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EVALUATION OF PHOTO-FENTON DEGRADATION OF REACTIVE BLACK 5 USING RESPONSE SURFACE METHOD

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Abstract: Photo-Fenton degradation of a reactive dyestuff, Reactive Black 5, was investigated in this study. The effects of UV light on Fenton Reagent process and the influence of reagents dosage, UV light intensity and initial dissolved oxygen concentration on photo-Fenton were explored. The experiments were conducted in a 3-L batch-mode reactor and were designed using Response Surface Method. The performance of the systems was assessed based on TOC removal. UV light was found to increase the efficiency of Fenton Reagent process by about 100%, reduce the reaction time by half and lessen the iron requirement by about 85%. Within the range used in the experiments, UV light intensity, and iron and hydrogen peroxide dosages were found to have significant positive influence on the efficiency of the photo-Fenton process. Iron dosage was significant in the early stage, peroxide dosage was significant at the later stage while UV light intensity was significant throughout the reaction period. The initial dissolved oxygen concentration was not a significant factor for photo-Fenton. Depending on the conditions of the reaction, TOC removal of 41.3% to 88.2% was obtained by photo-Fenton oxidation after 30 minutes.

Keywords: *Photo-Fenton; Response Surface Method; Initial Dissolved Oxygen Concentration; Reactive Dyestuff*

Abstrak: Kajian ini menyiasat keupayaan foto-Fenton dalam menguraikan pewarna reaktif, Reactive Black 5. Penilaian dibuat ke atas kesan sinaran UV kepada proses Reagen Fenton dan kesan dos reagen, keamatan sinaran UV dan kepekatan oksigen terlarut awal ke atas kelakunan foto-Fenton. Ujikaji makmal direkabentuk dengan menggunakan kaedah *Response Surface* dan dijalankan dengan menggunakan reaktor jujukan bersaiz 3 L. Kelakunan sistem dinilai berdasarkan kepada penyingkiran TOC. Sinaran UV didapati meningkatkan keberkesanan proses Reagen Fenton sebanyak 100%, mengurangkan masa tindakbalas kepada separuh dan mengurangkan 85% keperluan ferum. Berdasarkan kepada julat yang digunakan di dalam ujikaji, keamatan sinaran UV dan dos ferum dan hidrogen peroksida didapati memberi kesan positif yang signifikan kepada proses foto-Fenton. Dos ferum memainkan peranan penting di peringkat awal tindakbalas sementara dos peroksida menjadi penting di bahagian akhir tindakbalas. Keamatan sinaran UV memainkan peranan yang penting di semua peringkat tindakbalas. Kepekatan oksigen terlarut awal didapati tidak memainkan peranan yang penting kepada foto-Fenton. Selepas tindakbalas selama 30 minit, pengoksidaan foto-Fenton didapati mampu menyingkirkan TOC sebanyak 41.3% hingga 88.2%, bergantung kepada keadaan ujikaji yang dijalankan.

Katakunci: *Foto-Fenton; Kaedah Response Surface; Kepekatan Oksigen Terlarut Awal; Pewarna Reaktif*

1.0 Introduction

Fenton's Reagent (FR), a combination of H_2O_2 and Fe^{2+}, can be considered as the oldest Advanced Oxidation Processes (AOPs). Although the catalytic effect of Fe^{2+} on H_2O_2 was first observed by H.J.H. Fenton in 1894, the idea on the role of hydroxyl radical ($HO^{\bullet}$) was suggested by Haber and Weiss only in 1934. While many studies have been conducted on FR since the suggestion brought by Haber and Weiss, interest in exploring the feasibility of the process for treating contaminated water and wastewater is quite recent (i.e. about 20 years). Within this time frame, different types of model compounds, both simulated and actual wastewaters have been studied with FR. In general, degradation took place within reaction time of seconds to minutes while mineralization of the organics normally requires longer reaction time (Sun and Pignatello, 1993; Chamarro et al., 2001).

The benefits of UV light irradiation on FR have been reported by several researchers (e.g. Pignatello, 1992; Sun and Pignatello, 1993; Balanosky et al., 2000; Katsumata et al., 2004). Several mechanisms have been proposed on the role of UV light in enhancing the process. In general, the main mechanism has been attributed to the photoreduction of Fe^{3+} (Eqn. (1)). The reaction regenerates Fe^{2+} for subsequent Fenton reaction and also produces additional $HO^{\bullet}$. These enhance the process significantly and consequently reduce the iron requirement.

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \qquad (1)$$

The effect of O_2 purging on FR and photo-Fenton has been well documented (Cohen and Odofile, 1983; Sun and Pignatello, 1993; Huston and Pignatello, 1996; Hislop and Bolton, 1999). However, the effect of initial dissolved oxygen concentration (IDOC) on photo-Fenton seems to be lacking.

Using a lab-scale reactor, this study explored the influence of UV light on FR and the effects of IDOC, reagent dosage, and UV light intensity on photo-Fenton process. In order to determine the importance of each variable quantitatively and the possible synergistic or antagonistic effects between them, the study was conducted using Response Surface Method (RSM). A commonly reactive dyestuff, Reactive Black 5 (RB5) was used as the model compound.

2.0 Methodology

2.1 Materials and Analysis

The RB5 and other chemicals used were supplied by BDH or Aldrich. Solutions were prepared using deionized water generated by Elsgat Spectrum deionizer. The dye and ferrous solutions were freshly prepared prior to use while H_2O_2 solution was used as received. A 500 W medium pressure mercury lamp (Sei Myung Vactron, South Korea) was used as the UV light source. The lamp has a maximum intensity around 365 nm with a power loading of approximately 80 Wcm^{-1} (as provided by manufacturer).

The performance of the process was assessed by total organic carbon (TOC) analyzed using Shimadzu TOC-V CSH analyzer. For selected runs, samples were analyzed for H_2O_2 residual concentration with Titanium Sulphate Spectrophotometric Method (Mendham et al., 2000) using Lamda 10, Perkin Elmer UV/Vis spectrophotomer. The photonic flux of the UV light was analyzed using potassium ferrioxalate actinometry method (Calvert and Pitts, 1967). The concentration of ferrous ion for the actinomery was analyzed using phenanthroline method (Calvert and Pitts, 1967; APHA, 1999). A Mettler Toledo MO128 DO meter was used to monitor the dissolved O_2 concentration.

2.2 Experimental Procedure

The experiments were designed according to RSM with the aids of MINITAB™ (Version 13.32) statistical software. In particular, Central Composite Rotatable Design (CCRD) was used. As shown in Figure 1, the design consists of (a) a 2^k factorial- or ‘cube’-point runs (k represents the number of factors being considered); (b) star-point (also called axial points) runs and (c) centre-point runs.

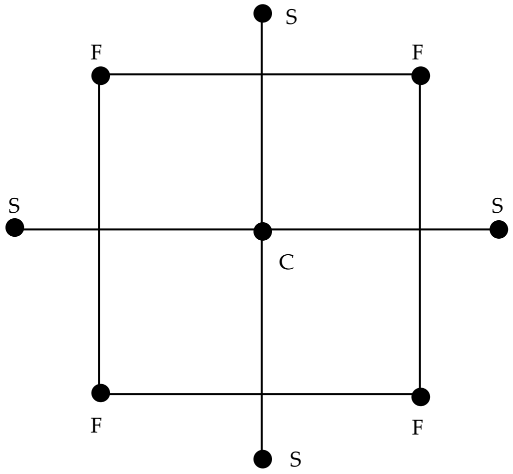

Figure 1: An example of a two-factor experimental setup according to Central Composite Rotatable Design (F: cube- or factorial-point; S: star-point; C: centre-point)

Table 1: List of experimental runs conducted in the study (not in random order)

[a]Run Code	H_2O_2 mg L^{-1} [mM] ( )[b]	Fe^{2+} mg L^{-1} [mM] ( )[b]	IDOC mg L^{-1} ( )[b]	UV Exposure %[b]
PFDO101	178.5 [5.25] (-1)	11.2 [0.20] (-1)	2.5 (-1)	25 (-1)
PFDO102	399.5 [11.75] (+1)	11.2 [0.20] (-1)	2.5 (-1)	25 (-1)
PFDO103	178.5 [5.25] (-1)	83.7 [1.50] (+1)	2.5 (-1)	25 (-1)
PFDO104	399.5 [11.75] (+1)	83.7 [1.50] (+1)	2.5 (-1)	25 (-1)
PFDO105	178.5 [5.25] (-1)	11.2 [0.20] (-1)	7.5 (+1)	25 (-1)
PFDO106	399.5 [11.75] (+1)	11.2 [0.20] (-1)	7.5 (+1)	25 (-1)
PFDO107	178.5 [5.25] (-1)	83.7 [1.50] (+1)	7.5 (+1)	25 (-1)
PFDO108	399.5 [11.75] (+1)	83.7 [1.50] (+1)	7.5 (+1)	25 (-1)
PFDO109	178.5 [5.25] (-1)	11.2 [0.20] (-1)	2.5 (-1)	75 (+1)
PFDO110	399.5 [11.75] (+1)	11.2 [0.20] (-1)	2.5 (-1)	75 (+1)
PFDO111	178.5 [5.25] (-1)	83.7 [1.50] (+1)	2.5 (-1)	75 (+1)
PFDO112	399.5 [11.75] (+1)	83.7 [1.50] (+1)	2.5 (-1)	75 (+1)
PFDO113	178.5 [5.25] (-1)	11.2 [0.20] (-1)	7.5 (+1)	75 (+1)
PFDO114	399.5 [11.75] (+1)	11.2 [0.20] (-1)	7.5 (+1)	75 (+1)
PFDO115	178.5 [5.25] (-1)	83.7 [1.50] (+1)	7.5 (+1)	75 (+1)
PFDO116	399.5 [11.75] (+1)	83.7 [1.50] (+1)	7.5 (+1)	75 (+1)
PFDO117	68.0 [2.0] (-1.682)	47.4 [0.85] (0)	5.0 (0)	50 (0)
PFDO118	510 [15.0] (+1.682)	47.4 [0.85] (0)	5.0 (0)	50 (0)
PFDO119	289.0 [8.5] (0)	2.8 [0.05] (-1.682)	5.0 (0)	50 (0)
PFDO120	289.0 [8.5] (0)	167.4 [3.00] (+1.682)	5.0 (0)	50 (0)
PFDO121	289.0 [8.5] (0)	47.4 [0.85] (0)	0.0 (-1.682)	50 (0)
PFDO122	289.0 [8.5] (0)	47.4 [0.85] (0)	10.0 (+1.682)	50 (0)
PFDO123	289.0 [8.5] (0)	47.4 [0.85] (0)	5.0 (0)	0 (-1.682)
PFDO124	289.0 [8.5] (0)	47.4 [0.85] (0)	5.0 (0)	100 (+1.682)
PFDO125 -131	289.0 [8.5] (0)	47.4 [0.85] (0)	5.0 (0)	50 (0)
Comparative experiments				
FDO101	178.5 [5.25]	11.2 [0.20]	2.5	0
FDO104	399.5 [11.75]	83.7 [1.50]	2.5	0
FDO121	289.0 [8.5]	47.4 [0.85]	0.0	0
FDO122	289.0 [8.5]	47.4 [0.85]	10.0	0
DO50C	289.0 [8.5]	0	5.0	50
DO50U	0	0	5.0	50

[a]Based on standard order designed by CCRD; [b]( ) – Coded value as assigned by CCRD

As four factors were considered and analysed in the study, the experiments were divided into 2^4 Hadamard matrix factorial runs, eight star-point runs and seven centre-point runs. To reduce the effect of bias due to unplanned factors, the experimental runs were carried out in a randomised order. The ranges of the variables were as follows: iron, 0.05-3.00 mM; H_2O_2, 2.0–15.0 mM; IDOC, 0-10.0 mg/L; and %UV exposure, 0-100%. As shown in Table 1, a total of 31 experimental runs were conducted for the RSM study. Additional experiments were conducted for comparative study.

The experiments were carried out batch-wise using a 3-L glass reactor. Mixing was provided by Rushton turbine impeller while the temperature was maintained at 25°C throughout the experiment. The UV lamp was enclosed in quartz immersion well placed in the solution. The UV light intensity was varied by controlling the percentage of UV lamp exposure to the solution, achieved by wrapping the lamp with aluminium foil.

The RB5 of 200 mg/L was used in all experiments. The initial pH was set to 3 using 1:1 (conc. acid : water) H_2SO_4. An appropriate dosage of Fe^{2+} solution was added into the vessel and mixed. The O_2 or N_2 gas was purged into the reactor until the required IDOC ($\pm$ 0.2) was achieved. The UV lamp was then turned on and the experiment started one minute later with the addition of appropriate dosage of peroxide. Samples were collected at predetermined intervals up to 30 minutes and analysed for TOC and residual peroxide.

3.0 Results and Discussion

3.1 General Overview

The results of the actinometry analysis are given in Table 2. The photonic flux ranges from 1.6×10^{-4} Einstein min^{-1} to 1.0×10^{-3} Einstein min^{-1} depending on the percentage of UV exposure. In general, as the percentage of UV exposure increases, the photonic flux produced also increases. However, the relationship between the percentage of UV exposure and photonic flux seems to be approximately exponential at higher UV exposure.

Table 2: The photonic flux of UV light at different UV exposure

%UV Exposure	F, photonic flux (Einstein min^{-1})
25	1.64×10^{-4}
50	3.04×10^{-4}
75	5.03×10^{-4}
100	1.00×10^{-3}

The results for TOC removal vary depending on the conditions of the experiment (see Table 1). The removal at 30 minutes for photo-Fenton process ranges from 41.3% to 88.2%. Only three runs exhibit TOC removal of lower than 70% (i.e. PFDO117, PFDO119 and PFDO123) which possibly due to the use of very low dosage of reagents or caused by the omission of UV light.

Figure 2 shows a comparison between different AOPs up to 30 minutes of reaction. As expected, photo-Fenton is the most effective process in the removal of TOC. This is followed by FR, UV/H_2O_2 and UV alone. Almost no TOC removal could be observed when the RB5 solution was irradiated by the UV light alone. A direct comparison between FR and photo-Fenton processes shows that even at relatively low UV intensity (25% exposure of 500 W), photo-Fenton process efficiency in term of TOC removal almost double those of FR. The TOC removal using 0.05 mM of Fe^{2+} by the photo-Fenton (56.3%) is even higher than using 0.85 mM by the FR (47.5%). Hence, the irradiation has the capability to increase the efficiency of the process by almost 100%, reduce the reaction time by half and lower the iron requirement by about 85%.

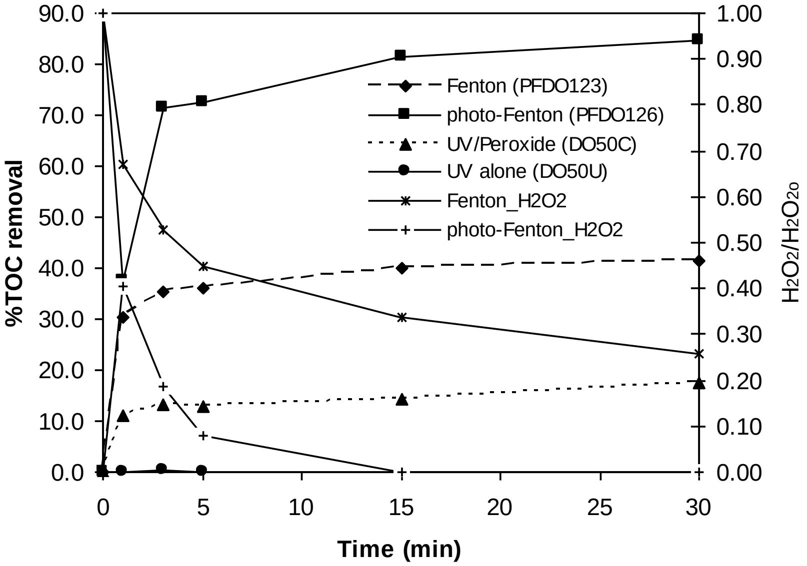

Figure 2: Performance of several AOPs on the removal of TOC and hydrogen peroxide degradation (H_2O_2: 8.5 mM; Fe^{2+}: 0.85 mM; IDOC: 5.0 mg L^{-1})

As mentioned earlier, the enhancement of FR by the UV light might be due to the reduction of Fe^{3+} to Fe^{2+} by the irradiation and simultaneous generation of additional $HO^{\bullet}$. In the presence of excess H_2O_2, the regenerated Fe^{2+} reacts with the peroxide to produce more $HO^{\bullet}$. Photolysis of H_2O_2 and ferric ions-catalysed decomposition of the peroxide followed by heat- or UV-induced may form ferrous ions and perhydroxyl radical ($HO_2^{\bullet}$) which could also contribute to the degradation of the dyestuff (Kang et al., 1999). These reactions continue until the peroxide is fully consumed. As shown in Figure 1, only about 11% of additional TOC was removed between the first minute and 30 minutes of the reaction in FR process as compared to more than 40% of additional TOC removal in the photo-Fenton process between the first minute and 15 minutes. This correlates with the H_2O_2 concentration profiles shown in the same figure. While more than 25% of the peroxide remained in FR process at 30 minutes, the peroxide in photo-Fenton process was completely utilised by 15 minutes. This indicates that the Fe^{2+} was regenerated in the photo-Fenton process much faster than in the FR. In the presence of Fe^{2+} the hydrogen peroxide is consumed in much faster rate in photo-Fenton than in FR. Further degradation (about 3% TOC removal) was also observed in the absence of peroxide (i.e. after the 15 minutes) possibly due to the radicals generated from the photoreduction of the remaining Fe^{3+}.

3.2 Characterisation of Dissolved Oxygen Profile

A comparison of the dissolved oxygen (DO) concentration profile between photo-Fenton and FR processes is illustrated in Figure 3. The profile of the runs irradiated with UV light (hollow mark) follows the same profile of the non-irradiated ones (solid mark) in the first few minutes. This is presumably due to the role of Fenton reaction which took place in the early stage of the process. For the runs with high IDOC (10 mg L^{-1}) a brief DO concentration drop was observed in the first minute. As the reaction progress, DO concentration increases until it reaches a maximum before it starts to decline.

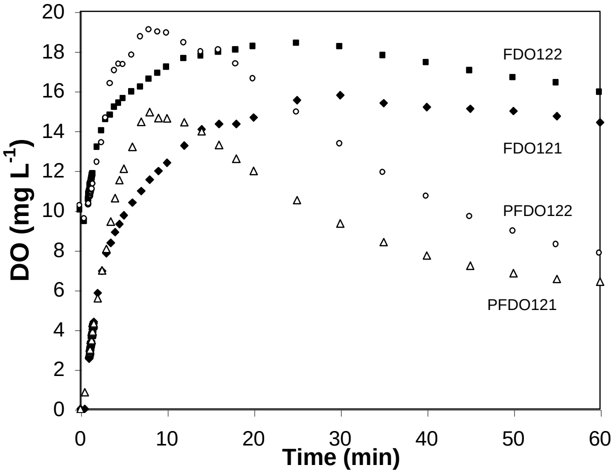

Figure 3: DO concentration profiles of photo-Fenton (hollow) and Fenton Reagent (solid) (H_2O_2: 8.5 mM; Fe^{2+}: 0.85 mM; DO_i: 0 and 10 mg L^{-1}; UV Exp.: 0 and 50%)

Several explanations have been given by the researchers with respect to the DO profile in FR systems (Cohen and Ofodile, 1983; Kiwi *et al*., 1993; Sychev and Isak, 1995). The decrease of DO concentration in FR and photo-Fenton processes is suspected to be due to the reaction of O_2 with the intermediate organoradicals (Eqn. 2) which is desirable for the completion of the oxidation process. Additionally, in photo-Fenton process, O_2 may react with the intermediate organoradicals to form photolabile Fe(III) complexes, creating additional pathway in mineralising the organics.

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} + H_2O \rightarrow ROH + HO_2^{\bullet} \qquad (2)$$

On the other hand, the evolution of O_2 in Fenton process is thought to be due to the catalytic reaction of $Fe^{2+/3+}$ with either $HO_2^{\bullet}$ or H_2O_2:

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (3)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (4)$$

$$Fe^{3} + 2H_2O \rightarrow Fe^{2+} + O_2 + 2H_2O \qquad (5)$$

For photo-Fenton process, as more $HO^{\bullet}$ is produced as compared to FR, more O_2 is released in the former due to reactions shown by Eqns. (3) and (4). Hence, the rise of O_2 is faster and the time to reach maximum O_2 concentration is shorter for the photo-Fenton process. Further depletion of O_2 towards the end of the reaction period could be due to the reaction of O_2 with the remaining organoradicals or/and due to natural phenomena which drive the O_2 to its equilibrium concentration.

It is also believed that both O_2 depletion and evolution reactions occur throughout the process. Depending on the availability of the reagents and some other factors, one of the reactions becomes dominant at different stages of the process.

3.3 Factorial Analysis

The factorial analysis was carried out on the 16 Hadamard matrix and seven centre point runs. The analysis was carried out based on TOC removal at reaction times of 3 and 30 minutes. Figures 4 and 5 show the Pareto chart and main effect plot of the study, respectively. Within the experimental conditions used in the study, the *p*-value (at 90% confidence level) indicates that only two factors, i.e. Fe^{2+} dosage and percentage of UV exposure (i.e. intensity) are significant to the process in removing TOC in the first 3 minutes. At 30 minutes, percentage of UV exposure and peroxide dosage are significant factors to the process while iron dosage becomes insignificant. Initial dissolved oxygen concentration was found to be insignificant during the study. Interaction effects between the factors also appear to be statistically insignificant. Based on the main effect plot on Figure 4, percentage of UV exposure, iron dosage and H_2O_2 dosage have a positive influence on the process. Increasing these factors would increase of the percentage of TOC removal.

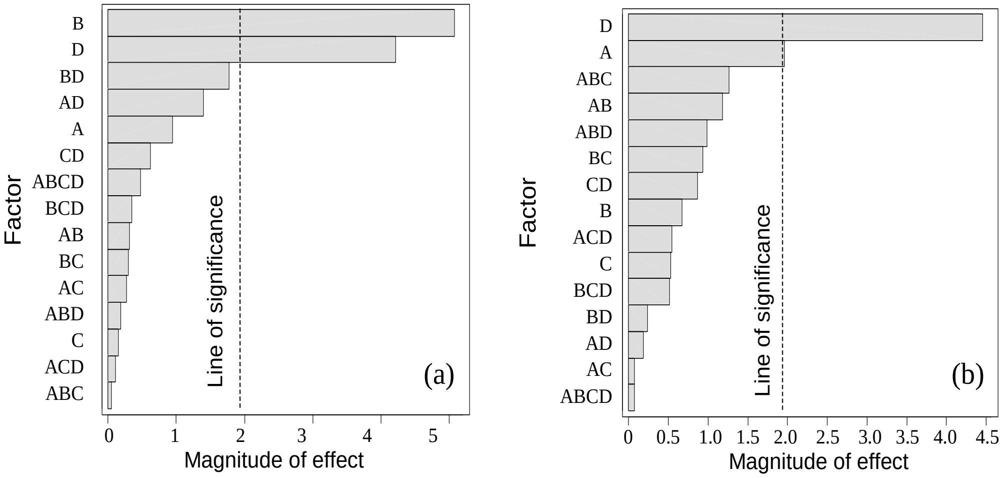

Figure 4: Pareto chart for TOC removal at (a) 3 minutes and (b) 30 minutes (α: 0.1; A: H_2O_2; B: Fe^{2+}; C: IDOC; D: UV Exposure)

3.3.1 Effect of UV Light Intensity

Although the relationship between the percentage of UV exposure and UV light intensity is slightly non-linear, the former can be interpreted as indicating the intensity of the latter. Hence, increasing the exposure of UV light to the RB5 solution increases the UV light intensity received by the solution.

The effects of UV light intensity on FR process at different reagents dosage are given in Figures 6 to 8. The influence of UV light on FR process was rather trivial during the first minute, i.e. the TOC removal for FR and photo-Fenton were about the same. However, after 3 minutes, the percentage of TOC removal by photo-Fenton markedly increased as compared to FR, indicating the effect of UV light. The removal of TOC increases from about 45% to more than 80%, depending on the percentage of UV light exposure to the solution. The influence of the UV irradiation also seems to be affected by the reagents dosage; the effect of UV light was greater at higher reagent dosage. As explained earlier, the UV light enhances the process through several mechanisms which include the photoreduction of Fe^{3+} to Fe^{2+}. Therefore, by increasing the UV intensity through increasing the UV light exposure to the solution, more photons become available to the solution. This promotes the photoreduction and other reactions to take place which ultimately cause more RB5 to be mineralised.

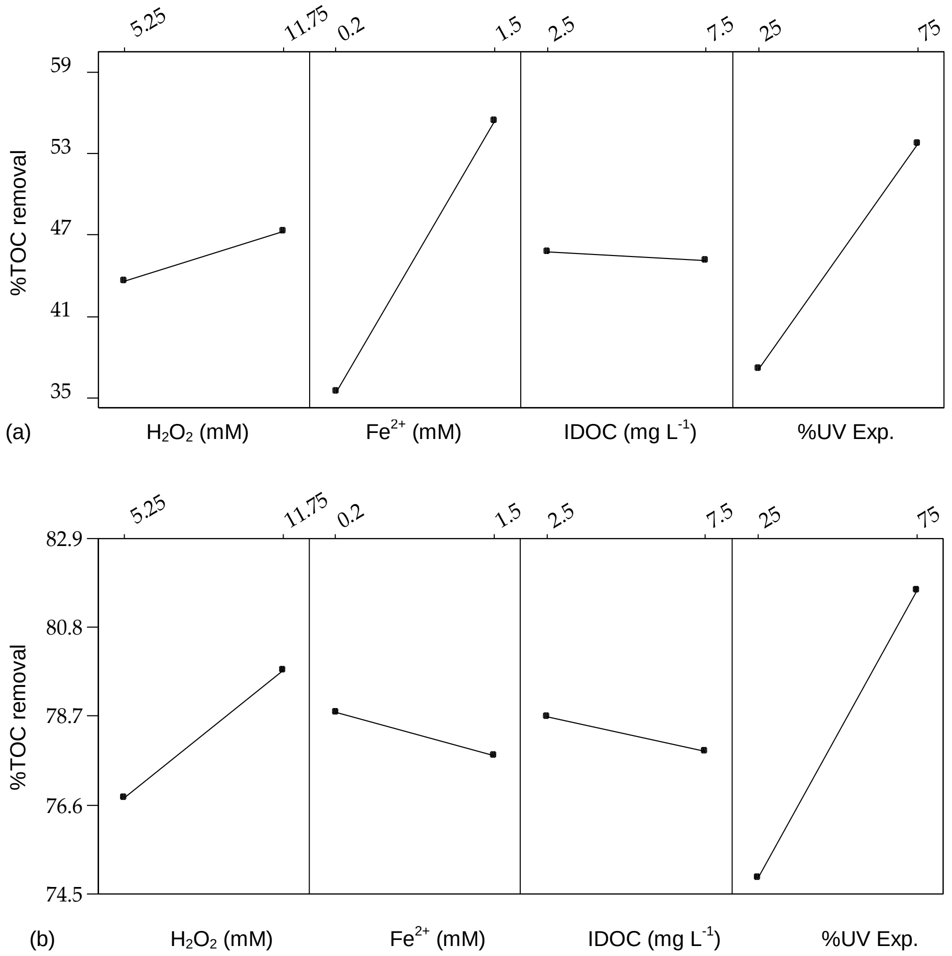

Figure 5: Main effect plot for TOC removal at (a) 3 minutes and (b) 30 minutes

3.3.2 Effect of Fe^{2+} and H_2O_2 Dosage

In general, in the presence of H_2O_2, the higher dosage of Fe^{2+} generated more $HO^{\bullet}$ and improved the degradation process. However, due to the catalytic activity of Fe^{2+}/Fe^{3+}, the effect of Fe^{2+} dosage becomes less significant over a long term (Aris, 2004). In photo-Fenton, the regeneration of Fe^{3+} to Fe^{2+} is much faster than that in the FR; hence, the lesser effect of the Fe^{2+} dosage to the process at the later stage is anticipated.

The significance of H_2O_2 at the later stage of photo-Fenton process could be attributed to the ability of UV light to regenerate Fe^{2+}. Since a higher concentration of Fe^{2+} is continuously available in photo-Fenton, the availability of H_2O_2 throughout the reaction period is an important factor in the process. The availability of the peroxide at this stage will determine the amount of $HO^{\bullet}$ generated and accordingly the efficiency of the process.

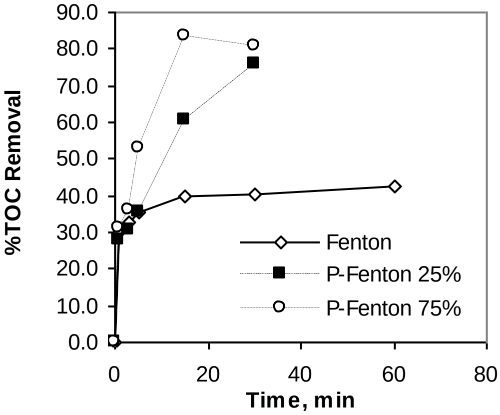

Figure 6: Effect of %UV light exposure on TOC removal (Fe^{2+}: 0.20 mM, H_2O_2: 5.25 mM, IDOC: 2.5 mg L^{-1}, %UV exp.: 0, 25, 75)

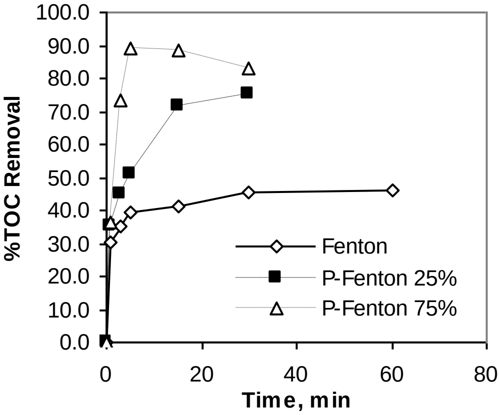

Figure 7: Effect of %UV light exposure on TOC removal (Fe^{2+}: 1.50 mM, H_2O_2: 11.75 mM, IDOC: 2.5 mg L^{-1}, %UV exp.: 0, 25, 75)

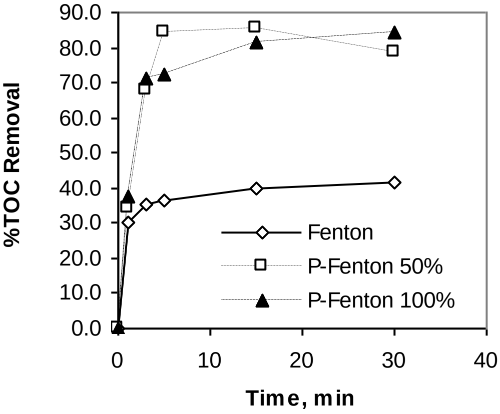

Figure 8: Effect of %UV light exposure on TOC removal (Fe^{2+}: 0.85 mM, H_2O_2: 8.5 mM, IDOC: 5 mg L^{-1}, %UV exp.: 0, 50,100)

3.3.3 Effect of Initial Dissolved Oxygen Demand

The effect of IDOC on FR process has been reported by Aris and Sharratt (2006). Reducing the IDOC was found to have significantly increased the efficiency of FR. The reduction of the IDOC from 7.5 mg L^{-1} to 2.5 mg L^{-1} has increased the removal of TOC by an average of about 10% while the reduction from 10 mg L^{-1} to 0 mg L^{-1} has enhanced the TOC removal by about 30%. The influence of IDOC however, appears to be insignificant to the photo-Fenton process. As shown in Figure 9, there is not much different in term of TOC removal between IDOC of 2.5 mg L^{-1} and 7.5 mg L^{-1}.

The insignificance influence of IDOC on the photo-Fenton process disagrees with the findings of Hislop and Bolton (1999) that did a similar study using UV-vis/ferrioxalate/H_2O_2 system. While the disagreement could be due to the differences in the experimental conditions (e.g. wastewater characteristics, reagents' dosage) and the system employed, the results of this study do not contradict to the explanation given by Aris and Sharratt (2006) on the effect of IDOC on FR process.

As shown in Eqns. (6) and (7), the reactions between the organoradicals ($R^\bullet$) and Fe^{3+} or H_2O_2 are anticipated to generate additional $HO^\bullet$ and regenerate the Fe^{2+} which enhance the FR process efficiency.

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \qquad (6)$$

$$R^\bullet + Fe^{3+} \rightarrow Product + H^+ + Fe^{2+} \qquad (7)$$

However, at high O_2 concentration, these reactions may be impeded due to the competition of $R^\bullet$ by the reaction with O_2 as given in Eqn. (2). This causes less $HO^\bullet$ being produced and thus reduces the efficiency of the FR process. This phenomenon is also expected to occur in photo-Fenton process. However, in photo-Fenton, there are other mechanisms that regenerate the Fe^{2+} and generate the $HO^\bullet$. These mechanisms such as photoreduction of Fe^{2+} seem to have much greater influence in enhancing the FR process than the effect produced by reducing the IDOC.

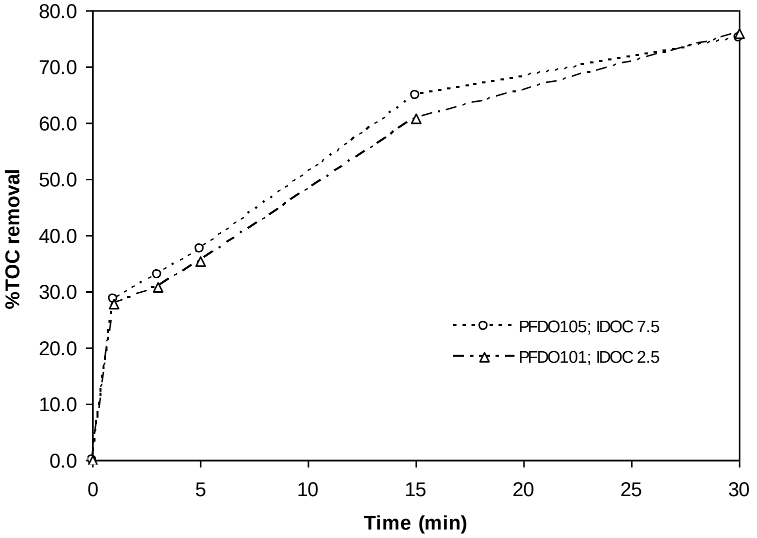

Figure 9: The profile of TOC removal of photo-Fenton process at different IDOC (H_2O_2: 5.25 mM; Fe^{2+}: 0.20 mM; %UV Exp.: 25%)

Therefore, the influence of IDOC appears to be insignificant to the photo-Fenton process as observed in this study. It should be noted that this could only be true within the experimental conditions of the study. The effect of IDOC at UV intensity lower than the one used in this study could be different and need further investigation.

3.4 Response Surface Analysis

A Response Surface Analysis (RSA) was carried out to model the relationship between the TOC removal and its associated factors. Additionally, the star- and centre-point runs that make up the RSM can be used to determine the pattern of the effect. The RSA was carried out based on TOC removal at 15 minutes since a significant portion of the removal in photo-Fenton study took place within this period.

The results of the analysis based on full quadratic terms indicate the inadequacy of the model in simulating the actual behaviour of the system. The R^2 is only 58.1% and *p*-value for the lack-of-fit[1] test is 0.003 suggesting the scantiness of the model (MINITAB™ User Guide, 2000; Montgomery, 2001). When the insignificant terms are omitted from the model, the R^2 and the *p*- value for the lack-of-fit test reduced to 54.6% and 0.000, respectively.

From these results, it can be deduced that the photo-Fenton process in this study could not be modelled statistically based on TOC removal at 15 minutes. It is possible that the process, which involves many catalytic chain-reactions and intermediate compounds, is too complicated to model using this approach. Due to such complex chain reactions, TOC removal at the later stage of the process could not be directly related to the factors being considered. It is plausible that a better model fit based on TOC removal at 3 minutes could be obtained. However, since the degradation process in photo-Fenton occurs over a much longer period, such a modelling exercise is not practically useful.

Figure 10 illustrates the profile of TOC removal after 30-minute reaction at different factors condition. The effect of UV intensity and reagents dosage on the removal of TOC follows a similar pattern while no remarkable effect of the IDOC on the percentage of TOC removal is observed. In general, increasing UV intensity and reagents dosage will increase the TOC removal. However, after certain limit, further increase of the intensity and dosage is expected to have marginal effect on the outcome of the process.

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[1] The low *p*-value (< 0.1) of lack-of-fit in the ANOVA table of RSA indicates the existence of lack-of-fit of the model at 90% confidence level. This implies the inadequacy of the model in simulating the actual scenario.

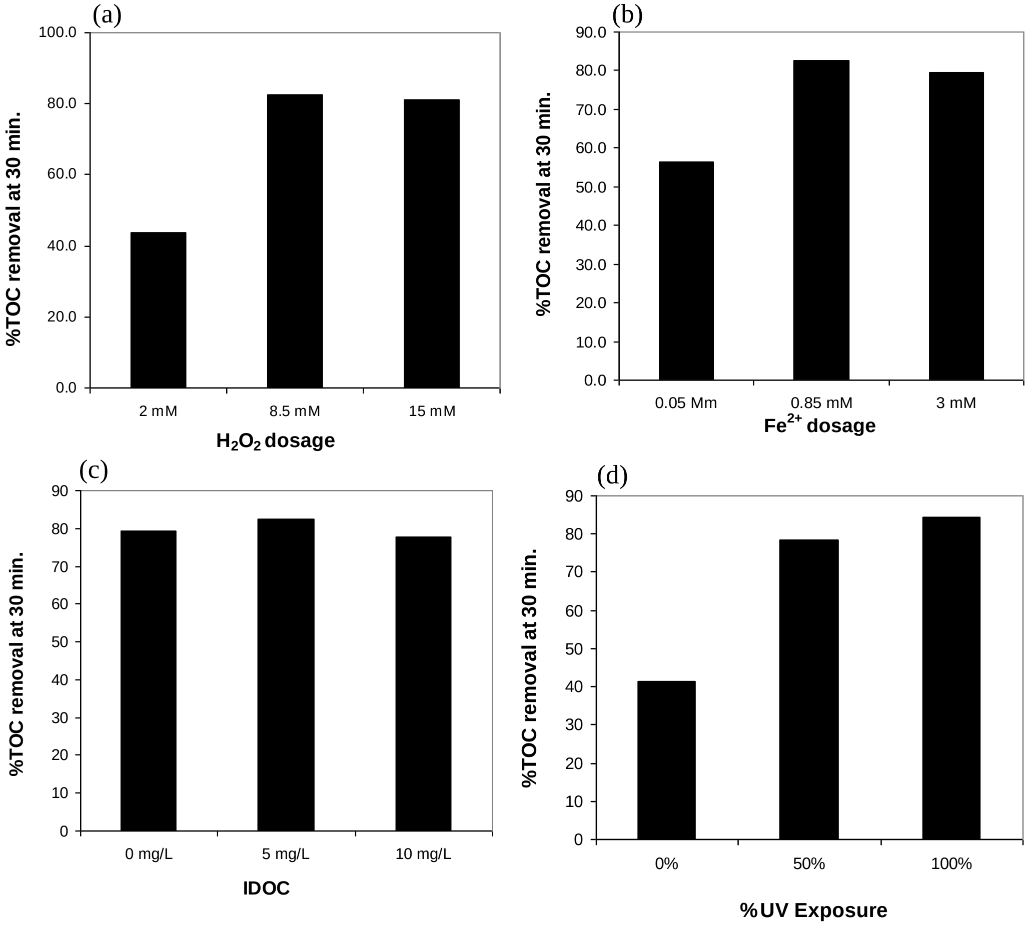

Figure 10: The pattern of TOC removal at 30 minute as a function of (a) H_2O_2 dosage, (b) Fe^{2+} dosage, (c) IDOC, and (d) %UV exposure

4.0 Conclusions

The followings conclusions are drawn from the study:

i. The participation of O_2 in photo-Fenton process can be observed based on the profiles of DO concentration. Dissolved O_2 is rapidly consumed in the early stage of the process and released in the later stages. The rate of O_2 liberation seems to be higher for photo-Fenton than FR and the rate at which DO reaches the equilibrium concentration also seems to be higher for the former than the latter.

ii. UV light greatly enhances the efficiency (i.e. TOC removal per unit time) of the FR process. The irradiation increases the efficiency of the process by about

100%, reduces the reaction time by half and reduces the iron dosage requirement by about 85%.

iii. The reagents dosage and UV intensity (based on percentage of UV exposure) are significant to the photo-Fenton process with regards to the experimental conditions of the study. Initial dissolved oxygen concentration has inconsiderable impact on the process. Fe^{2+} dosage is important at the early stage while H_2O_2 dosage is significant at the later stage of the process. UV intensity is important throughout the photo-Fenton process. The effect of the factors shows a non-linear pattern. Interaction effects between the factors are not significant.

iv. An acceptable model for photo-Fenton process based on TOC removal at 15 minutes could not be developed, most likely due to the complexity of the reactions occurring in the process.

References

APHA (1999) *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association.

Aris, A. (2004) *Fenton's Reaction System for the Treatment of Textile Dyeing Wastewater*. Ph.D. Thesis, UMIST, UK.

Aris, A. and Sharratt, P. N. (2006) Influence of initial dissolved oxygen concentration on Fenton's reagent degradation. *Environmental Technology,* 27: 1153-1161

Calvert, J. G. and Pitts, J. N. (1966) *Photochemistry*. Wiley.

Chamarro, E., Marco, A. and Esplugas, S. (2001) Use of Fenton reagent to improve organic chemical biodegradability. *Water Research,* 35: 1047-1051.

Cohen, G. and Ofodile, S. E. (1983) Activation of molecular oxygen during a Fenton reaction: A study with $^{18}O_2$. *Oxy Radicals and Their Scavenger Systems. Volume I: Molecular Aspects*. G. Cohen and R. A. Greenwald, Elsevier Science**:** 74-83.

Hislop, K. A. and Bolton, J. R. (1999) The photochemical generation of hydroxyl radicals in the UV-vis/ferrioxalate/H_2O_2 system. *Environmental Science and Technology,* 33: 3119-3126.

Huston, P. L. and Pignatello, J. J. (1996) Reduction of perchloroalkanes by ferrioxalate-generated carboxylate radical preceding mineralization by the photo-Fenton reaction. *Environmental Science and Technology,* 30: 3457-3463.

Kang, S. F., Liao, C. H. and Hung, H. P. (1999) Preoxidation treatment of dye manufacturing wastewater in the presence of ultraviolet light and ferrous ions. *Journal of Hazardous Materials,* B65: 317-333.

Katsumata, H., Kawabe, S., Kaneco, S., Suzuki, T. and Ohta, K. (2004) Degradation of bisphenol A in water by the photo-Fenton reaction. *Journal of Photochemistry and Photobiology A: Chemistry,* 162: 297-305.

Kiwi, J., Pulgarin, C., Peringer, P. and Gratzel, M. (1993) Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in waste water treatment. *Applied Catalysis B: Environmental,* 3: 85-99.

Mendham, J., Denny, R. C., Barnes, J. D. and Thomas, M. J. K. (2000) *Vogel's Quantitative Chemical Analysis*. Prentice Hall.

Minitab (2000) *MINITAB^{TM} User Guide 2: Data Analysis and Quality Tools*. Minitab Inc.

Montgomery, D.C. (2001) *Design and Analysis of Experiments*. John Wiley & Sons, Inc.

Pignatello, J. J. (1992) Dark and photoassisted Fe^{3+}, catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology,* 26: 944-951.

Sun, Y. and Pignatello, J. J. (1993) Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$. *Environmental Science Technology,* 27: 304-310.

Sychev, A. Y. and Isak, V. G. (1995) Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O_2 and H_2O_2 and of the oxidation of organic substrates. *Russian Chemical Reviews,* 64: 1105-1129.