Colour was analysed based on absorbance at wavelength 597 nm (as provided by manufacturer) using Perkin Elmer (Lamda 10) UV/Vis spectrophotometer. Total organic carbon was analysed using Shimadzu TOC-V CSH analyser. For selected runs, samples were analysed for  $\text{H}_2\text{O}_2$  residual concentration using Titanium Sulphate Spectrophotometric Method [10].

### Experimental Procedure

The experimental work was divided into three parts, namely mixing time study, mixing intensity effect study, and reagents addition strategy study.

#### Mixing time study

Mixing time is defined as the time required for a solution to achieve a defined degree of homogeneity when external material is added into the solution [11]. The mixing time study was preliminary work conducted to determine the effect of mixing intensity on mixing time in the vessel to be used in the subsequent studies. This calibrated the mixing behaviour of the vessel to allow the effect of mixing intensity on FR process to be established. Mixing time was determined using an inert tracer and probe method by means of conductivity measurement [11, 12]. A glass vessel, equipped with four symmetrically placed baffles was used and filled with 3 l of deionised water (Figure 1). The water was mixed using a Rushton turbine impeller with an adjustable speed drive. The conductivity of the solution was measured continuously using an Accumet Model 50 conductivity meter and the data were recorded using an on-line data logging system via RS232 port and WinWedge<sup>®</sup>32 software. A small volume of tracer, NaCl was then injected at the surface of the water and the conductivity of the solution was monitored until it reached a stable value. The time taken for the conductivity to reach permanently between 95% and 105% of the stable value (from the time the tracer was injected into the solution) was determined and noted as  $t_{95}$  (the 95% mixing time). Mixing times were determined at three mixing intensity levels, i.e. 70, 275 and 460 rpm which were verified using Lutron DT-2236 digital tachometer. For each intensity level, the mixing time was determined at eight different points (i.e. four points at the top and bottom of vessel) with eight repetitions at each point.

#### Mixing Intensity Effect Study

The experimental work of this study was statistically designed using Central Composite Rotatable Design (CCRD) with the aid of MINITAB<sup>™</sup> (Ver. 13.32) statistical software. The experiments were divided into a  $2^3$  Hadamard matrix

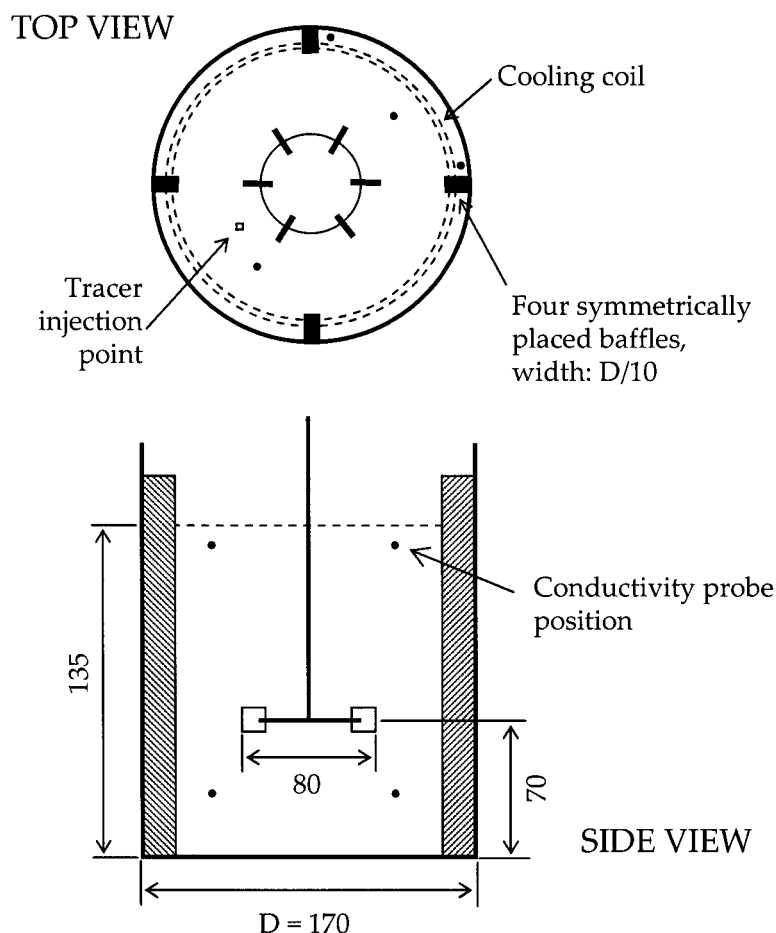


Figure 1. Schematic diagram of the vessel used in the study (units in mm).

factorial runs, star point runs and centre point runs. The effect and synergistic effect of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  and mixing intensity were determined based on Hadamard matrix runs, while the non-linear response behaviour was analysed using star point and centre point runs. The centre point run was also repeated six times in order to allow better estimate of the experimental error. As shown in Table 1, a set of 20 (randomised) experimental runs was carried out at different  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  initial concentrations and impeller speed with initial dye concentration of  $200 \text{ mg l}^{-1}$ . The  $\text{H}_2\text{O}_2$  initial concentration ranged from  $101 \text{ mg l}^{-1}$  to  $341 \text{ mg l}^{-1}$  while  $\text{Fe}^{2+}$  ranged from  $6.7 \text{ mg l}^{-1}$  to about  $166 \text{ mg l}^{-1}$ . Mixing intensity was varied from 70 rpm to about 560 rpm.

The experiments were conducted batch-wise using the 3-l glass vessel as described earlier. The impeller speed was set at the desired value and verified using the tachometer. The temperature of the dye solution was raised and maintained at  $25.0 \pm 1^\circ\text{C}$  throughout the experiment via a PTFE coil cooling/heating system. The initial pH of the solution was carefully adjusted to 3.0 using (1 : 1 = concentrated acid : water)  $\text{H}_2\text{SO}_4$ . A sample representing initial dye concentration (at  $t = 0$  minute) was drawn prior to

the addition of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . The experimental run started with a one-step, rapid addition (less than 3 secs) of the appropriate amount of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  solutions into the vessel. The reagents were injected at two points close to each other to simulate the typical situation in actual treatment plant. Samples were then drawn from the vessel at certain intervals up to 60 minutes. Each sample was immediately mixed with catalase solution to destroy the residual  $\text{H}_2\text{O}_2$  and analysed for colour and TOC.

#### Reagents Addition Strategy Study

Seven reagents addition strategy were tested at two different mixing intensities, i.e. 70 and 315 rpm (Table 2). The experimental runs were designed to analyse the effect of spatial reagent addition strategy (ME301 and ME302) and step addition or intermittent reagent addition strategy on FR performance. The detail of the experimental runs is as described in the previous section. The initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  were fixed at  $221 \text{ mg l}^{-1}$  and  $86.6 \text{ mg l}^{-1}$  respectively with initial dye concentration of about  $795 \text{ mg l}^{-1}$ .

Table 1. Experimental design to study the effect and synergistic effect of mixing intensity, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> initial concentration.

Run No.	Run Order	Run			% Removal	
		Fe <sup>2+</sup> , mg l <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> , mg l <sup>-1</sup>	RPM	TOC <sub>1 min</sub>	TOC <sub>60 min</sub>
ME101	18	39.1 (-1)	149.6 (-1)	169 (-1)	19.0	44.6
ME102	1	134.0 (+1)	149.6 (-1)	169 (-1)	38.4	50.0
ME103	17	39.1 (-1)	292.4 (+1)	169 (-1)	31.2	54.3
ME104	2	134.0 (+1)	292.4 (+1)	169 (-1)	38.7	49.7
ME105	13	39.1 (-1)	149.6 (-1)	461 (+1)	38.9	61.7
ME106	11	134.0 (+1)	149.6 (-1)	461 (+1)	39.7	58.3
ME107	9	39.1 (-1)	292.4 (+1)	461 (+1)	35.1	56.9
ME108	6	134.0 (+1)	292.4 (+1)	461 (+1)	46.6	57.3
ME109	10	6.7 (-1.68)	221.0 (0)	315 (0)	29.7	48.8
ME110	16	166.3 (+1.68)	221.0 (0)	315 (0)	44.5	64.5
ME111	20	86.6 (0)	101.0 (-1.68)	315 (0)	31.4	45.7
ME112	5	86.6 (0)	341.0 (+1.68)	315 (0)	43.2	63.2
ME113	19	86.6 (0)	221.0 (0)	70 (-1.68)	31.4	52.2
ME114	12	86.6 (0)	221.0 (0)	561 (+1.68)	37.1	51.6
ME115	8	86.6 (0)	221.0 (0)	315 (0)	44.9	62.8
ME116	7	86.6 (0)	221.0 (0)	315 (0)	42.6	62.9
ME117	3	86.6 (0)	221.0 (0)	315 (0)	45.5	65.5
ME118	4	86.6 (0)	221.0 (0)	315 (0)	44.0	64.1
ME119	15	86.6 (0)	221.0 (0)	315 (0)	48.4	67.4
ME120	14	86.6 (0)	221.0 (0)	315 (0)	44.0	64.6

( ) Coded value as assigned by central composite rotation design

Table 2 Lists of method used in reagents addition strategy study.

Run No.	Method
ME301	Simultaneous reagents addition at two close points
ME302	Simultaneous reagents addition at two distant points
ME303	Pre-dissolved H <sub>2</sub> O <sub>2</sub> followed by one-time Fe <sup>2+</sup> addition
ME304	Pre-dissolved Fe <sup>2+</sup> followed by one-time H <sub>2</sub> O <sub>2</sub> addition
ME305	Pre-dissolved H <sub>2</sub> O <sub>2</sub> followed by step addition of Fe <sup>2+</sup>
ME306	Pre-dissolved Fe <sup>2+</sup> followed by step addition of H <sub>2</sub> O <sub>2</sub>
ME307	Step addition of Fe <sup>2+</sup> and H <sub>2</sub> O <sub>2</sub> at two distant points

## RESULTS AND DISCUSSION

### Mixing Time Study

The results were analysed statistically using Analysis of Variance (ANOVA) to determine the significance of mixing intensity effect on mixing time. On average, increasing mixing intensity from 70 rpm to 460 rpm reduces mixing time from 8.3 secs to 4.4 secs for the top sampling points. For the bottom ones, the increase reduces the mixing time from 12.0 secs to 4.5 secs. An ANOVA table for top and bottom sampling points is shown in Table 3. At 0.05 level of significance, it can be deduced that mixing intensity has significant effect on mixing time as the F values (178.425 and 387.716 for top and bottom sampling points, respectively) are much higher than the F critical value (3.105). Based on this

analysis, it can be inferred that mixing intensity has a significant effect on the mixing behaviour of the reaction vessel. Furthermore, although the differences of mixing time seem to be small, the magnitude may be considered significant considering the reaction rate of HO<sup>•</sup> is very close to diffusion-controlled and the HO<sup>•</sup>-forming reactions are also fast. This in term suggests that the 3-l vessel can be used to deliver different mixing conditions to the vessel contents, and is thus suitable to investigate the effect of mixing intensity.

### Mixing Intensity Effect Study

A typical profile of colour and TOC removal is shown in Figure 2. As expected, removal of colour is much faster than TOC. Almost 100% of colour removal was achieved in

Table 3 ANOVA table for mixing time study.

Source of Variance	SS	df	MS	F	P-value	F-crit
<i>Top Sampling Point</i>						
Sample (rpm)	248.521	2	124.260	174.425	5.75E-31	3.105
Columns (position)	13.375	3	4.458	6.402	0.000586	2.713
Interaction	13.563	6	2.260	3.246	0.006432	2.209
Within	58.5	84	0.696			
Total	333.958	95				
<i>Bottom Sampling Point</i>						
Sample (rpm)	1020.063	2	510.031	387.716	3.83E-43	3.105
Columns (position)	79.25	3	26.417	20.081	6.65E-10	2.713
Interaction	92.188	6	15.365	11.680	1.78E-09	2.209
Within	110.5	84	1.315			
Total	1302	95				

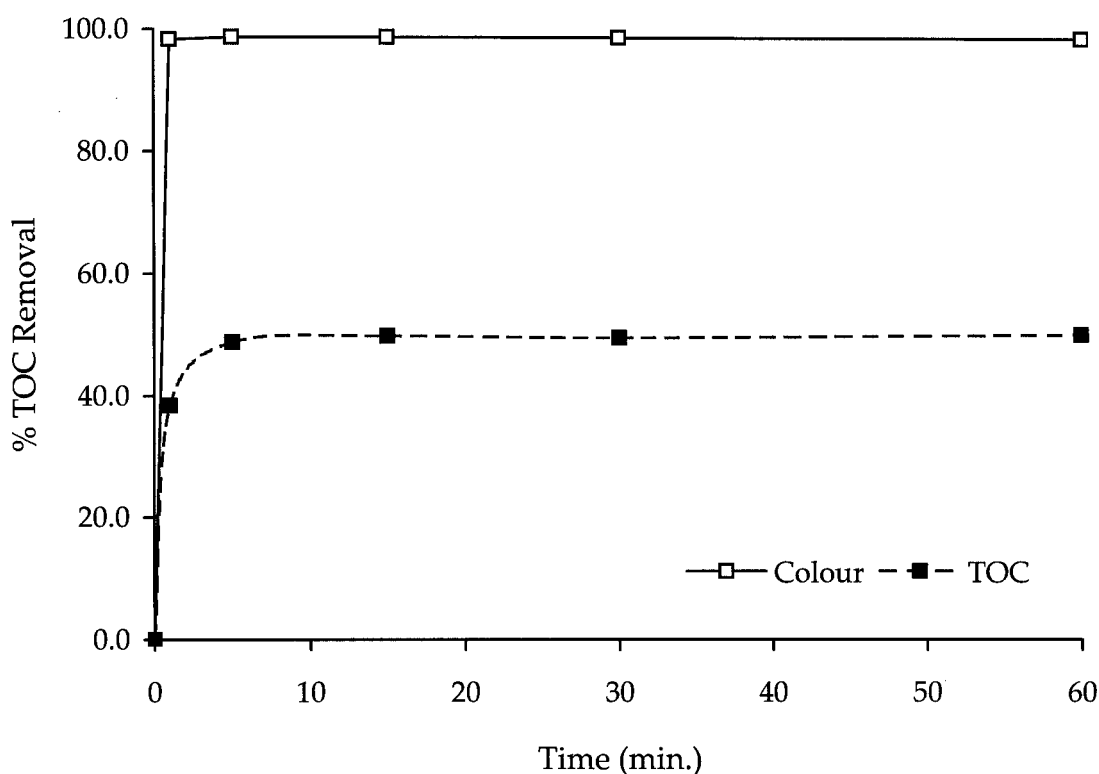


Figure 2. A typical profile of colour and TOC removal. Experimental condition: pH = 3.0; T = 25°C; RB5 = 200 mg l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 149.6 mg l<sup>-1</sup>; Fe<sup>2+</sup> = 133.9 mg l<sup>-1</sup>.

all runs after the first minute of reaction as compared to TOC removal of 44% to 67% (after 60 minutes). A significant portion of the removal took place in the first few minutes apparently due to the role of Fenton oxidation. As illustrated in Figure 3, the peak at  $\lambda = 597$  nm (which represents the dye chromophore) disappears almost completely after the first

minute. The smaller peak (at  $\lambda = 314$  nm), whilst reduced substantially during the first 15 minutes, shows persistence even up to 60 minutes. This could result from insufficient radicals being available in the last 45 minutes and also possibly due to the resistance of the compounds (which absorb at this lower spectrum range) to radical attack. Since

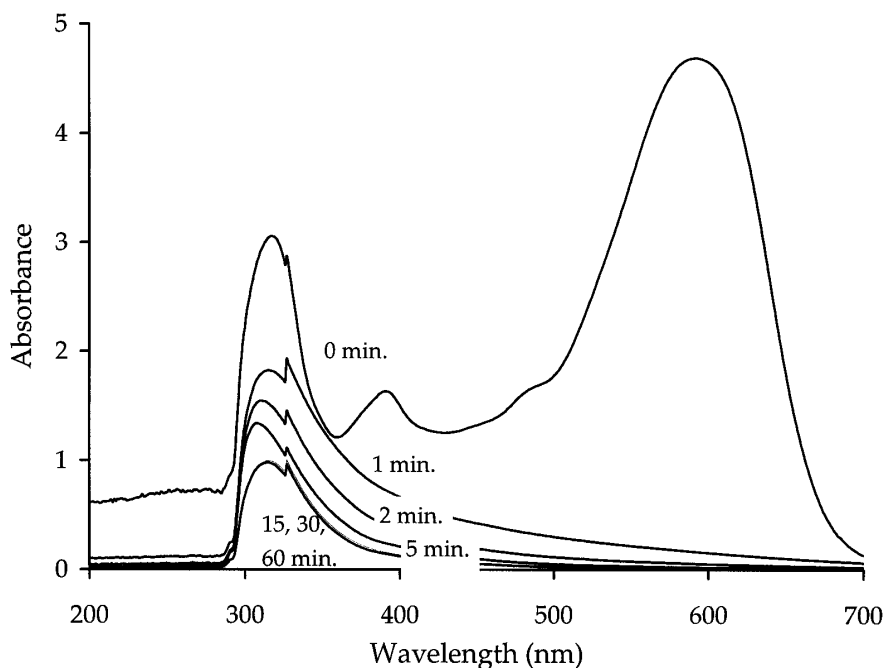


Figure 3. A typical absorption spectrum of RB5 at different Fenton oxidation reaction time. Experimental condition: pH = 3.0; T = 25°C; RB5 = 200 mg l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 149.6 mg l<sup>-1</sup>; Fe<sup>2+</sup> = 133.9 mg l<sup>-1</sup>.

colour was almost completely removed in all runs, the effect of mixing intensity on colour removal could not be observed. It seems that the RB5 (at 200 mg l<sup>-1</sup>) can easily be decolourised at the H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> dosage range used in this study. Therefore, the analysis of mixing intensity effect in the subsequent discussion will be based on TOC removal as given in Table 1. Based on the centre point runs, the results of TOC removal were reproducible within less than 10% experimental error.

A factorial analysis was carried on the Hadamard matrix and centre point runs based on TOC removal at reaction time of 1 and 60 minutes to elucidate the short and

long term effect of the factors being considered. A summary of the *p*-value (at 0.1 level of significance) of the main effects and their interactions at 1 and 60 minutes for the factorial analysis is given in Table 4. With respect to the experimental conditions used in the study, the *p*-value indicates that all factors, i.e. RPM, Fe<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub> (according to descending order) have significant effect on TOC removal in the FR process in the first minute of the reaction. The two-way interaction between Fe<sup>2+</sup> initial concentration and mixing intensity (Fe<sup>2+</sup>×RPM) and the three-way interaction (Fe<sup>2+</sup>×H<sub>2</sub>O<sub>2</sub>×RPM) are also significant. However, after 60 minutes of reaction, only mixing intensity effect (RPM)

Table 4 ANOVA for TOC removal at reaction times of 1 and 60 minutes.

Effect	t = 1 min		t = 60 min	
	P-Value	Significance <sup>a</sup>	P-Value	Significance <sup>a</sup>
<i>Main</i>				
Fe <sup>2+</sup>	0.001	yes	0.672	no
H <sub>2</sub> O <sub>2</sub>	0.038	yes	0.496	no
RPM	0.002	yes	0.001	yes
<i>Two-way interaction</i>				
Fe <sup>2+</sup> ×H <sub>2</sub> O <sub>2</sub>	0.838	no	0.262	no
Fe <sup>2+</sup> ×RPM	0.048	yes	0.473	no
H <sub>2</sub> O <sub>2</sub> ×RPM	0.153	no	0.027	yes
<i>Three-way interaction</i>				
Fe <sup>2+</sup> ×H <sub>2</sub> O <sub>2</sub> ×RPM	0.010	yes	0.037	yes

<sup>a</sup>significant at α = 0.1

remains significant in addition to the two-way interaction of  $\text{H}_2\text{O}_2 \times \text{RPM}$  and the three-way interaction. The Pareto chart and main effect plot generated by MINITAB™ given in

Figure 4 illustrate the degree of significance and effect graphically. As can be seen in the main effect plot, mixing intensity has much greater positive effect on TOC removal

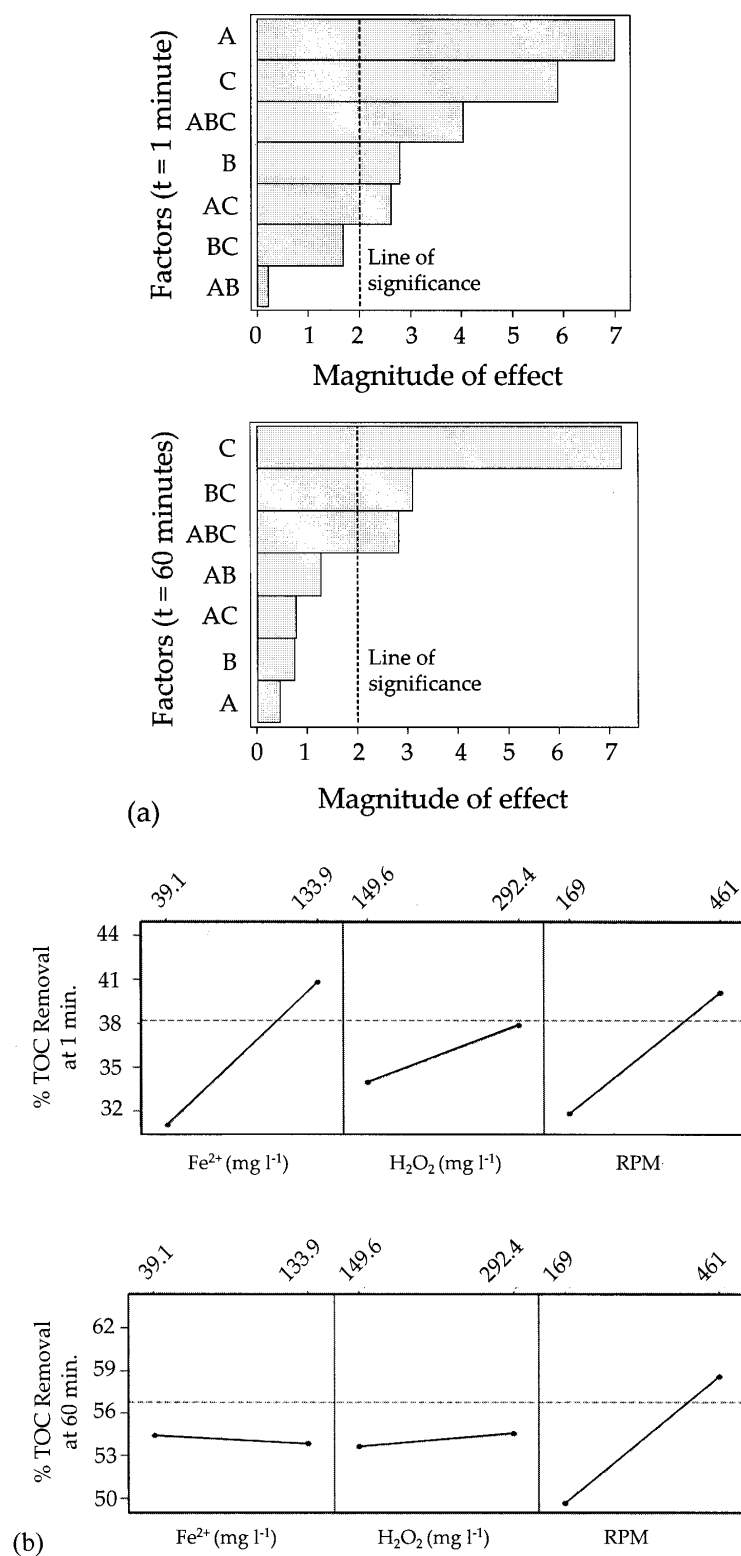


Figure 4. (a) Pareto chart and (b) main effect plot (based on data means) for TOC removal at 1 and 60 minutes ( $\alpha = 0.1$ ; A:  $\text{Fe}^{2+}$ ; B:  $\text{H}_2\text{O}_2$ ; C: RPM).



than the reagent's initial concentration.

The importance of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  dosages on FR process, which is very much related to the concentration of  $\text{HO}^\bullet$  generated, has been well documented in the literature [5, 6, 13, 14]. It has generally been observed that the efficiency of the process increases with the increase of reagent dosage. However, as the dosage goes beyond a certain limit, the reagents start to inhibit the reaction due to scavenging activity of the  $\text{HO}^\bullet$ , producing less reactive species (Equations (iii), (iv) and (vi)) giving marginal benefit to the process. It can also be deduced from the analysis that the benefit of increasing the reagents dosage can be short-term as also observed by Perez *et al.* [15]. As the reactions progress, the reagents dosage, particularly  $\text{Fe}^{2+}$ , becomes less significant. This is possibly due to the regeneration of these reagents from the catalytic reactions (Equations (v), (vi), (viii)) of the FR process which require more time to manifest. Additionally, the degradation may also be caused by the occurrence of much slower Fenton-like ( $\text{Fe(III)/H}_2\text{O}_2$ ) reaction (Equation (v)) which takes place at the later stage of the process.

The influence of mixing intensity on FR performance observed in this study is anticipated to be caused by the scavenging activity of  $\text{HO}^\bullet$ . As  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  solutions are added at two points close to each other, slow mixing apparently provides an environment for the chemicals to be "together" for a relatively longer period of time. This caused

the generation of high concentration of  $\text{HO}^\bullet$  but localised at certain areas within the vessel. Such a condition caused the radicals to react with each other or with the remaining available  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  producing less reactive species. Since the scavenging reactions of  $\text{HO}^\bullet$  with itself or other oxidants are as fast as the reactions of  $\text{HO}^\bullet$  with the dye compound and the intermediate organics (rate constant in the order of  $10^7$  to  $10^9 \text{ M}^{-1}\text{s}^{-1}$ ), it is possible that with poor mixing and reagents addition strategy used, the former occur in greater proportion than the latter. This view is supported by the profile of TOC and  $\text{H}_2\text{O}_2$  concentration shown in Figure 5 for two similar runs conducted at two different mixing intensities. As observed, while there is no significant difference with respect to  $\text{H}_2\text{O}_2$  concentration profile between the two runs, the TOC reduction for the run with higher mixing intensity is higher by more than 10%. It appears that although the decomposition of the  $\text{H}_2\text{O}_2$  is about the same for the two runs, the  $\text{HO}^\bullet$  generated by the run with slower mixing intensity seems not to be used effectively in degrading the organic compounds. Improving the mixing intensity possibly reduces the scavenging of  $\text{HO}^\bullet$  by distributing the reagents better and hence, enhances the TOC removal.

Figure 6 shows the interaction effect between mixing intensity and the reagents dosage after 1 and 60 minutes of reaction. At both reaction times, increasing mixing intensity from about 170 rpm to about 460 improves the performance of

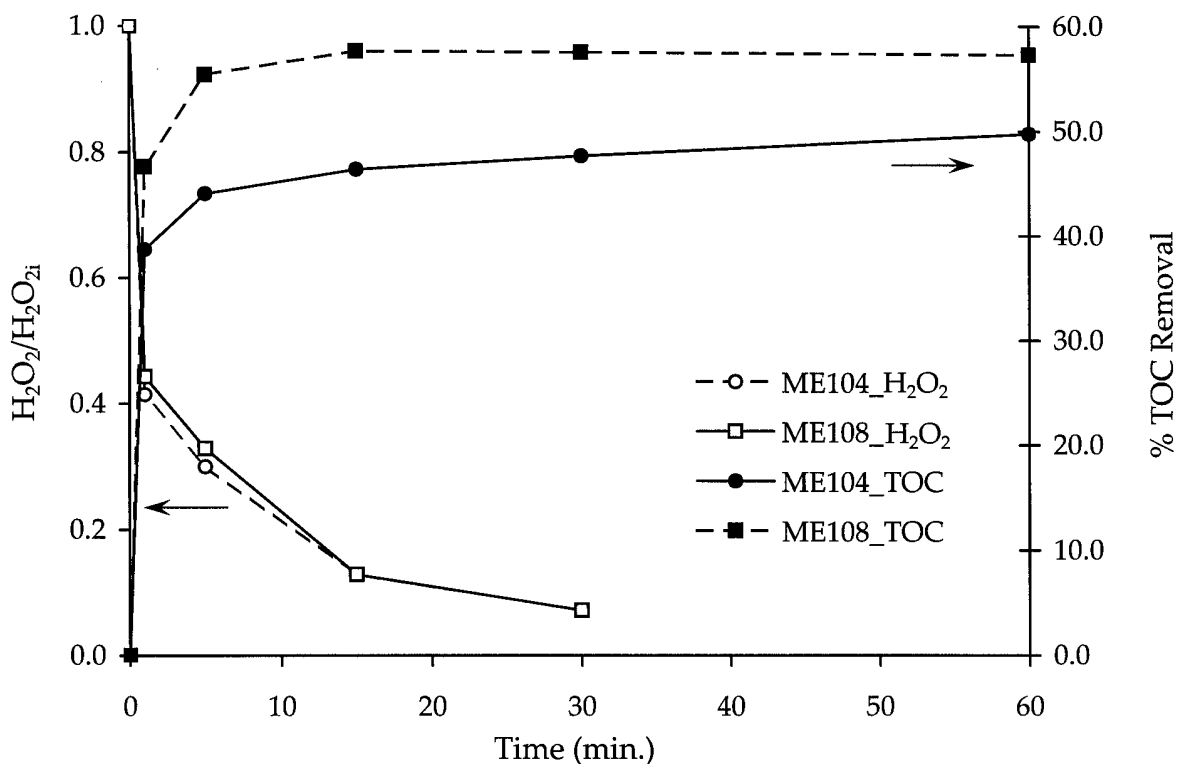


Figure 5. The profile of TOC and  $\text{H}_2\text{O}_2$  at two mixing intensities. Experimental condition:  $\text{pH} = 3.0$ ;  $T = 25^\circ\text{C}$ ;  $\text{RB5} = 200 \text{ mg l}^{-1}$ ;  $\text{H}_2\text{O}_2 = 292.4 \text{ mg l}^{-1}$ ;  $\text{Fe}^{2+} = 133.9 \text{ mg l}^{-1}$ ; rpm = 169 (ME104); rpm = 461 (ME108).

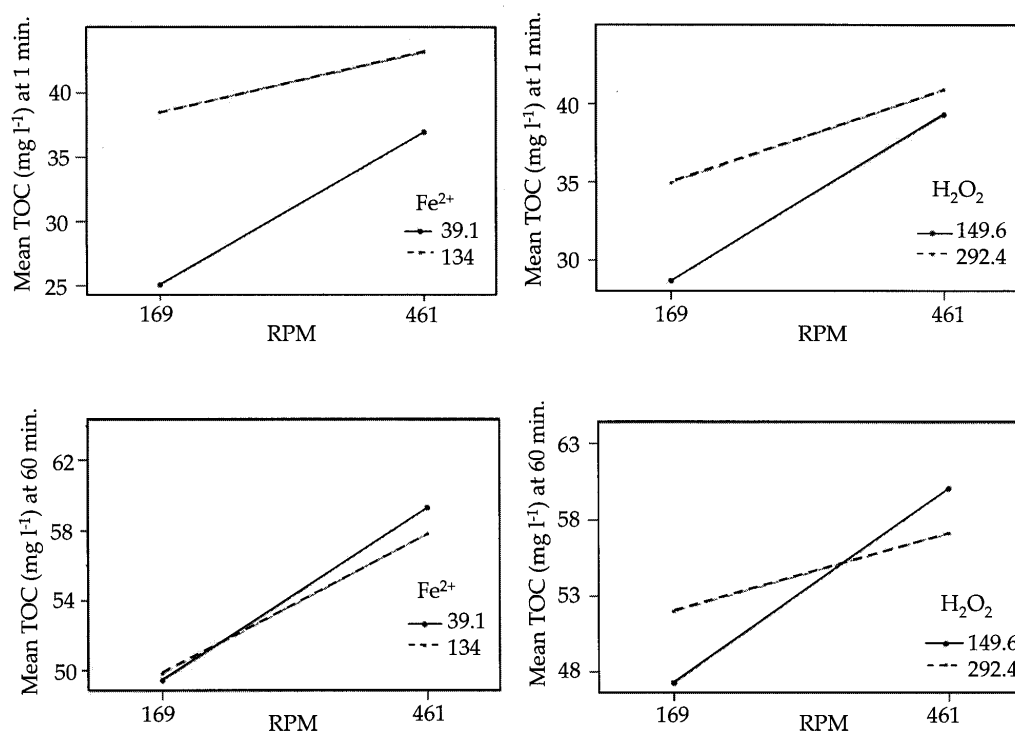


Figure 6. Interaction effect plot (based on data means) for TOC removal at 1 and 60 minutes.

the system. However, the improvement brought by increasing mixing intensity appears to be higher at lower reagent dosage. After 60 minutes of reaction, using higher mixing intensity at lower reagent dosage gave better TOC removal than the ones with higher reagent dosage. It is possible that the lower TOC removal at higher reagents dosage is due to the radical scavenging caused by the high reagents dosage as previously mentioned. Although the

higher mixing intensity managed to reduce the scavenging effect caused by the higher dosage, the scavenging effect is still higher than those of the lower dosage and therefore resulted in lower TOC removal.

Based on the star and centre point experimental runs, the effect of mixing intensity on TOC removal was found to be non-linear (Figure 7). Increasing impeller speed from about 70 rpm to 315 rpm improves the TOC removal by about 17%

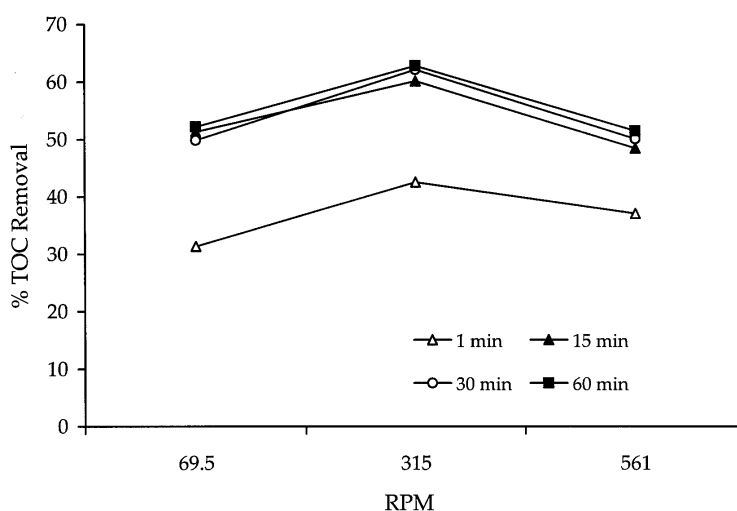


Figure 7. Effect of mixing intensity on TOC removal. Experimental condition: pH = 3.0; T = 25°C; RB5 = 200 mg l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 221.0 mg l<sup>-1</sup>; Fe<sup>2+</sup> = 86.6 mg l<sup>-1</sup>.

at 60 minutes. However, a still higher impeller speed (about 560 rpm) reduces the removal by about 18%. This result was reproduced in another repeated run. The reason for this phenomenon is presently not clear. It is possible that the very high mixing level has caused the dissolved oxygen (DO) concentration in the reactor to rise to a level that inhibits the Fenton oxidation as reported in several studies [16, 17]. Using UV/ferrioxalate system, Huston and Pignatello [16] observed a decreasing order of efficiency of air-saturated, oxygen-saturated and anoxic systems in degrading carbon tetrachloride. They suggested the phenomenon to be caused by the scavenging of the oxidants by DO. In degrading 2-propanol with UV/ferrioxalate/H<sub>2</sub>O<sub>2</sub> system, Hislop and Bolton [17] reported reduction in the process efficiency as the initial DO concentration was increased. They anticipated the reduction to be due to the decrease in Fe(III)/Fe(II) recycling reaction caused by the high DO content. However, as different systems were used by these researchers which may involve different pathways of oxidation and as DO concentration was not monitored during this study, the involvement of DO would need further investigation.

Alternatively, it is also possible that the maximum in TOC removal as a function of mixing intensity may be caused by the negative consequence of a very well mixed FR system on complete mineralisation. In the highly mixed system, the concentration of the HO<sup>•</sup> is well distributed. However, the intermediate mixed system is likely to have mixed regions of higher and lower concentrations of HO<sup>•</sup>. In regions with lower radical concentration, reaction with the dye molecules may generate more by-products and less mineralisation. On the other hand, in the higher HO<sup>•</sup> concentration region, a higher rate of mineralisation than those of the highly mixed system is expected and it may be that this exceeds the deficit in the HO<sup>•</sup>-lean regions. As TOC is a measure of compound mineralisation, better TOC removal was therefore observed in the intermediate mixed system than the highly mixed one. Then again, further study is needed to understand the phenomenon.

#### Reagents Addition Strategy

As the initial dye concentration was increased, colour and TOC removals were lower than those achieved in the mixing intensity effect study. However, rapid decolourisation could still be observed with about 90% and 95% of colour being removed in the first minute and 60 minutes of reaction, respectively. The removal of TOC after 60 minutes was between 40 to 45%.

The effects of reagents addition strategy on TOC removal after 2 and 60 minutes of reaction are shown in Figure 8. For the 2-minute reaction, four runs (ME301 to ME304) are considered as only in these had dosing of reagents been completed. As can be observed, simultaneous reagents addition at two distant points (ME302) gave the best TOC removal (29.1% at 315 rpm and 23.5% at 69 rpm) in the early stage of reaction while simultaneous addition at two close

points resulted in the lowest removal (21.1% at 315 rpm and 15.6% at 69 rpm). The effect of mixing intensity can also be observed at this stage of reaction as higher TOC removal can be observed with the runs with higher mixing intensity. Pre-diluting either Fe<sup>2+</sup> or H<sub>2</sub>O<sub>2</sub> did not improve the TOC removal but reduced the mixing effect.

At longer reaction time (60 minutes), the influence of addition strategy seems no longer to be significant particularly at higher mixing intensity. At 315 rpm, although the highest TOC removal was achieved by run ME302, it was not significantly different compared to other addition strategies. The removals were between about 42% and 45%. Pre-dissolving or intermittent addition of H<sub>2</sub>O<sub>2</sub> or Fe<sup>2+</sup> did not provide any positive effect on FR performance. With respect to intermittent addition of reagents, the results of this study confirm the findings of Kang *et al.* [18] who did not observe any benefit of multi-step addition of the reagents. At 69 rpm, TOC removal was not significantly different between runs ME302 to ME307. However, for ME301 (simultaneous addition at two close points), not only is there a significant difference in TOC removal (about 12%) between the two mixing intensities, the strategy also yields the lowest TOC removal. The results reveal that the effect of mixing intensity is affected by the reagent addition strategy and seems to support our earlier assertion with regards to the occurrence of localised generation of HO<sup>•</sup> causing the scavenging of HO<sup>•</sup>. By adapting different addition strategies which disperse the reagents better, the influence of mixing intensity was reduced. This then suggests that proper reagents addition strategy can be used to reduce the mixing intensity requirement, hence lowering the operational cost of the FR process.

#### CONCLUSION

The experimental results indicate that colour from RB5 can be more effectively removed than TOC using FR in the range of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> dosage tested. Within the experimental condition tested, mixing intensity was found to have significant effect on the outcome, and also was dependent on the reagents addition strategy applied. If the reagents are added close to each other, higher mixing intensity is needed to enhance the effectiveness of the removal process. A very high mixing level on the other hand, may cause reduction in the Fenton process performance if mineralisation of organics is the desired outcome. The results also show that there is an interactive effect between mixing intensity and Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> dosage and mixing intensity has a non-linear effect on the FR performance. The effect of reagents addition strategy was also found to be inter-dependent with mixing intensity. At higher mixing intensity, the reagents addition strategy has insignificant effect on the outcome in the longer term but this was not the case with lower mixing intensity.

The influence or the requirement of mixing intensity could be reduced through the use of a good reagents addition strategy, hence, lowering the operational cost of the process.

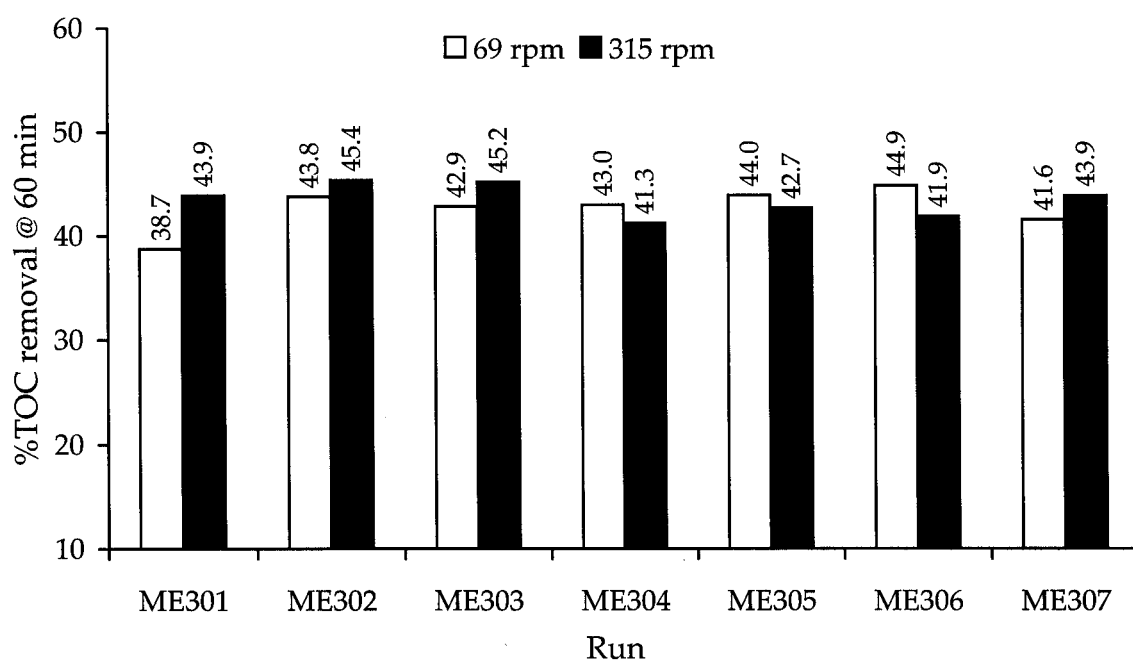
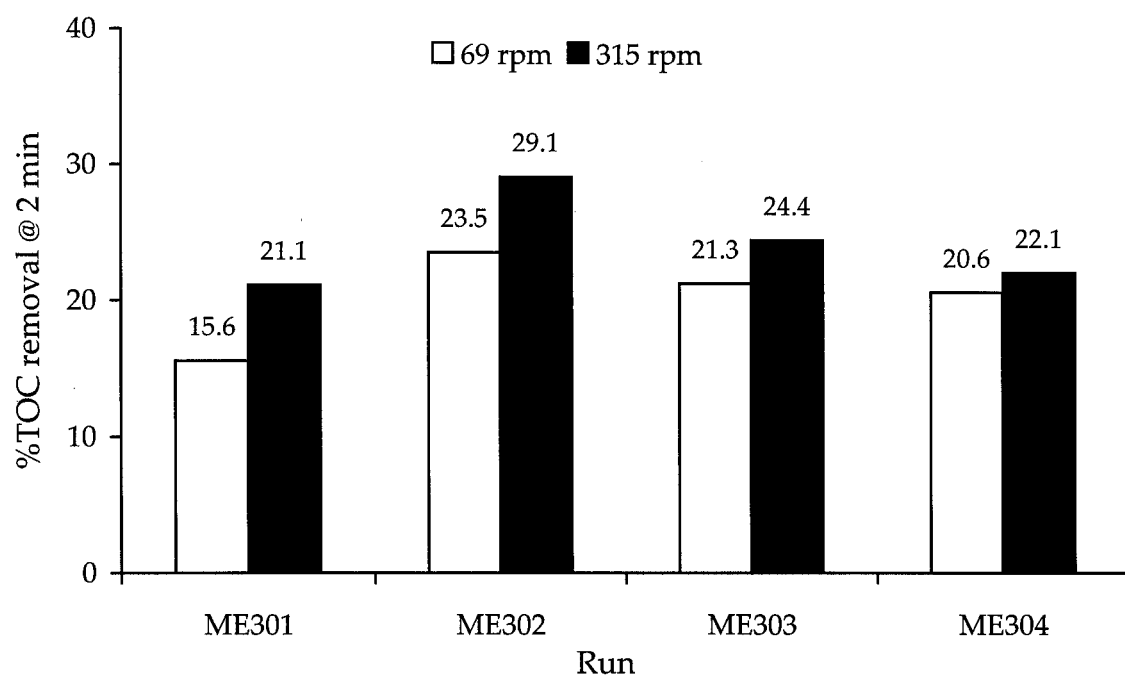


Figure 8. TOC removals using different chemical addition strategy after (a) 2 min-reaction and (b) 60 min-reaction. Experimental condition: pH = 3.0; T = 25°C; RB5 = 793.5 mg l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 221.0 mg l<sup>-1</sup>; Fe<sup>2+</sup> = 86.6 mg l<sup>-1</sup>.

While the study was conducted at laboratory scale, the effects can be expected to be greater and important in a bigger system where mixing times are likely to be longer. As this will affect the cost of operation, it is important that further study be carried out at larger scale.

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